

DEMONSTRATION AT ZELZATE

Written by Wikke Witteveen, Kris De Baere, Joeri Horvath, Flor Stoops, Thomas Bas, and Geert Potters – Antwerp Maritime Academy

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The demonstrator

Location

Output 5 compares the conditions and corrosion rates of different port environments. We chose these locations to obtain a wide variety of different conditions:

- The south coast of England (Shoreham, Newhaven) which are in direct contact with the Atlantic Ocean.
- The port of Vlissingen, at the bank of the Westerschelde (leading directly into the North Sea).
- The port of Den Helder in the North of the Dutch province of Noord-Holland.
- The marina of Zelzate, along the canal of Ghent-Terneuzen, which is situated much more inland, and which offers brackish water.
- The port of Ostend, close to the North Sea.

In the spring of 2021, significant damage was observed to several pleasure craft and other vessels in the marina of Zelzate, in the form of abnormally accelerated corrosion, correlated with a sudden development of bacteria of the genus *Gallionella*, *Rhodanobacter* and a number of sulfate-reducing bacteria. A series of tests with steel coupons in this marina and by extension along the Ghent-Terneuzen canal also showed accelerated pitting corrosion, indicating that this bacterium has spread further in the region and may have affected other assets in this industrial zone. Microbiologically induced corrosion (MIC) is a phenomenon for which there is an extensive scientific literature, but for which few practical solutions have been developed to date. The speed with which these bacteria manifest themselves (even within three days) and with which the damage occurs (with pitting at a rate of 3 mm per year) means that the standard monitoring and protection of assets is insufficient. That is why companies need a predictive system to determine or even predict the occurrence of MIC based on one or more environmental parameters.

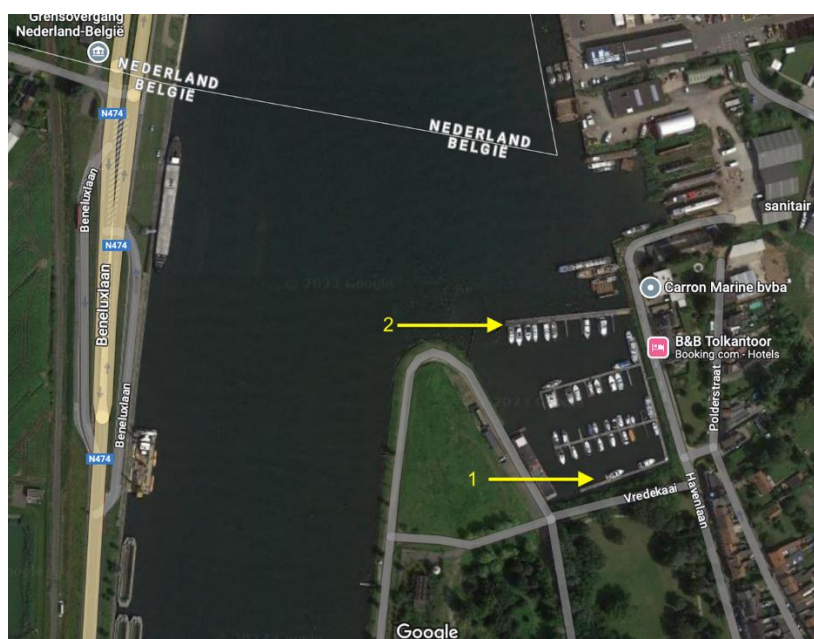


Figure 1. Location of the demonstrators in the marina of Zelzate

To investigate this effect, two identical setups were made to measure corrosion in the marina of Zelzate (Figure 1). One set-up was placed on the southern side of the harbour, indicated by number '1'. The other arrangement was placed on the northern jetty, indicated with number '2'. The arrangement on the south side is located on an overflow from which a constant stream of water comes. However, its origin is unclear. A pond south of the marina is believed to be responsible for this water supply. After all, there is less water circulation here because this part of the harbour is protected by the banks. The arrangement on the northern jetty, on the other hand, is more exposed to water circulation because there is clearly less bank protection here.

Sensor equipment

Both an environmental sensor (Scuba90) and a corrosion sensor (C-Cube) were used. By means of a specially designed distribution box, which was developed for the SOCORRO project, the uploading of data was optimized.



Figure 2. Sensor box on the north side (left) and the south side (right) of the Zelzate marina

A **Scuba90 sensor**, manufactured by Royal Eijkelpamp Soil & Water B.V., was used to measure the environmental parameters. (Giesbeek, The Netherlands). In the context of the SOCORRO project, only Scuba sensors were used, which measure specific environmental parameters that influence the corrosion rate. The measured physiochemical factors include temperature, pH, specific conductivity 25°C, salinity, dissolved oxygen, dry matter content, redox potential and chlorine content.

The Scuba90 sensor is 450mm in length and 90mm in diameter. The operating temperature varies within a range of -50°C to +50°C. The maximum operational depth of the sensor is 200 m, while the ion-selective electrode (ISE) can reach a maximum depth of 15 m. The sensor is supplied with a 12 V power supply and has a memory for 1,000,000 measurements (Royal Eijkelpamp, n.d.).

It is a multi-sensor probe equipped with several sensors capable of determining eight parameters (Royal Eijkelpamp, 2022).

- The **temperature** (Figure 3, 1) was measured by means of a thermistor whose resistance changes with temperature. Thermistors are very stable over time and therefore do not require calibration.
- **Dissolved oxygen** was measured using an optical sensor (Figure 3, 2). This sensor consists of a blue light source, a detection surface and a red-light receiver. When the detection surface is exposed to seawater, a reaction occurs between the oxygen in the seawater and the detection surface. The measurement principle is based on the phenomenon of fluorescence, where the detection surface absorbs light of a specific wavelength and then emits light of a different wavelength. In this case, the surface absorbs blue light and emits red light. During a measurement cycle, the blue light is turned on for a short time, after which the red-light receiver measures the time it takes for the fluorescence to extinguish. This length of time is proportional to the amount of dissolved oxygen in the seawater. It is important to emphasize that the presence of an oxygen active coating on the optical sensor can lead to inaccurate measurements. This is comparable to situations in which photosynthetic algae create a specific microenvironment of oxygen.
- The specific conductivity of water is determined by the four-electrode method. The sensor (Figure 3, 3) is equipped with two sets of graphite electrodes carefully positioned for stable measurement. A constant voltage is applied to one pair of electrodes and the current required to maintain this voltage is measured. The current strength increases as the conductivity of the water increases. The Scuba usually displayed specific conductivity, which is standardized to 25°C, representing the conductivity of the water as if the water had been heated or cooled to exactly 25°C. Conductivity can be expressed in different units, such as total dissolved solids (TDS) and salinity, expressed in Practical Salinity Unit (PSU). The values of either parameter were always derived from the specific conductivity.
- The acidity was determined by means of a pH glass electrode (Figure 3, 4). As a result of the ion exchange between the water and the pH glass membrane, a charge separation occurs across the glass. This charge separation creates a voltage difference that can be measured and corresponds to the pH value of the solution.
- The redox potential is measured using an oxidation-reduction potential (ORP) sensor (**Error! Reference source not found.**, 5). This sensor is located next to the pH sensor and can be noticed as a grey dot of 1 mm diameter. The redox potential is determined by measuring the voltage drop between the platinum membrane of the ORP electrode and the reference electrode. Because platinum does not react with the ions in the water, the redox potential can be derived from this voltage drop.

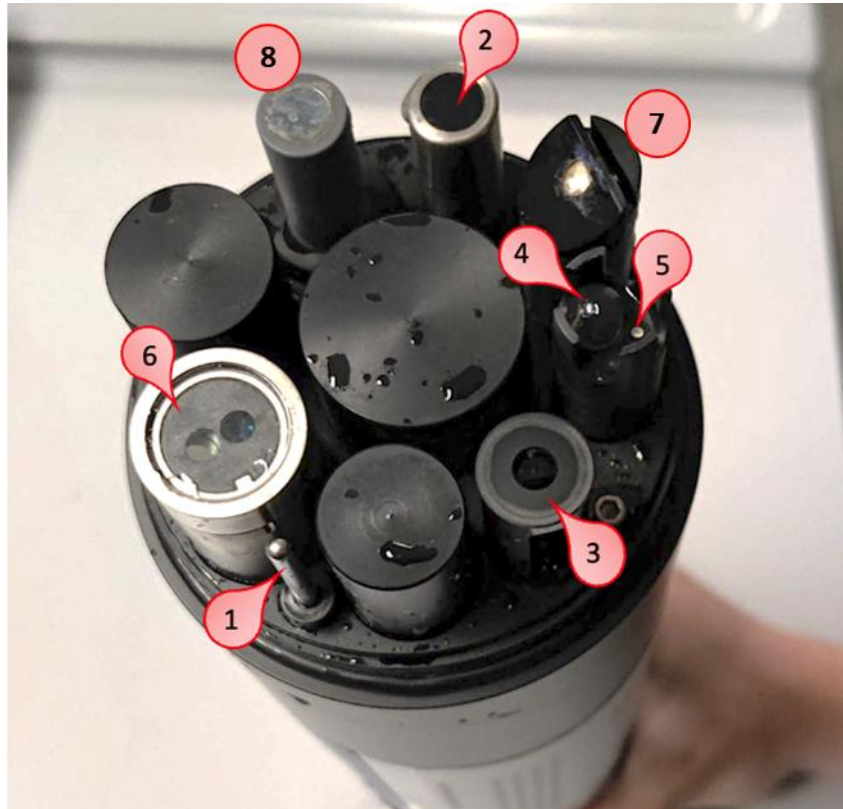


Figure 3. Different sensors of the Scuba Probe.

1: temperature sensor, 2: optical sensor (dissolved oxygen), 3: conductivity sensor, 4: pH glass, 5: ORP sensor, 6: fluorometer for chlorophyll determination; 7: reference electrode; 8: chloride sensor.

- An extra fluorimeter (Figure 3, 6) can be used to measure the chlorophyll concentration in the water. This is a measure of the presence of microalgae and therefore an indicator of the biological activity of the marine ecosystem.
- A reference electrode (supporting the other electrode measurements; (Figure 3, 7) and a chloride sensor (Figure 3, 8) complete the setup.

The Scuba probe furthermore comes with two different attachments that serve to protect the sensors. These attachments can be securely attached to the sensors using threads. A sealed capsule is available to store the probe. Since the sensors must be stored in a humid environment, the sealed capsule is partially filled with water before being attached to the probe.

An open capsule (Figure 4) is used when the probe is deployed. This capsule contains a weight to sink the Scuba Probe. The openings in the capsule serve on the one hand for the efficient passage of water and on the other hand for the protection of the sensors.



Figure 4. Open capsule for a Scuba probe

The capsule is fitted with a copper mesh, which acts as a biofouling-resistant barrier. The copper mesh exhibits a controlled solubility, slowly degrading and releasing copper ions. These copper ions cover the surfaces of the sensors and act effectively against the growth of biological organisms.

Scuba is connected to a 4G modem that uploads the data to the Telecontrolnet platform. Telecontrolnet is a platform where all data from the Scuba sensors come together. Here specific filters were applied to select only the sensors and parameters relevant for this project. Subsequently, a dataset was exported in the form of an Excel file. This Excel file was converted to a CSV file so that it was functional with the R program for the correlation analysis.

Calibration of the environmental sensors

When the secondary Scuba's readings differ from the in-water Scuba's readings, it was replaced or calibrated. The calibration procedure involves instructing the Scuba with the values it should indicate in a specific calibration situation, where the correct parameter value is known (Table 1). This practically implies the use of a liquid with a known value, which is indicated to the Scuba during immersion in this liquid.

Corrosion probes

For the SOCORRO project, a specific corrosion measurement system has been developed which measures corrosion of three different steel grades (S355, 316L and S235) and a micro-electrochemical cell that measures the rate of corrosion. These measurements are performed every 4 hours.

The working and reference electrodes are housed in a plastic housing filled with epoxy adhesive for protection against sea water. The LPR sensor from CCube (Delft, the Netherlands) has dimensions of 150 mm (length) x 60 mm (height) x 50 mm (width).

The sensor is connected to a separate CCube control box located in an easily accessible position. A potentiostat and a data logger are installed in the control cabinet. In addition, the control box contains a mobile antenna that transmits the measured data to the CCube network.

The company collects all sensor data and sends it to an online database that is accessible to all researchers of the SOCORRO project.

Table 1. Calibration of the different sensors on the Scuba 90

Sensor	Calibration method	Calibration points
Temperature	No calibration needed	Not applicable
pH	Two-/three-points	pH 4, pH 7, pH 10
ORP	1 point	ORP standard 200 mV
Conductivity	1 point	CD standard, 0.5 M, 58670 μ S (brackish – salt water) CD standard, 0.1 M, 12856 μ S (brackish water) CD standard, 0.01 Molar, 1412 μ S (freshwater) CD standard, 0.001 Molar, 147 μ S (fresh/glacial water)
Dissolved oxygen	1 point	100% saturated distilled water (shaken heavily to saturate water with O ₂)

Sensor box

A sealed electrical distribution box was designed and built within the SOCORRO partnership to power the sensors and support the Scuba while uploading data. To this end, the distribution box is equipped with an internal heating element (Figure 5, 2) to maintain a constant temperature of approximately 15-20 degrees Celsius. This heating element is connected to a thermostat (Figure 5, 3) that controls the activation of the element when the temperature falls below the desired value and switches it off when the maximum temperature is reached. To prevent short circuits and electrical damage to the equipment, the entire distribution box is fitted with fuses (Figure 5, 4). In addition, two CEE 16A plugs (Figure 5, 5) are provided to connect a laptop or other electronic devices on site if necessary.

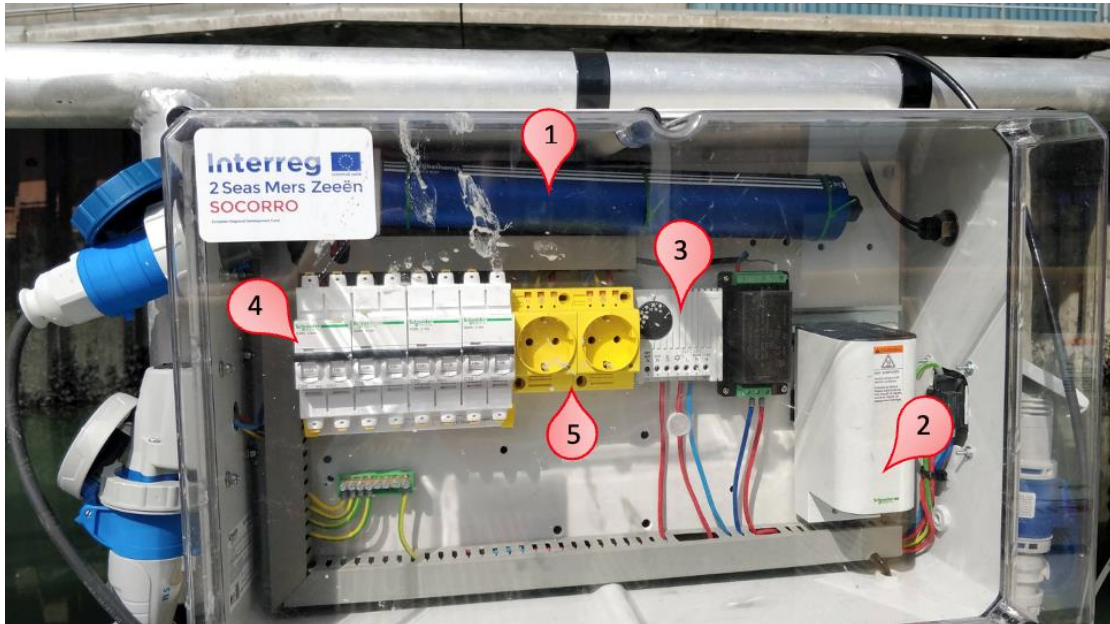


Figure 5. Electrical distribution box for sensors.
 1: 4G modem, 2: internal heating, 3: thermostat, 4: circuit breakers, 5: sockets

Data upload

For this purpose, a 4G modem (Figure 5, 1), namely the GDT-S Prime Plus, is integrated in the system (Figure 46). This allowed the data generated by the Scuba sensors to be initially stored and then forwarded to the GDT server at time intervals set by the user. Via this server, users not only had the possibility to view the data via the internet, but also to adjust the settings of the modem and sensors. This could be done via the Eijkelkamp web portal.

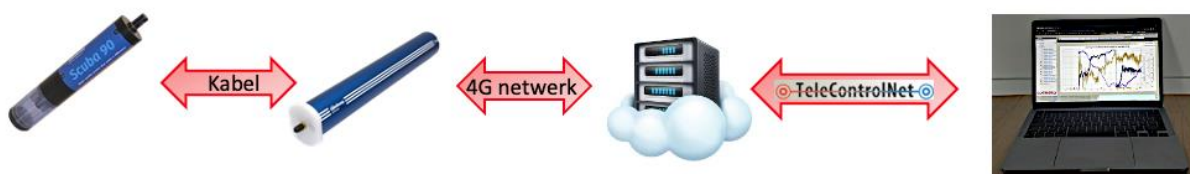


Figure 6. Overview of how data flows from sensor to web portal

Sensor maintenance

To ensure the accuracy of the measurements, it was essential to carry out a thorough maintenance of the sensors. At each visit to the rigs, the sensors were removed from the water and subjected to a thorough visual inspection. It was frequently found that the sensors suffered from biological fouling, which required careful and thorough cleaning. The cleaning process had to be carried out with extreme care to avoid possible damage to the sensors. It was crucial to clean specifically around the sensors and to avoid direct contact with the sensors. For the CCube corrosion probe, it was extremely important to have absolutely no contact with the LPR

sensors, as this would disturb the corrosion layers already present on the sensor, which could affect the measurements.

For the maintenance of the Scuba, the initial concern is the external condition of the device. In particular, the copper protective cover, intended to limit biological growth on the sensors, may need to be replaced. Then the Scuba's current readings were analysed using a secondary Scuba. A bucket was used to carefully collect a sample of water from the immediate vicinity of the setup, at a depth of about 1 meter. The bucket should be handled with care to minimize unwanted oxygen entry into the water. The Scuba was carefully placed in the bucket, to a distance of approximately 10 cm from the bottom, and then connected to a laptop computer running the Scuba Control Software. The direct measurement values could be observed via this software. After a certain period of time, the values stabilized. The software provided the option to copy a data series.

This data set was then compared to the data received from the Scubas in the water, allowing to calibrate or replace the Scuba to be determined. After the calibration procedure, the secondary Scuba was thoroughly rinsed with distilled water to remove any contaminants, and it was then safely stored, fitted with its protective cap, to maintain the integrity of the device.

Baseline measurements of environmental parameters

Seasonal measurements

Water conditions in the canal Ghent-Terneuzen and the marina of Zelzate (Figure 7) are monitored on an annual basis by the Vlaamse Milieumaatschappij (Flemish Environmental Agency, VMM). While there is a slow increase in the salinity of the water in the canal (caused by a heightened influx of seawater, as indicated by the concentrations of both chloride and sulfate), as well as of the dissolved oxygen content of the water, nitrate is on the other hand slowly decreasing over the last 20 years.

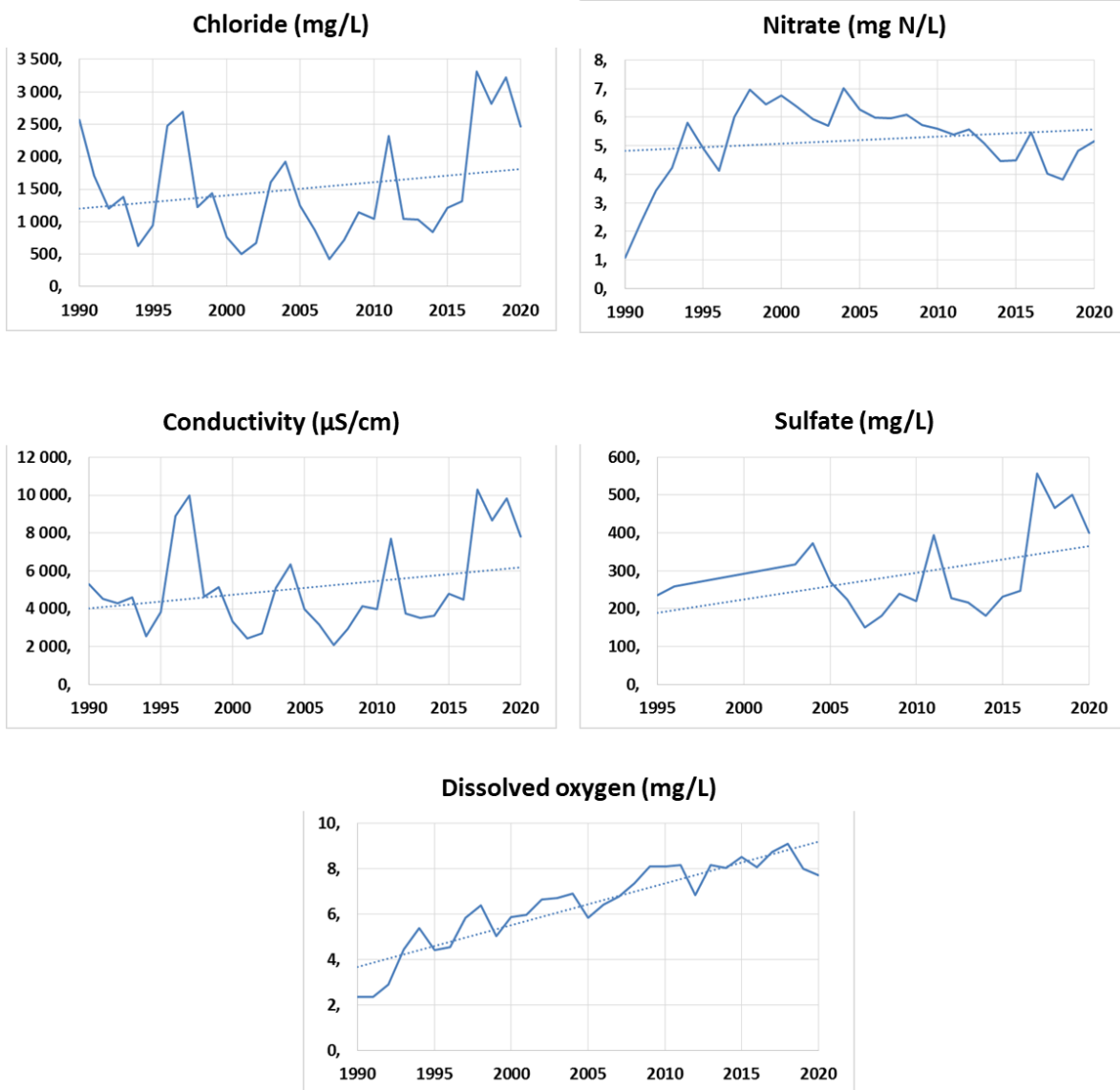


Figure 7. Physicochemical water parameters in the Zelzate marina
 Data obtained from VMM, Flanders.

Presence of corrosive bacteria around the demonstrators

In the spring of 2021, LP1 was contacted by surveyors from insurance companies and pleasure craft owners following some remarkable damage patterns found on several yachts, all moored in the marina of Zelzate. These vessels showed the presence of orange-red tubercles below the waterline (Figure 1). The morphology of these tubercles led us, by elimination, to MIC (Juntao et al., 2015; Phan et al., 2020). After removing the tubercles with grinding wheels and cup brushes, invariably deep corrosions were revealed with a shiny metal surface underneath. Pitting corrosion was found with pits of 3-4 mm deep in several places, developed over a term of (max.) 12 months. The deepest pit was 8 mm deep and was found in a rudderstock that was exactly one year old. Such a high corrosion rate can only be associated with microbially induced corrosion or MIC (Little et al., 2020; Mahlouf, 2018; Yingshao et al., 2020). The morphology also corresponds to what Phan et al., (2020) describe on a series of sheet piles with accelerated corrosion.

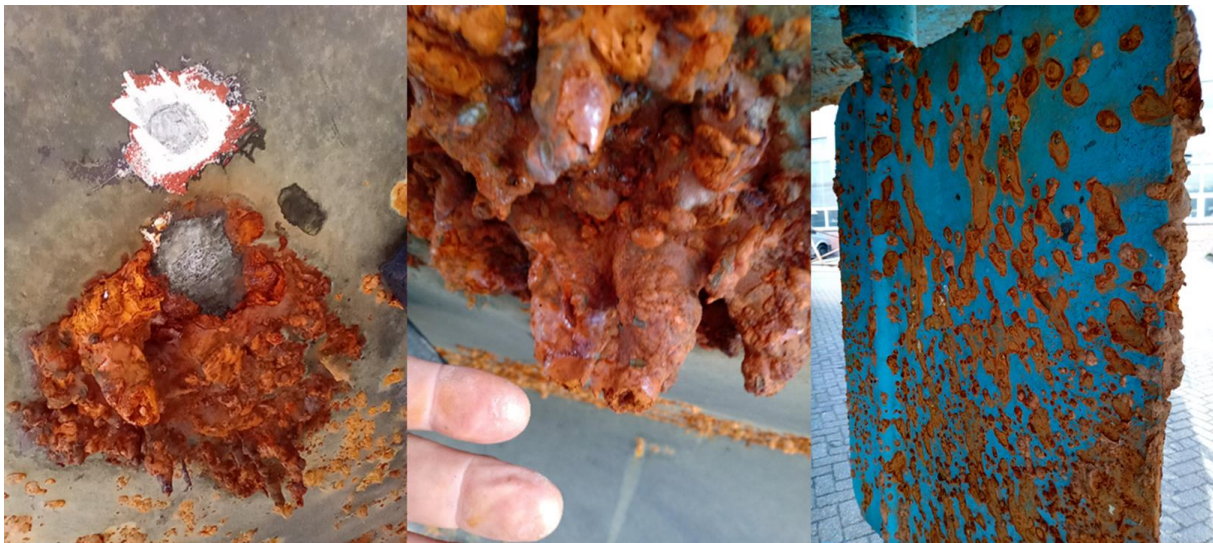


Figure 8. Microbiologically induced corrosion (left, middle) on the underwater hull of a ship docked in the marina of Zelzate, and (right) on the rudder of the ship



pitting corrosion on those plates. The presence of *Gallionella* was also determined in these communities by means of DNA sequence analysis.

- In addition, an accelerated corrosion test was carried out with water from the marina. Electron microscopy measurements demonstrated that the passivation layer disappeared on these plates and that even in this short time, very many small pits appeared in the material.

Several hypotheses can be derived from this information (and the on-site observations): (1) it concerns an exceptional symbiosis of bacteria, (2) an as yet unidentified bacterium is responsible, (3) there may be components in the water responsible for the aggressive behaviour of the water, or (4) a combination of these factors. In order to explain the observed damage, the reaction mechanism behind it must be found. Further research will have to show which hypothesis(es) is (are) correct.

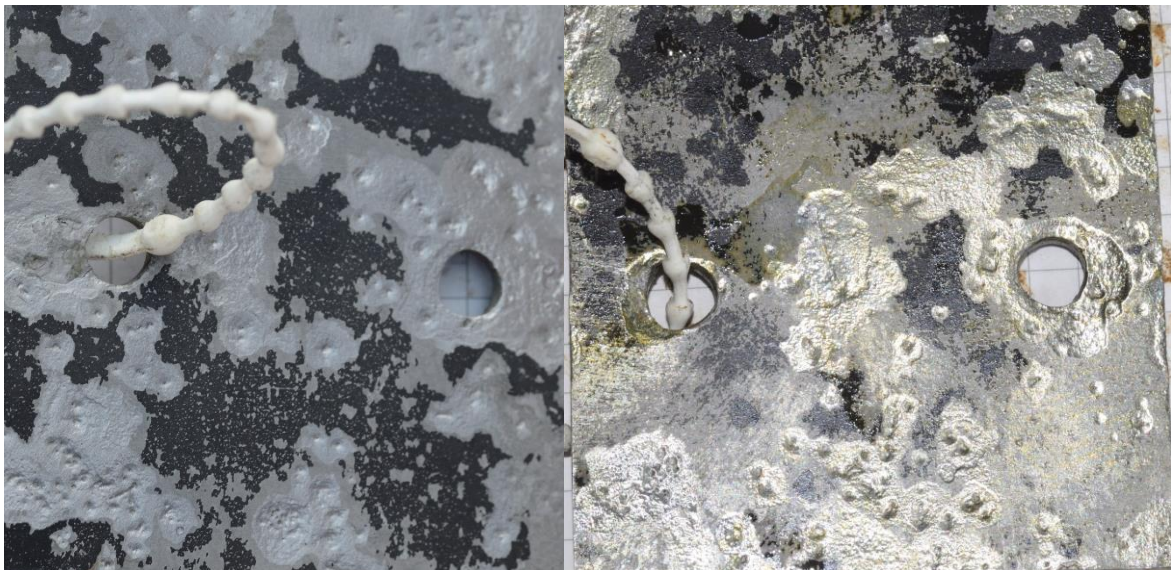


Figure 11. Pitting corrosion on S235 low carbon steel coupons in nearby Sas van Gent after (left) 3 months and (right) 6 months of exposure

Environmental parameters

Temperature (Figure 12) shows an (evident) increase during the measurements, from a value of 7.7°C in March 2023 to a maximum of 18.6°C at the end in June 2023. Both curves follow a similar course.

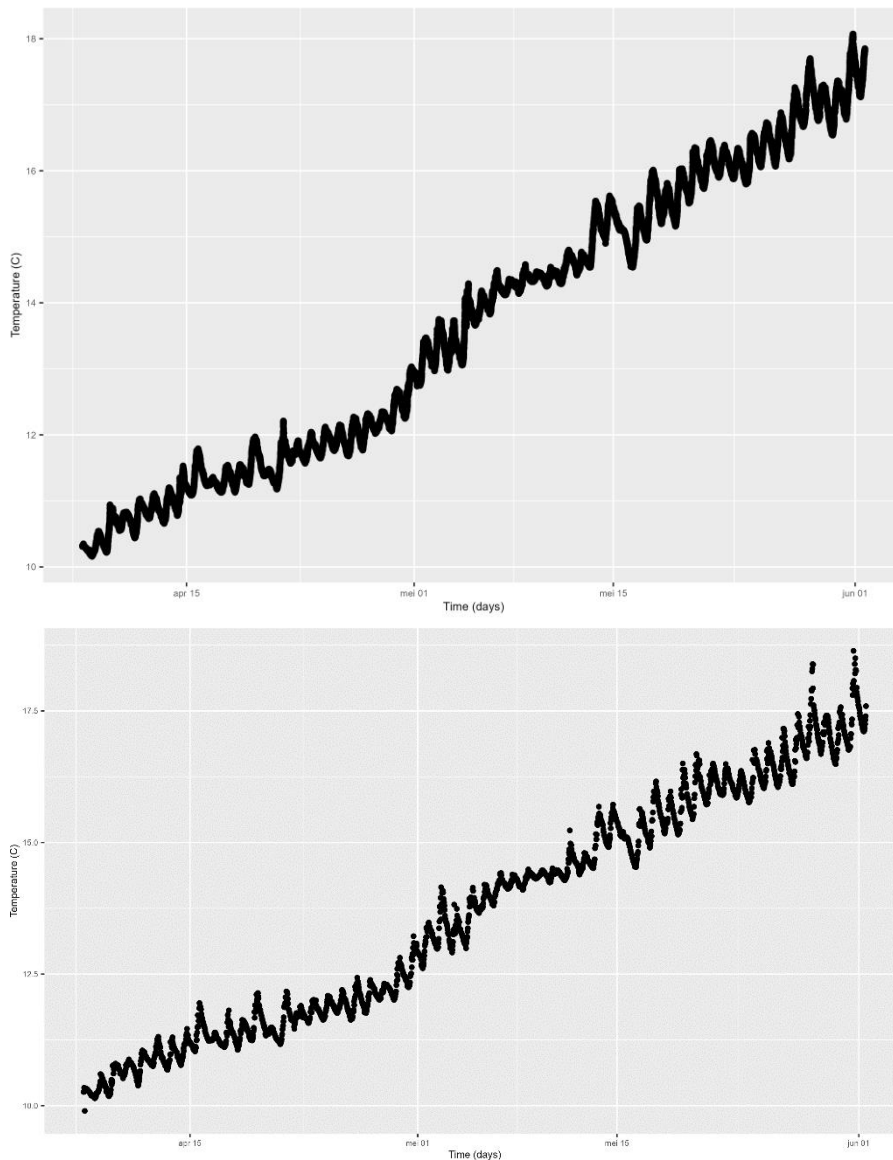


Figure 12. Temperature ,measured at the demonstrator at Zelzate North (top) and South (bottom)

The **dissolved oxygen concentration** (Figure 13) remains fairly constant in the first month, although parameter starts to drop during the month of May and shows a minimum around 20 May 2023 at which a saturation of less than 5 mg/L was reached.

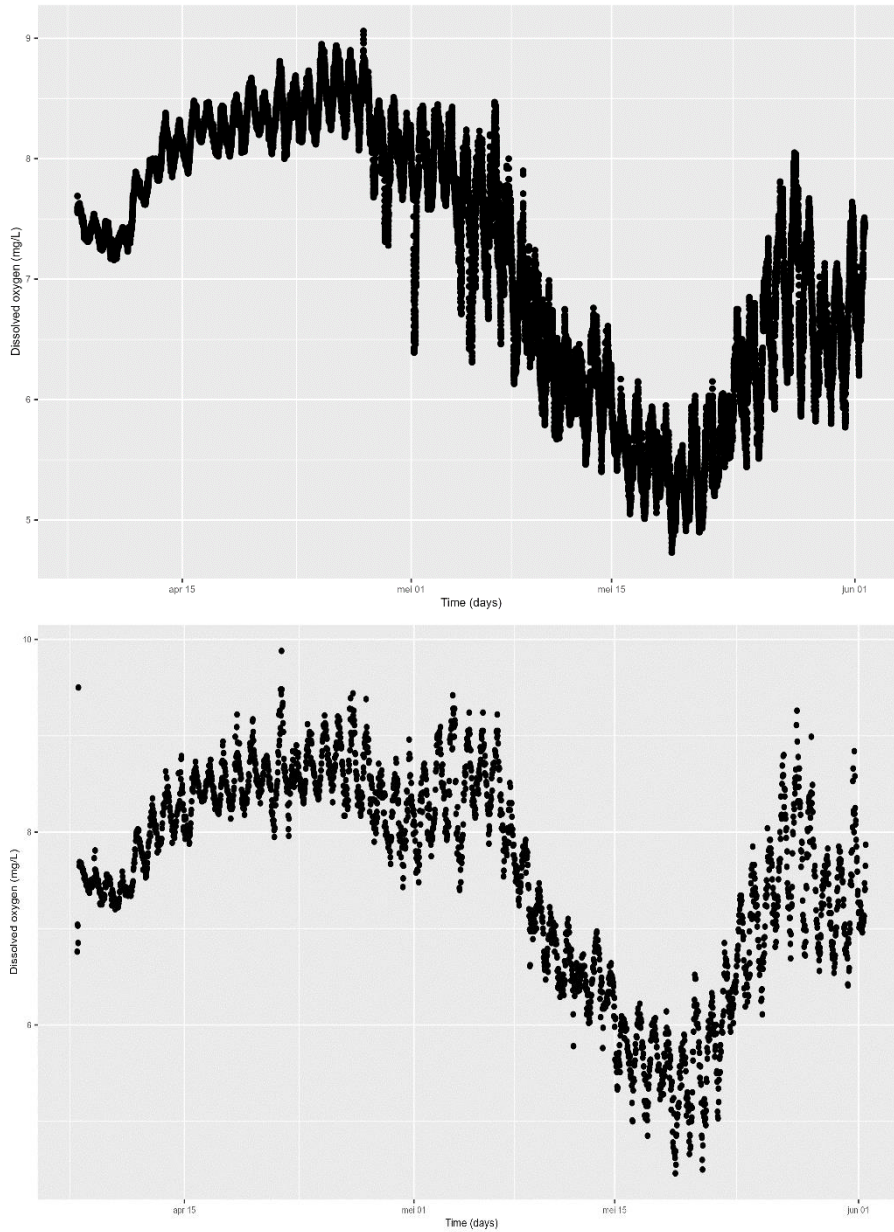


Figure 13. Dissolved oxygen, measured at the demonstrator at Zelzate North (top) and South (bottom)

Conductivity (and the derived value for salinity, see Figure 14 for Zelzate North and Figure 15 for Zelzate South) The maximum of this graph is 9134 and always remains above 5500 $\mu\text{S}/\text{cm}$. The salinity fluctuates between 3.09 and 4. This indicates mainly fresh water.

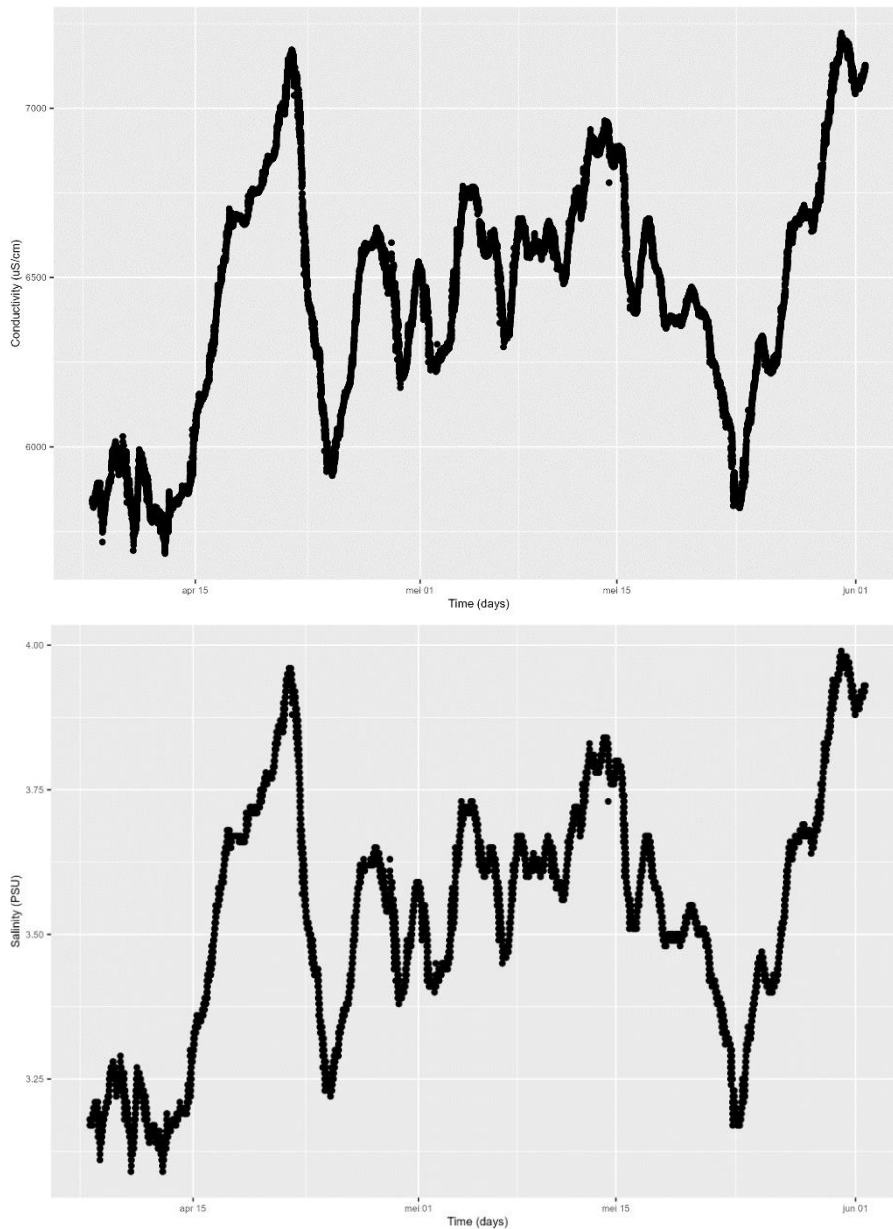


Figure 14. Conductivity (standardised at 25°C; top) and salinity (bottom), measured at the demonstrator at Zelzate North.

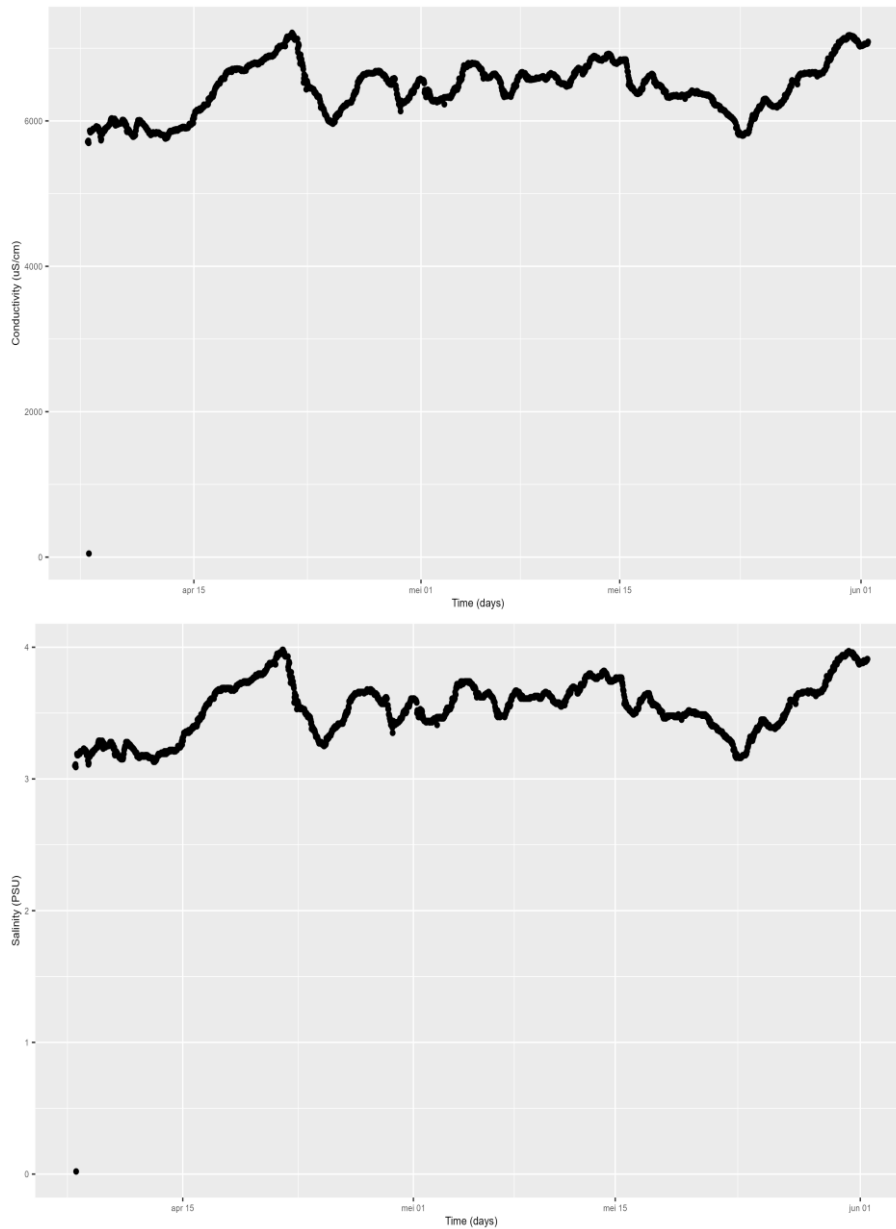


Figure 15. Conductivity (standardised at 25°C; top) and salinity (bottom), measured at the demonstrator at Zelzate South.

The pH values of the water fluctuates between 8 and 8.3, which again indicates the influx of seawater in the canal Ghent-Terneuzen. Pure water has a pH of 7 and seawater has a pH of 8.5, so the pH values of the water in the marina of Zelzate lie somewhere in between.

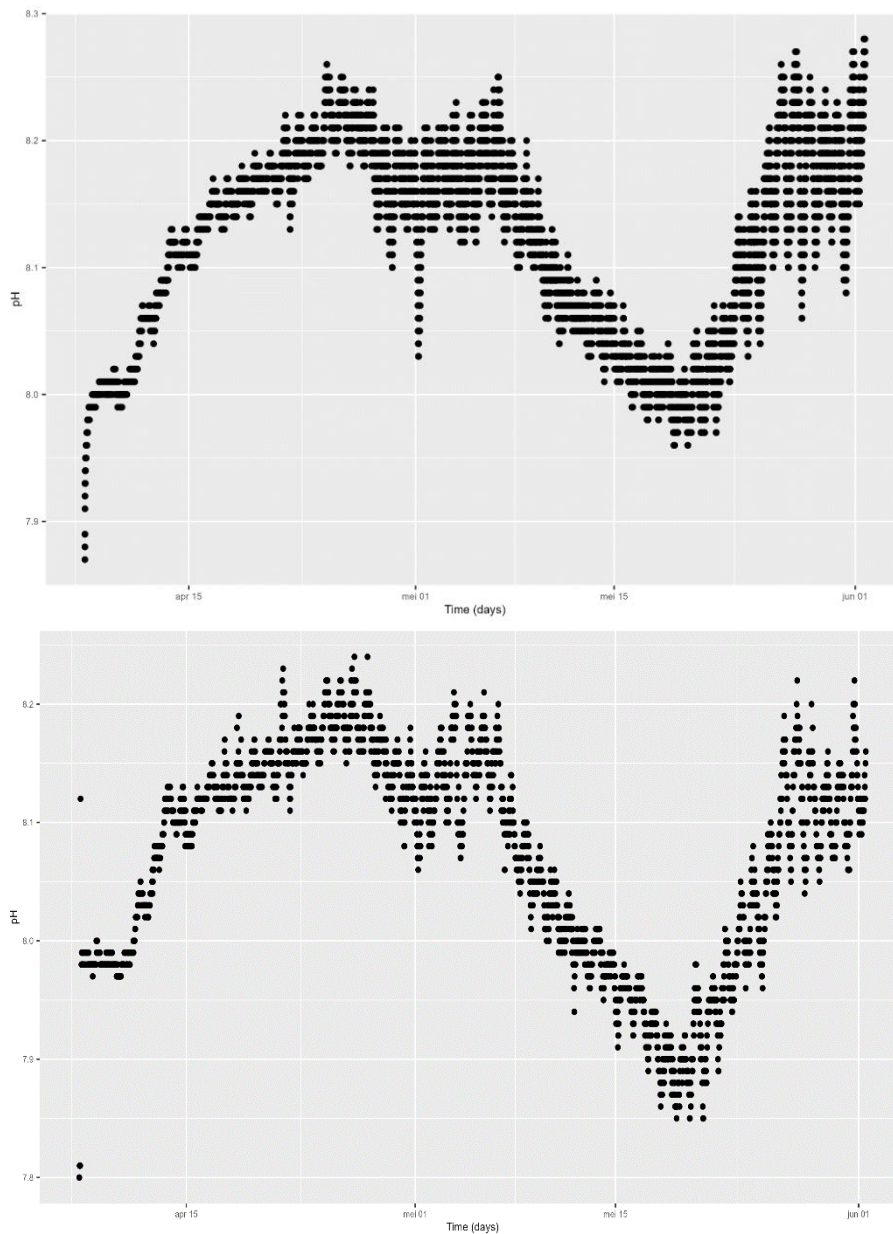


Figure 16. pH, measured at the demonstrator at Zelzate North (top) and South (bottom)

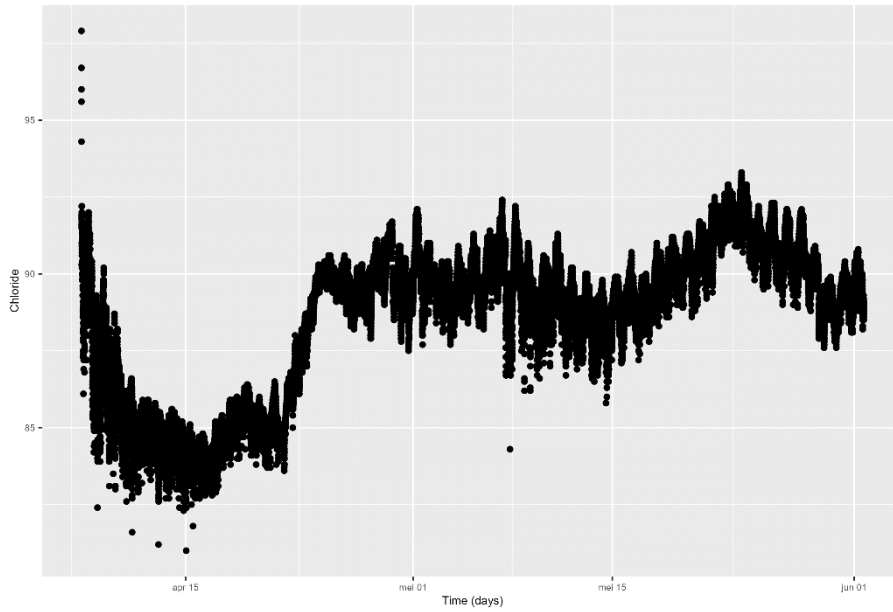


Figure 17. Chloride content, measured at the demonstrator at Zelzate North

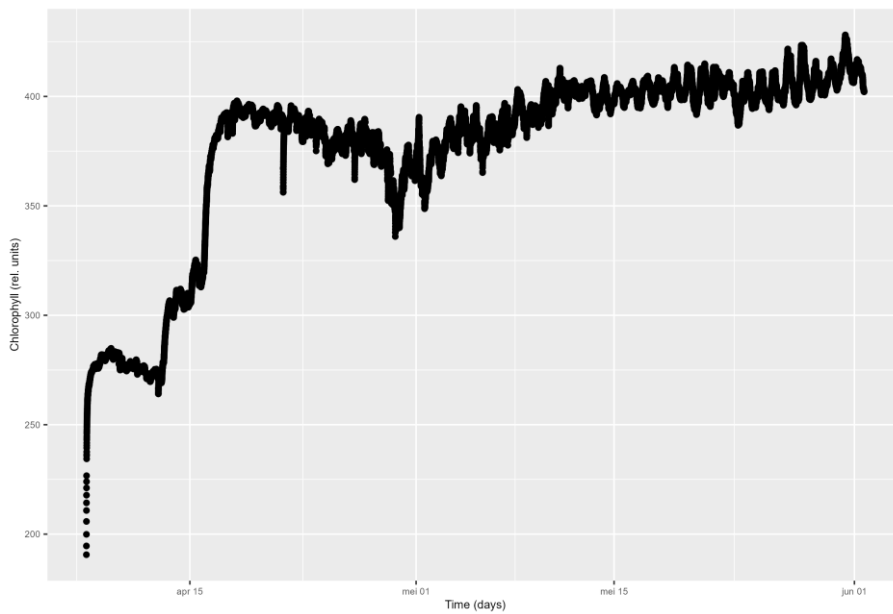


Figure 18. Chlorophyll content, measured at the demonstrator at Zelzate North

Corrosion measurements: experimental methodology

Steel types

Three specific steel types were selected for conducting the experiments: S235, S355 and 316L. In the following paragraphs, these individual steel types will be briefly described, explaining their characteristics and composition.

The first material is **S355 carbon steel**, which meets the European EN 10025:2 standard. This is a structural steel type (indicated by the "S" in the designation, which refers to "structural"). The value "355" stands for the minimum tensile strength of the material (355 MPa, for a sheet thickness of 16 mm). S355 can be classified as "mild steel" because of its relatively low carbon content, which makes it more suitable for welding work (de Jesus et al., 2012). The chemical and mechanical properties of the steel can be compared to those of the American standard variant ASTM A572/A709 (Igwemezie, Mehmanparast, & Kolios, 2018). S355 is widely used in various construction applications, including shipbuilding, bridge components, offshore structures and wind towers (Igwemezie et al., 2018).

S235 carbon steel follows the guidelines of the European Committee for Iron and Steel Standardization (ECISS), with a minimum tensile strength that is slightly lower than that of S355 for an equal thickness.

Both aforementioned structural steels belong to the category of low-carbon steels. The carbon limit for this category has been set at 0.30%, with both S235 with a maximum value of 0.22% C and S355 with a maximum value of 0.23% C more than comply. In addition to the carbon content, the American Iron and Steel Institute (AISI) also looks at the alloying elements in the steel. Since both S235 and S355 have a manganese content of up to 1.60%, they are classified as "plain carbon steel" (Singh, 2020). These classifications and limit values provide insight into the composition and properties of the steels. It is important to note that these low carbon steels will not perform optimally in terms of corrosion resistance. The material does not contain the crucial elements such as copper, chromium or nickel, which are of great importance for corrosion resistance. In the past, this material was available in a pickled and oiled form, which offered some degree of corrosion resistance.

Alloy 316L is a stainless steel with an austenitic structure containing chromium, nickel and molybdenum. The molybdenum improves corrosion resistance and resistance to pitting corrosion caused by chloride ion solutions, which often occur in water. In addition, it also increases strength at high temperatures. To provide protection against corrosion, a thin layer of metal oxides is applied to the surface, which acts as a barrier against corrosive substances. Typically, alloy 316L contains approximately 2-3% molybdenum, 16-18% chromium, 10%-14% nickel, 16-18% chromium, and 0.08% carbon. Other elements can be added to this alloy to modify the properties of the steel. Alloy 316L is widely used in marine equipment, refineries and chemical plants because of its excellent corrosion resistance, especially in highly corrosive environments.

Use of coupons for corrosion measurements

To completely submerge the metal coupons in water, racks were used to which the coupons were attached. To enable this attachment, two 8 mm diameter holes were drilled into the coupons. These holes were then used to securely fasten the coupons to the rack using tie wraps. Color coded tags were used to ensure that the different coupons could be identified throughout the study. These tags were attached individually to each plate, as well as to the rack itself. This made it possible to keep an overview of which coupons were still in the water and which had already been removed from the water. These identification tags were essential to enable proper tracking and analysis of the coupons throughout the research process.

The racks themselves were constructed using cut wire panels (*Figure 19*). This created a rectangular rack consisting of a grid of 3 by 9 compartments, resulting in a total of 27 coupons that could be attached to the rack. The racks themselves were also tagged, which were linked to specific locations. These tags were of a different color so that locations where the racks were used could be identified later. This tagging method was instrumental in maintaining traceability and facilitating the accurate identification of both coupons and racks throughout the research process.



Figure 19. Rack of S355 coupons to be exposed

The racks were attached by means of an eye splice made of three-strand twisted polypropylene rope, whereby the corners of the rack were attached to this rope. To keep the rope from fraying, tie wraps and duct tape were used to hold the ends of the rope together (*Figure 19*). This specific construction method and fasteners ensured a firm and reliable suspension of the racks, allowing the coupons to be attached and submerged in the aquatic environment in a stable and consistent manner during the study.

Depth profile for corrosion

Research by Jeffrey and Melchers (2009) shows that the corrosion in the splash zone was higher than on the parts on the waterline and in the atmosphere. An increased rate of corrosion was also found on the part just below the waterline. Their research was carried out in Australia, where steel strips of 1 meter long were suspended in the water at different heights. This investigation has shown that there is high corrosion around the zone where the steel is 25 cm above and below the waterline. A galvanic cell is created with the anode being the zone under water and the cathode being the zone just above the waterline. This clearly shows that the zone below the waterline (+- 25 cm) is heavily affected and the zone on and just above the waterline is flat. Because this forms a whole, free electron transfer is possible between the two zones. Higher up there is another anodic zone, namely the splash zone. Due to the constant humidity and ventilation, the oxidation of the steel goes smoothly. This again creates a galvanic cell between the relatively anodic splash zone in relation to the higher and less humid atmospheric zone.

The difference between the research described above and that in Zelzate and Sas van Gent is therefore that the steel is connected to each other over the entire depth, which means that the electrons can move freely over the entire depth. The setup of Jeffrey and Melchers also hung in salt water, the water in the Ghent - Terneuzen canal is brackish.

Long strings with coupons were hung in the marinas of Zelzate and nearby Sas van Gent. These strings were made from a plastic chain so that the coupons attached to them did not experience galvanic corrosion. The coupons, made of S235 mild steel, were attached to it at an equal distance from each other. 25 coupons were attached to each pendulum, each of which was weighed three times and provided with its own identification number. The garlands each have a length of 2 meters. The aim is to map the vertical distribution of corrosion as a function of water depth. By always hanging the first coupon above water and the second half submerged, the atmospheric and splash zones are simulated. An attempt was made to give the coupons an orientation when making the garlands. For example, each coupon is marked with a dot stroke in the top right corner. The coupons were mounted on the chains in such a way that they could not rotate a full 180°, but that does not preclude their orientation differing by a few degrees from the intended orientation.

Procedure for coupon measurements

Samples were collected at two, three and six months after the start of the exposure period. Whenever samples were taken, the rack was first taken out of the water to obtain a full picture of the rack. Subsequently, four samples per rack were taken.

Three coupons were thoroughly cleaned with water, dried with paper towels, wrapped in paper towels and placed in a sealed freezer bag with silica gel to prevent further corrosion. One coupon was not cleaned and was placed in a freezer bag without touching it. The purpose of this action was to perform a visual inspection on the coupon in the future. The date and location of sampling were documented on the pouch, after which the pouch was carefully sealed. The rack was then replaced under water.

The coupons were cleaned in accordance with the guidelines set forth in the ASTM G1 standard. After cleaning, the weight loss and corrosion rate of the coupons were evaluated to understand their corrosion behaviour. Measuring the weight loss and corrosion rate provides valuable information about the interaction between the coupon material and the environment in which they are exposed and can serve as an indicator of the durability and performance of the material in corrosive conditions. To determine the corrosion rate based on the mass loss, the corrosion products were first removed from the coupons. For this purpose, the metal coupons were placed in 200 ml 23% hydrochloric acid in glass beakers for 15 minutes. After the acid treatment, the coupons were thoroughly rinsed with demineralized water and dried with paper. To ensure the accuracy of the measurement, it was ensured that the coupons were completely dry before being weighed. At the start and after the cleaning process, the coupons were photographed with the corresponding tags.

Use of the CCube LP sensor

For the SOCORRO project, bespoke sensor systems been developed for corrosion measurement CCube (Delft, the Netherlands). The sensor is based on linear polarization resistance (LP) theory to measure the rate of corrosion. This is achieved by applying small voltages (less than ± 30 mV) to the metal just above and below the corrosion potential. Within this voltage range, the resulting current response is linear if the anodic and cathodic regions are equal (Campos-Silva & Rodríguez-Castro, 2015; Ropital, 2011). This makes it possible to determine the polarization resistance (R_p), which is defined as the slope of the current-potential curve according to the Stern-Geary equation (Stern & Geary, 1957):

$$I_{corr} = \frac{1}{R_p} * \frac{\beta_a * \beta_c}{2.303(\beta_a * \beta_c)}$$

with

$$B = \frac{\beta_a * \beta_c}{2.303(\beta_a * \beta_c)}$$

B is a constant that depends on the anodic and cathodic table diagram (β_a and β_c) obtained from polarization curves. In most cases, the values of β are between 60 and 120 mV (García-Galvan, Fajardo, Barranco, & Feliu, 2021).

$$I_{corr} = \frac{B}{R_p}$$

Faraday's law can then be applied to calculate the corrosion rate as follows:

$$CR = K_1 * \frac{I_{corr}}{dA} * EW$$

whereby CR = corrosion rate in mm/year, $K_1 = 3.27 * 10^{-3}$, d = density in g/cm^3 , EW = the equivalent weight, defined as the mass in grams oxidized by the passage of an electrical charge of 1 Faraday. EW values can be found for different metals in ASTM G102 (García-Galvan et al., 2021).

The CCube uses working electrodes made from the three different steel grades in the project (S355, 316L and S235) and a micro-electrochemical cell that measures the rate of corrosion. These measurements are performed every four hours. The working and reference electrodes are housed in a plastic housing filled with epoxy adhesive for protection against sea water, with dimensions of 150 mm (length) x 60 mm (height) x 50 mm (width).

The sensor is connected to a separate CCube control box located in an easily accessible position. A potentiostat and a data logger are installed in the control cabinet. In addition, the control box contains a mobile antenna that transmits the measured data to the CCube network. The company collects all sensor data and sends it to an online database that is accessible to all researchers of the SOCORRO project.

Corrosion: results

Visual observations

Figure 20 was taken on 8 March 2023 and shows the test coupons after one full month in the water of the marina of Zelzate. There is a dark colored slime layer on the rack, the rope and the pictures. On the plates with alloys S235 and S355 there is a clear orange-brown corrosion product. The 316L stainless plates show no corrosion.



Figure 20. Coupons after 1 month exposure in Zelzate North (February 2023). Yellow labeled plates are S355 alloy and white labeled plates are the S235 alloy. Red labels indicate 316L.

Table 2. Corrosion rate determinations per alloy, location and exposure duration. Values \pm standard error ($n = 3$). “”: $p < 0.01$; *** $p < 0.001$

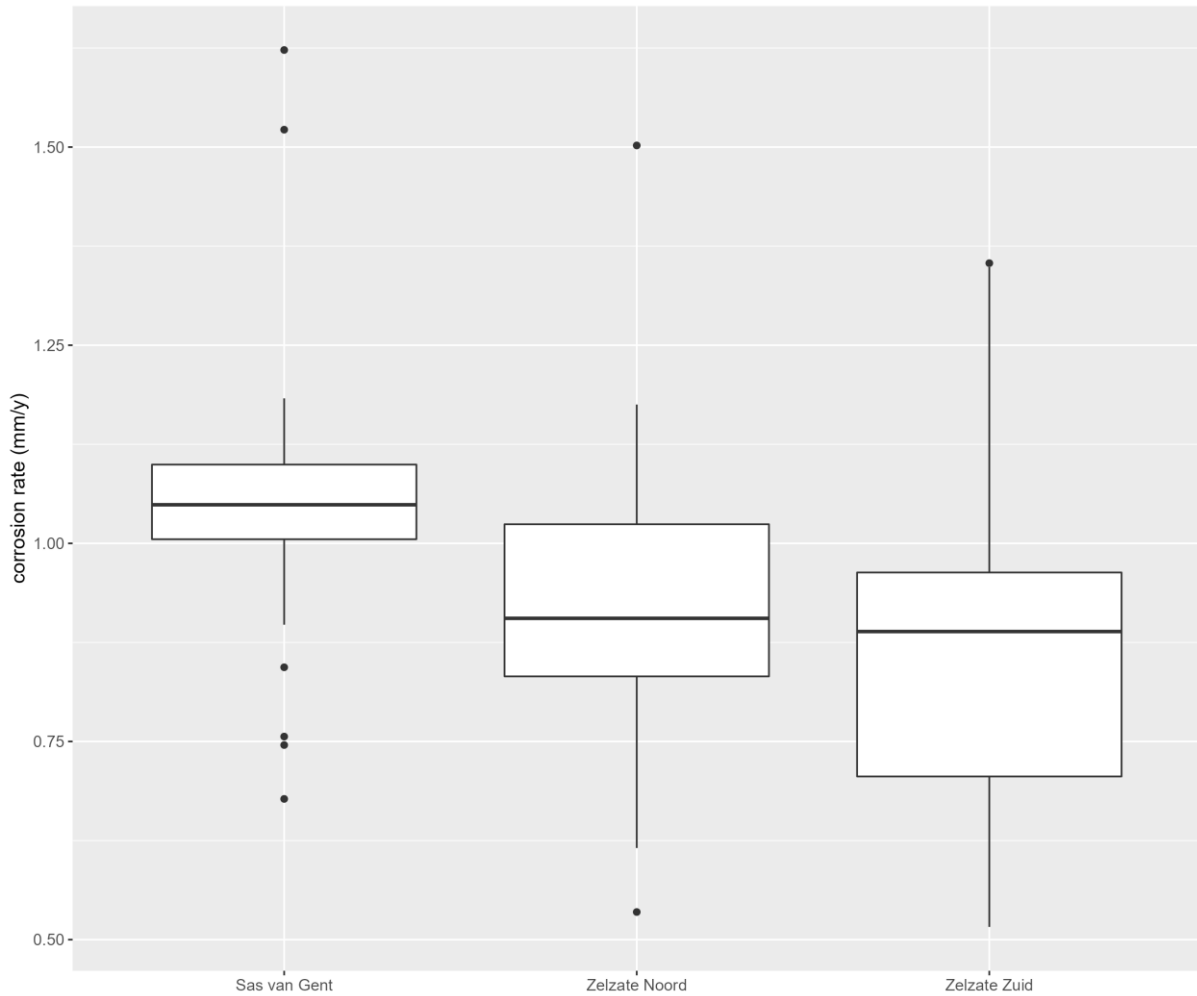
Alloy and location	Average corrosion rate (mm/year)		
	One month exposure (Feb 2023)	Two months exposure (Feb-March 2023)	One month exposure (April 2023)
316L North	0,001 \pm 0,001	0,000 \pm 0,000	0,001 \pm 0,001
316L South	0,001 \pm 0,001	0,001 \pm 0,001	0,002 \pm 0,000
S355 North	0,587 \pm 0,017	0,51 \pm 0,04	0,648 \pm 0,014
S355 South	0,544 \pm 0,027	0,51 \pm 0,04	0,621 \pm 0,025
S235 North	0,462 \pm 0,023	0,399 \pm 0,006	0,515 \pm 0,012
S235 South	0,347 \pm 0,005 **	0,314 \pm 0,007 ***	0,411 \pm 0,016 **

Coupon measurements

The average corrosion rates for the three alloys, for exposure for one or two months in The average corrosion rate for the alloy 316L is very small (0.001 millimeters per year). The corrosion rates for both carbon steels are much higher, with S355 in particular corroding quickly (between 0.51 and 0.648 mm/y). Corrosion is just as fast for S355 coupons on the north side as on the south side. Only for S235 is there a difference in corrosion rate between the north side of the marina and the south side, with the average mass loss on the north side being higher than in the south, for the three time periods.

Comparison with different S235 coupons¹, in a separate experiment that was meant to look at differences in depth at both Zelzate locations and nearby Sas van Gent (Netherlands) indicates that coupons at Sas van Gent corroded significantly faster than the ones in Zelzate ($p < 0.005$), whereas here, there was no difference between both Zelzate locations.

¹ The large differences in corrosion rate as well as in behaviour between this experiment and the previous one, even though we were using S235 coupons in both experiments, were noted after conclusion of the measurements. It was only then that we saw that this batch of coupons had not been sandblasted and still sported a mill scale layer on top. This may have distorted the corrosion processes.



A linear model analysis on these data, comparing the effect of both depth and location, indicated that depth of the coupons did not affect corrosion rate. However, we noted also that a few coupons, located right above the water, in the so-called splash zone, corroded faster than their submerged counterparts (data not shown).

Corrosion rates obtained through LP measurements

LP measurements in the brackish water of the Zelzate marina are generally underestimating corrosion rates, with an average of 0.0175 – 0.02 mm/year for S235 on the North side for April (Figure 21, top) compared to the 0.515 mm/year as determined by the coupon measurements (Table 2), or an average of 0.075 mm/year for the South demonstrator (Figure 21, bottom), compared to the 0.411 mm/year for coupons (Table 2).

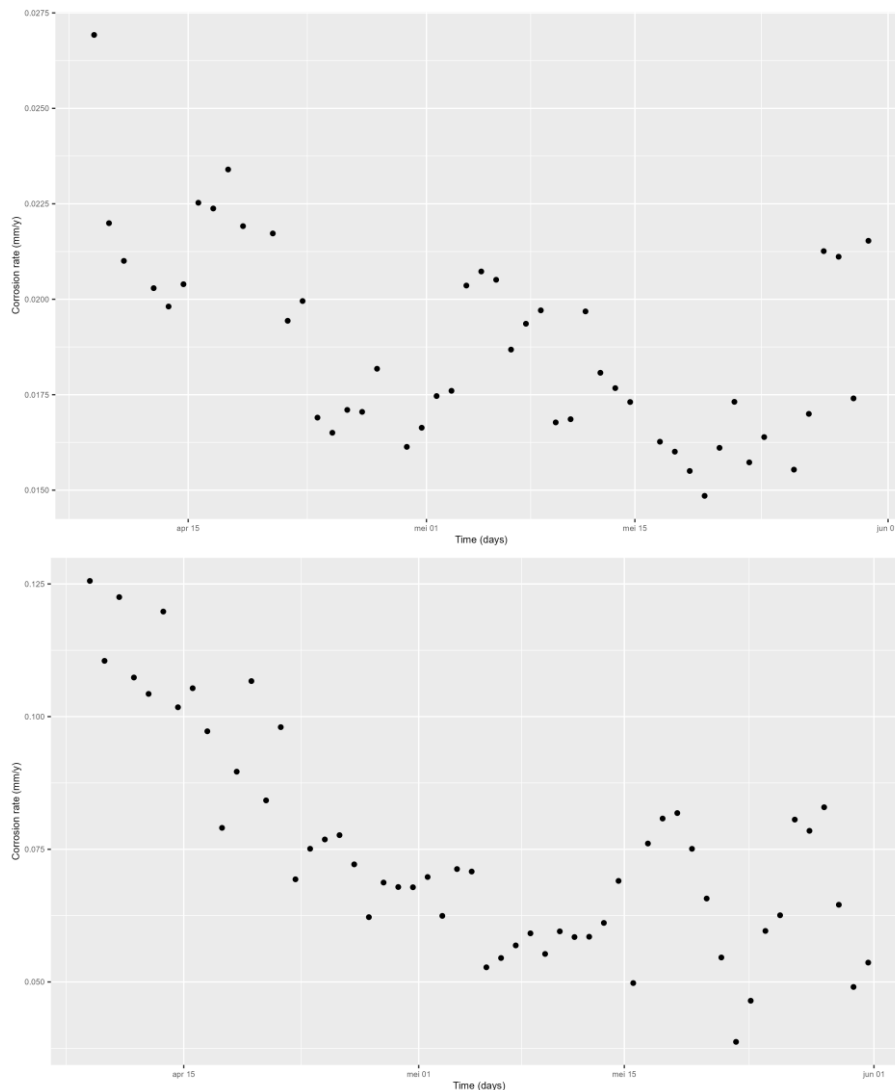


Figure 21. Corrosion of S235, measured at the demonstrator at Zelzate North (top) and South (bottom)

Pairwise correlations between parameters

The principal component analysis for Zelzate North (Figure 22, left graph), where extra environmental parameters were measured, shows a close correlation between dissolved oxygen, ORP and S235 corrosion, confirmed (though not entirely) by the one-to-one correlations on Figure 23 (where we see a correlation of 0.408 between dissolved oxygen and corrosion, and a correlation of 0.565 between ORP and corrosion). We also see two inverse correlations between corrosion and temperature or chloride, confirmed (though again not entirely) by the one-to-one correlations on Figure 23 (where we see a correlation of -0.607 between chloride and corrosion, and a more curious correlation -0.496 between temperature and corrosion). Neither pH nor conductivity/salinity were correlated with corrosion at all at the Zelzate North demonstration (R values of resp. 0.069, 0.010 and 0.009). The inverse correlation (R = -0.714) between temperature and dissolved oxygen could be expected (as the solubility of oxygen in water decreases with temperature), as well as the correlation between biological life (indicated by the chlorophyll parameter) and temperature (R = 0.699). There is also a curious correlation between dissolved oxygen and pH (R = 0.728), between conductivity and chlorophyll (R = 0.700) and an inverse relation between ORP and chloride content (-0.963). These cannot be explained for the moment.

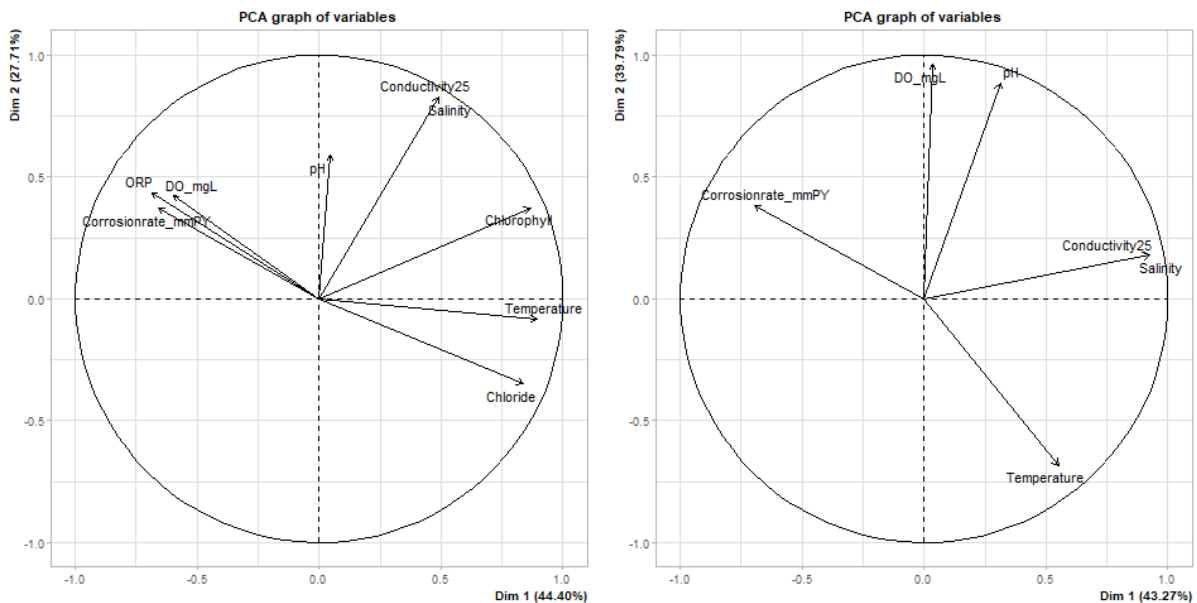


Figure 22. PCA analysis for the S235 corrosion rate and the environmental parameters measured at the demonstrator at Zelzate North (left) and South (right)

Analysis of the data at Zelzate South (Figure 22, right; Figure 24) show the same close correlation between dissolved oxygen and pH (R= 0.935) as well as the inverse relation between temperature and dissolved oxygen (R = -0.539). The corrosion rate is again curiously inversely related to temperature (R = -0.664) and conductivity measurements (R = -0.404). Corrosion is not correlated with dissolved oxygen and pH.

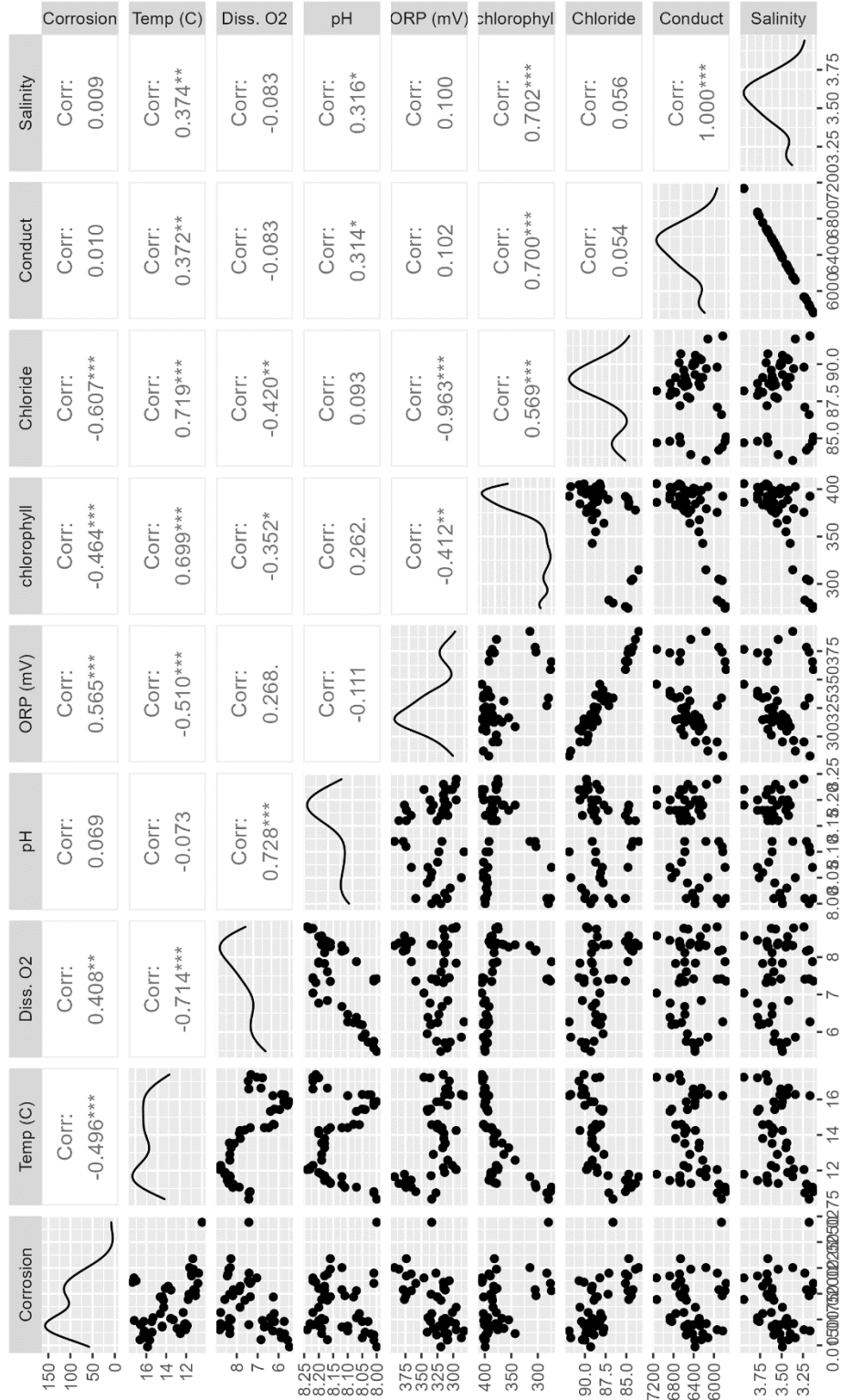


Figure 23. Pairwise correlations between the different environmental parameters and S235 corrosion (as measured by LP) for Zelzate North.

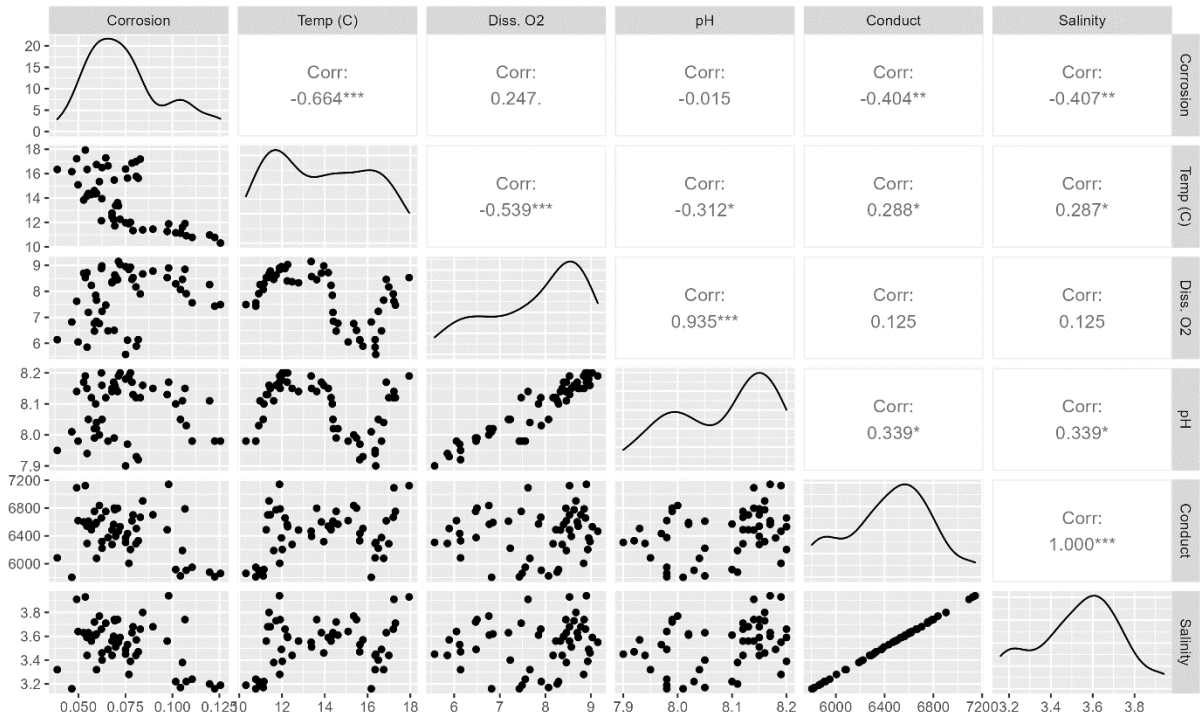
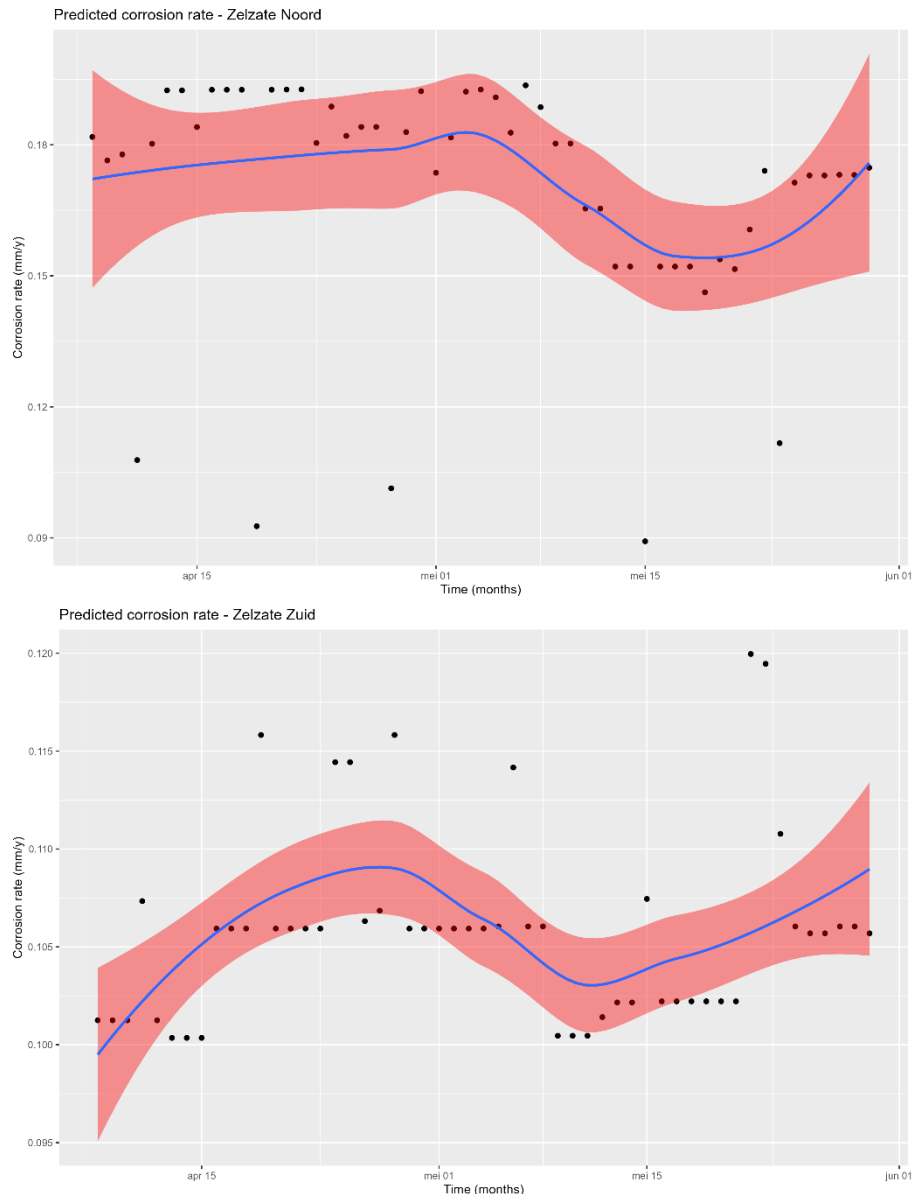


Figure 24. Pairwise correlations between the different environmental parameters and S235 corrosion (as measured by LP) for Zelzate North.

Use of the SOCORRO approach

To test the SOCORRO algorithm, the environmental parameters for Zelzate North and South were uploaded in the SOCORRO app (<https://app-c14q.onrender.com/>) and two models were chosen, the Seawater, Lab Trained model and the Seawater, Field Trained model.



*Figure 25. Predicted corrosion rates at Zelzate North (Sea water, lab trained model, top) and Zelzate South (Sea water, Field trained model, bottom)
 Blue line gives a loess regression line for the dataset with a red 95% confidentiality zone.*

Both models gave essentially the same outcome for each of the locations. The outcome for Zelzate North (Sea water, lab trained model, Figure 25 top) is significantly higher than the outcome of the sensor data and still significantly lower than the coupon data.

On the other hand, the average corrosion rate predicted for Zelzate South (Sea water, Field trained model, Figure 25 bottom) fits nicely with the data as measured by the LP probe (again, still significantly lower than the coupon data).

Plans for further use?

The Zelzate demonstrations are already being used in a new project as part of the Flemish TETRA project COMIC on the effect of the presence of corrosive microbial species on industrial assets. LP1, PP2 and PP3 collaborate here together with Endures (PP13); PP5 is part of the industrial committee.

In this project, the demonstrators will be expanded to analyse different ways to inhibit corrosion (and to protect industrial assets). This will not only help to optimise the demonstrator at Zelzate, but also to validate other outputs of the project (O6, the LCA and LCCA analyses). Given the large industrial committee, this will help us to present the outputs of SOCORRO to a larger audience.