# DEMONSTATION AT WASTEWATER TREATMENT PLANT

## Why this location

A wastewater treatment plant is a facility that removes contaminants from wastewater, making it safe to be released into the environment or reused. The treatment process involves physical, chemical, and biological treatment methods to remove pollutants such as organic matter, nutrients, bacteria, and pathogens. The industrial wastewater treatment plant being studied for work package 2 is located in Vilvoorde, at the company PB Leiner (https://www.pbleiner.com/en). PB leiner, also better known as PB gelatins, is a company within the Tessenderlo group that is specialized in the production of gelatin. This gelatin is a key ingredient for candy. Bones from animal origin are brought to PB Leiner by big trucks. In the chemical plant, gelatin is extracted from the bones by the use of strong acids (hydrochloric acid being the most important one). The wastewater is collected from the plant and send to the wastewater treatment plant, with a flow of a 7000 $m^3$ per day. The inlet of the wastewater treatment plant has an automated screw feeder. This ensures that if solid particles are present in the wastewater (like remnants of the bones), it is not blocking the inlet of the plant. The wastewater first passes through a DAF, an abbreviation for a dissolved air flotation. A strong flow of air at the bottom of the installation blows solid particles to the top surface, where it floats and where it is automatically removed. Common particles that are removed by the DAF are sand and fat particles inside the wastewater. After the DAF, the wastewater still has a low pH, somewhere between 3 and 8. The pH of in the inlet varies strongly due to the chemical (acidic) extraction of gelatin. To ensure a neutral pH, concentrated lime (calciumhydroxide) is added to the wastewater. When the pH is stable, around values of 6-7, the wastewater goes to the biological treatment where ammonium, nitrate and nitrite are converted to nitrogen gas. When the wastewater is aerated intensively, the ammonium is oxidized to nitrate (nitrification). Every 6 hours, the aeration inside the biological section is stopped. The redox potential drops significantly (to values of -200mV) and denitrification will occur. In this anoxic step, residual nitrate is converted to nitrogen gas. After the nitrification/denitrification process, the sludge is removed from the wastewater by a filter belt press. The wastewater is not harmful anymore and can be released into the environment (River Zenne).

***Figure: The site of PB Leiner in Vilvoorde with the wastewater treatment plant marked in yellow.***

Hydrochloric acid is used intensively in the gelatin extraction process. It is unavoidable that a small amount of the hydrochloric acid goes to the wastewater plant. Even when it neutralized by lime, the chlorides of the hydrochloric acid are still present in the wastewater. Hence, the wastewater of PB Leiner has a high chloride content of approximately 4000ppm. Such chloride concentrations can be considered as a maximum limit for biological treatment. Higher concentration of chlorides should be treated with a physico-chemical installation.

The wastewater treatment plant of PB Leiner works at an elevated temperature of 30°C. This ensures a high removal of nitrate, nitrite and ammonium. The high temperature and chloride content also create aggressive and corrosive conditions for the plant and the process equipment. Process engineers tell that corrosion resistant materials were used to build to plant, however, corrosion phenomena still occur. A good industrial site to measure corrosion/environmental parameters and see whether the Socorro AI model is able to predict the corrosion risk for this installation.

## Baseline/starting situation

Although the process engineers specified that corrosion resistant materials where used in their (wastewater treatment) plant, they don't have any information about the alloy type. From the Antwerp Maritime Academy, a portable XRF analyzer (Olympus Delta) was borrowed to investigate the used materials on-site. The XRF analyzer fires an (unharmful) X-ray beam to the material of interest. Characteristic X-rays are emitted by the sample and are measured by the XRF. From those measurements, the XRF analyzer can determine the chemical composition of the alloy. The XRF runs on Olympus software that automatically compares the found spectra with its internal database.

17 locations/parts of the wasterwater treatment were analyzed, the measurements can be found in table. Pipelines for aeration (section nitrification/denitrification) and the filter belt press are made out of AISI 304 and AISI 316 stainless steel. Most of flanges, pumps and valves in the nitrification/denitrification section are built out of carbon steel (with blue paint to protect it for

corrosion). Samples were taken from the nitrification/denitrification section and used to perform electrochemical tests. The chemical composition of the wastewater is shown in table. The accelerated tests should indicate that the materials, that are currently being used in PB Leiner, have sufficient corrosion resistance. Cyclic polarization curves were conducted in the wastewater. A potential was applied to the working electrode (material of interested), with respect to the used reference electrode (Ag/AgCl electrode). The current (density) is measured when the potential is step-wise increased with a rate of 600mV/h. If an exponential increase in current density is noticed, before the maximal potential of 1.2V, the material is susceptible to localized corrosion in the studied environment (i.e. wastewater of PB Leiner, section nitrification/denitrification). The results of the cyclic polarization curves are presented in figure.

***Table: Chemical composition (mean values) of the wastewater of the nitrification/denitrification section of PB Leiner***

| pH | Temp. (in °C) | $NO_3^-$ (in ppm) | $Cl^-$ (in ppm) | $SO_4^{2-}$ (in ppm) |
|---|---|---|---|---|
| 5.37 | 30 | 9±3 | 4324±230 | 503±37 |

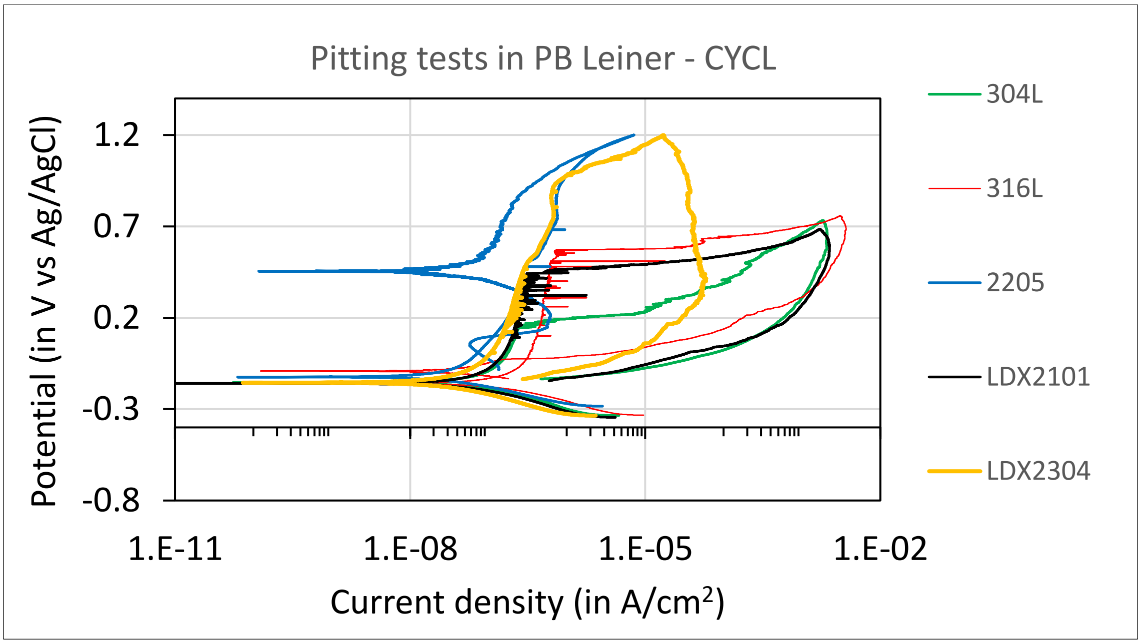



***Figure: Cyclic polarization curves of commonly used stainless steels in the wastewater of PB Leiner.***

The cyclic polarization plots of AISI 304 and AISI 316 show a strong increase in current density at a potential 160 and 577mV, respectively. It is therefore concluded that AISI 304 and AISI 316 stainless steel both show tendency to pit in the wastewater of PB Leiner. Even lean-duplex stainless steels (LDX2101 and LDX2304), a cheaper but more corrosion-resistant alternative for conventional stainless steels,  also show problems towards pitting. The only tested material that doesn't have problems in the wastewater, is a regular duplex stainless steel (DX2205). Microscopic analysis on the tested samples was performed, the SEM images are shown in figure.

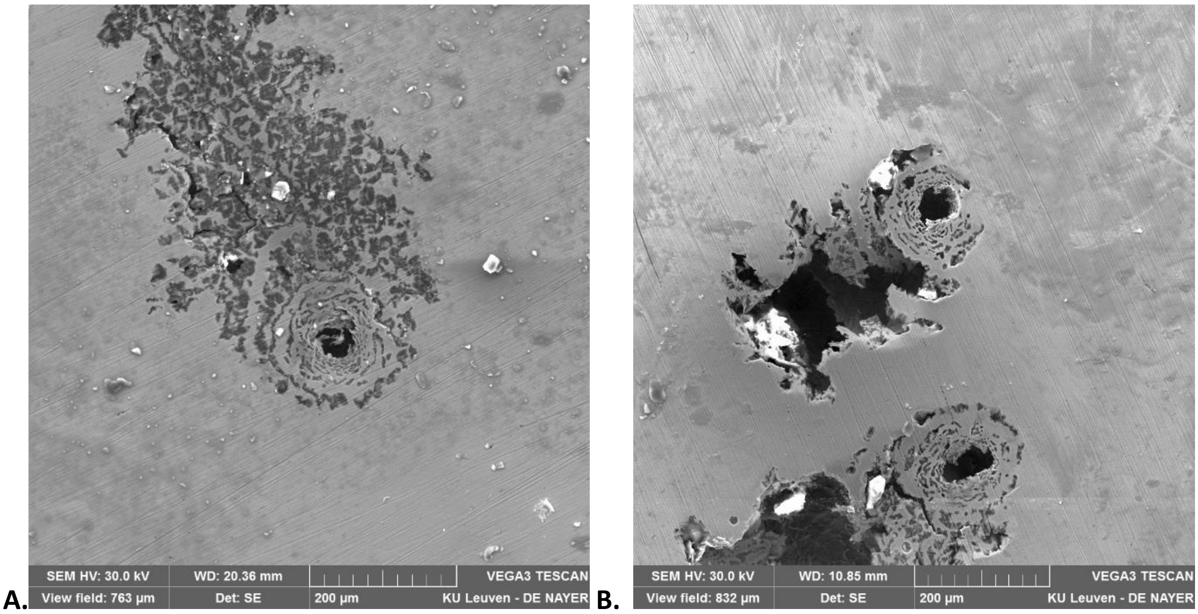



***Figure: Pitting corrosion found after polarization in the PB Leiner wastewater for A) AISI 304 and B) AISI 316***

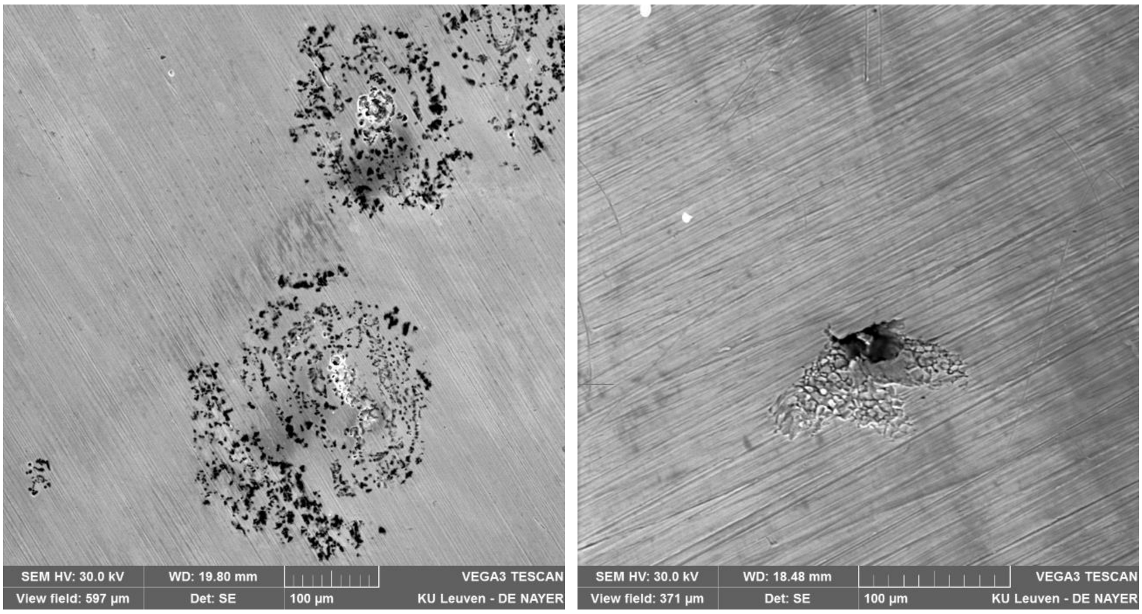



***Figure: Pitting corrosion found after polarization in the PB Leiner wastewater for A) LDX2101 and B) LDX2304***


***Figure: No pitting corrosion found after polarization in the PB Leiner wastewater for DX2205.***

A lot of chemical companies use AISI 304 or AISI 316 to build wastewater treatment plants. For both alloys, there is a lot of knowledge about surface treatment, machinability and weldability. Hence, the use of those stainless steels is a straight-forward choice. However, for very corrosive environments, those materials can still be unsuitable. PB Leiner was therefore interested to gain more knowledge about the corrosion performance of materials used in their process. The Socorro AI model predicts corrosion risk for 3 materials: Grade A carbon steel, S355 structural carbon steel and an AISI 316L stainless steel. The last grade is the material where PB Leiner is mostly interested in.

| Part of the installation | # | Alloy? | Fe | Cr | Ni | Mo | S | Si | Mn | Al | Cu | Zn | Co | P | Pb | V | Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pipeline for aeration | 1 | AISI 304 | 67.1 | 17.8 | 8.3 | 0 | 0 | 2.9 | 1.5 | 1.3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Pipeline for aeration | 2 | AISI304 | 69.3 | 18.0 | 8.5 | 0 | 0 | 1.9 | 1.4 | 0 | 0 | 0 | 0.5 | 0 | 0 | 0 | 0 |
| Flange | 3 | NA | 79.1 | 0 | 0 | 0 | 5.2 | 4.5 | 0 | 0 | 1.3 | 0 | 1.4 | 0 | 0 | 0 | 5.6 |
| Pipeline | 4 | AISI316 | 67.5 | 16.5 | 10.4 | 1.95 | 0 | 1.7 | 0.9 | 0 | 0 | 0 | 0.47 | 0 | 0 | 0 | 0 |
| Valve | 5 | Cast iron | 81.4 | 0.04 | 0 | 0 | 0 | 11.5 | 0.4 | 0 | 0.74 | 0 | 2.1 | 0 | 0 | 0 | 3.8 |
| Clarifier – tank | 6 | AIS304 | 68.9 | 16.9 | 8.3 | 0 | 0 | 1.7 | 1.4 | 0 | 0 | 0 | 0.63 | 0 | 0 | 0 | 0 |
| Clarifier – bridge | 7 | NA | 1.24 | 3.8 | 0 | 0 | 0 | 9.03 | 0 | 0 | 0 | 0 | 0 | 2.1 | 53.73 | 10.23 | 17.8 |
| Clarifier – pump | 8 | Steel + paint | 79.73 | 0 | 0 | 0 | 0.5 | 7.9 | 0 | 2.4 | 0 | 5.6 | 0 | 2.1 | 0 | 0 | 0 |
| Clarifier – pipeline | 9 | NA | 9 | 0 | 0 | 0 | 12.2 | 21 | 0 | 0 | 0 | 3.4 | 0 | 9,21 | 0 | 0 | 44.9 |
| Storage tank | 10 | NA | 47.1 | 0 | 0 | 0 | 0 | 0 | 0 | 7.9 | 0 | 9.6 | 1.9 | 0 | 0 | 0 | 31.7 |
| Pipeline dosage lime | 11 | AISI316 | 65.7 | 15.6 | 10.99 | 2.28 | 0 | 2.2 | 1.61 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Structural beam | 12 | Steel + paint | 20.1 | 0 | 0 | 0 | 0 | 1.97 | 0 | 0 | 0 | 4.8 | 1.87 | 1,32 | 1.42 | 0 | 67.4 |
| Pipeline with insulation | 13 | Aluminium 4XXX | 0.3 | 0 | 0 | 0 | 0 | 8.7 | 0 | 91 | 0 | 0.009 | 0 | 0 | 0 | 0 | 0 |
| Filter belt press – pipeline | 14 | AISI316 | 67.5 | 15.8 | 10.7 | 2.3 | 0.5 | 0 | 1.83 | 0 | 0.4 | 0 | 0 | 0 | 0 | 0 | 0 |
| Filter belt press – valve | 15 | Brass | 0.119 | 0 | 2.3 | 0 | 0 | 0.06 | 0 | 0 | 52.4 | 43.1 | 0 | 0 | 2.02 | 0 | 0 |
| Filter belt press – flange | 16 | AISI316 | 46.7 | 7.5 | 8.8 | 6.3 | 1.77 | 16.9 | 0 | 0 | 0 | 0 | 0 | 7.9 | 0 | 0 | 0 |

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Filter belt press – socket | 17 | AISI316 | 59.5 | 12.1 | 10.2 | 4.4 | 2.88 | 0 | 0 | 0 | 0 | 0 | 1.75 | 0 | 0 | 0 | 0 |






| | | | | | |
|---|---|---|---|---|---|
| **1** | **2** | **3** | **4** | **5** | **6** |

| | | | | | |
|---|---|---|---|---|---|
| **7** | **8** | **9** | **10** | **11** | **12** |





| | | | | |
|---|---|---|---|---|
| **13** | **14** | **15** | **16** | **17** |

## Construction

The wastewater treatment plant of PB Leiner is able to treat ±7000m³ per day. To ensure that all water quality parameters are OK to release into the environment, many probes are inserted into the concrete basin. The efficiency of the nitrification/denitrification are checked by titration experiments in the lab. Installing nitrate sensors was before, the sensors are unreliable when used in their aggressive wastewater. A few DO sensors are installed, but other than that, not a lot of other environmental sensors are present. To validate the Socorro AI model, the field demonstration dataset should contain the same environmental parameters as the dataset used for training. Hence, a Scuba 65 environmental probe was installed in the nitrification/denitrification section. The Scuba probe is more robust than the previous Aquaread probes. Other partners of WP2 are using a similar environmental probe. A scuba 65 probe normally runs on battery packs. Every 2-3 weeks, the battery packs should be changed by charged ones. Antwerp Maritime Academy adapted the Scuba 65 proces so that they could run on 230V. The Scuba probe is connected to an electrical box. The box supplies power to the Scuba and in addition, the data is logged to an Eijkelkamp modem. The Eijkelkamp probe was calibrated before its installation. Regular checks were performed to see if the probes were not damages because of the high flow inside the wastewater treatment plant. Next to an environmental probe, a C-Cube LPR sensor was installed to follow-up the corrosion rates of a grade A carbon steel, a S355 structural carbon steel and an AISI 316L stainless steel. Every 6 hours, a non-destructive LPR measurement is performed and corrosion rates are calculated for the 3 materials of interest. The Socorro AI model can predict the corrosion rate/risk based on the measured environmental variables, which than can be compared to the actual corrosion rates (measured by the LPR sensor). If there is good agreement between the LPR sensor and the AI model, it can be concluded that model is fine to use in (industrial) wastewater treatment plants.

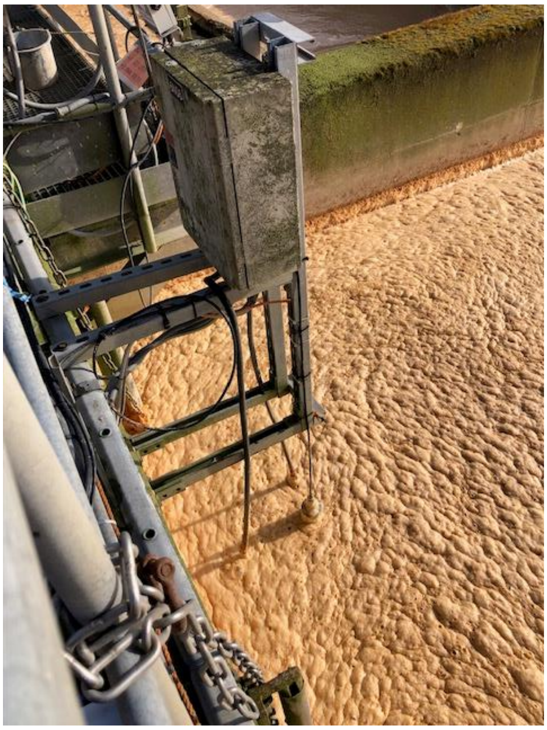


***Figure: The electrical box of the environmental probe (Scuba 65).***

To validate the measured corrosion rates of the C-Cube probe, a sample rack with coupons of the 3 grades was also immersed in the nitrification/denitrification section. Within this sample rack, each grade has 4 coupons (per month): 3 coupons are being used for weight loss determination, the last coupon can be used for microscopic analysis. The whole sample rack is made out of plexiglas to avoid any galvanic corrosion effects. After 1, 2, 3 and 6 months, samples were retrieved from PB Leiner and corrosion rates are calculated based on their weight loss and the active surface area.

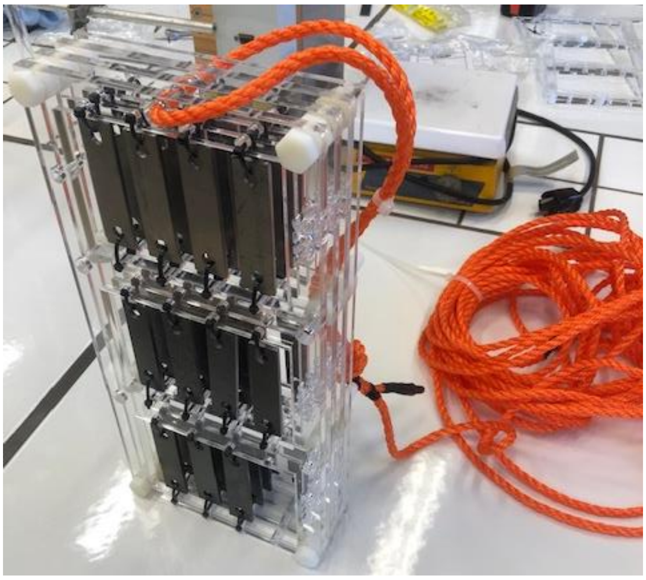


***Figure: Sample rack immersed in the MBBR for weight loss determination.***

Every 2 weeks, all sensors where checked for damage and/or contamination. If the sensor needed to be cleaned (perhaps when it completely covered by sludge), it was rinsed with distilled water. The environmental probe was running fine for 2-3 months before it started to collect bad data. Dissolved oxygen was not measured at all (0 mg/L), conductivity was acting strange and the measured pH went from a value of 7 (= 0 mV) to unrealistic values (pH 11-12). The sensor was, with the support of Eijkelkamp, completely checked. Water found a way to the electrical connector, where the probe is connected to the data cable (and power cable, see figure). Moisture can affect the measurements. All pin connectors were cleaned with pressurized air and extra gaskets were installed to avoid similar situations in future. Unfortunately, the sensor failed soon after, again because moisture affected the electrical connections. The sensor didn't run good for a while. It was changed by a new sensor and electrical box, that started to run well in April 2023.

A few issues were also noticed with the sample rack. After 1, 2, 3 and 6 months, samples should be recovered from the rack. The weight-loss of the coupons gives an accurate value for the corrosion rate inside the wastewater. After that data was retrieved for month 1, the cable of the sample rack snapped because of the high flow inside the basin (figure). Hence, there is no data for the immersion tests for month 2, 3 and 6. In future work, it is recommended to use a steel cable in rough/stormy environments. The C-Cube sensor in the wastewater of PB leiner didn't show intense corrosion phenomena as seen in the other demonstration site, the MBBR at the greenhouse. The electrodes of the LPR probe only showed little corrosion and required no cleaning (figure).

A.  B. 

***Figure: Issues in the field demonstration site in PB leiner A) Moisture inside the environmental probe and B) a cable snapped to which the sample rack was knotted.***

***Figure: The C-Cube LPR probe after being in the wastewater of PB leiner for 2 months without any cleaning.***

Results:

**1) Timeplots and boxplots of the environmental parameters**

The environmental parameters measured by the Scuba 65 inside the nitrification/denitrification basin are plotted in figure. All environmental parameters don' have data between March 2023 and April 2023 due to the previous mentioned issues with the Scuba probe. The temperature in the nitrification/denitrification basin is shown in figure A. The wastewater is continuously heated to temperature around 30°C. This temperature is ideal for the nitrate-reducing bacteria and therefore, the higher temperature increases the efficiency of the installation. In April 2023, the temperature outside is higher compared to January. Hence, with the same amount of heating, the wastewater reaches values up to 32°C. The conductivity, redox potential (ORP), the dissolved oxygen content, pH and salinity seem to have strong fluctuations inside their measured values. This is not due to malfunctions of the probe, this has to do with the cycli that are occurring inside the nitrification/denitrification basin. As mentioned before, nitrification and denitrification are conducted in the same basin. If nitrification should be the prior mechanism (conversion of ammonium to nitrate), the wastewater is strongly aerated. In this aerated cyclus, there is a strong flow inside the wastewater. However, each 6h, the aeration is stopped for approximately 2h. The dissolved oxygen content decreases fastly to anoxic values and denitrification will occur, nitrate will be converted to nitrogen gas. If the basin is in "nitrification" mode, the wastewater is aerated (figure). The dissolved oxygen content will go to values of 6mg/L. When the nitrate should be converted to nitrogen gas (denitrification), the aeration is stopped for 2h, the dissolved oxygen content will go to anoxic values (below 1mg/l, figure). The nitrification/denitrification also affect the ORP. If the bacteria are nitrifying, the water is aerated and the redox potential will be as high as 200mV. When denitrifying, the redox drops to values of -200mV. It is important to remark that those values are perfectly what we expect in a biological wastewater treatment plant (see table explained in the other demonstration site, WP2). Why conductivity (and thus salinity) and pH are affected by the cycli, is more difficult to explain from a theoretical point of view. When on-site, it is very clear in which cycli the basin is (figure). If the wastewater is not aerated, the wastewater is "denitrificated". A thick slude layers forms on top of the wastewater. A hypothesis is that the thick sludge blocks the environmental probes for the wastewater below. When the water is not aerated, sludge is only found at the probes which has a lower conductivity then the wastewater itself. When the water is aerated, the sludge is intensively mixed with the water and the conductivity at the probe will be higher. Following this hypothesis, it is reasonable to assume that the pH of the sludge will differ from the pH of wastewater itself. It will be interesting to see if the cycli, that are easily recognizable in the environmental parameters, are also recognizable in the measured corrosion rates.

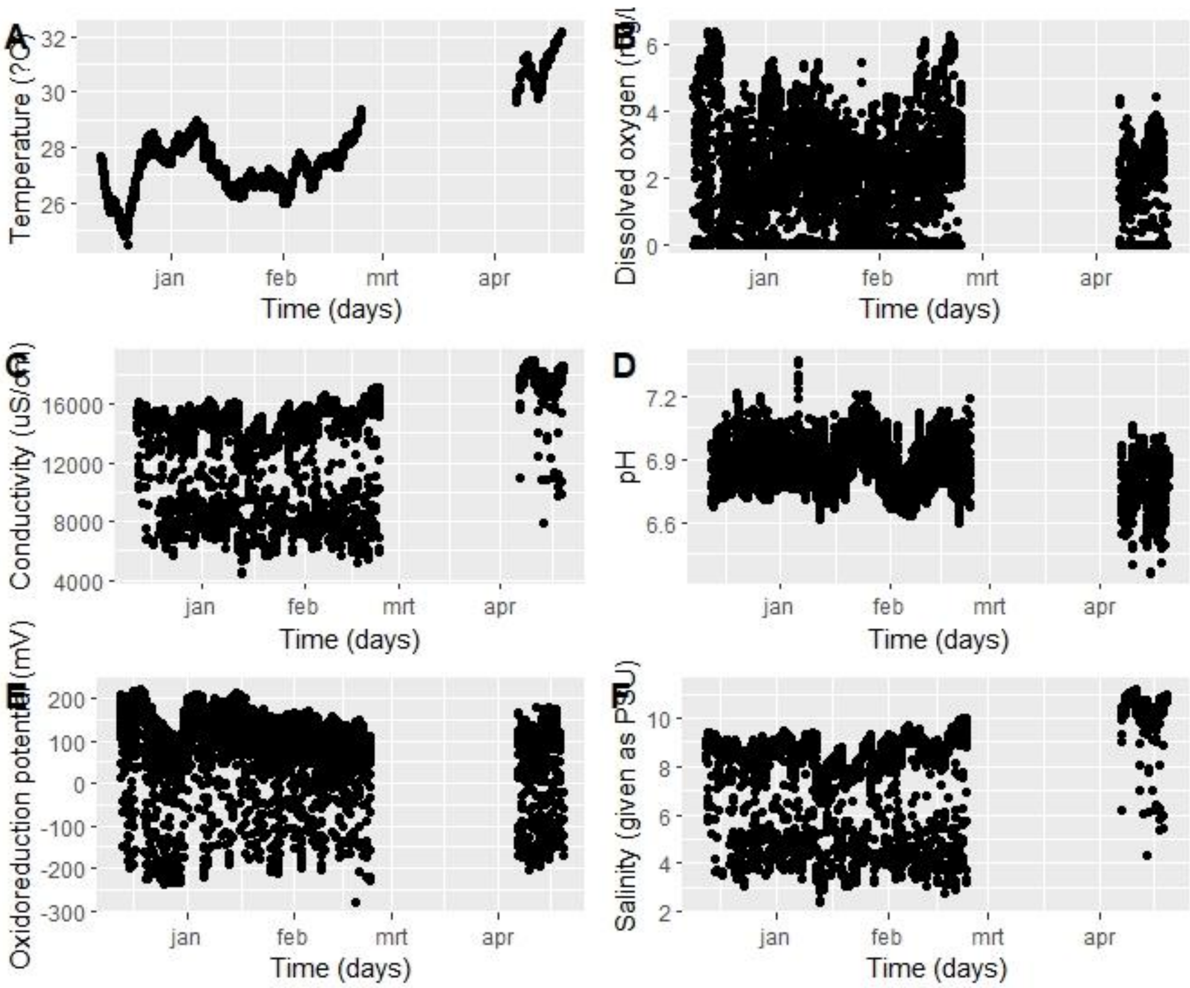



*Figure: Overview of the time plots in PB Leiner*

A.  B. 

***Figure: The basin of the PB Leiner wastewater treatment plant in A) nitrification modus and B) denitrification modus.***

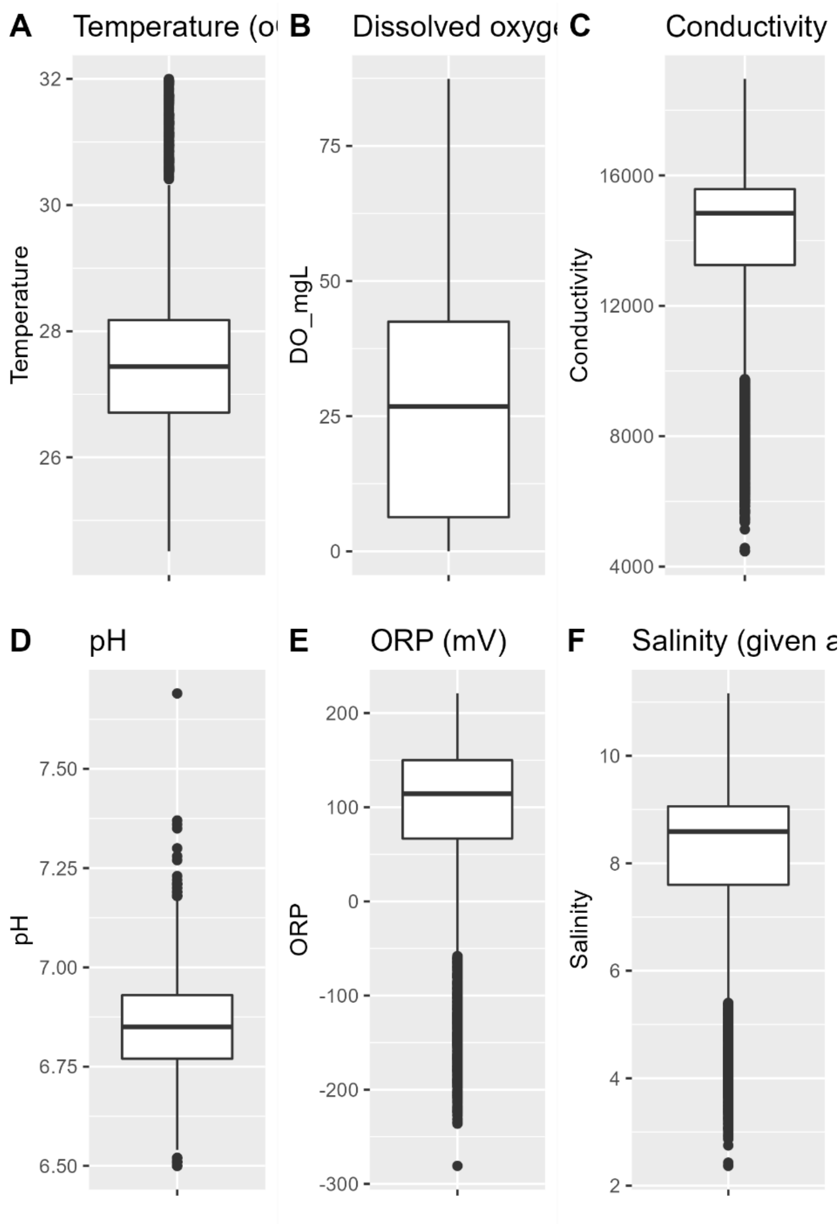



***Figure: Boxplots of the environmental parameters in PB Leiner***

## 2) Correlations between environmental parameters

In R studio, a correlation matrix was made to investigate correlations between the measured environmental parameters. The highest correlation coefficient was found between conductivity and salinity. Not really surprising as salinity is an immediate derivative of conductivity. The positive sign of the correlation coefficient indicates that if the conductivity increases, the salinity increases as well. Another strong correlation (coefficient between 0.4 and 0.6) is found between the ORP and the dissolved oxygen content. A correlation coefficient of 0.603 was determined. If the basin switches from nitrification to denitrification, the aeration is stopped. This results into a decrease of DO and lowers the ORP to values expected for denitrification (approximately -200mV). So that both parameters are correlated to each other makes sense, this is immediately explained by the biological processes that occur inside the basin. ORP is also reversely correlated to pH, with a correlation coefficient of -0.508. If the ORP decreases, the pH increases. This can be explained by the (bio)chemical reactions that occur when nitrifying or denitrifying, summarized below. When denitrification occurs, H+ ions are being produced which results into a lower pH value. Denitrification

uses H+ ions which will result into a higher pH values, like described in the correlation matrix. Because the nitrification/denitrication cycli also affect conductivity, it is normal that the parameters that fluctuate due to the cycli are correlated to conductivity.

***Table: The effect of nitrification/denitrification of the environmental parameters***

| Cycli | DO | ORP | pH | Conductivity | Salinity |
|---|---|---|---|---|---|
| Nitrification | ↑ | ↑ | ↓ | ↑ | ↑ |
| Denitrification | ↓ | ↓ | ↑ | ↓ | ↓ |

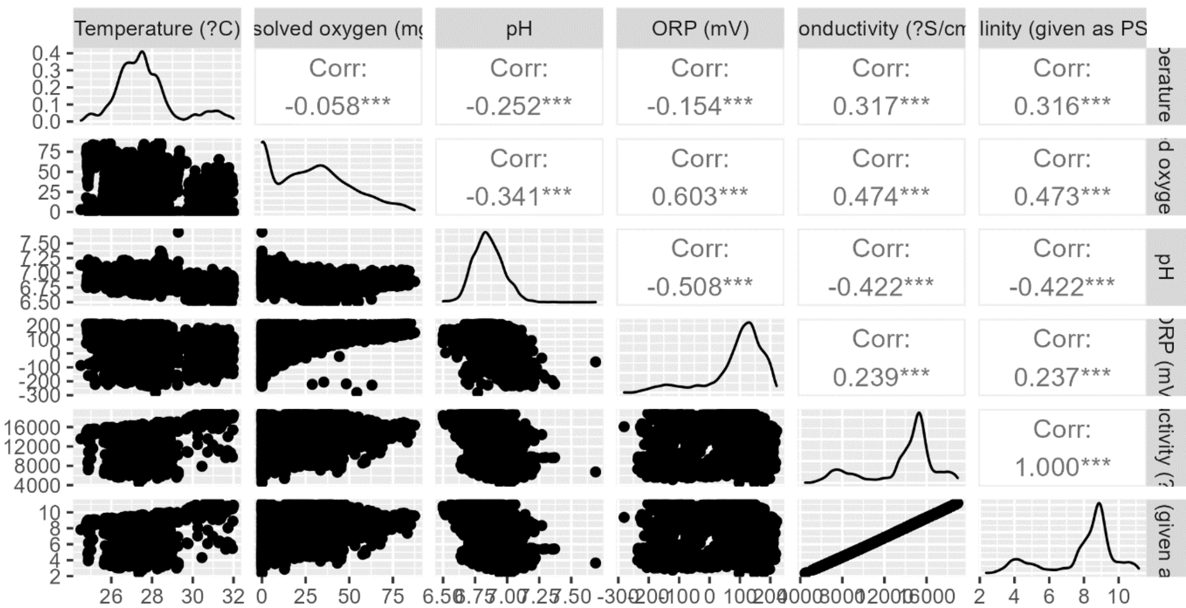
$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^-$$

***Reaction: Nitrification in the wastewater of PB Leiner***

$$2NO_3^- + 10e^- + 12H^+ \rightarrow N_2\ (nitrogen\ gas) + 6H_2O$$

***Reaction: Denitrification in the wastewater of PB Leiner***



### 3) Corrosion behavior of S235 steel (grade A) in PB Leiner

The uniform corrosion rate of S235 steel was measured each 6h by a LPR C-Cube probe. The C-Cube probe applies a potential 100mV below and above the open-circuit potential and measure the current (density). The result in a Linear Polarization Resistance measurement. The polarization resistance can be recalculated to a corrosion rate using the formula of Stern-Geary. Normally, a LPR measurement is not destructive and can be performed as frequent as needed to. However, most LPR measurements only apply 10-20mV of potential difference. C-Cube explained that with a higher potential (and thus a higher current density), the device calculates the corrosion rates more accurately. One side effect is that the frequency of conducting those measurements should be limited. According to lab tests of C-Cube, performing an LPR measurement every 6 hours with the current settings is acceptable. The corrosion rate for grade A, a carbon steel often used in maritime applications, is presented in the figure below. In the begin, a corrosion rate of only 0.004-0.05mm/y is found. This corrosion rate is really low, especially when compared to the other demonstration site (0.05mm/y) where the chloride content and temperature are remarkably lower ( < 200ppm $Cl^-$, temperature < 15°C) . Why the corrosion rate (around 100 days) suddenly increases to values of 0.15mm/y, is still unclear. Even the maximum values measured by the C-Cube probe are too low, considering that the wastewater contains 4000ppm of chloride at a temperature 30°C. From the sample rack, coupons where collected that were immersed for 1 month. Unfortunately, it was not feasible to determine the corrosion rate after 2, 3 and 6 months because the cable of the sample rack snapped. After 1 month immersion, a corrosion rate of 0.5mm/y was measured by the weight-loss. Much higher than measured by the C-Cube probe. A hypothesis why the corrosion rate of the LPR probe does not agree with the corrosion rate by weight-loss, is that the high amount of sludge (in the wastewater) covers the LPR electrodes. By periodic checks, it is noticed that sludge covers both installed probes: the LPR probe and the Scuba 65 environmental probe. The samples that were retrieved from the sample rack were also covered with a high amount of sludge. But for weight-loss, it doesn't matter that the active surface is partly covered with sludge. For a proper operation of the LPR probe, all three electrodes should be in electrical contact with each other: the working electrode (3 disk in the front of the LPR probe), the counter electrode (also in front of the LPR probe) and the reference electrode (zinc electrode at the side of the sensor). If one the electrodes is covered with sludge (and even if not all), the current density measured by applying a non-destructive potential difference will be lower than with sludge. The sludge is considered as an extra resistance where the current has to go through. If this is really the reason why the corrosion rates are too low, should be investigated in future work.

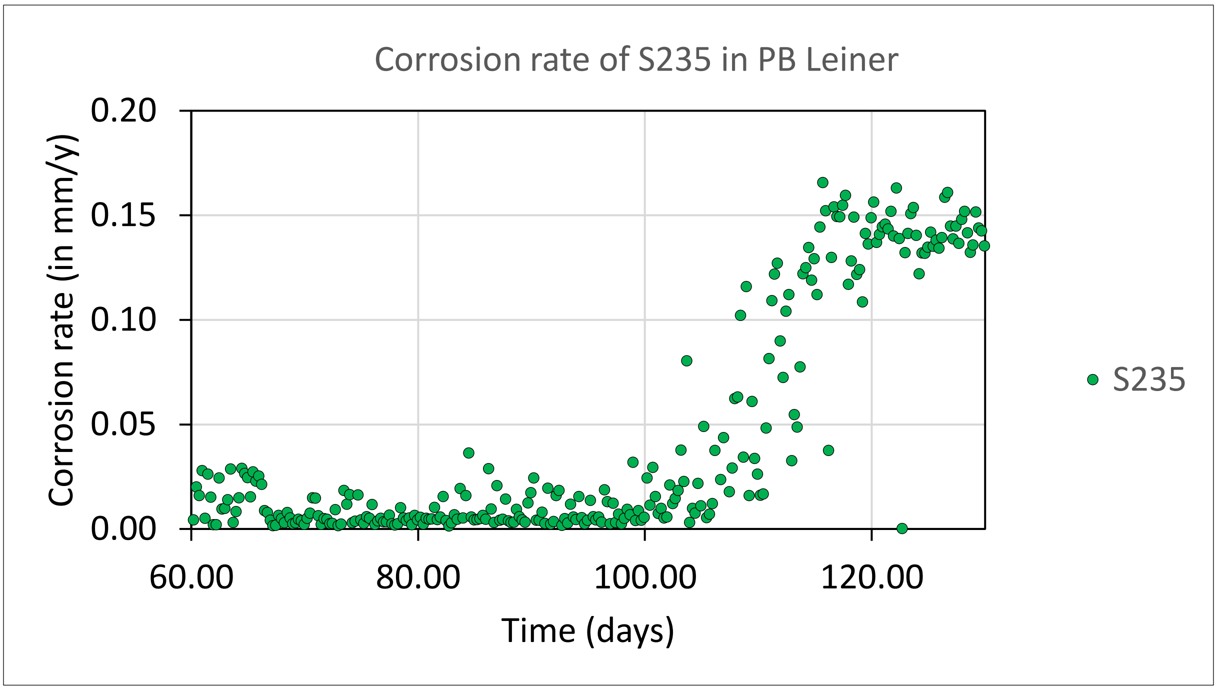



***Figure: Corrosion rate of the LPR C-Cube sensor (grade A) in PB Leiner***

Even though the corrosion rates, determined by the C-Cube LPR probe, are remarkably low, it is still interesting to see whether the Pearson test was able to find correlations with the environment parameters measured by the other probe (Scuba 65). The Pearson test revealed that at higher conductivity, salinity, DO, temperature and pressure, the corrosion rate will be higher as well. All previous parameters have a (statistical significant) proportional correlation with the measured corrosion resistance. A high turbidity and high pH results in a lower corrosion rate. It is normal that a higher conductivity/salinity results into a higher corrosion rates. A higher conductivity means that more salts (chloride, sulfate and nitrate being the most important salts present inside the PB Leiner wastewater) reach the steel surface and hence, the corrosion rates goes up. A higher temperature results in faster corrosion kinetics. A higher DO content inside the wastewater basin means that the unit is in “nitrification” mode. The wastewater is aerating, sludge will not cover the electrode as easy due to the high flow and therefore, conductivity increases (see correlation matrix). In “nitrification” mode, the pH also decreased because $H^+$ ions are generated (table). Why turbidity and pressure are correlated to the corrosion rate is still unclear.

| Parameter | p-value | Pearson coefficient |
|---|---|---|
| **Turbidity** | <0.001 | -0.43 |
| **pH** | <0.001 | -0.205 |
| ~~ORP~~ | ~~0.1413~~ | ~~-0.086~~ |
| **Conductivity** | 0.019 | 0.137 |
| **Salinity** | 0.017 | 0.14 |
| **DO** | 0.004 | 0.168 |
| **Temperature** | <0.001 | 0.198 |
| **Pressure** | <0.001 | 0.53 |

A Screeplot was made with the data collected from PB Leiner. It is clear that the two first principal components (PC1 and PC2) can explain more than 70% of the total variance seen in the original dataset. If PC3 is additionally included, more than 85% of the variance is included. PC1, PC2 and PC3 are used to generate a PCA plot and are shown in figure. According to the PCA plot (FactoMineR package), only the temperature is correlated to the corrosion rate of grade A.

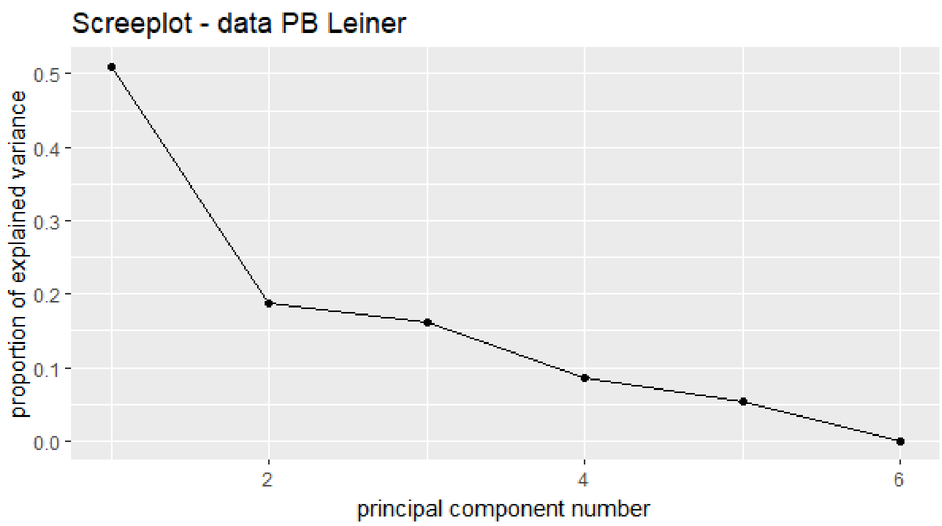



***Figure: Scree plot of the principal components – PB Leiner***

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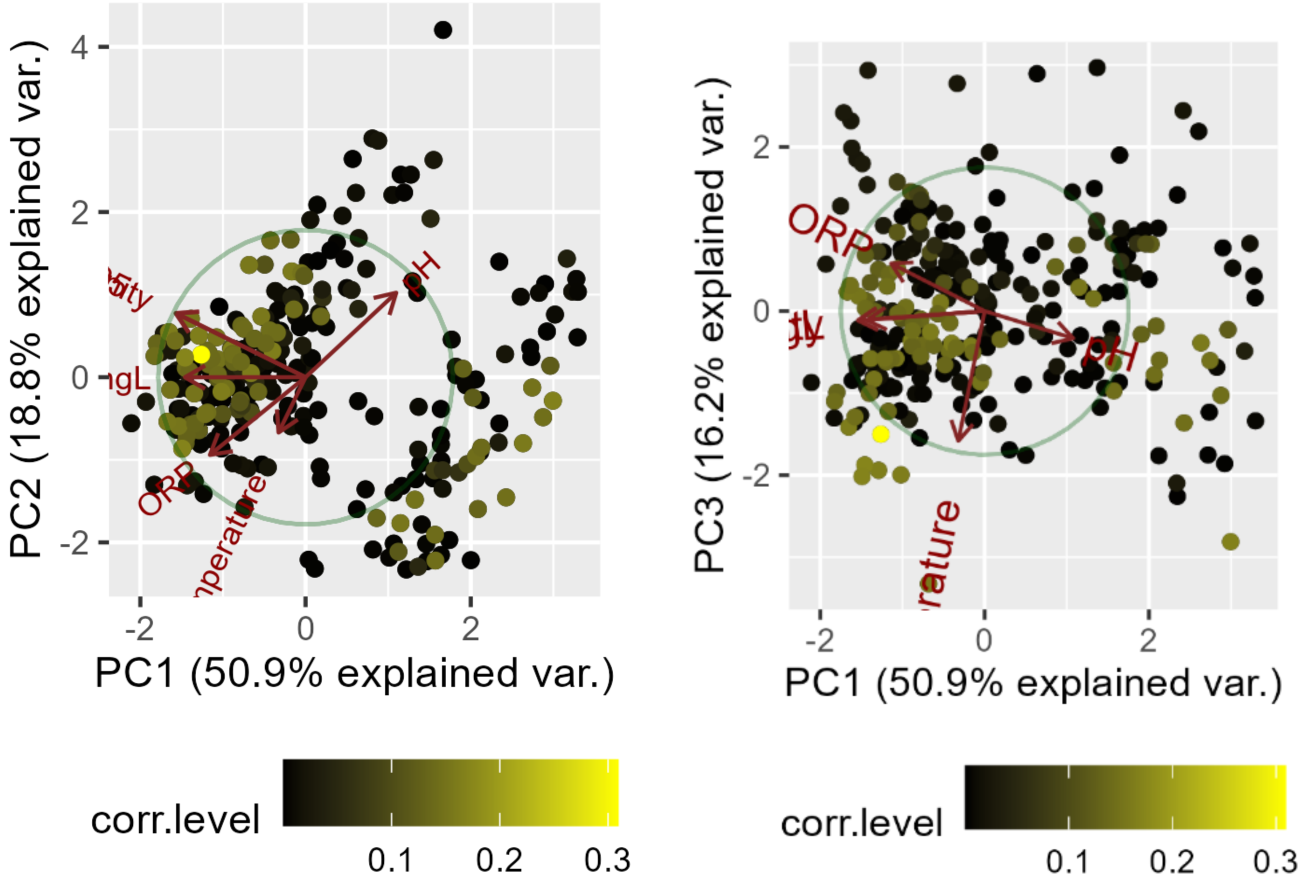


***Figure: PCA plots of PC1/PC2 (left) and PC1/PC3 (right) – PB Leiner***

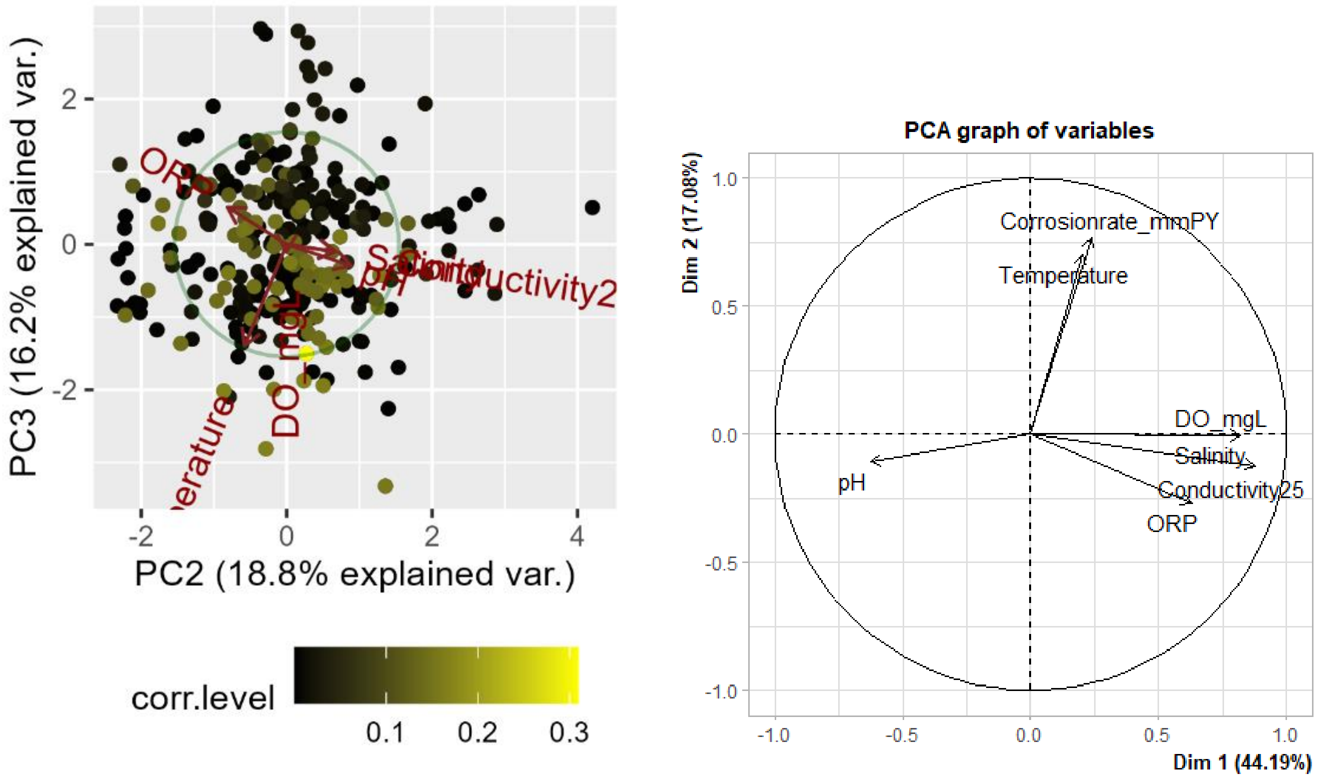


*Figure: PCA plots of PC1/PC2 – FactoMineR package – PB Leiner (Material S235, Grade A)*

## 4) Corrosion behavior of S355 steel in PB Leiner

The corrosion rate of the S355 steel measured by the LPR C-Cube is shown in the figure below. Corrosion rates vary between 0.03-0.08mm/y. The corrosion do not reach values as low as measured for grade A steel, neither do they reach maximum values of 0.15mm/y (like measured with grade A). Although the order of magnitude for the corrosion rate of grade A and S355 is the same, the trend of the corrosion rate is totally different. Grade A steel showed a strong increase in corrosion rate after 100days (after installation and first use). The S355 steel does not show such an increase, the corrosion rate acts more stable during the whole test period. With the immersed coupons, a corrosion rate of 0.5mm/y was calculated, which is the same rate calculated for grade A. This result is not unexpected as their chemical composition is very alike. A hypothesis why the immersed coupons have a significant higher rate than determined by the probe, is that the electrodes of LPR sensor are sensitive for contamination. If the LPR sensor is covered with corrosion product, or as expected in this case with a thick sludge layer, the additional layer will act as an extra resistance. More resistance results in a lower corrosion rate than the actual rate, accurately determined by the immersed coupons.

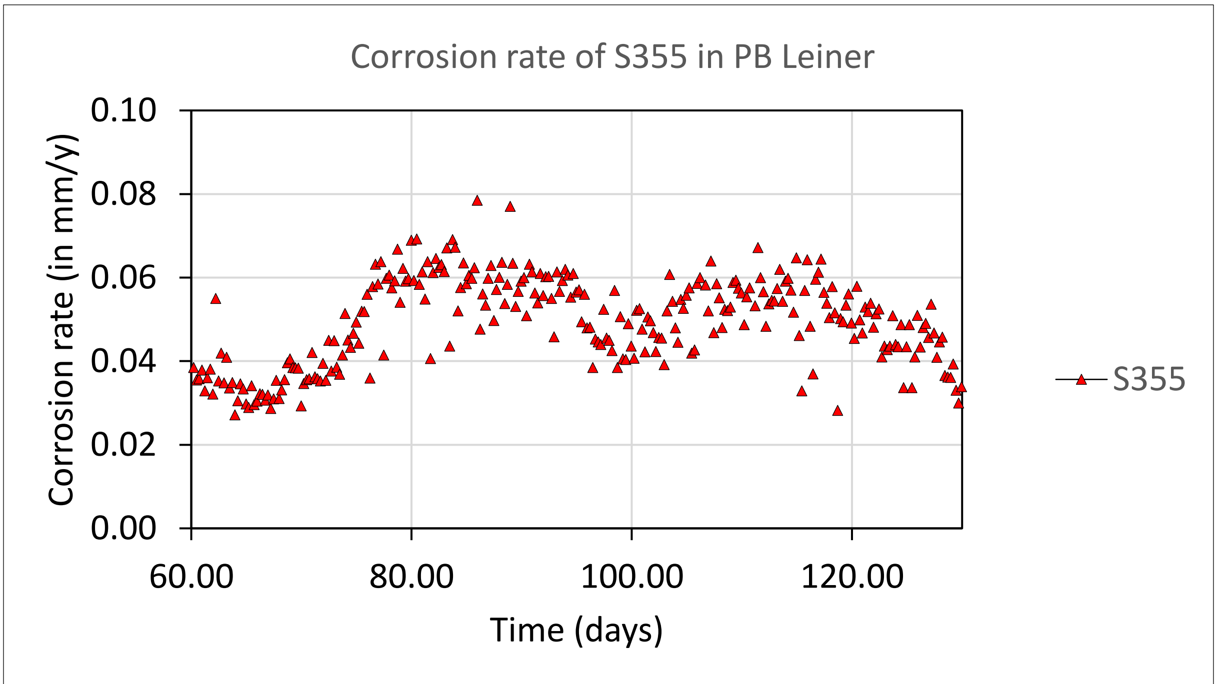


***Figure: Corrosion rate of the LPR C-Cube sensor (S355) in PB Leiner***

Between the corrosion rate (measured by the LPR probe) and environmental parameters, there are also few correlations that need further discussion. According to the Pearson test, the corrosion rate was only correlated to the pH, ORP and temperature. Turbidity, DO, salinity, conductivity and pressure didn't show a statistical significant correlations and hence, these variables will not be discussed in further detail. Corrosion rate is reversely proportional correlated to pH. A lower pH results in a higher corrosion rate. A high ORP values also results into a higher corrosion rate. In the wastewater basin, nitrification and denitrification cycli are carried out. Nitrification leads to a lower pH and a higher ORP value compared to denitrification. The correlations found insinuate that the corrosion rate of the S355 is higher during the nitrification cycli compared to the denitrification cycli. The reason why conductivity, salinity and ORP are not correlated to corrosion rate, these variables also vary within nitrification/denitrification, is still unclear. Next to the pH and ORP, the temperature was also positively correlated to corrosion rate. The higher the temperature, the higher the measured corrosion rate for S355 steel, probably due to the faster corrosion kinetics (that are temperature dependent).

***Table: Correlation between the corrosion rate (measured by the C-Cube LPR sensor, S355) and the environmental parameters.***

| Parameter | p-value | Pearson coefficient |
|---|---|---|
| **pH** | 0.016 | -0.141 |
| ~~Turbidity~~ | ~~0.44~~ | ~~-0.044~~ |
| ~~DO~~ | ~~0.601~~ | ~~-0.03~~ |
| ~~Salinity~~ | ~~0.855~~ | ~~-0.011~~ |
| ~~Conductivity~~ | ~~0.897~~ | ~~-0.007~~ |
| ~~Pressure~~ | ~~0.921~~ | ~~0.005~~ |
| **ORP** | <0.001 | 0.19 |
| **Temperature** | <0.001 | 0.283 |

Next the Pearson test, a Principal Component Analysis was performed to study the correlations between the corrosion rate and the environmental parameters in a more visual way. It is clear that vector "temperature" and "ORP" have the same direction and sense and vector "corrosion rate". This means that both environmental parameters are proportionally correlated to the measured corrosion rate. This is in perfect agreement with the result found by the Pearson test. pH has the same direction as vector "corrosion rate", however, the sense is the opposite. The PCA predicts that pH is reversely proportional correlated to corrosion rate, what again agrees with the Pearson test. Why pressure is found to be correlated to corrosion rate, something that was not found by the Pearson test, is still unclear is needs to be studied in future work.

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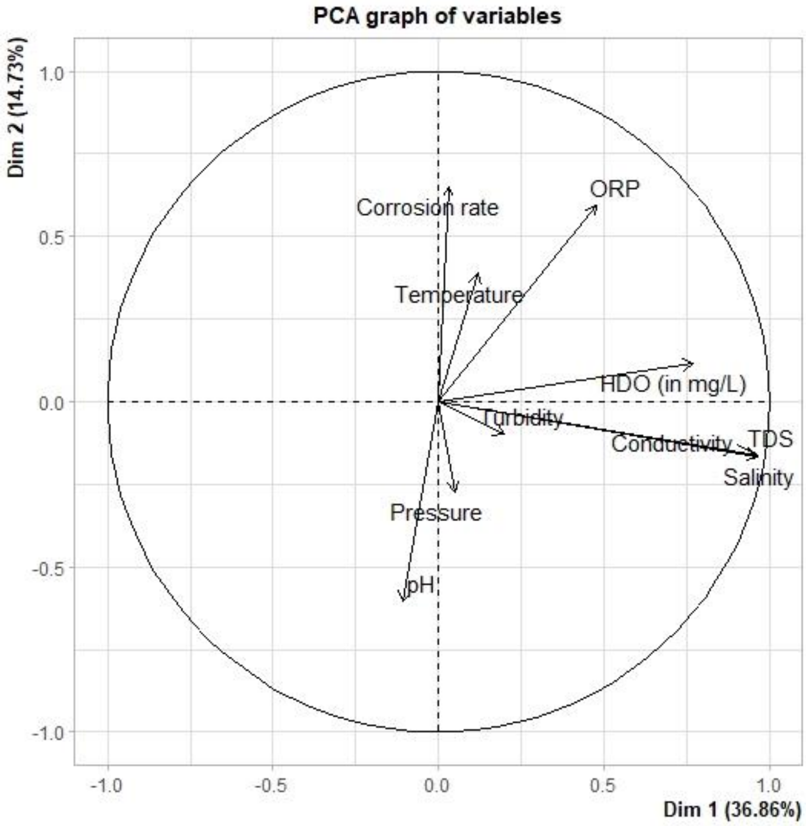



***Figure: PCA plots of PC1/PC2 – FactoMineR package – PB Leiner (Material S355)***

## 5) Corrosion behavior of AISI 316L in PB Leiner

The corrosion rates measured by the C-Cube LPR probe are shown in the figure below. The measured corrosion rates are expressed in µm/y, not unexpected because stainless steel will corrode much less than a steel grade because of its protective chromium-rich film. However, corrosion rates as low as $2.45*10^{-19}$ µm/y were measured for AISI 316 in the PB leiner wastewater. Maximum values go up to 0.4µm/y. It should be emphasized that measured corrosion rates lower than 0.1µm/y are not realistic. C-Cube LPR sensors with their electrical properties are normally not able to measure corrosion rates lower than 0.01µm/y. If such low corrosion rates need to measured accurately, the electrochemical equipment should be able to measure a corrosion current of 1nA/cm2 accurately. These corrosion currents are only measurable when using a faraday cage (like used in lab set-up), and not for electrochemical sensors for in-situ use. Another issue seen with the AISI 316 measurements is the strong fluctuation in corrosion potential within a few days. It is not normal that all environmental parameters are more or less stable and that the corrosion potentials shifts more than 300mV. This proves that the AISI 316 measurements are not good. Hence, it is not unusual that no correlations are found with the Pearson formula for all the measured environmental parameters (table). The PCA analysis does not agree with the Pearson test, however, it should be emphasized that a PCA does not take the statistical significance into account (p-value < 0.05 or not). It is a visual representation of the found correlation coefficients in a two-dimensional biplot.

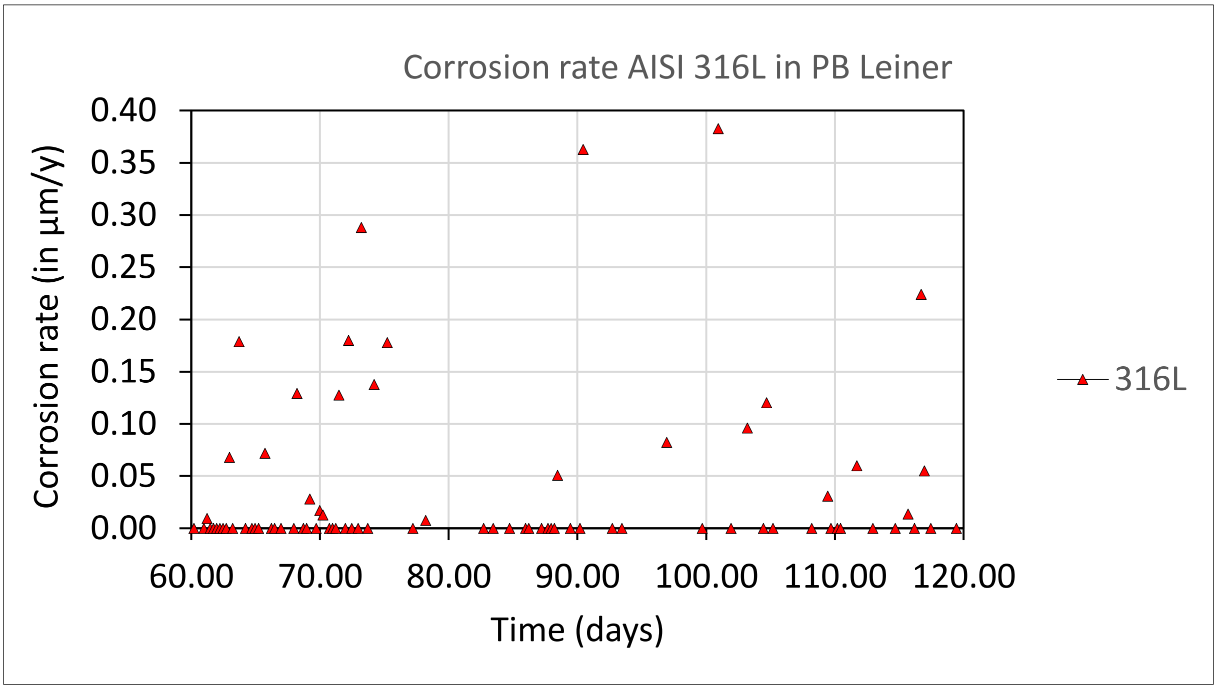



***Figure: Corrosion rate of the LPR C-Cube sensor (AISI 316) in PB Leiner***

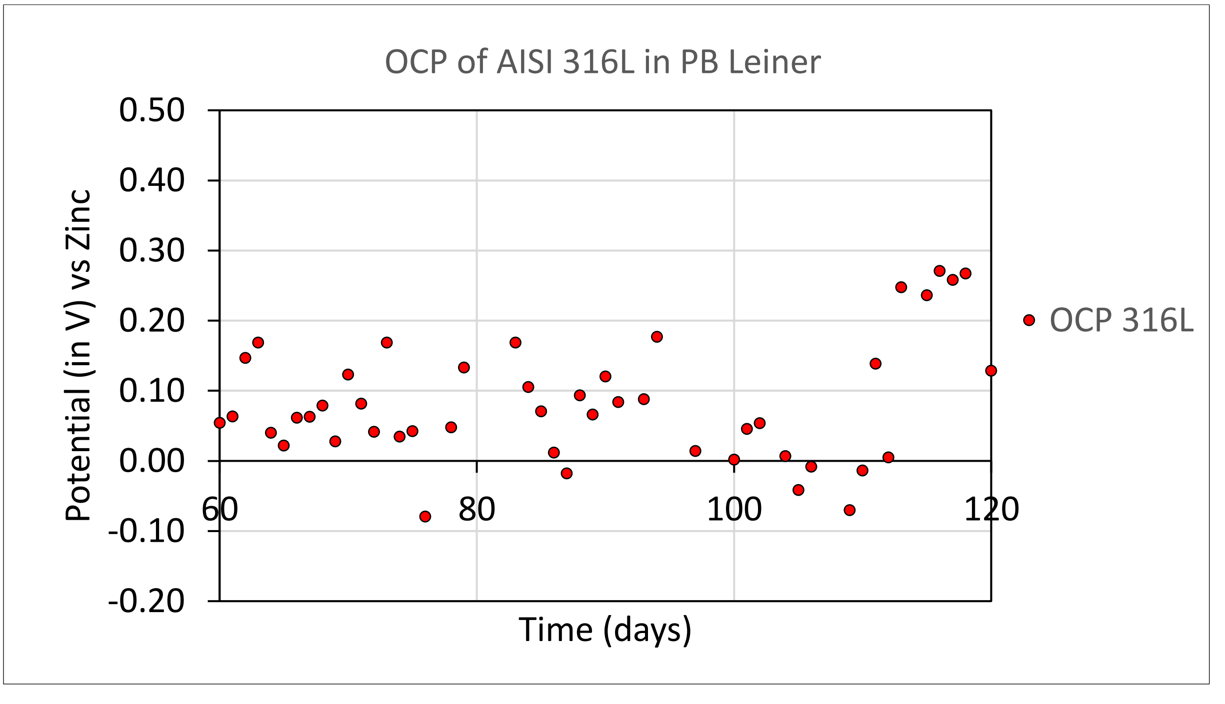



***Figure: Corrosion potential of the LPR C-Cube sensor (AISI 316) in PB Leiner***

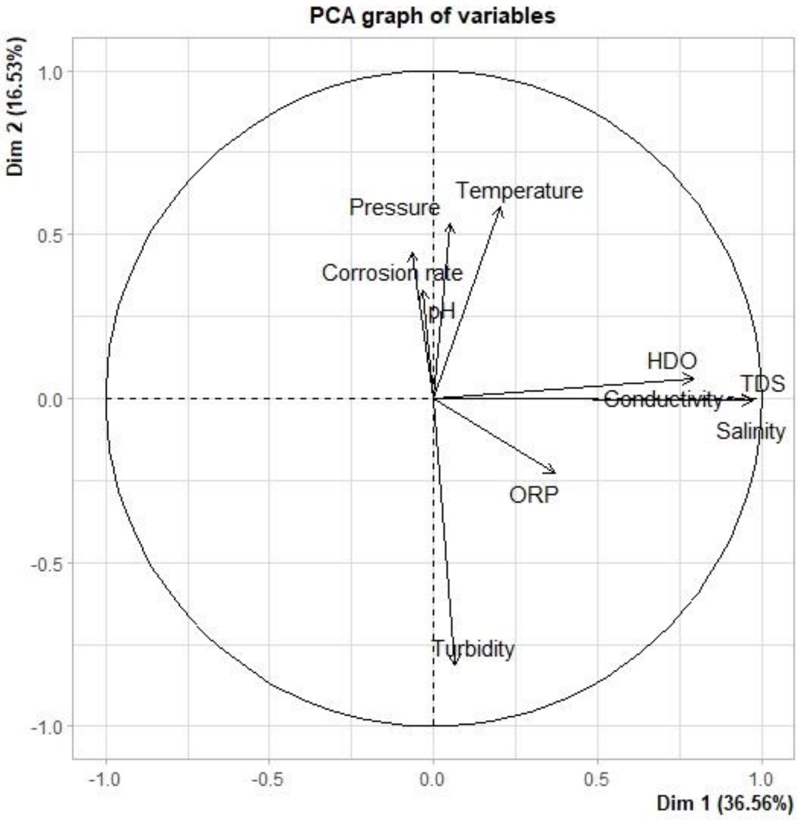
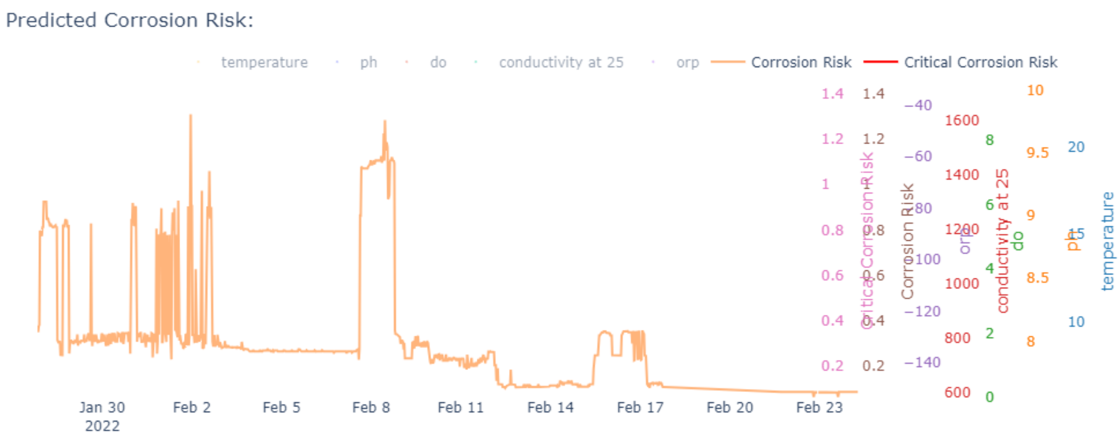
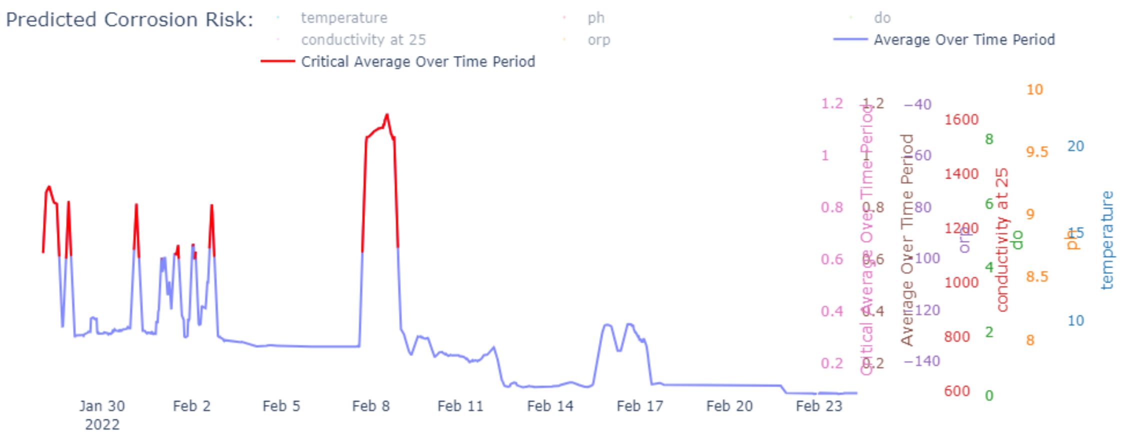
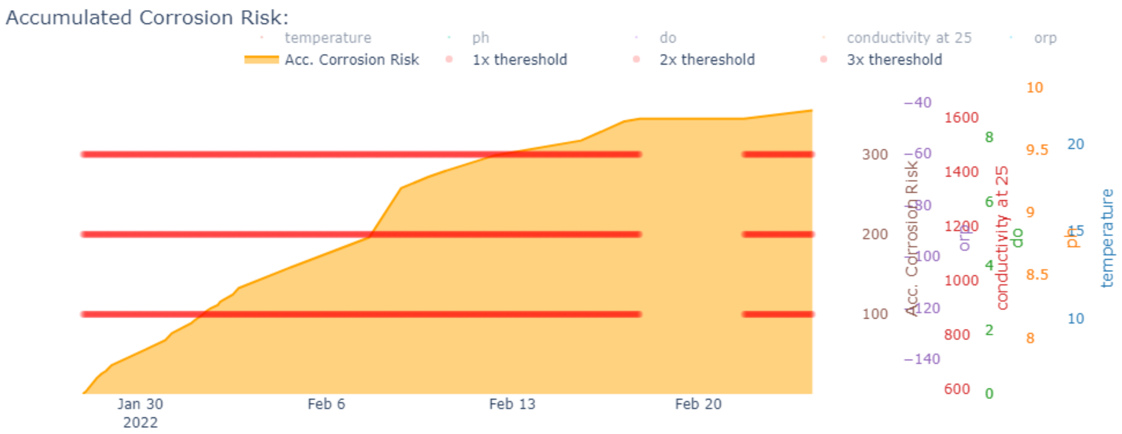



*Figure: PCA plots of PC1/PC2 – FactoMineR package – PB Leiner (Material AISI 316)*

Data analysis with SOCORRO data-app






## Plans for further use?

The environmental probe and the C-Cube LPR sensor are still installed in the PB Leiner wastewater treatment plant. We hope to let them run for a longer period of time so that we can learn more about the nitrifying/denitrifying cycli and their effect on corrosion.