MINKE

Metrology for Integrated marine maNagement and Knowledge-transfer nEtwork

INFRAIA-02-2020: Integrating Activities for Starting Communities

EUROPEAN COMMISSION

Project funded by the European Commission within the Horizon 2020 Programme (2014-2020)
Grant Agreement No. 101008724

Requirements

Water Station

Water Calibration and Replacement Solutions

Cable Seals

Computer

Arduino IDE (or other terminal software with UART)

USB

Distilled Water

File (tool)

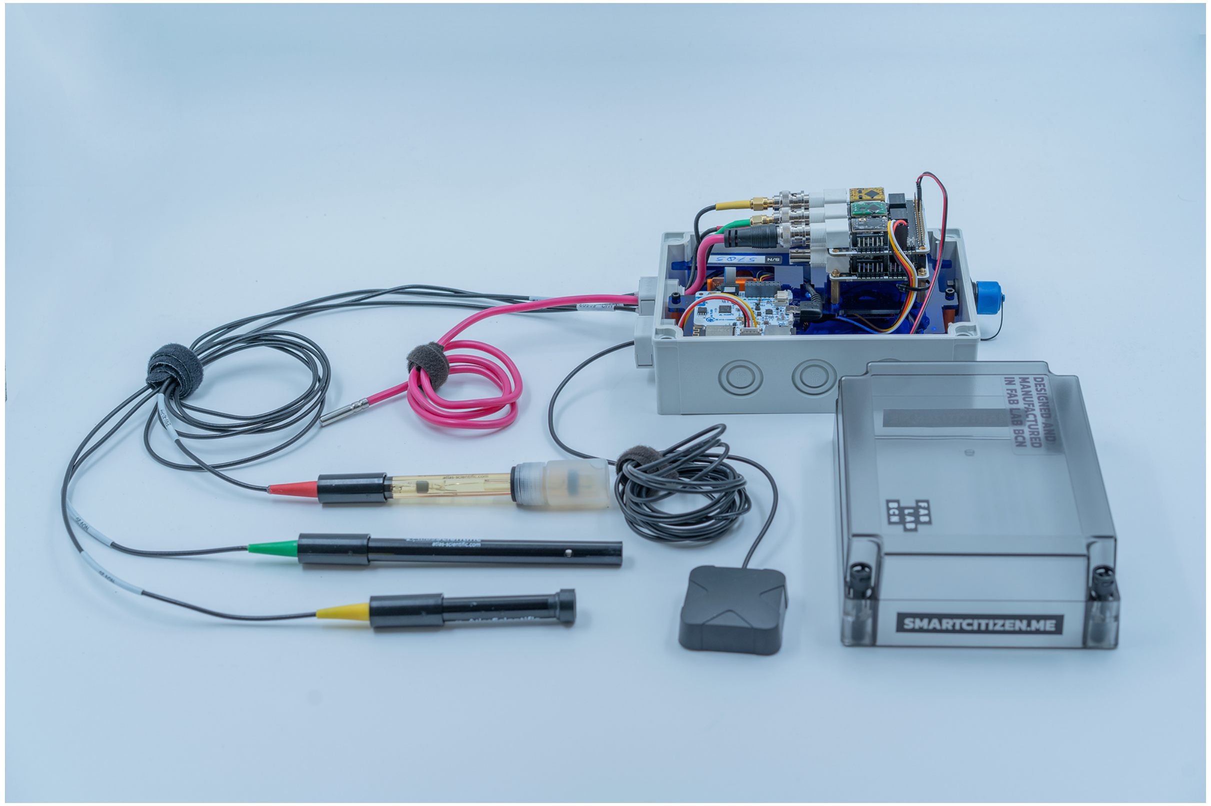
Water Sensors

Water Sensors

What are we measuring

The Water Sensors will measure physico-chemical parameters:

- pH
- Dissolved Oxygen
- Electric Conductivity
- Temperature
- Oxydation-Reduction Potential (ORP)



Extra material

A Citizen's Guide To Understanding And Monitoring Lakes And Streams:
https://apps.ecology.wa.gov/publications/documents/94149.pdf

USGS National Field Manual for the Collection of Water-Quality Data:
https://www.usgs.gov/mission-areas/water-resources/science/national-field-manual-collection-water-quality-data-nfm

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Water Sensors

pH basics

The **pH** of a sample of water is a **measure of the concentration of hydrogen ions**. At higher pH, fewer free hydrogen ions

The pH scale **ranges from 0 to 14**. A pH of 7 is considered to be neutral. Substances with **pH less than 7 are acidic**; substances with **pH greater than 7 are basic**.

The pH of water determines the **solubility** (amount that can be dissolved in the water) and **biological availability** (amount that can be utilized by aquatic life) of **chemical constituents** such as **nutrients** (phosphorus, nitrogen, and carbon) and **heavy metals** (lead, copper, cadmium, etc. - which can be toxic at higher concentrations).

Relationship with other metrics

pH also increases phosphorus solubility - making it more available for plant growth and higher Dissolved Oxygen demand in the long term.

Extra material (basics)

https://www.usgs.gov/special-topics/water-science-school/science/ph-and-water

https://www.usgs.gov/special-topics/water-science-school/science/alkalinity-and-water

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Water Sensors

pH basics in seawater

The degree of pH plays an important role in **oceanic carbon cycles.**

There is evidence that **ocean acidification has been caused by CO2 emissions**. The ocean absorbs about 30% of the CO2 emissions from the atmosphere, and when this happens, a chemical reaction takes place that generates hydrogen ions in the water.

- **More CO2**: Ocean acidification makes it harder for small marine organisms to trap CO2 when building their shells.
- **Less coral**: Ocean acidification causes the bleaching and disappearance of corals, which are home to 25% of fish species and support more than a billion people.
- **Less food**: Ocean acidification is corrosive to the shells of small marine snails, which are the first level of the food chain.

Impact and other metrics

The warming of the ocean as well as its acidification endanger the survival of phytoplankton, seagrass meadows, mangroves and marshes that are authentic CO2 traps.

Extra material (basics)

https://www.usgs.gov/special-topics/water-science-school/science/ph-and-water

https://www.usgs.gov/special-topics/water-science-school/science/alkalinity-and-water

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Water Sensors

Measuring pH: the Probe

pH values can change very quickly
If collecting samples, this parameter should be measured in the field immediately after collecting the sample. It can be measured a posteriori in the laboratory, but it will not be completely representative. To measure it, therefore, we will use a pH sensor.

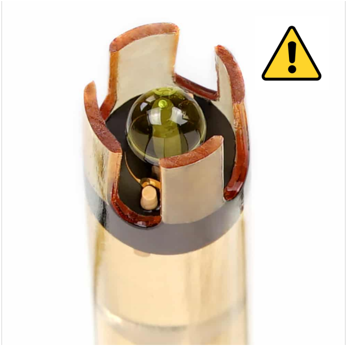
The pH probe is a very delicate submerged electrode in a thin glass bubble.

The sensor can be completely immersed:

Performance:

- pH range: 1 to 13
- Maximum depth in water: 35m
- Response speed: 95% in 4s
- Safe to use in food/beverages

https://files.atlas-scientific.com/consumer-grade-pH-probe.pdf



Difficulty of…

- Preparation
- Calibration
- Maintenance

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Water Sensors

Dissolved Oxygen basics

Dissolved oxygen (DO) is an indicator of how much oxygen is dissolved in the water (obviously) and available to living things.

The **movement of water**, or its impact against rocks or other elements increases DO. Other sources include for example exchange and **diffusion** with the atmosphere, **aeration** by wind and waves, or by **photosynthesis** of aquatic plants or concentration of life.

Dissolved oxygen is **essential for aquatic life**. The table below indicates the minimum amount of dissolved oxygen necessary for the life of different organisms.

Relationship with other metrics

Variations in temperature have an inversely proportional effect on dissolved oxygen: increases in temperature cause a decrease in dissolved oxygen and vice versa.

Organism	DO (mg/l)
Salmon	9-10
Trout	6.5
Sea Bass	6.5
Caddisfly Larva	4.0
Mosquito Larva	1.0

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Water Sensors

Dissolved Oxygen basics in seawater

The **organisms that live in the sea are generally acclimatized to a certain percentage of oxygen**. Fluctuations in this parameter can therefore have **devastating effects: if dissolved oxygen drops**, some species will be able to adapt, but it is quite possible that if the decline is not gradual enough, they will become **extinct**.

Dead zones (called hypoxic) in which oxygen is lacking **are multiplying** in the ocean. Global warming increases temperature of the water too – which consequently contains less oxygen – and the increasing presence of manure and fertilizers create the effect of fatal zones for marine animals.

Today, there are more than 245,000 km^2 spread over **400 dead zones**.

Impact and other metrics

Changes in water chemistry (at Oxygen and pH levels) can overwhelm the ability of aquatic organisms to acclimatize and survive. This can cause chain reactions, where habitats are degraded by losing biodiversity and biomass.

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Water Sensors

Measuring DO: the probe

This sensor is a **galvanic probe**, is made up of a teflon membrane and two electrodes, one of them in an **electrolyte solution**. This type of probe consumes a little bit of oxygen when taking readings. Therefore, **it is necessary to move the probe or the water around it a bit** (without aerating it).

Performance

- Range: 1-50mg/l
- Maximum depth in water: 70m
- Response speed: ~0.5 mg/l/per second

https://files.atlas-scientific.com/Mini_DO_probe.pdf

Dissolved Oxygen values are highly heterogeneous
If collecting samples, this parameter should be measured in **the field immediately after collecting the sample**. It can be measured a posteriori in the laboratory, but it will not be completely representative.

Difficulty of…

- Preparation
- Calibration
- Maintenance

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Water Sensors

Electric Conductivity

The conductivity of water is its ability to allow the flow of electrical charges. For there to be conductivity, the water needs to have dissolved ions (positive or negative electrical charges).

Conductivity, with **temperature**, is used to calculate **salinity**, and other parameters such as **dissolved solids** (TDS). **Salinity is the amount of salts contained in 1 kg of water**. It is expressed in PSU (Practical Salinity Unit, which is approximately equivalent to 1mg/g of salts).

The average salinity of seawater is 35 psu, or 35 g/kg.

Relationship with other metrics

Changes in conductivity are often derived from other metrics, directly impacted by the solubility of substances in the solution.

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Water Sensors

Electric Conductivity in seawater

In oceanography, conductivity is used as a measure to obtain the estimate of the salinity of seawater (in this case, it corresponds to the practical salinity).

Salinity is an ecological factor of great importance, and it influences the type of **organisms** (animals and plants) that can live in the water. It also has an impact on the formation of **deep water at the poles**. Finally, accompanied by a temperature measurement, it allows to define the **density of the water masses** and with this obtain information about the **currents and the buoyancy of water masses**.

In addition, variations in salinity can have an **impact on the absorption of CO_2** in the oceans (in saltier waters, CO_2 is less soluble).

Interest and other metrics

The temperature, salinity and density data are like the **identity card of the different masses of water contained in the oceans** and allow us to follow their path throughout their life (formation zone until they disappear or transform into another mass by diffusion or mixing processes).

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Water Sensors

Measuring EC: the probe

We will use a sensor called a conductivity meter.

Our conductivity sensor does not have an integrated temperature sensor, so we will have to use an additional temperature sensor to measure the temperature at which we are measuring. **This temperature sensor must be immersed at the same time when we take conductivity measurements.**

Taking samples or measuring directly

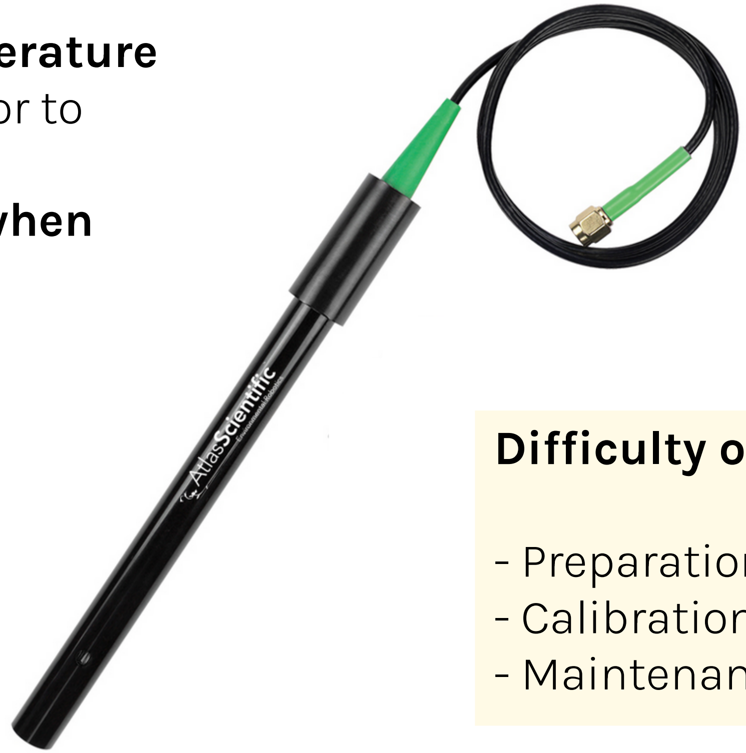
As a general rule, it is preferable to take measurements in situ, instead of taking samples and subsequent analysis in the laboratory, due to the possible chemical changes that may occur in the sample.

Performance (K10):

- Range: 10 µS/cm – 1 S/cm
- Accuracy: +/ - 2%
- Response time: 90% in 1s

Metrics:

- Conductivity
- Total Dissolved Solids
- Salinity
- Specific Gravity



Difficulty of…

- Preparation
- Calibration
- Maintenance

https://files.atlas-scientific.com/EC_K_10_probe.pdf

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Water Sensors

Oxydation Reduction Potential

The **ORP** of a sample of water is a **measure of the concentration of electron activity**. The ORP readings represents how strongly electrons are transferred to or from substances in a liquid. Readings **do not indicate the amount of electrons** available for transfer.

Knowing the redox conditions of water can help determine whether it **contains elevated levels of many contaminants**, including arsenic, nitrate, and even some manmade contaminants.

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Water Sensors

Measuring ORP: the probe

Difficulty of…

- Preparation
- Calibration
- Maintenance

An ORP probe is a passive device that detects a **current generated from the oxidation or reduction** of chemical substances in water. This current can be positive or negative.

Performance

- Range: -1100mV to 1100mV
- Accuracy: +/- 1.1mV
- Response time: 95% in 1s

https://files.atlas-scientific.com/consumer-grade-ORP-probe.pdf

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Water Sensors

Temperature

Temperature of water can be something very simple: it is a value that indicates how hot or cold the liquid is. However, **water, especially in large masses, can show enormous variations between different parts**: on the surface vs. in depth, or on the shore vs. in waters.

Temperature is a very important factor, because it conditions all the other factors of the water. It is an **ecological factor of considerable importance**, and has an influence on the types of organisms that can live in the water: normally, the higher the temperature, the greater the biological activity.

It is related to the salinity of currents in the ocean, and in general, changes in temperature in the oceans are due to exchanges with the atmosphere.

Interest and other metrics

It has a **direct impact on dissolved oxygen** (inverse - the higher the temperature, the lower the dissolved oxygen under equal conditions), in addition to **conditioning the speed at which chemical reactions** occur in the water. It has an impact on the **dissolution of salts and metals and therefore has an impact on electrical conductivity and ORP**.

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Water Sensors

Measuring temperature: the probe

If it is not possible to insert the sensor into the water, and you need to take a sample, stabilize the sampling container before measuring (by immersing it in water so that it is heated/cooled to the same temperature as the water).

For measuring temperature, we will use a **resistive sensor** (RTD, resistance temperature detector) of the PT1000 type (made of platinum, and with a resistance at 0°C of 1000Ω). This sensor is encapsulated within a stainless steel tip, to conduct heat very efficiently. **To be able to use it at more extreme temperatures, or to fix it in a pipe, we will use a thermowell (the metal capsule).**

Performance

- Range: -200 to 850°C (without thermowell -55°C to 125°C)
- Accuracy: ± (0.15 + (0.002*t))
- **Response speed: 90% in 13s**

https://files.atlas-scientific.com/PT-1000-probe.pdf

Difficulty of…

- Preparation
- Calibration
- Maintenance

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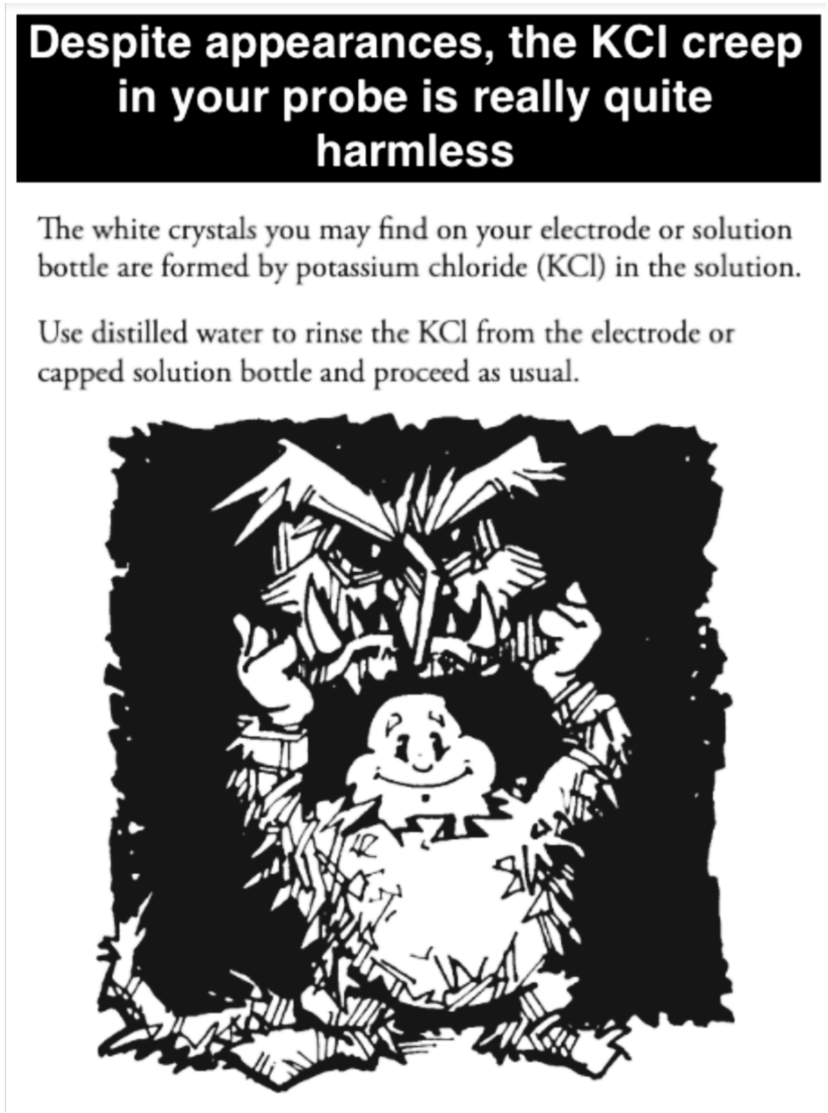
Sensor Preparation

Sensor Preparation

General requirements

- Some sensors require some preparation before usage
- We have to do this before calibrating and measuring
- This needs to be done periodically for some sensors (more on that on the maintenance section)
- pH, ORP, and DO sensors will "suffer" from **KCl "creep"**



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Sensor Preparation

Cables

You can use many different probe cable lengths.

It won't affect the measurement except for Temperature (it's a resistive sensor!). **If you change cable length, you have to recalibrate the temperature probe.**

Connectors for the sensors are not water proof

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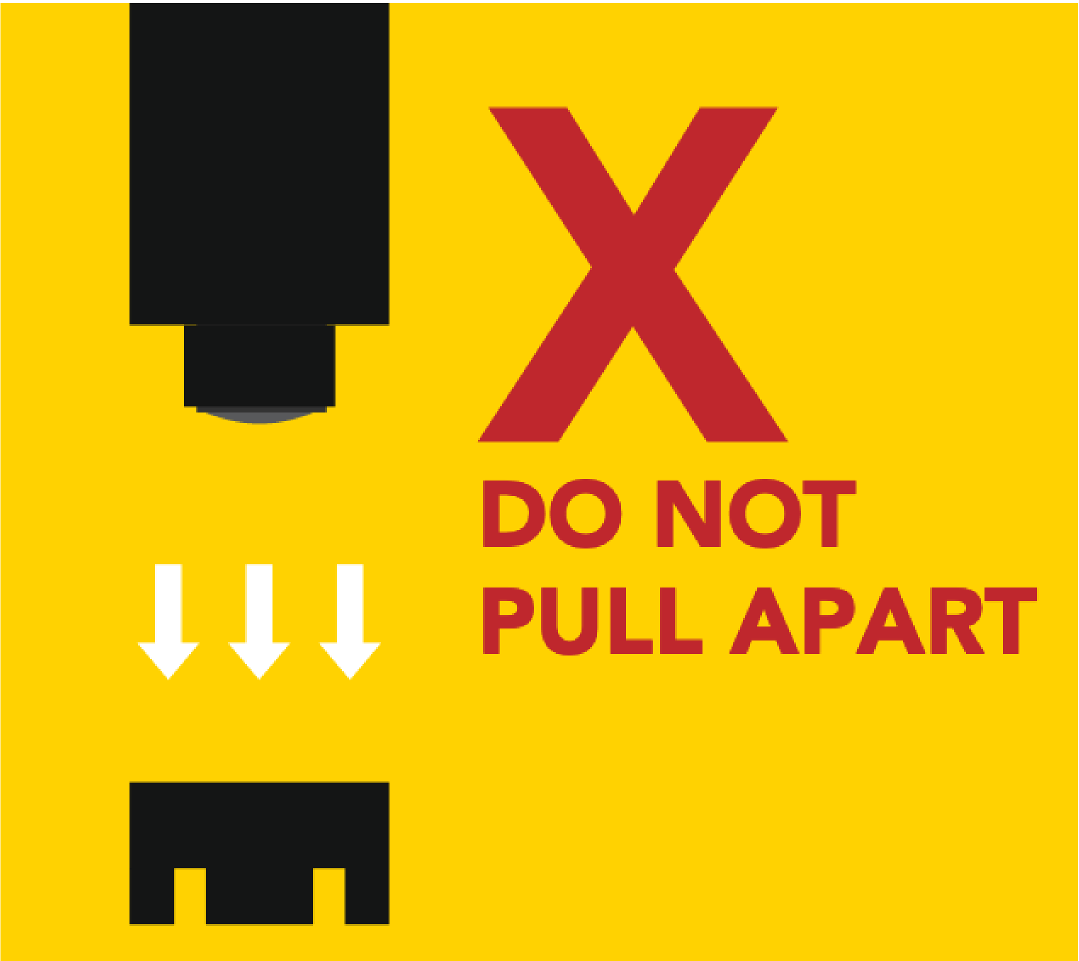
Sensor Preparation

Dissolved Oxygen Probe

If you **open the probe the first time**, make sure you only open the rubber cap protector, and **not any sensor component such as the membrane cap**



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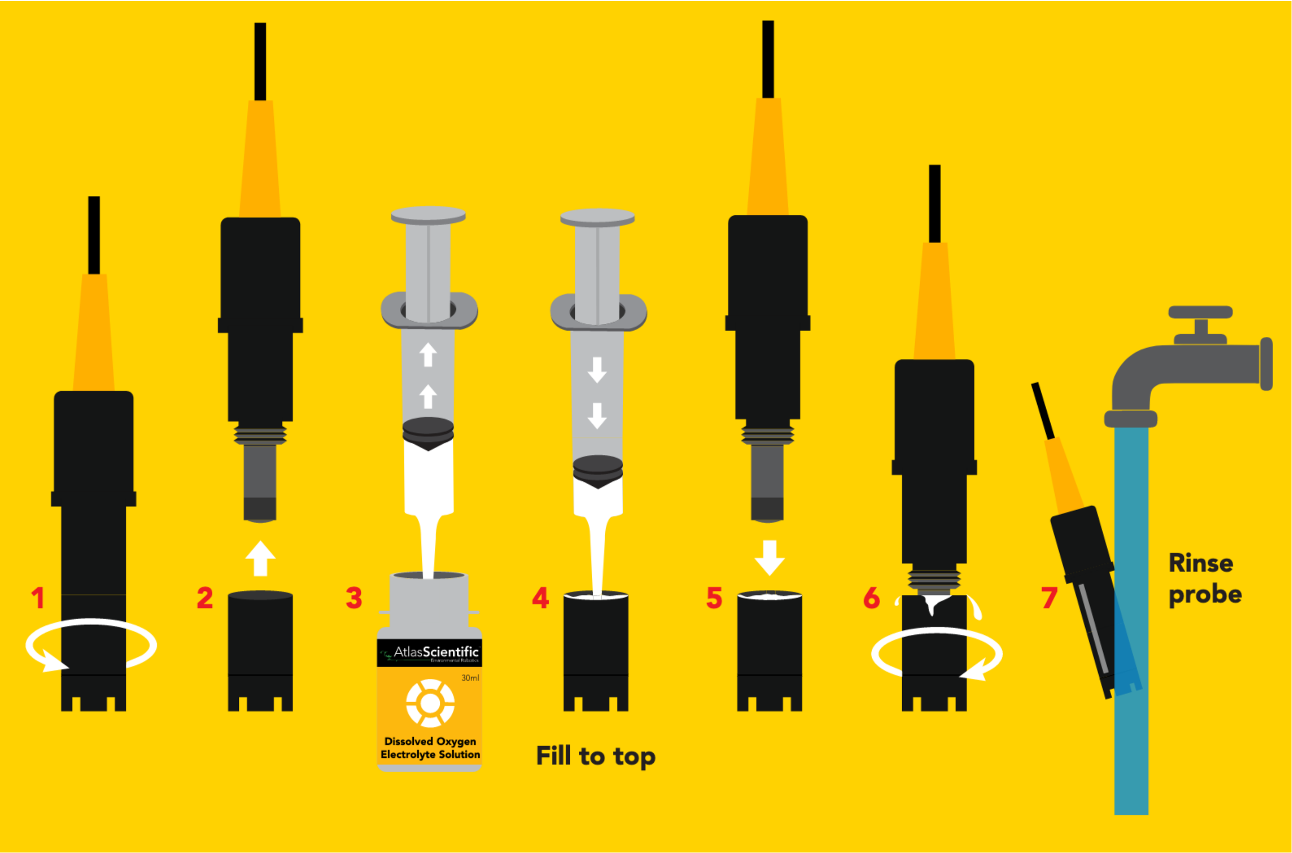
Sensor Preparation

Dissolved Oxygen Probe

The sensor **has an electrolyte solution inside to support the chemical reaction in the electrodes**.

This solution depletes over time, as the sensor is used and **it will generate a solid residue** that needs to be cleaned periodically (**roughly every 6 months for the Mini DO probe, but better to check**)

Even it the sensor is brand new, **you need to follow this process to avoid issues**.



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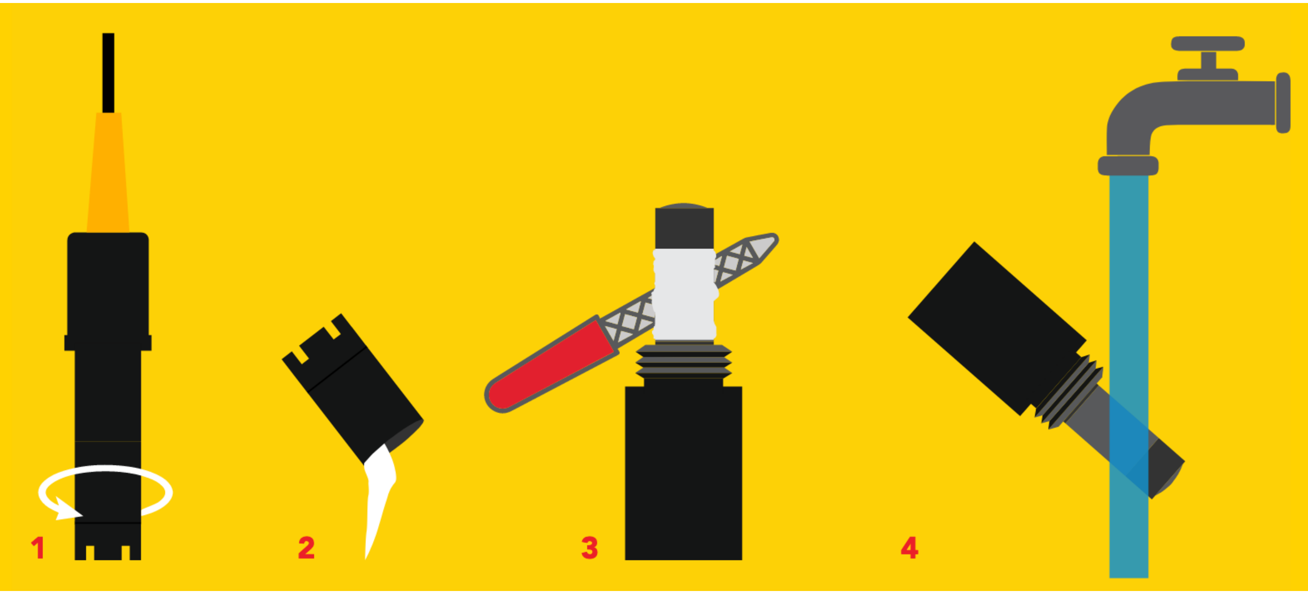
Sensor Preparation

Dissolved Oxygen Probe

You can **recondition the sensor with a small file and remove all Zinc Oxyde.**

Make sure that **the probe membrane is cleaned with a very soft brush both inside and outside**.

The membrane can be replaced if damaged. Make sure it is in good conditions because it will otherwise leak the electrolyte solution and the sensor will work erratically.



DO NOT USE A BRUSH TO CLEAN THE MEMBRANE

If the probes membrane is ripped it must be replaced, as it will cause irregular readings.

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Sensor Preparation

pH and ORP Probe

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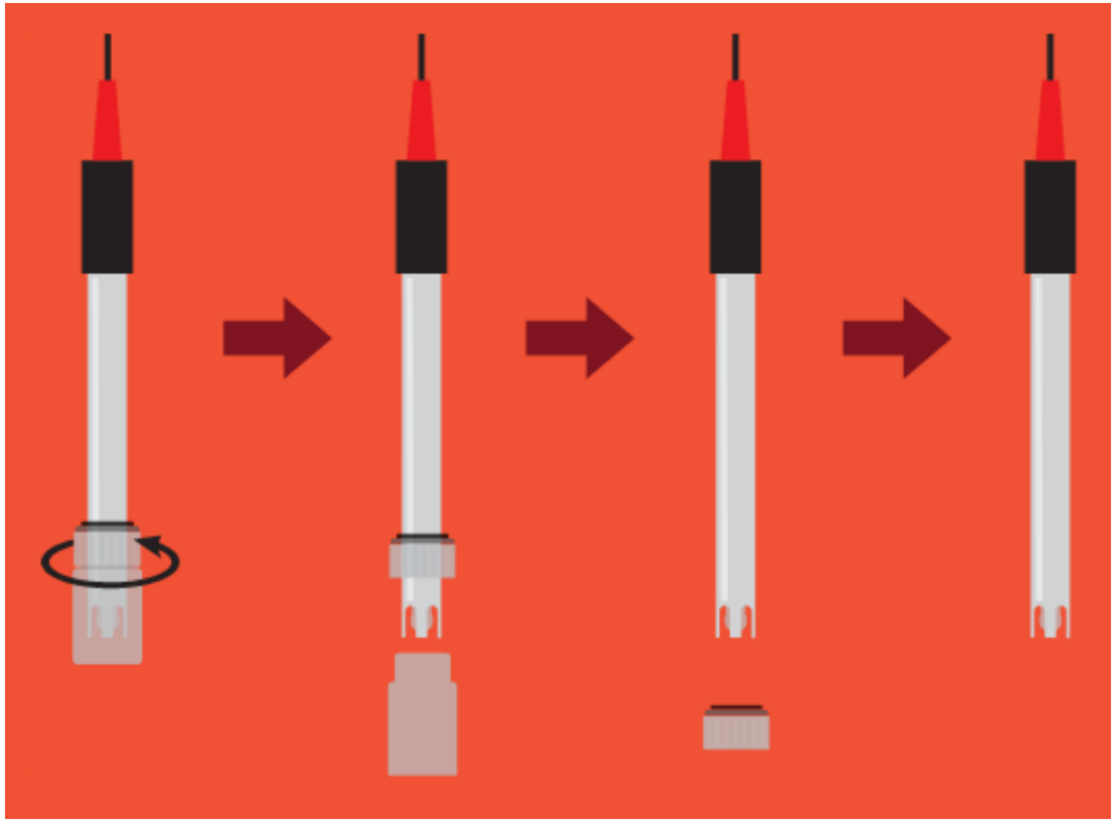
Sensor Preparation

pH and ORP Probes – Storage and usage

Both probes **need storage solution** in a small **soaker bottle** to prevent it from drying out.

If the probe is not being used you need to put the soaker bottle back on.



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Sensor Calibration

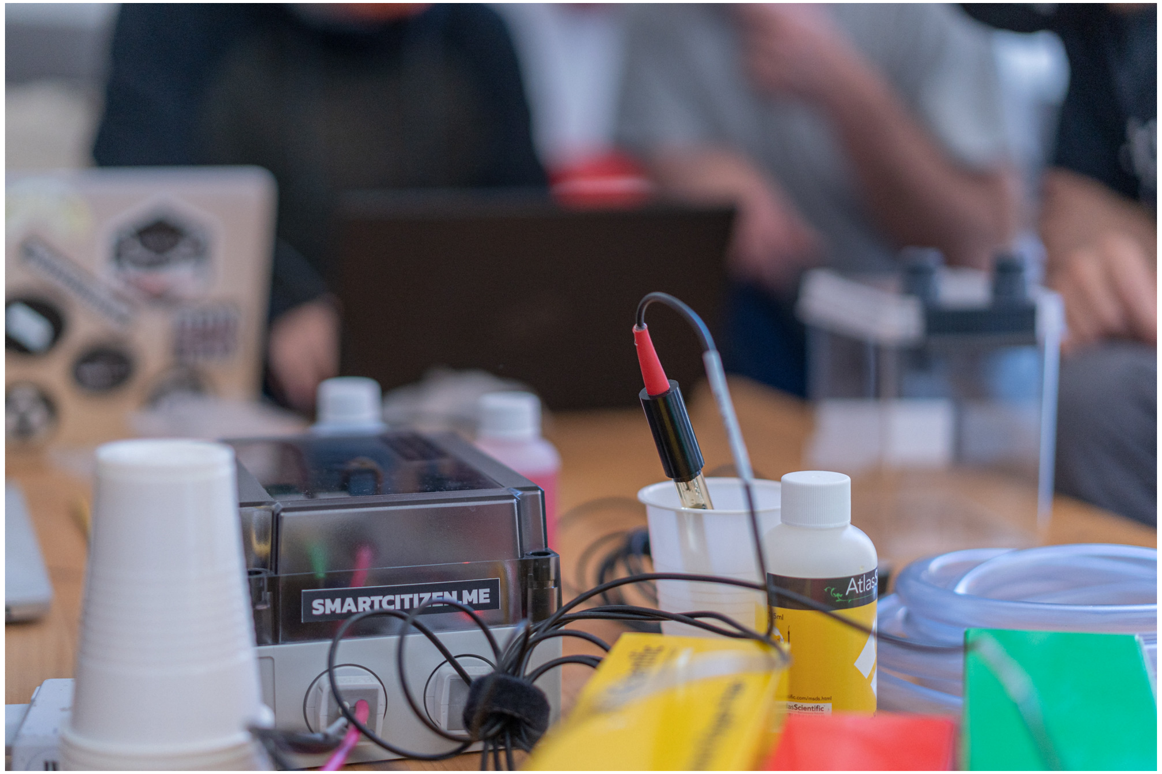
Sensor Calibration

What we need

- We will use a **terminal** or the **Arduino IDE** for calibrating the sensors.

- Before calibrating, make sure the sensors are ready by following the instructions on the **Sensor Preparation**

- We will use **calibration solutions** (these are standard) and **distilled water** (this too)



Calibration for the water sensors can't be done "a posteriori", except for the temperature sensor.

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Shell commands

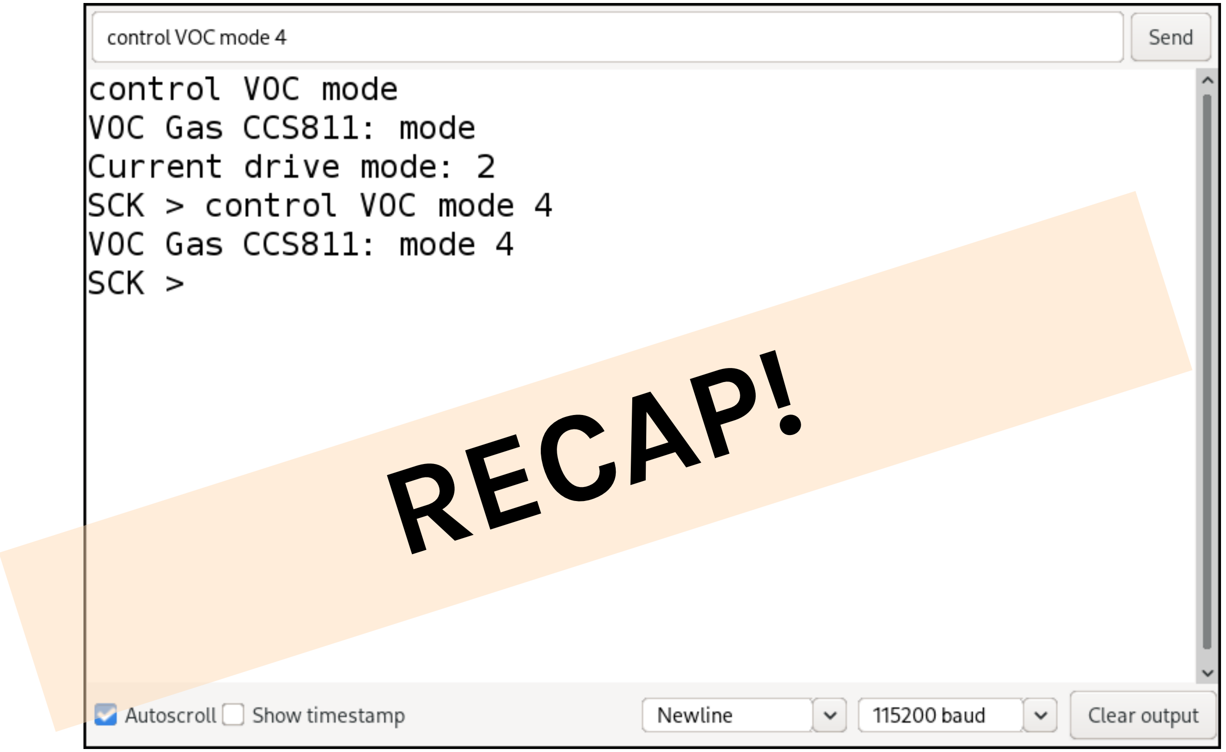
Sensor control

control

Allows custom control over some sensor properties.

Calibration of external sensor probes is one example of its use.

Check the documentation on your specific sensor for details.



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How often? 3 months

Sensor Calibration

pH Probe

- You need to perform a 3-point calibration with the calibration solutions.
- The **solutions vary their pH with temperature**, so make sure to check the temperature prior.
- The **pH value at current temperature can be found on the reference table** on the calibration solution bottle.

This is the order of the calibration:

- mid point **(always first! - it erases the rest!)**
- low point
- high point

Always clean the probe with distilled water between each calibration

Remove the soaker bottle and rinse off the pH probe. Pour a small amount of the pH 7.00 calibration solution into a cup. Let the pH probe sit in the calibration solution until the readings stabilize *(small movement from one reading to the next is normal).*

x 3 times!

First, read the sensor until stable (N times):

```
control ph com r
```

Issue calibration:

```
control ph com cal,[mid,low,high],[value]
```

Example:

```
control ph com cal,mid,6.99
```

Other useful commands:

```
control ph com cal,clear
control ph com cal,?
```

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How often? Long time (+5y)

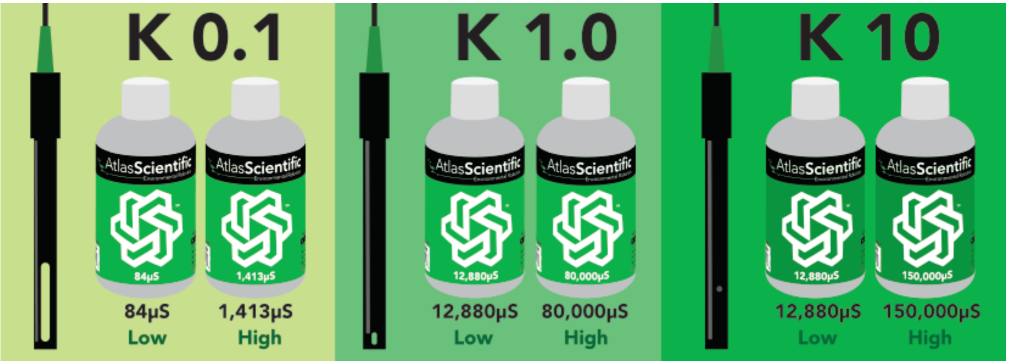
Sensor Calibration

EC Probe

You need to perform a **3 step calibration** with a **dry point** and a **2-point calibration** with the calibration solutions. This is the order of the calibration:

- set probe type
- dry point
- two-point calibration

Always clean the probe with distilled water between each calibration



Set the probe type (replace depending on your probe)

```
control conductivity com K,1.0
```

First, read the sensor until stable (N times):

```
control conductivity com r
```

Issue calibration of dry:

```
control conductivity com cal,dry
```

x 2 times!

First, read the sensor until stable (N times):

```
control conductivity com r
```

Issue calibration of low/high:

```
control conductivity com cal,low,[value]
```

Example

```
control conductivity com cal,low,12880
```

Other useful commands:

```
control conductivity com cal,clear
control conductivity com cal,?
```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How often? ~6 months. You need to replace the electrolyte probably sooner

Sensor Calibration

DO Probe

Make sure you have followed the probe reconditioning before proceeding with this calibration

You have two options for this calibration:

1) Single point calibration (dry point)
2) 2-point calibration (dry point and 0 mg/l point) - **only if you need accurate readings below 1mg/l**

First, read the sensor until stable (N times):

```
control dissolved oxygen com r
```

Issue the calibration command, after this the readings will change:

```
control dissolved oxygen com cal
```

If at any point of the calibration process you see akward readings (for instance, that using a 0mg/l solution for dissolved oxygen you see weirdly high values), it is better to start over.
For this, proceed with:

```
control dissolved oxygen com cal,clear
```

And start again

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How often? ~6 months. You need to replace the electrolyte probably sooner

Sensor Calibration

Make sure you have followed the probe reconditioning before proceeding with this calibration.

DO Probe

You have two options for this calibration:

1) Single point calibration (dry point)

2) 2-point calibration (dry point and 0 mg/l point) - **only if you need accurate readings below 1mg/l**

First, read the sensor until stable (N times):

```
control dissolved oxygen com r
```

Issue the calibration command:

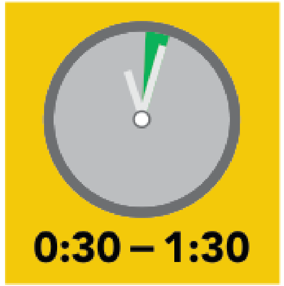
```
control dissolved oxygen com cal,0
```

If the readings during the 0mg/l go up, instead of down, start over. For this, proceed with:

```
control ox com cal,clear
```

And start again

After you have calibrated the EZO™ Dissolved Oxygen circuit using the "Cal" command; Place the probe into the Zero Dissolved Oxygen calibration solution and stir the probe around to remove trapped air *(which could cause readings to go high)*. Let the probe sit in Zero D.O. calibration solution untill readings stabalize. *(small movement from one reading to the next is normal)*.



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How often? At least once a year. More if you are on the extremes of the scale

Sensor Calibration

ORP Probe

- ORP probe can be calibrated with any calibration solution. **You can use a 225mV solution**

You only need to do a **single point calibration** this time

First, read the sensor until stable (N times):

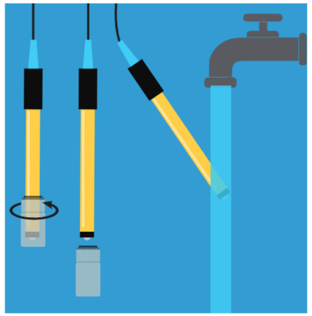
```
control orp com r
```

Issue calibration command:

```
control orp com cal,[value]
```

Example with default calibration solution

```
control orp com cal,255
```



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How often? Only if you change the probe cable or new probe

Sensor Calibration

Temperature Probe

This process is only necessary if you change the probe cable or the first time you use the sensor.

This is needed because the temperature probe is a resistive sensor – more cable → more resistance!

You will need a liquid which temperature is known – for instance, a pot of boiling water or calibrated sensor in the same liquid to be able to get a reference reading

The presence of a thermowell doesn't affect calibration or readings.

With a reference sensor (not mandatory)

First, read the **reference sensor** until stable (N times):

```
control atlas temp com r
```

Write the **[value]** down

First, read the **target sensor** until stable (N times):

```
control atlas temp com r
```

Issue calibration command

```
control atlas temp com cal,[value]
```


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Sensors in the wild

Sensor Installation

General considerations

You now have **bare probes** with shorter or longer cables.

- Probes **can't be simply submerged** and left unprotected

- They **need something to protect them and keep them at the desired depth**

- This enclosure needs to be **accessible for maintenance**

- This enclosure **shouldn't contaminate the environment**, or **affect the readings**!

Seawater

Seawater is corrosive and will destroy any material that is not ready for it.

- **Plastics**: HDPE, PVC, ABS, ASA,

- **Metals**: use of stainless steel **A4 316**

Tides change! You have to submerge the sensors **at least how ever much the tide moves!**

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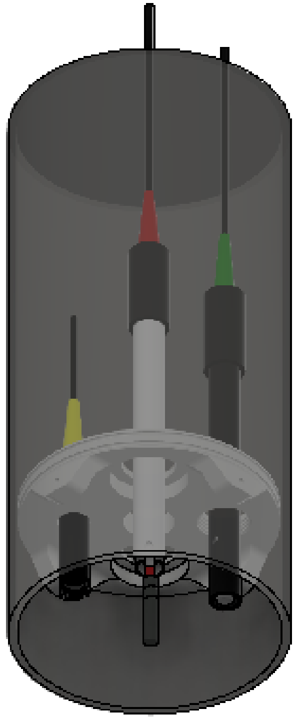
Sensor Installation

Design Options (prototypes)

Bulk type

Sensors are placed on a PVC pipe (110mm), with 3D printed ASA parts, diametrally on the pipe itself.

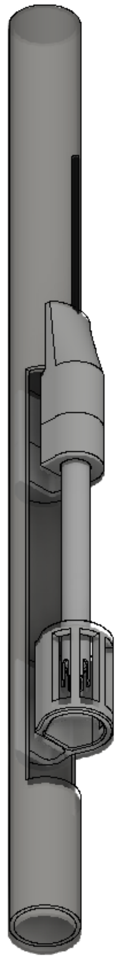
Good for wide spaces with shallow/deep deployments



Spear Type

Sensors are places on a PVC pipe (30mm), with 3D printed ASA parts, longitudinally on the pipe itself.

Good for small spaces with deep deployments



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Sensor Maintenance

Biofouling

Make sure that the sensors are cleaned frequently, specially if deployed on the field.

In some cases, sensors will be affected by biofouling and they will need more or less often cleanup - **in some cases weekly!**

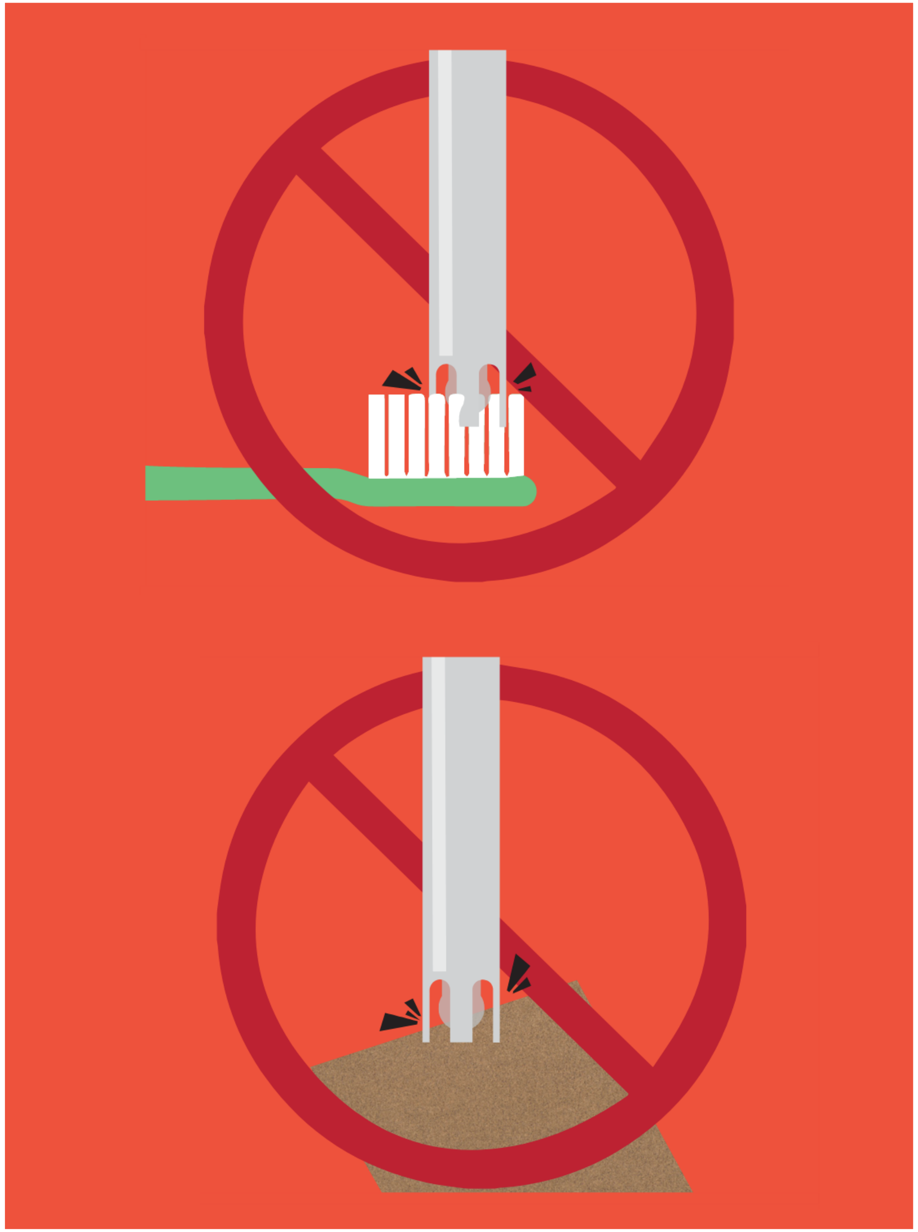
This will depend on the biological activity of your area!

Sensor Maintenance

pH Probe cleaning

Coating of the pH bulb can lead to erroneous readings including shortened span (slope).
The **type of coating will determine the cleaning technique:**
- **Soft coatings can be removed by vigorous** stirring or by the use of a s**quirt bottle**.
- **Organic chemical, or hard coatings**, should be **chemically removed using a light bleach solution**.

If cleaning does not restore performance, **reconditioning** may be tried. **Do not use a brush or abrasive materials on the pH probe**.



Sensor Maintenance

Conductivity Probe cleaning

Over time conductivity probes can become dirty and covered in deposits, which can change the basic electrical properties of the probe and cause inaccurate readings.

Soft coatings can be removed by lightly brushing around the conducting area.

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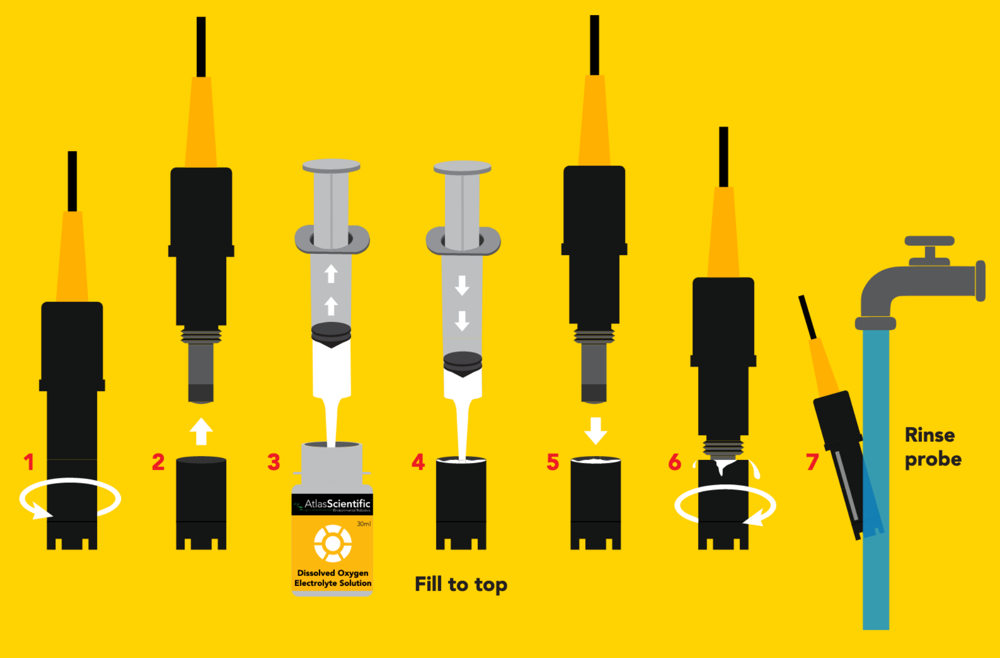
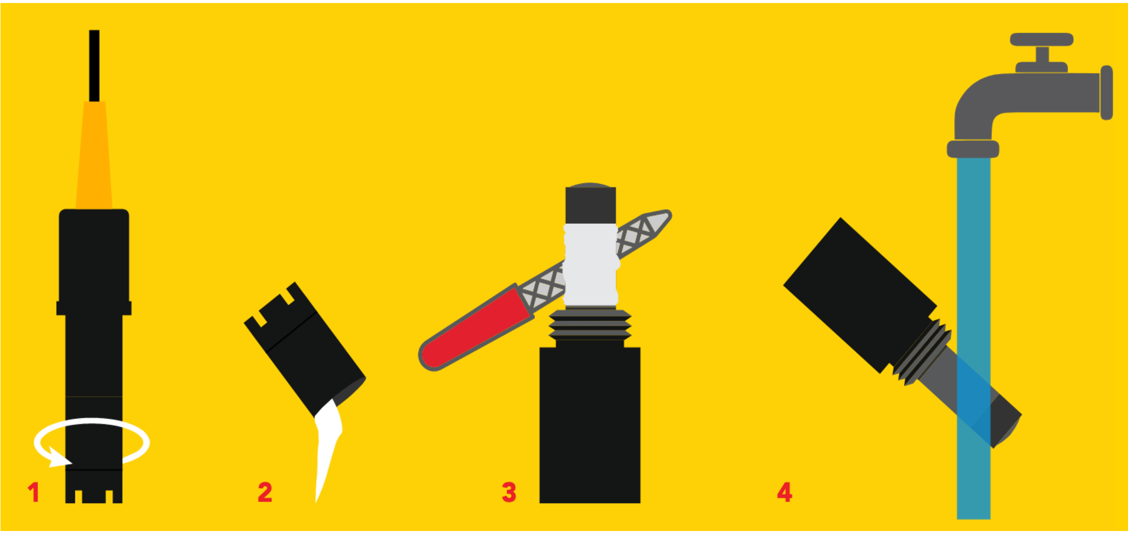
Sensor Maintenance

Dissolved Oxygen Probe

Revisit the sensor **preparation** for this.





DO NOT USE A BRUSH TO CLEAN THE MEMBRANE

If the probes membrane is ripped it must be replaced, as it will cause irregular readings.

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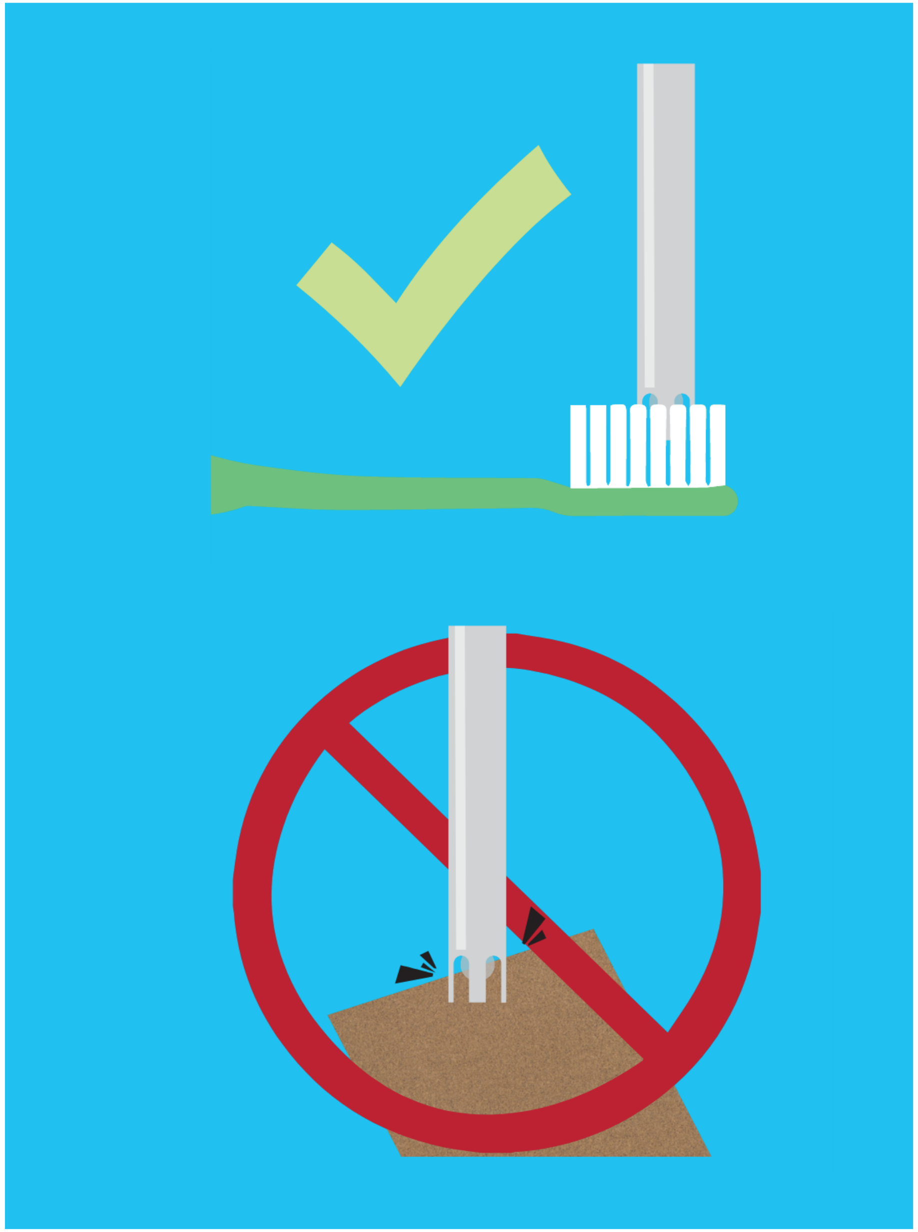
Sensor Maintenance

ORP Probe cleaning

Coating of the ORP bulb can lead to erroneous readings including shortened span (slope). The **type of coating will determine the cleaning technique:**

- **Soft coatings can be removed by vigorous** stirring or by the use of a s**quirt bottle**.
- **Organic chemical, or hard coatings**, should be **chemically removed. A light bleach solution or even a 5 – 10% hydrochloric acid (HCl) soak for a few minutes, often removes many coatings.**



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And on the next session...

And on the next session...

Getting data

Basic data access

Visual programming