In situ monitoring of ions with electrochemical sensors as a valuable source of information

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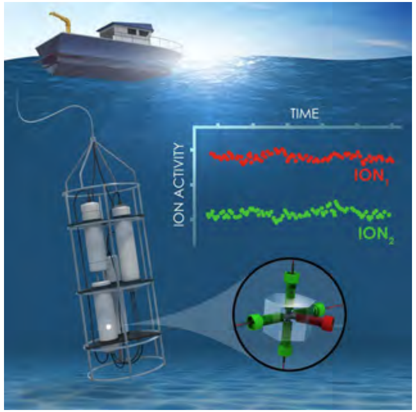
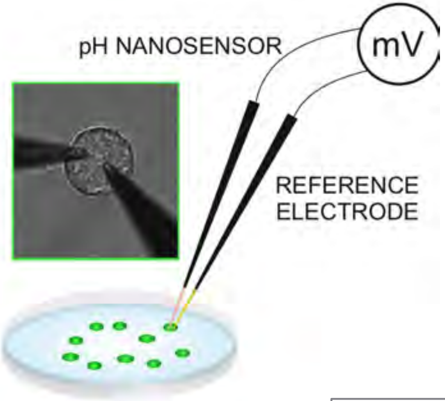
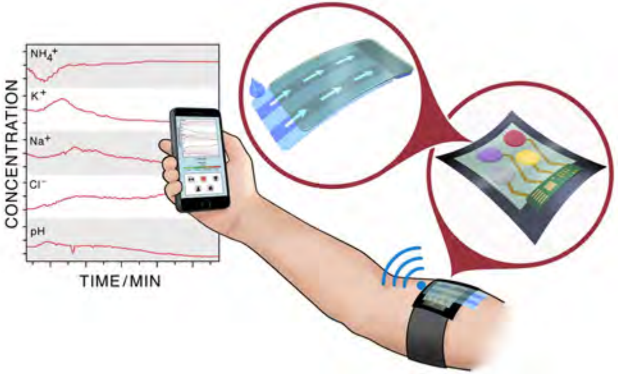


ChemSens

The Chemical Sensing Group





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The Baltic Sea suffers from eutrophication

Excessive **input** of nutrients to the marine environment enhances the growth of phytoplankton, leading to reduced light conditions in the water, oxygen depletion at the seafloor and a cascade of other ecosystem changes.

Water Quality?
Cleaner Water?

Early Diagnosis, Prediction, Recovery, Policies

↑

IoO

Internet of Oceans

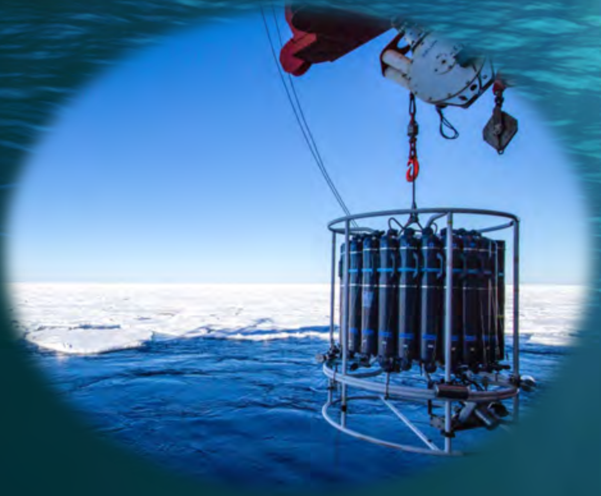
↑

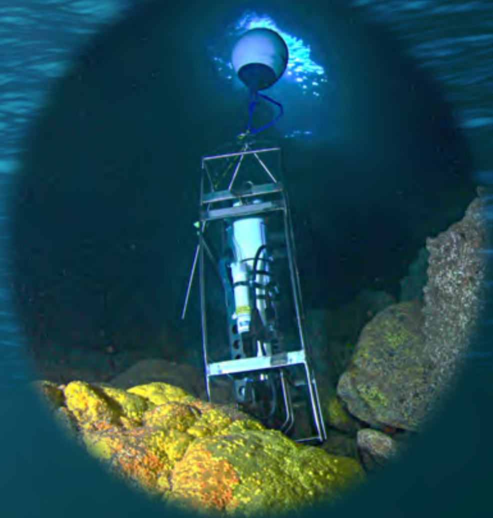
Massive Information

↑

??


Epichlorohydrin
Fluoride
Lead
Mercury
Nickel
Nitrate
Nitrite
Pesticides
Pesticides - Total
PAHs
Selenium
Pb
Hg
Ni
NO3
NO2
Se
0.01
250ml
200
150
100





CTD: pressure, temperature, conductivity (salinity), oxygen, pH and redox potential, sampling.

Early Diagnosis, Prediction, Recovery, Policies

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IoO

Internet of Oceans

↑

Massive Information

↑

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Early Diagnosis, Prediction, Recovery, Policies

↑

IoO

Internet of Oceans

↑

Massive Information

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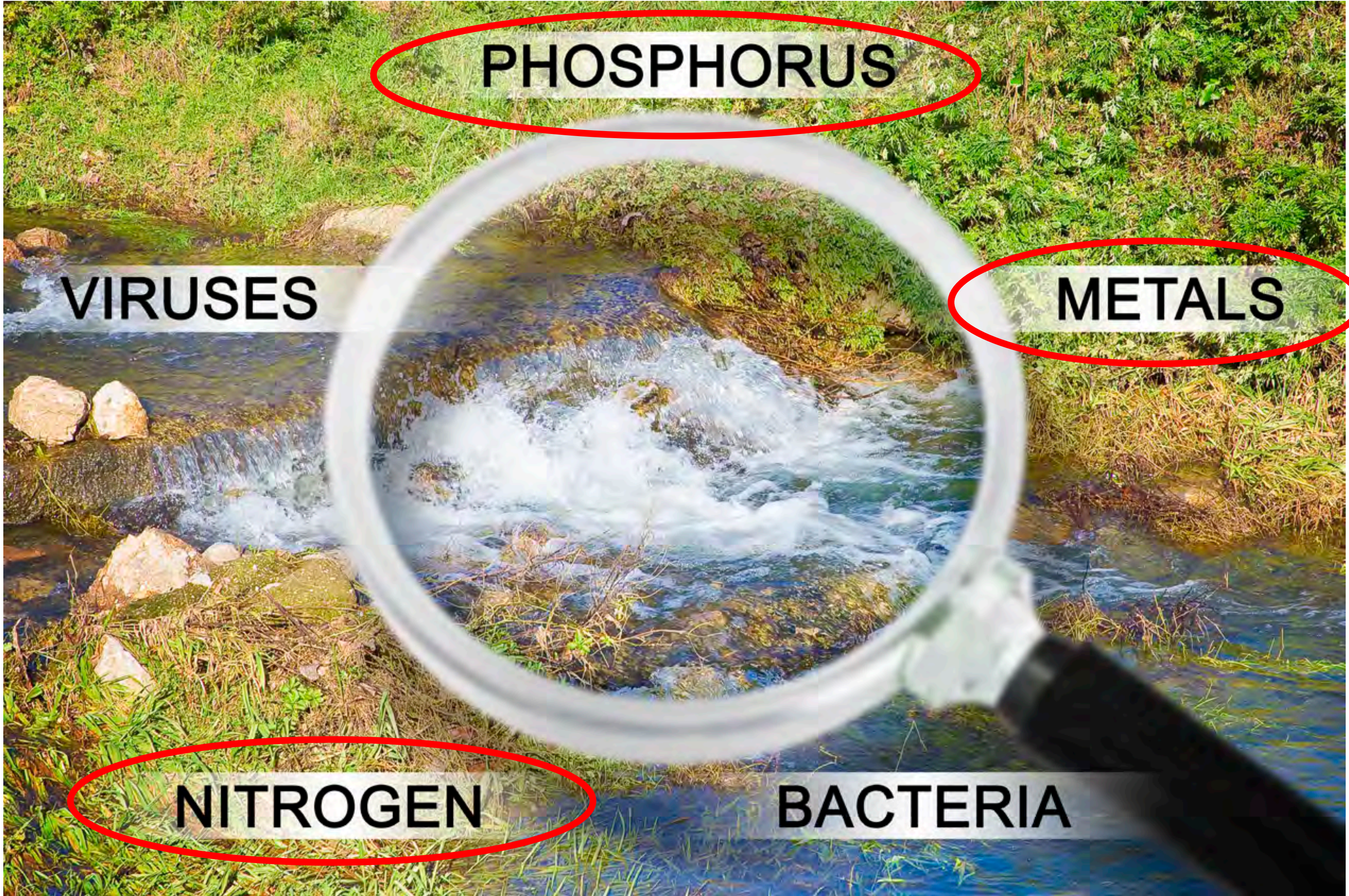
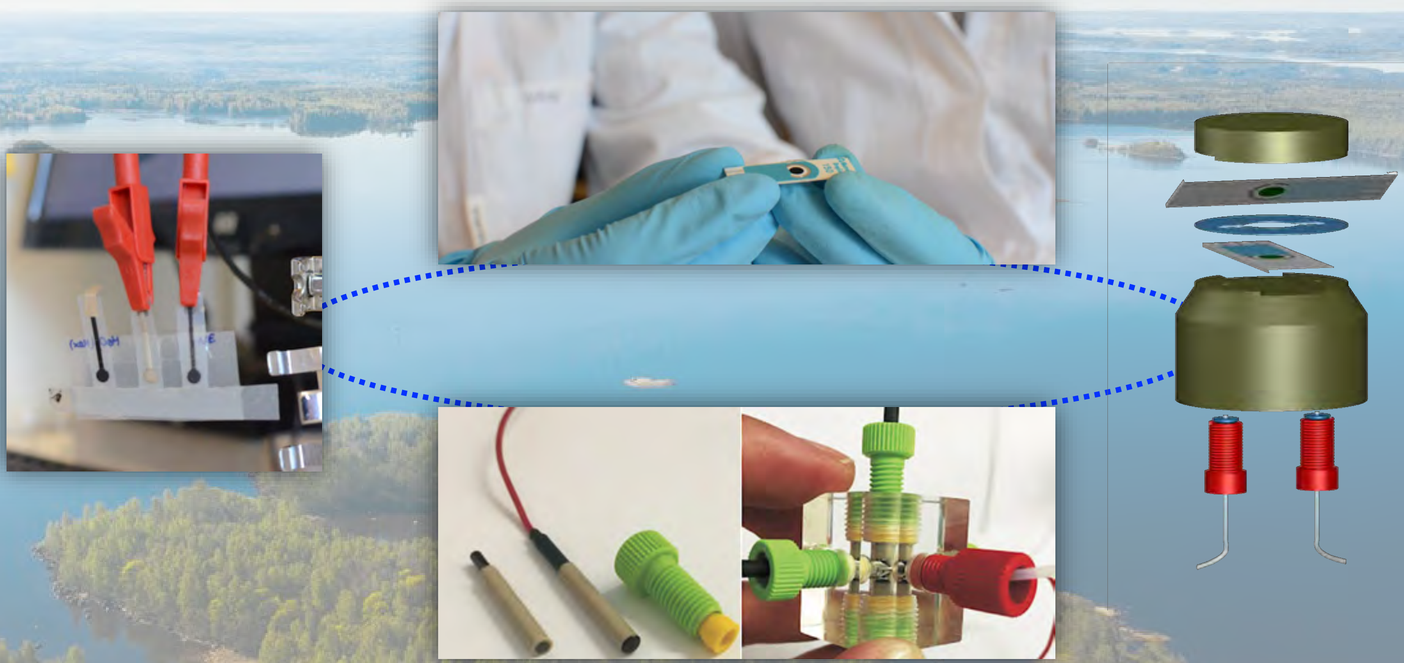
ELECTROCHEMICAL SENSORS

fast response, continue, easy to interpret, cheap, high temporal and spatial resolution, etc.

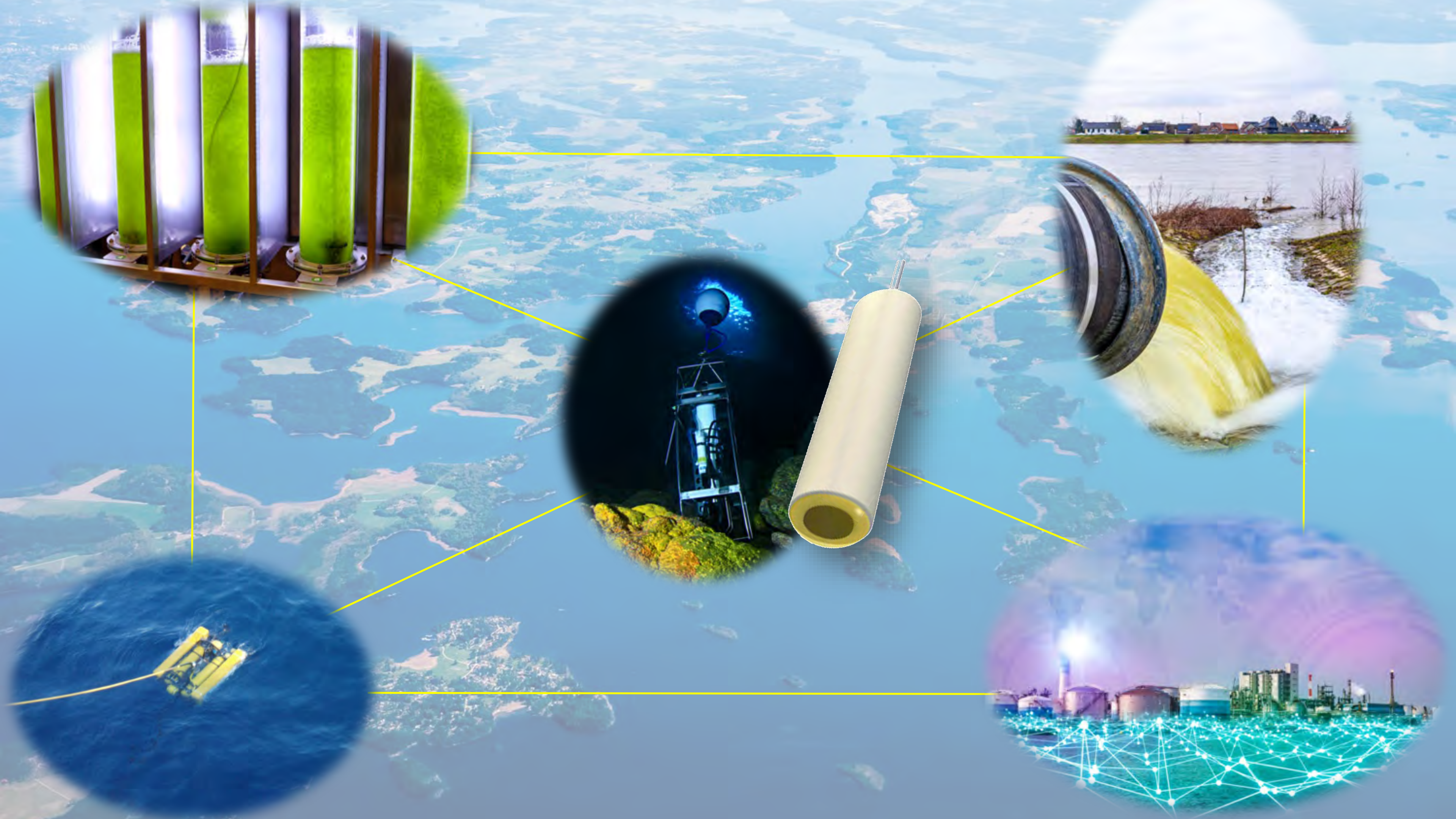

PHOSPHORUS
VIRUSES
METALS
NITROGEN
BACTERIA

TECHNOLOGY	IONS	INFORMATION	CURRENT TRL
Alkalinity-Module	Carbonates	Ocean's carbon uptake, in buffering, and in calcium carbonate production and dissolution.	TRL 4 Lab validted
P-Module	Inorganic P (phosphates)	Eutrophocation and algae bloom (toxins).	TRL 3 Lab proof-of-concept
C-Module	pH, carbonate, calcium, calculation of CO_2	The ocean is a sink for atmospheric CO_2, forming carbonate that increases water pH.	TRL 6 In Situ validated
N-Module	Ammonium, nitrate, nitrite	Eutrophocation and algae bloom (toxins).	TRL 3-4 Partially validated
Salinity-Module	Chloride	Higher salinity represents higher water density, which changes the movement of ocean currents.	TRL 6 In situ validated
ANC-Module	Acid Neutralizing Capacity: base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and acid anions (SO_4^{2-}, NO_3^{-}, and Cl^{-})	Water acidification: major role in the global ocean chemistry.	TRL 2 Formulated Concept
Metals-Module	Silver, Lead, Copper, Cadmium, Chromium, Nickel, Iron and Manganese	Pollution and toxicity	TRL 2 Formulated Concept

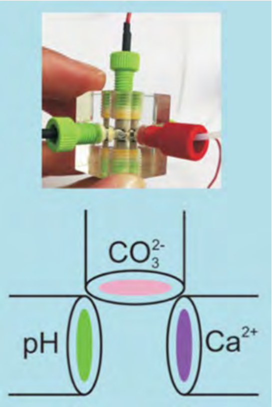
SMALL + IN SITU + REAL TIME + LOW COST




PH



C-MODULE
(Genoa Harbour)



DOI: 10.1021/acs.estlett.7b00388
Environ. Sci. Technol. Lett. 2017, 4, 410−415

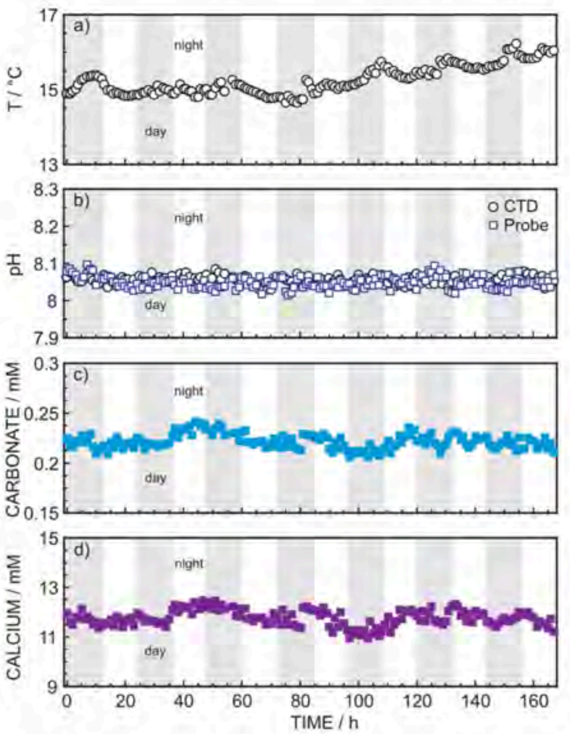
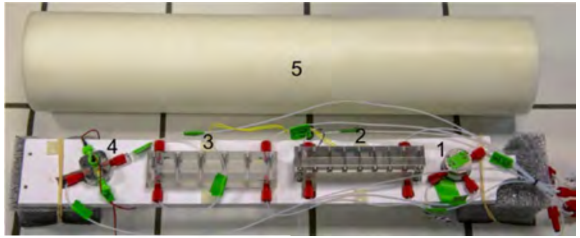


Figure 2. In situ profiles obtained for (a) temperature (CTD), (b) pH (CTD and developed electrodes), (c) carbonate, and (d) calcium during a 167 h deployment (from April 3, 2017, at 07:00 to April 10, 2017, at 12:00) in the CNR Station in Genoa Harbor (Italy). Note that additional sampling was performed for validation during the first 10 h. The average salinity was 37.95 PSU. The deployment depth was 4.2 m. The dissolved O_2 concentration was 6.4 ± 0.3 ppm, corresponding to 83.7 ± 3.3% for oxygen saturation within the monitoring window. Light hours are shaded in gray.[40]

N-MODULE (Arcachon Bay)



DOI: 10.1021/acs.analchem.7b05299
Anal. Chem. 2018, 90, 4702–4710

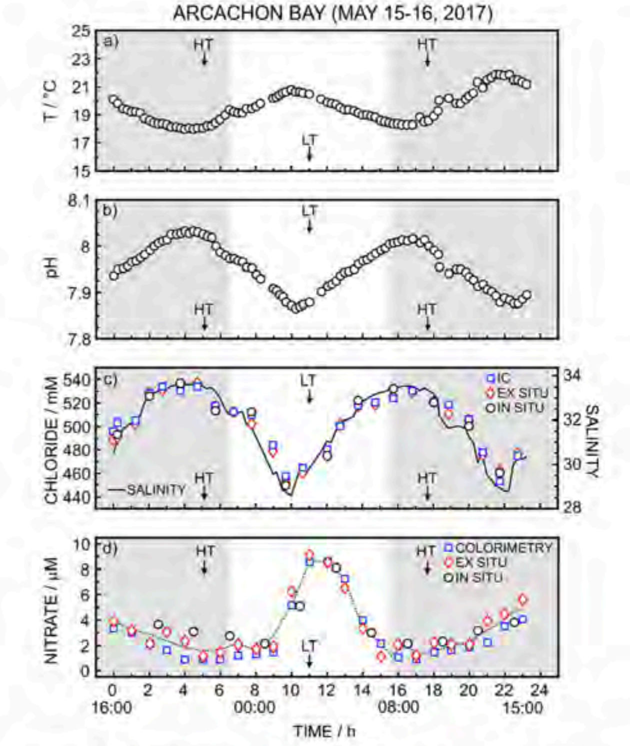
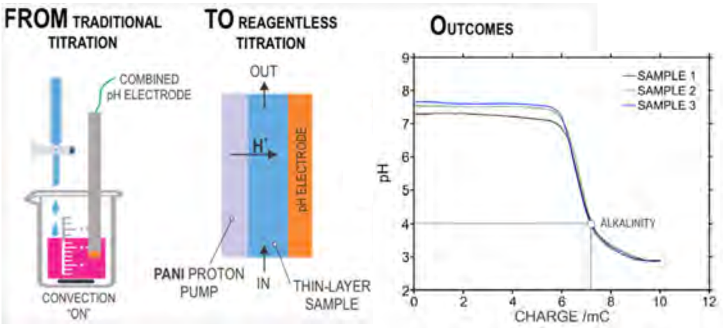
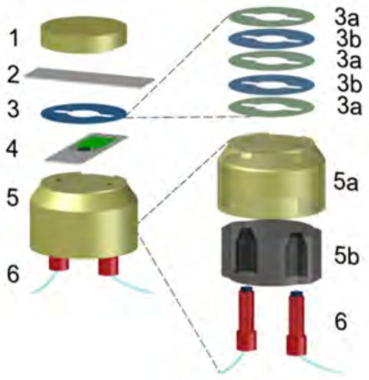


Figure 5. In situ temporal profiles obtained for (a) temperature (CTD), (b) pH (CTD), (c) salinity and chloride, and (d) nitrate during the deployment of 23 h (starting from May 15, 2017 at 16:00 to May 16, 2017 at 15:00) in the Arcachon Bay (44°40.822′N 1°06.007′W). The deployment depth was 2.3 ± 0.3 m. The dissolved O_2 concentration was 7.5 ± 0.3 ppm, corresponding to 101.2 ± 3.2% for oxygen saturation within the monitoring window. Light hours are shaded in gray.[51] The local times for high and low tides (HT and LT, respectively) were determined according to the tidal record at Jetée d'Eyrac (44°40′N 1°10′W) and considering the temporal evolution of the seawater level in the Arcachon Bay.[52,53]

Alkalinity-MODULE (Baltic Sea)





https://doi.org/10.1021/acs.analchem.1c02545
Anal. Chem. 2021, 93, 14130−14137

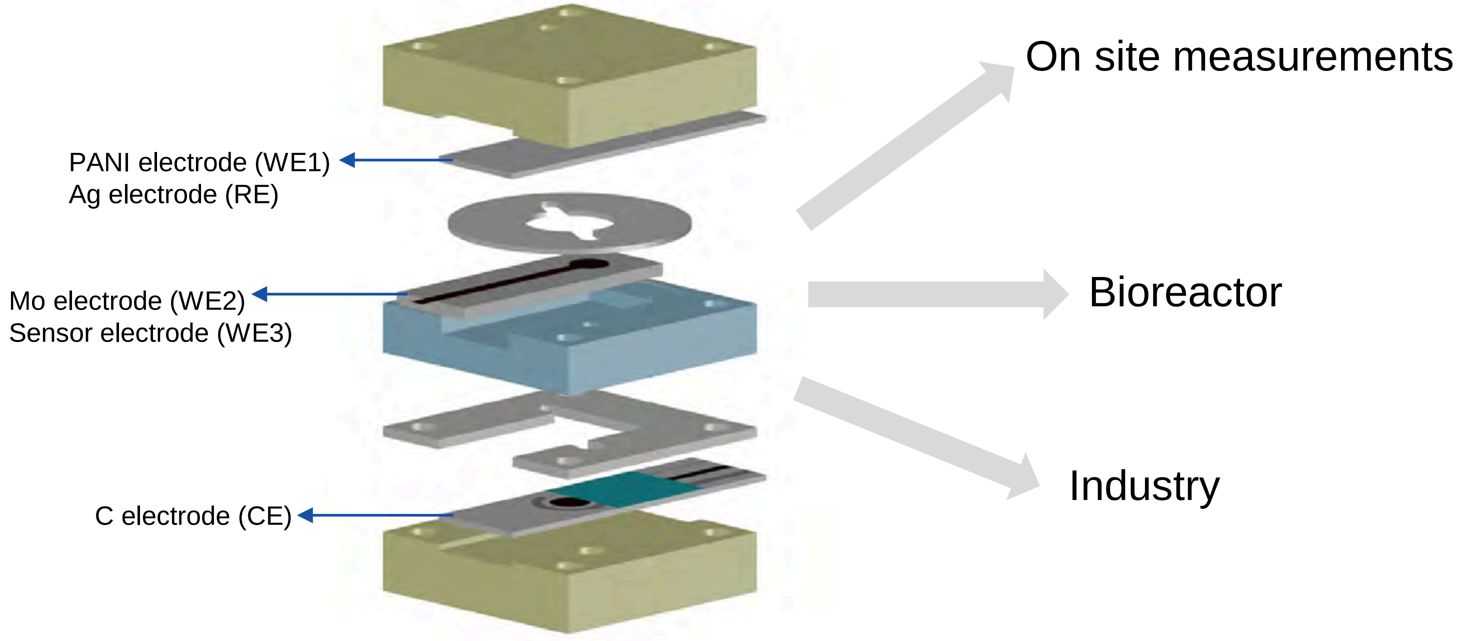
Table 1. Alkalinity Attained by Our Method and through Manual Titration

	initial pH		alkalinity (mM HCO_3^-)		
	pH meter	PANI sensor	new method[a]	titration[b]	difference (%)
1	7.3	7.3	1.57 ± 0.04	1.50	4.7
2	7.5	7.4	1.55 ± 0.05	1.48	4.7
3	7.3	7.6	1.63 ± 0.05	1.63	0
4	7.3	7.4	1.40 ± 0.09	1.54	9.1
5	7.3	7.5	1.40 ± 0.21	1.53	8.5
6	7.4	7.5	1.66 ± 0.05	1.46	12.0
7	7.2	7.4	1.49 ± 0.18	1.46	2.1
8[c]	7.6	7.7	2.75 ± 0.03	2.73	0.8
9[d]	7.8	7.9	3.30 ± 0.12	3.23	2.5

[a]Average ± standard deviation of n = 3 measurements. [b]Average of n = 3 measurements, with a standard deviation always lower than 0.04 mM. [c]Synthetic seawater. [d]Spiked synthetic seawater (+0.5 mM $NaHCO_3^-$).

Sample ID	Location	Coordinates
1	Stocksundet	59°22'56.1"N 18°02'30.8"E
2	Hägernäs Strand	59°26'32.3"N 18°07'46.1"E
3	Hustegafjärden	59°21'58.3"N 18°13'19.8"E
4	Näsbyviken	59°25'20.3"N 18°04'52.3"E
5	Edsviken	59°23'35.5"N 18°01'54.6"E
6	Grönstaviken	59°22'45.4"N 18°09'43.7"E
7	Torsviken	59°22'09.5"N 18°07'11.5"E

P-MODULE
(Baltic Sea)



Addressing the Detection of Ammonium Ion in Environmental Water Samples via Tandem Potentiometry–Ion Chromatography

Renato L. Gil, Célia G. Amorim, and Maria Cuartero* https://doi.org/10.1021/acsmeasuresciau.1c00056

Electrochemical sensors for *in-situ* measurement of ions in seawater

Maria Cuartero Sensors & Actuators: B. Chemical 334 (2021) 129635

Subnanomolar detection of ions using thin voltammetric membranes with reduced Exchange capacity

Kequan Xu, Gaston A. Crespo, Maria Cuartero* Sensors & Actuators: B. Chemical 321 (2020) 128453

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