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**ENVIRONMENTAL QUALITY ASSESSMENT  
AND MONITORING WITH WIRELESS SENSORS  
NETWORK – FINAL REPORT**



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## **acknowledgments**

For those who have experience doing field work in environmental hydrogeochemistry it is frequent to think about the advantages of an automatic and continuous monitoring, with remote and real-time data transmission. Not only because of the effort and cost of human resources, but also to improve the reliability and fidelity of the data, as it should lead to a better environmental quality assessment. Therefore, I must first acknowledge Dr. Carla Candeias and Dr. Paula Avila, as they envisioned the first steps in this direction. This work has aimed to contribute to this research approach, so that it may be further pursued in the future.

The interface of Sciences of Nature and Technology is an expanding universe, in which the sensors represent linking points. However it is desirable to select efficient links and test applications. Professor Vitor Santos played a key role in this matter. Without him, it wouldn't have been possible to assess the feasibility and capability of the different solutions available, of which only a few showed the desirable technical requirements.

I would like to thank Professor Eduardo Ferreira da Silva for the formal framework of this work, as well as the extensive research background dedicated to the study-area and environmental monitoring. His scientific work which has been published since the 80s, was the starting point of this study.

My acknowledgment to Madame Anne-Marie Guihard-Costa that showed me how multidisciplinary can be more than a mere theoretical concept. She became one of Estarreja's highest promoters, seeking to build a knowledge base that comes from disciplinary conjunction, rather than juxtaposition. My grateful thanks.

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## **palavras-chave**

Monitorização ambiental remota e de longo prazo, sensores em rede sem fios, medição contínua e em tempo real da qualidade da água, sensor químico, mercúrio, Complexo Químico de Estarreja, Ria de Aveiro

## **resumo**

Iniciado em Outubro de 2015, este projecto faz parte de uma linha de investigação da Universidade de Aveiro, dedicada à monitorização ambiental e com o apoio financeiro do OHM Estarreja (CNRS-França). O problema de partida foi o reconhecimento de uma tecnologia que promovesse o controlo à distância e, eventualmente, a amostragem automatizada de água, para obter dados geoquímicos em tempo real, integrada em programas de longo prazo. O equipamento seria constituído por uma rede de sensores químicos, imersos na água, sendo a comunicação sem fios – o sistema tem a abreviatura WSN.

O presente relatório apresenta o contributo desse estudo na definição e concepção do sistema de monitorização WSN, em alternativa aos métodos convencionais. Para isso, fez-se o levantamento do estado da arte, no domínio da geoquímica ambiental, para definir parâmetros regionais críticos em que o sistema tecnológico será instalado. E, bem assim, averiguar as soluções técnicas possíveis para estes sensores (disponíveis, ou não, no mercado).

A área de estudo onde os dispositivos deverão ser instalados é o Complexo Químico de Estarreja, ambiente contíguo ao sistema estuarino do Baixo Vouga Lagunar, com termo jusante na Ria de Aveiro. Estes ambientes têm vindo a ser sinalizados e caracterizados em trabalhos técnicos e científicos, desde a década de 1970, com elevada contaminação industrial em mercúrio, entre outros metais pesados.

Assim, este relatório fornece os elementos de estudo, referências e estratégias de pesquisa usadas na análise das soluções técnicas para a detecção metálica, compatíveis com as condições do meio, no desenvolvimento de um sistema integrado WSN e sensor electroquímico, como garantia de uma melhor avaliação e monitorização da qualidade do ambiente.

**keywords**

long-term remote environmental monitoring, wireless sensors network, autonomous real-time water quality sensing, chemical sensor, mercury, Estarreja Chemical Complex

**abstract**

Initiated in October 2015, this project is part of an Environmental Monitoring research line in Aveiro University, with the financial support of OHM Estarreja (CNRS-France). The initial problem was to identify a technology solution able to remotely control and perhaps automate sampling, to gather and transmit real-time data for long-term monitoring, as an efficient alternative to conventional monitoring. The selected system is named Wireless sensor network (WSN).

This study and Report aim to support the design of a monitoring system in superficial water based on WSN. First the state-of-the-art of the geochemical regional critical parameters was reviewed. In parallel, a market study was done to get an overview of types of chemical sensors (commercially available or not). The study-area where the equipment is to be installed is Estarreja Chemical Complex, contiguous to the important estuarine system Ria de Aveiro. Both environments have been associated with industrial contamination, mostly by mercury, and also other heavy metals.

Thus, the aim of this Report is to present research projects, strategies and other references, to review technical solutions in heavy metals sensing, taking into account the regional conditions, and to propose an integrated system comprising the WSN and electrochemical sensors, in order to ensure the environmental quality assessment and monitoring.

## **mots-clés**

surveillance de l'environnement à long terme et à distance, réseau de capteurs sans fil, détection autonome et en temps réel de la qualité de l'eau, capteurs chimique, mercure, Complexe Chimique d'Estarreja

## **résumé**

Débuté en octobre 2015, le projet s'intègre dans le cadre d'une recherche basée sur le suivi environnemental, à l'Université d'Aveiro, et financé par l'OHM Estarreja (CNRS-France).

L'objet initial visait à identifier une solution technologique capable de contrôler à distance et éventuellement prélever automatiquement des échantillons, mais aussi de rassembler et transmettre en temps réel des données dans le cadre d'une surveillance à long terme, alternative efficace à la surveillance classique. Le système choisi est un réseau de capteurs sans fil (Wireless Sensor Network (WSN)). Cette étude et rapport visent à appuyer la conception d'un système de surveillance des eaux de surface, à l'aide du WSN. Dans un premier temps, un état des connaissances des paramètres géochimiques critique régionaux a été fait. En parallèle, une étude de marché a été menée, afin d'obtenir une vue d'ensemble sur les différents types de capteurs chimiques (disponibles, ou non, sur le marché).

La zone d'étude où les dispositifs doivent être mis en place correspond au Complexe Chimique d'Estarreja, complexe contigu du grand estuaire de Ria de Aveiro (Portugal). Les deux entités ont été associées à des contaminations industrielles, principalement par le mercure, mais aussi par d'autres métaux lourds.

Par conséquent, le but de ce rapport est de présenter les projets de recherche, les stratégies et autres références pour réfléchir à des solutions techniques dans la détection des métaux lourds en tenant compte des conditions régionales, mais aussi de proposer un système intégré comprenant le WSN et les capteurs électrochimiques. Ceci dans le but de garantir l'évaluation et le suivi de la qualité environnementale.

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# 1. GENERAL INTRODUCTION

## 1.1. Motivation and Background

From the beginning of this post doc Project in September 2015 to its completion in September 2016, important technological advances were achieved in the development of environmental sensors for different kinds of pollutants. The national and international requirements for water quality and also the social pressure to improve health, safety and quality of life call for more effective and efficient systems to monitor and anticipate the environmental assessment.

On the other hand, the decision support must be based not only on theoretical approaches, (space-time studies, in a transversal analytical perspective), but also in long-term management programs (in a longitudinal approach), with automatic and continuously monitoring devices, capable of remote real-time data transmission. A Wireless Sensor Network (WSN) is able to achieve these goals.

The study-area of this project - Chemical Complex of Estarreja (CQE) – is in contiguity with the estuarine environment - Baixo Vouga Lagunar (BVL) – and it's downstream end Ria de Aveiro (referred to as RIA throughout this text). It has a strong industrial, agricultural and human pressure, with a dense fluvial drainage, a strong hydrodynamic flow and an inter-tidal influence. The main physicochemical changes in the environment are related both the salinity and to human impact, generated over the decades from the CQE.

The most significant environmental impact and the one that was first Reported in literature is industrial contamination by mercury (Hg) and arsenic (As). In CQE industries, Hg was present as a reagent, a by-product and as an effluent of industrial chemical processes, from the 1950s until the 1990s. Such Hg content persists in various media (sediment, soil, water, plants and animals) and found its way into the food chain. The As content is associated with waste treatment of mining raw materials (massive sulphide) is the past. Brought from the Iberian Pyrite Belt (Aljustrel mining complex) that raw material includes arsenic pyrite (up to 10% As in the crystalline lattice) bearing a wider range of trace metals, exceptionally high in those kinds of deposits.

OHM ESTARREJA encourages the study of complex phenomena in the field of natural and applied sciences, in a multidisciplinary approach, like this one. This project (referred to as OHM WSN project throughout this text) combines hydrogeochemistry with mechanical engineering and has a close association with another OHM project - "Wireless sensors network as a base solution for environmental water quality assessment and monitoring" (LabEx DRIIHM-280, Carla Candeias, Vitor Santos and Paula Ávila). This other project financially supported the equipment selected as the best solution.

## 1.2. Scopes and objectives

Several studies focussing on the RIA and the CQE have highlighted the flows and the biogeochemical cycles of some heavy metals, especially Hg. The complexity of the Hg contamination has been characterised in multiple transfer vectors at the ecosystem level. The scientific background of the RIA and CQE environment encompass diversified sampling media, with different sampling grids, describing a wide variety of interface phenomena, like chemical reactivity, exchange and transfer to the trophic food chain.



From the technological/sensing viewpoint, the study-area knowledge background may be seen as both the set of contingencies and operating requirements.

Thus, the combined study of environmental works published about RIA and CQE, and the review of environmental monitoring technology, which reflects the structure of this Final Report, was followed with the objective of analysing the best technology solution, able to remotely control, to gather and transmit real-time data for long-term monitoring, as an efficient alternative to the conventional approach, improving the detection of Hg concentration in water. In particular, this study aims to:

- i) contribute towards a better selection of the critical (direct and indirect) environmental parameters and a preferential location for the monitoring station through a review of the study-area established knowledge;
- ii) overview of state-of-the-art in water quality monitoring technology, specially relating with remote, and long term monitoring with wireless sensor networks (WSN);
- iii) review analytical instrumentation related with chemical and electrochemical sensors, the main applications and recent developments;
- iv) market study of WSN, chemical and electrochemical sensor technologies, and distinguish scientific and commercial solutions.

The approach to achieve the objectives listed above combines detailed reviews of the RIA and CQE bibliography in the scientific domains of geochemistry, chemistry, biology, and the market study through monitoring environmental technology, to evaluate a possible monitoring solution that guarantees cost savings and compliance assurance.

### 1.3. Report organization - Post Doc frame design

This Report is organized in 5 parts, including this (General Introduction). Besides introducing the Report and describing its structure, this first part also covers brief reviews of: i) the study-area CQE and its contiguous environment RIA, their geological, hydrological and hydrodynamic context; ii) the overview of environmental impact, in particular identifying the main analytic matrices; iii) national and international directives relating with standards for environmental monitoring.

In the second part, some options of monitoring technology are reviewed, regarding distance or remote long term monitoring, sampling and analytical methodology in the field. This part of the Report includes: i) state-of-the-art of WSN – concept and structure (with a discussion on autonomy and security for remote stations, the control of the devices, and the support structure or anchorage equipment); ii) national and International R & D projects of environmental sensing (examples of inter-governmental applications and funded projects by Community Research and Development Information Service (CORDIS); iii) critical parameters.

Analytical sensors are presented in the third part, with distinctions between physic-chemical, chemical and electrochemistal sensors (using potentiometry and voltammetry). Also in this part of the Report there is a brief

overview of technological developments in chemical sensing, and advances in research and application of specific innovative sensors, called screen printed electrode (SPE).

The concluding remarks and considerations for future trends are presented in the fourth part of the Report. In this part, the major contributions for the designing of the monitoring system based on WSN are highlighted and future suggestions for the OHM – WSN project improvements.

Finally, the References are organised chronologically and by topic, following the Report structure.

The appendixes with bibliographic maps complement the contents presented throughout the main parts of the Report. The last appendix details the Market Study, with the technical and commercial solutions found (producers / laboratories "Start Up" and distributors): i) bench equipment; ii) portable equipment; iii) panel equipment; iv) online automated equipment. A summary table organises these solutions.

### 1.4. Study-area – CQE and BVL/RIA brief characterization

Regarding the study-area review, the selected information that could be important to this study, can be divided in: i) natural environment (geologic, hydrologic, hydrodynamic) associated to BVL/RIA; II) environmental impact associated with CQE and its dispersion. Both types of references were analysed to identify the critical parameters (in direct and indirect association with the Hg contamination), how and where it could be measured continuously.

The study-area presents a strong environmental contrast between heavily contaminated areas by industrial activity, especially in the early 1950's (the Estarreja Chemical Complex - CQE) and lake-river environments in a mesotidal estuary (included in the BVL, contiguous to the RIA).

RIA is characterized by a saline introgression with variations in the tidal submersion regime (mesotidal). Specifically, the area corresponding to the CQE and its adjacent terrains, the lithostratigraphy consists of a sequence of Holocene and Plio-pleistocene sediment layers, with a considerable vertical and lateral heterogeneity and an increase in thickness from E→W and N→S. Generally, these sediments have a detrital nature and a silicate matrix (Barradas, 1993), are formed by variable grain size sands, by muddy sands and muds, based on pre-Ordovician shales (cloritic, sericitic and muscovite shales) specifically in the E of the CQE. In the W of the CQE, Cretaceous stoneware occurs. The CQE plants were built on a surface layer of very permeable sands (Branco, 2007). The type of hydrographic network is closely linked to the lithological nature of the terrain, which in turn affects the infiltration/surface runoff binome (Barradas, 1993).

Related with the hydrodynamic aspects, several studies show that RIA's origin and morphological evolution are associated with climate variability, which induces local fluctuations in mean sea level (Rodrigues, 2012; Vargas, 2012). A monitoring system like WSN could also give a useful contribution to distinguish between climate and tidal cycles, changes in weather patterns, in addition to detecting contamination spots or industrial operation cycles and their effluent discharges, which is the main focus in this work.

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However, the hydrodynamic aspects represent the main environment variations in superficial waters, which is an important factor for the monitoring station installation. On the other hand, geologic and hydrologic context may also cause interference with the equipment, mainly with the sensor.

Regarding the study-area natural context, the most significant references and related critical aspects for the present study, are summarised in the following **TABLE**.

Context	Critical aspects	References
Regional geology	The knowledge of the stratigraphic structure and the lithological units is relevant to predict rock-water interactions, and their influence in the sensor's measurements, are also relevant for making decisions about the support structure or the anchorage point of the equipment.	Teixeira and Zbyszewski (1976); Teixeira and Torre de Assunção (1963); Soares <i>et al.</i> (1982).
Superficial and quaternary hydrogeology	The characterization of the superficial waters (superficial aquifer) and of the water zone below (captive aquifer), its productivity, flows, networks and distribution in the study-area helps to define dilution sources, and the most persistent contaminants in the system.	Ferreira (1995). Dias <i>et al.</i> (1999) Branco, 2007
Cretaceous hydrogeology	The characterization and evolution of groundwater, and palaeowaters, their composition, chemical kinetics and rock-water interaction, helps to identify anomalies, persistent contamination, its distribution, the chemical content, and affected physicochemical parameters, which could be important to choose the sensor type and its location.	Saraiva <i>et al.</i> (1984); Condesso De Melo <i>et al.</i> (2001); Condesso De Melo (2002), Branco, 2007
Hydrodynamic	The knowledge of the river inputs on suspended sediment transport (fluxes between the lagoon and the ocean), the tidal export of particulate material and salinity patterns, the discrimination of the climatic factors and anthropogenic actions helps in the decision of where and how to install the monitoring station, evaluate their influence on the equipment anchorage and ensure the analytical conditions for the sensor operation.	Dias <i>et al.</i> (1998, 1999, 2000); Dias (2001); Abrantes <i>et al.</i> (2006); Lopes <i>et al.</i> (2001); Lopes (2009); Picado <i>et al.</i> (2011); Rodrigues (2012); Martins <i>et al.</i> (2013); Vargas (2012)
Sediment of the basin	The knowledge of the texture, mineral and chemical composition of the bed and suspended sediment allows to know about sediment-water interactions, and their influence on the device's maintenance and the reliability of sensor measurements.	Pereira (1996); Rocha <i>et al.</i> (2000); Abrantes <i>et al.</i> (2003); Martins <i>et al.</i> (2013)
Clay mineralogy	The chemical kinetics and mineral-water interaction of clay minerals could be a major influence on the sensor reliability, and may allow to anticipate requirements for the maintenance schedule if the sensor. These references could also support the decision on where the equipment should be installed.	Rocha and Gomes (1991, 1992); Delgado <i>et al.</i> (1992)

Regarding environmental contamination (not only by Hg, but also by As and other heavy metals), there is a large number of scientific publications, technical Reports, evaluation and control programs. Since the 80s the Hg problem has been referenced, the sources and sinks of Hg were associated with the CQE. The literature review provides important information, briefly listed below.

- 1) Past industrial raw materials, products, by-products, productions per year, chronology of the CQE installation and some processing diagrams were retrieved from Pássaro e Costa (1985); Vale *et al.* (1985); Lazaro and Silva (1985), Inácio (1993), Costa and Jesus-Rydin (2001), these works also Report the localization of the disposal sites and storage - channels, tanks and batteries. Queirós (1985) and Marnoto *et al.* (1985) present plans for pollution mitigation and effluent treatment, in a time of high environmental impact. Since 1994 the industrial operations began to include effluent treatment, with demercurization, to ensure discharges with a maximum of 50 µg/L Hg, and annual discharges in the order of 10 kg of Hg (Pereira, 1996). Until the 90s, the

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main industries were described by Inácio (1993), summarized below to highlight the complexity of the environmental problem of its various effluents:

- i. Uniteca since 1941 (now as CUF group), with the raw materials  $C_6H_6$ ,  $NH_3$ ,  $H$  produced  $C_6H_5NH_2$  (aniline) and  $C_6H_5OH$  (MNB), with  $NH_3$ ,  $HNO_3$ ,  $KCl$ ,  $(NH_4)_2HPO_4$  and  $Ca$ , produced  $(NH_4)(NO_3)$ , complex fertilizer (NPK and CAN), with  $(Hg, As)FeS_2$  (pyrite) produced  $H_2SO_4$  (until 1991); atmospheric effluents  $SO_2$ ,  $N_2O$ ,  $NH_3$ ,  $C_6H_5NO_2$ , suspended solids with  $Hg$  and  $As$ , liquid effluents  $C_6H_5NH_2$ ,  $NH_3$ ,  $C_6H_6$ ,  $C_6H_5OH$ ,  $As$ ,  $Hg$ ,  $Fe$ ,  $Zn$  and  $Pb$ ;
- ii. Quimigal since 1950 (now as CUF group) is a chlor-alkali production, with the raw materials  $NaCl$  (halite),  $HCl$ ,  $Hg$  (22 ton/year), produced paper and different by-products such as  $NaOH$ ,  $NaClO$ ,  $H$  and  $Cl$ , had as solid effluents  $Hg$ ,  $Ca$ ,  $Mg$ ,  $Fe$ ,  $CCl_4$  (most as sludge);
- iii. Cires since 1960, with the raw material  $C_2H_3Cl$  produced 70 000 ton/year of  $(C_2H_3Cl)_x$  (Polyvinyl chloride – PVC), effluents  $Ca(OH)_2$  (as a sludge).
- iv. Dow since 1978, with the raw material  $C_6H_5NH_2$ ,  $Cl$ ,  $NaOH$ ,  $CH_2O$  and  $CO$  produced  $NCO$  (60 000 ton/year),  $CCl_2O$  and  $ClH$  (byproducts), atmospheric effluents  $SO_2$  and  $NO$ , liquid effluents  $C_6H_5NH_2$ ,  $C_6H_5Cl$ ,  $Cl^-$ ,  $Na$ ,  $Hg$ .
- v. Oxinorte since 1990 (now as Air Liquide), with the raw material Naphtha produced  $CO$  and  $H$ , atmospheric effluents  $CO$ .

(It must be also considered other unit called Prozinco and with operation since 1978 (Branco, 2006).

- 2) The  $Hg$  content of the Industrial effluents, in 1985, was: 15,6 – 9,4 mg/L  $Hg$  effluent from Uniteca; 10,3 – 2,5 mg/L  $Hg$  effluent from Quimigal (Pássaro and Costa, 1985). In 1985, the total  $Hg$  industrial discharge reached 1100 kg (*cit por.* Pereira, 1996). The undifferentiated industrial discharges were analysed 10 years later by Pereira (1996): 12,5 – 2,5 pH range; 95 – 89% DO (dissolved oxygen) range; 31000 - 2570  $\mu S/cm$  EC (electric conductivity) range; < 30-167  $\mu g$   $Hg$  /L dissolved fraction; 32-3144  $\mu g$   $Hg$  /L particulate fraction.
- 3) Hydrogeoghechemical studies on the superficial aquifer Report anomalies in the CQE surrounding areas: in the “Esteiro de Estarreja”  $Cl^-$ ,  $Na$ ,  $Mg$ ,  $SO_4^{2-}$ , and in an area closer to the CQE  $Cu$ ,  $Pb$ ,  $Co$ ,  $Ni$ ,  $Zn$ , explained by effluents superficial runoff and groundwater (Ferreira da Silva, 1989). Cardoso da Fonseca *et al.*, (1992) Report s the contamination of the CQE groundwater with  $Fe$ ,  $Cu$ ,  $Zn$ ,  $Pb$ ,  $Co$  e  $Ni$ . Five different contamination zones were distinguished and characterized by Branco (2007). All of them included measurements of: EC >26000  $\mu S/cm$ ; pH with either very low values (<5) or very high (>10); <10 000 mg  $Cl$  /l; >100 mg  $NO_3$ /l; 10-600 mg  $Na$ /l; >2 000 mg  $SO_4^{2-}$ /l; > 45 mg  $NO_3^-$ /l; > 34 mg  $Al$  /l; >165mg  $Fe$  /l; < 50 mg  $Zn$  /l; > 9 mg  $As$  /l; > 20 mg  $Cu$  /l and > 0,65 mg  $Hg$  /l; traces of organic compounds were also detected (benzene, aniline, vinyl chloride, carbon tetrachloride, trichloroethene, tetrachloroethene and chlorobenzene, among others). Branco (2007) suggests an anomaly in EC values, calling it a “contamination plume” with NE-SW direction and origin in the CQE. The “plume” has an EC > 20 mS/m (apparent electrical conductivity - electromagnetic campaign data) (regional background < 5 mS/m and contamination indicators between 5 - 20 mS/m) - the “plume” generally follows the direction of groundwater flow, and the ditches contribute to the dispersion of contamination, especially “Vala do Canedo”. Mostly of the hydrogeochemical studies consulted the main relevant effluents reservoirs was: “Vala da Breja” (NW of CQE  $\approx$  1 km); “Vala de São Filipe” (SW of CQE  $\approx$  0,5 km); “Vala do

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Canedo" (WSW of CQE  $\approx$  1,5 km, connecting with "Lagoa de Vieiros", W of CQE  $\approx$  2Km); "Esteiro de Estarreja" SSW of CQE  $\approx$  2Km connecting with "Largo do Laranjo" (SW of CQE  $\approx$  2,5 km).

4) Two important CQE effluent receptors, contiguous to each other, are "Esteiro de Estarreja" (0.7 km<sup>2</sup>, 21% of the RIA) and "Largo do Laranjo" (1.7 km<sup>2</sup>, 61% of the RIA) (**MAP-APPENDIX**). Pereira (1996) has done, in both, important observations about the physicochemical parameters and the Hg concentration in sediments and in water (distinguishing between dissolved and particulate fractions). They are summarised below, since they are relevant to establish the sensor set-ups and the equipment location:

- i. Seasonal variability in water has more influence on the EC than on pH - peak values are related to low tides. The total suspended solid (TSS) depends on the flow rate, from which tidal inputs are responsible for an 80% increase. However, salinity does not influence TSS. Turbidity peaks were not observed.
- ii. During storm tides, the maximum amplitude of the water level is between 1.2 m and 1.4 m (in "Largo do Laranjo"). The maximum water speed is 0.5-0.7 m/s. Between the tidal cycles, the variation of salinity levels is 15. The water column in "Esteiro de Estarreja" is considered to be homogeneous relative to salinity and particulate fraction in suspension. The tidal currents intensity is estimated to produce a 70% increase of particulate fraction in suspension (Pereira *et al.*, 1998b).
- iii. In water, Hg concentration (dissolved and particulate fraction) depends on the effluent discharge cycle, and shows no dependence on tidal cycles, nor salinity. Higher values of Hg concentration occur in low tides (in the dissolved fraction  $<15 - 8\ 000$  ng/l and in the particulate fraction in suspension  $2 - 800$  µg/l). Hg concentration in water is more associated with the particulate fraction in suspension (80-90%) than the dissolved fraction. Hg transport in the dissolved fraction, from "Largo do Laranjo" to the rest of the RIA, was estimated to be lower than 11 kg per year, while in the particulate fraction is of 70 kg. In "Largo do Laranjo" the dissolved Hg content was generally difficult to quantify, as the measured quantities are  $< 15$  ng/l .
- iv. A relevant portion of Hg is retained in the sediments (88% in both reservoirs). In "Esteiro de Estarreja", the Hg accumulation in the sediment column is estimated to be 7 tons, and in "Largo do Laranjo" it is 20 tons. Hg accumulation in the sediment column for the whole RIA is estimated to be 33 tons (considering an annual average discharge of 730 Kg in 45 years).
- v. In the sediments, the highest value of Hg concentration is related to the "Esteiro de Estarreja", near the discharge area (200 mg/g). Areas further away from the discharge area show concentration values 70-500 times lower (4 km away from discharge Hg concentration is  $<100$  µg/g), while in "Largo do Laranjo" the Hg concentration decreases 6 to 40 times.
- vi. The sediments in "Esteiro de Estarreja" have a high capacity to retain Hg. The salinity variation in the water does not contribute to increase the Hg concentration in the water dissolved fraction, even with a high concentration in the sediments (348 µg/g) and a long period in solution (7 days). Also, the Hg concentration does not correlate with the sediment granularity. However, there is an affinity between Hg and sulphur, hence a higher percentage of fine particles ( $< 63$  µm) are Hg-sulphides.

- vii. The proximity of high concentrations of Hg with the discharge area is explained by the Hg mineralogical affinity, as it is found in the form of sulphides and also associated with organic matter – two forms that are stable and not very soluble. Also, the selective extraction of Hg from the particulate fraction shows an association between that Hg particulate fraction and Fe and Mn oxides. In the anoxide sediments the predominant form of Hg is the sulphide.
  - viii. The high quantity (4 – 14%) of organic matter (OM) in the superficial sediments is a factor that influences the sedimentation and transport of Hg. The correlation between the total Hg and the corresponding total OM in the sediment is of 0.8. Ramalhosa *et al.* (2002) study the association OM-Hg in the water, and Henriques, *et al.* (2013) in the soil.
  - ix. In the sediment column, the maximum concentration of Hg was observed at a depth of 40 cm, with a lower concentration of Hg at lower depths, which shows that more recent discharges have lower Hg content (the estimated natural recovery, for a 4 cm sedimentation rate per year, is 20 years - in accordance with an Hg dispersion model of “Esteiro de Estarreja”, suggested by Abreu (1996), with temporal predictions (1995 – 2035) for the Hg concentration.
- 5) Geochemical data of contaminated soils and the soil-plants interaction are studied by Inácio (1993); Inácio *et al.* (1998), Tavares (1995). The superficial layer of CQE soil (0-5 cm) was in the 117- 49 233 ppb [Hg] range while the regional background was 275 ppb [Hg]. The soil contamination was related preferentially with the atmospheric dispersion. Azevedo (1999) indicates different anomalies in the CQE soil and adjacent areas (As, Cu, Pb, Zn). The characterization of plants from the CQE (adjacent agricultural land) showed that the Hg biomagnification occurs consistently, and also showed the vectors that could be taken in the trophic chain (Tavares, 1995; Ferreira da Silva e Cardoso, 1996, Henriques *et al.* 2013), although the use of agricultural pesticides (PCB e DDT) also have their impact (Abrantes *et al.* 2005).
- 6) The clay minerals play an important role in the sediment-water interaction (Gomes and Delgado, 1993). The relationship of Hg content and those minerals could be associated with the early diagenesis, where clay mineral Hg adsorption occurs (Martins *et al.*, 2005).
- 7) The As content, associated with the contamination in water was first referred to by Pássaro and Costa (1985), and was later Report ed in the soil and sediments in “Lagoa de Veiros” (Cardoso da Fonseca *et al.*, 1995; Inácio *et al.*, 2007). Other heavy metals were also Report ed, such as Cu, Pb, Zn, Co, Ni, Cr, Cd (Costa and Jesus, 1999; Moreno *et al.*, 2000; Inácio *et al.*, 2008, Cardoso da Fonseca *et al.*, 1995; Ferreira da Silva, *et al.*, 1996; Rodrigues *et al.*, 2010).

The **TABLE** summarises the different media/matrix analysed in some of the reviewed scientific studies, to highlight the knowledge extent in the diversity of media influenced by the environmental impact, especially the sediments.

## 1. GENERAL INTRODUCTION

Hg analysing media	References
sediments	Hall <i>et al.</i> (1985); Lucas <i>et al.</i> (1986); Hall <i>et al.</i> (1988); Gomes e Delgado (1993); Delgado <i>et al.</i> , 1994, 1996; Pereira <i>et al.</i> , 1998a; 1998b, Delgado <i>et al.</i> , 2000, Rocha <i>et al.</i> (2000, 2005); Frangueiro <i>et al.</i> (2005); Abrantes <i>et al.</i> (2005), Anjum <i>et al.</i> (2011), Pastorinho <i>et al.</i> (2012); Martins <i>et al.</i> (2015)
superficial water and groundwater	Ferreira da Silva (1989); Barradas (1992); Pereira (1996); Patinha <i>et al.</i> (1998); Pato (2007) Cardoso da Fonseca <i>et al.</i> (1992), Branco (2006)
soil	Inácio (1993) e Inácio <i>et al.</i> (1998); Tavares (1995), Azevedo (1999)
soil – sediment – water	Barradas, 1992), Barradas <i>et al.</i> (1992); Pereira and Duarte, 1994
soil – plant	Inácio <i>et al.</i> , (2008); Tavares (1995)
air	Pio and Anacleto (1988);
dust	Reis, <i>et al.</i> (2013); Patinha, <i>et al.</i> (2014, 2015); Sousa, (2015).
fish,	Lima, (1985); Abreu <i>et al.</i> , (2000); Perez <i>et al.</i> (2001); Mieirol <i>et al.</i> (2011)
bivalves and	Vale, <i>et al.</i> (1985); Coelho <i>et al.</i> (2006)
crabs	Ferreira, <i>et al.</i> (1985)
microalgae	Coelho <i>et al.</i> (2005); Henriques <i>et al.</i> (2015); Figueira, <i>et al.</i> (2016)
foraminifera	Martins <i>et al.</i> (2013)
plants	Tavares, (1995); Pereira <i>et al.</i> (2007), Anjum <i>et al.</i> (2011, 2016)

Although most of these studies present specific characterizations, some of them present systematic sampling, with grids or nonuniformly distributed monitoring stations [e.g. Ferreira da Silva (1989) did 60 water sampling in large diameter wells; Azevedo (1999) obtained 985 water and soil samples with a 200m x 200m grid; Inácio *et al.* (2010) analysed soil collections from 1994, 2001 and 2008].

The first systematic approach specifically designed for a mitigation plan in CQE was the ERASE solution (ERASE, “Empresa Regeneradora de Águas e Solos de Estarreja”), Report ed by Costa and Jesus-Rydin (2001). It was created to solve/remove the CQE industrial dispersed wastes.

Other systematic approaches taken in CQE were the EU projects: BASELINE (to define chemical background in the groundwaters) and BRIDGE (to establish quality thresholds in groundwater, aimed for the EU directive, 2006/118 / EC for Groundwater Monitoring Stations). Both projects had the coordination of the University of Aveiro (Geoscience Dep.).

Also, municipal and inter-municipal initiative development plans for the superficial water-quality assurance (Município de Estarreja, 2012; Borrego *et al.*, 2006) established systematic approaches by designing environmental monitoring programs, in compliance with the national directives (transposed from the EU directives).

All these programs (with published sampling points or grids, protocol analysis and databases) are important contributions to define the best station characteristics, critical parameters, detection limits of water-quality monitoring system setups. Also this work could contribute to the municipal plans.

### 1.5. National and International DIRECTIVES

The Decree-Law N<sup>o</sup>. 236/98 established national water quality standards, but the most influential directive for environmental monitoring actions is the EU Directive 2000/60/EC, establishing a framework for EU action in the field of water policy (Water framework directive - WFD), transposed to the national regulation by Law N<sup>o</sup>. 58/2005, and recently updated by Decree-Law N<sup>o</sup>. 218/2015.

## 1. GENERAL INTRODUCTION

An example of an action aligned with the WFD purposes is the AMBI-Ria inter-municipal environmental assurance plan. In the plan (including 11 municipalities inside the RIA limits) water analysis have been conducted since 2006 (Borrego, *et al.* 2006). This monitoring program selected physicochemical parameters (pH, DO and EC) which have been measured with a multiparameter portable equipment, in 7 stations. These stations correspond to the network stations of the national program - “Rede de Qualidade da Água Superficial do Sistema Nacional de Informação de Recursos Hídricos (SNIRH)”.

The EU Decision No 2455/2001/EC established the list of priority substances in the field of water policy. Mercury (and its compounds) are identified as priority hazardous substances, also cadmium (and its contents), lead, níquel, Naphthalene, Benzene, all identified between the CQE contaminants. In addition, the EU has delineated a “Community Strategy concerning Mercury” (EC (2005). However, other international agencies have been focused on mercury contamination. The United Nations have a Global Mercury Assessment Program (UNEP, 2002). The United States Environmental Protection Agency, since the publication of Water Quality Criteria Documents (US EPA, 1996) includes mercury in primary standards (e.g. 0,002mg/l Hg as maximum level for drinking water quality, also 0,05 mg/l As, 0,01 mg/l Cd), and update documents are published to enforce tasks in the assurance plans, or new knowledge about the contaminants and impacts (e.g. US EPA-823-F-01-011, 2001), which is generally included in the recommended Water Quality Criteria (US EPA ,2006).

Environmental Quality Standards (in WFD). (Adapted from Pujol et al, 2014)

Substance	CAS number	EQS-AA <sup>a</sup> Inside surface waters <sup>b</sup> nM e[ $\mu\text{g L}^{-1}$ ]	EQS-AA <sup>a</sup> Other surface waters [ $\mu\text{g L}^{-1}$ ]	EQS MPC <sup>c</sup> Inside surface waters <sup>b</sup> nM [ $\mu\text{g L}^{-1}$ ]	EQS MPC <sup>c</sup> Other surface waters [ $\mu\text{g L}^{-1}$ ]
Cadmium and its speciation (according water hardness level d)	7440-43-9	$\leq 0.71$ (class 1) [0.08] $0.71$ (class 2) [0.08] $0.8$ (class 3) [0.09] $1.33$ (class 4) [0.15] $2.22$ (class 5) [0.25]	$1.78$ [0.2]	$\leq 4$ (class 1) [0.45] $4$ (class 2) [0.45] $5.34$ (class 3) [0.6] $8.09$ (class 4) [0.9] $13.3$ (class 5) [1.5]	$\leq 4$ (class 1) [0.45] $4$ (class 2) [0.45] $5.34$ (class 3) [0.6] $8.09$ (class 4) [0.9] $13.3$ (class 5) [1.5]
Lead and its speciation	7439-92-1	$34.7$ [7.2]	$34.7$ [7.2]	Groundless	Groundless
Mercury and its speciation	7439-97-6	$0.25$ [0.05]	$0.25$ [0.05]	$0.35$ [0.05]	$0.35$ [0.05]
Nickel and its speciation	7440-02-0	$341$ [20]	$341$ [20]	Groundless	Groundless

a Environmental Quality Standard—annual average.

b Inside surface waters include rivers, lakes and also water masses (artificial or seriously modified) related to them.

c Environmental Quality Standard—maximal permissible concentration.

d For cadmium and its compounds, EQS—AA values are functions of water hardness according to the five classes as follows: class 1:  $<40$  mg  $\text{CaCO}_3 \text{ L}^{-1}$  ; class 2:  $40\text{--}50$  mg  $\text{CaCO}_3 \text{ L}^{-1}$  ; class 3:  $50\text{--}100$  mg  $\text{CaCO}_3 \text{ L}^{-1}$  ; class 4:  $100\text{--}200$  mg  $\text{CaCO}_3 \text{ L}^{-1}$  ; class 5:  $\geq 200$  mg  $\text{CaCO}_3 \text{ L}^{-1}$  .

e Molar concentrations have been chosen as reference unit for the sake of comparison facility and regarding to the standards of the WFD (Water Frame Directive), even if this latter uses mass concentrations.



Following the WFD, standard criteria have been developed regarding environmental monitoring, and specifically for water quality monitoring, such as the “Common Implementation Strategy for the WFD Guidance” (EC 2000/60/EC, 2003), aimed to do a comparison of monitoring approaches for selected Priority Pollutants in surface Water. The considered aspects are: river water samples (whole procedure including sampling) and extract (measurement with real sample matrix); standard solutions (instrumental measurement only); harmonisation of analytical and sampling methods; matching sampling strategy with the system variability (water, sediment, biota); application of passive sampling approaches; application of sediment sampling/trapping approaches; emerging pollutant analysis. Considering these, it is recommended to setup water monitoring programs covering a wide range of possible contaminants, in order to identify risks, priority issues and needs for action, which had already been reinforced by the Environmental Protection Agency (EPA, 2006). Also, with the continued tightening of legislation in the field of water policy, online monitoring of pollutants (e.g. heavy metals) is likely to be compulsory for the European countries within a short period of time.

Thus, the harmonisation of sampling and analytical methods and instrumentation is highlighted by many environmental agencies, for instance CCME, with the publication of Guidelines and Standard Procedures, and considering the evaluation of potential standardization models for Water Quality Guidelines, or for optimizing water quality monitoring program design (e.g. CCME, 2007, 2006, 2009, 2014). The optimization even covers Field Measurement Methods (McNeill, 2004, focused on Arsenic in Drinking Water), or continuous water-quality monitors, considering station operation, record computation, and data Report ing, such as in Wagner, et al., (2006), still sensors or bio sensors as in Farré *et al.* (2009).

A specific EU directive recommends technical specifications for chemical analysis and monitoring of water status QA/QC (EC, 2009). Other countries have even more specific regulations, including sampling and analysis of waters, wastewaters, soils and wastes, such as the Industrial Waste Resource Guidelines (EPA Victoria, 2009).

A recent Report from the European Commission, to analyse the progress in the implementation of Programmes of Measures during the first planning cycle of the WFD (EC, 2015) in Portugal, Report s a low incidence of environmental monitoring programs and no Report ed strategies for remediation of contaminated sites (historical pollution including sediments, groundwater, soil).

This project contributes to define a monitoring system, as a priority issue, and responds to the demand for environmental actions with continuous water-quality monitors to assess the quality of surface water, and to immediately detect and warn about a contaminant discharge.

## 2. ENVIRONMENTAL TECHNOLOGY

Apart from the effort to regulate and standardize environment monitoring programs, the EU has also funded research projects in the field. In the context of FP7-ENVIRONMENT Specific Programme "Cooperation": Environment (including Climate Change), funding programs offered by the Community Research and Development Information Service (CORDIS) (2008-2018) include: FP7-KBBE - Specific Programme "Cooperation": Food, Agriculture and Biotechnology; FP7-ENVIRONMENT - Specific Programme "Cooperation": Environment (including Climate Change); OCEAN 2013.1: Biosensors for real time monitoring of biohazard and man-made chemical contaminants in the marine environment; OCEAN 2013.2: Innovative multifunctional sensors for in-situ monitoring of marine environment and related maritime activities (projects links listed at [http://cordis.europa.eu/programme/rcn/855\\_en.html](http://cordis.europa.eu/programme/rcn/855_en.html))

### 2.1.R & D International projects of environmental sensing

**HydroNet project** (2008-2012) ([http://cordis.europa.eu/result/rcn/90299\\_en.html](http://cordis.europa.eu/result/rcn/90299_en.html))

This project aimed to design, develop and test a new technological platform to improve the monitoring of water bodies based on a network of autonomous, floating and sensorised mini-robots, embedded in an Ambient Intelligence infrastructure. Chemical and biosensors, embedded in the mobile robots were developed and used for real time monitoring of physical parameters and pollutants in water bodies. The project developed mathematical models to simulate the pollutants transport and processes in rivers, lakes and sea.

The project partners designed a floating platform based on microelectronics and microfabrication of sensor technology (*i.e.* miniature sensors that are integrated into a network of independent floating robots and fixed buoys). The sensors were embedded in an ambient intelligent infrastructure for interactive configuration, tasking and monitoring. Based on EU Directives, it measured Physical and Chemical Parameters: Temperature, Salinity, pH, Turbidity: Hg, Hg++, HgCH<sub>3</sub>, Cr, Cd, Oil. The Sensor Technologies used were Enzyme Biosensors, Microfabricated Electrochemical Sensors and Optical sensors. The target average time for measurements and transmission to remote station was from real time (for most physical parameters) to 30 seconds.

The infrastructure was unmanaged, self-assembling and self-powered wireless, with an ever-decreasing cost per unit. It supports decision and managing bodies and system integrators in water bodies' resources. The Ambient Intelligence platform, which integrates not only sensors for water monitoring and robot tasks execution, but also communications backhaul systems, database technologies, knowledge discovery in databases (KDD) processes for extracting and increasing knowledge on water management.

**SenseOcean** (2013-2017) (<http://www.senseocean.eu/>)

This is a project to develop marine sensors, namely the communications system which allows high interoperability between sensors and the use of multiple platforms.

**SEA-on-a-CHIP** (2013-2017) (<http://www.senseocean.eu/>)

This project is a real-time monitoring system of sea contaminants by an autonomous Lab-on-a-chip biosensor, coordinated in Spain, but with portuguese participation, by the Instituto Português do Mar e da Atmosfera. The project aims to develop a miniaturized, autonomous, remote and flexible immuno-sensor platform, based on a fully integrated array of micro/nano-electrodes and a microfluidic system in a lab-on-a-chip configuration, combined with

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electrochemical detection for real-time analysis of marine waters in multi-stressor conditions. This system will be developed for an application in aquaculture facilities, including the rapid assessment of selected contaminants from a group of compounds (toxic, bioaccumulative, endocrine disruptors). Also those contaminants are produced by this type industry and affect environment and human health (antibiotics and pesticides).

Each device will be able to perform 8 simultaneous measurements in duplicates and it will be built in order to work with an autonomy of one-month, measuring in real time at least once per hour. Sensitivity for Sea-Water analysis is guaranteed by the gold microelectrodes arrays with metalocarborane doped functional polypyrrol.

The prototype will be tested throughout the lifetime of the project and calibrated with different chemical analytic setups: first in laboratory studies, second under artificial ecosystems and finally during field experiments in aquaculture facilities.

### **NeXOS** (2013-2017) (<http://www.nexosproject.eu>)

The project's title is "Next generation Low-Cost Multifunctional Web Enabled Ocean Sensor Systems Empowering Marine, Maritime and Fisheries Management". The project aims to improve the temporal and spatial coverage, resolution and quality of marine observations through the development of cost-effective innovative and interoperable in-situ sensors, based on optical and acoustics technologies deployable from multiple platforms, and Web Services for key domains and applications, including the measurement of critical parameters, for an improved assessment of fisheries.

### **ENVIGUARD** (2013-2018) (<http://www.enviguard.net/>)

This project's full title is "Development of a biosensor technology for environmental monitoring and disease prevention in aquaculture ensuring food safety". The chemical detection unit to be developed in this project is based on biophotonic sensing cells, called Bicells. These will use resonant nanopillars as transducers and monoclonal antibodies to detect toxins and man-made pollutants. The transducer will be integrated in a multiplexed chip with different sensing channels allowing the monitoring of several targets at the same time. A portable device will be developed so that the analysis can be performed in place.

### **SCHeMA** (2013-2017) (<http://www.schema-ocean.eu>)

With a title of "Integrated In Situ Chemical Mapping Probes", SCHeMA is expected to develop chemical solid state miniaturized sensors using analytical procedures to make electrochemical and optical measurements and high resolution mappings of pollutants such as Hg, Cd, Pb, As and Cu trace metal species, nitrate, nitrite, phosphate nutrients, volatile organic compounds, biotoxins, harmful algal blooms, species relevant to the carbon cycle, while trying to minimize chemical and physical interferences. It will also aim develop micro- and mini-analytical and mechanical fluidic systems. Another objective is to develop miniaturized multichannel probes, incorporating the sensors and fluidic systems, allowing their integration to moored or free floating devices, arranged in a chemical sensor network. The project also plans to develop remote control solutions for data transfer and mapping system reconfiguration, and web-based data information system for data storage, standardization, modelling and accessibility by third parties.

The plans to conduct field tests, as well as laboratory tests to compare results. Long-term field applications in estuary and coastal systems are also planned.

The project also aims to determine arsenic(III) in natural aquatic systems in the nanomolar range and at natural pH. In view of a future application of a gel integrated electrochemical detection approach to reduce fouling

and to control mass transport, a microelectrode will be used to quantify As(III). The microelectrode consists of a gold plated Ir-based microelectrode (Au-IrM), and operated with Square Wave Anodic Stripping Voltammetry. The obtained results demonstrate that the stripping peaks exhibit reproducible linear calibration curves at pH 8 for As(III) concentrations from 10 to 50 nM and from 1 to 10 nM, using 3 and 36 min preconcentration times, respectively. The interference by copper and chloride is negligible for an As : Cu concentration ratio of 1 : 20 and a chloride concentration of 0.6 M typically found in seawater. The gold layer exhibits a lifetime of 7 days. The measurements are reproducible over time for a given gold layer (RSD < 9%) and between renewed layers (RSD ≤ 12.5%)”

### **COMMON SENSE (2013-2017)** (<http://www.commonsenseproject.eu/>)

The project's title is "Cost-Effective Sensors, Interoperable With International Existing Ocean Observing Systems, To Meet Eu Policies Requirements". The project aims to provide interoperable, cost-effective, multi-functional sensors make in-situ measurements of critical parameters. This project focuses on eutrophication, contaminants, marine litter and underwater noise descriptors of the Marine Strategy Framework Directive. The project will design and develop sensors for the detection of nutrient analytes (with colorimetric chemistries for phosphate, ammonia, nitrate and nitrite), low concentrations of heavy metals (Pb, Hg Cd, Zn and Cu), surface concentration of microplastics and underwater noise (with an acoustic sensor). Other sensors (e.g. temperature, pressure, pH and pCO<sub>2</sub>) will be also integrated.

### **MARIABOX (2013-2018)** (<http://www.mariabox.net/>)

Under the title “MARINE environmental in situ Assessment and monitoring toolbox”, the project aims to develop a sensing and analysis box, a communication system, a power system, a software platform, and a cell phone application. The box will transmit the collected data in real time through different channels: according to local needs and geographical location: GSM/GPRS/3G, WiFi, WiMAX or satellite link. The box is to be remotely controlled, programmed, configured and updated. Biosensors will be developed for 5 man-made chemicals and for 4 categories of microalgae toxins relevant to shell fish and fish farming.

### **BRAAVOO (2013-2016)** (<http://www.braavoo.org>)

With the title “Biosensors for real time monitoring of marine contaminants”, the project aims to develop solutions for real-time in-situ measurement of high impact and difficult to measure marine pollutants, based on a combination of three types of biosensors, which will enable the detection of a number of specific marine priority pollutants and of general biological effects that can be used for early warning.

### **SMS (2013-2017)** (<http://www.project-sms.eu/>)

The project title is “Sensing toxicants in Marine waters makes Sense using biosensors”. This project uses commercially available sensors to measure temperature, pH, salinity, dissolved oxygen, nutrients and turbidity, to characterize the environment in which algal species, or target analyses tend to thrive. SMS will design a multi-modular miniaturized device with a Sampling Module and an Analysis Module. The device is to be installed in existing buoys in marine areas of Europe for continuous monitoring of the selected pollutants.

The device will be able to wirelessly transmit real-time data, and also allow remote access to collected data and remote management of biosensors. The device should be able to do automated water quality monitoring with an alarm system. SMS aims to develop low-cost devices, for future industrial exploitation and manufacturing.

**NANOMET** (2012-2014) (<http://www.mnt-era.net/mnt-era-net-success-stories/NANOMET.pdf>)

This project funding was a different source from the other projects described above, it was funded by the European Union through the MNT-ERA.Net programme. Also the coordination is not related to a country, but to a company, in this case, the Spanish Inkoa S.L., in partnership with the French / German company BeanAir. This project is more related to this OHM project (here Report ed), in comparison with previous projects, and was also a source of inspiration for the formulation of this one. NANOMET was a valuable indication in the selection of WSN equipment here Report ed.

The NANOMET project aimed to develop optical and/or electrochemical nanosensors for Cu, Cr, Zn, Hg and Cd integrated in wireless Embedded Sensing Platforms (ESPs) in order to deploy smart sensor systems for the monitoring and assessment of heavy metals in water resources as well as in Urban and Industrial Waste Water Treatment Plants. The project's main objectives was development of a Smart sensor system for Water Assessment based in Wireless Networks in order to obtain a systematic and analytic monitoring and prediction of the sites at risk of contamination, with unique features of unattended operation and reusability. Also it expected to develop and manufacture of a new generation of scalable wireless ESPs for distributed monitoring and assessment of water contaminants. The optical and/or electrochemical nanosensors must presented low-power consumption and rapid response, decreasing the cost of data collecting, especially in remote areas, and allowing a systematic risk assessment and control.

The system must worked on the Internet, such as a multi-platform, multi-channel open architecture system, ready to be integrated in both distributed and integrated data management systems. It enabled real time monitoring of heavy metals and information transmission in a secure, fast and reliable way to allow a rapid identification of pollution sources and to provide coverage of the changes in heavy metals concentration in water resources, which present a more accurate idea of long-term trends of heavy metals' levels.

In addition, it was design to help industries and wastewater treatment plants to ensure their discharges meet current water standards. The system aimed to benefit not only public institutions but also private companies, that need, or will required to install systems such online heavy metals sensors, which could be covered by NANOMET wireless sensor network.

Some NANOMET results are Report ed in Cases-Utrera *et al.* (2014), concerning the analyzer prototype, programmed and configured to detect simultaneously Cu and Zn in effluent waters, under flow conditions at glassy carbon electrodes, operating with electrochemical methods (*i.e.* stripping voltammetry). The work describes the development of a laboratory method into complete instrumentation.

The systems included a small to operate autonomously and unattended, with wireless embedded sensing platforms (ESP) The system requirements are portability, ease of use and maintenance, energy autonomy, and the possibility to be remotely controlled. Its external design was driven by the need to make it as compact as possible so it is easier to use and deploy, but also to make it more robust and resistant to outdoor weather conditions.

The final prototype was a small instrument (160×200×70 mm) and light (<2 kg), that can collect samples directly from a source such as a river or an effluent stream. The prototype was designed to be part of a larger network of electroanalytical stations. Experimental parameters such as solution pH (crucial in strpping analysis), electrode position potential, and electrodeposition time were optimized for the detection of Cu and Zn.

## 2. ENVIRONMENTAL TECHNOLOGY

Regarding the R&D projects described above, selected by the close study object with this OHMproject, *i.e.* the sensing of superfluous waters with environmental monitoring proposes, it was compile each project coordinate are summarised in the following **table**

Name	Subject	Period Start End	Total cost (€) EU contribution	Coordination
<b>HydroNet</b>	Floating Sensorised Networked Robots for Water Monitoring	2008-12-01 2012-01-31;	3 528 046 2 591 475	Italy
<b>SEA-on-a-CHIP</b>	Real time monitoring of SEA contaminants by an autonomous Lab-on-a-chip biosensor	2013-12-01 2017-05-31	7 594 206,08 5 751 459	Spain Project Partner: Instituto Português do Mar e da Atmosfera IP
<b>SenseOcean</b>	Marine sensors for the 21st Century	2013-10-01 2017-09-30	8 065 330,2 5 924 945	United Kingdom
<b>NeXOS</b>	Next generation, Cost-effective, Compact, Multifunctional Web Enabled Ocean Sensor Systems Empowering Marine, Maritime and Fisheries Management	2013-10-01 2017-09-30	8 104 266 5 906 479	Spain.
<b>ENVIGUARD</b>	Development of a biosensor technology for environmental monitoring and disease prevention in aquaculture ensuring food safety	2013-12-01 2018-11-30	7 177 126,82 5 523 461	Germany
<b>SCHeMA</b>	Integrated in situ chemical mapping probes	2013-10-01 2017-09-30	6 740 454,3 5 200 489	Switzerland
<b>COMMON SENSE</b>	Cost-effective sensors, interoperable with international existing ocean observing systems, to meet EU policies requirements	2013-2017	6 074 497,1 4 664 072	Spain
<b>MARIABOX</b>	MARINE environmental in situ Assessment and monitoring tool BOX	2014-02-01 2018-01-31	7 137 921,51 5 175 858	Cyprus
<b>BRAAVOO</b>	Biosensors for real time monitoring of marine contaminants	2013-12-01 2016-11-30	4 564 917 3 529 127	Switzerland.
<b>SMS</b>	Sensing toxicants in Marine waters makes Sense using biosensors	2013-12-01 2017-08-3	5 559 819 4 144 263	Italy
<b>NANOMET</b>	Wireless networks of heavy metals nanosensors for real time water pollution assessment	2012-04-02 2014-12-31	1 170 580	Inkoa S.L. (Spanish company) Project Partner: BeanAir (France)

### 2.2. Governmental run environmental sensing system

Some implemented projects/programs of environmental monitoring and sensing can be referenced, in compliance with governmental and/or international regulations.

Thus, the U.S. Department of Energy's Office of Legacy Management has more than 75 sites, transitioning from the remedial activity stage into long-term, post-closure monitoring (75 is a number from 2003, Report ed by Myers, et al., 2014). Those sites require long-term supervision of environmental parameters concerned to ensure the human health safety and the minimum environment impact. Initially these monitoring programs were expensive, labor intensive, and provide limited, periodic data, but with the technological evolution of sensors, communications, data storage, data security, and web interface platforms, substantial cost savings were achieved to mitigate the funding challenges. Myers, *et al.* (2014) describe field devices that generate the actual monitoring data from those remediated sites. The device composition extends beyond the sensors, probes, and wireless communications. Components include: 1) the remote terminal unit (*i.e.* the “brain” of the device); 2) the power supply (designed with an appropriate power budget); 3) the sensors to generate and capture data (a robust multiprobe); 4) communication links (satellite, cellular, etc.) to transmit data; 5) packaging to enclose and protect the device.

## 2. ENVIRONMENTAL TECHNOLOGY

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Similar to the previous program, for the case of Portuguese abandoned mining areas, a large number of them were recently targeted by remediation actions by the state company EDM. Nowadays, some of those areas have environmental monitoring programs with WSN systems or similar. Some mining sites, such as Lousal, Jales mines and uranium mines in Beira Baixa, have online sensing systems installations. The systems include potentiometers, PPA type (with pH, EC, T, Eh multiprobes), which operate unattended, with real-time data transmission, and with alarms and tele signals emitted to the central office in Lisbon and/or to the technical team cellphones. The field equipment has been subjected to vandalism (personal communication, Doutora Paula Ávila from LNEG, October 26, 2015)

Another national monitoring system implemented with EU and governmental support, is called SIMPATICO. It was initially designed for the Guadiana River (the estuary location), but nowadays other river stations are installed (Tejo River, in Salvaterra de Magos and Mondego River, in the estuary), with open data in: <http://webserver.mohid.com/simpatico/>. It is an autonomous system for in-situ monitoring of currents and water-quality parameters. The system is comprised of 3 main elements: a buoy, a multiparametric probe, and a current meter. The data is collected every 15 minutes and automatically downloaded via GSM. The data consists of hydrographic parameters (tides, waves, pressure and currents through the water column,) and near-surface water quality parameters (temperature, salinity, pH, dissolved oxygen, turbidity, chlorophyll and fluorescence). Other SIMPATICO specifications are Report ed in Garel, *et al.* (2009).

The international reference, with a few similarities with the SIMPATICO program, in water-quality monitoring, is the intergovernmental program between Germany and Netherlands, in Eijsden Station, called "Aqualarm" a warning system for land and sea, with open data in: <http://www.aqualarm.nl/eijsden.html> about the water quality of the Rhine and Meuse rivers. Aqualarm is an integrated water management/alarm system, used to monitor the rivers water quality, based on the measurement data collected by the system, managed by the Rijkswaterstaat entity (*i.e.* the responsible entity for the design, construction, management and maintenance of the main infrastructure facilities in the Netherlands). It complies with the European Water Framework Directive (WFD).

The monitoring on line water analyzing equipment is an On-line Metrohm (Process Analytics) operating with voltammetry for the chemical parameters, such as Cd, Cu, Pb and Zn. It also measures the following parameters: CE, acidity, turbidity, ammonium, oxygen, fluorine, algae, organic compounds and radioactive elements.

The projects and programs described above could be seen as a State-of-the-art of applied/implemented research for environmental technology. The next part of this Report will provide the monitoring background for the station site selection, the sampling requirements and the most common WSN setups, as it is considered to be the most relevant information for the Postdoc research.

### 3. REMOTE ENVIRONMENTAL MONITORING

The concept of “remote sensing” or “remote environmental monitoring” can have several meanings, such as “Hydrogeochemistry and Remote Sensing Yellowstone National Park”, with aerial photograph analysis (Planer-Friedrich *et al.*, 2003), or Remote-sensing monitoring of environmental impacts, with hyperspectral image analysis (as in MINEO project, Chevrel *et al.*, 2003). In this Report the meaning is related to distance monitoring, detecting and measuring environmental parameters, without a human operator, by automated sensing and sampling.

In fact, monitoring techniques and equipment for sampling, analyzing and signaling an environmental risk can be efficiently validated in the CQE context, because there are many field experiences of environmental characterization, Reported by several academic researches, papers, technical Reports (presented in the first part of this Report), and also many indicators of the environmental impact, which can be measured with different sensors. However, in all of these studies, only a few parameters were measured in the field, in one or some campaigns. The traditional approach to environmental monitoring for surface water requires periodic field sampling at fixed locations. The field samples are labeled, preserved, cooled, and shipped to laboratories to be analyzed according to prescribed methods and protocols, with bench/Lab equipment.

Slightly extending the concept of traditional or conventional approach to environmental monitoring, as described by Jiang, *et al.* (2009), the methods for monitoring water environments can be defined as:

1) “Artificial sampling” with portable water quality measurement devices and subsequent lab analysis - only sampling on specific points, grids or cross-sections of water bodies, with a sampling frequency ranging from several times a day to seasonally.

2) Automatic and continuous monitoring of water environment parameters by a system consisting of monitors (or control centers) – could be an online system with high power consumption and a built infrastructure, or an immersed probe with external data logging and antenna (no external power required). In both cases, data can be remotely and automatically transferred, providing real-time water parameters. These systems can be costly and have a surrounding ecological influence.

3) Monitoring with remote images sensing technology, detecting the spectrum specifics of an electromagnetic wave (radiation, reflection and scattering) in a water contactless method - after information processing of the collection of illustrative spectra, its physics and chemical characteristics are identified (this is a low accuracy method and doesn't provide real-time monitoring).

4) Water quality monitoring bio-technology using aquatic organisms' sensitivity - in the presence of poisonous substances in water bodies, by measuring or analyzing the change of activities of different organisms.

For instance, Myers, *et al.*, (2014) describe a remote monitoring system as a chain of complex technologies, that requires a sensor and platform interfacing, a communications platform design and configuration, web interface customization, cyber security, packaging design and testing, and device maintenance, highlighting the experience in deploying, debugging and maintaining devices that contribute to the success of remote monitoring.



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### 3. REMOTE ENVIRONMENTAL MONITORING

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The proposal of this OHM project was to implement a continuous water monitoring system with *in situ* wireless sensors, providing real-time information on the critical parameters (*i.e.* Hg or As content, pH or EC values) on water streams and assessing the risk of events of metal effluent inputs or upticks. The advantage of these devices is the long distance monitoring that will alert for specific contamination events, allowing mitigation measures.

On the other hand, remote environmental monitoring, and its on-site analysis, also addresses other issues associated with traditional sampling approaches. For example, Myers *et al.* (2014) refers resamples for upticks in contaminant concentrations becoming automatic procedures with the use of field sensors:

- If an actual uptick or release has occurred, the real-time sensor data will provide “up-to-the-minute” Report s on the state of the environment.
- If the uptick is a false positive due to field sampling or laboratory error, the automated sampling system’s subsequent measurements will confirm immediately that compliant levels are actually present in the aquifer.

Myers *et al.* (2014) highlight that the sensor data becomes essentially self-validating due to the large volume of data produced. It is desirable to design a remote environmental monitoring program with all this aspects in mind.

#### 3.1. Design of remote environmental monitoring program

The monitoring programmes considering by WFD (Directive 2000/60/EC; EC, 2006) cover three modes of monitoring, *i.e.*: surveillance, operational and investigative. These are distinguished by Alan, et al, (2006), as follows:

- Surveillance monitoring is designed to provide information to supplement and validate impact assessment procedures, assess long-term changes in natural conditions or as a result of anthropogenic activity (data and information collected (12-month) provides the basis for the production of national-regional river-basin management plans (as AMBI-Ria, Borrego, 2006).
- Operational monitoring aims to provide information to be used to classify the status of water bodies identified as being at risk and to assess any changes resulting from these actions (as this OHM project intends).
- Investigative monitoring may be undertaken when surveillance monitoring shows an occasional event that causes some environmental impact. It is designed to assess the extent of the impact of accidental pollution events (possibly derived from this program)

The environmental monitoring program considered in this Report , can be seen as an operational monitoring system. It is to be designed to determine the impacts of anthropogenic outputs, to detect potential impacts that may not be found through conventional chemical monitoring, and to use systems that provide early warnings of water contamination and early changes in aquatic organism health due to intermittent, accidental or deliberate releases of contaminants (theoretically defined by Alan, et al, 2006) .

#### 3.1.1. Operation mode

In the case of accidental pollution, a rapid response is required from the on-site monitoring tools, which could use WSN technology, with data acquisition from a physicochemical and/or chemical sensor, data logging and wireless transmission in real-time. The different types of possible sensors will be reviewed in the next part of the Report . Here, WSN technology is analyzed as a key feature for remote environmental monitoring, in an unattended mode.

Two distinct kinds of operation modes exist for detection or measurement - attended and unattended. A distinction is given by Katznelson *et al.* (2010):

1. **Attended** (discrete measurements): each measurement is recorded manually into a data sheet, or the readings of all sensors are logged as one discrete 'sample.'
2. **Unattended** (continuous, or time-series measurements): the probe/system is programmed for automatic measurements and data logging at specified intervals, then deployed for a given time period, and then retrieved for downloading of the logged data as a deployment-episode file or also includes real-time transmission of the data (telemetry).

The operation mode in this monitoring proposal will be unattended (*in continuum*). The time interval selected between repeated measurements must be sufficiently small for the resulting water-quality record to be considered continuous (Wagner, et al., 2006). This choice is highly related with the sensor setup selected, but environmental conditions must be considered, such as the tidal cycles (that repeat approximately every 6 hours). To infer an industrial (daily) discharge the environmental patterns must first be understood, and they depend on the tidal cycle.

#### 3.1.2. Critical parameters or Key parameters

The configuration of a common monitoring-system for water-quality data collection to assess the quality of surface waters, used by the U.S. Geological Survey has a four-parameter monitoring system (temperature, specific conductance, dissolved oxygen, and pH) which can also be configured to measure other properties with continuous water-quality monitors (Wagner, *et al.* 2006).

Environmental monitoring is required to protect the public and the environment from contaminants grouped into the following categories:

- 1) metals,
- 2) radioisotopes,
- 3) volatile organic compounds, and
- 4) biological contaminants.

This work was focused on the metal contaminants, even though other contaminants were Reported at the CQE.

### 3. REMOTE ENVIRONMENTAL MONITORING

In a study called “Long-life Heavy Metal Ions Sensor Based on Graphene Oxide-anchored Conducting Polymer” Pandey, *et al.* (2016) define the general group of heavy metals (HMs) as main analytes, the elements which have metallic nature and belong to the family of transition metals, metalloids, lanthanides, and actinides; having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.

Some HMs such as Fe, Cu, Co, Mn, Mo, and Zn are life-essential, required for proper growth of plants and animals (micronutrients), however excessive levels could also lead to detrimental effects on living organisms. Other HMs like Hg, Cr, Cd, As and Pb are poisonous and highly undesirable, even at low concentrations (<2 ppb). The table below shows environmental standards for HM contents in drinking water and industrial effluent discharges. These national and international standards (discussed in the first part of this Report) have extremely high importance as promoters of the development of state-of-the-art metal sensing, including from countries that have a modest record of environmental concerns like India and China.

Heavy metals	Drinking water Standard (mg/L)		Maximum permissible limit for industrial effluent discharges in India (mg/L) [25,26].	
	US EPA (MCL)[23]	Indian standard (IS:10500)* [24]	Into inland surface IS-2490	Into Public sewers IS-3306
Arsenic	0.010	0.01–0.05	0.2	0.2
Cadmium	0.005	0.003-NR	2.0	1.0
Chromium	0.1	0.05-NR	0.1	2.0
Copper	1.3	0.05–1.5	3.0	3.0
Lead	0.015	0.01-NR	0.1	1.0
Mercury	0.002	0.001-NR	0.01	0.01
Iron	0.3	0.3-NR	3.0	3.0
zinc	5.0	5.0–15.0	5.0	15.0

\* Lower limit is the desirable value and upper limit is permissible on

Considering the CQE/RIA study area, the first part of this Report highlighted the necessary information to identify the chemical and physicochemical parameters more related to the problem of pollution and its sources, considered in the environmental monitoring program design. These are the critical parameters with significance to the monitoring that could be divided in: contamination direct parameters – Hg, As, Zn, Pb and other heavy metals related with the industrial impact; and the contamination indirect parameters – pH and EC, and water level. This last physicochemical and hydrodynamic parameters – pH, EC and water level - could be the key parameters to find, which steered the market study towards sensing solutions to operate the pilot tests – first in Lab conditions and after in RIA conditions (ex-situ), the next phase of this OHM project.

#### 3.1.3. Station site selection and setup

As Reported by the U.S. Geological Survey - Guidelines and standards Procedures for Continuous Water-Quality Monitors (Wagner *et al.*, 2006) - the Environment Monitoring Station selection and setup must attend to : 1) site selection, 2) monitor configuration (which means all units associated sensing/acquisition, data logging, transmitter, coordinate) including types of sensors and instrument acceptance criteria; 3) placement of sensors in the aquatic environment; 4) use and calibration of field meters; 5) monitor operation and maintenance, 6) sensors field cleaning. Specifically, the factors that influence in the placement and installation of continuous water-quality monitoring station are:

- Site characteristics – CQE surrounding areas;
- Monitor installation – also called data monitor mode,
- Maintenance requirements - depending on the complexity of the system and equipment IP.

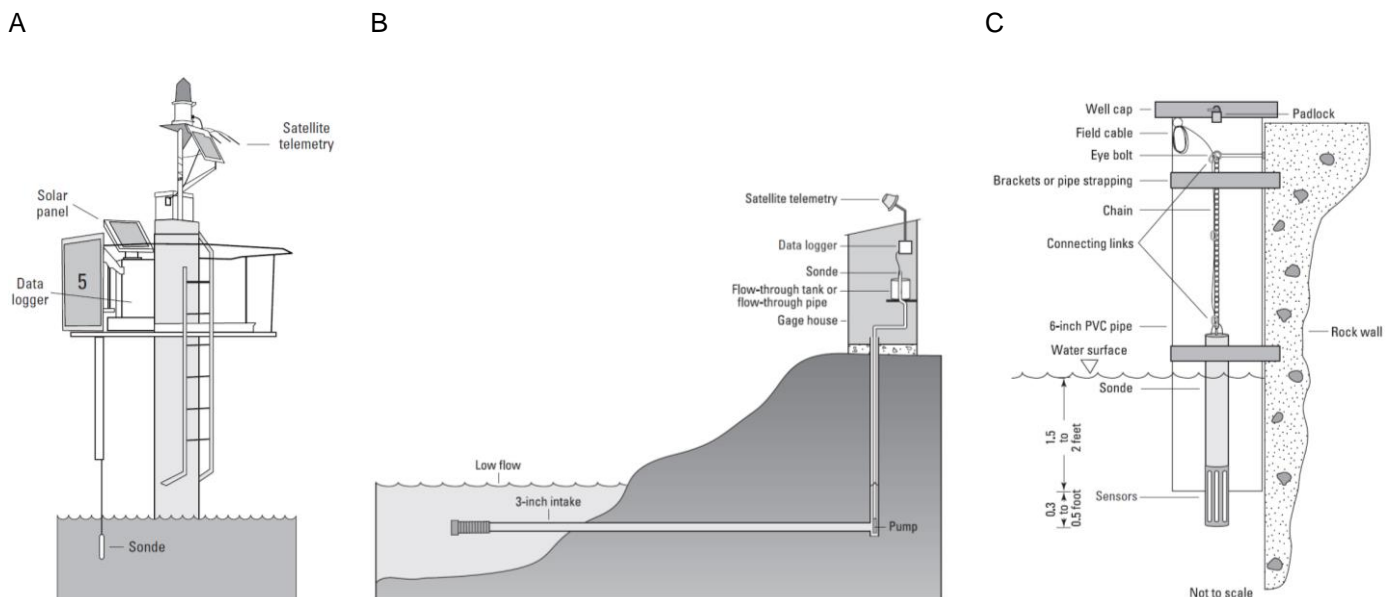
### 3. REMOTE ENVIRONMENTAL MONITORING

Site characteristics must consider: 1) water-quality measurements at the site to be representative of the location being monitored. 2) Degree of cross-section variation and vertical stratification. 3) A channel configuration that may pose unique constraints. 4) Range of stream stage (from low flow to flood) that can be expected for water velocity. 5) Presence of turbulence that will affect water-quality measurements. 6) Conditions that may enhance the rate of fouling, such as excessive fine sediments, algae, or invertebrates. 7) Range of values for water-quality field parameters. 8) Need for protection from high-water debris damage. 9) Need for protection against vandalism.

Monitor installation includes: 1) Type of state or local permits required before installation can begin (the most promising field coordinator base is the municipality – “Junta de Freguesia” de Vieiros ou Beduido -, or one of it's buildings). 2) Safety hazards relevant to monitor construction and installation. 3) Consideration of unique difficulties (private properties) or costs of installation (no budget for infrastructure and construction).

Maintenance requirements must include: 1) site accessibility; 2) Safe and adequate space to perform maintenance; 3) Presence of conditions that increase the frequency of servicing intervals needed to meet data-quality objectives; 4) For stream sites, proximity to an adequate location for making cross-section measurements; 5) Accessibility and safety of the site during extreme events (for example, floods or high winds); 6) Availability of electrical power or telephone service; 7) Need for real-time Report ing.

Different quality monitor station are described / illustrated by Wagner, *et al.* (2006), and shown in FIGURE: A - In situ water; B – flow-thought, with a pump (require 110-volt alternating current (AC)) that delivers water from the measuring point to the sensor(s) or probe housed in a shelter; C - internal-logging and recording system (combined sensor and recording probe that is entirely immersed and requires no external power)



The best location for a monitoring site is often the one that is best suited for measuring surface-water discharges. Although hydraulic factors in the site must be considered, it is more important to consider factors that affect water-quality conditions. The same hydraulic factors that must be considered when selecting a specific site for measuring discharges in a channel should also be considered in selecting a water-quality monitoring location. Both purposes require a representative site that approaches uniform conditions across the entire width of the

stream. Streams subjected to substantial bed movement can result in the sensors being located out of the water following a major streamflow event, or at a point that is no longer representative of the flow. A site may be ideal for monitoring high flow but not satisfactory during low flows. Site selection often is a choice of meeting as many of the applicable criteria as possible.

#### 3.1.4. Conventional sampling and automated sampling

The analytical objectives for environmental samples differ from those for other samples in that reproducible measurements must be obtained from very low analyte concentrations - some species occur at the part-per-million or even part-per-trillion level in highly complex samples (Pérez-Bendito and Rubio (1999). Environmental control and protection usually rest on the measurements that encompass long periods of time and wide geographical areas. Valid conclusions on a situation and its changes can be drawn only through correct sampling and accurate analytical results.

USGS (2015) National Field Manual for the Collection of Water-Quality Data, discriminates all possible considerations to take with sampling, given the importance that it has is a conventional or artificial type of environmental monitoring program. It covers: 1) Selection and Cleaning of Equipment for Water Sampling; 2) Collection and Processing of Water Samples (Syringe-Filter Procedure for processing Samples for "Organic Compounds", "Wastewater", "Pharmaceutical, and Antibiotic Compounds", "Arsenic Speciation", "Low-level Mercury"; 3) Field Measurements (recurrent parameters as temperature, dissolved oxygen, Specific Electrical Conductance, pH, Reduction-Oxidation Potential-Electrode, Alkalinity and Acid Neutralizing Capacity, Turbidity with the use of multiparameter instruments for routine field measurements

For operational monitoring, passive sampling is referred to as an innovative monitoring tool, with advantages in this kind of operational environmental programs (Alan, et al, 2006). Passive samplers are a monitoring tool for time-integrated measurement of bioavailable contaminants in water and sediment. It has proved to be a reliable, robust and cost-effective tool that could be used in regional – local or extended monitoring programs. These devices are now being considered as a part of an emerging strategy for monitoring a range of priority and emerging pollutants (ICE, 2004).

In situ passive sampling techniques appear better adapted than conventional monitoring to test for trends or differences between sites, especially in water bodies with highly variable conditions or subject to seasonal anthropogenic impacts, such as the CQE. However, this could be more relevant in water bodies with persistent fluctuations in concentration over a period of time, rather than irregular peaks of concentrations when an episode would not be detected because of the response time of passive samplers, with no interest for this case study.

Sampling and its settings are a controversial subject. IT is increasingly accepted that the sampling step and the transport to the laboratory are not essential to monitoring, and the development of technological solutions for in situ analysis should be encouraged. Therefore, Pawliszyn (2006) defends on-site (or *in situ*) analysis, against any sampling, as a more efficient approach than taking a sample, transporting it to a laboratory and then performing the analysis. This reduces errors, and avoids the possibility of sample change and the time delays associated with transport and storage. So on-site analysis is more accurate, more precise and the analytical is quickly available.

Moreover, there are technological developments in automatic sampling, for example project PISCIS (FEUP-DEEC, CORDIS, 2004) "Prototype of an Integrated System for Intensive sampling of the Coastal Ocean". The project addresses the design and implementation of an advanced modular and cost effective system for collecting oceanographic data that includes two autonomous underwater vehicles with an acoustic positioning system and sensors. The PISCIS system is configurable for oceanographic applications in real time, bathymetry, underwater archeology and monitoring of effluents.

Myers et al., (2014) Report s the application of automated sampling in a U.S. Remote Environmental Monitoring site. It produces real-time data for long-term monitoring, with cost savings and compliance assurance. Automating the sampling process offers multiple advantages over the traditional approach.

This OHM WSN project recognizes the need for automated sampling, as metal sensing has several problems in field operation. Key parameters were chosen to detect a contamination event and a sampling device (automated box, which could be called s-box) will collect the water extract if and when such a contamination is identified.

#### 3.1.5. WSN – Background and Literature review

A wireless sensor network (WSN) operates in an unattended environment with sensing, computation and communication capabilities (Bhattacharyya et al., 2010). It could have spatially distributed autonomous sensors to monitor physical or environmental conditions, such as temperature, sound, vibration, pressure, motion or pollutants (Martin and Islam, 2012). It is self-configured (Cai et al., 2011), and can cooperatively pass it's data through the network to a main location or sink, where the data can be observed and analysed.

A base station acts like an interface, between users and the field network. It has various application domains such as: pollution monitoring (air, water, soil); forest fires detection; greenhouse monitoring; landslide detection, industrial process monitoring, home automation and environmental monitoring

As Farooq and Kunz (2011) referred "WSN is a highly dynamic network because nodes die due to severe environmental conditions and battery power depletion". Furthermore, a WSN is composed of miniaturized motes equipped with scarce resources (limited memory and computational capabilities). WSNs invariably operate in an unattended mode and it is impossible to replace sensor motes after deployment (*idem.*) Therefore, a fundamental objective to the sensing research is to optimize the sensor motes' life time.

The technology is very suitable for the monitoring and prediction of the heavy metal pollution (Cai et al., 2011), even if the big challenge for WSN is that the sensor nodes often have to survive the elements of nature and function for long periods of time, so the wireless sensor node should be extremely low power and low cost.

For designing a WSN, different factors need to be considered such as: fault tolerance, scalability, hardware production costs, constraints in sensor network topology, transmission media, power consumption (Matin and Islam, 2012). In particular, power consumption, is the challenge. The size of the nodes limits the size of the battery and miniaturisation could be the future trend. Also, the software and hardware design needs to carefully consider the issues of efficient energy use. For instance, data compression might reduce the amount of energy used for radio transmission, but uses additional energy for computation and/or filtering (*idem.*). The energy policy also

### 3. REMOTE ENVIRONMENTAL MONITORING

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depends on the application; in some applications, it might be acceptable to turn off a subset of nodes in order to conserve energy while other applications require all nodes operating simultaneously,

Simultaneous HM detection (already a very demanding electrochemical process), or different physicochemical parameters (operating in the sensor nodes) represent a high power consumption in the WSN supply.

In the WSN system, sensor nodes are micro-electro-mechanical systems that produce a measurable response to a change in some physical or physicochemical or chemical condition in the area to be monitored. The continuous analog signal sensed can be digitized by an analog-to-digital converter and sent to controllers for further processing. Every sensor node in a WSN has a sensor, a microcontroller and a transmitter/receiver (Bi, et al., 2008). It is able to acquire data from a specific point in a real environment and transmit it through the WSN. In the literature, very few works address sensing different parameters using a single sensor.

In the description of other authors (Jiang *et al.* 2009), a WSN node with: 1) sensing and computing module (the sensor unit can be an ADC - Analog to Digital Converter), 2) processing module (as CPU), 3) communication module (as radio transceivers) and 3) a power unit.

The individual nodes in a WSN are inherently resource constrained, they have limited processing speed, storage capacity, and communication bandwidth. After the sensor nodes are deployed, they are responsible for self-organizing an appropriate network infrastructure. This is not pursued in this project, as the monitoring station (the pilot-station) only has a single node.

Bhattacharyya *et al.* (2010) distinguishes between three categories of sensor nodes:

- Passive, Omni Directional Sensors: passive sensor nodes sense the environment without manipulating it by active probing. In this case, the energy is needed only to amplify their analog signals. There is no notion of "direction" in measuring the environment.
- Passive, narrow-beam sensors: these sensors are passive and they are concerned about the direction when sensing the environment.
- Active Sensors: these sensors actively probe the environment.

Wireless communication systems transmit data to secure storage locations behind firewalls or in the internet cloud for user access and analytics (Myers et al., 2014). "Smart" systems also can be programmed to send instant alerts via phone, text, or email messaging if predefined contaminant thresholds are breached. The user interface incorporates data from traditional field sampling-fixed laboratory analysis to provide systems integration efficiency for multiple aspects of environmental monitoring and regulatory compliance (*idem.*).

Recent developments in the area of micro-sensor devices have accelerated advances in the sensor networks field, leading to many new protocols specifically designed for WSN (Bhattacharyya, et al., 2010). These sensor nodes have some constraints due to their limited energy, storage capacity and computing power. Data is routed from one node to other using different routing protocols. Routing techniques are required for sending data between sensor nodes and the base stations for communication. Different routing protocols are proposed for wireless sensor networks. These protocols are classified according to different parameters. Protocols can be classified as proactive, reactive and hybrid based on their mode of functioning and type of target applications. In a proactive protocol the nodes switch on their sensors and transmitters, sense the environment and transmit the data to a BS through the predefined route.

### 3. REMOTE ENVIRONMENTAL MONITORING

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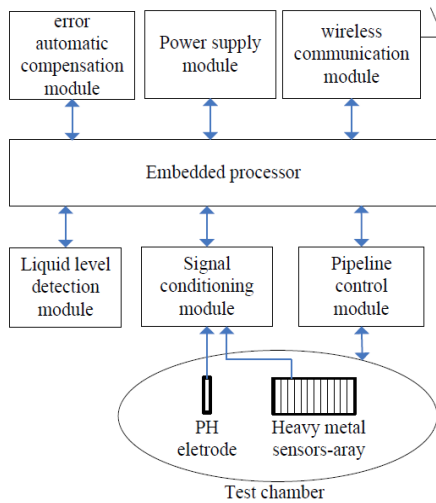
Some examples of WSN applications, relating with monitoring, chemical sensing, water quality monitoring systems, are listed below:

- Water Quality Monitoring System, based on WSN, applied to waste treatment is described by Wang (2012). The station consists of: 1) Analog inputs/outputs for water parameter transmission; 2) Control pumping and 3) Controls alarm system - all digital inputs/outputs. Data can be exchange from a station to monitoring center via TCP / IP protocol, but with WSN Platform in PLC input/output ports, the data can be communicated with center directly. The technical requirements include in the WSN node are directly connected to the analyzer, through analyzer' s communication interface protocols (such as MODBUS / PROFIBUS / JBUS/RS 232/RS 485); Output signal: 4~20 mA; Power: 220V 50Hz, response time:  $\leq 30$  seconds. It was present the parameters used as standard indicators, sensing targets and range, e.g.  $\leq 0.0005$  mg Hg/l;  $\leq 0.005$  mg Cd/l (parameters under Fishery Water Quality Standard, China, GB 11607-89, *cit by* Wang, 2012).
- A kind of WSN is Report ed by Steinberg *et al.* (2005), the wireless chemical sensors (WCSs), that is an analytical device that combine chemical sensing ability with integrated wireless data transfer. They are particularly suited to mobile and wearable applications where size, weight, power consumption, battery lifetime and connectivity are key factors beyond analytical performance. A wireless amperometric potentiostat represents a wireless data connectivity that exists between simple low-cost mobile and wearable chemical sensors and powerful ubiquitous computing products (e.g. Smart-phones, tablets and computers). By providing a seamless digital interface, this potentiostat could assist in the commercial realisation and wides pre-adadoption of wearable and mobile electrochemical sensors. The potentiostat is semi-autonomous and operates as a stand-alone chronoamperometric datalogger, with data analysis performed externally on the Smartphone, tablet or computer.
- Autonomous real-time water quality sensing as an alternative to conventional monitoring to improve the detection of ecosystem indicators are Report ed by Dong *et al.* (2015). Which have potential to provide data to understand the symbiosis between food, energy and water (FEW) systems. Precision timing, synchronization, and security must be considered. In particular, precision timing with microsecond or nanosecond accuracy is able to define high-speed, low-latency networked devices and applications. Communication among sensing devices requires precision timing to ensure accurate data time stamping and handoffs during transmission.
- For soil moisture measurement Morais *et al.*, 2004; present a wireless RF CMOS interface, which comprises a Delta-Sigma ( $\Delta\Sigma$ ) modulator for acquiring an external sensor signal, and a RF section where data is transmitted to a local processing unit. The interface can also be used with other kinds of environmental sensors in a wireless sensors network. The CMOS mixed-signal interface has been implemented in a single-chip using a standard CMOS 0.7 $\mu$ m process.
- A heavy metal monitoring system is described by Lin and Huang (2014), the system was composed by a monitoring terminal, a gateway, a General Packet Radio Service (GPRS) network and upper computer monitoring center. The system detected the heavy metal ion concentrations by ion-selective electrode array and came into the system error automatic compensation method (develop by the authors) in the detection process. The system hardware mainly includes the gateway and monitoring terminal. The monitoring terminal was consisted of embedded processor, test chamber, pH electrode, heavy metal sensor array, liquid level



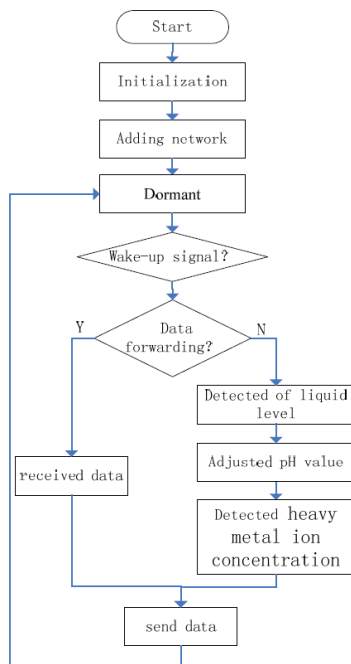
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detection module, signal processing module, pipeline control module, error compensation module, voltage management module and wireless communication module.



**Hardware block diagram of monitoring terminal (Lin and Huang, 2014)**

Heavy Metal Sensors-array and pH electrode were in a test chamber. Pipeline control module which composed of the peristaltic pump and the electromagnetic valve was used to control the instrument pipeline. The Pipeline control module would input a different fluid to the test chamber in the detection process, empty and clean the test chamber and pipeline in the after test. Heavy metal sensors-array was composed of multiple ionic electrodes, which can simultaneous measurement of multiple heavy metals such as lead, cadmium, mercury information, copper etc. The data of heavy metal sensors-array was I/V converted, filtered, amplified through signal conditioning circuit, and then was A/D transformed by embedded processor conversion. According to the weak acid requirement of the testing water samples, the system uses pH electrode to detect water pH value, and adjust the pH value of testing samples by Pipeline control module, so as to realize the accurate measurement of HM ions.



**Program flow chart of monitoring terminal (Lin and Huang, 2014)**

The system can meet the requirement of long time monitoring:

- The monitoring terminal software mainly included network management, data transmission, information collection and data processing.
- The sampling period (refresh rate) was 1 h and wake-up interval of the monitoring terminal was 2 s.
- Sending and receiving data interval was 30 seconds. The total power consumption of 1 hour was 503550 mA\*ms which about 0.14 mAh.
- A Lithium battery with a capacity of 1200 mAh make the nodes works 357days.

**Power consumption of working status (Lin and Huang, 2014)**

State	Current (mA)	Duration (ms)	Times	Power consumption (mA*ms)
Collection	50	3000	1	150000
Send or receive	35	20	120	84000
Wake-up	10	5	1800	90000
Sleep	0.05	1995	1800	179550
Total				503550

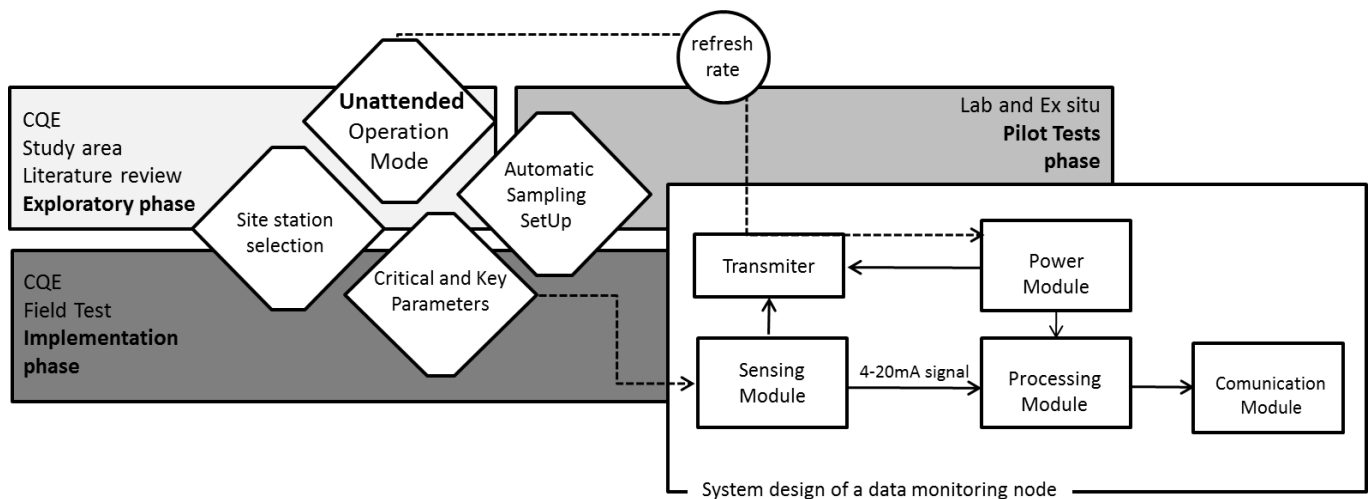
- The sensor nodes often have to survive the elements of nature and function for long periods of time, so the wireless sensor node should be extremely low power, and low cost. Cai *et al.* (2011) relates a hybrid chemical sensor (DPASV), combining six microelectrode arrays (MEA) and four light-addressable potentiometric sensors (LAPS) on the same silicon chip, used to get redundant data about the concentrations of HM and pH in water environment. The sample tested consisted of  $Zn^{2+}$ ,  $Pb^{2+}$  and  $Cu^{2+}$  (concentrations respectively 70  $\mu g/L$ , 10  $\mu g/L$  and 5  $\mu g/L$ ). The solutions of  $Zn^{2+}$  and  $Pb^{2+}$  were separately ranging from  $10^{-7}$  to  $10^{-2}$  mol/L. It was monitoring the HM pollution of a real lake in real-time. According to the experience, DPASV applied to MEA is suitable for on-line monitoring. The PVC membranes coated on LAPS were not very stable.

#### 3.2. Diagram of the WSN Environmental Monitoring Program

The different components and background concepts described above contribute to the design of the remote environmental monitoring program that this Report proposes.

Considering a three phase program, the main factors analyzed in this part of the Report are listed and illustrated below:

- The defined operation mode – unattended (as initially defined in the proposed research program), as well as specific considerations related to the environmental conditions, pose constraints for the sensing module, the processing module, the refresh rate of the transmitter, and the power module;
- The selection of critical parameters, responsible for the environmental contamination (explicit in the literature review) and the key parameters (indirect critical parameters) must be reanalyzed specifically to test the monitoring equipment system in a field test following the literature review.
- The selection of a station site, an important step in the monitoring program, might result from the literature review, although the field tests (and conventional campaigns for validation parameters) should confirm the best location.
- The development of the automated sampling device, an innovative aspect of the program, mainly in the closely related project within the OHM WSN research, is another important challenge with a decisive impact on the program as a whole, with necessary adaptations and improvements in the Pilot and Field test.
- Most importantly, the WSN system design of the data monitoring node must include: the Processing Module (monitor or acquisition and data logger linked, with a 4-20mA, with the sensor and transmitter); the Sensing Module with one or more probes (to measure the key parameters) immersed in the water; the Power Module; the Communication Module (the wireless coordinator or gateway device, located in an office station, connecting wirelessly with the processing mode). This WSN system design proposal must be tested both in a second phase of the project, in Lab and ex situ (Campus de Santiago), as well as in the study area field (the CQE surroundings) in a third phase.



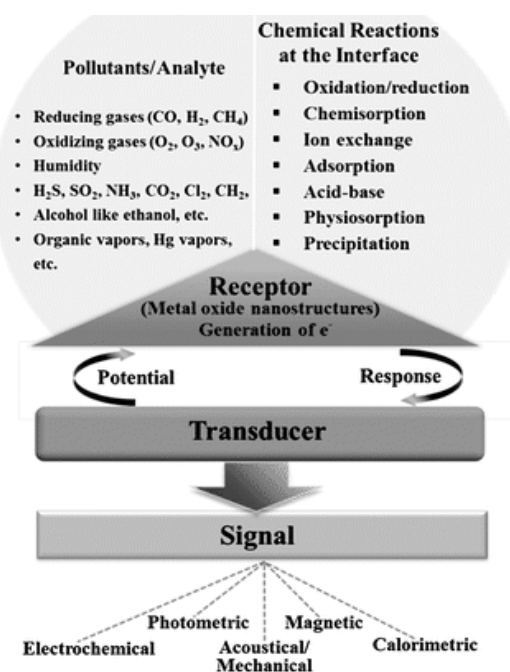
Configuration of a common monitoring-system for water-quality data collection

## 4. ANALYTICAL SENSOR

The state-of-the-art of sensor technologies for real-time water quality monitoring includes fiber-optic sensors, biosensors, microelectrode-based sensors (thin-film plated electrodes, micro and nano sized solid electrodes, screen-printed electrode type), lab-on-a-chip system, and electromagnetic wave sensors, among others. Other alternatives include cell-based sensors, which can detect the presence of a wide range of toxicants by monitoring the cell's viability. In this part of the Report will be present some relevant characteristics of sensors for the environmental monitoring instrumentation. Also it is presented an overview of the chemical and electrochemical sensors types (considered in the OHM project) and some applications and recent developments.

Sensor technologies are currently unable to measure all analytes in all media at acceptable detection limits (**FIGURE:** Hahn *et al.*, 2012). Nevertheless, many environmental parameters and contaminants may be measured today (even more via surrogate indicators, like the key parameters in this OHM project) and market demand continues to drive sensors development by commercial firms. It was continues an extensive research into miniaturized sensors that offer promise for measuring any kind of contamination (Ho *et al.*, 2005)).

A sensor is any kind of transducer that transforms the magnitude that must be measured in another which is easier to measure. There can be direct indication sensors (e.g. a mercury thermometer) or there can be connected to an indicator (possibly by means of an A/D converter) (Bri *et al.*, 2008)



In : Hahn *et al.*, 2012

Another definition is from Alwakeel (2015), the sensor is a device that detects a physical quantity and converts it into an analogue quantity which can be measured electrically such as voltage, capacitance, inductance and OHMmic resistance. The output needs to be operated, interfaced & regulated by the system designer (*idem.*). The transducer is considered as the heart of the sensor. It is a device that convert the measured quantity into a standard electrical signal such as 0-10V DC, -10 to +10V DC, 4 to 20mA, 0 to 20mA, 0-25mA etc. The output of the transducer can be directly used by the system designer. Transducers are used in electronic communication systems to convert signals of different physical forms to electronic signals (*idem.*)

Sensor and probe components are today smaller and more rugged than ever, making them capable of withstanding harsher environments. In addition, detection limits, sensitivity, and selectivity are advancing similarly. New generations of sensor technologies are emerging at an unprecedented rate, opening the door for automated sampling in long-term monitoring programs (Pujol, *et al.*, 2014).

#### 4. ANALYTICAL SENSOR

Ho et al (2005) identify and describe sensor technologies that may be applicable to monitoring of different contaminants, organized according to analyte, which include: trace metals, radioisotopes, volatile organic compounds, and biological pathogens, presented in the **TABLE** below.

**Summary of potential sensor technologies that can address environmental monitoring needs (Adapt from Ho et al., 2005))**

Sensor Technology	Application	Analyte	Comments
LIBS Laser-induced breakdown spectroscopy	Drinking Water, Storm Water, Pretreatment	Trace Metals	High cost of the laser and spectrometer. Additional development needs to bring the price down Need package for use in water applications. Could potentially be used to simultaneously identify 9 metals and As. Sampling interval ranges from 1 s to ~1 minute (for signal averaging). Can be run continuously.
Nanoelectrode Array	Drinking Water, Storm Water, Pretreatment	Trace Metals	Less selective than LIBS. Sampling interval on the order of seconds. Still under development to discern among multiple target analytes present.
Miniature Chemical Flow Probe Sensor	Drinking Water, Storm Water, Pretreatment	VOCs, Trace Metals	Expensive because of spectrometry (like LIBS). Reagents need to be supplied. Need to acquire sample to introduce reagent in a side-stream.
RadFET	Drinking Water	Radioisotopes	Need to use filters to allow speciation. Sensitivity in water for alpha and beta emitters is questionable given the attenuation through water.
Low-energy Pin Diodes Beta Spectrometer	Drinking Water	Radioisotopes	Commercially available. May not need any additional development. Sensitivity in water for alpha and beta emitters is questionable given the attenuation through water.
Cadmium Zinc Telluride Detectors	Drinking Water	Radioisotopes	Commercially available. Sensitivity in water for alpha and beta emitters is questionable given the attenuation through water.
SAW surface acoustic wave	Drinking Water, Storm Water, Pretreatment, Air	VOCs	Sensitivity can get down to ~ppm, but fluctuations in environmental parameters (e.g., humidity, temperature) can reduce the sensitivity and accuracy. Sensor signal drifts over time. Cannot analyze more than three contaminants at once.
Chemiresistors	Drinking Water, Storm Water, Pretreatment, Air	VOCs	Sensitivity is limited (hundreds of ppm). Needs pre-concentration. These can also be used to monitor in-situ remediation activities (patent pending)
IMS MicroHound/Ion Mobility Spectrometer	Drinking Water, Storm Water, Pretreatment, Air	Semi-Volatile Organic Compounds	Gas-phase detection; Need to develop a sampling system to introduce water samples to IMS. Should be able to detect semi-volatile chlorinated hydrocarbons (e.g., polychlorinated biphenyls (PCBs)). Can detect pesticides, organic nitrates.
MicroChemLab (gas)	Drinking Water, Storm Water, Pretreatment, Air	VOCs	High cost Additional development work is needed to adapt these systems for VOCs.
MicroChemLab (liquid)	Drinking Water	Biological	High Cost
FAME Fatty acid methyl esters analyzer	Drinking Water	Biological	Sampling is currently done manually.

## 4. ANALYTICAL SENSOR

### 4.1. Relevant characteristics of sensors for the instrumentation system

Various types of sensors and transducers are available to choose from like analog or digital. The type of input or output transducer being used depends upon the kind of signal sensed. Basically, a sensor or a transducer can be defined as they convert one physical quantity to another. In short, a device which processes an input is called sensor because it senses a physical change of a stimulus, while transducer is also a device, however it converts the energy from one form to another (**TABLE**).

**Relevant characteristics of sensors for the instrumentation system**

Sensor interface	Analog	Digital
Most common types	Current (4-20 mA)	RS232
	Voltage (different ranges: 0-5 V, 0-12 V, etc)	SDI-12
		RS485
		USB, etc
Sensor physical link	Dedicated - one cable per sensor	May be dedicated (RS232, USB), <i>i.e.</i> one cable per sensor, or integrated in a data bus for multiple sensors, as with SDI-12 or RS485
Parametric sensors	Not possible in general, one cable per sensor	Multiparametric sensors may be available, as data is already in digital format and the communication protocol should be able to identify data sources
Acquisition unit	Needs signal conditioning systems and data acquisition systems	Interfaces with PCs or microcontrollers are more versatile
	In general, requires specific hardware from the manufacturer	Interfacing hardware may be optional or not needed
	Usually there is hardware to interface with the sensor and to log data	In some cases, data logging may be done by the sensor itself if internal memory is available
Software	In general requires proprietary software to interface with the data logger	May need specific software but is potentially more versatile to work with custom or standard software
	Does not require the knowledge of communication protocols between the application and the hardware	To work with generic software or custom software, knowledge of the communication protocols used by the sensors is needed
Data logging	The data logger, when with connectivity, transmits the data to the remote system directly to a computer or to a network, usually through wireless gateway	If there is an intermediate data logger, the solution could be similar to using an analog sensor, but the more common case would be for the sensor to act as a logger while it is not connected to a computer. Data will later be transferred when the sensor is connected to a computer.

A choice was made to use analog sensors, so that the data logger would not need to support specific digital transmission protocols, which could potentially be different for the sensors of different parameters.

To enable the use of the sensor with the selected acquisition system, it would have to be compatible with the input channels of the BeanAir (ref. BND-XTD-AN420-4CH), 4-20mA current output. If the sensor did not have these rating, a conversion stage would have to be added.

The sensors could be of two different types:

- Sensors with signal conditioning (amplification, filtering, etc.)
- Sensors without signal conditioning, (like thermocouples or extensometers).

Sensors with signal conditioning would be preferable, as they simplify the overall system. Sensors without signal conditioning would obviously pose additional problems and further complicate the system design.

If the sensors would have signal conditioning and current outputs, only a direct connection would be needed between the sensor and the acquisition unit, and the only concern would be to use suitable connectors. If the sensors have voltage outputs, or even digital outputs, these would have to be converted to current outputs, which could be achieved through the use of additional hardware, such as microcontrollers.

### 4.2. Physic-chemical, chemical and electrochemical sensors

Electrochemical sensors are suitable for measurements at remote location, due to their portable nature. Despite prominent advantages of electrochemical techniques, Omanović *et al.*, (2015) describe the development of fully equipped autonomous systems are scarce. Few systems were assembled in recent years which were successfully applied for real-time monitoring of trace metals in clean and polluted waters, demonstrating the advantage of automated systems for monitoring of trace metals temporal variations. The benefit of continuous and remote sensing was recently highlighted by Noyhouzer and Mandler (*cit por* Omanović *et al.*, 2015) who developed a new electrochemical flow cell as a part of an autonomous flow system for HM analysis in aquatic environments.

The follow sensors descriptions (literature review) refer fist to those type of sensors which could measure the key-parameters selected (pH, EC, water level) and then to the chemical sensors which generally measure the HM.

**pH sensors** (described by Macekova and Žiga, 2014) are a potential difference between electrodes immersed in a tested solution is directly proportional to pH. The calibration of measuring equipment must be considered and realized before measurement campaign. Calibrating process consists of two or more times repeated sequential immersions of the probe into calibrating solutions (buffers), with the aim to gain more calibration data. Buffers are stable solutions with exactly defined pH at the defined temperature. Buffers used for calibration must have different pH, but in the interval of the supposed value of the measured solution. Two- or more-points calibration is known, depending on the required accuracy or on expected shape of the pH-voltage relation, graphically illustrated by diagram. Mostly the dependency is considered roughly linear and then, it is demanding only two calibration points. After calibration, mathematical estimation of pH (by microcomputer) is applied at the temperature of tested liquid. Consideration of temperature is necessary condition for a correct evaluation and comparison, so the temperature is usually measured simultaneously with the pH.

**EC sensors** includes two basic types of sensors for conductivity measurement (described by Macekova and Žiga, 2014) a contacting (conductive) sensor and an electrode-less (inductive) sensor. The contacting sensors consist of two metal electrodes (stainless steel, titanic, or platinum) immersed in electrolyte solution. Depending on the concentration of ions in the solution (and also on geometric parameters, and temperature), a current of certain value starts to flow between the electrodes and can be recalculated into the value of conductivity. Precise equipment can utilize four electrodes and/or the AC-current principle. This principle provides wider dynamic range and reduces errors due to the recombination of the ions on the electrodes, serial impedance of the wires and effect

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of contaminations of electrode surface. The conductivity of liquids is measured with a measuring system that has two coaxially arranged electrodes. In inductive conductivity measurement equipment, a transmitting toroid coil generates magnetic alternating field that induces ionic current in the ambient solution, depending on the conductance of the solution. In the receiver toroid coil, the current is induced, measured and evaluated by an analyzer. The advantages of such design are as follows: the material of coils does not need to touch the solution and the solution can also contain big dispersed solid particles. This principle is suitable for measurement of the conductivity greater than approximately 15  $\mu\text{S}/\text{cm}$ .

As Katznelson *et al.* (2010) referrer all EC and pH probes also contain a thermistor and have a built-in automatic temperature compensation (ATC) capability; those compensation algorithms may vary in level of sophistication (e.g., some pocket instruments may simply correct the reading by 2% for each degree  $^{\circ}\text{C}$ ). All monitoring results must be Reported after compensation for temperature, salinity, and atmospheric pressure as relevant.

Today, several producers in the area of water quality measurements offer freestanding probes, and also the sophisticated so called multiprobe systems, or multiparameter probes. The multiprobe system has a common base with the powering and communication interface, optionally it can connect 3 or more (more than 10) probes for several water quality indicators. The multiprobe can have its own battery, a cleaning brush with automatic function, a protective cage and an outgoing connecting cable for the power supply and communication. These systems can be fastened to a buoy, and can measure continuously during intervals of a few weeks without maintenance.

Multi-parameter multi-channel devices can measure a few parameters simultaneously. They can generate alarm at the exceeding limits, or in case, when it is needed to calibrate or maintenance the pH probe. A number of hand-held measurement devices (like multimeters) are known, which are connectable to more types of probes, and can show or recalculate parameters mentioned above. They can serve for combined measurement methods (without and with a man attendant), and also for the calibration and the reference measurement.

**Water level sensors** was reviewed by Loizou and Koutroulis (2016) with the past-proposed techniques for liquid level sensing revealing that either they have been applied for liquid level sensing over a relatively low range, or special scientific equipment of high cost is required for conditioning and processing the electric signal produced by the liquid level sensor, or they are not convenient for transportation, installation and long-term maintenance in multiple large-scale water storage tanks of water distribution networks in cities, communities etc. Then, the operational characteristics and performance of a novel capacitive-type water level measurement system have been investigated through simulations and experimental tests conducted in two water storage tanks of a city-scale water distribution network. It has been demonstrated that the proposed capacitive water level measurement system achieves equivalent performance with that of a commercially-available ultrasound sensing device and simultaneously exhibits a much lower manufacturing cost.

**Chemical sensor**, according to the International Union of Pure and Applied Chemistry, is “a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. The chemical information, mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated”. In other words,

chemical sensors cover all-encompassing devices employed to monitor, measure and analyze chemical signal as generated due to changes in analyte concentration (Pandey, et al, 2016)

The chemical information originated by the physical property of the system or by the reaction of the species present in the analyte was utilized in the receptor unit (working electrode), which further transformed in electrical signal by the potentiostat/galvanostat based electrochemical work station as transducer system.

The final analytical useful results can be deliberated by applying various modes of signal amplifications techniques such as potentiometry, voltammetry, conductometry and electrochemical impedance spectroscopy. Different modification of working electrode can be carried out for enhancing the sensitivity, selectivity and reproducibility of the electrochemical sensor.

Thus, the electrochemical sensor provides low detection limit, high sensitivity, high surface area, good reproducibility, better signal to noise ratio and selective sensing of more than one metal ion. It is a tool that adapts the chemical information of sample and converts it into an analytical signal.

Although the progress in electroanalysis of trace metals has been made, only few of new techniques are suitable for analysis at (ultra)trace levels application (Omanović, et al, 2015). The requested concentration ranges are extremely broad, no on-line chemical analyser can cope with it. The measured span usually covers 2-3 orders of magnitude, e.g. 0.1 to 100 ppb.

### 4.2.1. Electrochemistry principles

Sensors and probes work mostly on electrochemical principles, as mentioned by Macekova and Žiga (2014). They are applied in the glass electrodes or generally in the so called ISE electrodes (Ion-Selective Electrodes).

There are three components of a ISE: an indicative electrode, a reference electrode and a semipermeable membrane, sensitive to a special chemical environment. The indicative electrode shows out some little electric potential when it is attended in the measured environment (gas, liquid, ground, etc.), depending on the activity of the measured ions. Ideally, the reference electrode does not change its electro-chemical potential during the measurement. The electrodes are mostly rod like shaped, and can be used separately or can be set in the compact combined double electrode. A relevant potential difference between of two electrodes appears and is measured by a voltmeter. This voltage is then computationally transformed into the value of a measured parameter and indicated on a display.

The common voltammetry systems must provide a range of scan, step and pulse techniques that are of importance in analytical electrochemistry, microelectrode studies, sensor research, electrodeposition and battery/fuel cell analysis. A basic voltammetry system provides some of the fundamental techniques as a low cost alternative. The advanced system includes: normal and differential pulse voltammetry - used in analytical electrochemistry applications e.g. for trace metal analysis. Recurrent pulse techniques (used in battery / fuel cell analysis) including equivalent series resistance ESR analysis and GSM / CDMA mobile phone pulse test applications (Pujol *et al.* (2014)).

Even if techniques based on anodic stripping voltammetry (ASV) are the most frequent, a good analytical performance (low n-sensitivity) could result from other two techniques considered (adsorptive cathodic stripping



voltammetry – AdCSV and stripping chronopotentiometry – SCP), meaning that the mode of voltammetric procedure is not the most critical point explaining its efficiency.

The cyclic voltammetry (CV) method is widely used for understanding there do x processes and reaction intermediate comparatively less sensitive for quantification. The square wave voltammetry (SWV) method has been proved to be more sensitive and faster than the CV and differential pulse voltammetry (DPV) methods for determination of trace metal ions.

In common SWV voltammetry, the accumulation of metal ions is mainly due to sorption of complexes at the surface of the electrode in open circuit condition. For instance, metal ions like Cr and Al were quantified by adsorptive stripping voltammetry after complexation with *cupferron* and Ni and Co were detected after complexation with *dimethylglyoxime* (Pandey, et al., 2016). The significance of electrochemical sensors belongs to their high sensitivity, selectivity, low detection limit and good reproducible results.

### 4.2.2. Electrochemistry in a study market perspective

The most common chemical sensors for *in situ* measurements, with portability and power supply autonomy, are the called “multiparametric probes”, which measure most of the physicochemical parameters: pH, Redox, DO (optical and electrochemical), EC, salinity, turbidity, TSS, temperature, etc. Some of commercial models (Producers brands and probes models) can be listed: OTT Hydromet (Hydrolab HL4); Xylem analytics (WTW IQ 2020XT e NET 182 XT); YSI (YSI ProDSS Multi-Parameter Water Quality Meter); Ponsel (ODEON X Handheld); Hach Lange (sensION + MM150); In-Situ, USA (smarTROLL MP Handheld); Thermo Orion, USA (Star A329); Amel, ITA (346), among others. Those prices are in order of 10 k eur (summary tables of the Market study are available in the Appendix).

Some of those “multiparametric probes” models operate with ISE, detect and/or measure some cations contents, such as ammonium, nitrate, nitrite, chloride, fluoride, phosphate (e.g. Hydrolab HL4; Xylem WTW IQ 2020XT; Orion 9512BNWP; Hach Lange, SL1000). Also for the measurement of alkali metals determinations it is common the dedicate ISE (common for Na and K) and for some transition metals (Cu and Pb), indeed, only used for a first screening. The results of those electrodes have low precision and do not operate continuously (e.g. Amel 346; Mettler Toledo, USA, perfectION™ e DX series).

Moreover, for in-situ applications, even with low precision and low detection limit (accuracy to 1 ppb and range detection below 0,5ppb) the Skyray Analyzer (HM 3000P – Portable Water Quality Heavy Metals) can measure simultaneously Cu, Cd, Pb, Zn, Hg, As, Cr, Ni, Mn and Ta, with electrochemical methods as anodic stripping voltammetry. The price of this portable device is more than 20k eur.

Many of these devices have telemetric capabilities and data processing. The most complete probes models also include data-logging system (e.g. Hydrolab HL4 has 4GB for logging, the equivalent to 5 years of continuous measurements for 15min refresh rates). They also have remote real-time transmission, as well as remote control and alarm management. The autonomy of this equipment can be ensured with great longevity lithium batteries (e.g. Hydrolab HL4: about 75 days with 30 s refresh rate and 3 sensors measuring simultaneously - T, EC, pH). Another feature to highlight is the associated equipment to the probe, including self-cleaning (with ultrasonic methods) to ensure the maintenance of the probe and the reliability of the measurements (cleaning cycles could be programmed, as the measurement refresh rate).

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Another type of electrochemical sensors is the online analyzers, which employing anodic stripping voltammetry methods, and provide real-time data on the concentration of metal/s. The designation assigned to sensors measuring in continuous with programmable refresh rate. Usually, online analyzers needs high power supply, and have high instrumental complexity with analytical requirements as sample pretreatment, pre-concentration or dilution, reagents and standard solutions for calibration, also an hard maintenance. However this is the best technical solution to measure metals *in situ*, such as in natural as in industrial environment.

The online analyzers always have custom lines, addressed to the custom measurement requirements, it can include all metals or physicochemical parameters. All commercial online equipment require ongoing maintenance, and the development and installation costs are in the order of 100k euro.

The main commercial brands and equipment models are: Alliance Instruments, FRA (PROXIMA-SFA); Mercury Instruments, USA/UK (Mercury Process Analyzer); Sensolytics, DEU (OLGA - On-Line General Analyser); SPECTRO, DEU (SPECTROBLU); Arizona Instrument LLC, USA (Jerome® 451, Gold Film Fence-line Mercury Monitoring System); Lumex Instruments, DEU (RA-915M Mercury Analyzer); Istran, SLO (EcaMon SaFIA); PSAnalytical, UK (10.225 online systems); Trace2O, UK (Metalyser On-line HM6000), Metrohm Applikon (2035 Process Analyzers); Applitek (EnviroLyzer® Series II e VPA® Voltammetric Process Analyzer); Modern Water, UK (OVA7000 Dual Cell and OVA5000).

Considering the market study (summarized in the Appendix) and the budget of the OHM project, it was proposed the ISE probes (*in situ* equipment and with continuous measurements). Namely the pH sonde (Hanna HI-1006-2005 pH electrode with PTFE junction) with a pH Transmitter (Hanna HI98143-20) designed for long distance measurements, it can be either panel or wall mounted. Has an output 4-20mA current transmitter (active and/or passive output). The equipment could be used for the pilot tests – in laboratory and in the RIA field conditions - in an early stage of the OHM WSN work project.

### 4.3. Advances in Research and Applications

The future perspective in the development of HMs sensor is towards the manufacture of miniaturized devices employing as hand held tools for day-to-day on-site monitoring with a nano-molar range of the detection limit. In spite of obtaining prominent achievements, the complicated procedures and inconvenience in the fabrication of platform apparently hindered their sensing applications.

For environmental applications, as mention in recent reviews (Justino et al, 2015; Cinti and Arduin, 2016) develop and applying a metal sensor it is a difficult task, the recognition elements should be improved, since they should be tolerant to environmental conditions. However, the utilization of nanomaterials, also the synthesis and application of graphene to the fabrication of graphene-based electrochemical sensors is emergent and the main develop direction, accompanying the printed technology, microfluidic in electroanalysis (Cinti and Arduin, 2016).

Emerging sensor for various environmental monitoring applications are fabricated by technologies or processes that combining electrochemistry methodologies, such potentiometry and voltammetry, in a miniaturized support, with different electrode materials and assemblies, it can be distinguished as:

- Thin-film plated electrodes,
- Micro and nano sized solide electrodes;
- Screen-printed electrode type.

Nowadays this field of knowledge and technology goes through a period called the "Electroanalysis Renaissance" (Escarpa, 2012 in Cinti and Arduin, 2016).

A recent study refers the electrochemical sensing performance of the nanocarbon highly dependent upon on its unique electronic and structural properties (Pandey, et al, 2016).

On the other hand, Pujol *et al.* (2014) remember that the properties of the conventional mercury electrode have been at the origin of considerable efforts with respect to electrochemical methods devoted to HMs detection in water. But, nowadays, the great experience in polarographic techniques coupled with the improvements in data processing for the monitoring of pulsed potential sequences is still encouraging to exploit the background on this electrode. Nevertheless recent trends have focused on mercury-free electrodes, because this metal will be totally prohibited in the next few years (EU Directive2008/105/EC).

The research and technological progress, as refereed by Omanović *et al.* (2015) was centered on the development of new "green" sensors, as well as well-established electroanalytical methods, comprising improvements in sensitivity, robustness, versatility, disposability and reliability.

On the other hand, the detection of trace metals requires more sensitive methods. In that way the chemically modified electrodes (CMEs) represent a good alternative toward expensive, inconvenient analytical methods developed in laboratory. The combination of amperometric transduction with the specificity induced by the modifier makes it possible to propose reagent less sensors exhibiting high sensitivity and good selectivity. Furthermore the large range of available strategies for surface modification allows multielectrodes or micro array sensors to be designed for simultaneous multicomponent analysis in complex media.

A new generation of analytical devices called "micro total analysis system" ( $\mu$ TAS) is being developed for the online monitoring of real samples. These devices integrate not only the sensing element but also some complementary actuators (pumps, valves, micro fluidic channels) to obtain an all-integrated automatic monitoring system which includes a calibration procedure.

### 4.3.1. Screen-printed electrode types

As recognize in the market study (summarized in the Appendix), the screen-printed electrodes (SPE) became very attractive for the broad range of applications including the sensing of trace metals. SPE are commercial available, those suppliers are commonly R & D laboratories, associated with universities: DropSens, ESP; Micrux Fluidic, ESP; PalmSens, NLD; BVT, CZE; ItalSens, ITA; etc. The cost of all instrumental SPE system is in the order of 3-5 k euros. Suppliers are mostly R & D laboratories, associated with universities. They are receptive to develop specific solutions for the required parameters and the specific support matrix, but with high costs, above 10 k euro).

The formats of screen-printed sensors are changeable in line with the requirements of a specific analyte. Also, the surface of a screen-printed sensor can be easily modified to fit many different pollutants and to achieve a variety of improvements. Screen-printed sensors combine ease of use and portability with simple, inexpensive

#### 4. ANALYTICAL SENSOR

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analytical methods. It can be based on carbon, gold, platinum, silver or carbon nanotubes inks, they are disposable devices, designed to work with micro-volumes of sample (general dimensions: 3.4 x 1.0 x 0.05 cm).

The analytical performance of these sensors could not compete with classical electrodes, due to portability they could be used for field applications, but it loses in accuracy and reproducibility. Some recent studies enhanced analytical performance of the commercially available SPE of gold nanoparticle-modified carbon nanotubes for As(III) determination in real samples, the results show that it could be attractive for portable systems and in-situ measurements (Zhang et al., 2009). But, perhaps, the major limitation of the device is the lack of robustness due to its disposable nature.

A long-life electrochemical sensor for the continuous analysis of heavy metal ions (Zn(II), Cd(II), Pb(II), Cu(II), and Hg(II)) was developed by Park *et al.* (2016), using the graphene oxide (anchored-functionalized polyPATT composite). Modern stripping voltammetry has used Bi and other inorganic materials as an alternative of Hg to preconcentrate trace heavy metal ions on the electrode surface. Besides of these, various materials including carbon, carbon nanotubes, graphite, metal nanoparticles, graphene oxide, and other organic ligands have been also used as electrode materials to achieve more environment friendly and less interference methods.

The sensor surface was characterized by Park *et al.* (2016) using field emission-scanning electron microscopy (FE-SEM), energy dispersive x-ray spectroscopy (EDXS), and x-ray photoelectron spectroscopy (XPS). To improve the cationic exchange capacity and protect the surface of sensor probe, *Nafion* was coated onto the modified electrode. The sensor was applied for continuous monitoring of HMIs in tap and local surface water using the SWASV and CC methods. The observed values of Zn(II), Cd(II), Pb(II), Cu(II), and Hg(II) all of the ions were detected in the samples, and the results of both methods were in a good agreement. Therefore, this method has a great possibility for the practical determination of these five ions in various kinds of real samples. The sensor was successfully applied for the simultaneous determination of those metals using SWASV and CC. Compared with SWASV, CC has an advantage with regards to the dynamic range and analysis time, even without a predeposition step. The results conclude this sensor probe can be used as a green electrode (with no bio-toxicity). In addition, the proposed CC method is efficiently applicable to the on-site network analysis of the HM ions in environmental samples within a few seconds, and the continuous wireless detection system for the environmental field monitoring (*op cit.*).

Duarte *et al.* (2016) highlight that disposable sensors are economical in nature and designed to be one-shot, so they do not experience so-called memory effects. Some few do not require further pre-treatment prior to use or cleaning between measurements and they are very versatile in different applications. Various disposable sensors for environmental monitoring of Pb, Cd and Hg were fabricated using different technologies, such as screen-printing, toner transfer, and lithography, which we discuss in the following sub-sections.

Li *et al.* reviewed the recent developments and applications of screen printed electrodes (SPEs) in environmental assays, including the determination of Pb, Cd and Hg, but they did not cover disposable screen-printed devices. According to Arduini *et al.* (2016), sensors for Pb detection are usually modified with carbon, bismuth(Bi), gold or other materials in order to improve sensitivity. The modifiers can be transplanted onto the surface of SPEs Bi is one of the most used modifiers in electrochemical sensing due to its good analytical performance and its environment friendly characteristics. The modification of an electrode/sensor with a Bi film for lead detection essentially involves electroplating a film of Bi onto the surface of the electrode/sensor. This process can be performed in three different ways(ex situ, in situ and bulk). The performance of the sensor was evaluated

#### 4. ANALYTICAL SENSOR

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using real samples of tap water and river water, and was found to be comparable with ICP-MS. To study the stability of the sensors after fabrication, several sensors were prepared and stored at room temperature. A solution of  $10\text{ }\mu\text{g L}^{-1}$  of Hg was measured for different days of fabrication. The sensor lost 15% of the analytical signal measured on the day of its fabrication, but then remained constant during the first 30 days.

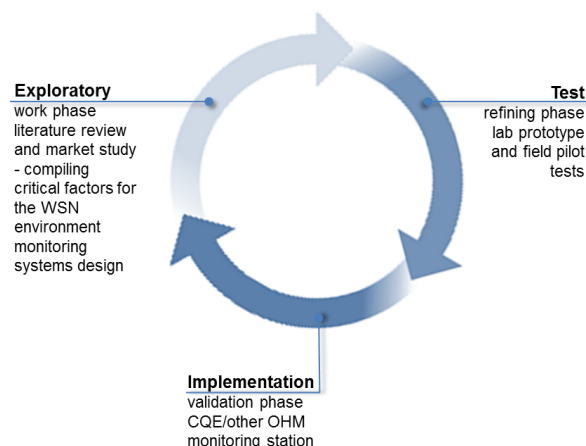
With carbon nanomaterials (with focus on graphene and carbon nanotubes) endowed with unique physiochemical properties Duarte *et al.* (2016) found to be most suitable for electrochemical detection of HM in various sources of water, soil, and foods, due to their ease to modify, high sensitivity, good selectivity and high reproducibility (Pandey, *et al.*, 2016). As graphene has several properties that make it interesting for use as a modifier that increases sensor sensitivity, including high conductivity, large surface area, and fluorescence quenching; it also offers the possibility of functionalization for increasing detection capability and efficiency. Graphene can be employed as a support material for dispersion and stabilization of other materials and the incorporated material can also prevent the problem of the aggregation of graphene. It was developed gold-nanostructured screen printed transducers modified with graphene for the detection of Hg(II).

The disposable sensors used for one-shot measurements of Pb(II), Cd(II) and Hg(II) in environmental samples showed adequate inter sensor reproducibility, sensitivity and selectivity, achieving very low LODs (Duarte *et al.*, 2016). These disposable sensors detect Pb(II), Cd(II), and Hg(II) and are best suited to speciation analysis and monitoring of those cations, rather than the determination of total elemental composition, as done with standard methods based on atomic absorption spectroscopy, atomic fluorescence spectrometry, ICP-MS, and ICP-OES development of simple, cost effective, rapid, sensitive and selective disposable sensors for detection of trace concentrations of Pb(II), Cd(II) and Hg(II) under field conditions, ensuring that in-situ results are comparable with those of laboratory instruments. Due to the great interest and high performance of disposable sensors in environmental applications, their commercialization is likely to come in the near future.

## 5. CONCLUSIONS AND FUTURE TRENDS

This Report covers a year of exploratory work, with literature review, market study of commercially available systems and technological solutions developed in academia, and compiling and reviewing the critical factors for the design of successful WSN environment monitoring systems.

The overall project should include the three phases depicted in the diagram, combining this first concluded exploratory phase of literature review and market study with a second phase of testing and refining, both the lab prototype and the field pilot tests, and a third phase with implementation of the CQE monitoring station using the knowledge generated by the first two phases.



### 5.1. Main contributions

In one year of research it was possible to do an extensive bibliographic review of geological, hydrological, hydrodynamic background, and environmental impact studies in the CQE, to select superficial water critical indicators of the industrial contamination (e.g. reference contamination values selected from Branco, 2006):

- direct parameters) Hg (0,1 – 224  $\mu\text{S}/\text{cm}$  “Vala de São Filipe”); As (0,76 – 3,26 mg/L “Vala de São Filipe”); Zn (6,92 – 22,37 mg/L “Vala de São Filipe”) and Cu (8,46 – 21 mg/L “Vala da Breja”) and
- indirect parameters (Key-parameters) pH (< 4,5 “Vala do Canedo”), EC (even this presents a local anomaly, the range values in the most affected area are higher than the regional background EC range values (9 270 – 13 556  $\mu\text{S}/\text{cm}$  in “Vala de São Filipe”).

Also, the importance of the fine sediment (< 63  $\mu\text{m}$  fraction) must be considered in the bed basins and in suspension in the water column. They could compromise the operation of the sensor, and normally require the pre-treatment of the water sample. Also the SST, whose increase is related to the high tidal fluctuation or industrial discharges, also affect the sensor operation. For this reason, it is highly recommended also to consider a flow level sensor connected with the WSN, to take measurements simultaneously with the physicochemical parameters.

The most affected areas, addressed in the different scientific references, are: “Vala de São Filipe” > “Vala do Canedo” (and “Lagoa de Vieiros” its confluent) > “Vala da Breja” > “Esteiro de Estarreja” (and “Largo do Laranjo” its confluent). Each of these locations could be a good choice for the installation of an internal-logging type monitoring station. In a next phase of this research line/OHMproject, field work should be done to analyse local variations of the critical parameters considered, and to identify the equipment support structures and potential influence of external factors not recorded in the literature review.

## 5. CONCLUSIONS AND FUTURE TRENDS

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In water monitoring technology, specially relating with superficial water, the technical solution analysed for remote and long term monitoring was an WSN equipment (Datalogger and Wireless data acquisition platform with 4-20mA Analogic Output + Gateway Data acquisition and storage device with Ethernet & GSM/GPRS). This WSN equipment must be compatible with the analytical device – the chemical sensor – considering a 4-20mA output current and input passive signal.

The instrumentation of chemical and electrochemical sensors has been highly developed in recent times. The technological solution that better complies with the aim of environmental monitoring purposes is a “Lab-on-a-chip” type device, with thin-film plated electrodes, or micro and nano sized solid electrodes or even screen-printed electrodes (SPE). Operational requirements of these solutions are very restrictive for their use in the field. They require flow analysis, in a specific cell, sample pre-filtering and possible dilution. The commercial SPE devices identified in the market study have no analytical protocol established for metal (ionic species) quantification. And at this moment, it is still difficult to integrate the classical electrodes in the microfluidic systems.

### 5.2. Considerations for Future Research

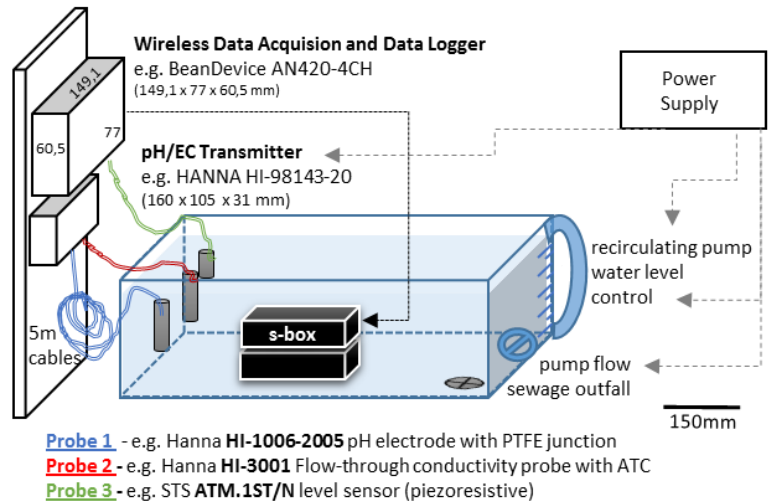
Once this exploratory study is concluded, a pilot study should be conducted to determine whether the monitoring program can meet the objectives defined above (**Lab Pilot Test “cqeAquarium”, divided in 4 phases listed below**). Analysis of preliminary data allows a first estimate of temporal sequence of values (unattended data acquisition) of the monitored parameters, and of the accuracy requirements for the sensors in terms of their ability to detect environment changes. Furthermore, conducting a pilot study allows for a more realistic and accurate evaluation of the resources and costs involved than any advance estimate, as pointed out by Moreira and Cunha, (2007) about Long-term Monitoring Programmes.

After that, if preliminary data analysis reveals that the available budget is sufficient to achieve the objectives, it is reasonable to proceed with the implementation of the program. If not, further refinement is needed before monitoring begins. This refinement can involve reducing the number of parameters to be monitored,

Another pilot test must be developed - **Field Pilot-Test “Santiago-site”** - to test the self-powered wireless data logger in an outdoors setting, and the communication with the WSN coordinator in the project office (LAR – Dep. Mec. – UA).

### 1. Lab Pilot Test “cqeAquarium” Scheme - design and equipment measurements

- 1.1. Aquarium construction
- 1.2. Panel construction for the aquarium and external equipment connections (IP compatible with field work)



### 2. Lab Pilot Test equipment

- 2.1. Installation – the “cqeAquarium” setup
- 2.2. provide sewage and channelling to the aquarium
- 2.3. choose the location of the power source and provide access develop the battery and/or solar panel support

### 3. Lab Pilot test – Installation and Maintenance – first parameters detection (pH/T; flow level)

- 3.1. test signal acquisition (active)
- 3.2. program and control sampling rate (refresh rate)
- 3.3. test the parameters and variation detection (pH/T; flow level)
- 3.4. test the probes calibration
- 3.5. program the critical level signal/alarm
- 3.6. develop flow system in the aquarium
- 3.7. test the automatic sampling device (s-box)
- 3.8. monitor probe coating/fouling deposition, and the influence in signal acquisition

### 4. Standard Reference Samples (SRSs) to use in Lab Pilot Test “cqeAquarium”

- 4.1. Select the laboratory\* to purchase SRSs [such Sigma Aldrich (USA/UK); Merckmillipore (USA/CANADÁ); Inorganic Ventures (USA/Spain)]
- 4.2. Establish analytical procedures - dilution / saturation
- 4.3. Develop attended (discrete measurements) and unattended tests (continuous, or time-series measurements)



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## APPENDICES - STUDY MARKET

- Bibliographic Maps
  - Technical and commercial solutions (Producers / laboratories and distributors)
    - Bench equipment
    - Portable equipment
    - Online Automated equipment
- Synthesis table