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# Environmental quality assessment and monitoring with wireless sensors network - Final Report

Raquel Alves

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## FINAL REPORT / RELATÓRIO FINAL DO PROJETO INTEGRADO / RAPPORT FINAL DU PROJET

Raquel Maria Cepeda Alves Silveira de Brito

20 october 2016

### 1. TITLE OF THE PROJECT | TITRE DU PROJET

#### Environmental quality assessment and monitoring with wireless sensors network

Avaliação e monitorização da qualidade ambiental com um sistema de rede de sensores sem fio

*Évaluation et monitoring de la qualité environnementale avec un système de réseau de capteurs sans fil*

### 2. REF | RÉFÉRENCE

Project Post-Doctoral ref. 296

### 3. FUNDING YEAR | ANNÉE DE FINANCEMENT

- 2015-2016
- 01 octobre 2015 (Project Start Date | Date de Commencement du Projet)

### 4. OHM-WSN PROJECT TEAM | ÉQUIPE IMPLIQUÉE DANS LE PROJET

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For those who have experience in hydrogeochemistry field work 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 well to assess a better environmental quality. Therefore, I must first acknowledge Dra. Carla Candeias and Dra. Paula Ávila, 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 1980s, was the starting point of this study.

My acknowledgment to Madame Anne-Marie Guihard-Costa, who 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.

I thank colleagues and friends who generously agreed to join the many discussions and disciplinary explanations, many times supported, corrected and made improvements to the work and the text production in both English and French: José Brito, Aurora Araujo, Carla Barbosa, Theresa e Christopher Zach, Bianca Rapple, Margaux Mauclair, Rui Miguel Ribeiro.

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

## Abstract

Initiated on October 2015, this project is part of an Environmental Monitoring research line in the University of Aveiro, 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 at supporting 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 the types of chemical sensors (commercially available or not).

The study-area where the equipment is to be installed is the Estarreja Chemical Complex, contiguous to the important Ria de Aveiro estuarine system. Both environments have been associated with industrial contamination, mostly by mercury, and also by 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.

**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.



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## 5. BACKGROUND AND OBJECTIVES | CONTEXTE ET OBJECTIFS

From the beginning of this post doc Project in October 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.

Thus, the environmental decision support must be based not only on theoretical approaches, (technical or academic sporadic studies, in a transversal analytical perspective), but also, in long-term management programmes (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 its 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 the 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 the related project in Guihard-Costa *et al.* (2012) and Inácio *et al.* (2011 a,b) or even this project. This Postdoc research (referred to as OHM Project throughout this text) combines hydrogeochemistry with mechanical engineering and has a close association with another OHM Project named “Wireless sensors network as a base solution for environmental water quality assessment and monitoring” (LabEx DRIIHM-280, coordinated by Carla Candeias and with Vitor Santos and Paula Ávila collaboration). This project financially supported the equipment selected as the best solution in this postdoc work year (both projects will be referred generally to as OHM-WSN Project throughout this text). The OHM-WSN Project also aims to replicate their technological developments to other OHM DRIIHM, having as a first approach to analyse some geological and mining maps specifically of Vicdessos (1/50 000), Marseille (1/250 000) and Toulouse - Pyrénées occidentales et contrales (1/500 000), purchased for this purpose, but this issue will not be subject to analysis in this Report.

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 locations for the monitoring station through a review of the study-area/region 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 electrochemical sensors, the main applications and the recent developments;
- iv) market study of WSN, environmental and electrochemical sensor technologies, identify 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.

## 5.1. Report organization | Organisation du Rapport

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

The second part briefly explains the methodological approach of this work (**METHODOLOGICAL ASPECTS**).

The third part is the main part of the Report, detailing the research conducted throughout the year. As there was no experimental work, the results of this research consist of the literature review on the study area, reference projects in the sensing area and technological aspects, and their interpretation in the scope of an environmental WSN monitoring system.

Therefore, the third part (**RESULTS AND INTERPRETATION**) of the Report is divided in: **ENVIRONMENTAL TECHNOLOGY** with some options of monitoring technology, regarding 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); **REMOTE ENVIRONMENTAL MONITORING** distance or remote long term monitoring, sampling and analytical methodology in the field, this part of the Report includes the state-of-the-art of WSN systems, with a discussion on autonomy and security for remote stations, the control of the devices, and the support structure or anchorage equipment; **ANALYTICAL SENSOR** are presented in this part, with distinctions between physic-chemical, chemical and electrochemical sensors, also it is done a brief overview of technological developments in chemical sensing, advances in research and application of specific innovative sensors called screen printed electrode (SPE).

The concluding remarks and considerations for the future are presented in the fourth part of the Report (**4- CONCLUSIONS AND FUTURE WORK**). In this part, the major contributions for the designing of the monitoring system based on WSN are highlighted, as well as, and future suggestions for a next desirable OHM – WSN project.

The **REFERENCES** are organised chronologically and by topic, following the Report structure. To the study area/region was referenced not only the cited studies but all it was analysed in this research year, as well as the technological literature. The participation in the international Labex DRIIHM Seminar is mentioned in **CONFERENCES, SCIENTIFIC DISSEMINATION**.

In the end of the Report, the **APPENDIX** includes: 1) bibliographic maps that complement the contents presented throughout the main parts of the Report (MAPs 1-52); 2) official cartography, land use plans and orthophotos of CQE/RIA (MAPs 53-56); 3) main remarks of the market study (TABLES 1-11). This last appendix, with several summary tables, details technical and commercial solutions (systems / manufactures and/or distributors) including: i) WSN equipment; ii) electrochemical sensing system; iv) online equipment; v) SPE technology (note: whenever it is indicated the nationality of the manufacturers it's used the ISO 3166-1 codes, with three letters). Also it is presented some datasheets of the selected and/or purchased equipment for this OHM one year project.

## 5.2. Study-area – brief characterization | Étude de zone - caractérisation brève

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, Appendix - MAP1; MAP2; MAP3).

RIA is characterized by a saline introgression with variations in the tidal submersion regime (Appendix – MAP4). 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 (Appendix – MAP5; MAP6) 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 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 the RIA water level (Rodrigues, 2012; Vargas, 2012, Appendix – MAP7) as well as the setting of the estuary basin depth (Vaz and Dias, 2011; Appendix – MAP8). 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. However, the hydrodynamic variables could represent the main environment influences in superficial waters (Appendix – MAP 9 to MAP 15), which factors must be considered for the monitoring station installation. On the other hand, geologic and hydrologic context (Appendix – MAP5; MAP16 to MAP19) may also cause interference with the equipment, mainly with the sensing module. Regarding the study-area natural context, the most significant references and related critical aspects for the present study, are summarised in the following Table 1.

**Table 1. Significant references and related critical aspects for the present study**

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 knowing about sediment-water's 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 anticipating requirements for the maintenance schedule of 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 programmes dedicated to CQE (Appendix – MAP20). 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) (Appendix – MAP21), Costa and Jesus-Ryding (2001) (Appendix – MAP22), 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 90's, the 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<sub>2</sub> (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, H, atmospheric effluents CO.

It must be also considered other unit called Prozinco, 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) (Appendix – MAP23, MAP24). 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 µS/cm EC (electric conductivity) range; < 30-167 µg Hg /L dissolved fraction; 32-3144 µg Hg /L particulate fraction (Appendix – MAP25, MAP26).

- 3) Hydrogeogchemical studies on the superficial aquifer report anomalies in the CQE surrounding areas: in the “Esteiro de Estarreja”  $\text{Cl}^-$ , Na, Mg,  $\text{SO}_4^{2-}$ , 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) reports 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  $>26000 \mu\text{S}/\text{cm}$ ; pH with either very low ( $<5$ ) or very high values ( $>10$ );  $<10\ 000 \text{ mg Cl}/\text{l}$ ;  $>100 \text{ mg NO}_3/\text{l}$ ;  $10\text{-}600 \text{ mg Na}/\text{l}$ ;  $>2\ 000 \text{ mg SO}_4^{2-}/\text{l}$ ;  $>45 \text{ mg NO}_3^-/\text{l}$ ;  $>34 \text{ mg Al}/\text{l}$ ;  $>165 \text{ mg Fe}/\text{l}$ ;  $<50 \text{ mg Zn}/\text{l}$ ;  $>9 \text{ mg As}/\text{l}$ ;  $>20 \text{ mg Cu}/\text{l}$  and  $>0,65 \text{ mg Hg}/\text{l}$ ; 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 (Appendix – MAP27). The “plume” has an EC  $>20 \text{ mS}/\text{m}$  (apparent electrical conductivity - electromagnetic campaign data) (regional background  $<5 \text{ mS}/\text{m}$  and contamination indicators between  $5\text{-}20 \text{ mS}/\text{m}$ ) - the “plume” generally follows the direction of groundwater flow, and the ditches contribute to the dispersion of contamination, especially “Vala do Canedo”. Mosa que horas devereitly of the hydrogeochemical studies consulted the main relevant effluents reservoirs was: “Vala da Breja” (NW of CQE  $\approx 1 \text{ km}$ ); “Vala de São Filipe” (SW of CQE  $\approx 0,5 \text{ km}$ ); “Vala do Canedo” (WSW of CQE  $\approx 1,5 \text{ km}$ , connecting with “Lagoa de Vieiros”, W of CQE  $\approx 2 \text{ km}$ ); “Esteiro de Estarreja” SSW of CQE  $\approx 2 \text{ km}$  connecting with “Largo do Laranjo” (SW of CQE  $\approx 2,5 \text{ km}$ ).
- 4) Two important CQE effluent receptors, contiguous to each other, are “Esteiro de Estarreja” ( $0,7 \text{ km}^2$ , 21% of the RIA) and “Largo do Laranjo” ( $1,7 \text{ km}^2$ , 61% of the RIA) (Appendix – MAP24, MAP25). 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:
- 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.
  - 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).
  - In water, Hg concentration (dissolved and particulate fraction) depends on the effluent discharge cycle, and shows no dependence on tidal cycles, nor on salinity. Higher values of Hg concentration occur in low tides (in the dissolved fraction  $<15\text{-}8\ 000 \text{ ng}/\text{l}$  and in the particulate fraction in suspension  $2\text{-}800 \mu\text{g}/\text{l}$ ). 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 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 (Appendix – MAP49, MAP50). 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 within 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 non-soluble. The selective extraction of Hg from the particulate fraction also shows an association between that Hg particulate fraction and Fe-Mn oxides. In the anoxide sediments the Hg predominant form 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 0.8. Ramalhosa *et al.* (2002) study the association OM-Hg in the water, and Henriques, *et al.* (2013) in the soil (Appendix – MAP28, MAP29).
- 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. Barradas (1993) reports Cu, Zn and Pb anomalies in the soil (Appendix – MAP31 to MAP33). Azevedo (1999) indicates different anomalies in the CQE soil and adjacent areas ( $As_{soil}$ , As, Zn, Pb, Cu, Mn, Ni, Cr, Co, Fe,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{3-}$ )(Appendix – MAP34 to MAP48). The characterization of plants from the CQE (adjacent agricultural land) showed that the Hg biomagnification occurs consistently (Appendix – MAP30, MAP49), 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 could be associated with the early diagenesis, where 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 reported in the soil and sediments in “Lagoa de Vieiros” (Cardoso da Fonseca *et al.*, 1995; Inácio *et al.*, 2007). Other heavy metals were also reported, such as Cu, Pb, Zn, Co, Ni, Cr, Cd, and also in different matrices [Barradas, 1993 (Appendix – MAP31 to MAP33), 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 2 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.

**Table 2. Different media/matrix identified in some of the reviewed scientific studies devoted to CQE/RIA**

HG ANALYSING MEDIA	REFERENCES
sediments	Hall <i>et al.</i> (1985); Lucas <i>et al.</i> (1986); Hall <i>et al.</i> (1988); Gomes and 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); 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 dust	Pio and Anacleto (1988); Reis <i>et al.</i> (2013); Patinha <i>et al.</i> (2014, 2015); Sousa (2015).
fish, bivalves and crabs	Lima (1985); Abreu <i>et al.</i> (2000); Perez <i>et al.</i> (2001); Mieirol <i>et al.</i> (2011) Vale <i>et al.</i> (1985); Coelho <i>et al.</i> (2006) 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)

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”), reported 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 programmes, in compliance with the national directives (transposed from the EU directives).

All these programmes (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.

### 5.3. National and international directives | Les directives nationales et internationales

The Decree-Law Nº.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.º. 58/2005, and recently updated by Decree-Law Nº. 218/2015. 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 programme selected parameters (pH, DO and EC) which have been measured with a multiparameter portable equipment, in 7 stations. These stations correspond to the network national programme - “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, nickel, 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 has a Global Mercury Assessment Programme (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). IUGS/IAGC Global Geochemical Baselines (FOREGS) are also a key initiative (Appendix – MAP51-52).

Following the WFD, standard criteria have been developed regarding environmental monitoring, and specifically for water quality, such as the “Common Implementation Strategy for the WFD Guidance” (EC 2000/60/EC, 2003), aimed to make a comparison of monitoring approaches for selected Priority Pollutants in surface water (Table 3). 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.

**Table 3. Environmental Quality Standards (WFD), adapted from Pujol *et al.* (2014).**

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

<sup>a</sup> Environmental Quality Standard—annual average; <sup>b</sup> Inside surface waters include rivers, lakes and also water masses (artificial or seriously modified) related to them; <sup>c</sup> Environmental Quality Standard—maximal permissible concentration; <sup>d</sup> For cadmium and its compounds, EQS—AA values are functions of water hardness according to the five classes as follows: class 1: <40 mg CaCO<sub>3</sub>/L; class 2: 40–50 mg CaCO<sub>3</sub>/L; class 3: 50–100 mg CaCO<sub>3</sub>/L; class 4: 100–200 mg CaCO<sub>3</sub>/L; class 5:  $\geq$  200 mg CaCO<sub>3</sub>/L; <sup>e</sup> Molar concentrations have been chosen as reference unit for the sake of comparison facility and regarding to the standards of the WFD

Considering these, it is recommended to setup water monitoring programmes 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 programme design (*e.g.* CCME 2007, 2006, 2009 and 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 reporting, such as in Wagner *et al.*, (2006), still sensors or bio sensors as in Farré *et al.* (2009).

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A specific EU directive recommends technical specifications for chemical analysis and monitoring of water, with QA/QC status (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 implementation progress of the Programmes of Measures in Portugal, during the first planning cycle of the WFD (EC, 2015) reports a low incidence of environmental monitoring programmes and doesn't refer any strategies for remediation of contaminated sites (historical pollution including sediments, groundwater and soil). This OHM Project contributes to define a monitoring system, as a priority EU issue, and responds also to the EU demands for environmental actions relating with continuous water monitoring.

## 6. METHODOLOGICAL ASPECTS | ASPECTS MÉTHODOLOGIQUES

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This research year can be seen as an exploratory phase in a technological development of an environmental WSN monitoring system. As many two-stage EU project applications (*e.g.* H2020 Grants with different schemes: two-stage; continuous and multi-step applications), this project was developed as a first-stage. It represents a first input of technical and scientific information and a market study, both to find technical and commercial solutions for the WSN system, and to recognise gaps in the market or even technological trends. Also, some equipment was purchased, following the WSN system design found in the literature review and according to the knowledge of the study area environmental parameters. Thus, the methodological approach of this post-doctoral research did not include experimental procedures, but encompassed:

- 1) literature review of the study area (firstly studying the CQE area with reviews of hydrogeochemical works related, directly or indirectly, with the environmental impact; secondly studying the associated area RIA with similar ecological, hydrological, hydrodynamic and geological attributes) – the scope of the study included works from the 80's up to the current research, some of them already funded by OHM;
- 2) state-of the-art of the environmental technology, compiling R&D recent or ongoing EU funding projects; remote environmental monitoring (namely WSN systems); extrapolation of a WSN system design to be implemented, in a future phase of the project – for this purpose, an overview was done about electrochemical sensing (and the different environmental systems and equipment used nowadays);
- 3) market study of the commercial solutions available, taking into consideration the advances in new technology and instrumentation, to support the selection of the WSN equipment including the processing module (a computer with the required software to supervise and control the system); the communication module (gateway device); the sensing module (analytical sensor to measure pre-selected critical or key parameters and acquisition /data logging device); as well as, the associated hardware needed, like cables, antennas, etc.

The selected equipment was purchased and will be installed and used only in a second phase of this project, to operate within the conceptual design proposed in this work, in pilot tests in the laboratory and on the field (with CQE similar environmental conditions). Only after these tests should be possible implement the WSN system in the CQE field.



## 7. RESULTS AND INTERPRETATION | RÉSULTATS ET INTERPRÉTATION

### 7.1. ENVIRONMENTAL TECHNOLOGY | TECHNOLOGIE DE L'ENVIRONNEMENT

Apart from the effort to regulate and standardize environment monitoring programmes, the EU has also funded research projects in the field. In the context of FP7-ENVIRONMENT Specific Programme "Cooperation": Environment (including Climate Change), funding programmes 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 [www.cordis.europa.eu/programme/rcn/855\\_en.html](http://www.cordis.europa.eu/programme/rcn/855_en.html))

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

**HydroNet project** (2008-2012) ([www.cordis.europa.eu/result/rcn/90299\\_en.html](http://www.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 sensor-equipped mini-robots, embedded in an Ambient Intelligence infrastructure (All). 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 All for interactive configuration, tasking and monitoring. Based on EU Directives, it measured Physical and Chemical Parameters: Temperature, Salinity, pH, Turbidity: Hg, Hg<sup>++</sup>, 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 All platform, which integrates not only sensors for water monitoring and robot tasks execution, but also communications backhaul systems, database technologies, knowledge discovery in databases processes for extracting and increasing knowledge on water management.

**SEA-on-a-CHIP** (2013-2017) ([www.senseocean.eu/](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 (IPMA). 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 electrochemical detection for real-time analysis of marine waters in multi-stressor conditions. This system will be developed

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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 on-month 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 lab studies, second under artificial ecosystems and finally during field experiments in aquaculture facilities.

**NeXOS** (2013-2017) ([www.nexosproject.eu](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) ([www.enviguard.net/](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) ([www.schema-ocean.eu](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 moor 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 are 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 pre-concentration 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)** ([www.commonsenseproject.eu/](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)** ([www.mariabox.net/](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)** ([www.braavoo.org](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)** ([www.project-sms.eu/](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

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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)** ([www.mnt-era.net/mnt-era-net-success-stories/NANOMET.pdf](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 German company BeanAir. This project is much related to this OHM Project (here reported), in comparison with previous projects, because was also a source of inspiration for the formulation of this one. NANOMET was a valuable indication in the selection of WSN equipment here reported.

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 were the 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. It is also 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 present 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 work in 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 designed to help industries and wastewater treatment plants to ensure their discharges meet current water standards. Some NANOMET results are reported in Cases-Utrera *et al.* (2014), concerning the analyser 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 prototype to operate autonomously and unattended, with wireless embedded sensing platforms (ESP) The system's 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 stripping analysis), electrode position potential, and electrodeposition time were optimized for the detection of Cu and Zn.

The R&D projects described above were selected because they have a study object similar to this OHM project, (*i.e.* probing/analysing superficial waters for environmental monitoring), the main coordinates of those projects are summarised in the following Table 4.

**Table 4. R & D projects of environmental sensing (examples of inter-governmental applications, funded by CORDIS)**

NAME	SUBJECT	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 Portuguese Partner: IPMA, IP
<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 <i>in situ</i> 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 <i>in situ</i> 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. (Spain company) Project Partner: BeanAir (GER/FRA)

### 7.1.2. Governmental run environmental sensing system

Some implemented projects/programmes 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, reported by Myers *et al.*, 2014). Those sites require long-term supervision of environmental parameters concerned to ensure the human health safety and the minimum environmental impact. Initially these monitoring programmes were expensive, labour-intensive, and provided 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

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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 protect the device.

Similar to the previous programme 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 programmes 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’s cell phones. However, the field equipment has been subjected to several vandalism actions (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 reported in Garel, *et al.* (2009).

An important international reference for environmental monitoring technology is the intergovernmental programme between Germany and The Netherlands, in Eijsden Station, called “*Aqualarm*” a warning system for land and sea, with continuous open data in: [www.aqualarm.nl/eijsden.html](http://www.aqualarm.nl/eijsden.html) about the water quality/parameters 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 (*i.e.* the responsible entity for the design, construction, management and maintenance of the main infrastructure facilities in The Netherlands). It complies, also with the European Water Framework Directive (WFD). The monitoring water analysing equipment is Online (process analytic) from *Metrohm Applikon*, NER (referred model in the Appendix – Table7). That equipment operates with voltammetry for measure 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 programmes described above could be seen as a state-of-the-art of applied/implemented systems for environmental technology. The next part of this Report will provide some background in remote monitoring, and recent approaches and trends mainly in practical subjects such as: the station site, the sampling requirements and the most common wireless sensor network systems, as it is considered to be the most relevant information for the Postdoc research.

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## 7.2. REMOTE ENVIRONMENTAL MONITORING | SURVEILLANCE DE L'ENVIRONNEMENT À DISTANCE

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.

For instance, Myers, *et al.*, (2014) describe *remote monitoring system* as a chain of complex technologies, which require a sensor and a 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.

Thus, slightly extending the concept of traditional or conventional approach to environmental monitoring, as described by Jiang *et al.* (2009), different methods for monitoring water environments can be defined as, in which this OHM Project could assume the second point:

- 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 environment parameters by a system consisting of monitors (or control centres) – could be an online system with high power consumption and a built infrastructure, or, with no external power required, an immersed probe (with or without external data logging) and antenna. 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) *Quality monitoring bio-technology* using aquatic organisms' sensitivity - in the presence of poisonous substances in water bodies, by measuring or analysing the change of activities of different organisms.

In fact, different monitoring approaches, techniques and equipment for sampling, analysing and signaling an environmental risk can be efficiently validated in the CQE context, because there are many field experiences/dataset of environmental characterization, stated by several academic researches, papers, technical reports (identified 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 surface water environmental monitoring requires periodic field sampling at fixed locations. Thus, the field samples are labelled, preserved and sent to laboratories to be analysed according to prescribed methods and protocols, usually with bench equipment.

On the other hand, remote environmental monitoring, and its onsite analysis, also addresses other issues associated with traditional sampling approaches. For example, Myers *et al.* (2014) refer 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” reports 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 water body.

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 programme with all this aspects in mind.

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 and even self-validate the environmental monitoring system.

### 7.2.1. Design of remote environmental monitoring programme

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 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.



The environmental monitoring programme 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 geochemical 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 (as theoretically defined by Alan *et al.*, 2006). The design here proposed includes the consideration of the operation mode, the critical and Key parameters selected, the station site selection, the sampling issues, the wireless sensor network (WSN).

### 7.2.1.1. 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 analysed 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 selected sensor setup, but also the environmental conditions must be considered, such as the tidal cycles (that in RIA repeat approximately every 6 hours). To infer an industrial (daily) discharge the environmental patterns must first be understood, as it was done in the first phase of this project.

### 7.2.1.2. Critical parameters and 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, that could be grouped into the following categories, suggested by Ho *et al.* (2005): 1) metals, 2) radioisotopes, 3) volatile organic compounds, and 4) biological contaminants. This work was focused on the metal contaminants, namely some heavy metals (assumed as the *critical parameter* for environmental monitoring), even though other contaminants were reported at the CQE (as seen above).

But, more specifically, the term "heavy metal" refers to what? In a recent study, related with long-life Heavy Metal Ions Sensor, 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 5 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 and environmental monitoring programmes design, including from countries that have a modest record of environmental concerns like China and India (Pandey *et al.*, 2016).

**Table 5. HM defined in the US EPA and India drinking water standards and Indian industrial effluents (in: Pandey *et al.*, 2016).** Symbology: \* Lower limits is the desirable value and upper limit is permissible only in the absence of alternate source. NR – no relaxation.

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

Considering the CQE/RIA study area/region, 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 programme design. These are the *critical parameters* with significance to the monitoring that could be divided in: the contamination direct parameters – Hg, As, Zn, Pb (other HM, related with the industrial impact could be also considered in CQE, attending some local anomalies, Appendix, Map 31-33 and Map 36-45); and the contamination indirect parameters – pH and EC. These physicochemical and also hydrodynamic parameters, such as the water level, could be seen as the *key parameters* in the environmental monitoring programme design here proposed. These will steer the market study towards sensing solutions to operate the pilot tests – in Lab conditions and after in RIA conditions (*ex-situ*) – a desirable next phase of this OHM project.

### 7.2.1.3. 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 module 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 main site selection factors of the continuous monitoring station are: i) site characteristics – CQE surrounding areas; ii) monitor installation setup – also called data monitor module, iii) maintenance requirements - depending on the complexity of the system and the equipment IP (waterproof index, up to IP56).

Site characteristics must consider: 1) water-quality measurements must to be representative of the location being monitored; 2) degree of cross-section variation and vertical stratification in the water body; 3) channel configuration; 4) range of stream stage (from low flow to flood) attending the water velocity; 5) presence of turbulence; 6) conditions that may enhance the rate of turbidity, such as excessive fine sediments, algae or invertebrates; 7) range of values for water-quality field critical parameters; 8) need for protection from high-water debris damage; 9) need for protection against vandalism.

In the monitor module installation (*i.e.* WSN devices including probes and antenna) it is important to attend: 1) local permits required before installation can begin (the most promising site is some municipality build or land, belonging to – “Junta de Freguesia” – of Vieiros or Beduido; 2) safety hazards relevant to monitor construction and installation. 3) consideration of specific installation difficulties related with private lands and land use constrictions (Appendix – MAP53, MAP54, MAP55); 4) costs of installation (no budget for infrastructure and construction).

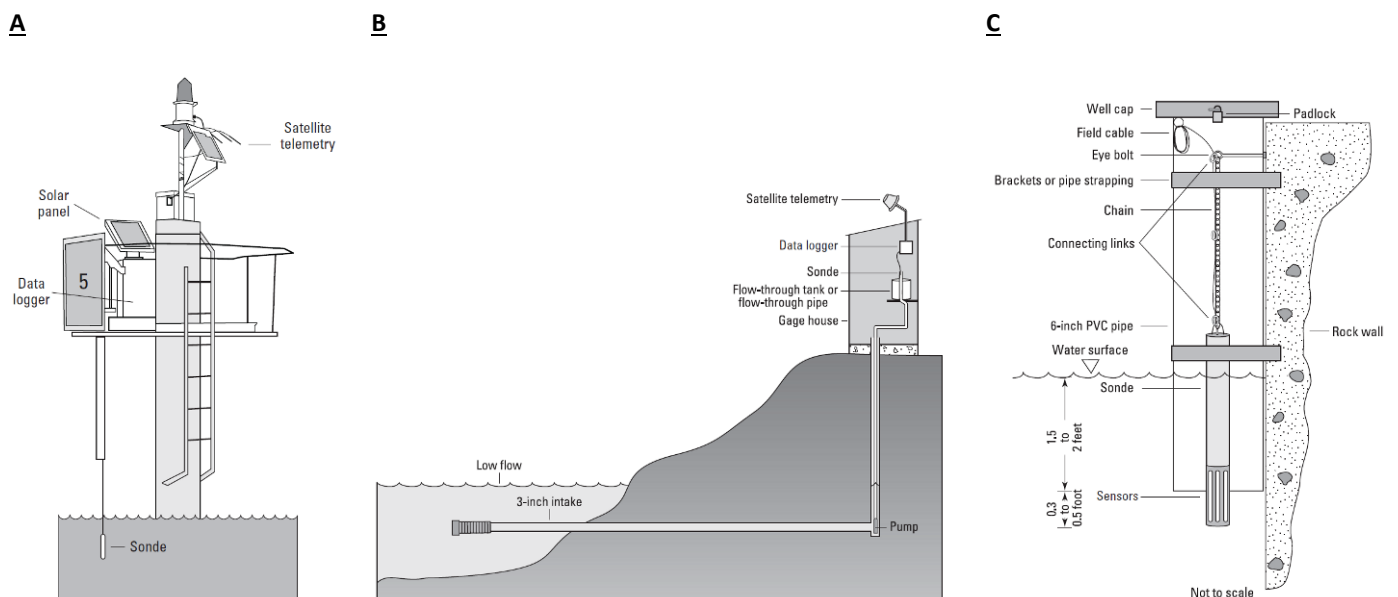
Different quality monitor station are described and illustrated by Wagner *et al.* (2006), shown in Figure 1. For this OHM monitoring station the type of the monitor module station must include internal-logging and recording system, combined data acquisition/logging + transductor not immersed and probe immersed (no external power), such as Figure 1A.

The maintenance of the monitoring station must be considered in the environmental programme design, which requirements include: 1) site accessibility and safety (even during extreme pluvious events); 2) safe and adequate space to perform maintenance; 3) conditions that increase the frequency of servicing intervals needed to meet data-quality objectives; 4) proximity to an adequate location for making cross-section measurement tests and validations; 5) availability of electrical power.

The best location for a monitoring site is often the one that is best suited for measuring surface-water industrial discharges, also considering hydraulic 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. Wagner *et al.* (2006) refer that 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. Site selection often is a choice of meeting as many of the applicable criteria as possible (*idem.*).

**Figure 1. Different quality monitor station (adapt. from Wagner *et al.*, 2006): 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 recommended location to install the monitoring station, suggested in this OHM project, must be associated with the walled watercourses margins in the main relevant effluents reservoirs, and their adjacent drainage courses: “Vala da Breja” (NW of CQE  $\approx$  1 km); “Vala de São Filipe” (SW of CQE  $\approx$  0,5 km); “Vala do Canedo” (WSW of CQE  $\approx$  1,5 km); “Lagoa de Vieiros”, (W of CQE  $\approx$  2Km); “Esteiro de Estarreja” (SSW of CQE  $\approx$  2Km). The site selection must considered walls or other fixed structures through his borders (as in Figure 1A).

#### 7.2.1.4. 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

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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 in a conventional or artificial type of environmental monitoring programme. 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 (or EC), pH, reduction-oxidation potential-electrode (REDOX), alkalinity and acid neutralizing capacity, turbidity with the use of multiparameter instruments for routine field measurement.

For operational monitoring, it is referred the passive sampling as an innovative monitoring tool, with advantages in this kind of operational environmental programmes (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 programmes. 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 (even disadvantageous) to monitoring, and the development of technological solutions for *in situ* analysis is being encouraged. Therefore, Pawliszyn (2006) defends onsite (or *in situ*) analysis, against any sampling, as a more efficient approach. Onsite analysis will reduce errors and avoids the possibility of sample change and the time delays associated with transport and storage. Thus, onsite analysis would be more accurate, more precise and the analytical result is quickly available. Myers *et al.*, (2014) report the application of automated sampling in a U.S. Remote Environmental Monitoring site, associated to real-time data for long-term monitoring with cost savings and compliance assurance.

Moreover, there are technological developments in automatic sampling, *e.g.* the project PISCIS (FEUP-DEEC, CORDIS, Lobo Pereira, 2014), the abbreviation means "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 archaeology and monitoring of effluents.

This OHM Project recognizes the importance and need for automated sampling, although it was not necessarily associated with *in situ* analysis. It could be considering an helpful approach by two reasons: 1) for the immediate water sampling during an industrial discharge (signalized by an abrupt change of the key parameters, relating with that contamination); 2) for the contaminated sample preservation and to be able for complete laboratory characterization, attending to the difficult determination of critical parameters (Hg, As, Zn, Pb, etc.) in the field. The automatic sampling would be triggered by the key parameter sensor, which data acquisition and processing would promote a mechanical action of floodgates for trapping the sample in a sealed recipient (develop box), and report the event wirelessly, using the WSN system. The automated system (with developed floodgates and open box, which could be called s-box) will collect the water extract if and when such a contamination is identified by the sensor (programed for key parameters critical level with specific alarms). The prototype must be developed attending not only the mechanical automatism, but also the box and floodgates materials and their interaction with the water and environmental characteristics and conditions.

#### 7.2.1.5. 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 its 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 of HM 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 (Martin and Islam, 2012). In particular,

power consumption is 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 depends on the application. 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 (such 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 can also be programed 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.*).

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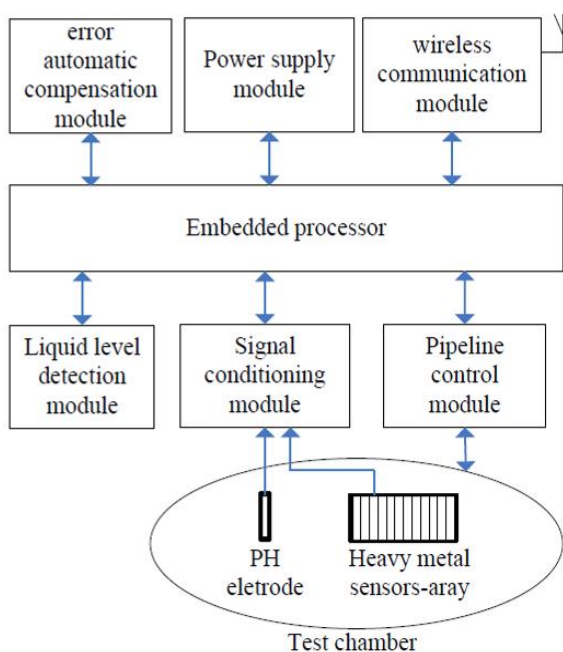
Recent developments in the area of micro-sensor devices have accelerated advances in the sensor networks field, leading to many new protocols specifically designed for WSN (Bhattacharyya *et al.*, 2010). These sensor nodes have some constraints due to their limited energy, storage capacity and computing power. Data is routed from one node to another 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.

Some examples of WSN applications, related to 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 exchanged from a station to the monitoring centre via TCP / IP protocol, but with WSN Platform in PLC input/output ports, the data can be communicated directly with the centre. The technical requirements included in the WSN node are directly connected to the analyser, through analyser'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 reported 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-adoption of wearable and mobile electrochemical sensors. The potentiostat is semi-autonomous and operates as a stand-alone chronoamperometric data logger, with data analysis performed externally on the Smartphone, tablet or computer.



- 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 HM 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 centre. The system detected the HM ion concentrations by ion-selective electrode array and came into the system error automatic compensation method (developed by the authors) in the detection process. The system hardware mainly includes the gateway and monitoring terminal. The monitoring terminal consisted of an embedded processor, test chamber, pH electrode, HM sensor array, liquid level detection module, signal processing module, pipeline control module, error compensation module, voltage management module and wireless communication module.



**Figure 2. Example of an hardware block diagram of monitoring terminal (Lin and Huang, 2014)**

HM Sensors-array and pH electrode were in a test chamber. Pipeline control module 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. HM sensors-array was composed of multiple ionic electrodes, which can perform simultaneous measurement of multiple HMs such as lead, cadmium, mercury, copper etc. The data of HM 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 and adjusts the pH value of testing samples by pipeline control module, so as to realize the accurate measurement of HMs ions.

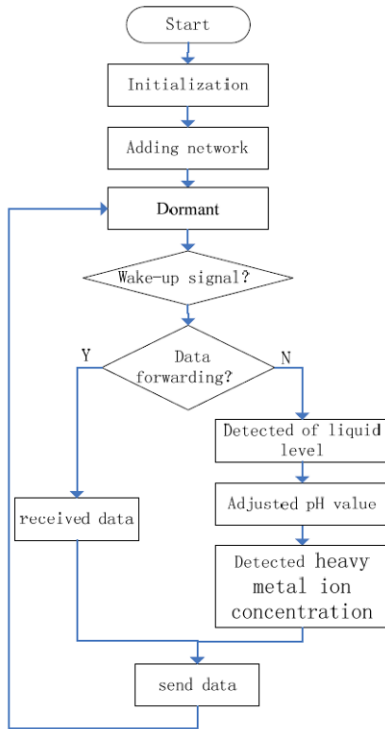


Figure 3. Example of a programme flow chart of monitoring terminal (Lin and Huang, 2014)

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, works 357days.

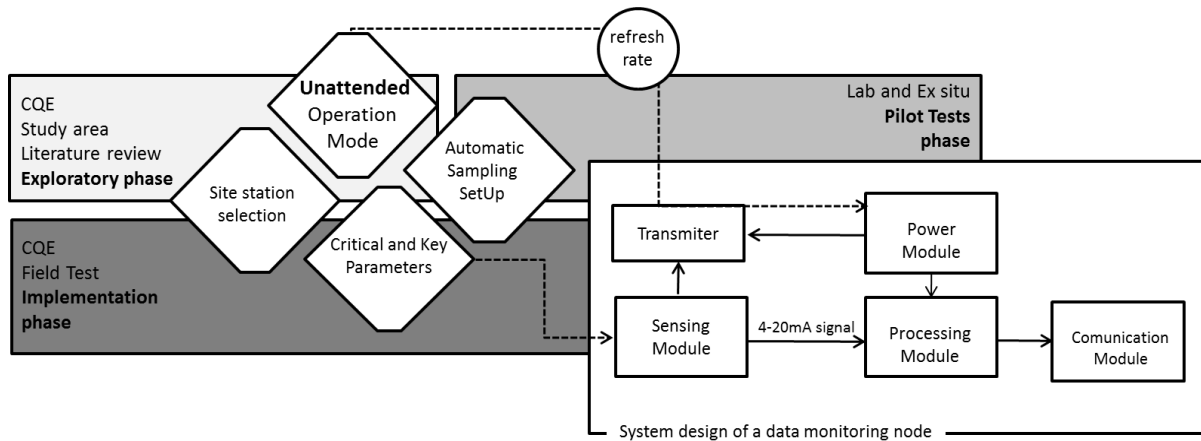
Table 6. Example of power consumption data in long time monitoring working status (Lin and Huang, 2014)

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
<b>Total</b>				<b>503550</b>

- Autonomous real-time water quality sensing as an alternative to conventional monitoring to improve the detection of ecosystem indicators are reported by Dong *et al.* (2015), which has the 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.
- 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<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup> (concentrations respectively 70 µg/L, 10 µg/L and 5 µg/L). The solutions of Zn<sup>2+</sup> and Pb<sup>2+</sup> were separately ranging from 10<sup>-7</sup> to 10<sup>-2</sup> 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.

### 7.2.2. Diagram of the WSN Environmental Monitoring Programme

The different components and background concepts described above contribute to the design of the remote environmental monitoring programme which this Report proposes (synthetized in the Figure 4).



**Figure 4.** Design diagram of this OHM WSN Environmental Monitoring Project, including three research phases: I) Exploratory phase with CQE study area and RIA region, environmental monitoring technology and sensing literature review and market study for unattended equipment; II) Pilot Tests phase with Laboratorial and *ex situ* field installations to improve the equipment and the WSN system; III) Implementation phase with equipment installation in CQE for *in situ* field test and on-site operation. For the phase II and III is proposed the design of the monitoring-system for water-quality data collection (monitoring node), adapted from Jiang *et al.*, 2009.

Considering a three-phase programme, the main factors analysed in this part of the Report are present below:

- The defined operation mode – unattended (as initially defined in the proposed research programme), 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 reanalysed 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 programme, 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 programme, mainly in the closely related project within the OHM WSN research, is another important challenge with a decisive impact on the programme 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.

### 7.3. ANALYTICAL SENSOR | CAPTEUR ANALITIQUE

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. Will be presented, as well as, 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, considering different complex environments and reactions. 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. An extensive research will be continued into miniaturized a sensor that offers promise for measuring any kind of contamination (Ho *et al.*, 2005).

A sensor is any kind of transducer (Figure 5) 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 a connection to an indicator (possibly by means of an A/D converter) (Bri *et al.*, 2008)

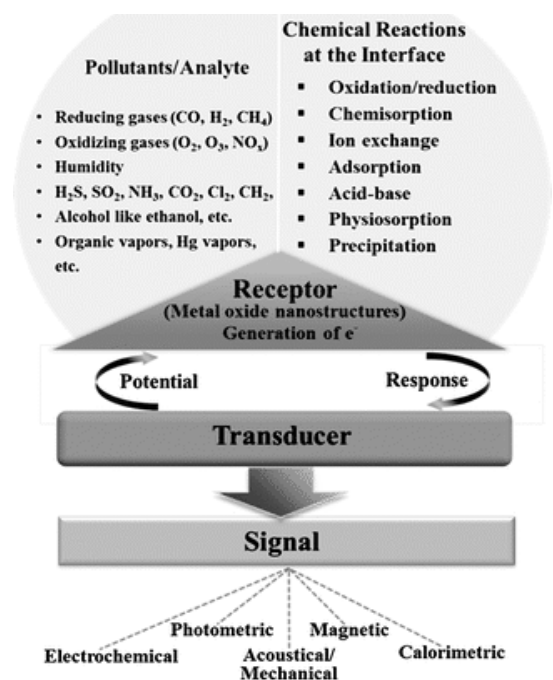


Figure 5. Analytical sensor (seen as a transducer) overview (Hahn *et al.*, 2012)

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 OHMIC resistance. The output needs to be operated, interfaced and regulated by the system designer (*idem.*). The transducer is considered as the heart of the sensor. It is a device that converts 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.

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 8 below.

**Table 7. Summary of potential sensor technologies that can address to the environmental monitoring needs, adapted 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, Pre-treatment	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, Pre-treatment	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 analyse more than three contaminants at once.
Chemiresistors	Drinking Water, Storm Water, Pre-treatment, Air	VOCs	Sensitivity is limited (hundreds of ppm). Needs pre-concentration. These can also be used to monitor <i>in situ</i> remediation activities (patent pending)
IMS (MicroHound/Ion Mobility Spectrometer)	Drinking Water, Storm Water, Pre-treatment, 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, <i>i.e.</i> PCBs). Can detect pesticides, organic nitrates.
MicroChemLab (gas)	Drinking Water, Storm Water, Pre-treatment, 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 analyser)	Drinking Water	Biological	Sampling is currently done manually.

### 7.3.1. 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 9). The technological review and the market study start by these considerations, attending the WSN system selection.

**Table 8. Relevant characteristics of sensors for the instrumentation system (Santos, 2016, written communication)**

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, it 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 WSN equipment, namely with the data acquisition system – the BeanAir solution (ref. BND-XTD-AN420-4CH, Appendix – TABLE 3, Datasheet 1-3), it would have to be compatible with the input channels of the BeanDevice,

4-20mA current output. If the sensor did not have these rating, a conversion stage would have to be added. Thus, to the selection of the sensing node of this OHM project, it must be considering the pH – key parameter. An adequate solution and choice could be the combination of transmitter + pH probe, such as the HANNA equipment (HI 98143 transmitter; pH HI-1006-2005; Appendix – TABLE 3, Datasheet 4) which must to be tested.

It should also be taken to analyse this selection that 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's design.

If the sensors had 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 had 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.

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

Electrochemical sensors are suitable for measurements at remote locations, 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 Table 10, below, presents different monitoring parameters and supporting sensors which could be found in the market, referring some models and those main features (supported range, measure accuracy and power supply). Leading sensor manufactures for different applications and parameters, and some examples of prototype for different sensor network areas and applications are listed in Appendix – TABLE 1 and TABLE 2.

**Table 9. Different Monitoring Parameters and Supporting Sensors for Marine Applications, in: Alwakeel (2015)**

MONITORING PARAMETER	SENSOR	SUPPORTED RANGE	ACCURACY	POWER SUPPLY	PRODUCT REFERENCE
Pressure (bar)	AST4000	up to 10,000 PSI	<±0.5% BFS	4-20 mA	<a href="http://www.astensors.com">www.astensors.com</a>
	DCT 533	0-400 bar	0.35 % FSO	N/A	<a href="http://www.bdsensors.de">www.bdsensors.de</a>
	SBE 50	20 to 7000 dbars	± 0.1%	8 - 30 VDC	<a href="http://www.seabird.com">www.seabird.com</a>
Temperature (°C)	109-L	-50° to +70°C	±0.2° Cover	2500 mA	<a href="http://www.campbellsci.com">www.campbellsci.com</a>
	MBT 5560	-50 °C - +200°C	N/A	4 - 20 mA	<a href="http://www.danfoss.com">www.danfoss.com</a>
	Si7050	-40 to +125 °C	± 1.0 °C	195 nA	<a href="http://www.silabs.com">www.silabs.com</a>
Conductivity/ Salinity (S/m)	SBE 4	0.0 to 7.0 S/m	± 0.0003 S/m	6 - 24 VDC	<a href="http://www.seabird.com">www.seabird.com</a>
	OBS-3A	0 to 65 mS/cm	1% of reading	2500 mA	<a href="http://www.campbellsci.com">www.campbellsci.com</a>
	SAL-BTA	0 to 50 ppt (salinity)	±3%	N/A	<a href="http://www.vernier.com">www.vernier.com</a>
Turbidity (NTU)	WQ730	0-50 NTU	+ 1%	10-36 VDC	<a href="http://www.globalw.com">www.globalw.com</a>
	OBS500	0 to 4000	±2%	9.6 to 18 Vdc	<a href="http://www.osil.co.uk">www.osil.co.uk</a>
	TurbiLux	0 to 1,00 NTU	<±2%	9 to 36 Vdc	<a href="http://www.chelsea.co.uk">www.chelsea.co.uk</a>
pH	SeaFET	6.5 - 9.0 pH	0.02 pH	6 - 18 VDC	<a href="http://www.satlantic.com">www.satlantic.com</a>
	WQ201	0-14 pH	2%	10-30 VDC	<a href="http://www.globalw.com">www.globalw.com</a>
	SBE 18	0 to 14 pH	± 0.1 pH	6 - 24 VDC	<a href="http://www.seabird.com">www.seabird.com</a>
Dissolved Oxygen(mg/L)	Hydrolab DO	0 to 50 mg/L	±0.2mg/l	N/A	<a href="http://www.osil.co.uk">www.osil.co.uk</a>
	SBE 63	120% of surface saturation	±3 µmol/kg	6 - 24 VDC	<a href="http://www.seabird.com">www.seabird.com</a>
Pollution/CO <sub>2</sub>	pCO <sub>2</sub> Sensors	1 – 25 % CO <sub>2</sub>	± 5 %	18 VDC	<a href="http://www.presens.de">www.presens.de</a>
	SAMI-CO <sub>2</sub>	150-700 µatm	± 3 µatm	N/A	<a href="http://www.sunburstensors.com">www.sunburstensors.com</a>
Oxidation (mV) Reduce Potential	CSIM11-ORP	700 to +1100 mV	±0.1%	3 VDC	<a href="http://www.campbellsci.com">www.campbellsci.com</a>
	ORP Sensor	-450 to + 1100 mV	N/A	7 mA (5VDC)	<a href="http://www.vernier.com">www.vernier.com</a>

The follow sensors descriptions (literature review) refer first 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 directly proportional to the pH. The calibration of measuring equipment must be considered and realized before the measurement campaign. The calibrating process consists of two or more repeated sequential immersions of the probe into calibrating solutions (buffers), with the aim of obtaining 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 calibration points are known, depending on the required accuracy or



on the expected shape of the pH-voltage relation, graphically illustrated by diagram. Mostly the dependency is considered roughly linear and then, it demands only two calibration points. After the calibration, a mathematical estimation of pH (by microcomputer) is applied at the temperature of the liquid tested. Consideration of temperature is a 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 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 analyser. The advantages of such a 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 when the pH probe needs calibration or maintenance. 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 (with or without and with a man attendant), and also for the calibration and the reference measurement.

**Water level sensors** were 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 analyse chemical signals 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 a few of the new techniques are suitable for analysis at (ultra)trace levels application (Omanović *et al*, 2015). The requested concentration ranges are extremely broad, no online chemical analyser can cope with it. The measured span usually covers 2-3 orders of magnitude, *e.g.* 0.1 to 100 ppb.

### 7.3.2.1. 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 an ISE: 1) an indicative electrode, 2) a reference electrode and 3) 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, soil, 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 transformed into the value of a measured parameter, 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 (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 is due to their high sensitivity, selectivity, low detection limit and good reproducible results.

### 7.3.2.2. Electrochemistry in a market study 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 (Manufactures and probes models) can be listed: OTT Hydromet, GER (Hydrolab HL4); Xylem analytics, USA (WTW IQ 2020XT and NET 182 XT); YSI, USA (YSI, ProDSS Multi-Parameter Water Quality Meter); Ponsel, FRA (ODEON X Handheld); Hach Lange, ITA (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 this Market Study are available in the Appendix TABLE 3, TABLE 4 ).

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 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) e.g. the Skyray Analyser (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 equipment associated 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).

Another type of electrochemical sensors is the online analysers (or process analysers), which employ voltammetric methods, and provide real-time data on the concentration of metal/s. Specifically for mercury analyses it could be referred manufactures such as Mercury Instruments (USA/UK); Arizona Instrument LLC (USA); Lumex Instruments (GER); P S Analytical (UK), with dedicated instrumentation (Appendix TABLE 5, TABLE 6). These sensors measure in continuous, with programmable refresh rate. Usually, online analysers needs high power supply, and have complex instrumentation, with analytical requirements as sample pre-treatment, pre-concentration or dilution, reagents and standard solutions for calibration, and also an hard maintenance, with automated cleaning sensors. However, this could be the best technical solution to measure metals *in situ*, both in a natural and in an industrial environment, but is very expensive (namely up to 20k eur for one parameter, as the Istran, SVK base solutions).

On the other hand, the online analysers always have custom lines, addressed to the custom measurement requirements; which can include all metals or physicochemical parameters. All commercial online equipment requires ongoing maintenance, and the development and installation costs are in the order of 100k eur. Some manufactures and equipment models are: Alliance Instruments, FRA (PROXIMA-SFA); Mercury Instruments, USA/UK (Mercury Process Analyser); SPECTRO, GER (SPECTROBLU); Arizona Instrument LLC, USA (Jerome® 451, Gold Film Fence-line Mercury Monitoring System); Lumex Instruments, GER (RA-915M Mercury Analyser); Istran, SLK (EcaMon SaFIA); PSAnalytical, UK (10.225 online systems); Trace20, UK (Metalysers On-line HM6000), Metrohm Applikon, NER (2035 Process Analysers); Applitek, BEL (EnviroLyzer® Series II e VPA® Voltammetric Process Analyser); Modern Water, UK (OVA7000 Dual Cell and OVA5000) (Appendix TABLE 5 to TABLE 8 ).

Considering the WSN/electrochemical sensing market study, and the budget of the OHM project, it was proposed the ISE probes (equipment for continuous measurements). The pH sensor combining probe + transmitter: (Hanna probe HI-1006-2005) and pH/EC Transmitter (Hanna HI98143-20) is designed for long distance measurements. It can be either panel or wall

mounted. It 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.

The WSN system selected, as said above, is a BeanAir solution including the instrumentation: 1) BeanDevice AN420 data acquisition and data logging platform, wireless transmission and linked to the sensor by a cable; 2) BeanGateway® Ethernet & GSM/GPRS (Data acquisition and storage device, wireless transmission IEEE 802.15.4 with antenna); 2) BeanScape® (WSN supervision and monitoring software), operating in a personal computer, specifically purchased for this purpose (HP EliteBook 840 G2 - Intel Core i7-5500U), with an extended battery (HP Inc. Battery 50Wh 3 CELLS 4.5AH) and an extra storage disc (Toshiba CANVIO CONNECT II 2.5" 1TB).

### 7.3.3. Advances in Research and Applications

The future perspective in the development of the HMs sensor is towards the manufacture of miniaturized devices employed 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 the platform apparently hindered their sensing applications.

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

Emerging sensors for various environmental monitoring applications are fabricated by technologies or processes that combine electrochemistry methodologies, such potentiometry and voltammetry, in a miniaturized support, with different electrode materials and assemblies, it can be distinguished as: i) Thin-film plated electrodes; ii) Micro and nano sized solid electrodes; iii) 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). However, the electrochemical sensing technology, including devices, remote, continuous and voltammetric analytical methods has decades of development from the earliest patented findings, as can be seen in the Table 10. There is presented some selected examples of the first technical approaches (US, EP, WO patents) to the analyzed solutions in this OHM Project; it is highly recommended consulting those open files (available in <https://patents.google.com/>) for the OHM WSN Project furtherance.

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 Directive 2008/105/EC).

**Table 10. Electrochemical Sensing Patents, attending devices, remote, continuous and voltammetric analytical methods.**

PATENT	PRIORITY YEAR	NAME OF THE INVENTION	INVENTOR(S)	ASSIGNEE(S)
US2913386 A	1959	Electrochemical Device for Chemical Analysis.	Leland C. Clark, Jr.	Yellow Springs, Ohio.
US4329649 A	1982	Ion Sensor Probe.	Kenneth D. Scoates	Gibbs & Hill, Inc.
US5489371 A	1991	Sensor for Electrochemical Measurements.	Jose P. Joseph, Arvind Jina, Michael J. Tierney	Teknekron Sensor Development Corporation, California
US5676820 A	1995	Remote Electrochemical Sensor.	Joseph Wang, Khris Olsen, David Larson	New Mexico State University Technology Transfer Corp.
US5643797 A	1997	Process of Continuously Controlling the pH of an Acid Liquid Including Measuring the pH Continuously with a Glass Electrode.	Hans J. Schmidt and Bertold Stegemann	
WO1997032203 A1	1997	Carbon screen printed electrodes and uses thereof.	John William Dilleen and Jonathan Mark Slater	EA Technology Limited
EP0969281 A2	1998	The use of screen printed electrodes in the electrochemical analysis of electroactive species.	Martin Jude Mary Hill, William Lane, Hazel Victoria Newton	University College Cork National University of Ireland, Cork
US 8177958 B2.	2004	Electro Chemical Sensor.	Nathan Lawrence, Andrew Meredith, Markus Pagels	Schlumberger Technology Corporation
WO 2009123645 A1	2009	Simultaneous electrochemical detection of multiple heavy metal ions in liquid.	Telis Dimitrakopoulos and Joseph Wang	Arizona Board of Regents, acting for and on behalf of Arizona State University, Millipore Corporation
US20110139636 A1	2011	Gold plated screen printed electrodes and their use as electrochemical sensors.	Rebecca Y. Lai and Weiwei Yang	
US 20100326845 A1	2010	Method and electrochemical sensing strip with screen for determining concentration of dissolved oxygen in a solution printed three electrodes.	Meng Shan Lin, Hoang Jyh Leu, Chien Hung Lai	Tamkang University
WO2012125016 A1	2012	Alloy electrode sensor for detecting heavy metal.	Rais Ahmad Mohd and Azera Tuhaime Nur	Mimos Berhad
US20150212059 A1	2015	Method and device for detection of heavy metals in water using dye nano complexants and a polymeric film.	Israel Schechter and Bella Dolgin	Technion Research & Development Foundation Ltd.

The research and technological progress, as referred by Omanović *et al.* (2015) was centred 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 to 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.

### 7.3.3.1. Screen-printed electrode (SPE)

As recognized in the market study (summarized in the Appendix, Table 9 to Table 11) the screen-printed electrodes (SPE) became very attractive for the broad range of applications including the sensing of trace metals, although its discovery already has nearly two decades (Patent WO1997032203 A1, in Table 10, above). Nowadays 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 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 HM 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 pre-concentrate trace HM ions on the electrode surface. Besides these, various materials including carbon, carbon nanotubes, graphite, metal nanoparticles, graphene oxide, and other organic ligands have also been 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 photoelectro 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) highlighted that disposable sensors are economical in nature and designed to be one-shot, so they do not experience so-called memory effects; some 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 technologies, such as screen-printing, toner transfer, and lithography.

Li *et al.* reviewed the recent developments and applications of 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, 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 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  $10 \mu\text{gL}^{-1}$  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.

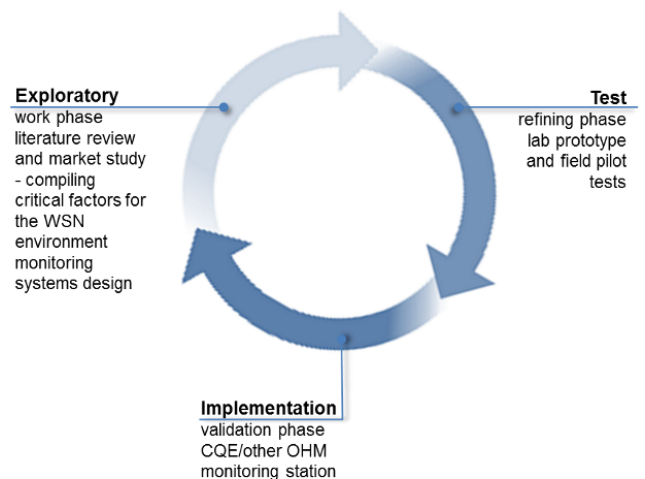
With carbon nanomaterials (with focus on graphene and carbon nanotubes) endowed with unique physiochemical properties Duarte *et al.* (2016) were found to be most suitable for electrochemical detection of HM in various sources of water, soil, and foods, due to their easiness to modify, high sensitivity, 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. 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 (*idem.*). These sensors 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 AAS, AFS, 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.



## 8. CONCLUSIONS AND FUTURE WORK | CONCLUSIONS ET TRAVAUX FUTURS

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.



**Figure 6. The three phases implicit in the OHM - WSN Project (overview). The present Report closes the first phase – Exploratory.**

### 8.1. 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 (as 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 affects 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 (OHM - WSN Project), 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.

In water monitoring technology, specially related to 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.

## 8.2. Considerations for Future Research

Once this exploratory study is concluded, a pilot study should be conducted to determine whether the monitoring programme 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 programme. 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).

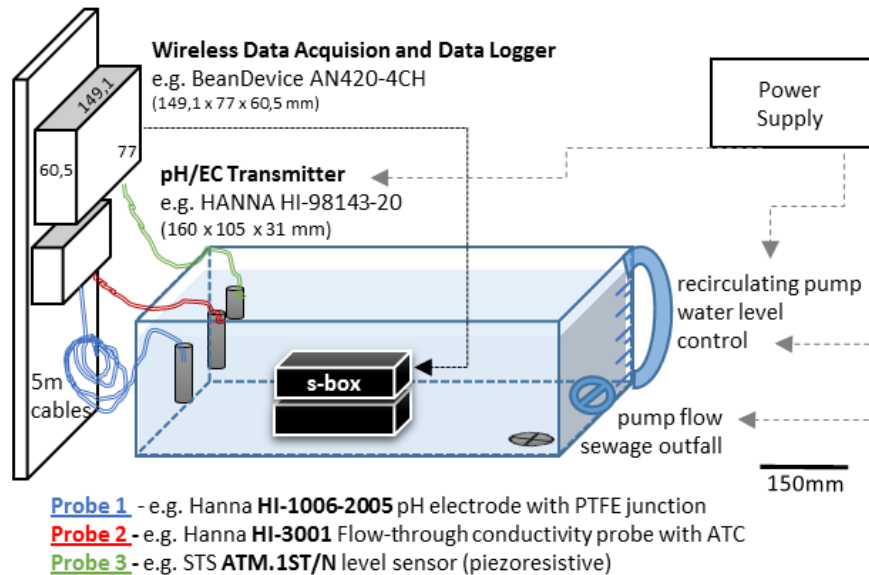


Figure 7. Propose Scheme for the second phase of the OHM-WSN Project –the Laboratory Pilot Test with possible instrumentation operate in the “cqeAquarium”

#### Lab Pilot Test “cqeAquarium”, to implement in the 4 phases:

##### 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/CAN); Inorganic Ventures (USA/ESP)];
- 4.2. Establish analytical procedures - dilution / saturation;
- 4.3. Develop attended (discrete measurements) and unattended tests (continuous, or time-series measurements).

## 9. REFERENCES | BIBLIOGRAPHIE

### STUDY REGION RIA

- Teixeira, C. and Torre de Assunção, C. (1963) - Notícia Explicativa da Folha 13-C, Ovar. *Serviços Geológicos de Portugal*. Lisboa.
- Teixeira, C. and Zbyszewski, G. (1976) - Notícia Explicativa da Folha 16-A, Aveiro. *Serviços Geológicos de Portugal*. Lisboa.
- Soares, A.; Barbosa, B.; Pena dos Reis, R. (1982) - Esboço de enquadramento cronostratigráfico das unidades líticas pós-Jurássicas da Orla Meso-Cenozóica Ocidental entre os paralelos de Pombal e Aveiro. *Memórias e Notícias, Publ. Mus. Lab. Min. Geol. Univ. Coimbra*, nº 93 - Coimbra.
- Saraiva, M. ; Barradas, J.; Marques Da Silva, M. (1984) - Aquífero cretácico de Aveiro: subsídios para a sua caracterização hidrogeológica. *III Simpósio de Hidrogeologia*, Madrid.
- Hall, A.; Lucas, M.; Caldeira, M.; Duarte, A. (1985) - Presença de mercúrio nos sedimentos da Ria de Aveiro, Portugal. *Jornadas da Ria de Aveiro*. Câmara Municipal de Aveiro, 1:103-125.
- Vale, C.; Barros, M.Cortesão, C.; Ferreira, A.; Castro, O. (1985) – Contribuição para a avaliação da poluição química na Ria de Aveiro através da análise de Bivalves filtradores. *Jornadas da Ria de Aveiro*. Câmara Municipal de Aveiro, 1:129-136.
- Lázaro, D. and Silva, J. (1985) – Poluição na Ria de Aveiro – Poluição dos seus afluentes. *Jornadas da Ria de Aveiro*. Câmara Municipal de Aveiro, 1:39-59.
- Ferreira, M.; Vale, C.; Castro, O.; Cortesão, C. (1985) – Metais pesados e organoclorados em caranguejos da Ria de Aveiro. *Jornadas da Ria de Aveiro*. Câmara Municipal de Aveiro, 1:147-153.
- Sampayo, M. (1985) – Microalgas para tratar efluentes que desaguam na Ria de Aveiro. *Jornadas da Ria de Aveiro*. Câmara Municipal de Aveiro, 1:165-174.
- Queirós, M. (1985) – Possibilidade de resolver a curto prazo os problemas da poluição fluvial originados pela fábrica da Portucel em Cácia. *Jornadas da Ria de Aveiro*. Câmara Municipal de Aveiro, 1:165-174.
- Marnoto, M.; Vinagreiro, J.; Lemos, J. (1985) – Redução da Poluição no centro fabril de Cácia, da Portucel. *Jornadas da Ria de Aveiro*. Câmara Municipal de Aveiro, 1:177-204.
- Sobral, F.; Carvalheira, A.; Santos, H. (1985) – Rio Vouga – Estabelecimento de um plano de qualidade da água. *Jornadas da Ria de Aveiro*. Câmara Municipal de Aveiro, 1:225-268.
- Lima, C. (1986) - Impacto da Poluição por Mercúrio nos Organismos Aquáticos da Ria de Aveiro. *Relatório INIP n.º 66*, Lisboa.
- Lucas, M.; Caldeira, T.; Hall, A.; Duarte, A.; Lima, A. (1986) - Distribution of Mercury in the Sediments and Fishes of the Lagoon of Aveiro, Portugal. *Water Science & Technology*. 18 (4-5): 141-148.
- Hall, A.; Duarte, A.; Caldeira, M.; Lucas, M. (1987) - Sources and sinks of mercury in the coastal lagoon of Aveiro, Portugal. *Science of the Total Environment*. 64, 1-2: 75-87.
- Hall, A.; Duarte, A.; Oliveira, S.; Lucas, M. (1988) - Particulate mercury in coastal area of Aveiro, Portugal. Heavy metals in the hydrological cycle. M. Astruc and J. Lester (Eds.) *Selper Ltd*. London, 507-512.
- Vinhas, T. and Valença, M. (1991) - Vigilância da qualidade da água na ria de Aveiro (1990). *Instituto Hidrográfico, Divisão de Química e Poluição*. Lisboa.
- Barradas, J.; Ferreira da Silva, E.; Cardoso da Fonseca, E. (1991) - Impacte Ambiental versus actividade industrial: poluição em metais pesados numa zona envolvente da Ria de Aveiro. [\*]
- Rocha, F. and Gomes, C. (1991) - Clay mineralogy used for the definition of paleosurfaces in the Tertiary and Quaternary of the Aveiro sedimentary basin. *Mémoires des Sciences de la Terre, Ecole des Mines de Paris*. 18: 31-38.

- Delgado, H., Rocha, F. and Gomes, C. (1992) - Evolution of the Aveiro Lagoon during the last 500 years based on clay mineralogy. *Min. Petr. Acta*, Vol. XXXV-A: 105-110.
- Rocha, F. and Gomes, C. (1992) - Fibrous clay minerals as morphoclimatic markers in the Aveiro sedimentary basin. *Min. Petr. Acta*, Vol. XXXV-A: 217-226.
- Ferreira da Silva, E. and Cardoso da Fonseca, E. (1993-94) - Comportamento do Zinco, Níquel e Cromio na espécie *zea mays* (vulgo milho) no perímetro industrial de Águeda [\*]
- Marques, L.; Cruz, M.; Moreira, M.; (1993) - Estudo de impacte ambiental. Desassoreamento da Ria de Aveiro, *Rel. JAPA*, Aveiro.
- Gomes, C. and Delgado, H. (1993) - Heavy metals in the sediments of the Aveiro lagoon (Portugal): sources and relationships with clay minerals. *Chem. Geol.* 107(3-4): 423-426
- Delgado, H.; Rocha, F.; Gomes, C. (1994) - New data on heavy metals in the sediments of the Aveiro Lagoon. *Proc. Littoral 94 (Eurocoast, Lisbon)*: 516–518.
- Ferreira da Silva, E. (1995) - Geoquímica de elementos maiores e vestigiais em sistemas perturbados [texto policopiado] : contribuição para caracterização ambiental do concelho de Águeda utilizando meios amostrais diferenciados. *Tese de Doutoramento*. Univ. Aveiro, 386 p.
- Ferreira, P. (1995) - Hidrogeologia do Quaternário da região norte da Ria de Aveiro. *Tese de Mestrado*. Univ. de Aveiro.
- Ferreira da Silva, E.; Reis, P.; Cardoso da Fonseca, E. (1995) - Identificação das fases suporte do Cu, Pb, Ni e Cr em amostras de solo colhidas no perímetro industrial de Águeda. [\*]
- Pereira M. (1996) - Distribuição, reactividade e transporte do Mercúrio na Ria de Aveiro, *Ph.D. Thesis*, Univ. Aveiro, 284p.
- Delgado, H.; Rocha, F.; Gomes, C. (1996) - Statistical data analysis relating heavy metal concentrations and distribution to recent sediment nature and composition in the Aveiro Lagoon (Portugal). *Proc. IVth Intern. Symp. on the Geochemistry of the Earth's Surface*, Int. Assoc. Geochem. Cosmochem. Univ. Leeds: 383-388.
- Pereira, M. and Duarte, A. (1997) - Contaminação da Ria de Aveiro com Mercúrio. *Indústria da Água*. 24: 47-57.
- Pereira, M.; Duarte, A.; Millward, G.; Abreu, S.; Vale, C. (1998a) - An estimation of industrial mercury stored in sediments of a confined area of the Lagoon of Aveiro (Portugal). *Water Science and Technology*. 37 (6–7): 125–130.
- Dias, J.; Lopes, J.; Dekeyser, I. (1998) - An exploratory study of the dynamics of Ria de Aveiro, Portugal, Kim H., Lee S.H., Lee S.J. (Eds.), *Hydrodynamics*: 619 – 624.
- Pereira, M.; Duarte, A.; Millward, G.; Vale, C.; Abreu, S. (1998b) - Tidal export of particulate mercury from the most contaminated area of Aveiro's Lagoon, Portugal. *Science of The Total Environment*. 213 (1–3): 157–163.
- Patinha, C.; Ferreira da Silva, E.; Cardoso da Fonseca, E. (1998) - Componente solúvel do solo versus componente dissolvida da água interrelação em áreas contaminadas. [\*]
- Dias J.; Lopes J.; Dekeyser I. (1999) - Hydrological characterization of Ria de Aveiro, Portugal, in Early Summer. *Oceanologica Acta*. 22: 473 – 485.
- Marques da Silva, M. (1990) - Hidrogeologia del sistema multiacuífero del Bajo Vouga - Aveiro (Portugal). *Tese de doutoramento*. Facultad de Geologia, Univ. Barcelona.
- Delgado, H.; Rocha, F.; Gomes, C. (2000) - Modelos de dispersão de metais pesados nos sedimentos recentes da laguna de Aveiro e sua relação com a composição e textura dos sedimentos. In: A. Duarte, C. Vale and R. Prego (eds.), *Estudos de Biogeoquímica na Zona Costeira Ibérica. Actas IX Sem. Ibérico Quím. Marinha* - Univ. Aveiro: 325–336.
- Rocha, F.; Bernardes, C.; Delgado, H. (2000) - Caracterização textural e mineralógica dos sedimentos da Laguna de Aveiro, Portugal. (Abstr.) *3º Simp. Margem Contin. Atlant. Ibérica*. Univ. Algarve: 17–18.
- Dias, J.; Lopes, J.; Dekeyser, I. (2000) - Tidal Propagation in Ria de Aveiro Lagoon, Portugal. *Phys. Chem. Earth (B)* 25, 369–374. DOI.org/PII:S1464-1909(00)00028-9.

- Abreu, S.; Pereira, E.; Vale, C.; Duarte, A. (2000) - Accumulation of mercury in sea bass from a contaminated lagoon (Ria de Aveiro, Portugal). *Mar. Pollut. Bull.* 40 (4): 293–297. DOI.org/10.1016/S0025-326X(99)00187-3).
- Lopes, J.; Dias, J.; Dekeyser, I. (2001) - Influence of tides and river inputs on suspended sediment transport in the Ria de Aveiro lagoon, Portugal. *Physics and Chemistry of the Earth, Part C: Solar, Terrestrial & Planetary Science*, 26( 9): 729-734.
- Dias, J. (2001) - Contribution to the Study of the Ria de Aveiro Hydrodynamics. *PhD Thesis*, Univ. Aveiro, 288pp.
- Perez Cid, B.; Boia, C.; Pombo, L.; Rebelo, E. (2001) - Determination of trace metals in fish species of the Ria de Aveiro (Portugal) by electrothermal atomic absorption spectrometry. *Food Chemistry*. 75: 93–100.
- Bastos, C; Ferreira da Silva, E.; Cardoso da Fonseca, E. (2001) - Biogeoquímica do tomateiro em amostras contaminadas por Ni – Agueda, Centro de Portugal. [\*]
- Condesso De Melo, M.; Carreira Paquete ,P.; Marques Da Silva, M. (2001) - Evolution of the Aveiro Cretaceous aquifer (NW Portugal) during the Late Pleistocene and present day: evidence from chemical and isotopic data. *Geological Society, London, Special Publications*. 189:139-154, DOI:10.1144/GSL.SP.2001.189.01.09.
- Batista, A.; Ferreira da Silva, E.; Azevedo, M.; Sousa, A.; Cardoso da Fonseca, E. (2002) - Soil data analysis from central Portugal by principal component analysis and geostatistical techniques. *Geochemistry: Exploration, Environment, Analysis*. 2: 15–25.
- Condesso de Melo, M. (2002) - Flow and hydrogeochemical mass transport model of the Aveiro Cretaceous multilayer aquifer (Portugal). *PhD Tesis*, Univ. Aveiro.
- Ramalhosa, Segade, Pereira, Vale, Duarte, A. (2002) - Effect of Organic Matter on Determination of Reactive Mercury in Contaminated Water. *Intern J Environ Anal Chem*. 83: 81-88.
- Abrantes, I.; Rocha, F.; Dias, J. (2003) - Distribuição e composição dos sedimentos em suspensão na Ria de Aveiro. *Thalassas*. 19(2 B): 27-28.
- Rocha R; Ferreira da Silva, EA; Bernardes, C; Vidinha, J; Patinha, C. (200?) - Trace Elements on sediments from Aveiro Lagoon channels (Portugal) [\*]
- Antunes, P. and Gil, O. (2004) - PCB and DDT contamination in cultivated and wild sea bass from Ria de Aveiro, Portugal. *Chemosphere*. 54: 1503–1507.
- Silva, J.; Duck, R.; Catarino, J. (2004) - Seagrasses and sediments response to changing physical forcing in a costal lagoon, *Hydrology and Earth System Sciences*. 8(2): 151-159.
- Abrantes, I.; Rocha, F.; Vidinha, J.; Dias, J. (2005) - Influence of Aveiro Lagoon heavy metal contents in the adjacent continental shelf (Portugal). *Ciencias Marinas*. 31(1B): 149–160.
- Rocha R; Ferreira da Silva, EA; Bernardes, C; Vidinha, J; Patinha, C. (2005) - Chemical and mineralogical characterisation of the sediments from the Mira, Ilhavo and Ovar Channels Of the Aveiro Lagoon (Portugal). [\*]
- Fangueiro, D.; Bermond, A.; Santos, E.; Carapuça, H.; Duarte, A. (2005) - Kinetic approach to heavy metal mobilization assessment in sediments: choose of kinetic equations and models to achieve maximum information. *Talanta*. 66: 844–857.
- Coelho, J.; Pereira, E.; Duarte, A.; Pardal, M. (2005) - Macroalgae response to a mercury contamination gradient in a temperate coastal lagoon (Ria de Aveiro, Portugal). *Estuarine, Coastal and Shelf Science*. 65: 492-500.
- Silva, J. and Oliveira, F. (2005) - The eutrophication in the river Vouga basin – impacts on the quality of water for public supply. *The Fourth Inter-Celtic Colloquium on Hydrology and Management of Water Resources*, Guimarães, Portugal, July 11-14.
- Coelho, J.; Rosa, M.; Pereira M.; Duarte, A.; Pardal, M. (2006a) - Pattern and annual rates of *Scrobicularia plana* mercury bioaccumulation in a human induced mercury gradient (Ria de Aveiro, Portugal). *Estuar. Coast. Shelf Sci.* 69: 629–635 DOI.org/10.1016/j.ecss.2006.05.027.
- Coelho, J.; Pimenta, J.; Gomes, R.; Barroso, C.; Pereira, M.; Pardal, M.; Duarte, A. (2006b) - Can *Nassarius reticulatus* be used as a bioindicator for Hg contamination? Results from a longitudinal study of the Portuguese coastline. *Marine Pollution Bulletin*. 52 : 674–680.

- Borrego, C (ed.); Coutinho, M.; Marques da Silva, Fidélis, T.; Figueiredo, J.; Leão, F.; Pinho, R.; Bento, S.; Mata, P. (2006) – Plano Municipal da Água – Diagnóstico – Relatório Final. Estudos Estratégicos e de Planeamento. *AMRia – Associação de Municípios da Ria*.
- Lopes, J. and Silva, C. (2006) - Temporal and spatial distribution of dissolved oxygen in the Ria de Aveiro lagoon. *Ecological Modelling*. 197 (1–2): 67–88.
- Lopes, J.; Dias, J.; Dekeyser, I. (2006) - Numerical modelling of cohesive sediments transport in the Ria de Aveiro lagoon, Portugal. *Journal of Hydrology*. 319: 176–198.
- Abrantes, I.; Dias, J.; Rocha, F. (2006) - Spatial and temporal variability of suspended sediments concentration in Ria de Aveiro and fluxes between the lagoon and the ocean. *Journal of Coastal Research*. 39: 718 e 723 (special issue).
- Pato, M. (2007) - Variability of mercury distribution and exchanges between the Ria de Aveiro and the Atlantic Ocean. *Tese de doutoramento*. Univ. Aveiro. 134p.
- Pereira, P.; Rodrigues, M.; Videira Castro, I.; Simões, F. (2007) - Identification of an arsenic resistance mechanism in rhizobial strains. *World Journal Microbiology and Biotechnology*. 23 (10): 1351-1356.
- Pereira, M.; Lillebø, A.; Pato, P.; Válega, M.; Coelho, J.; Lopes, C.; Rodrigues, S.; Cachada, A.; Otero, M.; Pardal, M.; Duarte AC. (2008) - Mercury pollution in Ria de Aveiro (Portugal): a review of the system assessment. *Environ Monit Assess*. 155(1-4):39-49.
- Lemos, C. (2008) - Base de Dados Geoambiental SIG para apoio à Gestão do Risco em Aveiro. Aveiro, Portugal. *Tese de Mestrado*, Univ. Aveiro 189p.
- Sousa, L. (2008) - Metodologias de Ordenamento do Espaço Marinho: Aplicação à Ria de Aveiro. Aveiro, Portugal. *Master's thesis*, Univ. Aveiro, 102p.
- Pereira, E.; Rodrigues, S.; Otero, M.; Válega M.; Lopes C.; Pato P.; Coelho J.; Lillebø A.; Pardal M.; Rocha R.; Duarte A. (2008) - Evaluation of an interlaboratory proficiency-testing exercise for total mercury in environmental samples of soils, sediments and fish tissue. *Trends In Analytical Chemistry*. 27(10): 959-970.
- Pato, P.; C. Lopes, M. Válega, A.I. Lillebø, J. Dias, E. Pereira, A.C. Duarte (2008) - Mercury fluxes between an impacted coastal lagoon and the Atlantic Ocean. *Estuarine, Coastal and Shelf Science*. 76 (4): 787-796.
- Lopes, J. F.; Silva, C. I.; Cardoso, A. C. (2008) - Validation of a water quality model for the Ria de Aveiro lagoon, Portugal. *Environmental Modelling & Software*. 23 (4): 479-494.
- Vidinha, J.; Rocha, F.; Ferreira da Silva, E.; Patinha, C.; Andrade, C. (2009) - Geochemical beach sediments studies - a contribution to a standard definition useful for public health. *Journal of Coastal Research*. SI 56 (Proceedings of the 10th International Coastal Symposium): 905 - 908.
- Condeso de Melo, M. and Marques da Silva, M. (2009) - The Aveiro Quaternary and Cretaceous Aquifers. *Portugal Natural Groundwater Quality*: 233-262.
- Lopes, C. (2009) - Impactos da subida do nível médio do mar na Ria de Aveiro no séc. XXI. Departamento de Física. *Dissertação de mestrado*. Univ. Aveiro: 55p.
- Rodrigues, S.; Glegg G.; Pereira, M.; Duarte, A. (2009) - Pollution problems in the northeast Atlantic: lessons learned for emerging pollutants such as the platinum group elements. *Ambio*. 38(1):17-23.
- Rodrigues, S.; Henriques, B.; Coimbra, J.; Ferreira da Silva, E.; Pereira, M.; Duarte, A. (2010) - Water-soluble fraction of mercury, arsenic and other potentially toxic elements in highly contaminated sediments and soils. *Chemosphere*. 78: 1 301-1 312.
- Carvalho, T. (2010) - Modelo de Governação para os Planos de Ordenamento dos Estuários. Aveiro, Portugal. *Master's thesis*. Univ Aveiro
- Picado, A.; Lopes, C.; Dias, J. (2011) - Alterações hidrodinâmicas na Ria de Aveiro – Cenários futuros. Almeida, A.; Alves, F.L.; Bernardes, C.; Dias, J.; Gomes (Eds.). *Centro de Estudos do Ambiente e do Mar*: 115-122.
- Queiroga, H.; Serôdio, J.; Vaz N. (Ed.), Atas das Jornadas da Ria de Aveiro 2011, Univ. Aveiro, *Centro de Estudos do Ambiente e do Mar*: 115-122.

- Almeida, A.; Alves, F.L.; Bernardes, C.; Dias, J.M.; Gomes, N.; Pereira, E.; Queiroga, H.; Serôdio, J.; Vaz, N. (Eds.), (2011) - Actas das Jornadas da Ria de Aveiro 2011. Univ. Aveiro. *Centro de Estudos do Ambiente e do Mar*. 373 pp.
- Anjum, N.; Ahmad, I.; Válega, M.; Pacheco, M.; Figueira, E.; Duarte, A.; Pereira, E. (2011) - Impact of seasonal fluctuations on the Sediment-Mercury, its accumulation and partitioning in *Halimione portulacoides* and *Juncus maritimus* collected from Ria de Aveiro Coastal Lagoon (Portugal). *Water, Air, & Soil Pollution*. 222 (1-4): 1-15.
- Mieiro, A.; Duarte, M.; Pereira, M.; Pacheco, M. (2011) - Mercury accumulation patterns and biochemical endpoints in wild fish (*Liza aurata*): A multi-organ approach. *Ecotoxicology and Environmental Safety*. 74 (8): 2225–2232.
- Rodrigues, M. (2012) - Effects of the climatic factors and anthropogenic actions in the Ria de Aveiro. *Tese de doutoramento*. Univ. Aveiro.
- Vargas, C. (2012) - Salinity patterns adjustment to climate change in Ria de Aveiro. *Dissertação de Mestrado*. Univ. Aveiro, 72p.
- M. Ramiro Pastorinho; Trevor C. Telfer; António J. A. Nogueira; Amadeu M. V. M.; James F. Ranville. 2012 - An evaluation of trace metal distribution, enrichment factors and risk in sediments of a coastal lagoon (Ria de Aveiro, Portugal). *Environmental Earth Sciences*. 67(7): 2043-2052.
- Ahmad, I.; Coelho, J.; Mohmooda, I.; Anjum, N.; Pacheco, M.; Santos, M.; Duarte, A.; Pereira, E. (2012) - Mercury contaminated systems under recovery can represent an increased risk to seafood human consumers – a paradox depicted in bivalves' body burdens. *Food Chem*. 133: 665–670. DOI.org/10.1016/j.foodchem.2012.01.047.
- Reis, A.; Coelho, J.; Rodrigues, S.; Rocha, R.; Davidson, C.; Duarte, A. (2012) - Development and validation of a simple thermo-desorption technique for mercury speciation in soils and sediments. *Talanta*. 99: 363–368.
- Martins, M.; Frontalini, F.; Tramonte, K.; Figueira, R.; Miranda, P.; Figueira, C.; Fernández-Fernández, S.; Dias, J.; Yamahita, C.; Reno, R.; Laut, L.; Sobrinho, F.; Rodrigues, M.; Bernardes, C.; Nagai, R.; Sousa, S.; Mahiques, M.; Rubio, B.; Bernabeu, A.; Rey, D.; Rocha, F. (2013) - Assessment of the health quality of Ria de Aveiro (Portugal): heavy metals and benthic foraminifera. *Marine Pollution Bulletin*. 70: 18-33.
- Coelho, J.; Mieiro, C.; Pereira, E.; Duarte, A.; Pardal, M. (2013) - Mercury biomagnification in a contaminated estuary food web: Effects of age and trophic position using stable isotope analyses. *Marine Pollution Bulletin*. 69: 110-115.
- Martins, V.; Dias, J.; Bernardes, C.; Rubio, B.; Bernabeu, A.; Rey, D.; Soares, A.; Sobrinho, F.; Laut L.; Frontalini, F.; Terroso, D.; Miranda, P.; Fernández, S.; Rodrigues, M.; Figueira, R.; Sousa, S.; Amaral, P.; Mahiques, M.; Rocha, F. (2013) - The ITRAX core scanner, an useful tool to distinguish anthropic vs. climatic influences in lagoon of Aveiro (N Portugal). *J Coastal Res*. 65: 70-75.
- Martins, V.; Dias J.A., Laut L.M., Sobrinho F., Santos J.F., Rodrigues M. A., Frontalini F., Miranda P., Terroso D., Fernández-Fernández S., Bernardes C., Figueira R., Sousa S., Amaral P., Mahiques M., Bernabeu A., Rey D., Rubio B., Rocha F. (2013) - Speciation of rare earth elements in surface sediments of Lagoon of Aveiro (N Portugal). *Journal of Coastal Research*. SI 65: 64-69.
- Henriques, B.; Rodrigues, S.; Coelho, C.; Cruz, N.; Duarte, A.; Römkens, P.; Pereira, E. (2013) - Risks associated with the transfer of toxic organo-metallic mercury from soils into the terrestrial feed chain. *Environ Int*. 59: 408–417.
- Rocha, L.; Lopes, C.; Borges, J.; Duarte, A.; Pereira, E. (2013) - Valuation of unmodified rice husk waste as an eco-friendly sorbent to remove mercury: a study using environmental realistic concentrations. *Water Air Soil Pollut*. 224(7): 1–18.
- Patinha, C., Reis, A.; Dias, A.; Abduljelil, A.; Noack, Y.; Robert, S. (2014) - The mobility and human oral bioaccessibility of Zn and Pb in urban dusts of Estarreja (N Portugal). *Environmental Geochemistry and Health*. 37, 115–131.
- Martins, M.; Mane, M.; Frontalini, F.; Santos, J.; Silva, F.; Terroso, D.; Miranda, P.; Figueira, R.; Laut, M.; Bernardes, C.; Mendonça Filho, J.; Coccioni, R.; Alveirinho Dias, J.; Rocha, F. (2015) - Early diagenesis and clay mineral adsorption as driving factors of metal pollution in sediments: the case of Aveiro Lagoon (Portugal). *Environmental Science and Pollution Research*. 22 (13): 10019-10033.
- Henriques, B.; Rocha, L.; Lopes, C.; Figueira, P.; Monteiro, R.; Duarte, A.; Pardal, M.; Pereira, E. (2015) - Study on bioaccumulation and biosorption of mercury by living marine macroalgae: prospecting for a new remediation biotechnology applied to saline waters. *Chem Eng J*. 281: 759–770.



- Reis, A.; Duarte, A.; Henriques, B.; Coelho, C.; Batista Lopes, C.; Miei-ro, C.; Tavares, D.; Ahmad, I.; Coelho, J.; Rocha, L.; Cruz, N.; Monteiro, R.; Rocha, R.; Rodrigues, S.; Pereira, E. (2015) - An international proficiency test as a tool to evaluate mercury determination in environmental matrices. *TrAC Trends in Analytical Chemistry*. 64: 136–148.
- Patinha, C.; Duraes, N.; Sousa, P.; Dias, A.; Reis, A.; Noack, Y.; Ferreira da Silva, E. (2015) - Assessment of the influence of traffic-related particles in urban dust using sequential selective extraction and oral bioaccessibility tests. *Environ Geochem Health*. 37: 707–724. DOI 10.1007/s10653-015-9713-0
- Sousa, P (2015) - Distribuição dos metais nas poeiras colhidas em Estarreja: estudo da mobilidade e impacto potencial dos metais no ambiente – *Dissertação de Mestrado*. Univ. Aveiro. 104p.
- Figueira, P.; Henriques, B.; Teixeira, A.; Lopes, C.; Reis, A.; Monteiro, R.; Duarte, A.; Pardal, M.; Pereira, E. (2016) Comparative study on metal biosorption by two macroalgae in saline waters: single and ternary systems. *Environmental Science And Pollution Research*. 23, 12, 11985-11997.
- Anjum, N.; Duarte, B.; Caçador, I.; Sleimi, N.; Duarte, A.; Pereira, E. (2016) - Biophysical and biochemical markers of metal/metalloid-impacts in salt marsh halophytes and their implications. *Frontiers In Environmental Science*. 4, 24.
- Rocha, L.; Almeida, A., Nunes, C.; Henriques, B.; Coimbra, M.; Lopes, C.; Silva, C.; Duarte, A.; Pereira, E. (2016) - Simple and effective chitosan based films for the removal of Hg from waters: Equilibrium, kinetic and ionic competition. *Chemical Engineering Journal*. 300, 217-229.

#### STUDY AREA CQE

- Pássaro, D. and Costa, A. 1985 - Poluição na zona de Estarreja - Convenção de Paris. *Jornadas da Ria de Aveiro*. Câmara Municipal de Aveiro. Vol. I – Poluição: 61-70.
- Barrosa, L. (1985) – Principais fontes poluentes da Ria de Aveiro com origem na zona de Estarreja. *Jornadas da Ria de Aveiro*. Câmara Municipal de Aveiro. Vol. I – Poluição: 73-86.
- Pio, C.A. e Anacleto, M.T. (1988). Deposição atmosférica na Zona Industrial de Estarreja. In: Borrego, C. (Ed.) - *1.ª Conferência Nacional Sobre a Qualidade do Ambiente*, Vol. 2, Univ. Aveiro: 574-587.
- Ferreira da Silva, E A. (1989) - Impacte ambiental de elementos maiores e vestigiais no aquífero superficial de Estarreja: caracterização da zona envolvente ao complexo químico. *Dissertação P.A.P.C.C.* Univ. Aveiro: 103p.
- Ferreira da Silva, EA; Barradas, J; Cardoso Fonseca, E. 1990 - Contribuição para a caracterização da componente polutiva no aquífero superficial de Estarreja. [\*]
- Barradas, J. (1992) - Geoquímica de elementos maiores e vestigiais em amostras de solos, sedimentos de valas e águas subterrâneas. Contribuição para a caracterização ambiental da zona envolvente ao Complexo Químico de Estarreja. *Tese de Doutoramento*. Univ. Aveiro.
- Barradas, J.; Cardoso Fonseca, E; Ferreira da Silva, E. (1992) - Identification and mapping of pollution indices using a multivariate statistical methodology, Estarreja - Central Portugal. [\*]
- Cardoso Fonseca, E.; Barradas, J.; Ferreira da Silva, E. (1992) - Partitioning of Fe Cu Zn Pb Co and Ni in groundwater sample Estarreja Central Portugal [\*]
- Inácio, M.M. 1993 – Mercúrio em solos da área do complexo químico de Estarreja. *Dissertação de Mestrado*, Aveiro, Univ. Aveiro, 139p.
- Pereira, M.E. e Duarte, A.C. (1994). Variabilidade das concentrações de mercúrio no Esteiro de Estarreja. Santana, F. *et al.* (Ed.) - *4.ª Conferência Nacional sobre a Qualidade do Ambiente*. Vol. 3, Lisboa, Univ. Nova de Lisboa: 239-243.
- Senos Matias, M.; Marques da Silva, M.; Carvalho, R.; Teles Roxo, G. (1994) - Estudo geofísico preliminar dos aquíferos quaternários a Oeste de Estarreja. *Actas da IV Conferência Nacional sobre a Qualidade do Ambiente*. Vol. I: 184-198.
- Cardoso Fonseca, E.; Barradas J.; Ferreira da Silva, E.; Reis, A (1995) - Distribuição do As em solos e sedimentos de vala no envolvente do Complexo Químico de Estarreja Implicações de ordem ambiental [\*]

- Tavares, C. (1995) - Contaminação por Hg do solo e plantas dos campos marginais do Esteiro de Estarreja. *Tese de Mestrado*, Univ. Aveiro, 132 pp
- Ferreira da Silva, E.; Patinha, C.; Cardoso da Fonseca, E. (1996) - Sorption/desorption of Zn, Ni and Cr in industrial polluted stream sediments - Central Portugal. Luis Enrique Lesmes Moscoso, Gloria Prieto Rincón y Carlos Julio Cedeño (Eds). *Simposio Internacional de Geoquímica Ambiental en Países Tropicales*.
- Abreu, S. (1996) - Modelação da dispersão do Mercúrio no Esteiro de Estarreja, *MSc. Thesis*, Univ. Aveiro, 90p.
- Inácio, M.; Pereira, V.; Pinto M. (1998) - Mercury contamination in sandy soils surrounding an industrial emission source. *Geoderma*. 85 (4): 325-339.
- Costa, C. and Jesus, C. (1999) - Case study of heavy-metals pollution in Estarreja (Portugal). *International Conference on Investigation Methods on Soil Contamination*, Lisbon, 10.
- Azevedo, M. (1999) - Contribuição para a caracterização ambiental da área envolvente do Complexo Químico de Estarreja. *Dissertação de mestrado*. Univ. Aveiro. 109p.
- Costa, C. and Jesus, C. (1999) - Case study of heavy-metals pollution in Estarreja (Portugal). *International Conference on Investigation Methods on Soil Contamination*, Lisbon, 10.
- ERASE (2000) - Estratégia de Redução dos Impactes Ambientais associados aos resíduos industriais depositados no Complexo químico de Estarreja. *Estudo de Impacte ambiental, Memória Geral*. Estarreja.
- Moreno, F.; Ferreira da Silva, E.; Cardoso Fonseca, E. (2000) - Cu, Pb, Zn, Co, Ni, Cr, Cd e As em sedimento de corrente da Bacia Hidrográfica do Rio Antuã – Portugal - um estudo usando a extracção química selectiva sequencial [\*]
- Costa, C. and Jesus-Rydin, C. (2001) - Site investigation on heavy metals contaminated groundwater in Estarreja-Portugal. *Engineering Geology*. 60:39–47.
- Moreno, F.; Ferreira Silva, E.; Cardoso da Fonseca E. (2001) - Aplicação de um índice de enriquecimento/contaminação na cartografia de elementos vestigiais em sedimentos de corrente da bacia hidrográfica do Rio Antuã – Portugal [\*]
- Inácio, M.; Pereira, V.; Pinto, M. (2001) - Metais Pesados, Arsénio e Selénio em solos e vegetação da zona industrial de Estarreja. *Revista de Ciências Agrárias*. 24 (3/4): 307-314.
- Branco, C. (2007) - Estudo de contaminação do aquífero superior na região de Estarreja. *Dissertação de Mestrado*. Univ. Coimbra. 191p.
- Cachada, A.; Rodrigues, S.; Pereira, E.; Ferreira da Silva, E.; Duarte, A. (2007) - The origin and distribution of potentially toxic metals in soils from the town of Estarreja, Portugal. *VI Congresso Ibérico de Geoquímica, XV Semana de Geoquímica*, Vila Real, Portugal: 301-304 (CD-Rom)
- Inácio, M.; Pereira, V.; Ferreira da Silva, E. (2007) - Evolução espaço/temporal dos níveis em metais pesados e As na zona envolvente do Complexo Químico de Estarreja (Portugal) – Um estudo Preliminar. *XI Congresso Brasileiro de Geoquímica*. Atibaia, Brasil. CDROM, 4 p.
- Inácio, M.; Pereira, V.; Ferreira da Silva, E. (2008) - Arsénio e mercúrio em solos e vegetação da envolvente da zona industrial de Estarreja. *XV Semana - VI Congresso Ibérico de Geoquímica*: 373-376.
- Cachada, A.; Rodrigues, S.; Mieiro, C.; Ferreira da Silva, E; Pereira, E.; Duarte, A. (2009) - Controlling factors and environmental implications of mercury contamination in urban and agricultural soils under a long-term influence of a chlor-alkali plant in the North–West Portugal. *Environ Geol*. 57:91-98.
- Reis, A., Rodrigues, S.; Araújo, C.; Coelho, J.; Pereira, E.; Duarte, A. (2009) - Mercury contamination in the vicinity of a chlor-alkali plant and potential risks to local population. *Sci Total Environ*. 407(8): 2689-700.
- Reis, A.; Rodrigues, S.; Davidson, C.; Pereira, E.; Duarte, A. (2010) - Extractability and mobility of mercury from agricultural soils surrounding industrial and mining contaminated areas. *Chemosphere*. 81: 1369–1377.
- Inácio, M.; Ferreira da Silva, E.; Pereira, V. (2010) - Heavy metals contamination in sandy soils, forage plants and groundwater surrounding an industrial emission source (Estarreja, Portugal). *Proceedings 15th International Conference on Heavy Metals in the Environment*, Gdansk, Poland: 856-859.

- Inácio, M.; Ferreira da Silva, E.; Pereira, V.; Guihard-Costa, AM.; Valente, S. (2011a) - Accumulation of potentially harmful elements in soils and forage plants in the Industrial area of Estarreja, Portugal. *Geophysical Research Abstracts*. 13: EGU2011-13568.
- Inácio, M., Ferreira da Silva, E., Pereira, V.; Guihard-Costa, AM.; Valente, S. (2011b) - Evaluation of urinary arsenic in children and their mothers living near an industrial complex (Estarreja, Portugal). *Fourth International Conference on Medical Geology*, Bari, Italy, 20-25 September.
- Rocha, L.; Rodrigues, S.; Lopes, I.; Soares, A.; Duarte, A.; Pereira, E. (2011) - The water-soluble fraction of potentially toxic elements in contaminated soils: relationships between ecotoxicity, solubility and geochemical reactivity. *Chemosphere*. 84(10): 1495-505.
- Guihard-Costa, AM.; Inácio, M.; Valente, S.; Ferreira da Silva, E. (2012) - Méthode d'étude spatialisée des effets de la contamination industrielle sur la santé des populations locales, région d'Estarreja (Portugal). *Sud-Ouest Européen*. 33: 69-76.
- Município de Estarreja (ME) (2012) - Avaliação Ambiental Estratégica da Proposta de Revisão do Plano Director Municipal de Estarreja – *Relatório Ambiental*. Estarreja: Município de Estarreja. 418p.
- Anjum, N.; Ahmad, I.; Rodrigues, S.; Henriques, B.; Cruz, N.; Coelho, C.; Pacheco, M.; Duarte, A.; Pereira, E. (2013) - Eriophorum angustifolium and Lolium perenne metabolic adaptations to metals- and metalloids-induced anomalies in the vicinity of a chemical industrial complex. *Environ Sci Pollut Res Int*. 20(1): 568-81.
- Inácio, M.; Neves, O.; Pereira, V.; Ferreira da Silva, E. (2013) - Concentração de As, Cu, Hg e Zn em solos e produtos agrícolas (Brassica oleraceaL., Lycopersicon esculentumMill e Zea maysL.) numa área industrial no NW de Portugal. *Revista de Ciências Agrárias*, 36(2): 229-237.
- Instituto Nacional de Estatística (INE) (2013) - Carta Administrativa Oficial de Portugal 2013 e Censos 2011, Ano de refª 2012.
- Rodrigues, S.; Coelho, C.; Cruz, N.; Monteiro, R.; Henriques, B.; Duarte, A.; Römkens, P.; Pereira, E. (2014) - Oral bioaccessibility and human exposure to anthropogenic and geogenic mercury in urban, industrial and mining areas. *Sci Total Environ*. 496: 649-61.
- Sousa, P. (2015) - Distribuição dos metais nas poeiras colhidas em Estarreja: contribuição para o estudo da mobilidade e potencial impacto dos metais no ambiente. *Dissertação de Mestrado*. Univ. Aveiro.

#### NACIONAL AND INTERNACIONAL DIRECTIVES

- US EPA-820-B-96-001 (1996) - Water Quality Criteria Documents for the Protection of Aquatic Life in Ambient Water. Washington, DC, USA.
- Decree-Law Nº. 236/98 of the Portuguese Ministry of the Environment of 1 August establishing water quality standards. *Diário da República*: I Série L176:3676–3722.
- EC (2000) - Directive 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL - Establishing a framework for Community action in the field of water policy (WFD). *Official Journal of the European Communities*. L327: pp. 1-72.
- US EPA-823-F-01-011 (2001) - Mercury Update: Impact on Fish Advisories. EPA, Washington. 10 pp.
- EC DECISION No 2455/2001/EC(2001) DECISION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL - Establishing the list of priority substances in the field of water policy. *Official Journal of the European Communities*. L331: pp. 1-5.
- UNEP (2002) - Global Mercury Assessment, United Nations Environment Programme, Chemicals, Geneva, Switzerland, (*available in*: <http://www.chem.unep.ch/MERCURY/>).
- EC 2000/60/EC (2003) - Common Implementation Strategy for the water framework directive Guidance Document No 7. Monitoring under the Water Framework Directive. Policy Summary to Guidance No. 7. With assistance of Produced by Working Group 2.7 - Monitoring. 160 pp.
- McNeill, L. (2004) - Field Measurement Methods for Arsenic in Drinking Water. *American Water Works Association (AWWA)*. 74 p.
- Law N.º. 58/2005 de 29 de Dezembro from the Directiva 2000/60/CE do Parlamento Europeu e do Conselho, de 23 de Outubro de 2000, called Diretiva Quadro da Água.
- EC (2005) - Community Strategy concerning Mercury, COM (2005) 20 final. Brussels, Belgium (*available in*: [http://eur-lex.europa.eu/LexUriServ/site/en/com/2005/com2005\\_0020en01.pdf](http://eur-lex.europa.eu/LexUriServ/site/en/com/2005/com2005_0020en01.pdf)).



- Environmental Protection Agency (EPA) (2006). Water Framework Directive Monitoring Programme. Prepared to meet the requirements of the EU Water Framework Directive (2000/60/EC) and National Regulations implementing the Water Framework Directive, Published by the *Environmental Protection Agency, Ireland*, Version 1.0.
- US EPA (2006) - National Recommended Water Quality Criteria, March 6 (*available in*: <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table>)
- Wagner, R.J.; Boulger, R.; Oblinger, C.; Smith, B. (2006) - Guidelines and standard procedures for continuous water-quality monitors— Station operation, record computation, and data reporting: *U.S. Geological Survey Techniques and Methods 1–D3*, 51 p. + 8 attachments.
- CCME (Canadian Council of Ministers of the Environment) (2006) - Canadian Water Quality Guidelines for the Protection of Aquatic Life. Update, July, 2005.
- CCME (2007) - A Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life. CCREM (Canadian Council of Resource and Environment Ministers). 1987. *Canadian water quality guidelines*. Prepared by the Task Force on Water Quality Guidelines.
- Moreira, L. and Cunha, I. (2007) - Guidelines for a Long-term Monitoring Programme (Task7.3.1). WP 7: Environmental Monitoring. CIIMAR-EROCIPS (Emergency Response to coastal Oil, Chemical and Inert Pollution from Shipping). Supported by the *European Union*, Project co-financed by the ERDF. 13p.
- EC (2009) - COMMISSION DIRECTIVE 2009/90/EC - Technical specifications for chemical analysis and monitoring of water status QA/QC. *Official Journal of the European Communities*. L201: pp. 36-38.
- EPA Victoria (2009) - Sampling and Analysis of Waters, Wastewaters, Soils and Wastes. The Regulations - Industrial Waste Resource Guidelines (IWRG). Publication IWRG701
- CCME (2009) - Evaluation of Potential Standardization Models for Canadian Water Quality Guidelines (WQG). Prepared by the Zajdlík & Associates Inc., G. Craig & Associates, I. Middelraad and D.G. Dixon. 64p.
- EC 2013/39/EU (2013) - Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. *Official Journal of the European Communities*. L226: pp. 1–17
- CCME (2014) - Guidance Manual for Optimizing Water Quality Monitoring Program Design. PN 1543 ISBN 978-1-77202-020-5 PDF.
- EC (2015) - Report on the implementation of the Water Framework Directive River Basin Management Plans - Member State: PORTUGAL. Communication from the European Commission to the European Parliament and the Council. *Commission Staff Working Document*. 103p.
- Decree-Law Nº. 218/2015 of the Portuguese Ministry of Environment and Spatial Planning of 10 July Establishing the environmental quality standards in the field of water policy. *Diário da República*: I Série L196/2015.

## R&D SENSORS PROJECTS

- Garel, E.; Nunes, S.; Magalhães Neto, J.; Fernandes, R.; Neves, R.; Marques, J.; Ferreira, O. (2009) - The autonomous SIMPATICO system for real-time continuous water-quality and current velocity monitoring: examples of application in three Portuguese estuaries. *Geo-Marine Letters*, 29 (5): pp 331-341.
- Lobo Pereira, F. (2004). PISCIS - Protótipo de um Sistema Integrado para a Amostragem Intensiva d Oceano Costeiro. Faculdade de Engenharia da U.P. - *Departamento de Engenharia Electrotécnica e de Computadores*.
- Community Research and Development Information Service (CORDIS) (2008-2018) - FP7-ENVIRONMENT Specific Programme "Cooperation": Environment (including Climate Change) - OCEAN 2013.1and 2: Biosensors for real time monitoring of biohazard and man-made chemical contaminants in the marine environment; Innovative multifunctional sensors for in-situ monitoring of marine environment and related maritime activities (projects links from : [http://cordis.europa.eu/programme/rcn/855\\_en.html](http://cordis.europa.eu/programme/rcn/855_en.html))HydroNet (2008-2012), i.e.: BRAAVOO (2013-2016); SEA-on-a-CHIP (2013-

2017); SenseOcean (2013-2017); NeXOS (2013-2017); SCHeMA (2013-2017); COMMON SENSE (2013-2017); MARIABOX(2014-2018); SMS (2013-2017); ENVIGUARD (2013-2017)

## ENVIRONMENTAL MONITORING SYSTEM

- Pérez-Bendito, D and Rubio, S. (1999) - Chapter 2 - Quality assurance in environmental analysis. *Comprehensive Analytical Chemistry*. 32: 35-57,
- Chevrel, S.; Kuosmanen, V.; Groesel, K.; Marsh, S.; Tukiainen, T.; Schaeffer, U.; Quental, L.; Vosen, P.; Loudjani, P.; Kuronen, E.; Aastrup, P. (2003) - Remote-sensing monitoring of environmental impacts. *Mining Environmental Management*. 11 (6): 19-23.
- Planer-Friedrich, B.; Becker, J.; Böhme, B.; Seidel, M.; Merkel, B. (2003) - Hydrogeochemistry and Remote Sensing Yellowstone National Park. *Preliminary scientific research status report for the field trips*. June, 5<sup>th</sup> to July, 16<sup>th</sup> and September, 2<sup>nd</sup> to October, 10<sup>th</sup>.
- Jiang, P.; Xia, H.; He, Z.; Wang, Z. (2009) - Design of a Water Environment Monitoring System Based on Wireless Sensor Networks. *Sensors* 9, 6411-6434; DOI:10.3390/s90806411
- ICES (2004) - ACME Report of the Working Group on the Statistical Aspects of Environmental Monitoring (WGSaEM). *International Council for the Exploration of the Sea (ICES)*, Copenhagen, Denmark: 1–56.
- Ho, C.; Robinson, A.; Miller, D.; Davis, M. (2005) - Overview of Sensors and Needs for Environmental Monitoring. *Sensors*. 5: 4-37.
- Pawliszyn, J. (2006) - Why move analysis from laboratory to on-site? (Editorial) *Trends in analytical Chemistry*. 25 (7):633-634.
- Allan, I.; Vrana, B.; Greenwood, R.; Mills, G.; Knutsson, J.; Holmberg, A.; Guigues, N.; Laschi, S.; Fouillac, A.; Laschi, S. (2006) - Strategic monitoring for the European Water Framework Directive. *Trends in Analytical Chemistry*. 25 (7): 704-716.
- Guilhermino, L.; Moreira, S.; Cunha, I. (2007). Guidelines for a Long-term Monitoring Programme (Task7.3.1). WP 7: Environmental Monitoring. EROCIIPS (Emergency Response to coastal Oil, Chemical and Inert Pollution from Shipping). Supported by the European Union, Project co-financed by the ERDF. 13p.
- Bri, D.; Coll, H.; Garcia, M.; Lloret, J. (2008) - A Multisensor Proposal for Wireless Sensor Networks. *The Second International Conference on Sensor Technologies and Applications*. IEEE Computer society: 270-276.
- Farré, M.; Kantiani, L.; Pérez, S.; Barceló, D. (2009) - Sensors and biosensors in support of EU Directives. *Trends in Analytical Chemistry*. 28 (2): 170-184.
- Katznelson, R. et al. (2010) - Quality Assurance (ACRR) Matrix. QA Checklist for Calibration, Quality Checks, and Record Keeping. to Ensure that Data Are of Known and Documented Quality. Methods and Data Comparability Board. *Aquatic Sensor Workgroup*. 22p
- Lin, K. and Huang, T. (2014) - Design of Heavy Metals monitoring System in Water Based on WSN and GPRS. *Sensors & Transducers*. 168, (4): 150-154
- Myers, J.; Hoffman, D.; Boerste, M. (2014) - Remote Environmental Monitoring: Applying Automated Sampling to Produce Real-Time Data for Long-Term Monitoring Cost Savings and Compliance Assurance. *Waste Management Symposia*. WM2014 Conference, 9p.
- USGS (2015) - National Field Manual for the Collection of Water-Quality Data. Techniques of Water-Resources Investigation. Handbooks for Water-Resources Investigations. *U.S. Geological Survey TWRI Book 9: Chapter A1*. Preparations for Water Sampling: 65p.
- Chaulya, S. and Prasad, G. (2016) - Sensing and Monitoring Technologies for Mines and Hazardous Areas: Monitoring and Prediction Technologies. *Elsevier*: 432 p.
- Loizou, K. and Koutroulis, E. (2016) - Water level sensing: State of the art review and performance evaluation of a low-cost measurement system. *Measurement*. DOI:org/10.1016/j.measurement.2016.04.019.
- Dong, Z.; Li, F.; Beheshti, B.; Mickelson, A.; Panero, M.; Anid, N. (2016) - Autonomous real-time water quality sensing as an alternative to conventional monitoring to improve the detection of food, energy, and water indicators. *J Environ Stud Sci*. DOI: 10.1007/s13412-016-0383-8.

Oikonomou, P.; Botsialas, A.; Olziersky, A.; Hadjigeorgiou, E.; Katsikas, S.; Dimas, D.; Sotiropoulos, G.; Raptis, I.; Sanopoulou, M. (2016) - A selfcalibrated Wireless Sensing System for monitoring the ambient industrial environment. From lab to real-time application. *Sensors and Actuators B: Chemical*. DOI: org/10.1016/j.snb.2016.06.118.

#### WSN – CONCEPT AND STRUTURE

Morais, R.; Valente, A.; Couto, C.; Correia, J. (2004) - A wireless RF CMOS mixed-signal interface for soil moisture measurements. *Sensors and Actuators, A* 115: 376–384.

Wang, S. (2007) - Theory and application of wireless sensor network. *Beihang Univ. Press*, Beijing.

Do, J. and Ahn, J. (2008) - A polymer lab-on-a-chip for magnetic immunoassay with on-chip sampling and detection capabilities. *The Royal Society of Chemistry. Lab Chip*. 8: 542–549.

Bhattacharyya, D.; Kim, T.; Pal, S. (2010) - A Comparative Study of Wireless Sensor Networks and Their Routing Protocols. *Sensors*. 10: 10506-10523. DOI:10.3390/s101210506

Farooq, M. and Kunz, T. (2011) - Operating Systems for Wireless Sensor Networks: A Survey. *Sensors*. 11: 5900-5930.

Cai, W.; Zhao, H.; Ha, D.; Guo, H.; Zhang, W.; Wang, P. (2011) - Design of wireless sensor node based on a novel hybrid chemical sensor for heavy metal monitoring. *Transducers'11*. 5-9: 2114-2118.

Matin, M. and Islam, M. (2012) - Overview of Wireless Sensor Network. *Wireless Sensor Networks – Technology and Protocols*: 3-24.

Wang, T. (2012) - Water Quality Monitoring System based on WSN. Master Thesis. *KTH Royal Institute of Technology*. Sweden: 59p.

Maceková, L. and Žiga, M. (2014) - The wireless sensor network concept for measurement of water quality in water streams. *Acta Electrotechnica et Informatica*. 14 (2): 60–67.

Lin, K. and Huang, T. (2014) - Design of Heavy Metals monitoring System in Water Based on WSN and GPRS. *Sensors & Transducers*. 168 (4): 150-154

Zhang, Y.; Yang, W.; Han, D.; Kim, Y. (2014) - An Integrated Environment Monitoring System for Underground Coal Mines—Wireless Sensor Network Subsystem with Multi-Parameter Monitoring. *Sensors*. 14: 13149-13170.

Alwakeel, M. (2015) - Sensors and Sensor Network Applications. *Journal of Theoretical and Applied Information Technology*. 82 (2): 321-334.

#### ANALYTICAL SENSORS

Hulanicki, A.; Glab, S.; Ingman, F. (1991) - Chemical sensors. Definitions and classification, *Pure Appl. Chem*. 63: 1247–1250.

Ervin, A.; Ewing, K.; Lamontagne, R.; Aggarwal, I.; Rowley, D. (1993) - Development of a fiber-optic sensor for trace metal detection in aqueous environments. *Applied Optics*. 32: 4287

Preininger, C. and Wolfbeis, O. (1996) - Disposable cuvette test with integrated sensor layer for enzymatic determination of heavy metals. *Biosensors Bioelectronics*. 11: 981.

Beinrohr, E.; Dzurov, J.; Annus, J.; Broekaert, C. (1998) - Flow-through stripping chronopotentiometry for the monitoring of mercury in waste waters. *Fresenius J Anal Chem*. 362: 201–204.

Vlasov, Y.; Legin, A.; Rudnitskaya, A. (1997) - Cross-sensitivity evaluation of chemical sensors for electronic determination of heavy metal ions. *Sens. Actuators*. B44: 532.

Achterberg, E. and Bnmugardt, C. (1999) - Stripping voltammetry for the detennination of trace metal speciation and in-situ measurments of trace metal distributions in marine waters. *Analytica Chimica Acta*. 400: 381-397.

Prestel, H.; Gahr, A.; Niessner, R. (2000) - Detection of heavy metals in water by fluorescence spectroscopy: On the way to a suitable sensor system, *Fresenius J. Anal. Chem*. 368: 182.

- Metters, J.; Kadara, R.; Banks, C. (2011) - New directions in screen printed electroanalytical sensors: an overview of recent developments. *Analyst*. 136: 1067–1076.
- Li, M.; Li, Y.; Li, D.; Long, Y. (2012) – Recent developments and applications of screen printed electrodes in environmental assays – A review. *Analytica Chimica Acta*. 734: 31–44.
- Hahn, Y.; Ahmada, R.; Tripathya, N. (2012) - Chemical and biological sensors based on metal oxide nanostructures. *Chem. Commun.* 48: 10369-10385. DOI:10.1039/C2CC34706G
- Hayat, A. and Marty, J. (2014) - Disposable Screen Printed Electrochemical Sensors: Tools for Environmental Monitoring. *Sensors* 14: 10432-10453. DOI:10.3390/s140610432
- Pujol, L.; Evrard, D.; Groenen-Serrano, K.; Freyssinier, M.; Ruffien-Cizsa, R.; Gros, P. (2014) - Electrochemical sensors and devices for heavy metals assay in water: the French groups' contribution. *Frontiers in Chemistry*. 2 (19): 1-24. DOI: 10.3389/fchem.2014.00019
- Cases-Utrera, J.; Escudé-Pujol, R.; Ibáñez-Otazua, N.; del Campo, J. (2015) - Development of an Automated Heavy Metal Analyser. *Electroanalysis*. 27: 929– 937.
- Duarte, K.; Celine I.; Justino, A.; Freitas, A.; Gomes, A.; Duarte, A.; Rocha-Santos, T. (2015) - Disposable sensors for environmental monitoring of lead, cadmium and mercury. *Trends in Analytical Chemistry*. 64: 183–190
- Lawal, A. (2015) - Synthesis and utilisation of grapheme for fabrication of electrochemical sensors. *Talanta*. 131: 424–443
- Steinberg, M.; Kassal, P.; Kereković, I.; Steinberg, I. (2015) – A wireless potentiostat for mobile chemical sensing and biosensing. *Talanta*. 143: 178–183.
- Omanović, D.; Garnier, C.; Gibbon–Walsh, K.; Pižeta, I. (2015) - Electroanalysis in environmental monitoring: Tracking trace metals—A mini review. *Electrochemistry Communications*. 61: 78-83.
- Parat, C. and Pinheiro, P. (2015) - ISIDORE, a probe for *in situ* trace metal speciation based on DODonnan membrane technique with related electrochemical detection part 1: equilibrium measurements, *Anal. Chim. Acta*. 896: 1–10.
- Cinti, S. and Arduini, F. (2016) - Graphene-based screen-printed electrochemical (bio)sensors and their applications: efforts and criticisms. *Biosensors and Bioelectronics*. *Bioelectronic*. DOI:org/10.1016/j.bios.2016.07.005
- Park, M.; Noh, H.; Park, D.; Yoon, J.; Shim, Y. (2016) - Long-life Heavy Metal Ions Sensor Based on Graphene Oxide-anchored Conducting Polymer. *Electroanalysis*. DOI:10.1002/elan.201600494.
- Pandey, S.; Singh, P.; Singh, J.; Sachan, S.; Srivastava, S.; Singh, S. (2016) - Nanocarbon-based electrochemical Detection of Heavy Metals. *Electroanalysis*. DOI:10.1002/elan.201600173.
- Velmurugan, M.; Thirumalraj, B.; Chen, S. (2016) - Development of electrochemical sensor for the determination of palladium ions (Pd<sup>2+</sup>) using flexible screen printed un-modified carbon electrode. *J Colloid Interface Sci* 2017 Jan 29: 485:123-128. epub 2016 Dec 29. DOI:org/10.1016/j.jcis.2016.08.073.
- Shuai, H. and Lei, Y. (2016) - Graphene Ink Fabricated Screen Printed Electrode for Cd<sup>2+</sup> and Pd<sup>2+</sup> Determination in Xiangjiang River. *Int. J. Electrochem. Sci.* 11: 7430 – 7439, DOI: 10.20964/2016.09.38.
- Bartona, J.; González García, M.; Hernández Santos, D.; Fanjul-Boladob, P.; Ribottic, A.; McCauld, M.; Diamond, D.; Magnic, P. (2016) - Screen-printed electrodes for environmental monitoring of heavy metal ions: a review. *Microchimica Acta*. DOI: 10.1007/s00604-015-1651-0.

## 10. CONFERENCES, SCIENTIFIC DISSEMINATION | COLLOQUES, DIFFUSION SCIENTIFIQUE

- Alves, R. (2016) - Évaluation et surveillance de la qualité de l'environnement avec le réseau de capteurs sans fil - analyse longitudinale. 4<sup>ème</sup> Séminaire annuel du Labex DRIIHM. 23, 24 et 25 mai 2016, Toulouse.

## 11. APPENDIX

In this last part of the Report will be present:

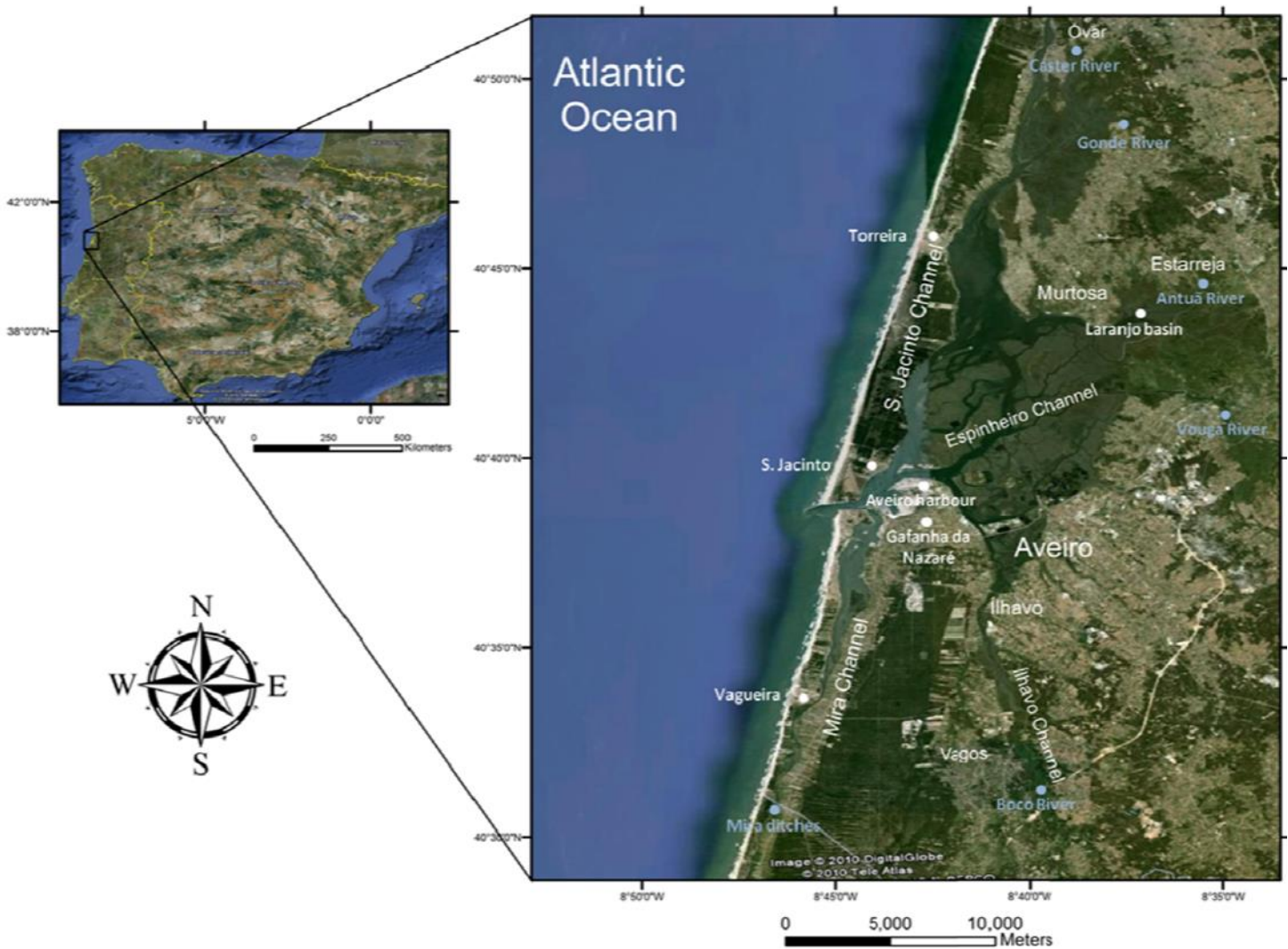
- Bibliographic maps (MAP 1 to MAP 52) to complement the contents presented throughout the Report  
(**note:** some maps show a format deformation, which it is due to an bad reproduction from the original document, *i.e.* photocopy and photography, those productions should be repeated with appropriate means, as scanner);
- Official cartography, land use plans and orthophotos of COE/RIA (MAP 53 to MAP 56) to locate the main study areas and their territorial constraints;
- Market study synthesized in several summary tables:
  - literature references (TABLE 1 and TABLE 2);
  - technical details and commercial solutions (systems / manufactures and/or distributors) about:
    - WSN equipment (TABLE 3);
    - Electrochemical sensing system (TABLE 3-11) with different techniques:
      - Portable probes and multiprobes (TABLE 3-4);
      - Online equipment – panel or portable (TABLE 5-8);
    - SPE technology (TABLE 9-11);

(**note:** whenever it is indicated the nationality of the manufacturers it's used the ISO 3166-1 codes, with 3 letters)
- Datasheets (and equivalent technical notes) of the selected and/or purchased equipment for the OHM-WSN Project;
- Quotations examples required in this year of Postdoc research, that support the market study references of some equipment costs.



## 11. APPENDICES

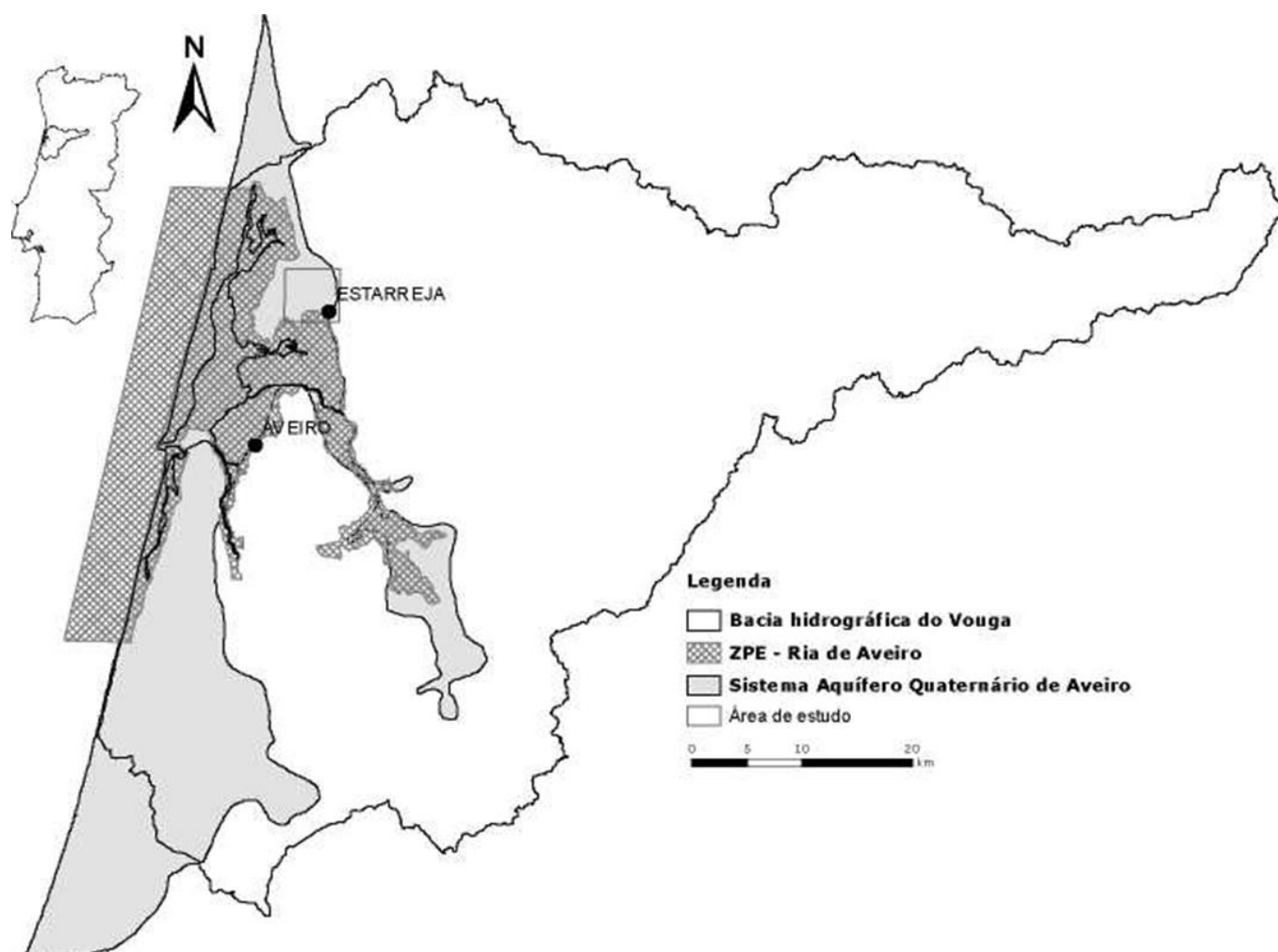
### Bibliographic Maps



**Map 1** – Imagem satélite da RIA com a localização das principais zonas abordadas na bibliografia, incluindo Estarreja. 40°44'29,36"N, 8°33'37,83"W, Goolge Earth™ 7.0.3.8542. *In*: Vargas (2012)

## 11. APPENDICES

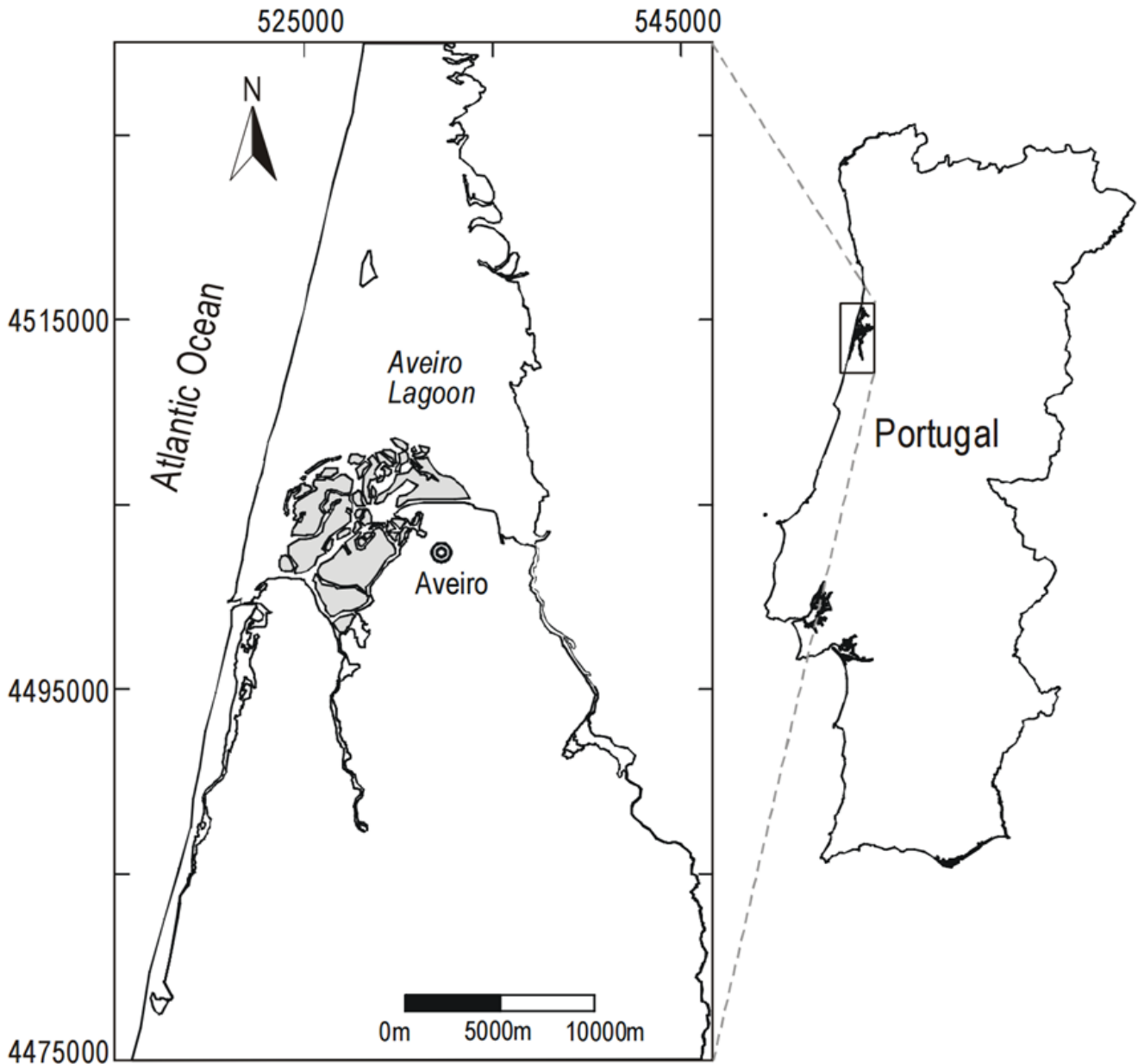
### Bibliographic Maps



**Map 2** – Localização e limites da Bacia hidrográfica do Vouga, incluindo BVL e RIA, a área com estatuto nacional de conservação - Zona de Protecção Especial (ZPE), os limites do Sistema Aquífero Quaternário de Aveiro e da área de estudo Estarreja, onde sita o CQE. *In*: Branco (2007)

## 11. APPENDICES

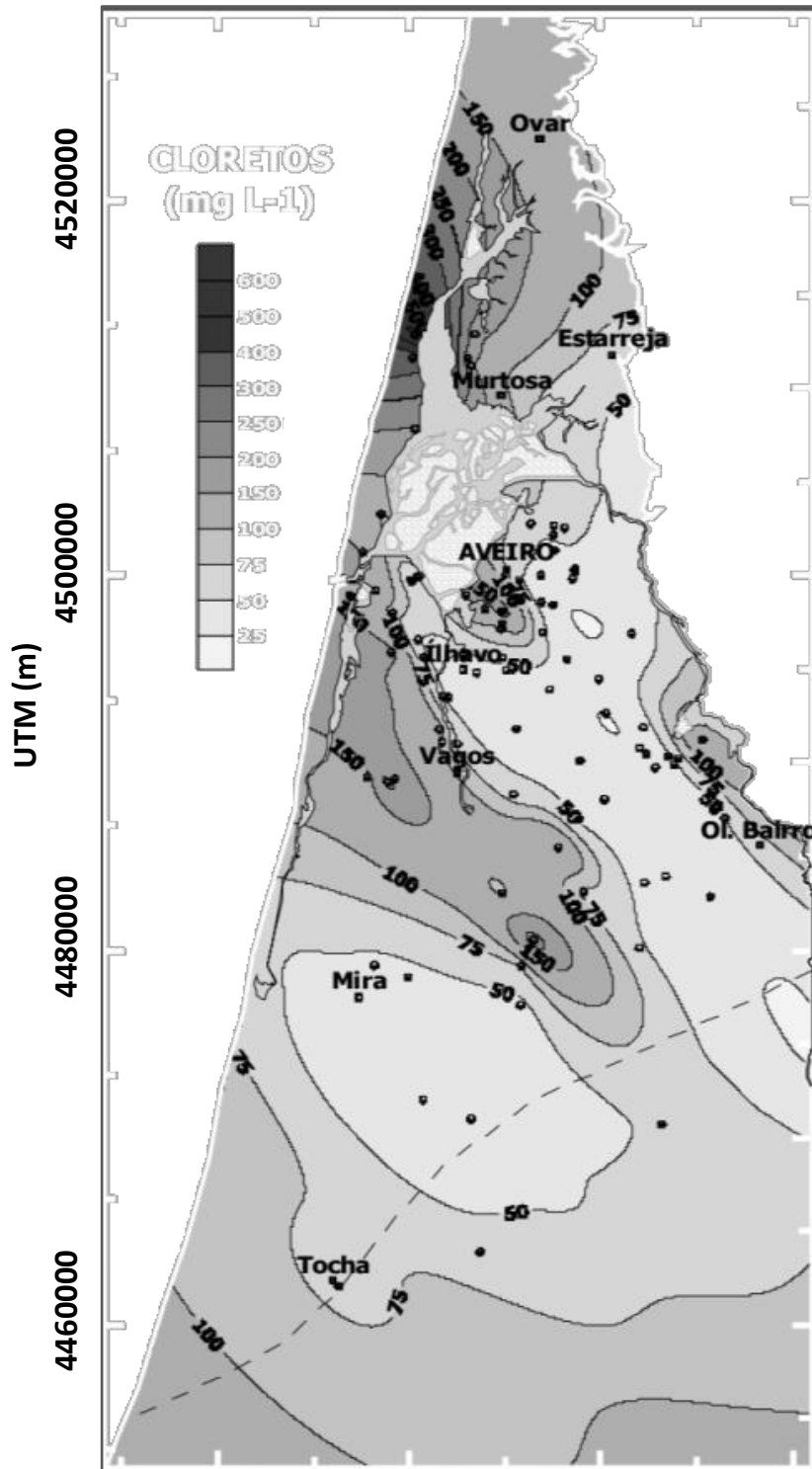
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**Map 3** – Localização da RIA (Aveiro Lagoon). *In: Rocha et al. (2005)*

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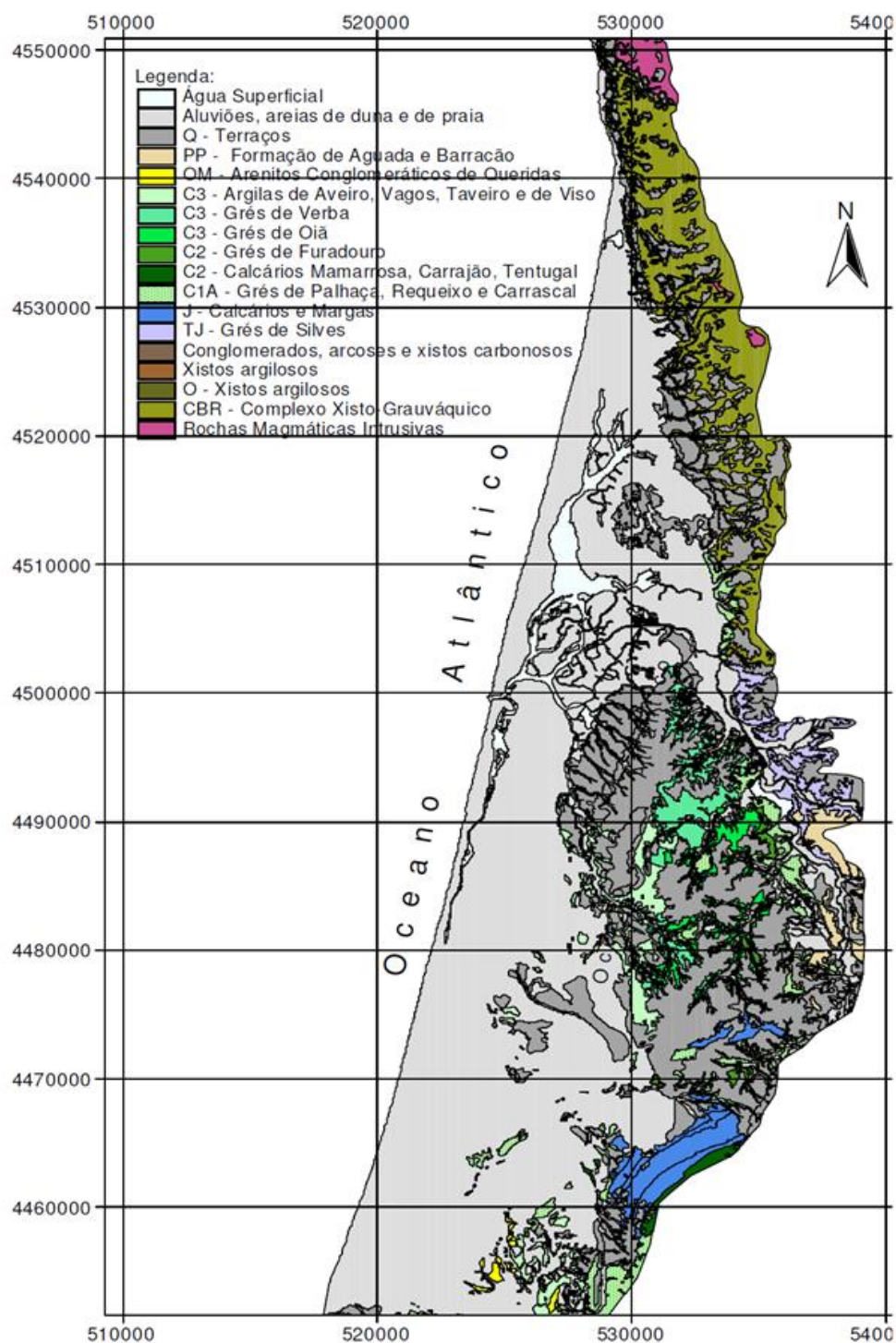
### Bibliographic Maps



**Map 4** – Intrusão salina evidenciada pela dispersão do conteúdo de cloretos. *In*: Condesso de Melo, (2002).

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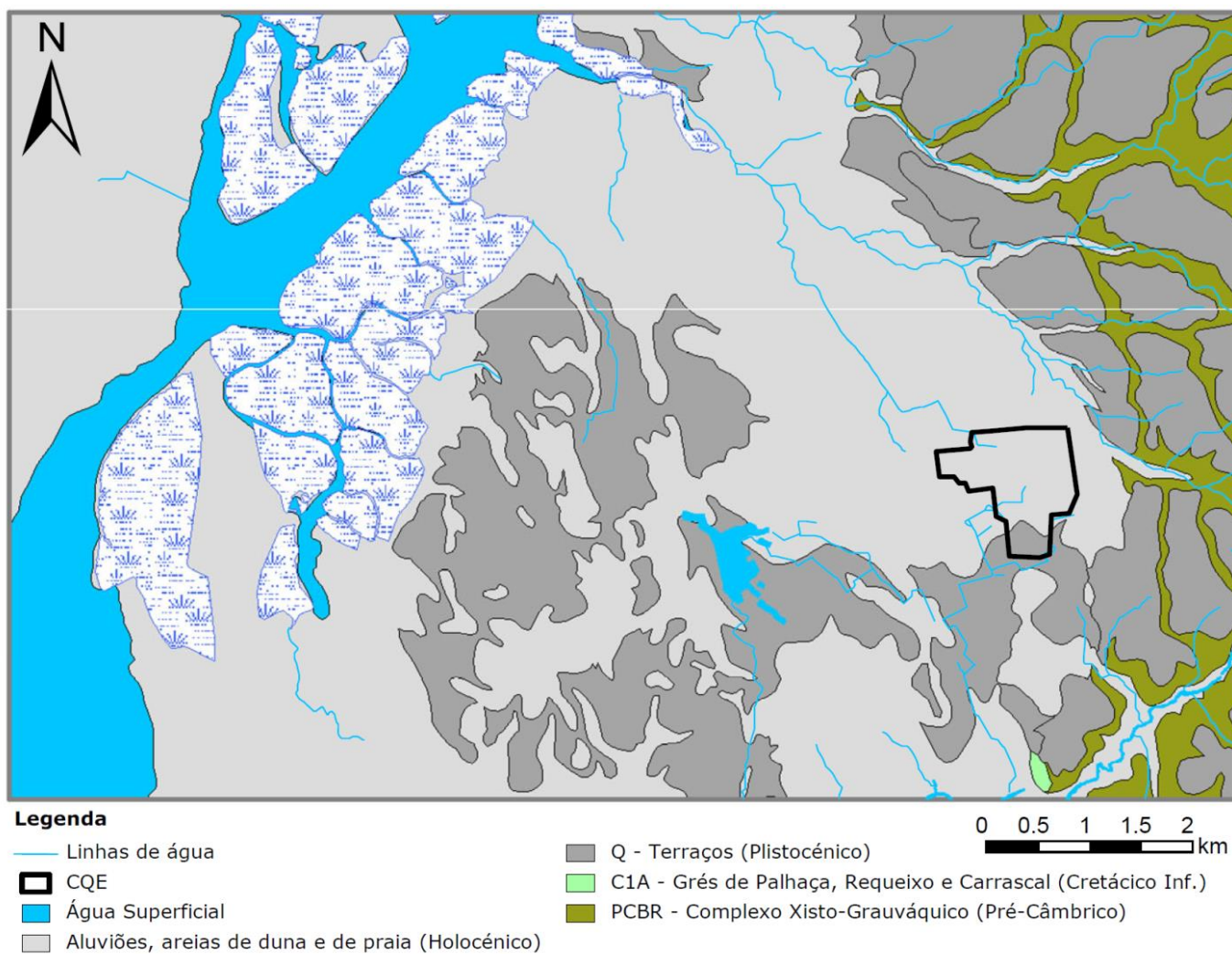
### Bibliographic Maps



**Map 5** – Mapa Geológico da RIA (Codesso de Melo, 2002). *In*: Comunidade Intermunicipal da Região de Aveiro (2006): Plano Municipal da Água – Fase de diagnóstico.

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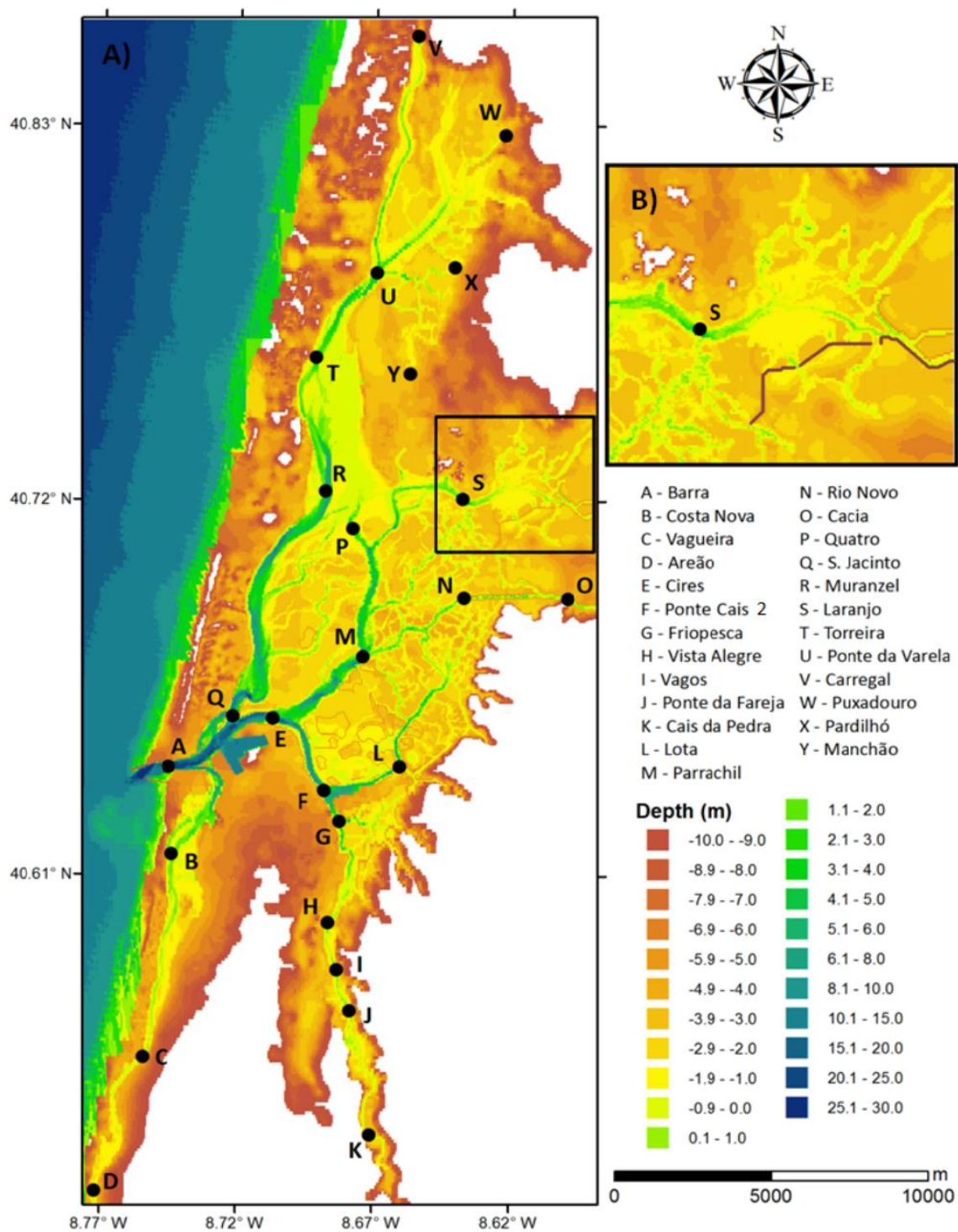
### Bibliographic Maps



**Map 6** – Mapa geológico da área envolvente do CQE (Carta Geológica de Portugal, Folha 13 C – Ovar; escala 1: 50 000) . *In*: Branco (2007).

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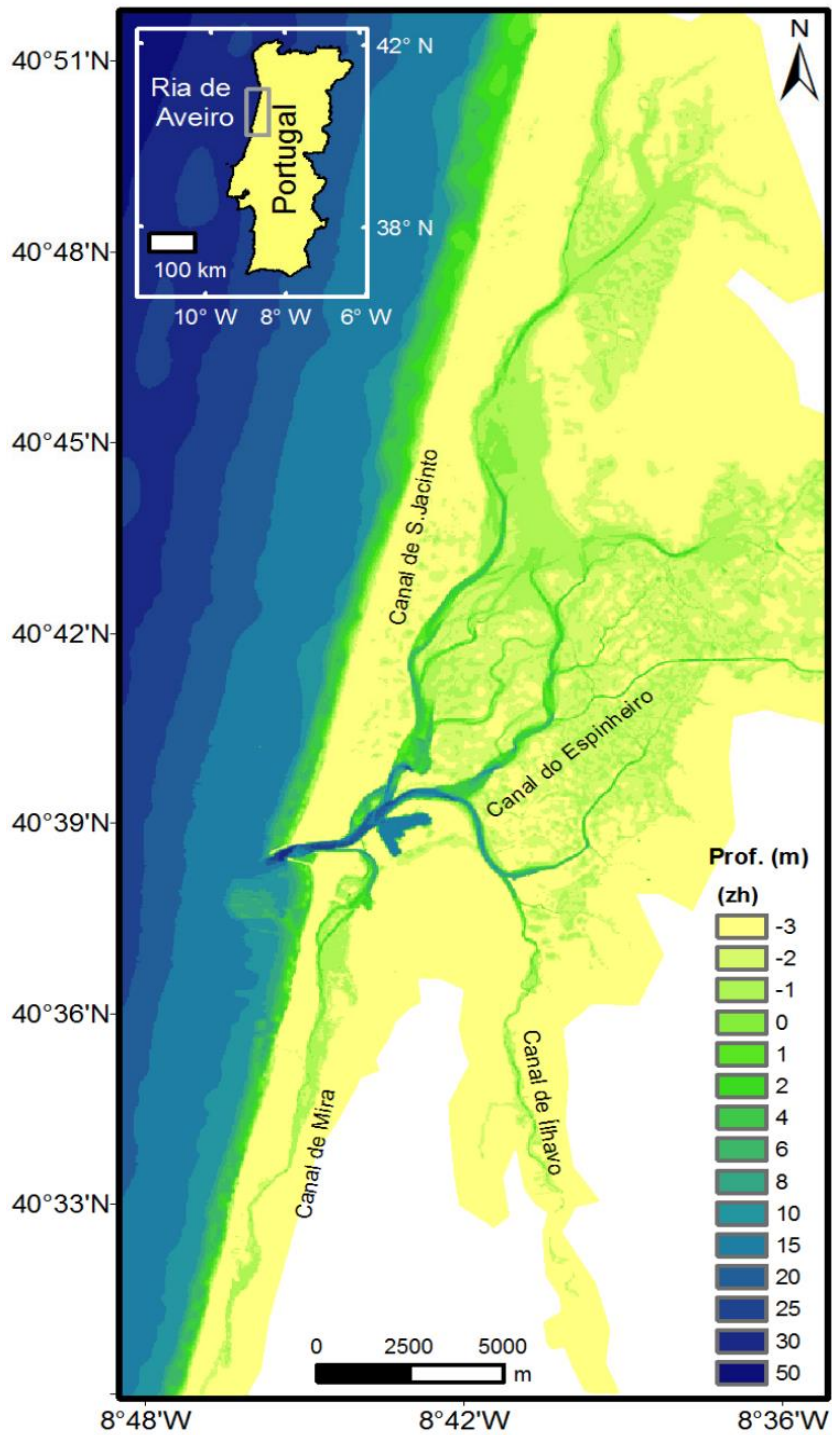
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**Map 7** – Batimetria numérica da RIA, com a localização das estações de levantamento de dados (A); detalhe do dique do BVL (B). *In*: Vargas (2012)

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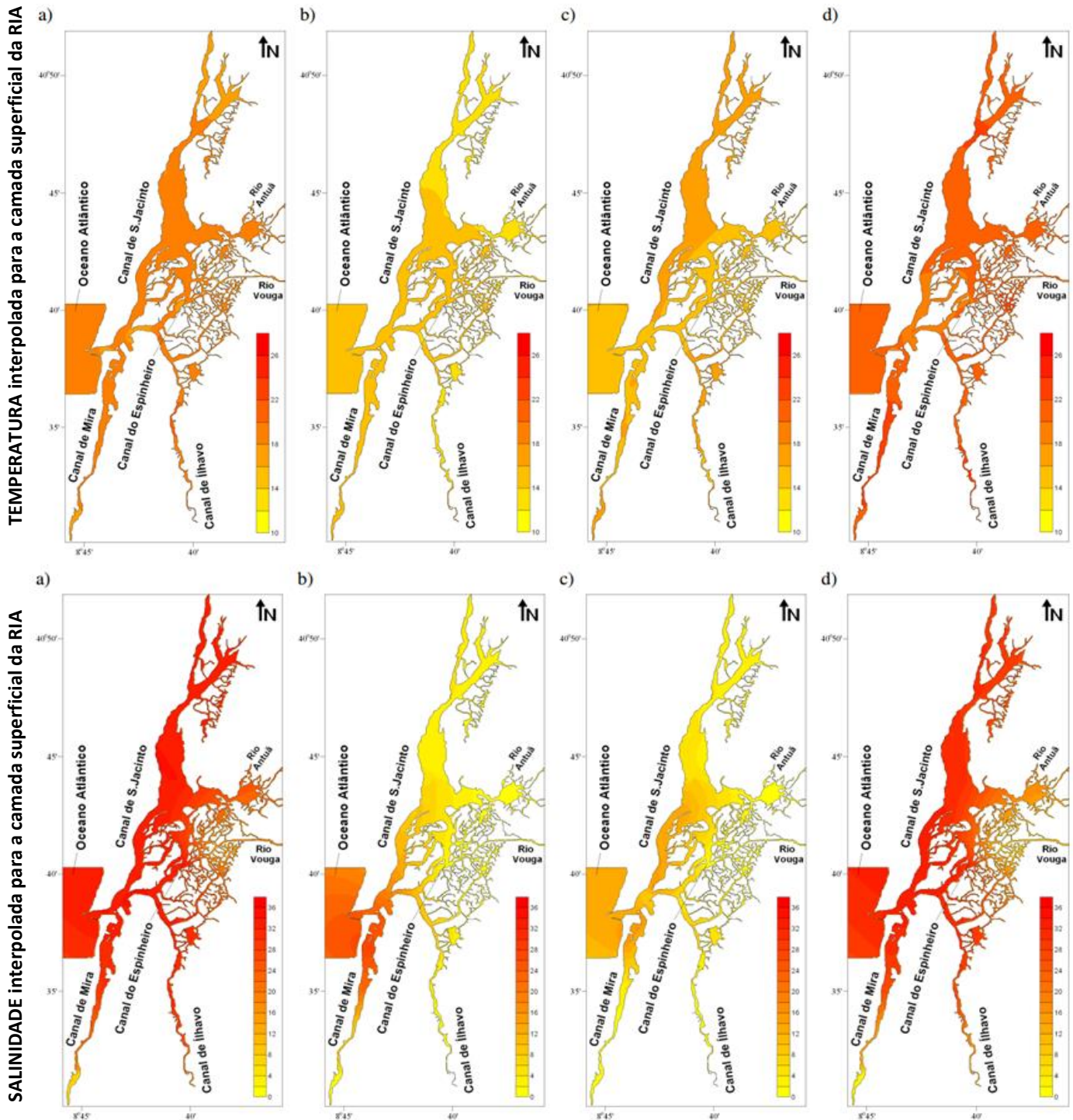


**Map 8** – Batimetria numérica da RIA, localização na Costa Portuguesa. *In*: Vaz and Dias (2011).



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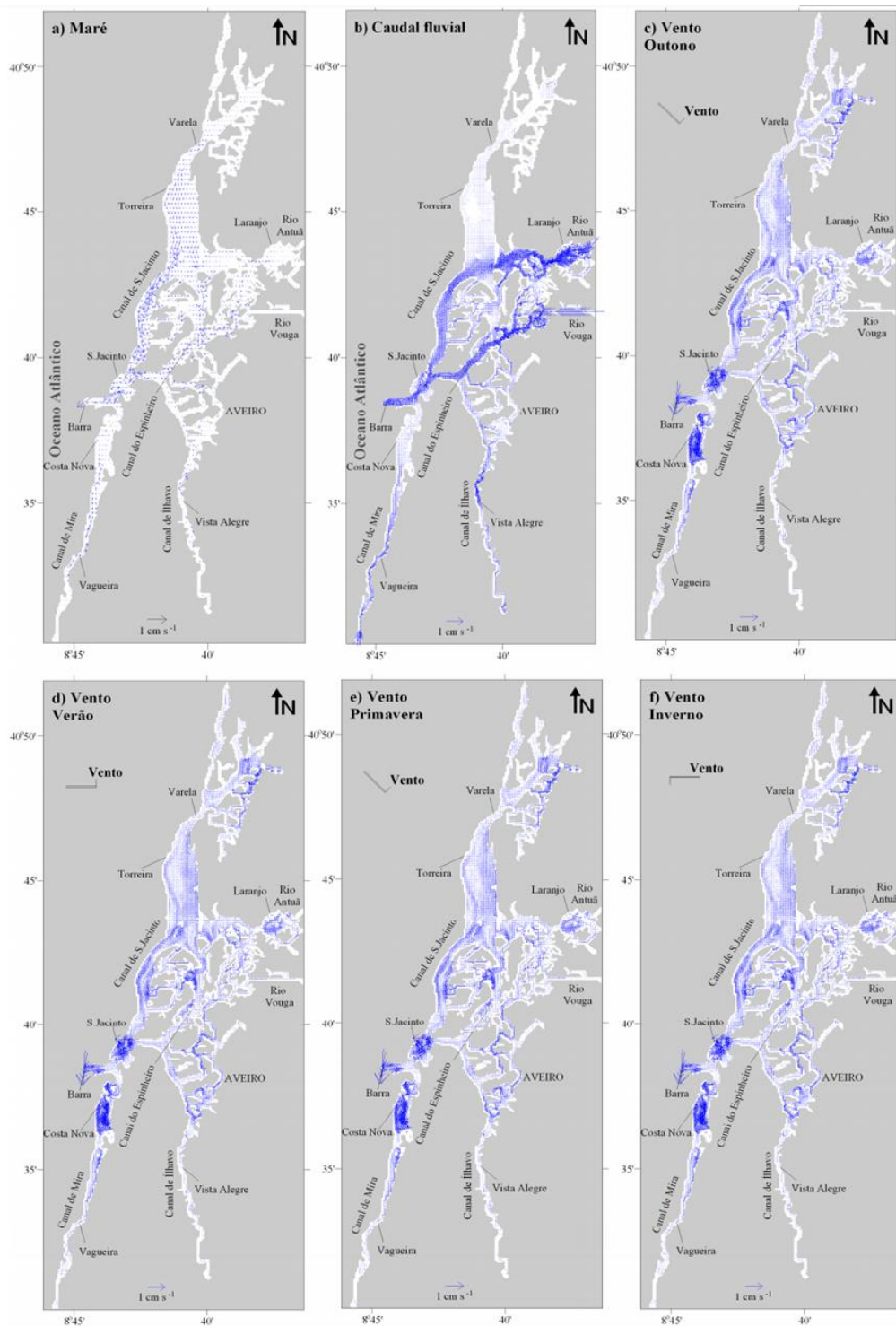
### Bibliographic Maps



**Map 9** – Estrutura horizontal da temperatura e da salinidade da água interpolada para a camada superficial da Ria de Aveiro, para cada estação do ano: a) Outubro de 2000; b) Inverno de 2000; c) Primavera de 2001; d) Verão de 2001. *In: Dias et al. (2011).*

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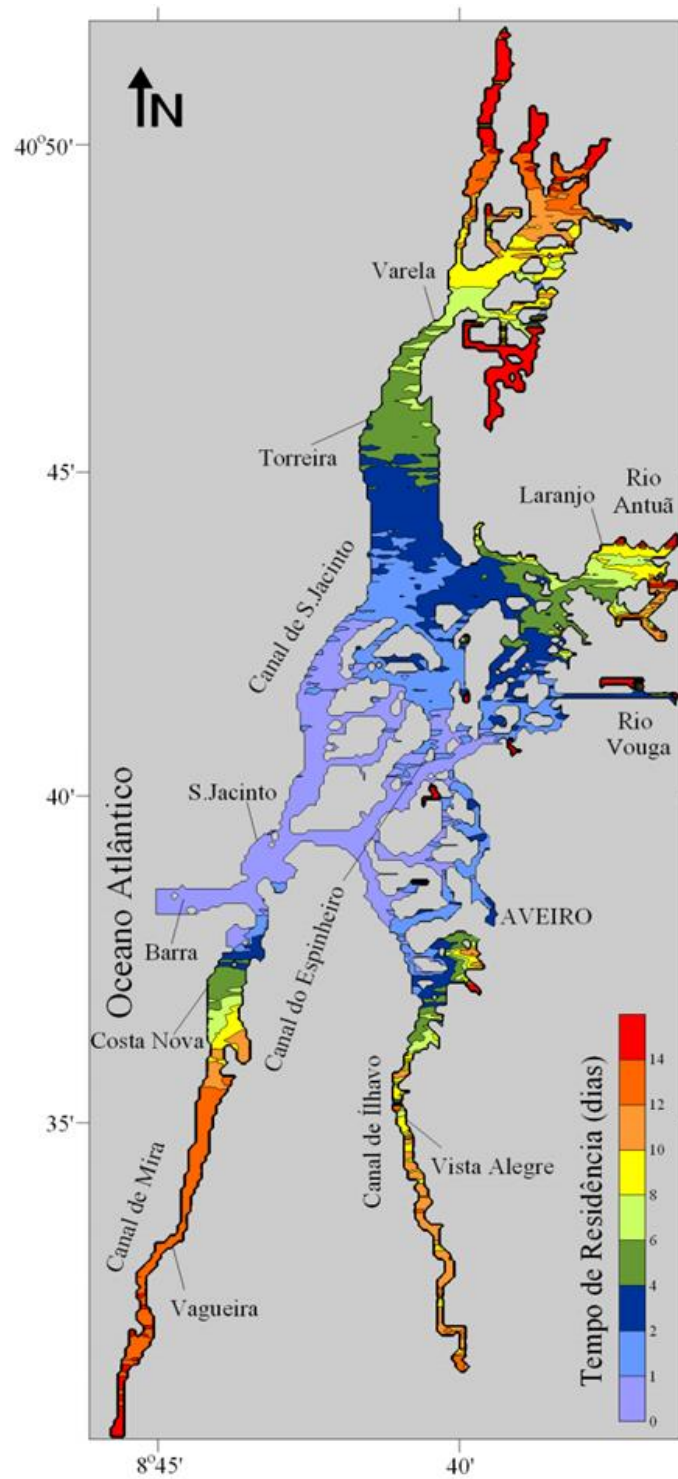
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**Map 10** – Circulação Residual de sedimentos introduzida pela maré (a), caudal fluvial (b) e por ventos característicos de cada estação (c-f) na RIA. *In*: Lopes and Dias (2011).

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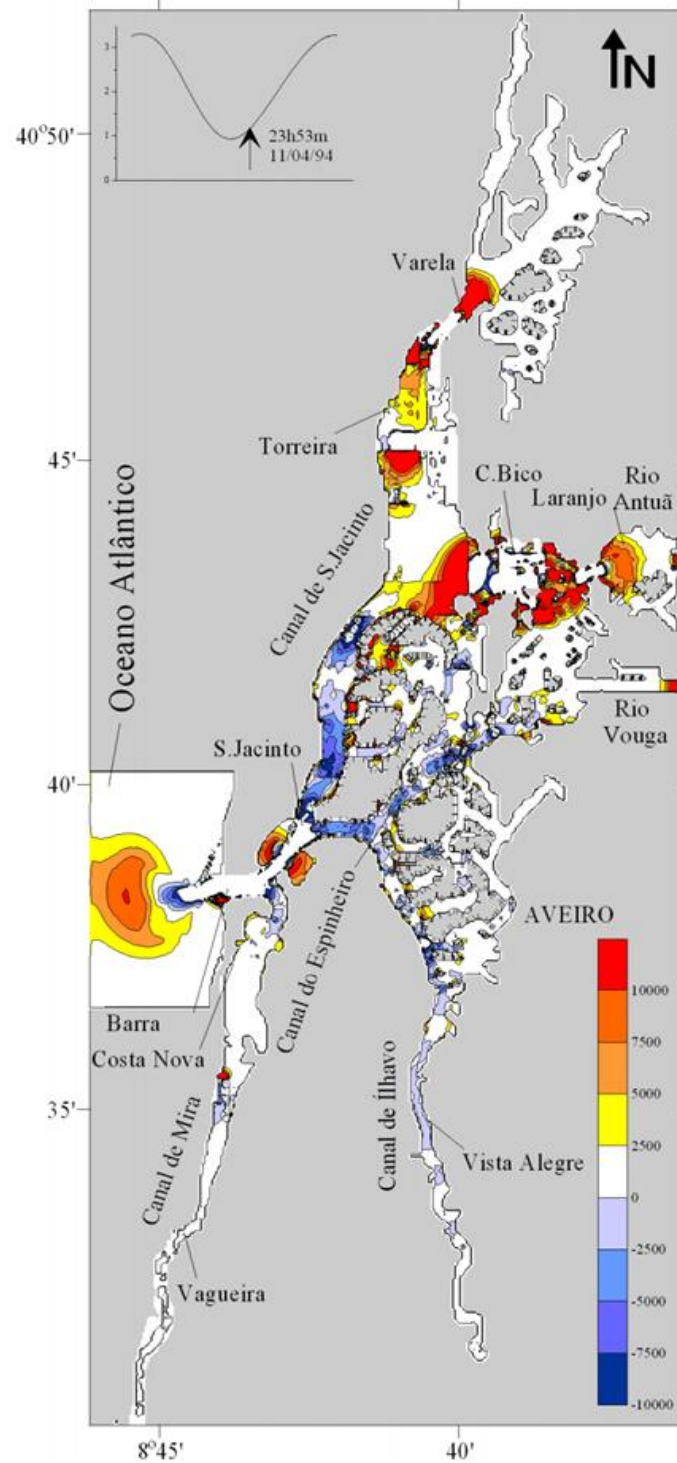
### Bibliographic Maps



**Map 11** – Tempo de residência de sedimentos na RIA. *In*: Lopes and Dias (2011).

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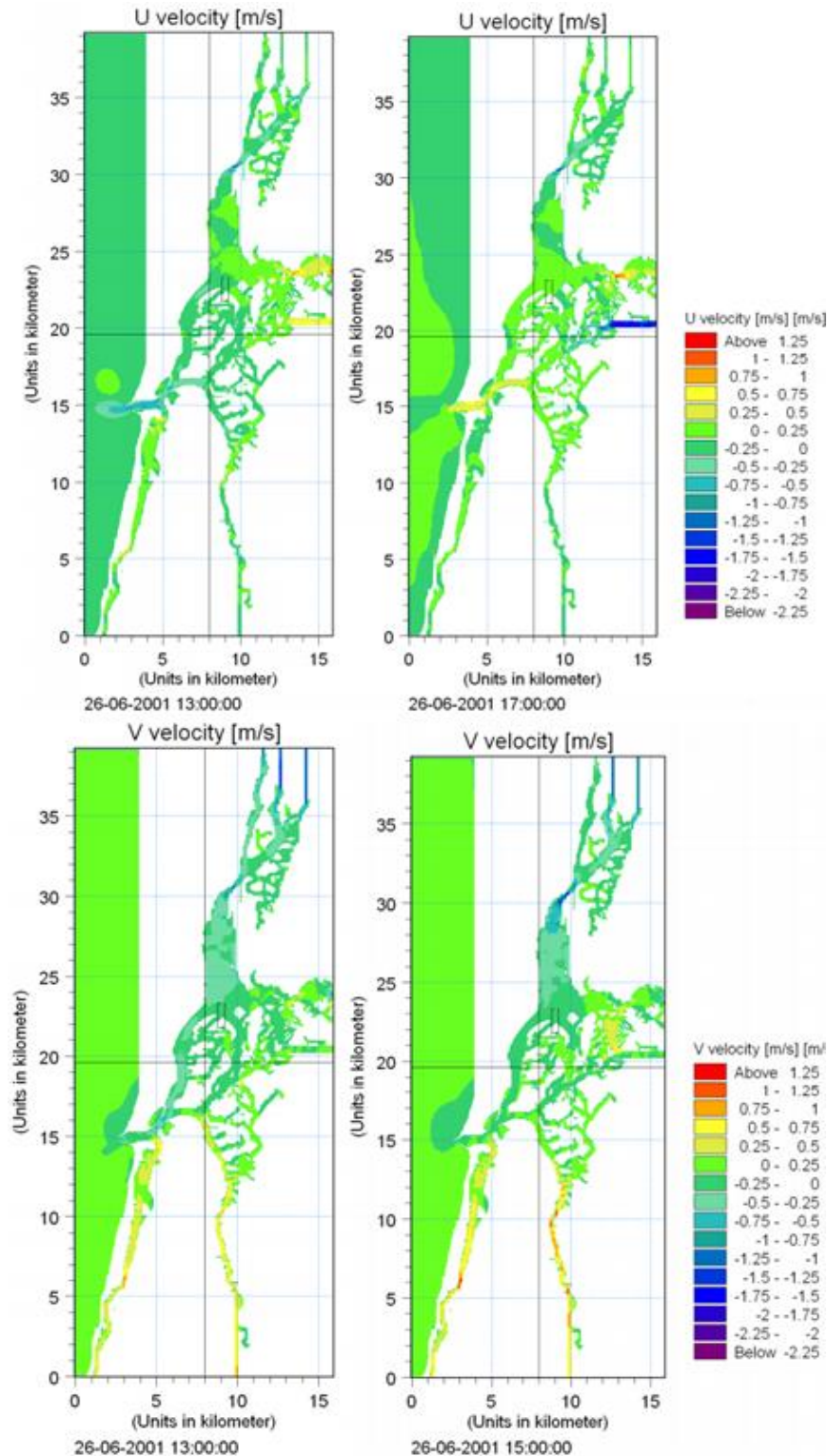
### Bibliographic Maps



**Map 12** – Balanço erosão-deposição (g/m<sup>2</sup>) na RIA: erosão (valores negativos); deposição (valores positivos). *In*: Lopes and Dias (2011).

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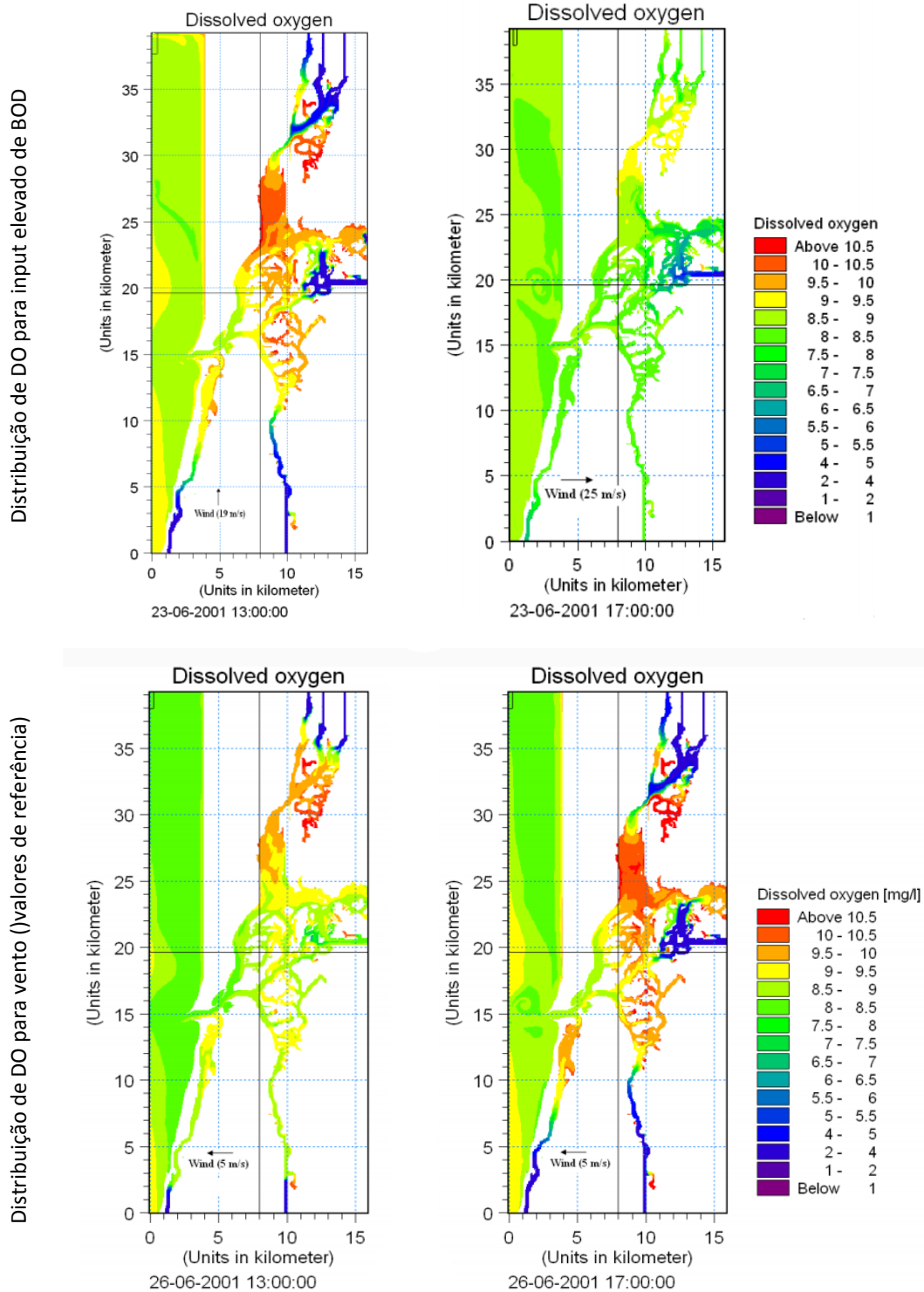
### Bibliographic Maps



**Map 13** – Mapa de correntes da RIA (componente U e V). *In: Lopes et al. (2011).*

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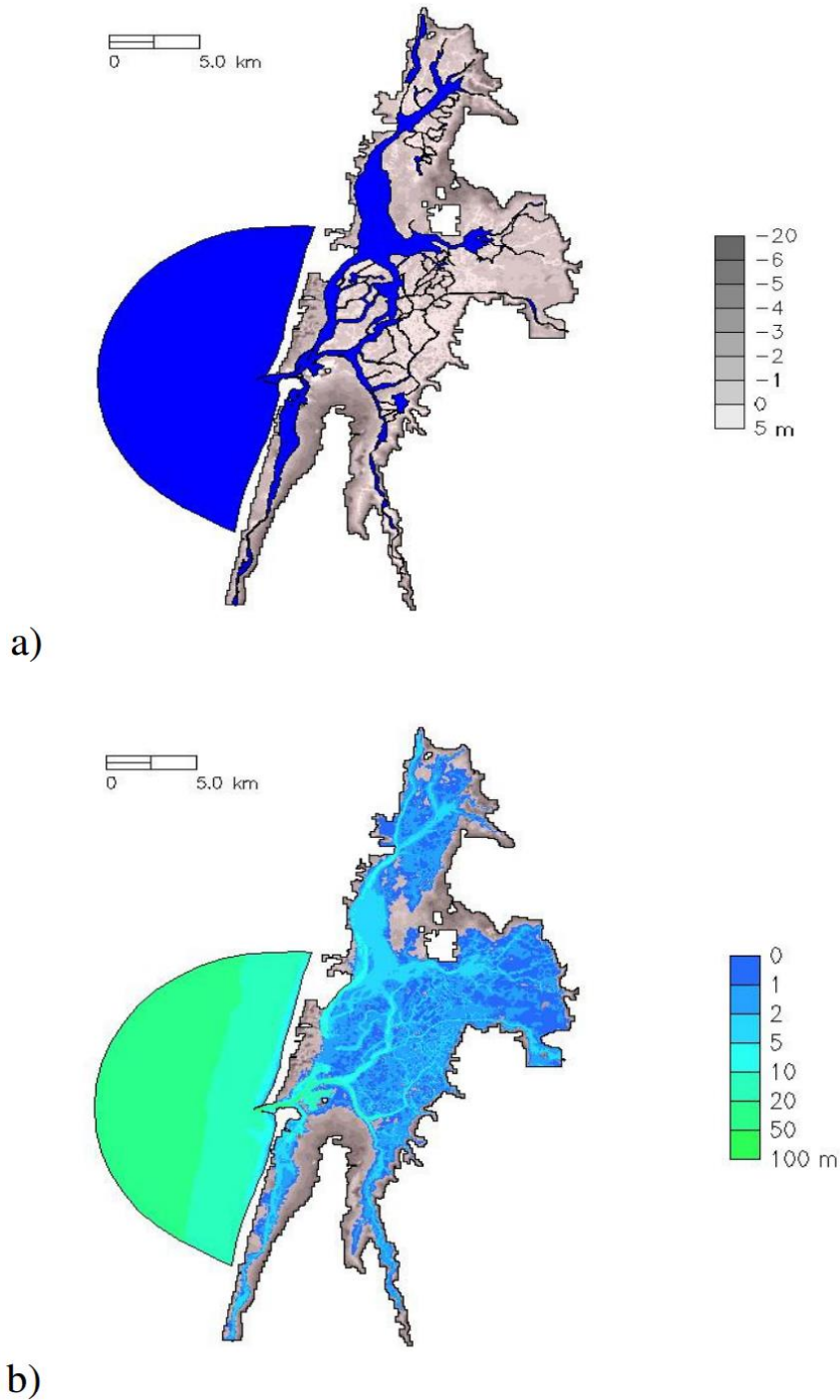
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**Map 14** – Distribuição de DO para input elevado de BOD (Biochemical oxygen demand) e para vento (valores de referência). *In: Lopes et al. (2011).*

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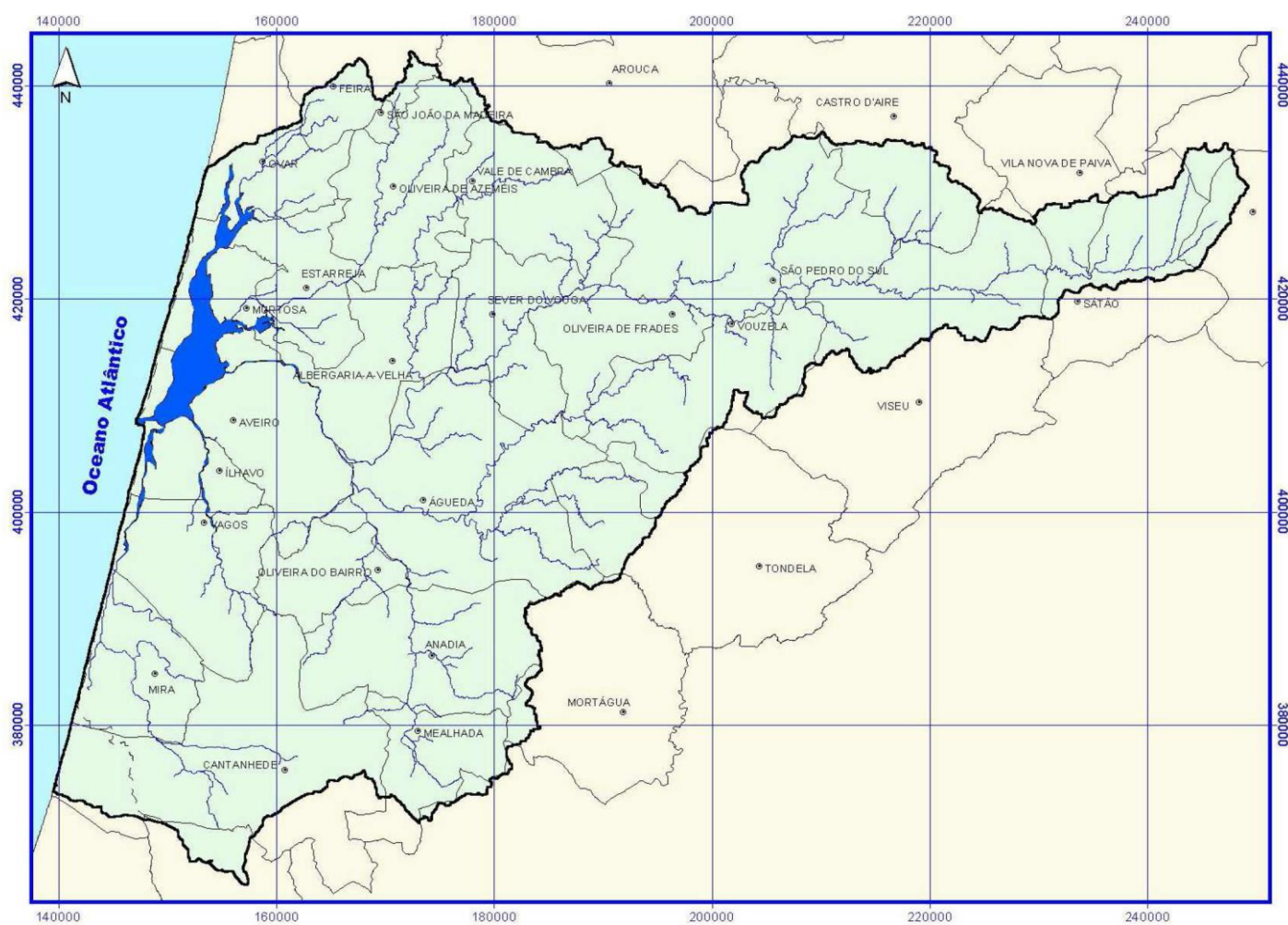
### Bibliographic Maps









**Map 15** – Simulação da inundação da RIA. a) topo-batimetria e zona sob efeito da maré e caudal médio (sem zonas inundáveis mas incluindo zonas intertidais); b) exemplo de alturas de água simuladas com malha alargada às zonas inundáveis, durante uma inundação. *In: Oliveira et al. (2011).*

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#### LEGENDA

-  Limite do Plano de Bacia Hidrográfica do Rio Vouga
-  Limite da Bacia Hidrográfica do Rio Vouga
-  Ria de Aveiro
-  Rede Hidrográfica Principal
-  Limite de concelho
-  Sedes de concelho

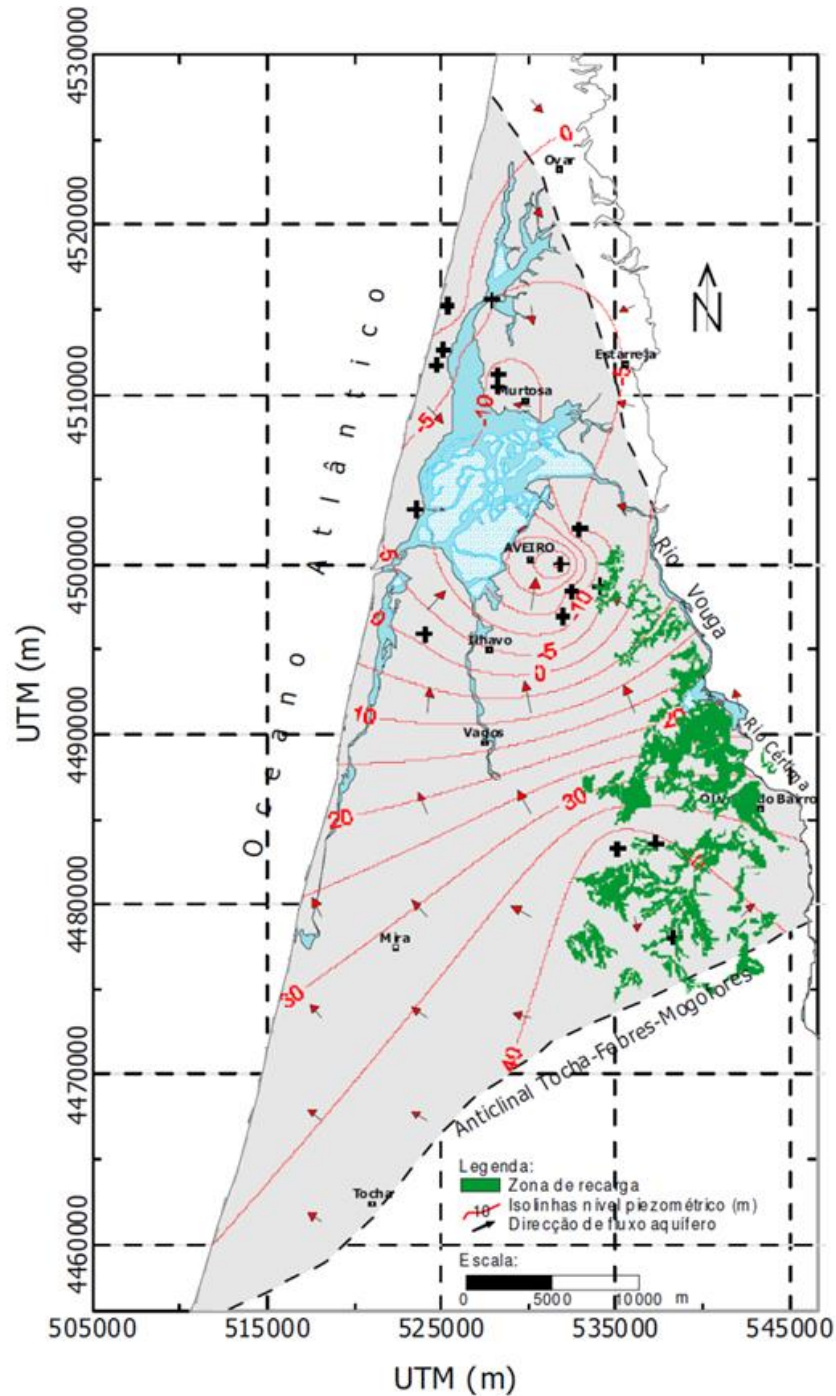
Map 16 – Bacia hidrográfica do Rio Vouga. *In: Lillebø et al. (2005).*





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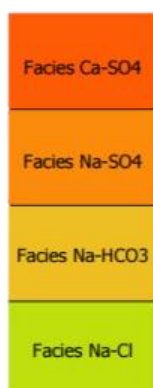
**Map 18** – Superfície piezométrica regional e principais direcções de fluxo actual no aquífero Cretácico da RIA (segundo Condesso de Melo, 2002). Nota: Valores dos níveis piezométricos dados em relação ao nível médio do mar. *In*: Comunidade Intermunicipal da Região de Aveiro. (2006) - Plano Municipal da Água – Fase de diagnóstico

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#### CLASSIFICAÇÃO

águas subterrâneas



#### ZONA DE RECARGA

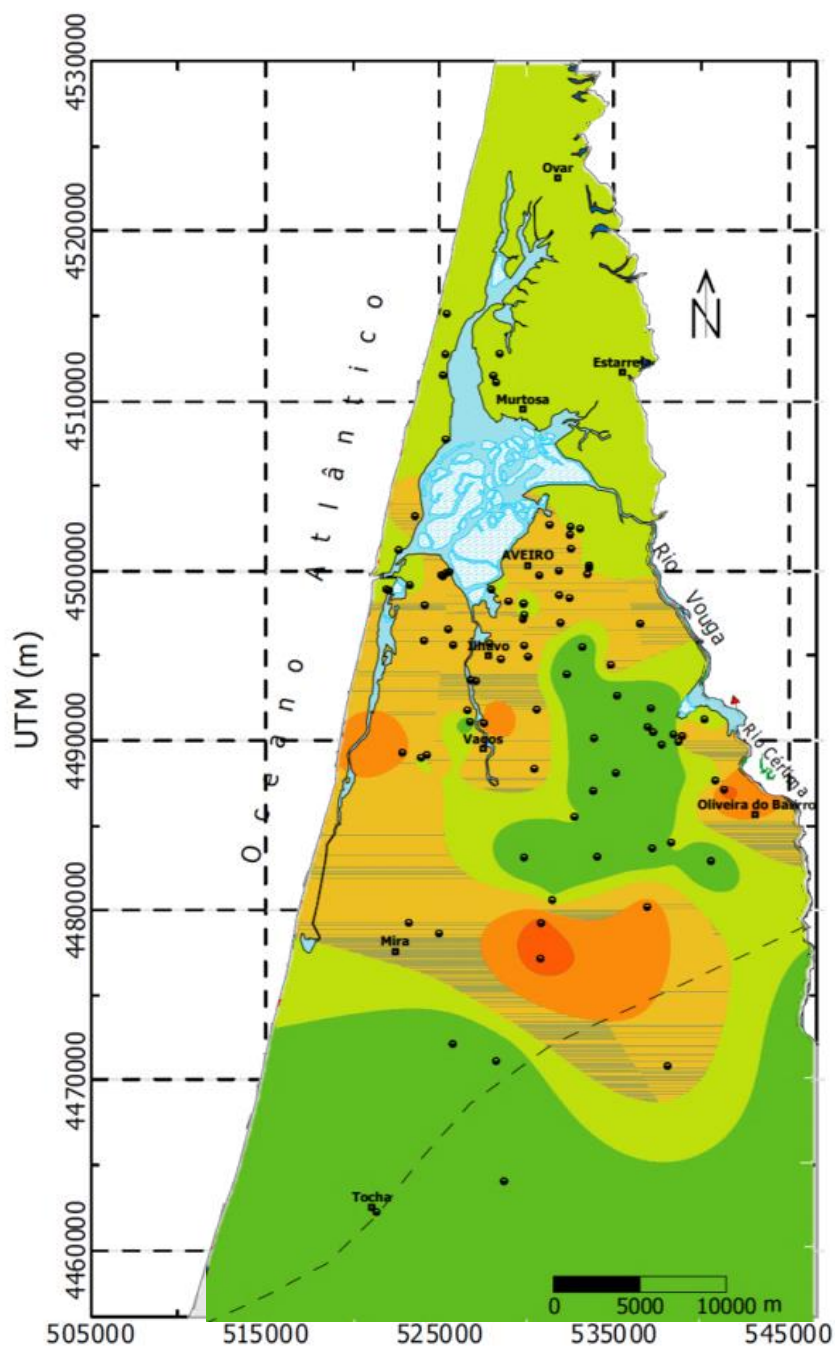
(Ca-HCO<sub>3</sub>;  
pH<7,0;  
T<20°C;  
Cl~30mg/L;  
t<sub>R</sub><5 000 anos

#### ZONA INTERMEDIA

Ca-Na-HCO<sub>3</sub>;  
6,0<pH<8,0;  
T~21,3°C  
Cl~40mg/L;  
t<sub>R</sub><3 500-18 000 anos

#### ZONA DA COSTA

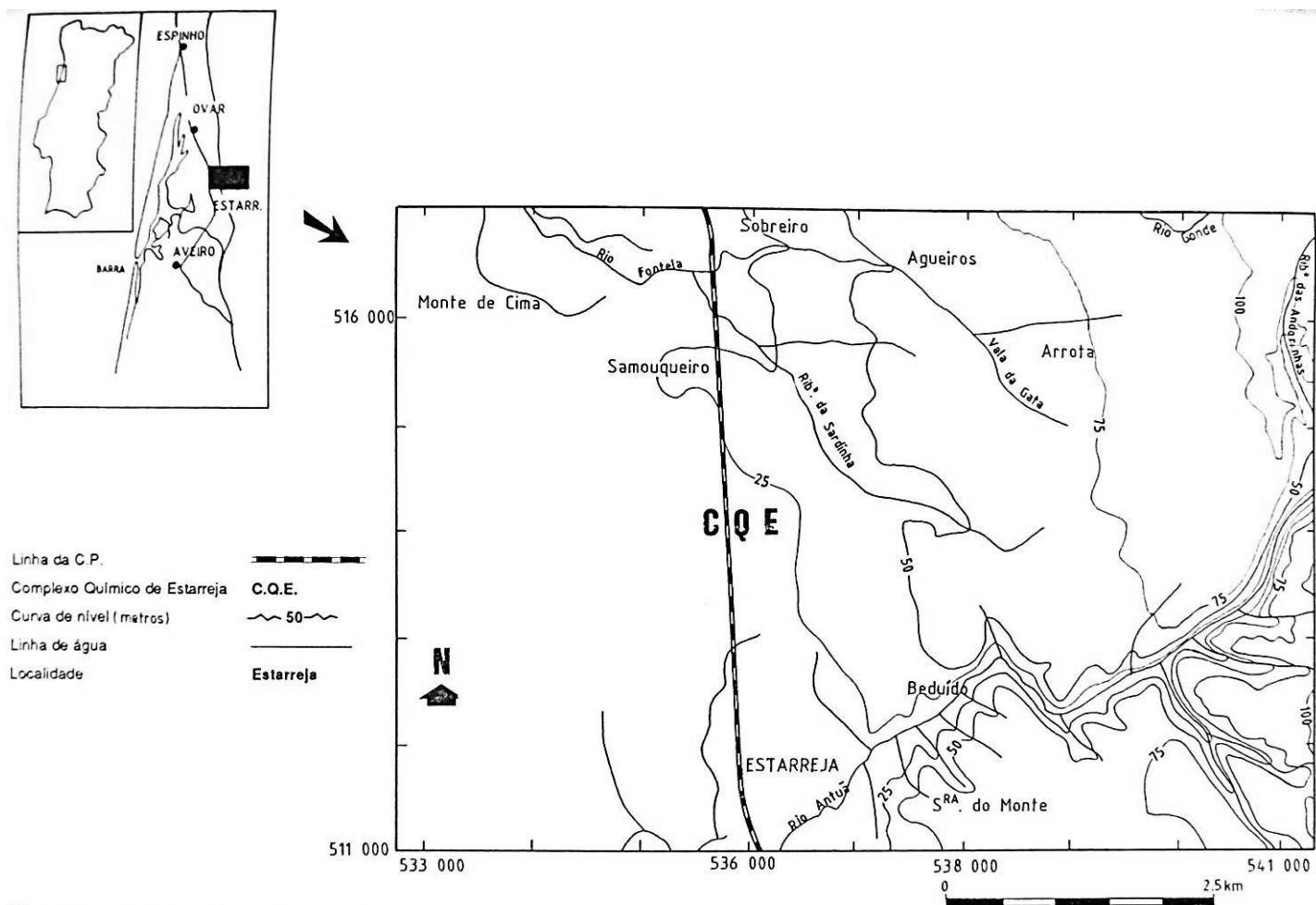
Na-HCO<sub>3</sub>-Cl;  
7,1<pH<8,9;  
T>22°C;  
Cl~100mg/L;  
t<sub>R</sub>>18 000 anos



**Map 19** – Classificação da águas subterrâneas (segundo Condesso de Melo, 2002). *In*: Comunidade Intermunicipal da Região de Aveiro (2006) - Plano Municipal da Água – Fase de diagnóstico.

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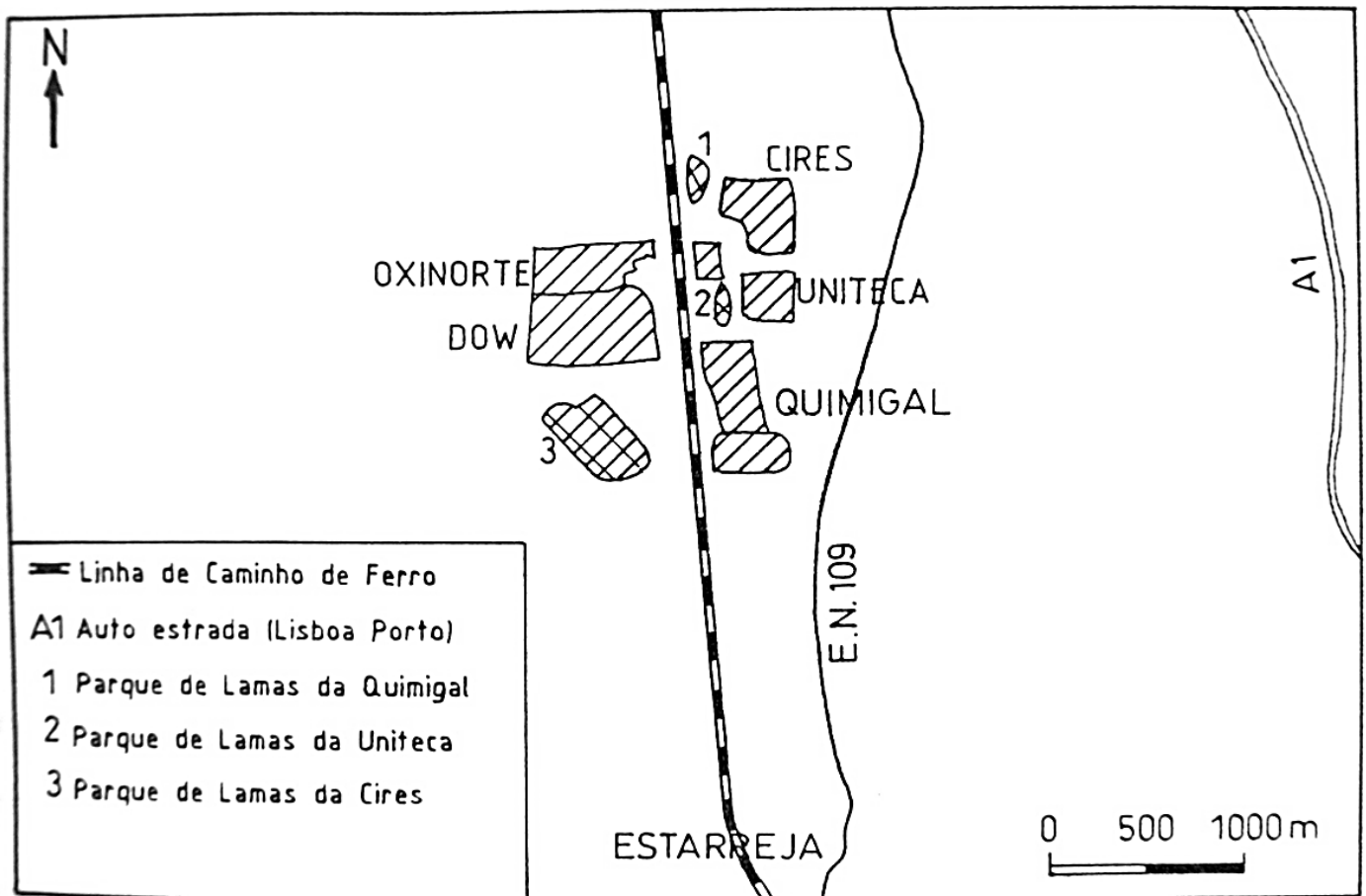
### Bibliographic Maps



**Map 20** – Enquadramento geral da Área de Estudo - envolvente do CQE. *In:* Inácio (1993)

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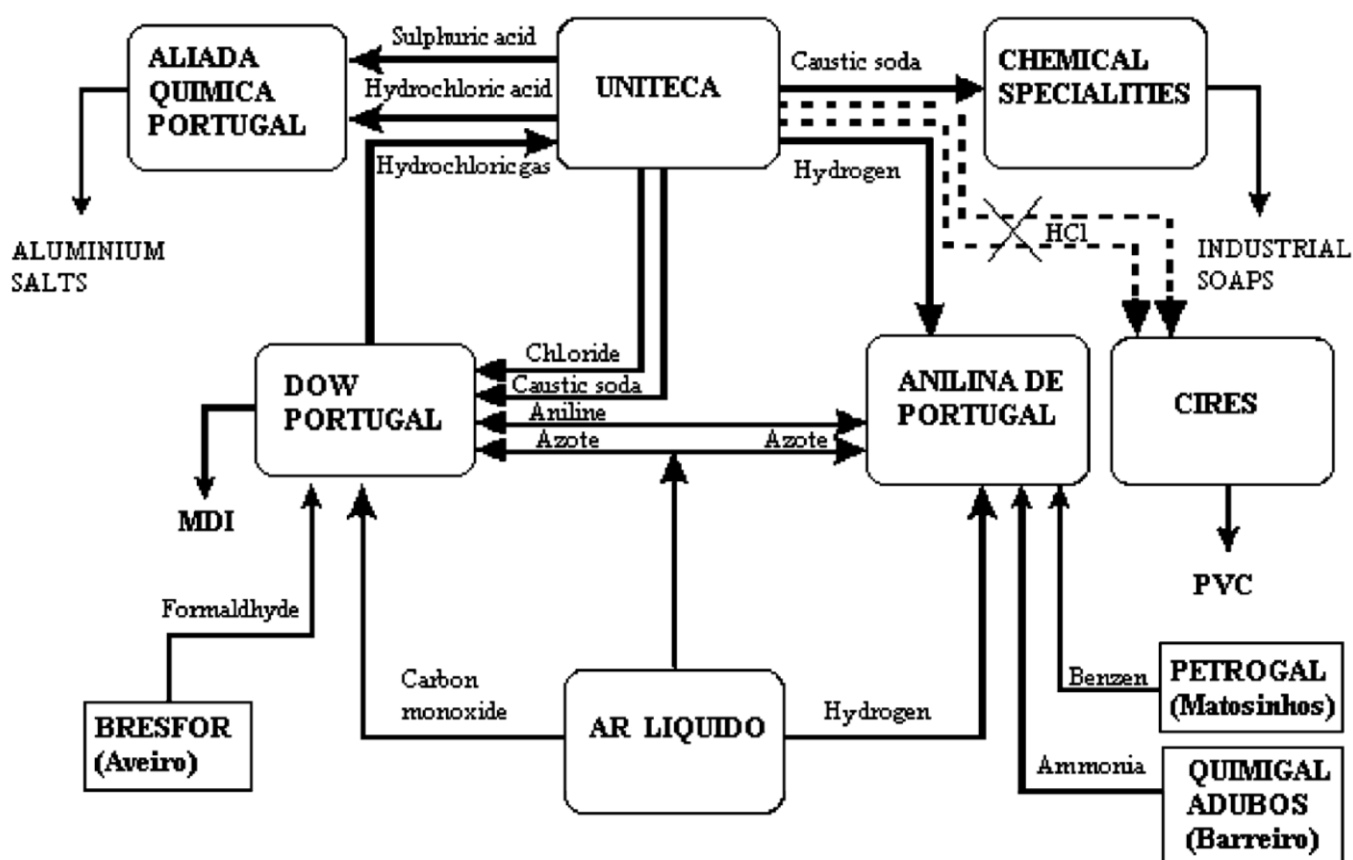
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**Map 21** – Localização da principais unidades fabris a operar no CQE na década de 90 e respectivos parques de lamas. *In*: Inácio (1993).

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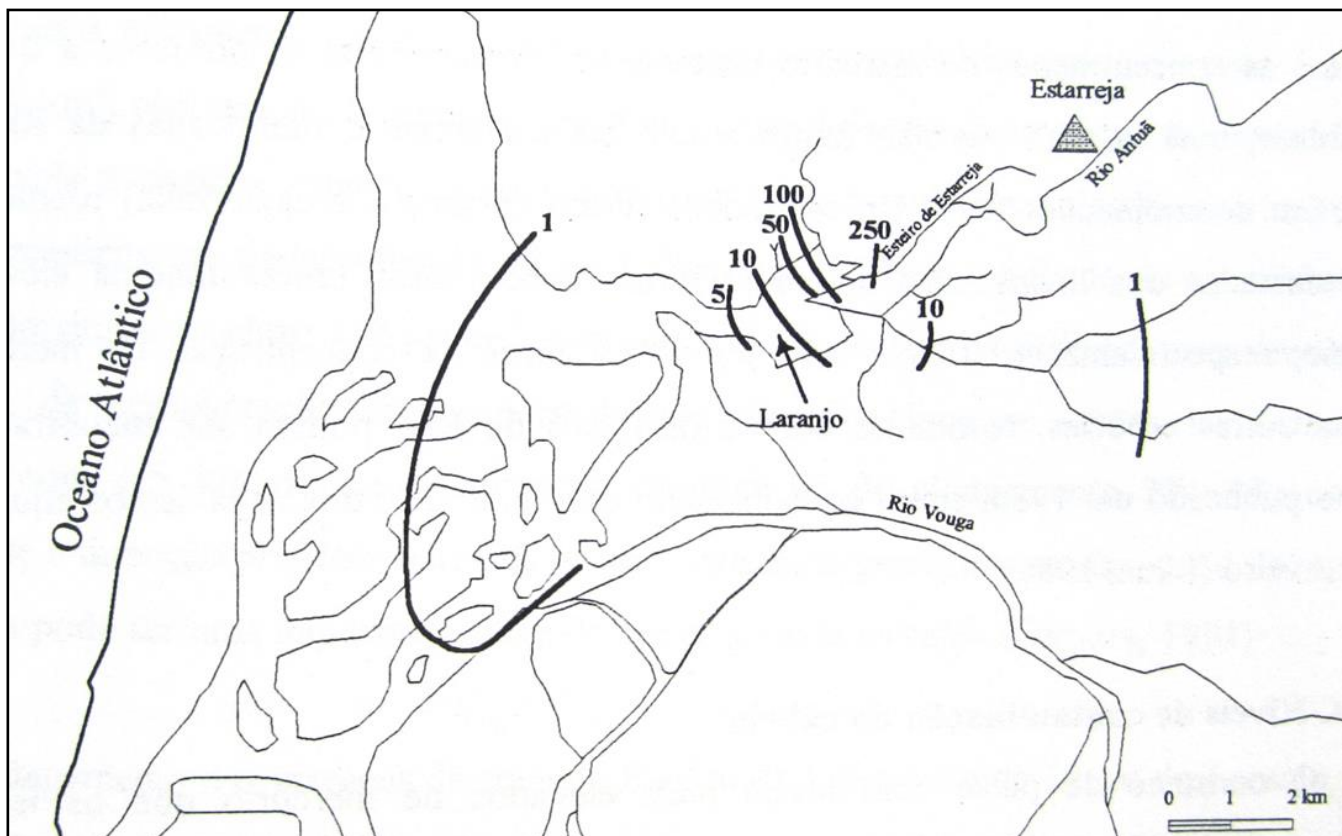
### Bibliographic Maps



**Map 22** – Unidades industriais a operar no CQE na década de 90, seus produtos e relações de fornecimento entre as indústrias do mesmo complexo. *In*: Costa e Jesus-Rydin (2001)

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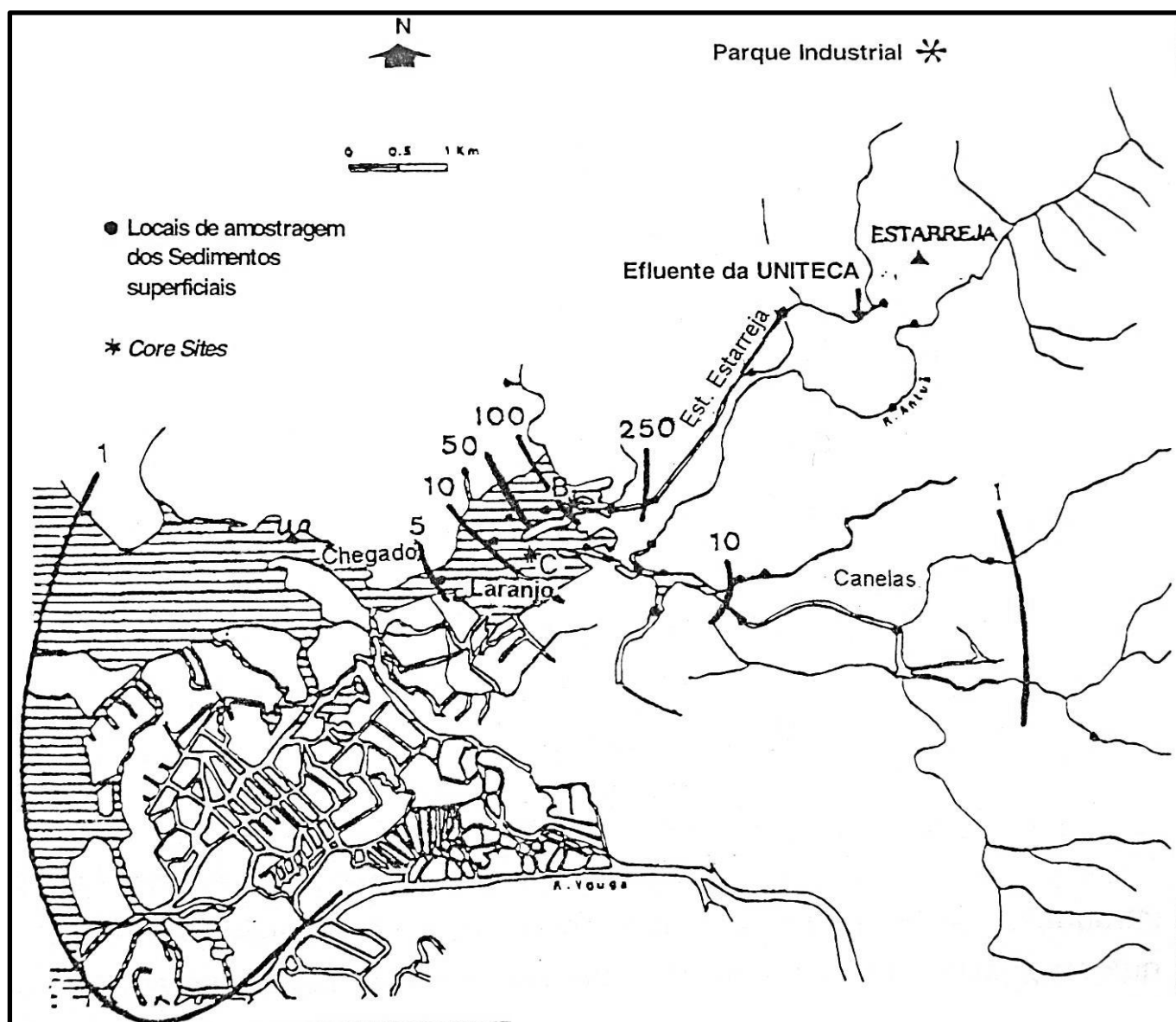
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**Map 23** – Linhas de isoconcentração de Hg ( $\mu\text{g/g}$ ) nos sedimentos superficiais da Zona do Largo de Laranjo (Lucas *et al.*, 1986). *In*: Pereira (1996)

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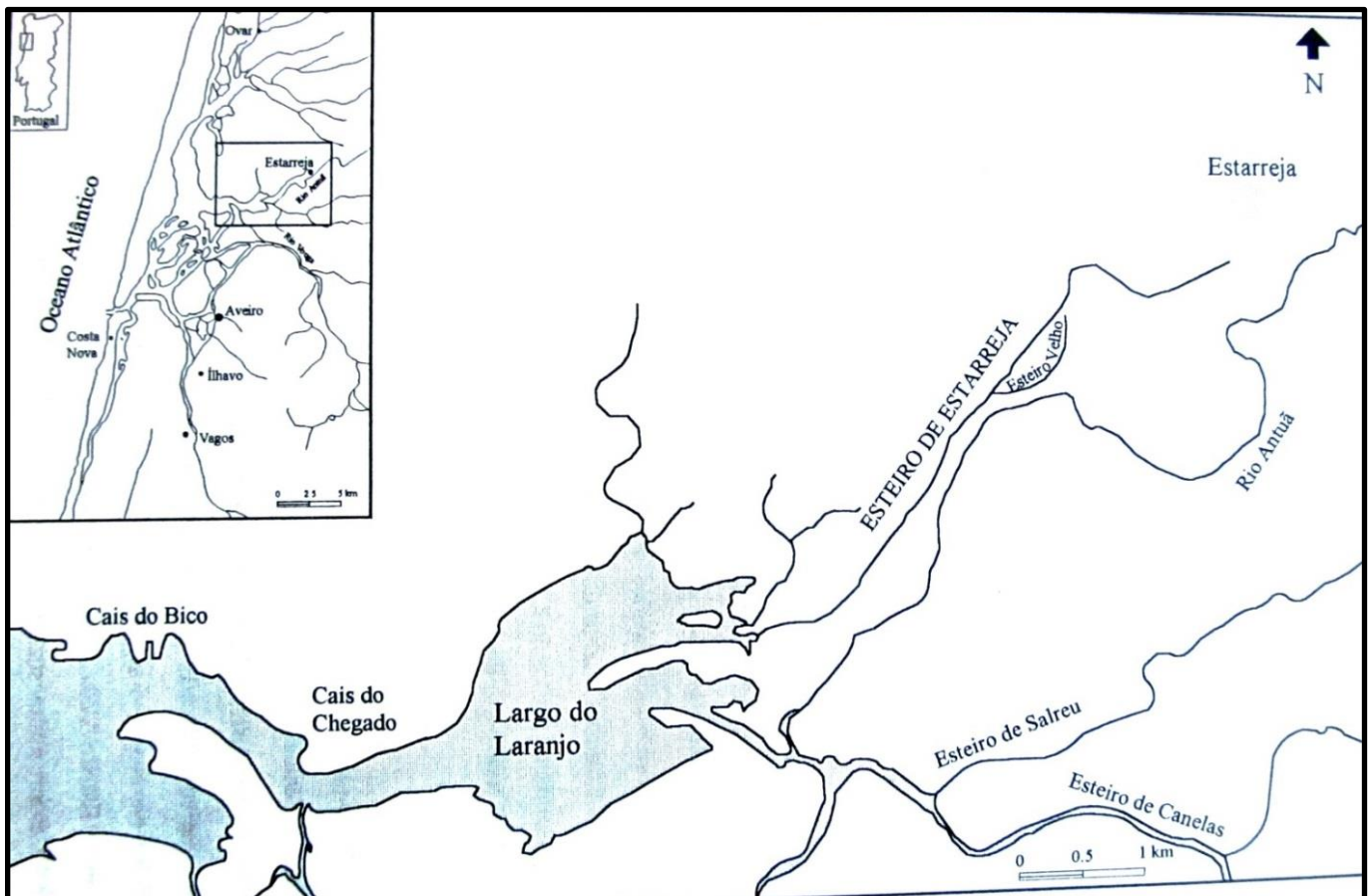


**Map 24** – Linhas de isoconcentração de Hg (mg/kg peso seco) dos sedimentos do largo do Laranjo (Hall *et al.*, 1987). *In:* Tavares (1995)



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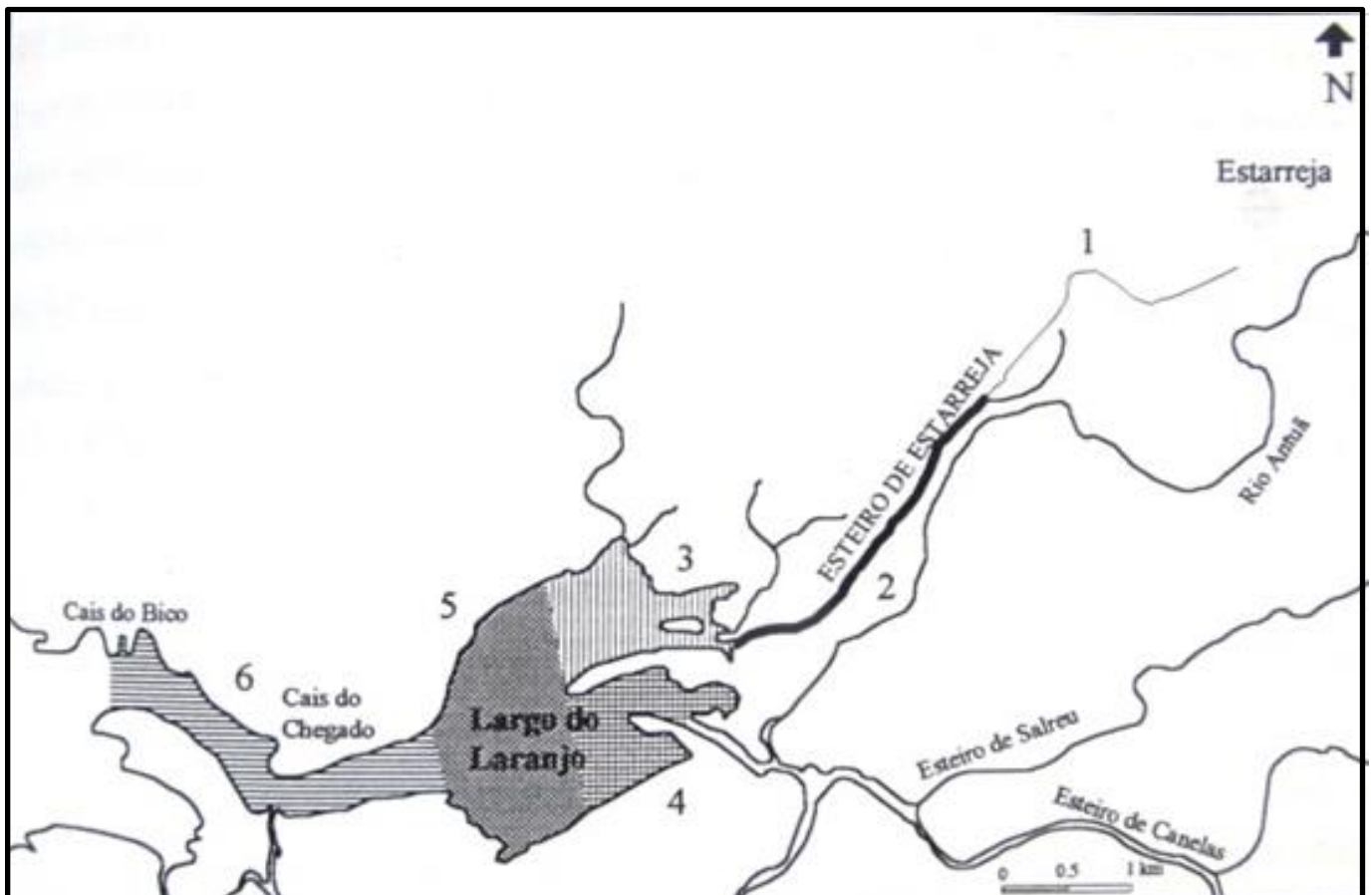
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**Map 25** – Reservatórios de contaminação directa do CQE – “Esteiro de Estarreja” e “Largo do Laranjo”, alvos de estudos dedicados à carga sedimentar. *In*: Pereira (1996)

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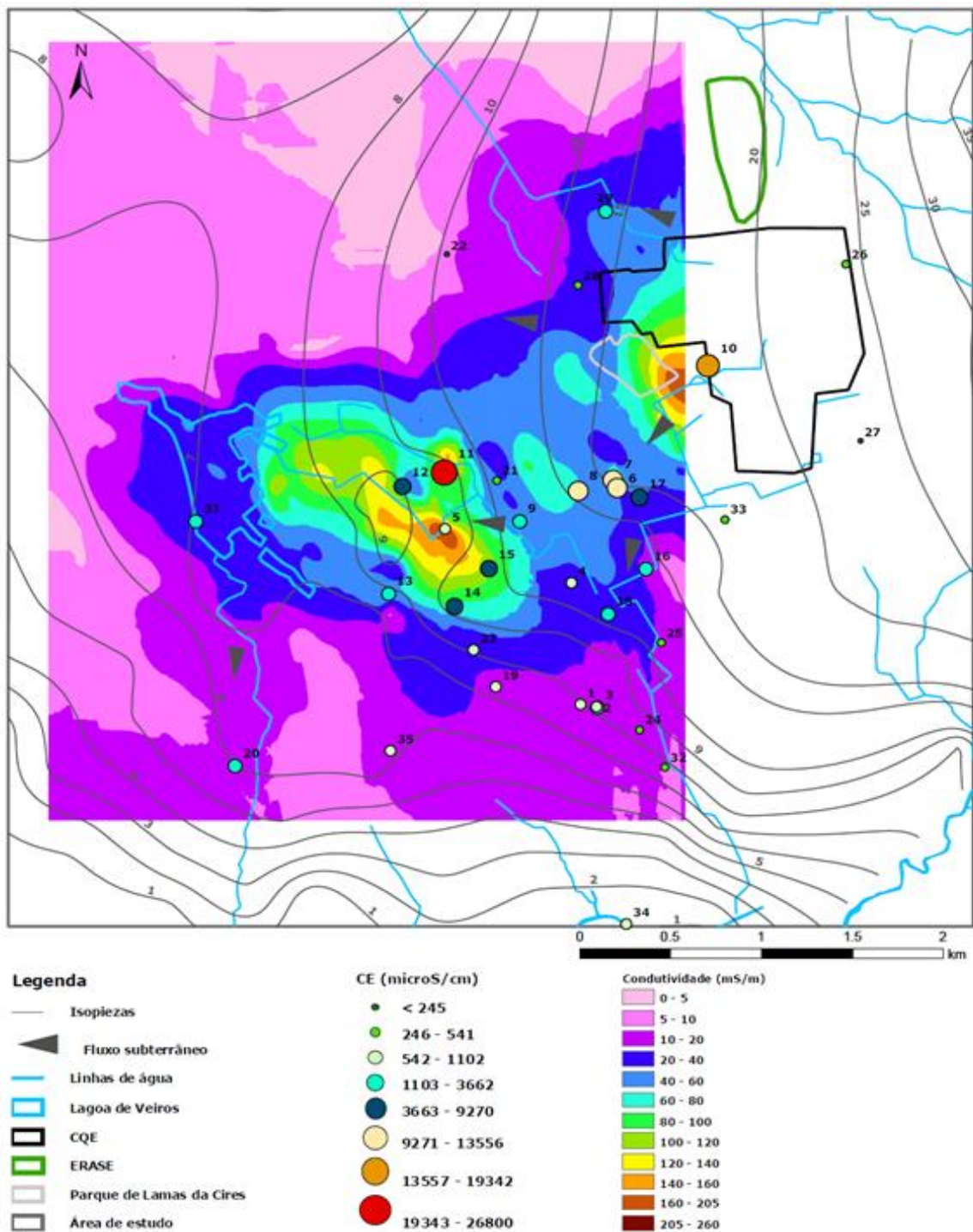
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**Map 26** – Identificação das secções em que foi dividida a área da Ria mais contaminada com Hg, para a estimar a quantidade de metal acumulado nos sedimentos nesse reservatório. *In:* Pereira (1996)

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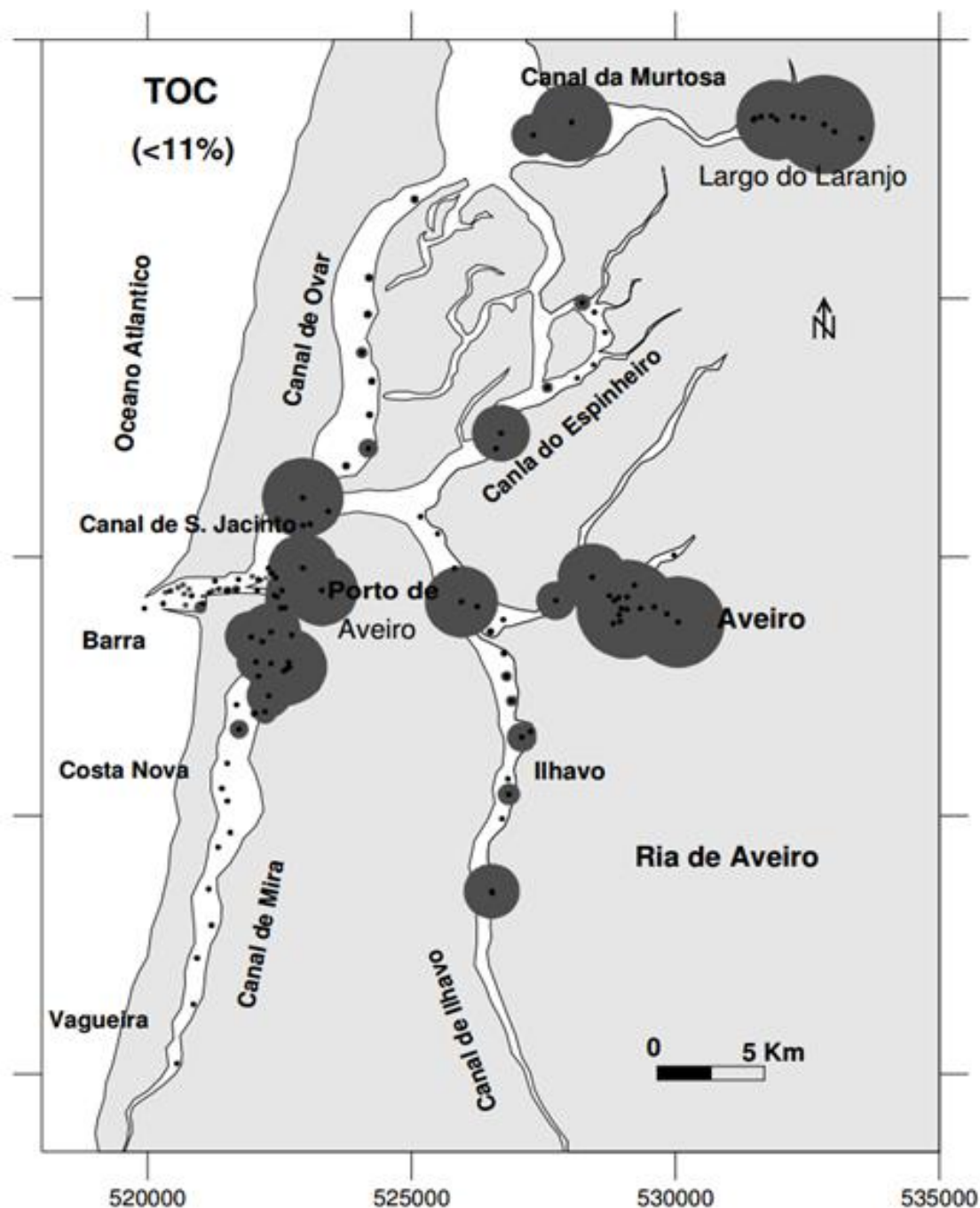
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**Map 27** – Mapa de condutividade eléctrica aparente da medida V20 (dados de campanha electromagnética) e de CE da água subterrânea. *In*: Branco (2007)

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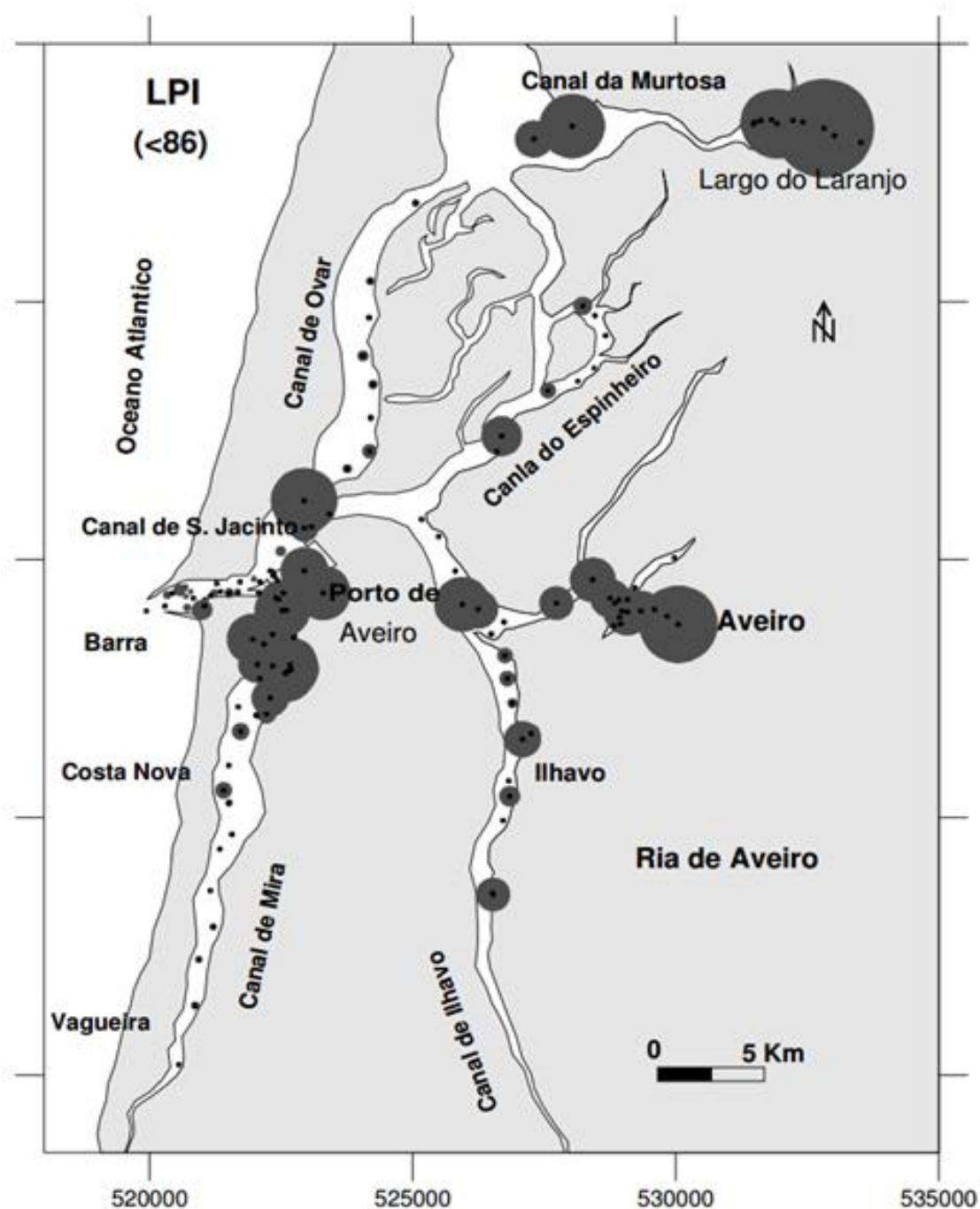
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**Map 28** – Mapa de distribuição da proporção de TOC (Total Organic Carbon). A dimensão das marcas circulares cinzentas é proporcional aos valores de cada local de amostragem. *In*: Martins *et al.* (2011)

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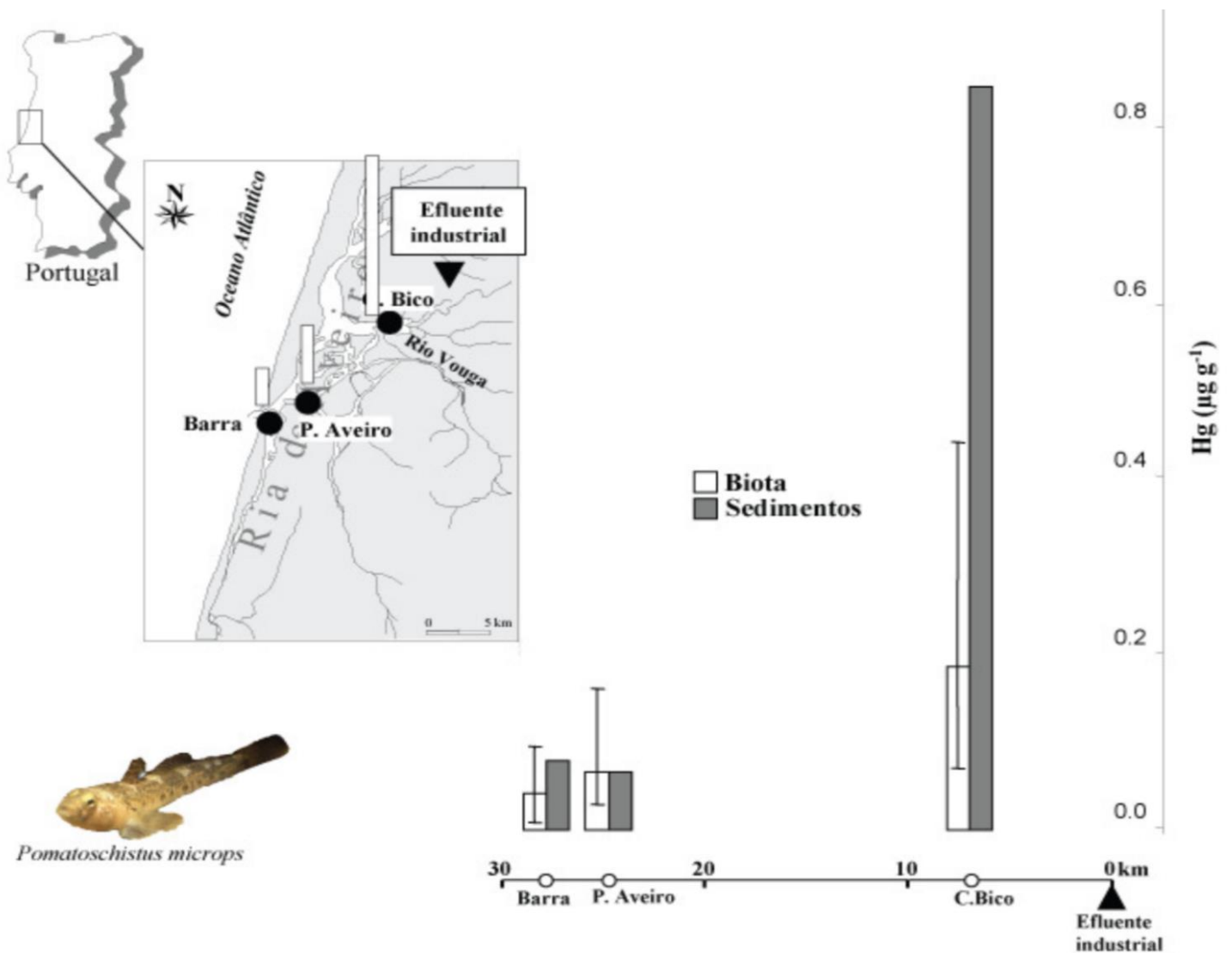
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**Map 29** – Índice de carga poluente (Leachate Pollution Index , LPI). Valores baseados nas concentrações (obtidas por digestão total dos sedimentos) de: As, Cu, Cr, Ni, Pb, Zn e Cd. A dimensão das marcas circulares cinzentas é proporcional aos valores de cada local de amostragem. *In: Martins et al. (2011)*

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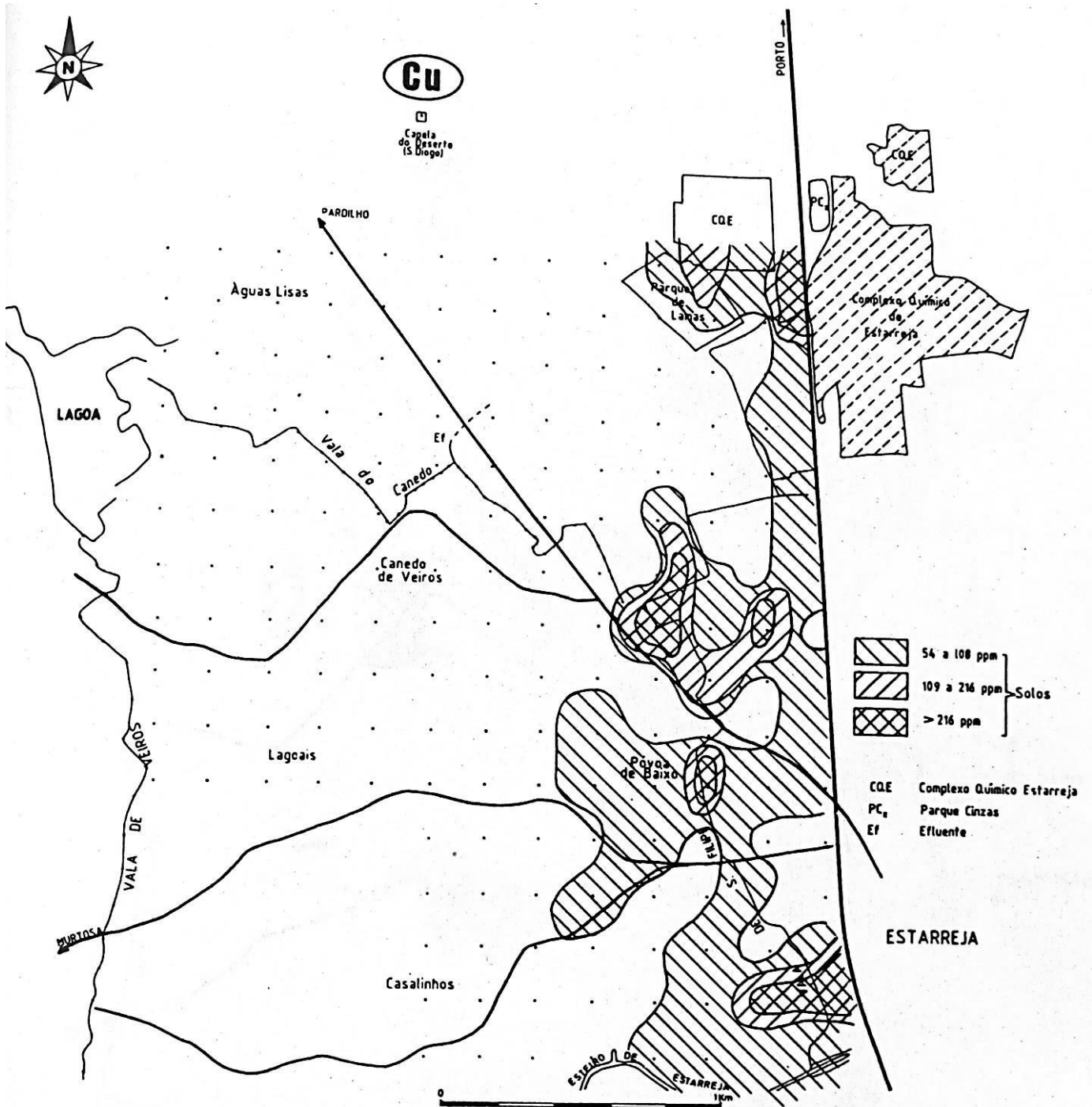
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**Map 30** – Concentrações de Hg em sedimentos superficiais finos ( $<63\mu\text{m}$ ) e no biota *P. microps*, presente na RIA (estações C. Bico, P. Aveiro e Barra, gradualmente afastadas da área mais contaminada). In: Abreu *et al.* (2011)

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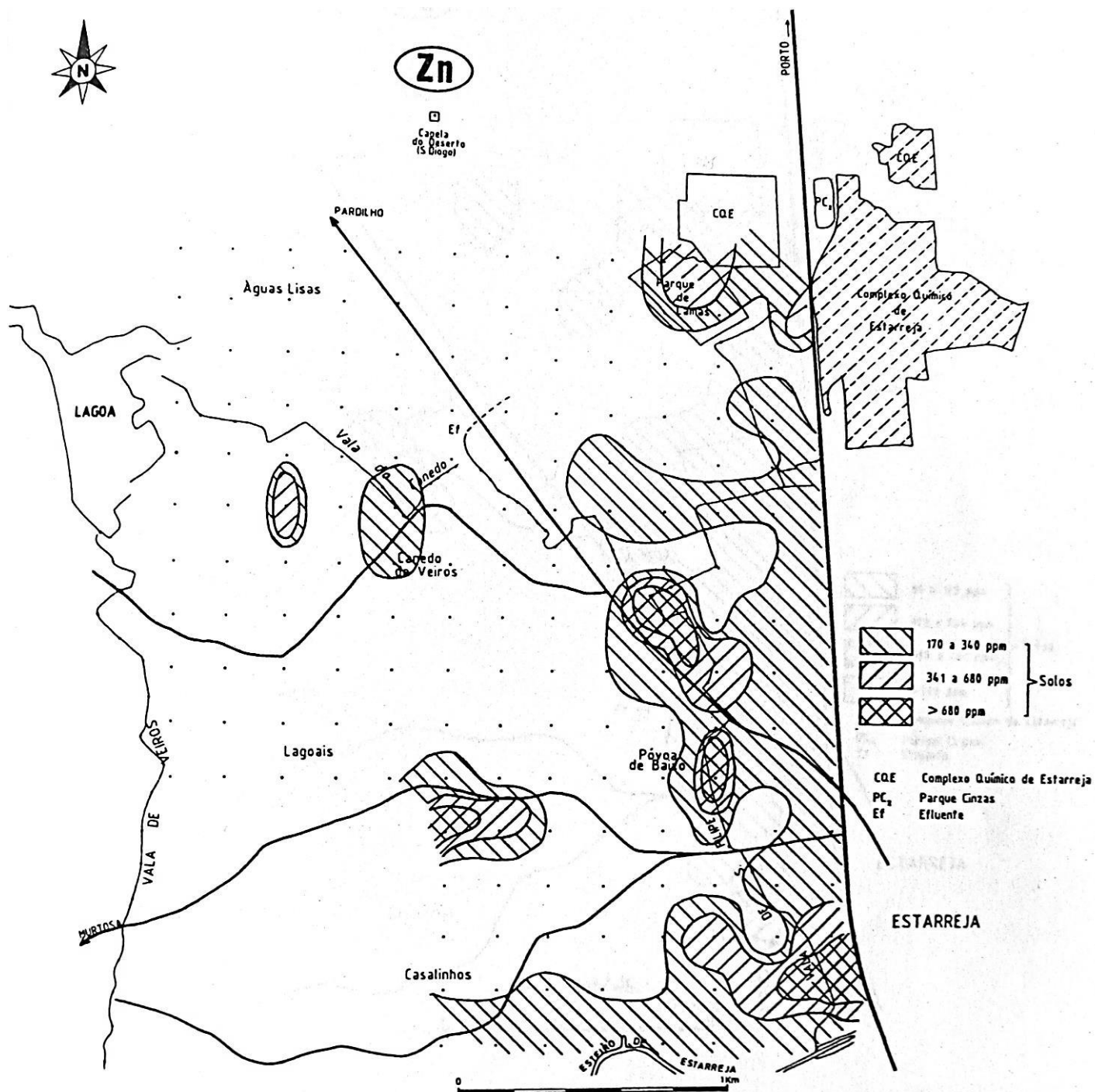
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**Map 31** – Cartografia dos teores de Cu no solo sa envolvente do CQE. *In*: Barradas (1993)

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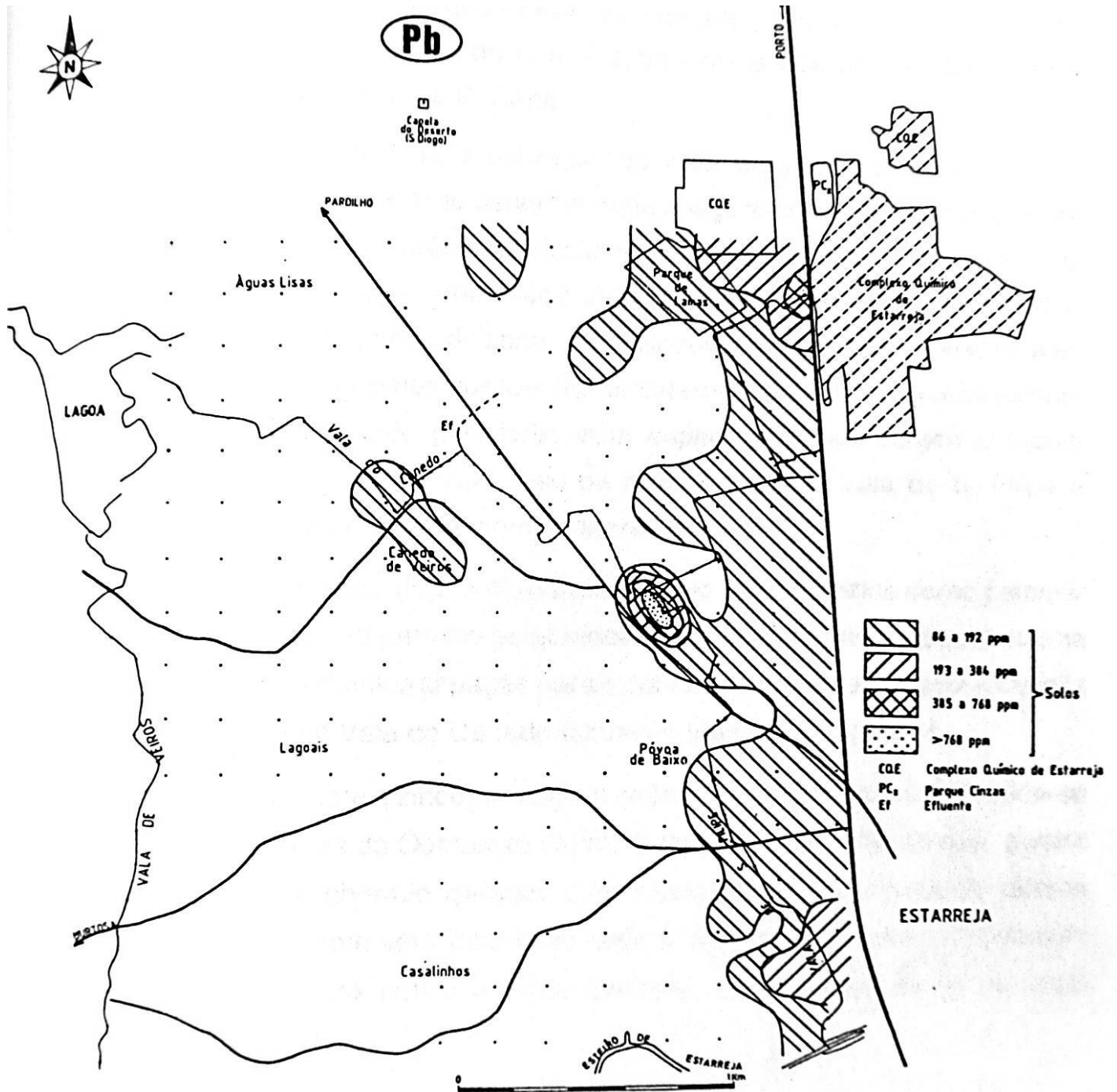


Map 32 – Cartografia dos teores de Zn no solo sa envolvente do CQE. *In*: Barradas (1993)



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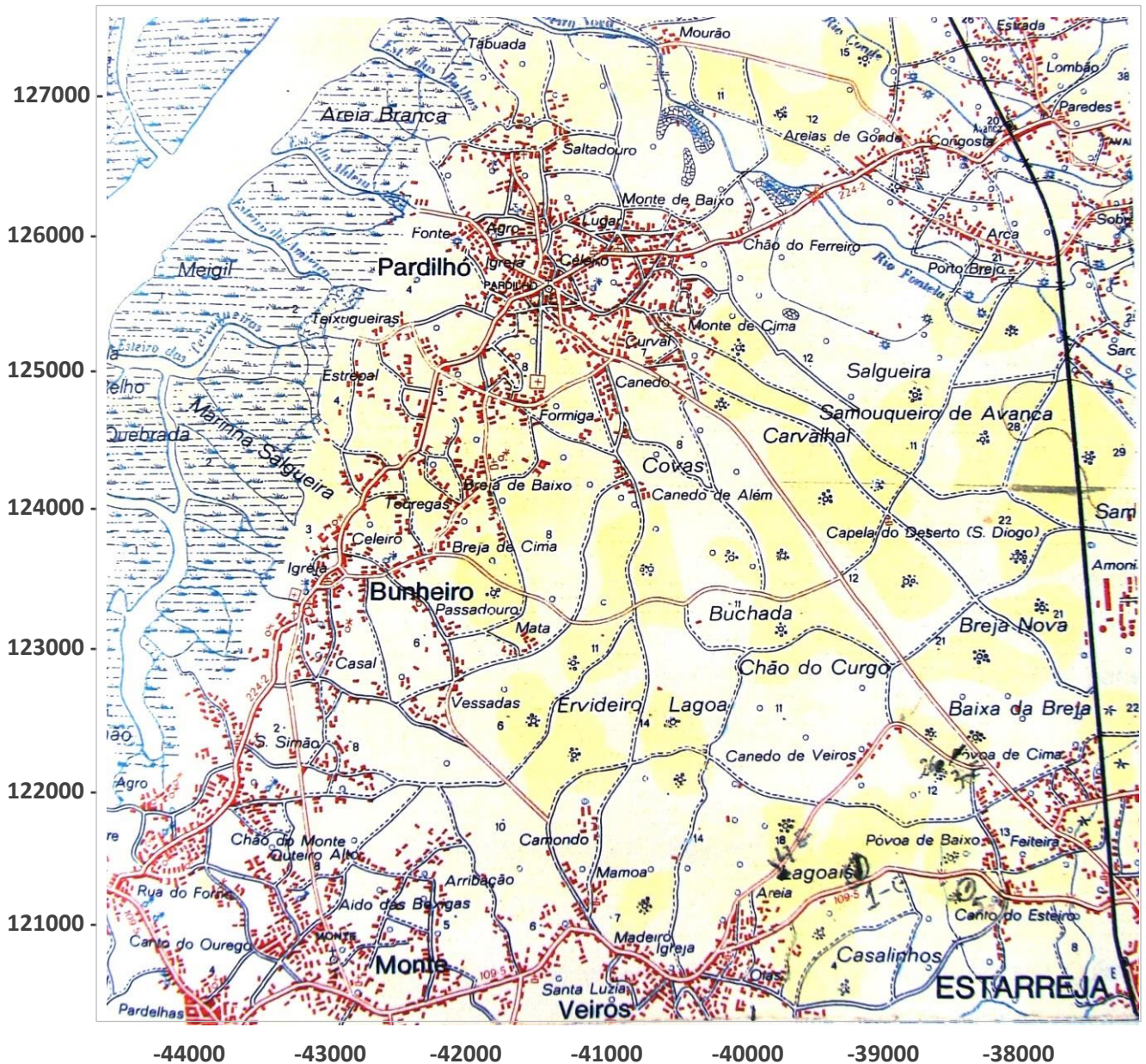
### Bibliographic Maps



**Map 33** – Cartografia dos teores de Pb no solo da envolvente do CQE. *In*: Barradas (1993)

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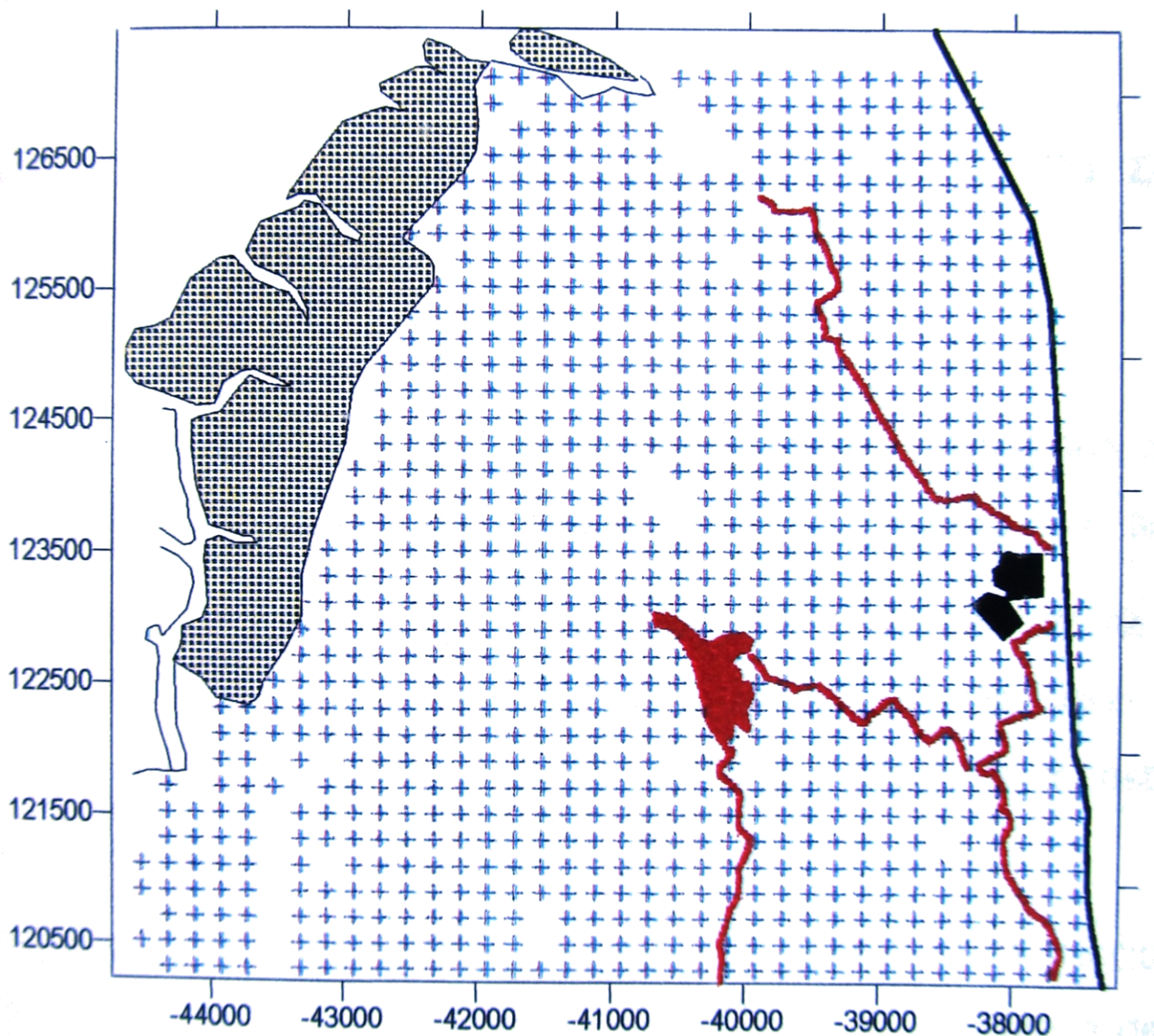
**Bibliographic Maps**



**Map 34** – Localização da área de estudo na envolvente do CQE (Adaptado da carta topográfica, folha 19-C de Ovar, Instituto Geográfico e Cadastral, 1963). In: Azevedo (1999)

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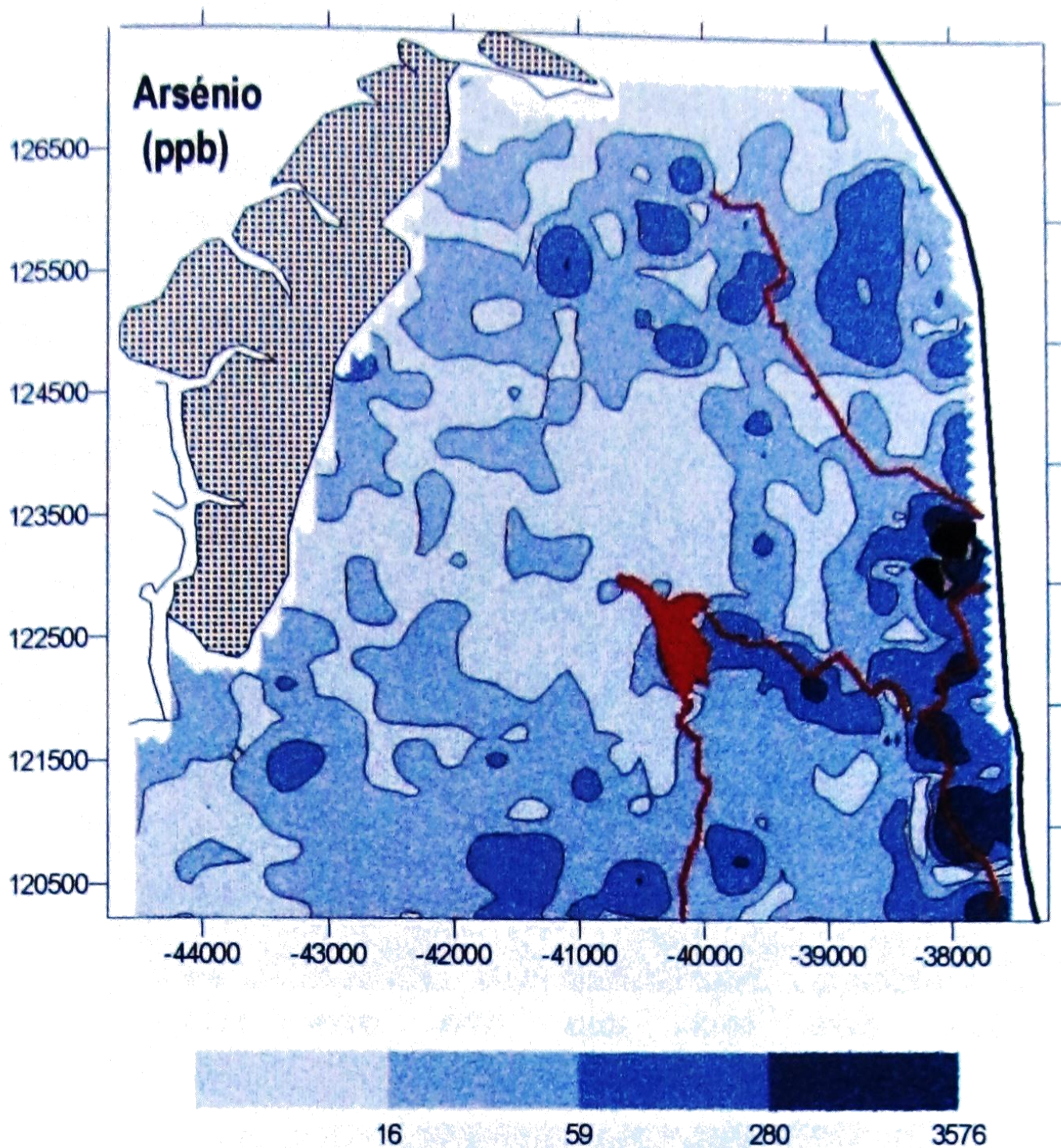
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**Map 35** – Grelha de amostragem de solos (985 amostras numa malha de 200 x 200m), com ilustração de cursos e receptores de contaminação (a vermelho) e de duas áreas-fonte de poluição (a preto) , na envolvente do CQE. *In: Azevedo(1999)*

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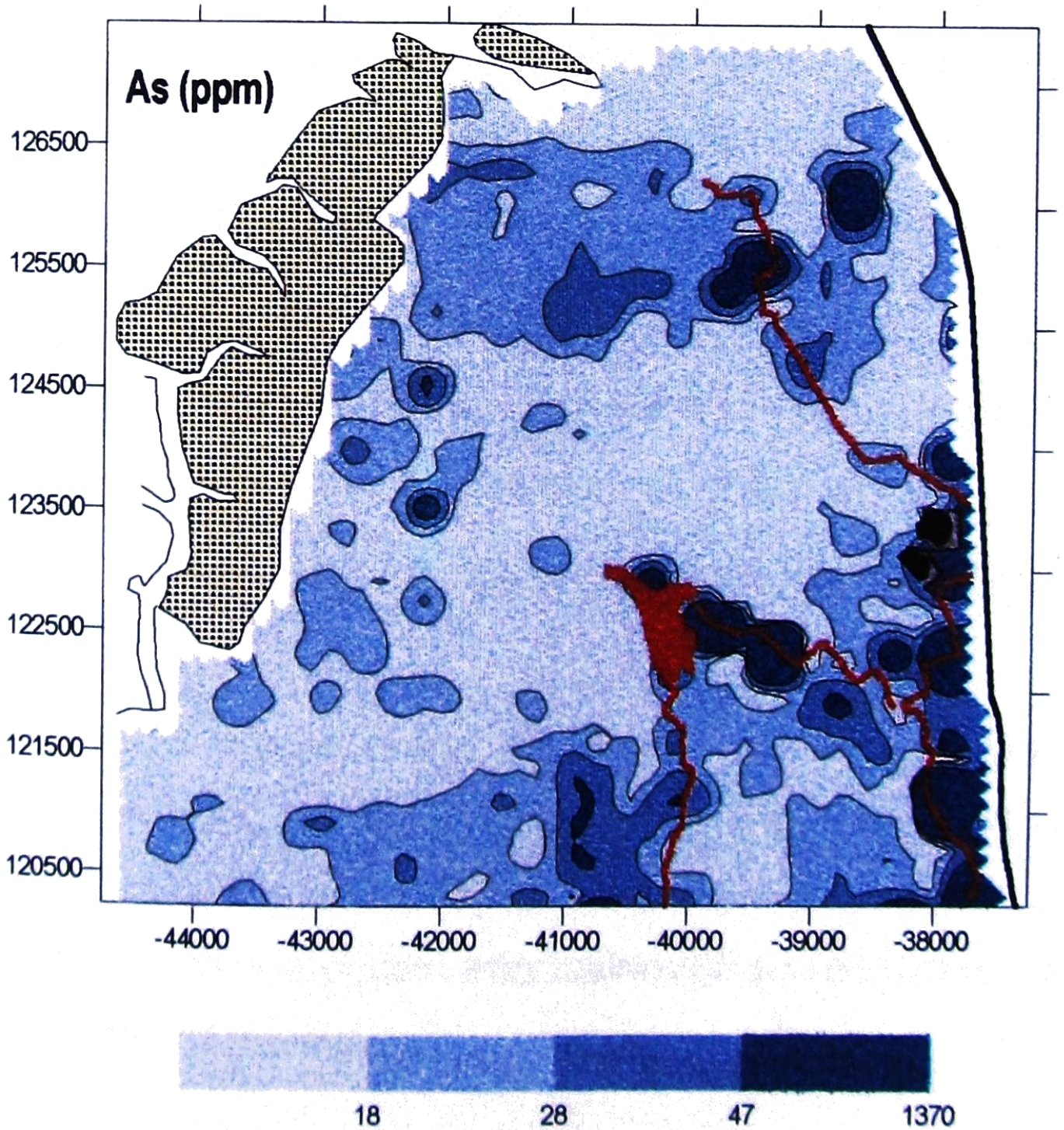
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**Map 36** – Cartografia de teores de As solúvel em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*

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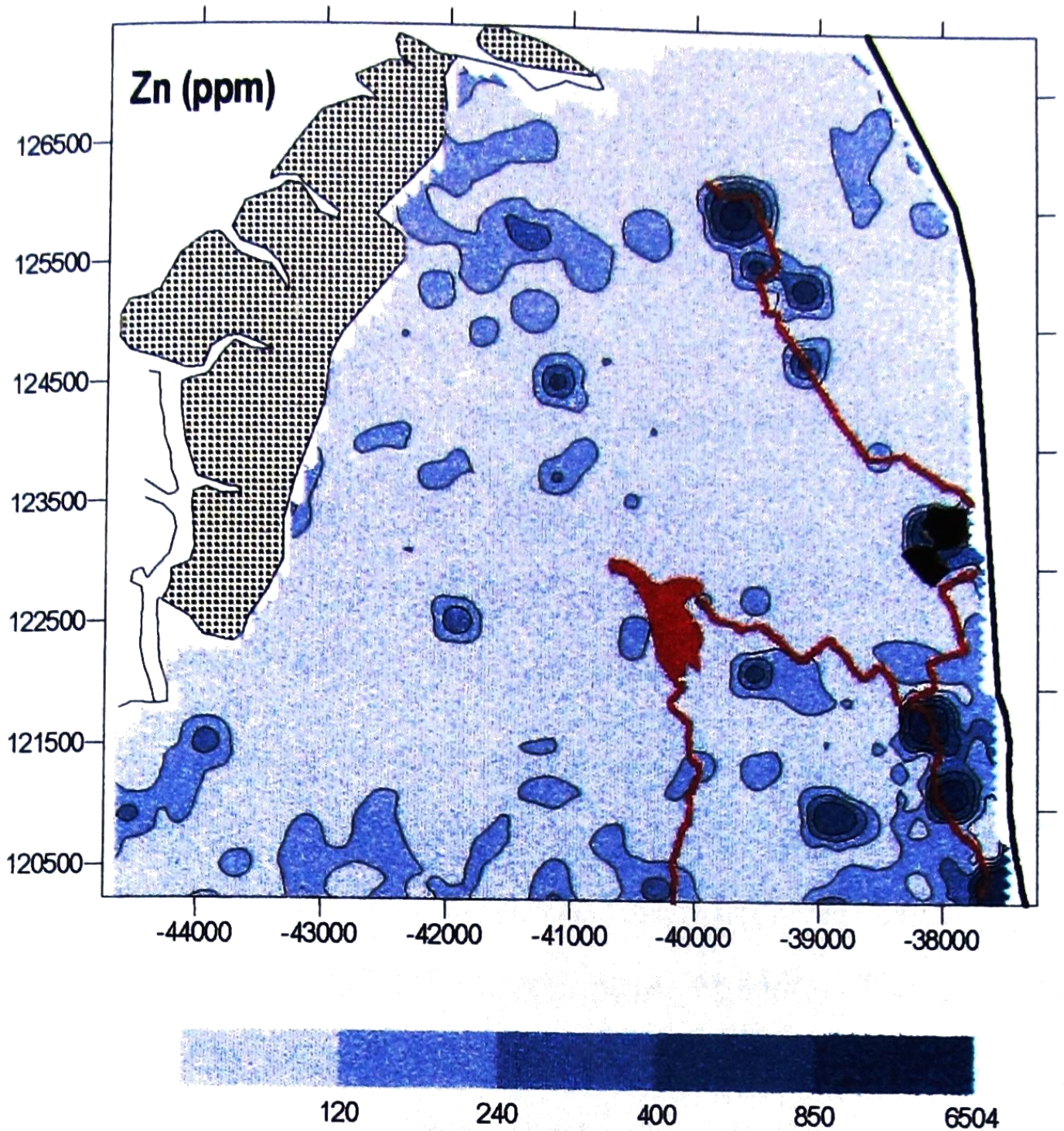
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**Map 37** – Cartografia de teores de As em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*

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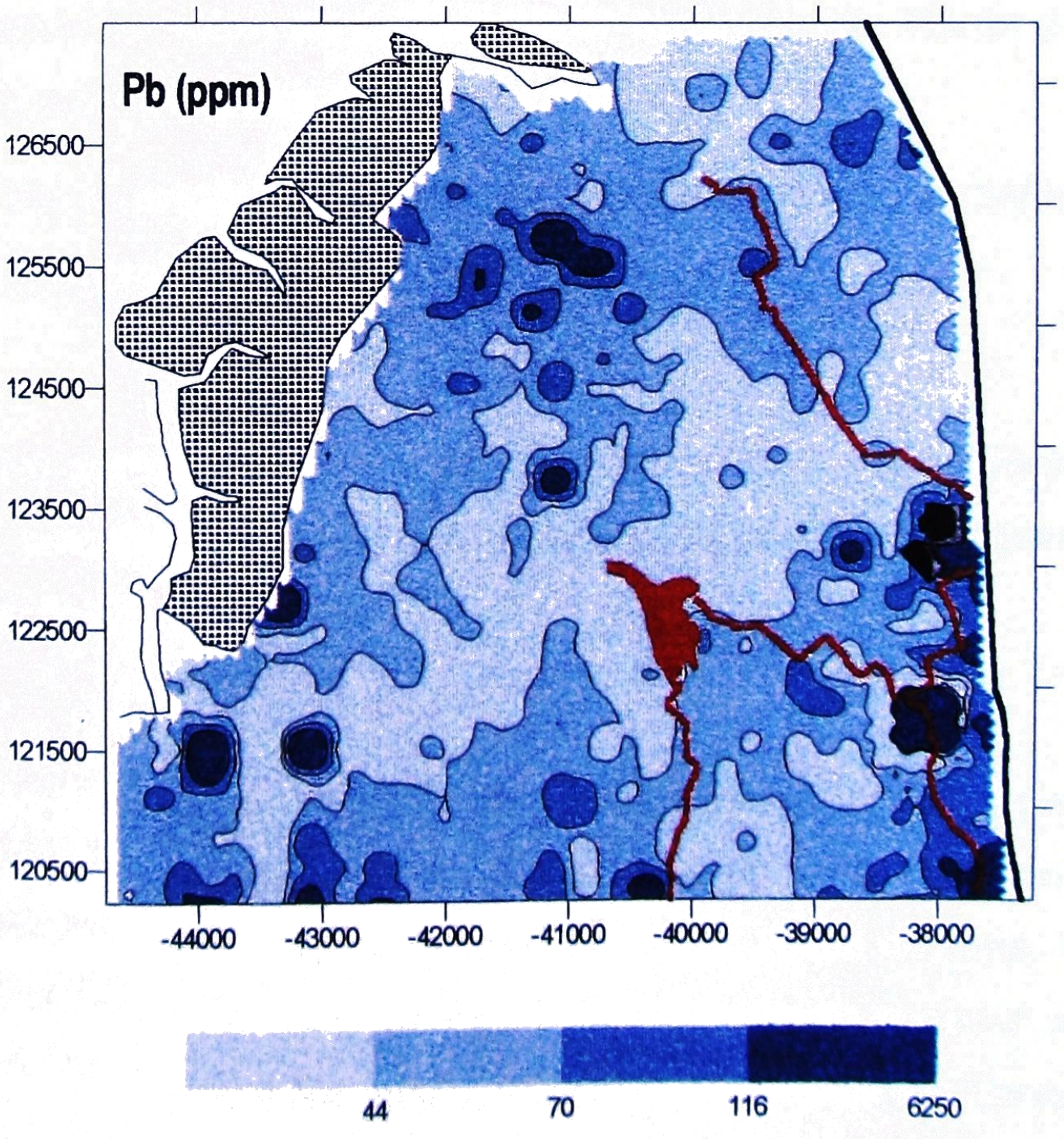
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**Map 38** – Cartografia de teores de Zn em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*

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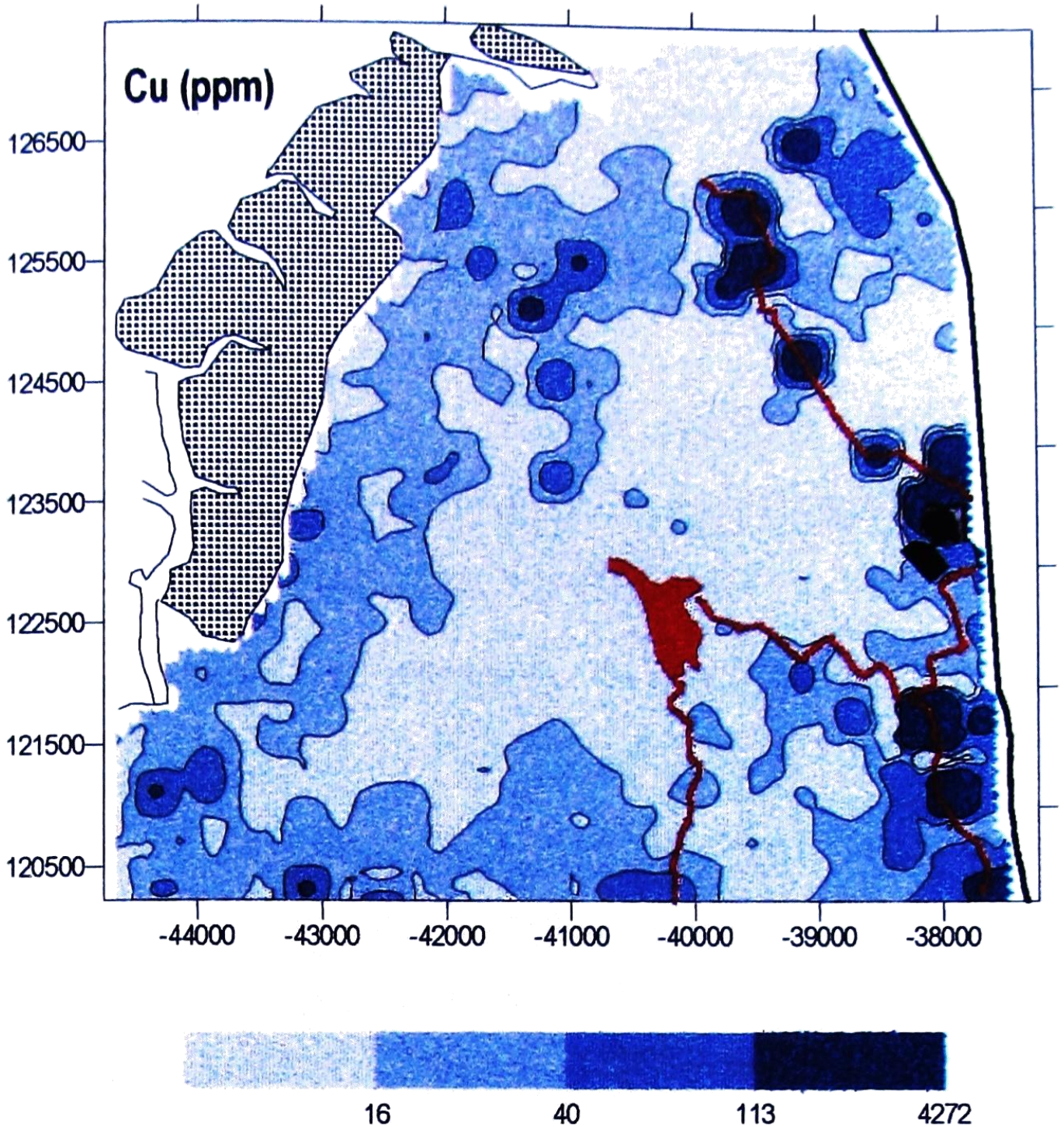
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**Map 39** – Cartografia de teores de Pb em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*

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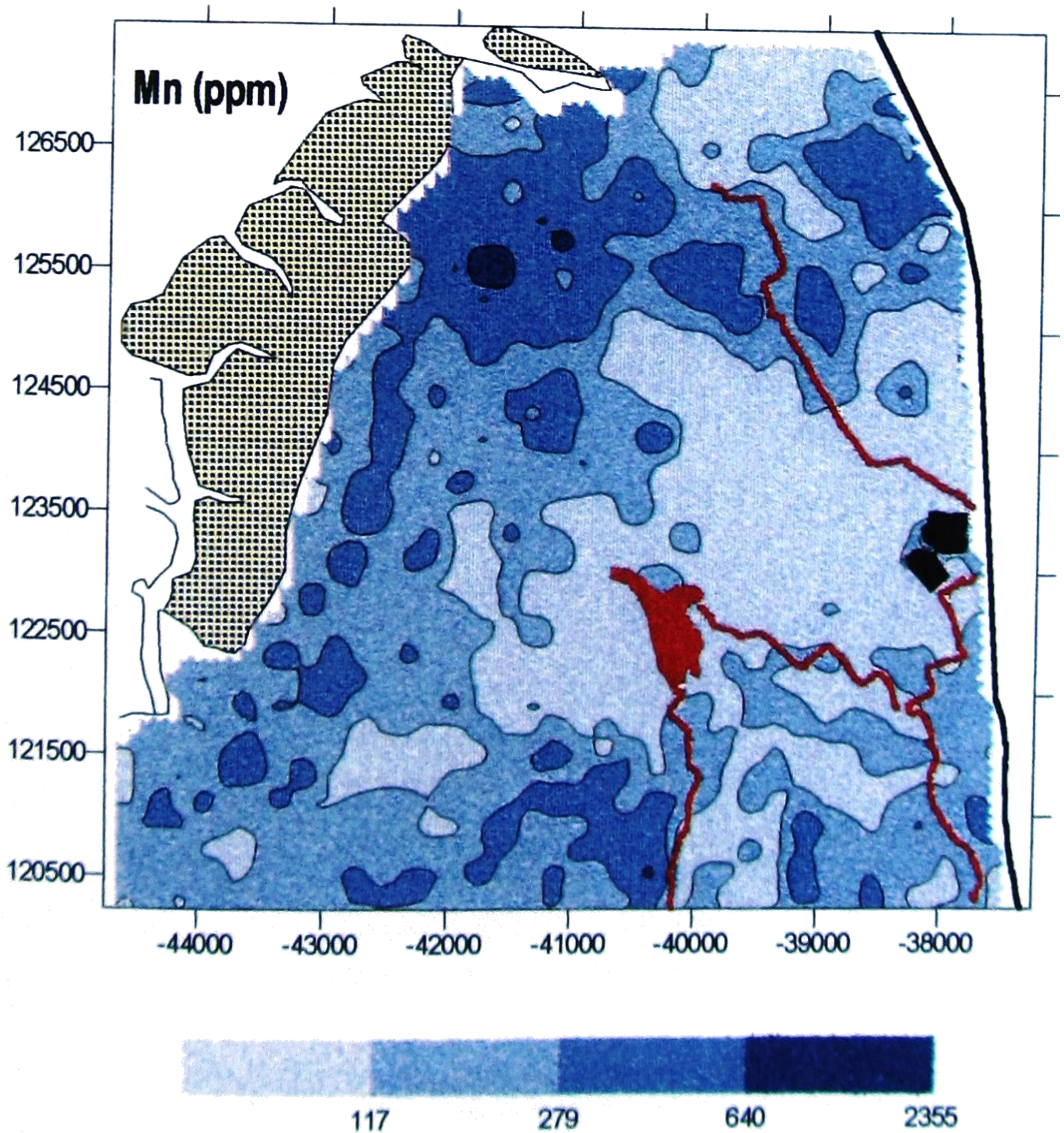


**Map 40** – Cartografia de teores de Cu em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*



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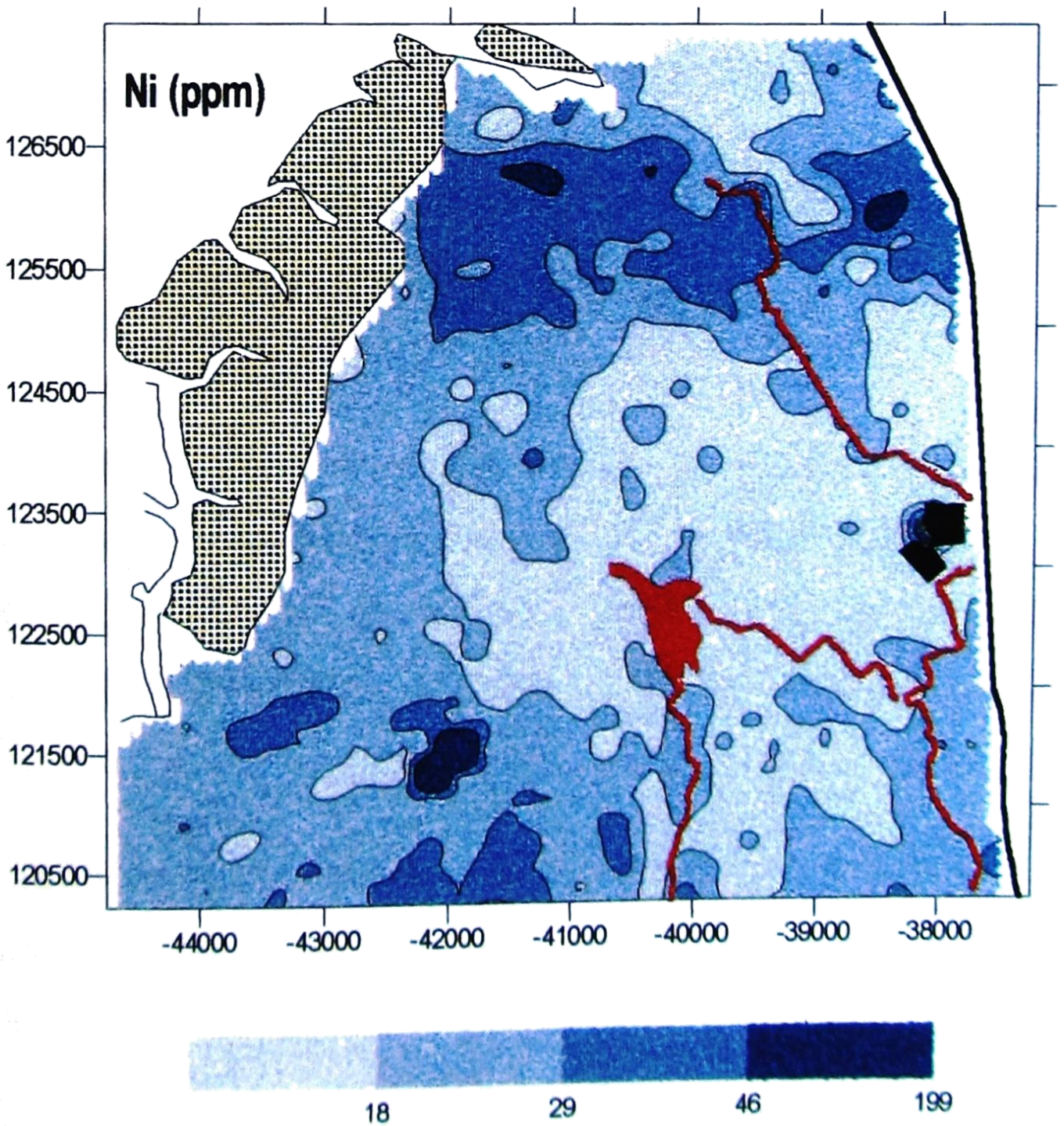
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**Map 41** – Cartografia de teores de Mn em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*

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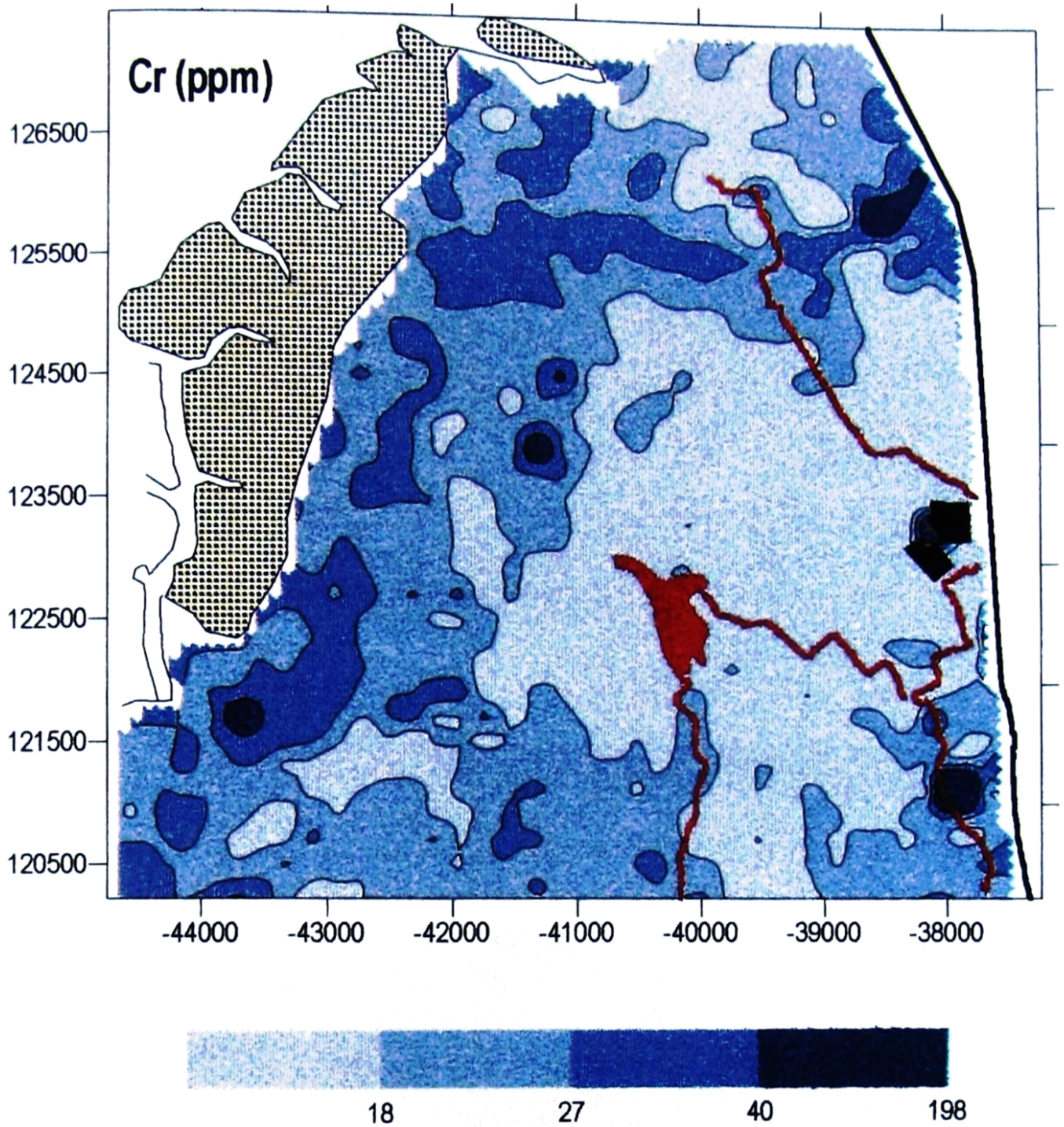
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**Map 42** – Cartografia de teores de Ni em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*

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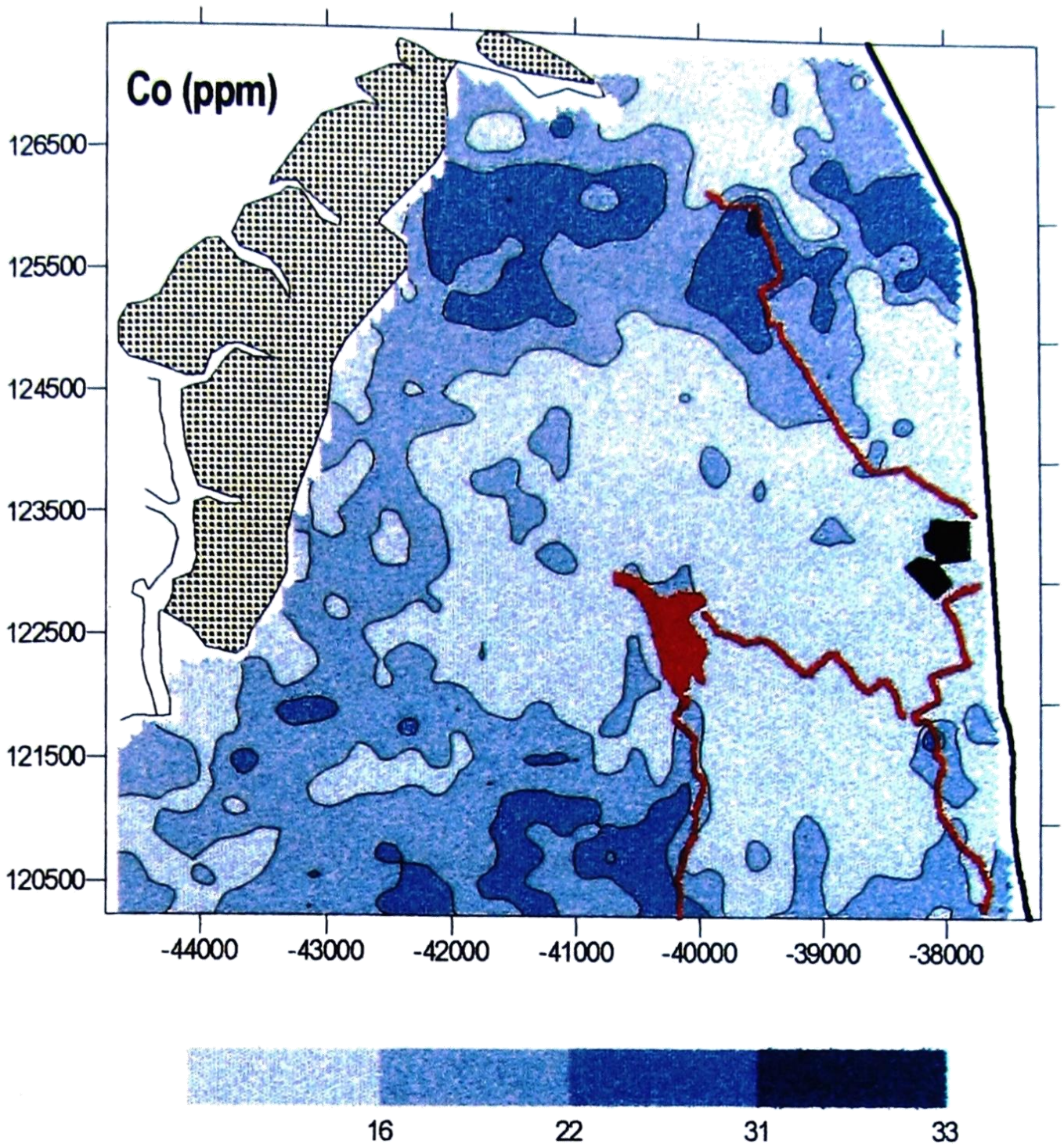
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**Map 43** – Cartografia de teores de Cr em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*

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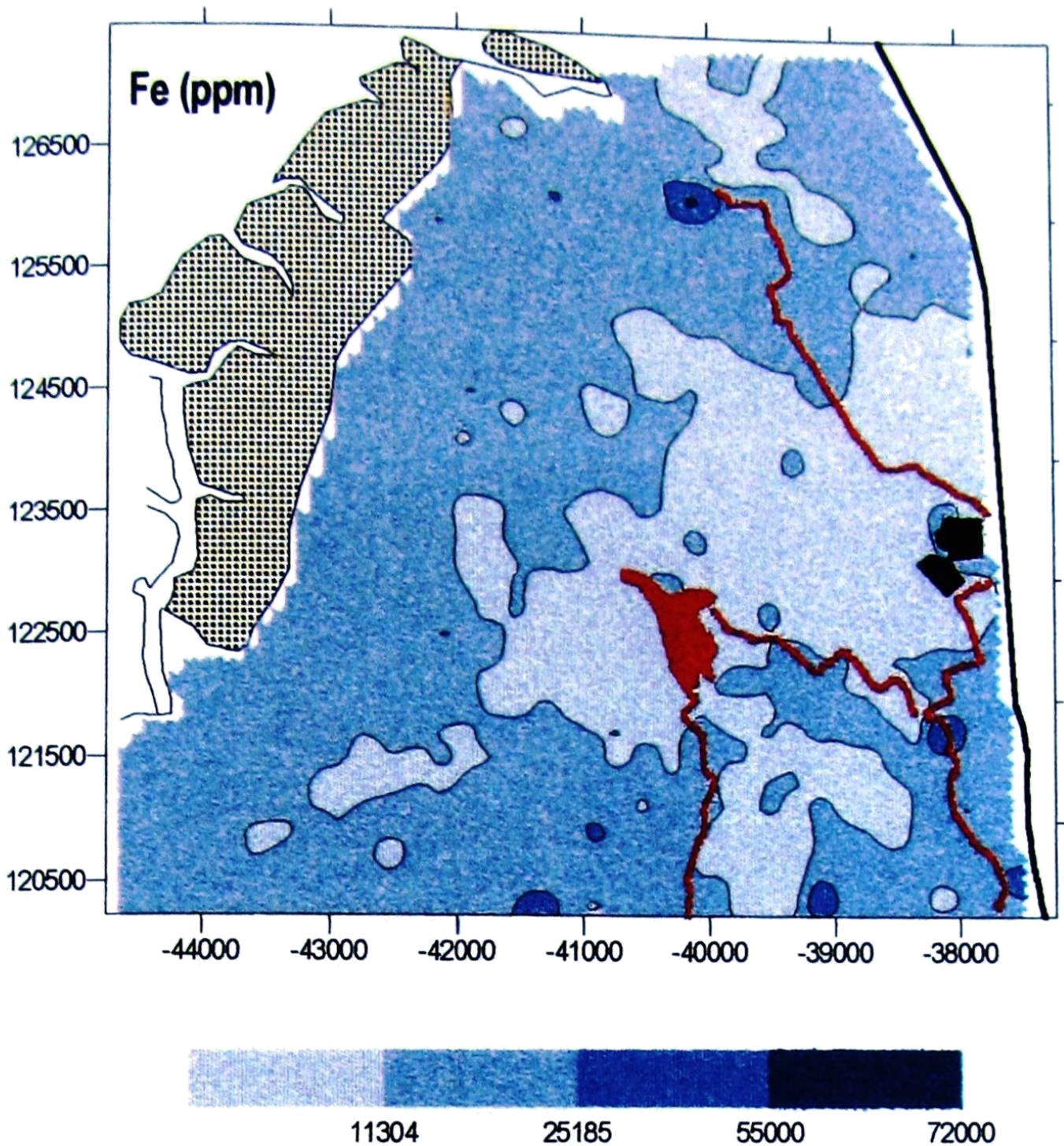
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**Map 44** – Cartografia de teores de Co em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*

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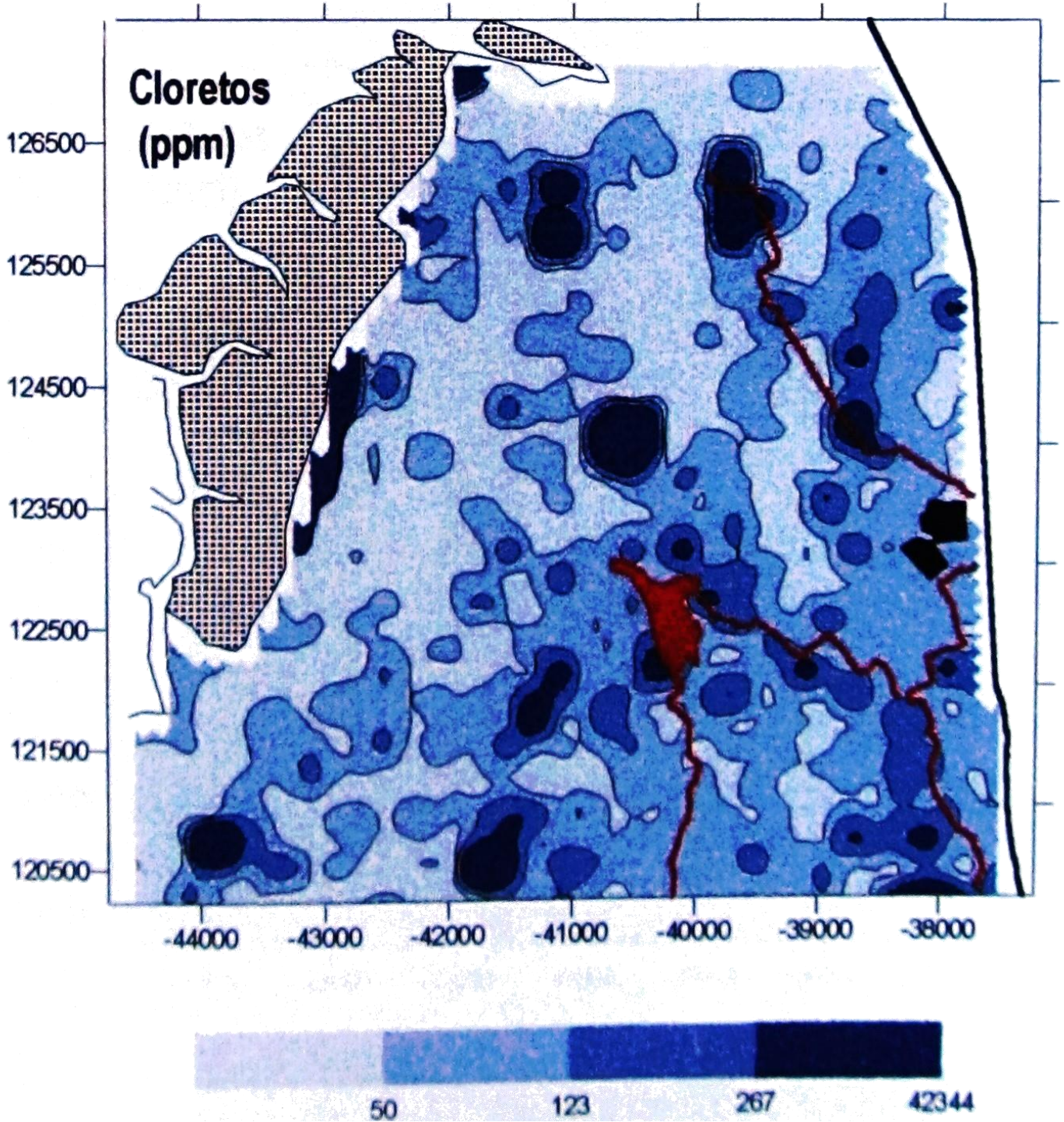
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**Map 45** – Cartografia de teores de Fe em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*

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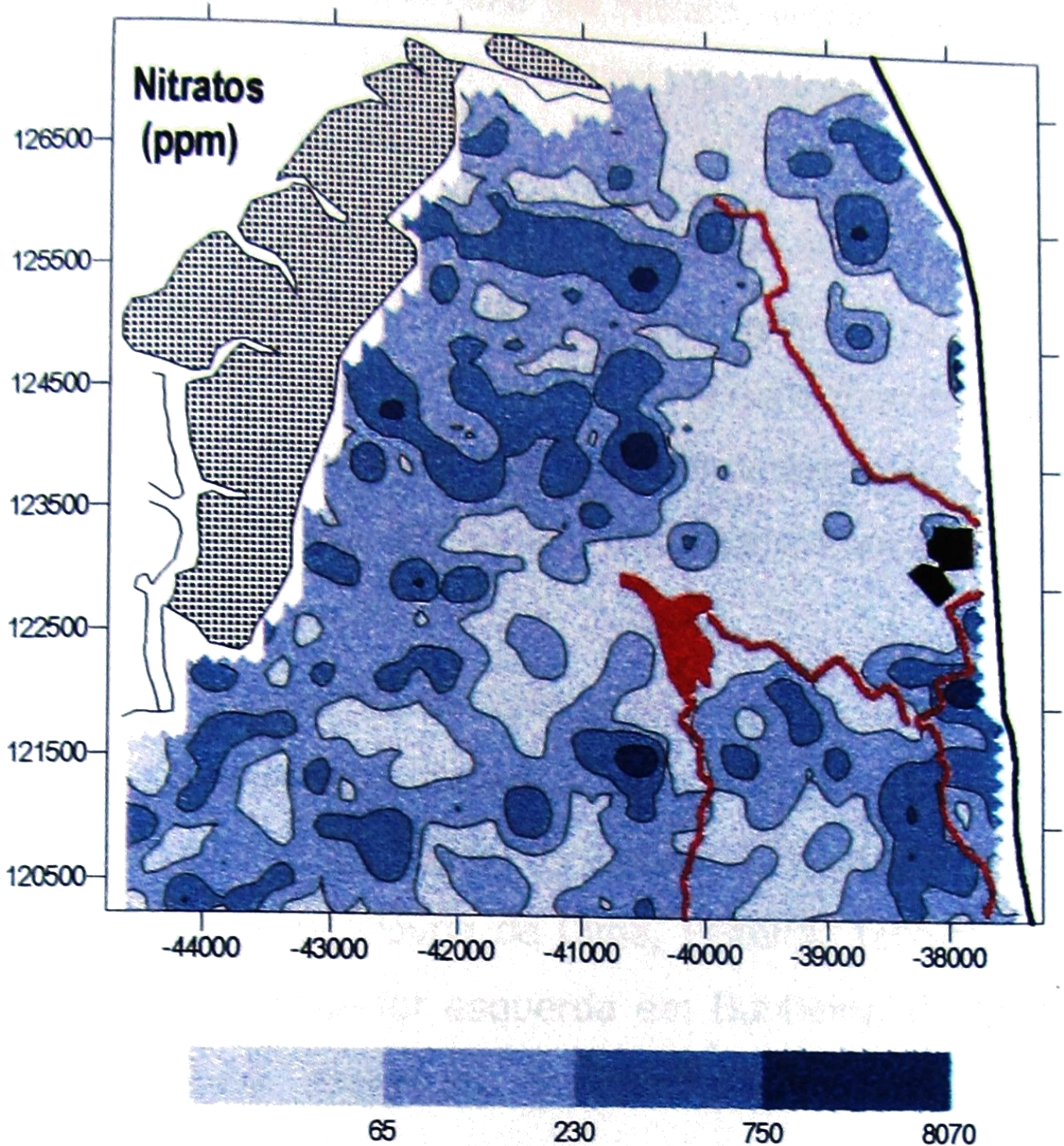
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**Map 46** – Cartografia de teores de Cl<sup>-</sup> em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*

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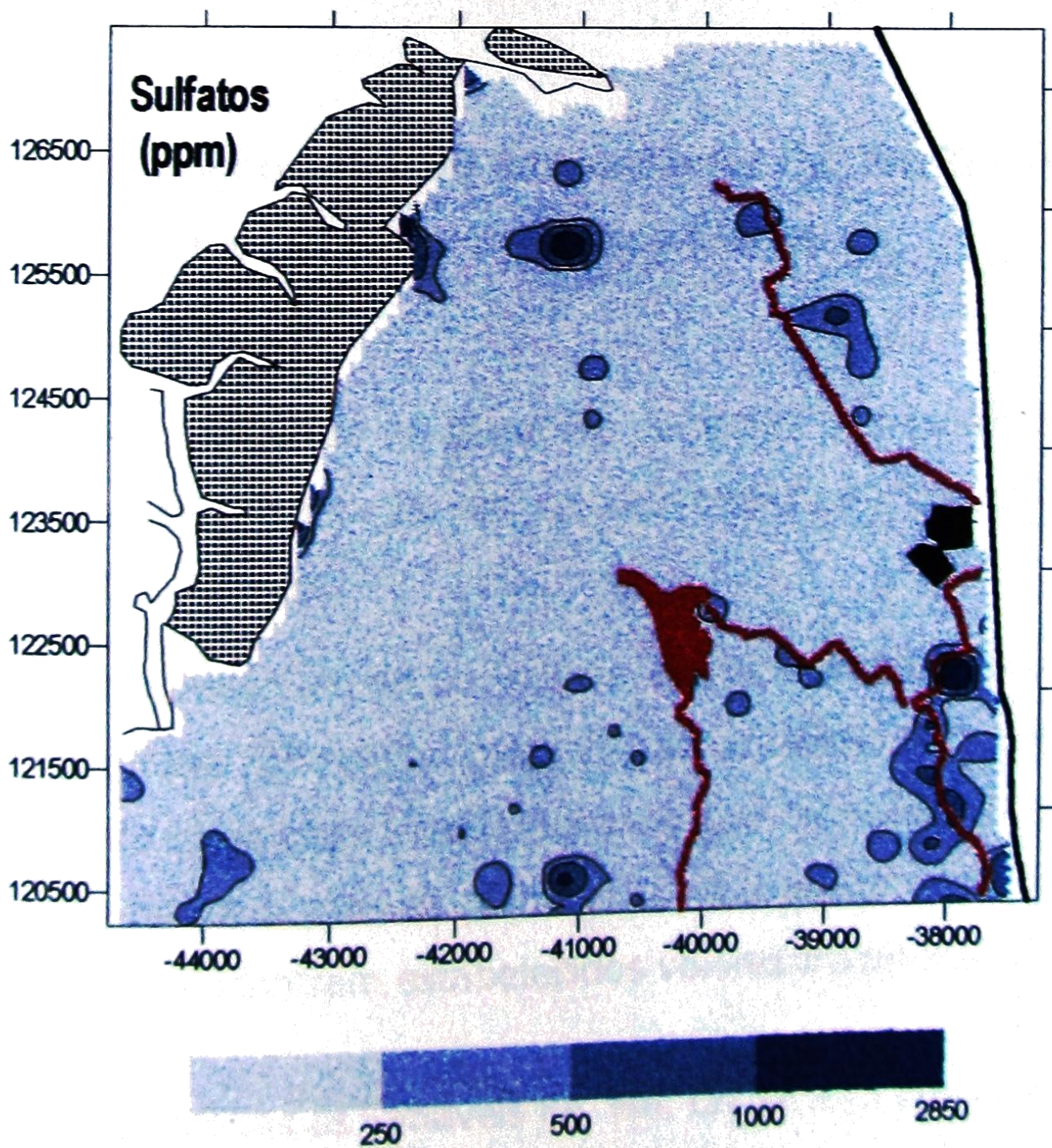
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**Map 47** – Cartografia de teores de  $\text{NO}_3^-$  em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*

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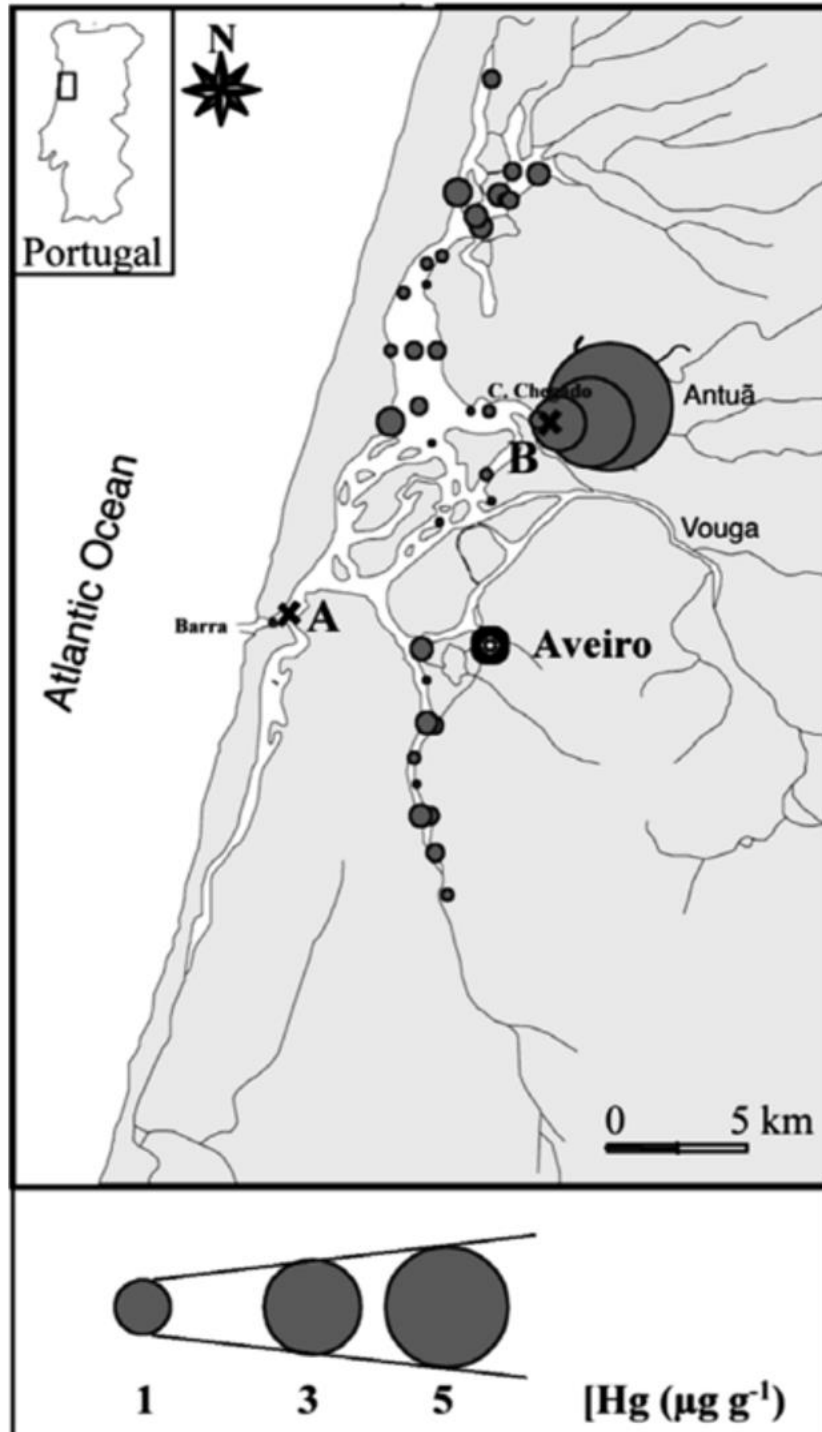


**Map 48** – Cartografia de teores de  $\text{SO}_4^{2-}$  em amostras de solo (na envolvente do CQE).  
*In: Azevedo(1999)*



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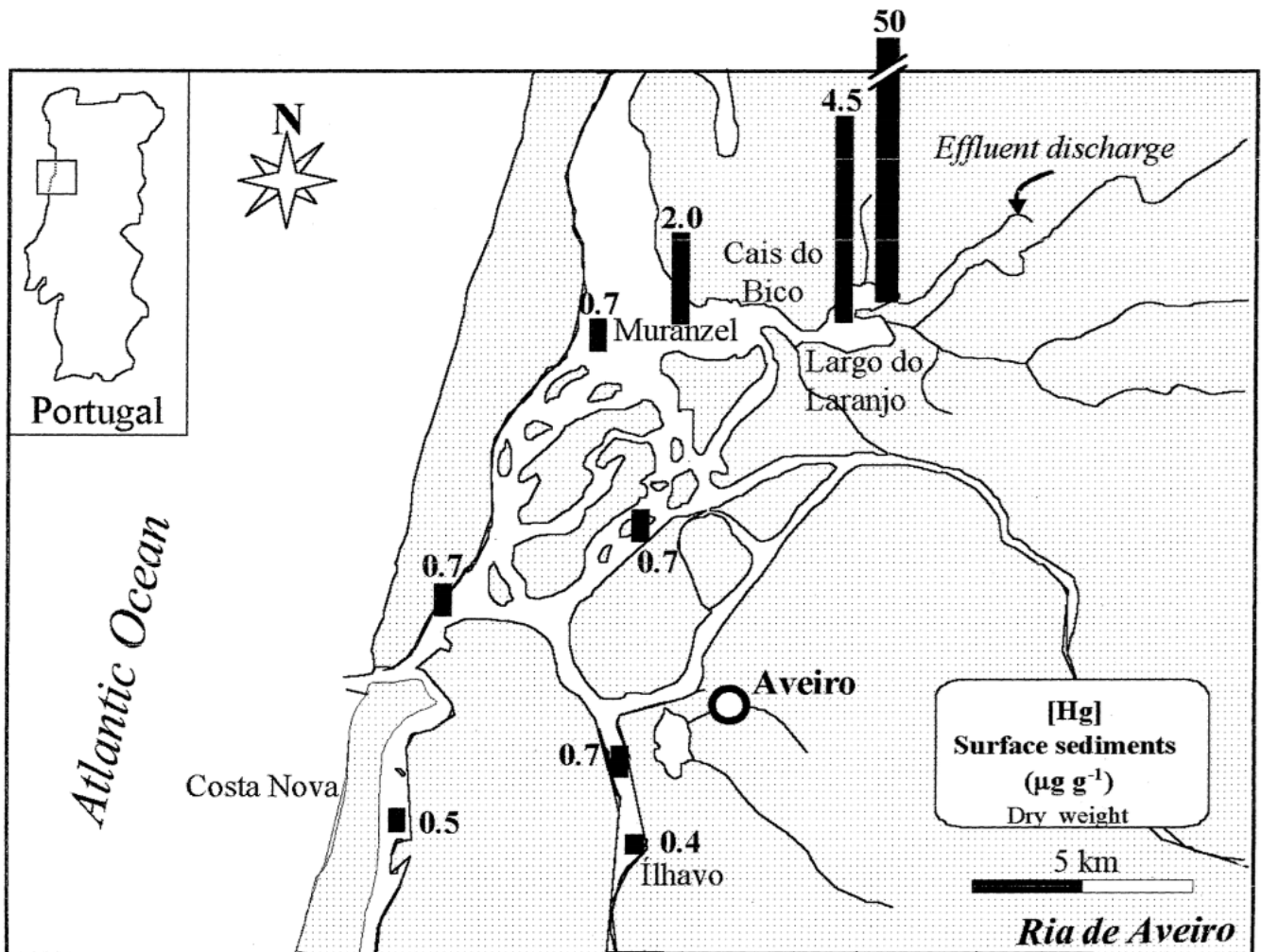
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**Map 49** – Total mercury concentrations ( $\mu\text{g/g}$ , dry weight) in surface sediments of RIA, and sampling sites for *C. maenas* (A and B). *In*: Pereira *et al.* (2006)

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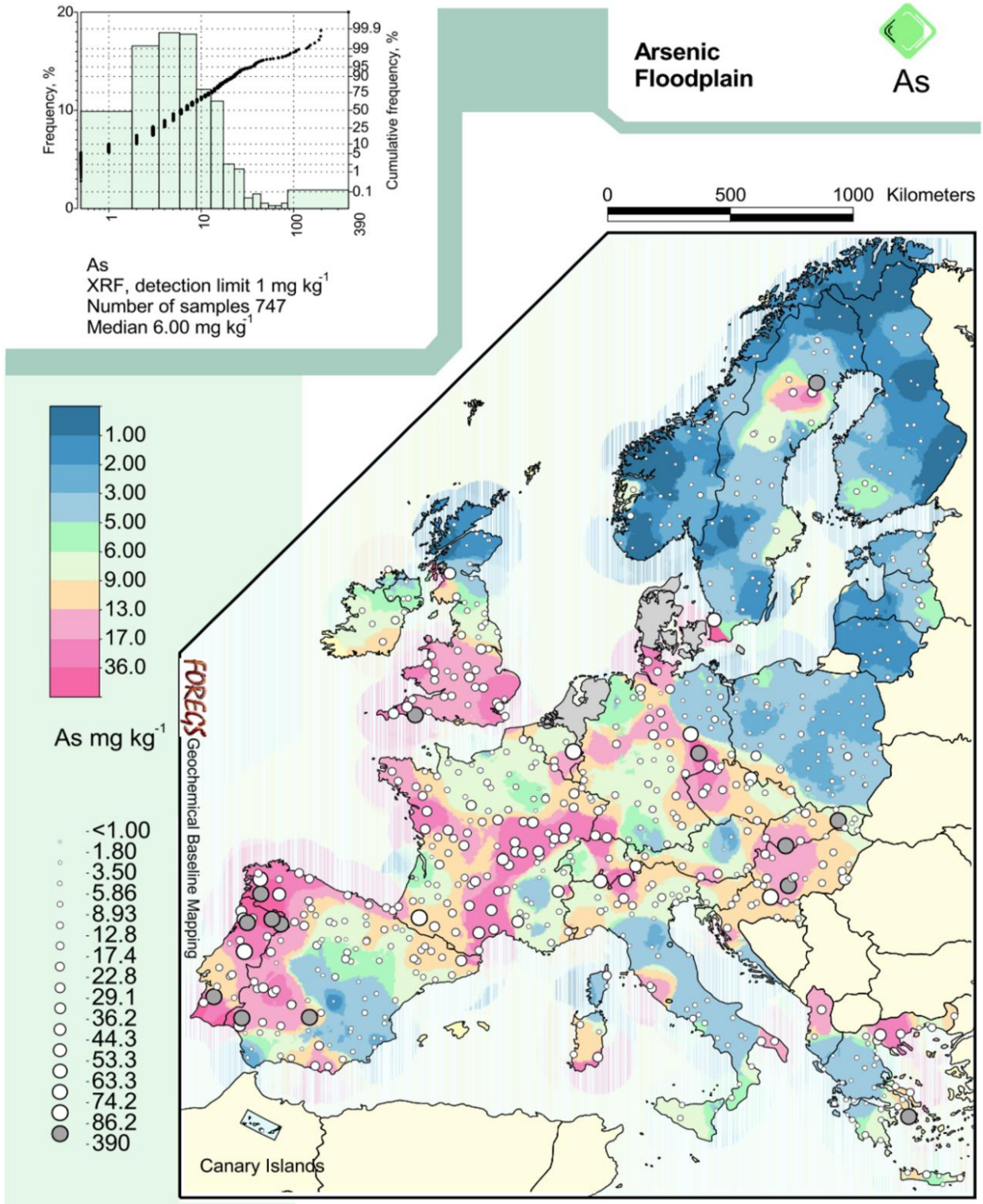
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**Map 50** – Sampling sites (Largo do Laranjo, Muranzel, Cais do Bico, Costa Nova and Ilhavo) and Hg concentration (µg/g) in surface sediments of RIA. *In: Abreu et al. (2000)*

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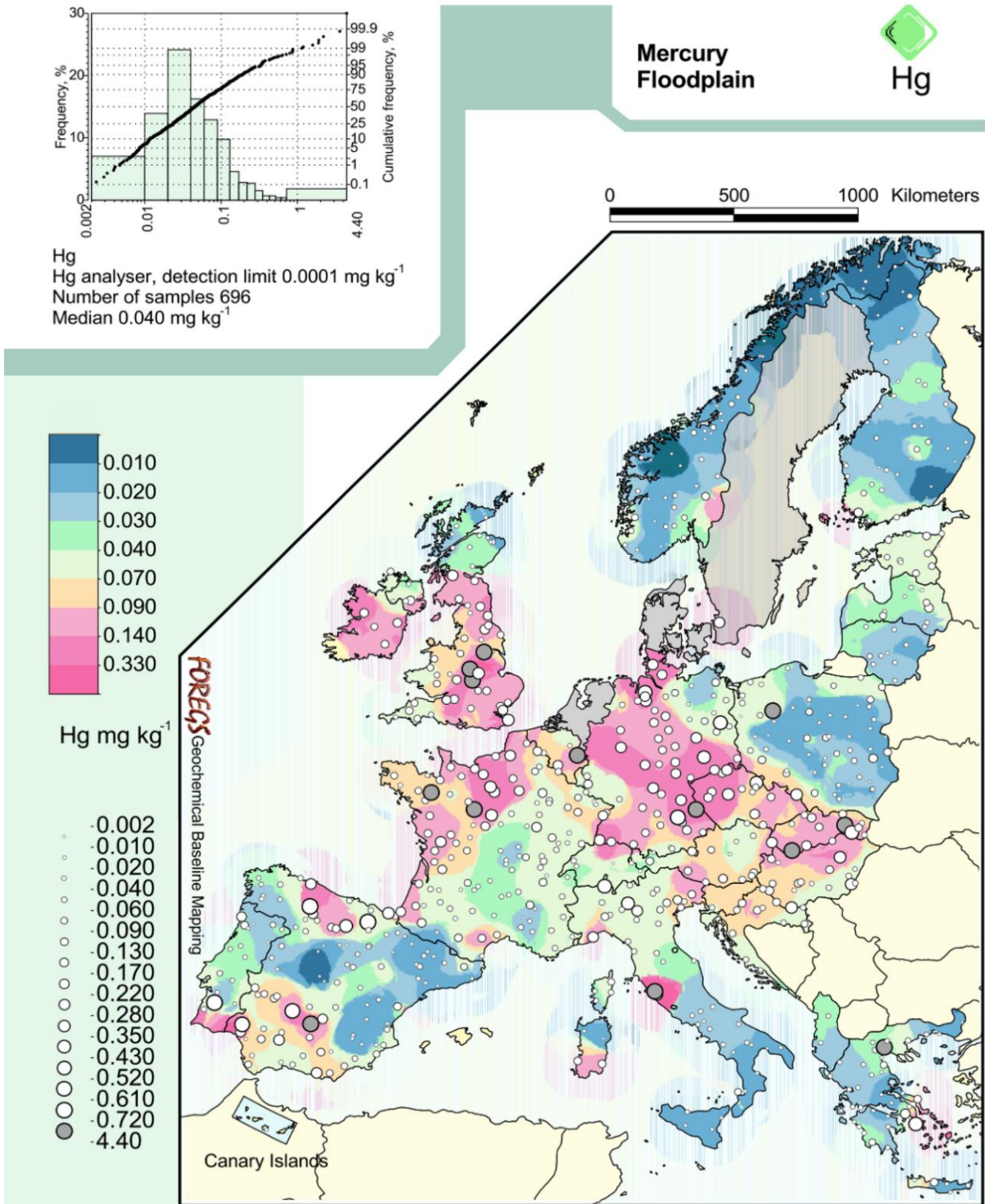
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**Map 51** – Arsenic floodplain sediment - geochemical distribution map - a contribution to IUGS/IAGC Global Geochemical Baselines (FOREGS). *In*: Salminen (ed.), 2005 – electronic version available in: <http://weppi.gtk.fi/publ/foregsatlas.html>

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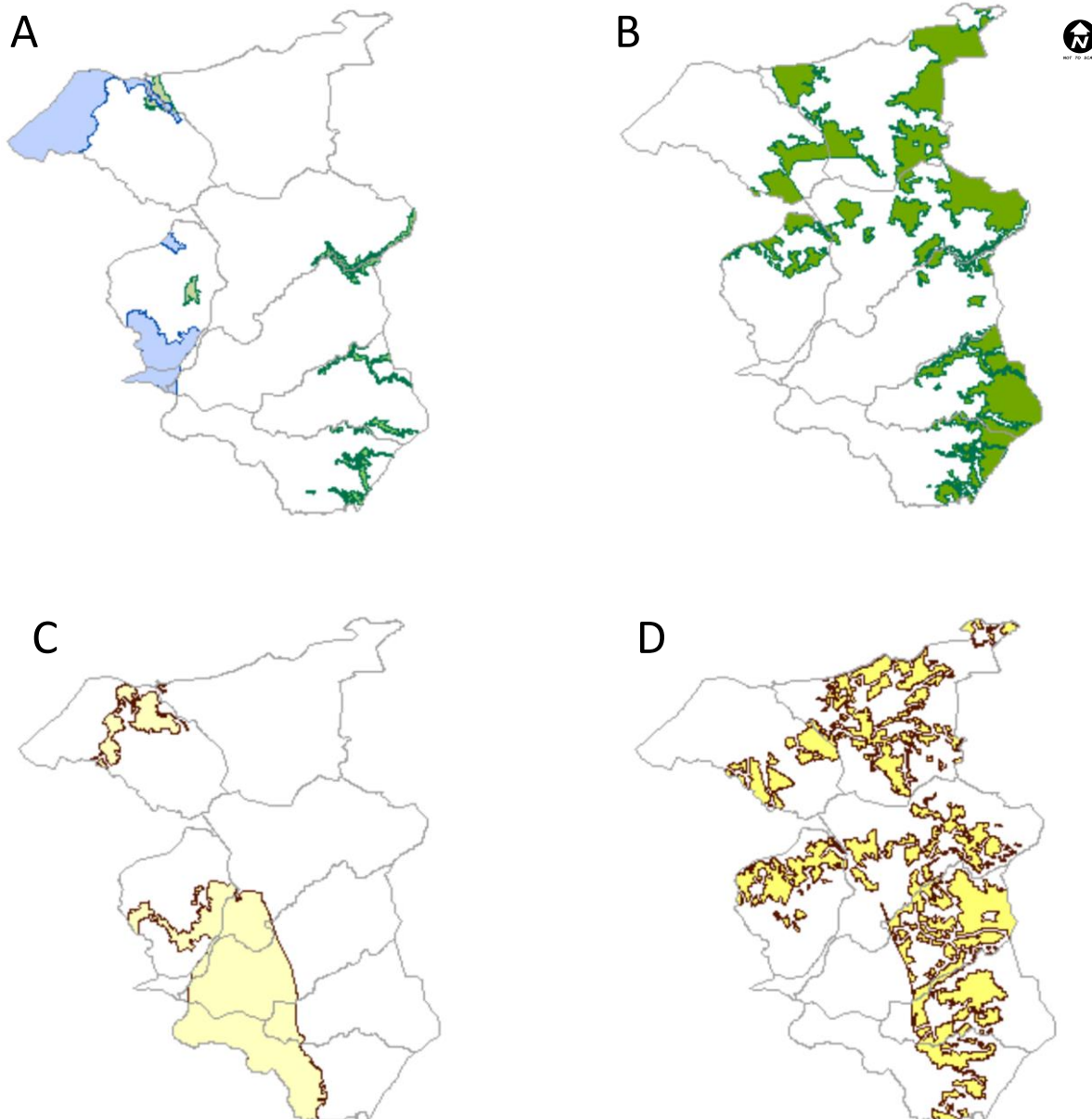
### Bibliographic Maps



**Map 52** – Mercury floodplain sediment - geochemical distribution EU map - a contribution to IUGS/IAGC Global Geochemical Baselines, FOREGS). *In*: Salminen (ed.), 2005 – electronic version available in: <http://weppi.gtk.fi/publ/foregsatlas.html>

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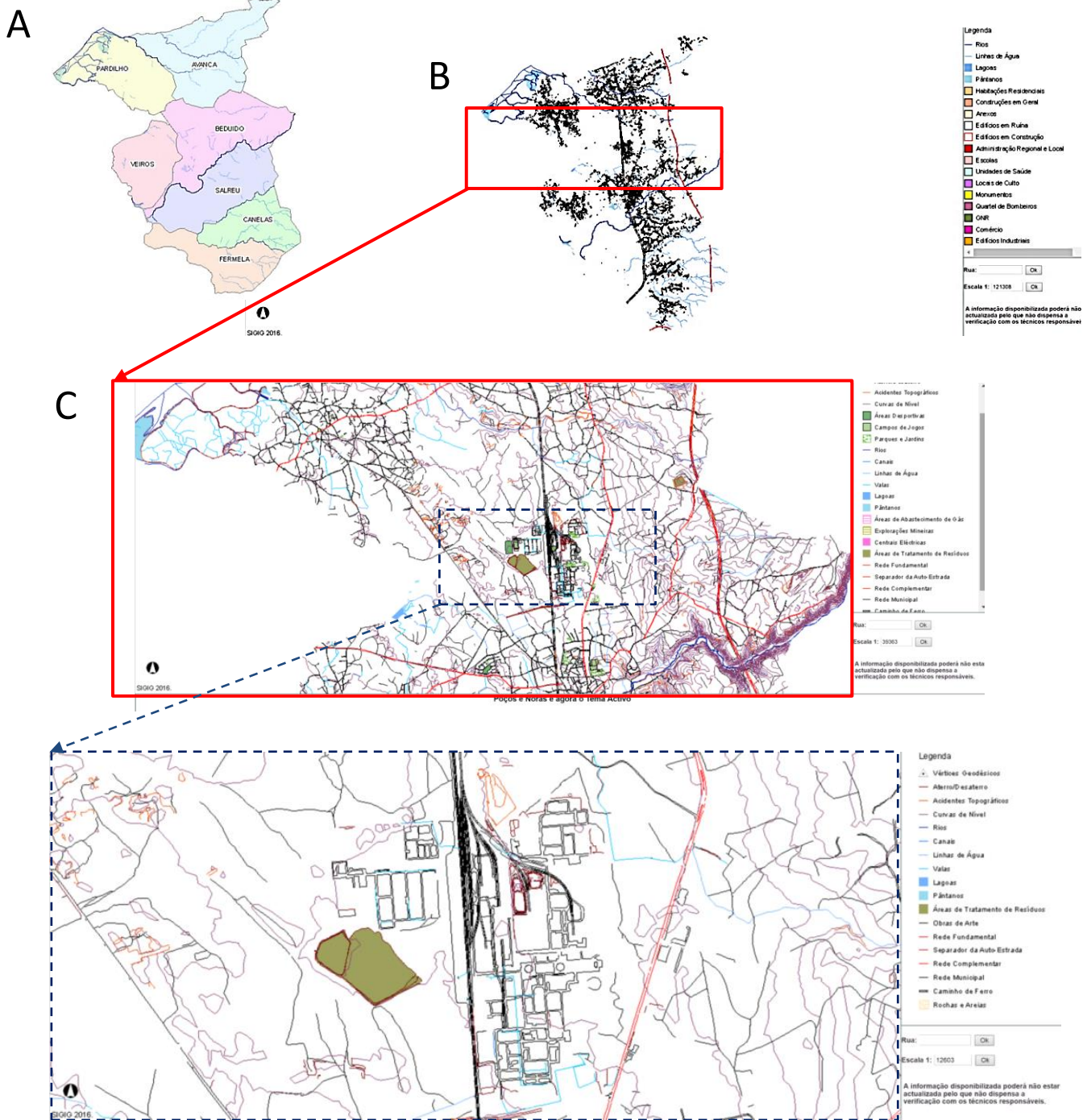
Official cartography, planning maps



**Map 53** – Concelho de Estarreja: A – Espaço Natural (Azul); Espaço floresta de conservação estrita e de protecção (verde claro e escuro respectivamente) e com estatuto de conservação; B – Espaço Florestal de Produção; C – Espaço agrícola de conservação; D – Espaço agrícola de produção (escala 1:121200). SIG of the Intermunicipal Community Region and Tourism Centre of Portugal, available in: [http://sig.cm-estarreja.pt/website/ordenamento\\_new/viewer.htm](http://sig.cm-estarreja.pt/website/ordenamento_new/viewer.htm)

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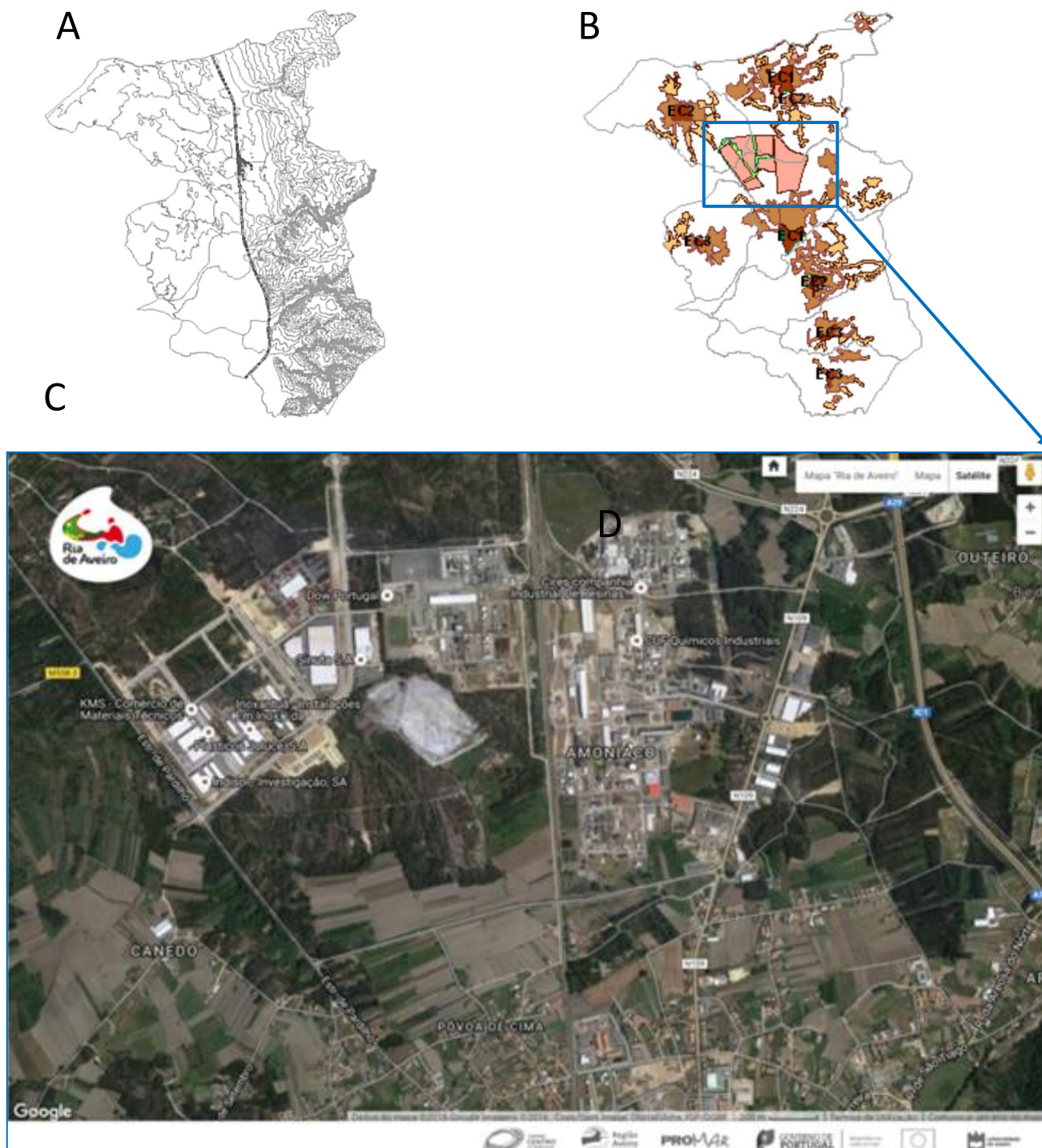
Official cartography, planning maps and orthophotomaps



**Map 54** – Enquadramento do CQE: A -Limites administrativos de Estarreja e suas freguesias; B - distribuição de edificado, infraestruturas viárias e principais cursos de água (escala 1:121200); C – Detalhe da envolvente do CQE, área verde – tratamento de resíduos industriais (escala 1:39500); D – CQE (escala 1:12600). SIG of the Intermunicipal Community Region and Tourism Centre of Portugal, available in: <http://sig.cm-estorreja.pt/> and <http://sig.riadeaveiro.pt/web/#>

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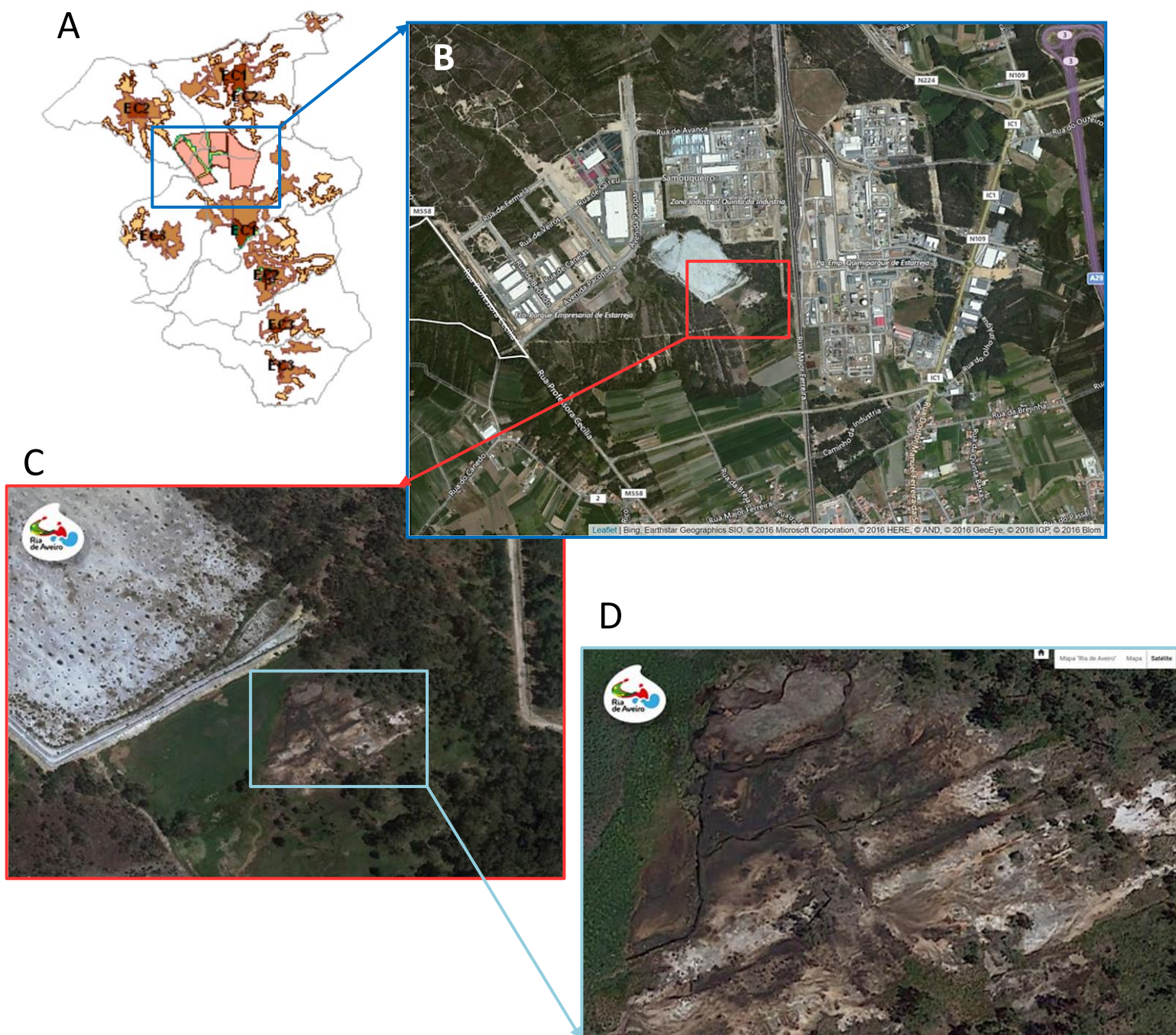
Official cartography, planning maps and orthophotos



**Map 55** – Enquadramento do CQE: A – Altimetria do concelho; B – Núcleos urbanos e áreas associadas, (escala 1:121200); C – Ortofoto da envolvente do CQE. Cartografia Oficial Escala 1:10000, SIG of the Intermunicipal Community Region and Tourism Centre of Portugal, *available in:* <http://sig.cm-estarreja.pt/> and <http://sig.riadeaveiro.pt/web/#>

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Official cartography, planning maps and orthophotos



**Map 56** – Enquadramento do CQE: A -Núcleos urbanos e áreas associadas, (escala 1:121200); B – Ortofoto do CQE (EPSG 27493, escala 1:10000, voo de Julho de 2000, resolução de 1m); C – Detalhe da envolvente do CQE, termo SE da área de tratamento de resíduos industriais; D – Detalhe da envolvente do CQE, zona de drenagem e precipitação de produtos ocre, exterior à zona de tratamento, a SE. Cartografia Oficial Escala 1:10000, Aveiro Region Intermunicipal Community, *available in:* [http://sig.regiaodeaveiro.pt/website/ortofotos/default\\_en.htm](http://sig.regiaodeaveiro.pt/website/ortofotos/default_en.htm)



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### Market Study – Literature references

TABLE 1 - Leading sensor manufactures for different applications and parameters, *in*: Alwakeel (2015)

APPLICATION AREA	MANUFACTURER	PRODUCTS/ COMPONENTS	SENSING PARAMETERS/ APPLICATIONS	REFERENCES
Agriculture	SensaTrack	Sensor, Adaptors, Gateways	Saving water, Soil moisture, Temperature, Humidity, light	<a href="http://www.sensatrack.com">www.sensatrack.com</a>
	Stevens	Sensor, Data loggers	Irrigation, Golf courses/ sports turf	<a href="http://www.stevenswater.com">www.stevenswater.com</a>
Marine Environment	Satlantic	Sensors, Radiometers, Observing Systems	Depth, Density, Salinity, pH, Fluorescence, UV Absorbance	<a href="http://www.satlantic.com">www.satlantic.com</a>
	Sea Bird Elec.	Sensors, Buoys, AUVs, ROVs, Underway systems	Water samples, Wave, Tide, pH and Oxygen sensors, Dredging, Oil spills	<a href="http://www.seabird.com">www.seabird.com</a>
Healthcare	SOL-CHIP	Tracking Sensors, Medical wristband and bracelets	Tracking elders and children, Monitoring, Hearing aids	<a href="http://www.sol-chip.com">www.sol-chip.com</a>
	MICRO- EPSILON	Measurement, Sampling and positioning tools	Dental samples, Tablet color, Surgical equipment position.	<a href="http://www.micro-epsilon.com">www.micro-epsilon.com</a>
Environment Monitoring/ Forecasting	ACURITE	Weather Sensor and station, Rain gauges	Environment, Weather forecasting, Rain, Humidity, Lunar cycle	<a href="http://www.acurite.com">www.acurite.com</a>
	Stevens	Weather stations, Gauges, Wind sensors	Rain gauges, Wind direction and speed, Solar radiation, Evaporation	<a href="http://www.stevenswater.com">www.stevenswater.com</a>
Gas and Petroleum	RigStat	Sensors, Cameras, GPS, Horns, Obstruction lights	Rig and Met-Ocean monitoring, Inspection, Emergency operations, Tracking	<a href="http://www.rigstat.com">www.rigstat.com</a>
	Gems Sensors & Controls	Sensor, Level-Indicators, Switches, Gauges. Valves	Flow and Presser sensing, Level measuring, Boiler control, Indications	<a href="http://www.gemssensors.com">www.gemssensors.com</a>
Safety and Security	PURELINK	Sensors, Badges, Tags, Severs, Software	Anti-Aggression, Visit control, Zone access, Emergency, Safety, Prevention	<a href="http://www.purelink.ca">www.purelink.ca</a>
Home Automation	SOL-CHIP	Sensors, Meters, Switches, Alarms	Remote home control, Smoke detection, Motion, Gas leakage	<a href="http://www.sol-chip.com">www.sol-chip.com</a>

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### Market Study – Literature references

TABLE 2 - Examples of prototype for different sensor network areas and applications, *in*: Alwakeel (2015)

APPLICATIONS	PROTOTYPE	MONITORING PARAMETERS	SCALE AND DENSITY	DATA AMOUNTS/ FREQUENCY	YEAR	COUNTRY
Agriculture	Root Zone Irrigation	Irrigation, moisture, Water Salinity	6 number of nodes and 3 repeaters	Depends on irrigation interval, 5 months duration	2008	Italy
	Smart Irrigation System	Irrigation, Moisture	2-sensor motes, 1 EC-5 soil humidity sensors	Small amount of data. After every 4.40 hours, Continue for 2 days	2011	Greece
Healthcare	Three Layer WBSN	Different physical activities in elderly	Few shimmer nodes on Body, Smart phone as base station	Minimal, Periodically data transmission	2010	Germany
	Smart Healthcare Clothing	Body temp., Heart beat, Respiration	Sensors and RFID tags, Cloths	Small amount of data, React only during emergency	2007	South Korea
Marine Environment	Ocean-TUNE UCONN Testbed	Acoustic channel behavior, Conductivity	Sensors are sparsely deployed, 3 surface buoys	Frequently, Mostly with 15 mints sampling, Stayed for 7 months.	2013	USA
Safety and Security	SASA	Structure Variations, Detect collapses locations	27 mica- 2 motes. Large number of sensors nodes.	Large amount of data packets are generated, Frequent transmission	2006	Hong Kong
	WINS Area Monitoring	Area monitoring, Surveillance, Security	Few nodes in area of Interest, can support 100m range.	Depends on app. requirement and network's current status.	1999	USA
Weather	Great Duck Island	Habitat monitoring, Data collection, Sampling	32 sensor motes Over 1 KM2	Frequently, 2-4 hour intervals, Stayed for 4 weeks	2002	USA
Transportation	Multi-sensor Automated Highway	Intelligent transport, Embedded control	4 vehicles equipped with 2 different classes of sensors	Case depended	2006	France
Livestck	Monitoring Wildlife Passages	Safe animal crossing, Target identification	Variable node density in 40 m of radius (Detector, Cameras)	Whenever target detected, Real time action is not required	2009	Spain

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TABLE 3 – WSN system (BeanAir) and a sensor solution (HANNA). Integrated System – sensing, data acquisition, and telemetry (OTT Hydromet) – main features. COST based in quotation request (Jan-April 2016)

SYSTEM MANUFACTURE	PRODUITS COMPONENTS	PARAMETERS/ PROBES	COMMUNICAT. INTERFACES	POWER SUPPLY	STORAGE	REFERENCE COST
<b>BeanAir GmbH (GER)</b>	<a href="#">BeanGateway</a> ® Ethernet & GSM/GPRS (Data acquisition and storage device) => Wireless Transmission IEEE 802.15.4 with antenna and <a href="#">BeanScope</a> ® (WSN supervision and monitoring software) and <a href="#">BeanDevice AN420</a> Wireless data acquisition platform	-	Analog current loop measurement (4-20mA)	Integrated Sensor Power Supply, software configurable 4.5V to 20V  Integrated Rechargeable Lithium-Ion battery ou Integrated Lithium-thionyl chloride primary cell 6,5Ah	Embedded Data Logger up to 1.000.000 data acquisitions records	<a href="http://www.beanair.com">www.beanair.com</a> BeanAN420 495€ BeanGateway 495€ BeanScope 430€
<b>HANNA (ITA)</b>	pH/EC isolated Transmitter (for long distance measurements of pH and EC. It can be either panel or wallmounted)	pH probe pH Electrode with PTFE junction, general purpose glass bulb, BNC connector  CE probe Flow-through Conductivity Probe with ATC, four-ring probe measures conductivity with a platinum sensor	pH 4-20 mA (isolated) EC 4-20 mA (isolated)	External, 12 to 24 VDC (not included)	-	<a href="http://www.hannaco.com">www.hannaco.com</a> HI 98143 transmitter 433 €  pH HI-1006-2005 346 € EC probe HI 3001 187€
<b>OTT Hydromet GmbH (GER)</b>	Hydrolab HL4 Multiparameter Sonde (portable device for attended, unattended monitoring)  It has on-board data logging and dedicated communications modules for easy integration with external loggers and telemetry	Communications modules and data logging integrated with a multiprobe, available to measure: Temperature, Conductivity, Depth, pH, Oxygen Reduction Potential (ORP), Dissolved Oxygen (LDO), Dissolved Oxygen (Clark Cell), Turbidity, Chlorophyll a, Blue-Green Algae, Rhodamine WT, Ammonium, Nitrate, Chloride, Total Dissolved Gas (TDG), Ambient Light	Hydrolab communications modules: USB, SDI-12, RS232, RS485, or TTY	External: 6 ... 30 VDC (12 VDC nominal) applied to the communications module, 12 VDC: 250 mW average, 19 W peak  Internal: (Optional) Internal alkaline D-cell battery, non-rechargeable.	4 GB of internal memory; 1 second interval minimum Sufficient memory to keep 5 years of continuous measurements with a 15 minute logging interval	<a href="http://www.ott.com">www.ott.com</a> Hydrolab HL4 10.095,00 €  Possible to add a Copper Anti-Fouling Solutions

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TABLE 4 - Data acquisition and sensing systems – main features. COST based in a quotation request (Jan-April 2016)

SYSTEM MANUFACTURE	PRODUTS COMPONENTS	PARAMETERS/ PROBES	COMMUNICAT. INTERFACES	POWER SUPPLY	STORAGE	REFERENCE COST
IMO GmbH PCE Instruments (GER)	SMART WG-2 pH/mV measuring and control device  (wall mounting housing)	CE probe ISSO-Amplifier and EC probe LMP1-4E-PP (measuring range: ...200ms)	Outputs: 3 potential- free relay contacts (switch): 250VAC / 8A resistive load can be assigned as desired 2 Analog outputs Standard signal 0/4 ... 20mA; 0 ... 5V/10V by parallel connection of a 250/500 Ohm resistor; Freely allocate the display value; Max burden: 500 Ohm	Operating voltage: 85 ... 264 VAC 50 / 60Hz Power consumption <5 VA	-	<a href="http://www.imo-ag.biz/gx2/">www.imo- ag.biz/gx2/</a>  SMART WG-2 pH/mV 355€  EC probe 326€
YSI – Xylem analytics (USA)	YSI IQ SENSORNET SYSTEM NET 182 XT (modular water quality terminal for continuous monitoring and process control – possible modular expansion from 1 to 4 sensors/ probes) <b>Adding the probes:</b> SensoLyt® 700 IQ/SET (SEA pH electrode) IQ SensorNet TetraCon® (submersible probe)	It is available to measure (with additional sensors): Dissolved Oxygen (optical or electrochemical) pH ORP/Redox Conductivity/Salinity Temperature Turbidity* TSS (total suspended solids)* Ammonium Nitrate Potassium COD (chemical oxygen demand)* TOC (total organic carbon)* DOC (dissolved organic carbon share of TOC)* SAC (spectral absorption coefficient)* BOD (biochemical oxygen demand)* * Available ultrasonic cleaning for sensors	With 5 analog outputs and 6 relays. Up to 4 sensors be connected. Comprehensive EMC shield control; cable topology; within network can be in the form of a line, tree, star or multiple star; Total cable length max. = 1000 m (3280 ft) without signal amplifying; with signal amplifying module MIQ/JBR add an additional 1000 m Radio transmission Class 1 with a range of 100 m (328 ft); max 300 m (984 ft)	2-wire with shield for power supply and comm. Electrical 100 to 240 VAC (50/60 Hz), 24 V AC/DC (Used for connecting sensors or as an input/output or for looping through/bran ching of the IQ SensorNet cable)	-	<a href="http://www.ysi.com">www.ysi.com</a>  IQ Sensor NET 182 2.975,00€  PH e T probe WTW 109173 1400€  CE probe TetraCon 700 IQ 1850€
Skyray Instrument (USA)	HM-3000P Portable Water Quality Analyzer- Heavy Metals  Analyzer is based on the authority- approved standard method, anodic stripping voltammetry (ASV), which features low cost and high precision and are replacing traditional atomic absorption method in Europe.	Simultaneously test heavy metals in artificially contaminated water sample (with given content of Cd, Pb, Cu) - in this case, artificially contaminated water sample (with given content of 100 ppb Cd, Pb, Cu) will be tested and the testing results will be calculated through single standard addition method.	With USB port and PC software. Connected to Bluetooth printer for on-site printing of measurement results (Bluetooth optional)	Large capacity of lithium battery for 10 hours of unremitting working or more than 100 times of continuous testing (with function of indicating remaining power.	Achieve functions of hardware inspection, electrode maintenance, testing, submitting history data, polargram analysis, algorithm application and analysis and other operations More than 2000 groups of testing data	<a href="http://www.skyrayinstrument.com">www.skyrayin strument.com</a>  \$30,500  With accessories: Electrode cleaner, professional analysis cups, pipette&pipette tube, charger and cigarette lighter adapter, portable suitcase, portable Bluetooth printer and accessories

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TABLE 5 – Electrochemical mercury sensing systems – main features . COST based in a quotation request (Jan-April 2016) .

SYSTEM MANUFACTURE	PRODUITS/ MODELS	EQUIPMENT DESCRIPTION	REFERENCE (COST)
Mercury Instruments (USA/UK)	Mercury Process Analyser PA-2 / PA-2 Gold	Continuous Detection of Mercury in Water and Aqueous Solutions Fields of Application: Fully automatic system; Easy menu-driven operation; Proven and reliable detection method: <u>UV absorption</u> ; Measuring ranges from 10 ppt to 100 ppm; High flexibility of sample pre-treatment procedure; Right for complex sample compositions. Low reagent consumption; Corrosion-protected construction; Automatic self diagnosis system for reliable operation. The detection of mercury contained in the sample occurs in an optical cell made of fused silica (Suprasil). In a first step mercury is reduced to the elementary state by means of tin(II)chloride or NaBH <sub>4</sub> . Subsequently mercury is stripped from the aqueous phase with an air stream and carried into the optical cell. Here the UV absorption measurement is conducted at a wavelength of 253,7 nm. This analytical technique called "cold vapor atomic absorption spectroscopy (CVAAS)" shows extreme sensitivity and selectivity. It has been reliable and proven for many years. In contrast to the occasionally recommended atomic fluorescence method the analytical technique utilized by the PA-2 is extremely low in interference and does not require an amalgamation step nor expensive noble gas as a carrier.	<a href="http://www.mercury-instruments.de">www.mercury-instruments.de</a>
Arizona Instrument LLC (USA)	Jerome 451 - Gold Film Fence-line Mercury Monitoring System - Unattended	The Jerome® 451 monitoring system from Arizona Instrument provides long-term monitoring even in extreme weather conditions; it can be stationed at any location that requires monitoring. Multiple units can also be linked to form a perimeter monitoring system. <u>Data logging and radio telemetry capabilities</u> make downloading data convenient and easy from a remote PC; User Selectable Time-Weighted Average (TWA) Reporting and Alarms with Email Alerts   Relay for Audible/Visual Alarm   Programmable Alarm Points; Enhanced reporting function for: compliance need maintenance tab for system verification and calibration reminders site view tab to monitor all locations at once, displaying last and data logging; user-friendly PC software; wall or post mounting   outside temperature monitoring; inherently stable gold film sensor; wind speed and direction monitoring; Temperature Controlled Interior for Increased Accuracy; Linear Response throughout Entire Detection Range; SCADA interface capabilities via 4-20ma; Functional Test Kit (FTK) verifies instrument functions correctly between recommended annual factory calibrations. <u>Output: SPECTRA RADIO-MODEM SPECIFICATIONS</u> ; Frequency: 2.4 – 2.4835 GHz (2400 MHz), 49 selectable channels; Serial Interface: RS-232; Power Requirement: 10 – 30 VDC, 450 mA; Operating Temperature: -40 – 75°C; Range: Up to 4 miles (6.4 km) "line of sight", longer distances may be obtainable through use of a high gain antenna or by using the Radio Repeater. The 451 is a detachable hand-held mercury analyser is contained within the unit for pinpointing a gas source; Define alarm points that meet needs and receive email notifications and warnings; Measurement data is transmitted wirelessly from 451 stations to the user's PC; It is housed in a steel casing, insulated, air conditioned and ready for any environment.	<a href="http://www.azic.com">http://www.azic.com</a>
Lumex Instruments (GER)	Mercury analyzer RA-915M	It is a high sensitivity analytical instrument for measuring mercury, especially for the real time detection of mercury vapor in air, mercury detection in water, natural and stack gases, oil and condensate, solid and sediments, foodstuff. <u>RA-915M Mercury Analyzer</u> is a portable multifunctional atomic absorption spectrometer with Zeeman background correction, which eliminates the effect of interfering impurities. It is the only high sensitivity and selectivity instrument that does not require gold amalgam pre-concentration and subsequent regeneration steps. This enables the user to conduct real time monitoring and detection of a mercury vapor. Being combined <u>with an RP-92 Cold Vapor accessory for water and PYRO-915+ pyrolysis attachment</u> for solid sample testing, the instrument is designed to determine mercury content in ambient air, water, soil, natural and stack gases, dental and medical testing and diagnostics, analysis of food and marine life, etc., the mercury detection limits being as low as 0.5 ng/m <sup>3</sup> in air and 0.5 ng/l in water.	<a href="http://www.lumexan-alytics.de">www.lumexan-alytics.de</a>

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TABLE 6 – Electrochemical sensing systems – main features . COST based in a quotation request (Jan-April 2016) .

SYSTEM MANUFACTURE	PRODUITS MODELS	EQUIPMENT DESCRIPTION	REFERENCE (COST)
P S Analytical (UK)	PSA 10.225 Online Hg Analyser PSA 10.255 Online Analyser (As/Se/Sb) systems ONLINE MERCURY IN LIQUID STREAMS	The system has been designed for the determination of mercury in a wide range of samples from waste water and chemical processes. The analytical method for measuring is Cold vapor atomic fluorescence spectroscopy, chemistry section can be supplied with both a UV Cracker and a conventional heater. As standard only UV is utilised, however a heater option and also a UV + heater option are available. The PSA 10.225 online systems can be wall-mounted or free standing and for convenience consists of the following three sections: 1- Touch screen user interface; 2- Chemistry section; 3- Electronic section. The Touch screen and the electronic section provides the system control and user interface whilst the chemistry section takes the actual sample and oxidises all of the mercury to the +2 in the digestion manifold prior to reduction to Hg <sup>0</sup> in the gas liquid separator and detection by atomic fluorescence spectroscopy. The system can be used with a wide range of chemistries such as bromination, aqua regia and permanganate depending upon the customer's requirements. <u>The system can also run in either continuous flow or discrete injection modes to add further flexibility.</u> The system is supplied with the P S Analytical C210S007 Online software package as standard, to complete flexibility of control with full multi tier multi user operation set up. The software gives full control and results with user determined alarms covering all possibilities. As standard the PSA 10.225 online system comes with 4 off 4x4-20mA outputs and 1 and 3 digital outputs (upgradable to contact closure) for alarms. Additional 4-20mA and contact closures and digital outputs can be easily added, as well as MODBUS RTU, RS 232, OPC Server and OPC Client. The online system has been designed with remote access in mind. The software can be configured to routinely send data, alarms and reminders via email. It also has the ability to be remotely controlled over Ethernet /Internet enabling remote diagnostics to be carried out. <u>There are 3 main considerations for sampling systems</u> with this equipment: 1. sample must be representative of the sample stream, in the bulk sample flow; 2. sample must be at atmospheric pressure, to ensure correct operation of the analyser and to prevent leaks; 3. sample must be particulate free, as particles and suspended solids can lead to blockages which can affect sample flow and analytical results, cause leaks, corrosion and damage to valves.	<a href="http://www.psanalytical.com/">www.psanalytical.com/</a>
Trace20 (UK)	Metalyser On-line HM6000	Remote monitoring station for heavy metals in process and environmental waters. The system uses the proven <u>photometric analysis method</u> , coupled with a panel PC, and an optional telemetry unit to provide a remote system. With the HM6000, pollution events can be detected through continuous 24/7 monitoring. The HM6000 is configured and controlled using the built-in waterproof 8.4" touchscreen panel PC. <u>The optional telemetry unit logs and transmits results from the system using Quad-band GSM/GPRS network, to a secure server with web browser access.</u> Alarm levels can be configured to trigger sending of alarm SMS messages to up to 10 mobile phone numbers. The user interface consists of an industrial PC with a touch screen. The control Software is simple and intuitive, enabling new users to rapidly familiarise themselves with all of the functions and commands. BENEFITS: Simple set-up; Low running and maintenance costs; 300 tests between reagent changes; Simple monthly maintenance; Self cleaning; Real-time data; SMS alarms that requires telemetry unit.	<a href="http://www.trace20.com/">www.trace20.com/</a>
Modern Water (UK)	OVA7000, OVA7000 Dual Cell and OVA5000	The systems are automated on-line metal monitors to provide continuous or intermittent monitoring of metals in process streams, effluent discharges, river and potable water. OVA 7000, OVA7000 Dual Cell and OVA5000 utilise internationally recognised voltammetry (ASV and CSV) technology, which provides quick and accurate determination of metals at the µg/L (ppb) level, directly comparable with laboratory analysis using AAS or ICP. On-line analysers (OVA5000-7000) can provide real-time monitoring of several concurrent sample streams, configured to individual customer requirements. Sample pre-treatment may include digestion for elimination of potential interferences, although ASV is not affected by Al, Na, Ca, Mg, chlorine or other salts, often present in complex samples which can cause problems with other analysis methods. Modern Water's OVA7000 can be fitted with a variety of options for pre-treatment and sampling to enable accurate analysis of most types of water. Features: 24 hour monitoring of up to 3 sample streams in effluent or (6 in drinking water); Pre-treatment options of acid/UVdigest to eliminate interferences and allow total and dissolved concentrations to be monitored; Modular construction; Results stored on solid-state internal memory; Programmable alarm outputs for out-of-range samples or system faults; Solid electrodes – no hazardous elemental mercury; Multi-element analysis configurations available	<a href="http://www.modernwater.com/">www.modernwater.com/</a>

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TABLE 7 – Electrochemical sensing systems – main features. COST based in a quotation request (Jan-April 2016) .

SYSTEM MANUFACTURE	PRODUITS/ MODELS	EQUIPMENT DESCRIPTION	REFERENCE (COST)
Istran (SVK)	EcaMon SaFIA and <u>EcaMon 10s</u>  High-performance one parameter on-line system for unattended monitoring of metals and some nonmetals in the lowest, medium and high concentration range, addressing concentrations from the low µg/L (ppb) range up to several g/L concentration.	EcaMon system is an unattended monitoring system for a continuous measurement of trace and high concentrations of heavy metals and some non-metals in waters, waste waters and technological liquids. There is a possibility to measure several species simultaneously with stripping voltammetry or coulometry. The system is controlled by a built-in industrial PC and facilitates virtually all kinds of In/Out signal flow including remote control through internet. Electrochemical cell with compact electrode system is automatically flushed by the supporting electrolyte during all analyses. <u>EcaMon 10s</u> enables the monitoring of tap water, sea water, river waters, mineral waters, some waste waters and cleaned waste waters for metals such as As, Hg, Pb, Cu, Bi, Tl, Cd, Zn, Se, Mn, Fe, Ni, Cr down to the µg/L concentration levels as well as for some non-metals (Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> , S <sub>2</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , NH <sub>3</sub> , hydrazine, EDTA, bromate, chlorite, ascorbic acid, etc.). The flow-through pneumatic system with peristaltic pump provides continuous sampling of the analysed sample and supplementary solutions (supporting electrolyte, calibration solution), their accurate dosage and transport during the whole analysis. The closed electrochemical cell with compact electrode system is automatically flushed by the supporting electrolyte during all analyses. The sample is taken from a compact siphon (loop) continuously filled with the sample ensuring fast response. The basic version comprises: Instrument rack IP54 (IP55 option); Industrial PC with colour monitor, Windows 2000; Analytical unit; Sample inlet module 1; Analog output, 4 - 20 mA; Digital IN/OUT signal interface (dry contacts)	<a href="http://www.istran.sk">http://www.istran.sk</a>  EcaMon 10s (with installation) 26000 €
Metrohm Applikon (NED)	2035 Process Analyzers	Modular wet part means greater flexibility for applications, with three basic configurations for potentiometric, photometric, and thermometric determinations. An integrated solution for 24/7 online monitoring of critical chemical parameters in industrial processes and wastewater streams. Additional measuring techniques can be integrated (pH, conductivity); IP66/NEMA 4-rated: protection in harsh environments; Customizable, user-friendly interface with several security levels; Remote control capability makes evaluating results and inspecting diagnostics easier. The 2035 Analyzer can be automatically calibrated as an option using the proven Metrohm auto-dilution technique: If a sample is outside the calibration range, it is automatically re-analyzed after an appropriate dilution factor is applied. Auto-calibration – specific to your analytical parameters – ensures that your results are always accurate.	<a href="http://www.metrohm-autolab.com/">http://www.metrohm-autolab.com/</a>  Distributor <a href="http://www.mtbrandao.com/">www.mtbrandao.com/</a> ADI2045Va similar to 2035 Process Analyzer (without installation) 86000eur
AppliTek (BEL)	AppliTek On-line Analyzers Suite - The EnviroLyzer® Series II	AppliTek's range of on-line water analyzers allow to measure virtually any possible parameter in water matrices, in a wide range of applications: from sum parameters in waste water up to specific parameters in boiler feed water and water safety and toxicity. VPA® Voltammetric Process Analyzer is the latest addition in AppliTek's portfolio of xPA Process Analyzers.  <u>Stripping Voltammetry</u> , as incorporated in the new analyzer system, is considered as one of the most sensitive techniques for the determination of trace metals, and enables you to detect and measure the elements of relevance in all sorts of water matrices, from the lowest (µg/l) ranges up to highly contaminated (g/l) samples. The method is also insensitive to interference, from which colorimetric determinations can suffer. The <u>VPA® is available as a single-parameter unit or as a multichannel configuration</u> (up to 6 channels). One "channel" represents one single stream with one single parameter measured in one specific measuring range. Likewise, a 4-channel configuration can measure for example two types of heavy metals with each of them having two measuring ranges. Several combinations are possible, according to your application.	<a href="http://www.applitek.com/">http://www.applitek.com/</a>

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TABLE 8 – Electrochemical sensing systems – main features . COST based in a quotation request (Jan-April 2016) .

SYSTEM MANUFACTURE	PRODUTS/ MODELS	EQUIPMENT DESCRIPTION	REFERENCE (COST)
Originalys (FRA)	LandSat	A Potentiostat, Galvanostat and Impedencemeter measurments (1 up 2 channels 17.5V 100mA z=1MHz). General specifications: Auxiliary voltage: $\pm 17.5$ V, Maximum current: $\pm 100$ mA, Applied voltage: $\pm 5$ V. Current measurement: 9 ranges from 1 nA to 100 mA; Best resolution 30 fA; Auto ranging configurable; Acquisition speed: 1 Million samples / second; Scanning performances: Acquisition times $\geq 100$ $\mu$ s. Ohmic drop compensation: "Feed-back" manual or automatic; Electrochemical impedance (EIS): 100 $\mu$ Hz to 5 MHz; 20 frequencies / decade; Applied potential step resolution 1 mV for 1 V. Power supply:90 to 264 Vac – 47 to 63 Hz – 30 VA; Or 24 V battery; Or 12 V battery using a converter This instrument is a cabin luggage that can be transported easily for field experience. It includes a computer allowing immediate analysis.	<a href="http://www.originalys.com/">www.originalys.com/</a>
Uniscan Instruments (FRA)	Potentiostat- Galvanostat Model PG581	The PG581 potentiostat – galvanostat is connected to a PC via its USB port in the laboratory for electrochemical experiments such as cyclic voltammetry, chronoamperometry and square wave voltammetry with unsurpassed ultra low noise performance. In addition you can now upload those same techniques directly to the PG581 to collect data in the field without a computer.	<a href="http://www.uniscan.com">www.uniscan.com</a> Distributors: Bio-Logic SAS <a href="http://www.bio-logic.info">www.bio-logic.info</a> ec-lab Ltd <a href="http://www.ec-lab.co.uk">www.ec-lab.co.uk</a>
Ivium Technologies B.V. (NED)	CompactStat™ with a PDA and DataSecure module	It combines swept dc and FRA / Impedance Analyzer into a USB-powered, lightweight unit (<600 grammes). The integrated design delivers measurement capabilities not available to use separately. Driven shield technology and opto-isolated USB complement the low-noise circuit design.	<a href="http://www.ivium.com">www.ivium.com</a> CompactStat 9200€ PDA module: 1200€ DataSecure module: 1200€
Alliance Instruments (FRA)	PROXIMA Segmented Flow Analysis (SFA)	PROXIMA, SFA technology system can analyse between one and five analytes simultaneously by a colorimetric method. The two, 26 position pumps (52 tubes in total) are operated by the software. Options like automatic startup, automatic shutdown, and leak detection enable longer walk-away times. For user safety, the reagent drawer located below the instrument, allows one to store all reagents "inside" the instrument and will reduce the risks due to handling of hazardous reagents and also saves space required by the system. High analytical throughput - will allow to run all of the analysis at the optimum throughput. With its reduce reagents consumption (micro or macro-flow), and its high sensitivity detector ( digital colorimeter with 24 bit A/D converter). The PROXIMA system gives consistent results even when working at very low detection limits. <u>Fast analytical manifold change over</u> - Using the PROXIMA will also allow to use the unique rapid "Alliance system" to measure other parameters with the same instrument. In less than 5 minutes, it can replace a manifold (simply disconnect the tubes and pull away the complete plate with the pump tube holder). To eliminate the opportunity for mistakes, each manifold is supplied with its own pump tube holder. Up to <u>500 results per hour</u> - When the instrument is ready to run, just load your sampler and place the reagents in the drawer. The instrument will run the analysis at a speed from 20 to 100 analyses per channel (according to the method). In a five channels configuration, it will be able to run up to 500 results per hour. PROXIMA automates the most complex colorimetric methods and the toughest sample matrices (phenol, cyanides, TN,TP...). <u>All types of sample preparation</u> are used (dialysis, in-line distillation, heating-bath, liquid-liquid extraction, autoclave, UV digestion) to reduce time and cost of analysis according to standards (ISO, EPA). In addition, with the XYZ sampler (360 positions) and optional dilutor, it will be able to use the dilutor to automatically dilute out of range samples or standards solutions.	<a href="http://www.alliance-instruments.com/">www.alliance-instruments.com/</a>



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TABLE 9 – Electrochemical sensing systems – main features. COST based in a quotation request (Jan-April 2016) .

SYSTEM MANUFACTURE	PRODUTS/ MODELS	EQUIPMENT DESCRIPTION	REFERENCE (COST)
PalmSens (NED)	<p>PalmSens3 allows the application of most of the relevant voltammetric and amperometric techniques, as well as impedance analysis (EIS)</p> <p>Electrochemistry Kit, EmStat Blue (EKS-ES3BLUE):</p> <ul style="list-style-type: none"> <li>• TC4 cell (a glass cell with 5 openings),</li> <li>• 3 stoppers (for the glass cell),</li> <li>• stirrer ST1 designed for TC4,</li> <li>• BVT Sensor connector</li> <li>• (conical plug for the glass cell with integrated connector);</li> <li>• BVT Starter Kit (various BVT electrodes),</li> <li>• Rugged plastic case</li> </ul>	<p>It is a flagship instrument, a Potentiostat, a Galvanostat and a EIS Analyser</p> <p>PalmSens3 is a battery powered potentiostat, galvanostat and Frequency Response Analyser (FRA) for Electrochemical Impedance Spectroscopy (EIS) with low noise, a large potential range and high current resolution, over 9 current ranges.</p> <p>A laboratory instrument, with a rugged design for field work. Standard packaging includes a shielded cable with connections for a working, a counter and a reference electrode by means of 2 mm banana connectors and mini-crocodile clips and a USB cable.</p> <p>Standard software for all single channel instruments PStouch comes standard on a CD and available to download. For controlling PalmSens3 using a phone or tablet download PStouch for Android.</p> <p>PalmSens can be extended by a multiplexer, BiPot and other accessories</p>	<p><a href="http://www.palmsens.com/en/">www.palmsens.com/en/</a></p> <p>EmStat3 Blue 1850 eur</p> <p>Electrochemistry Kit EmStat3 Blue e BVT eq. 2495 eur</p>
BVT (CZE)	<p>ELECTROCHEMICAL SENSOR Type AC1.W*.R* (*) with LINEAR PUMP Type: LP.*)</p> <p>LINEAR PUMP Type: LP.*) - pump without pulsation and with easy connection of syringe. It is designed for extremely small flow rates. It is optimized for flow supply in electrochemical measurement.</p>	<p>SENSOR Type AC1.W*.R* (*) - The sensor is formed on a corundum ceramic base. Onto this surface the working, the reference and the auxiliary electrodes are applied. The working and the auxiliary electrodes are made of variety of materials. At the end of the sensor there is a contacting field which is connected with the active part by the silver conducting paths which are covered by a dielectric protection layer.</p> <p>The LINEAR PUMP LP.*) consists of miniature motor with digital encoder and planetary gear, which is in aluminium body of pump. The motor drives the screw which moves the piston in syringe in both directions. The pump is designed for extremely small applications. It can be used in hand-held devices. The main advantage is no pulsation and easy connection with syringe piston. The pump can supply liquid through flow cells FC2/FC3. Linear pump is delivered with optional Hamilton syringe holder. Parameters Flow rate: 0 - 250 µl/min; Portable device • Hand-held device • Low power application</p> <p>FLOW CELL Type: FC2.*) - Experimental Accessories • Peristaltic Pump • Linear Pump Cell Usage • Flow measurement • Flow-injection analysis Example of Order • 5 pieces – FC2.1 Ordering Information • The order is specified by whole product code • Minimum order quantity – 1 cell • Delivery time for standard FC2 cell is 4 weeks from receipt of order • Delivery time for non-standard FC2 cell depends on final technical specification of order</p>	<p><a href="http://www.bvt.cz/">http://www.bvt.cz/</a></p>

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TABLE 10 – Electrochemical sensing systems – main features. COST based in a quotation request (Jan-April 2016) .

SYSTEM MANUFACTURE	PRODUTS/MODELS	EQUIPMENT DESCRIPTION	REFERENCE (COST)
DropSens (ESP)	<p>μStat 400</p> <p>It can be used with one- or two-working electrodes configuration and can be applied for voltammetric, amperometric or potentiometric measurements, including 18 electroanalytical methods.</p>	<p>Analytical Methods: voltammetry, amperometry, galvanostat, mix Tech</p> <p>POTENTIOSTATS for <i>in situ</i> or field electrochemical analysis, they can be used with SPE or with any other conventional electrode. Controlled by DropView Software, which provides powerful functions such as experimental control, graphs or file handling, among others.</p> <p>μStat400 bipotentiostat/galvanostat is Li-ion Battery powered (USB charger adapter compatible) and it can be easily connected to a PC via USB, RS232 and Bluetooth ®</p> <p>(SPE made of <u>carbon</u>, gold, platinum, silver, carbon nanotubes or gold nanoparticles based inks. Innovative strips manufactured for electrochemical analysis in environmental, clinical or agri/food areas.</p> <p>Thin layer flow-cell SPE, circular working electrode - integrated in one channel flow-cell, where working electrode is circular shaped with a diameter of 4 mm. They are suitable for working with Flow Injection Analysis systems and also in batch mode. The transparent cover allows you an easy control of the sample volume.)</p>	<p><a href="http://www.dropsens.com/">www.dropsens.com/</a></p> <p>μStat 400 3675€</p>
Micrux Fluidic, (ESP)	<p>Electrochemical flow-cell (ref. ED-FLOW-CELL)</p> <p>All-in-One cell (ref. ED-AIO-CELL) (Minimal order for the customized thin-film electrodes are 230 units that can include different electrode designs and materials)</p> <p>Drop-cell connector (Ref. ED-DROP-CELL)</p>	<p>Analytical methods: electroforese, voltammetry</p> <p>Microfluidic electrophoresis chips (SU-8 / GLASS SINGLE-CHANNEL MICROFLUIDIC CHIPS WITH ELECTRODES) are Reusable microfluidic electrophoresis chips manufactured in different designs with integrated (micro)electrodes for electrochemical measurements = Electrochemical Sensors - Reusable metal-based (micro)electrodes fabricated by <u>thin-film technologies on a glass substrate</u>.</p> <p>Microfluidic &amp; electrochemical platforms for interfacing MicruX microfluidic chips and electrochemical sensors. The interfaces enable the use of the MicruX microfluidic devices and sensors. <u>The innovative All-in-One cell</u> provides an unique multipurpose interface with movable add-ons that can be interchanged for using the standard (10 x 6 mm) thin-film (micro)electrodes supplied by MicruX. The AIO-cell enables the use of the thin-film (micro)electrodes in static (Drop / Batch-cell) or dynamic (Flow-cell) conditions, fulfilling the requirements of multiple analytical applications.</p> <p>Portable Instrumentation and compact analytical instruments (high voltage power supplies, potentiostats...) for an easy use of microfluidic chips and electrochemical sensors. MicruX instruments bring a solution for multiple in-situ applications in microfluidic and electrochemistry research field.</p>	<p><a href="http://www.micruxfluidic.com/">www.micruxfluidic.com/</a></p> <p>Electrochemical flow-cell - cell including the base and one add-on (+20 free electrodes) 725 €</p> <p>All-in-One cell (+20 free electrodes) 895 €</p> <p>2 channels peristaltic pump 3.000 €</p>

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TABLE 11 – Electrochemical sensing systems . Manufacture references of recent technology in the SPE devices.

MANUFACTURE REFERENCE	TECHNOLOGY DESCRIPTION
GoSense Wireless (UK) - NFC and RFID Mobile Sensors <a href="http://www.gosense-wireless.com">www.gosense-wireless.com</a>	It is a privately owned technology company located near the city of Cambridge, UK. GoSense Wireless develops mobile wireless sensors. pH & Ions – in development. A dual channel node designed for use with any standard pH electrode or ion selective electrode (ISE). Two separate input channels plus internal temperature reference, with an NFCv/RFID compatible interface and 1Mb memory.
Electrochemical Detectors ED, Ltd. <a href="http://www.elektrochemicke-detektory.cz/">www.elektrochemicke-detektory.cz/</a>	Standard offer includes ion selective electrodes, silver metal electrodes, platinum electrodes, glass pH electrodes, plastic bodied pH electrodes, reference electrodes, polarographic electrodes working, auxiliary, reference and combined ones, redox electrodes glass or plastic bodied, electrolytic conductivity sensors, dissolved oxygen and custom manufactured atypical electrodes. For application of the above mentioned sensors are offered auxiliary materials and accessories, as reference electrolytes, salt bridge solutions, calibration solutions, ionic strength and pH adjustors, storage and cleaning solutions, polishing kit for solid state polarographic electrodes, apparatus for measuring, renovation of ion selective electrodes, connecting cables with various commonly used connectors, electrodes with atypical dimensions for various measuring devices
VisioAMV (GER) <a href="http://www.amvtechnics.cz">www.amvtechnics.cz</a> ; <a href="http://www.visiotec.info/">www.visiotec.info/</a>	It is concerned with complete development, production and service of our own special devices for Health Care in a line of infusion technology (syringe pumps, volumetric pumps, enteral pumps, etc), job-order production of high precision machine parts produced on lathe and milling 5 - axis CNC machines and complete batch production of special devices for chemical laboratories. Complementary production is composed of design and production of electronics and SW for direct-current stepping motors for special applications.
Probe Scientific <a href="http://www.probescientific.com">www.probescientific.com</a>	it develops innovative products to solve clinical problems and improve healthcare. The company has a substantial product pipeline based on its proprietary technologies and is seeking to commercialise this range to simultaneously benefit clinicians and the community in general. Probe Scientific Ltd is a private company, founded in 1998 and is based in the West Midlands, UK. Probe Scientific has grown steadily since its origins as a research organisation and has recently recruited experienced senior executives with a commercial focus.
Čerpadla Kouřil <a href="http://www.cerpadlakouril.cz/">www.cerpadlakouril.cz/</a>	Manufacturers of metering pumps and dispensers. Company manufactures and supplies peristaltic metering pumps and dispensers with capacity up to 2 l / min. Pumps and dispensers are designed for pumping liquids in laboratories and production processes. They also supply accessories for peristaltic čerpadla PCD (tubing, connectors ...)
BST (GER) <a href="http://www.bst-international.com/">www.bst-international.com/</a>	It develops and produces electrochemical sensors and instruments. Thick film sensors and flow cells are available from PalmSens.
ItalSens (ITA) <a href="http://www.italsensor.com/">www.italsensor.com/</a>	It provides screen printed electrodes developed by the University of Florence which are suitable for a range of voltammetric methods and ideal for functionalization as used by many biosensors. (SEE: Mercury analysis using the ItalSens Au sensor, Quantification of mercury in aqueous solutions, 2015. Available in: <a href="http://www.palmsens.com/media/files/Applications/Detection%20of%20mercury%20IS-Au%202015-12-16.pdf">http://www.palmsens.com/media/files/Applications/Detection%20of%20mercury%20IS-Au%202015-12-16.pdf</a> )
Rusens (RUS) <a href="http://www.rusens.com/">www.rusens.com/</a>	It develops and produces screen printed sensors. The sensors have a working and a counter electrode of graphite and Ag reference electrode. Modified sensors are available for hydrogen peroxide, glucose and lactate. A flow cell is available for these electrodes.
CHI electrodes and cell (USA) <a href="http://www.chinstruments.com/">www.chinstruments.com/</a>	It has a range of working, reference and counter electrodes available as well as a proper cell stand
GWENT Group (UK) <a href="http://www.gwent.org/">www.gwent.org/</a>	It can offer a full screen-printing prototype service for base electrode manufacture in a class 100 clean room. Many customers use this route before purchasing their own screen-printing equipment.

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EXEMPLES OF SOME DATASHEETS (and equivalent technical notes consulted) AND EQUIPEMENT QUOTATIONS.

#### DATASHEETS (AND EQUIVALENT)

- BeanDevice AN-420-XTD
- BeanGateway Ethernet-outdoor
- BeanScape
- Hanna Transmitter HI98143-20
- BVTcz\_SPEelectrod-AC1n

#### QUOTATIONS

- 01 multiprobe HYDROLAB modelo HL4 - instrutech
- 02 transmitterIQ Sensor NET 182 and pH and EC probes - instrutech
- 03 BeanAIR system - instrutech
- 04 SPE and BiPotentiostat P-70002449 - DropSens
- 05 CuElectrodeMET51344812 – MetterToledo - SoQuimica
- 06 pH and EC probes and transmitters - HANNA
- 07 EC probe and transmitter - OnSet
- 08 EC, pH probe and transmitter - HACH
- 09 HM-3000P Portable Water Quality Analyzer HM - SKYRAY
- 10 waterLevel\_pH\_EC\_probes - AGC