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session: Accidents & Hazards

Chair: Paraskevi Nomikou

14:15 – 14:30 **Michail Chalaris**
International Hellenic University | Hellenic Fire Corps
Novel Systems for Detection and Monitoring of Dangerous Substances in Water Environmental Sensitive Areas
Nikos Tsalas, Giorgos Katsouras, Michalis Chalaris, Stelios Samios, Efthymios Lytras, Kostas Papadopoulos, Nikos Kouris, Simos Malamis, Costas Noutsopoulos5, Danos Mamais5, Andreas Andreadakis

14:30 – 14:45 **Markela Giannousopoulou**
NCSR DEMOKRITOS
Maritime accidents and environmental hazards. Creating a dynamic model for predicting maritime accidents and environmental pollution
Markela Giannousopoulou, Myrto Konstantinidou

14:45 – 15:00 **Konstantina Bantouvaki**
Harokopio University of Athens
Earth Observation for Coastal Erosion Monitoring in Europe: the Space for Shore Project

15:00 – 17:00 **Poster Session (p. 13-14)**

17:00 – 19:00 **Round Table:**
Legislative Framework and its Role for Local Authorities
Panel:
Gerassimos Papadopoulos (Coordinator)
Konstantinos Kokolakis, Decentralized Adm. of Macedonia – Thrace Civil Protection former Director
Kostas Chouvardas, Region of Eastern Macedonia & Thrace, Civil Protection Department, Head
Elena Rapti, Legal Adviser to the Deputy Minister for Civil Protection and Crisis Management

NOVEL SYSTEMS FOR DETECTION AND MONITORING OF DANGEROUS SUBSTANCES IN WATER ENVIRONMENTAL SENSITIVE AREAS

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ABSTRACT

This publication presents the innovative system of autonomous robotic boats and their ability to detection heavy metals in surface waters. Initially, reference is made to the technology used and then the results of copper and lead detection in two Greek water bodies, Lake Koumondourou and river Asopos, are presented.

Keywords: INTCATCH, Robotic boats, Heavy Metals, Dangerous Substances

1. INTRODUCTION

Within the framework of INTCATCH H2020 project, the application of the robotic boats and their integrated sensors allowed monitoring and sampling of water quality in a large area of a catchment with far greater frequency than current sampling methods. By using the continuous monitoring system, potential sources and pollution pathways could be identified and the results provided EYDAP the opportunity to have a more comprehensive picture of the quality of the water body in real time and take immediate countermeasures. The possible effect from anthropogenic pollution can be thoroughly investigated with the use of the robotic boats and their integrated innovative systems. The INTCATCH autonomous boats through demonstration activities in Greek catchments [1] provoked a paradigm shift in the monitoring of physicochemical parameters, with regard to water quality and trophic status. Besides their basic sensors kit, the autonomous and radio controlled boats were equipped with an innovative Heavy Metal System [3], which was tested in Lake Koumoundourou and Asopos River (Figure1).

Lake Koumoundourou, is located on the northern side of the Gulf of Elefsina, within an industrial area. Its surface is 1m higher than the surface of the sea and has an area of 143 acres. Marine and freshwater from muddy sources are mixed, creating a wetland, brackish environment that has many characteristics in common with the formation of a coastal lagoon. The Asopos is a river in Greece that flows along the borderline between Boeotia and Attica counties [1]. Actually, in antiquity it formed the natural border between the cities of Thebes and Plataea. Along the Asopos River human activities –mainly agricultural and industrial ones take place. Those activities produce effluents resulting in polluting the river, aquifer

and soil of the area. The above-mentioned situation forms a negative but typical example of the impact to both humans and environment caused from non-sustainable use of natural resources

Figure 1. HM boat campaign in Asopos river, Oropos

2. EXPERIMENTAL METHOD

The INTCATCH architecture is divided in 4 main components: Bluebox, E-board, smartphone and tablet. The Bluebox communicates directly with the sensors and is responsible for interpreting the electrical signals, converting them to significant values and uploading the data to the Cloud database for permanent storage via a 3G connection. The E-Board is controlled by an Arduino Due that reads the physicochemical values from the Bluebox via a serial port and sends them to the smartphone, via a custom protocol via USB. The smartphone is the main computer unit of the boat. It controls all the autonomous behaviors of the platform and communicates with the tablet via WiFi to show the sensor values in real time and to receive commands from the operator. The tablet is an interface for the operator to control the vessel, displays the state of the vessel (eg position on the map) and the sensor values and allows the user to manage the data collection mission [2]. The architecture and components of the INTCATCH are shown in figure 2.

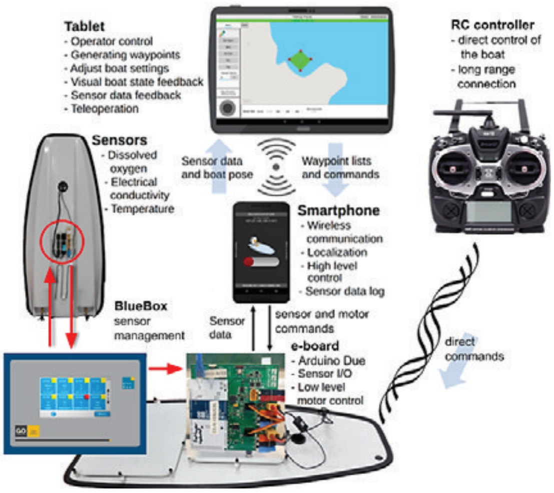

Figure 2. Architecture of the boat control system showing options for manual RC control and autonomous operation through the Control App running on the tablet (Bloisi,D. 2020).

2.1. Boat Equipment

The basic sensor kit for INTCATCH boats includes DO, pH and EC and a more specialized ISA sensor (UV / VIS Spectra in the range 200 - 720 nm). Additional sensors: chlorophyll and hydrocarbons and innovative sensors: Heavy metals (copper and lead), Escherichia Coli, Pesticides / Toxicity, Genomic analysis. A sampler is placed at the back place of the boat and contains 4 jars, of a volume of 500 ml each that can be activated individually with the tablet or independently [2].

2.2. Square Wave Anodic Stripping Voltammetry

This method consists of the several sequential steps [3]:

1. Conditioning step: a positive (or at least 0.0 V) potential is applied to the working electrode.
2. Deposition step: It is characterized by a deposition potential that is applied in order to reduce metal onto the working electrode surface. Depending on the exact value of the deposition potential, certain metals in free ionic form (or any specie/compound in real sample able to be reduced) will be reduced and deposited onto the working electrode surface. Deposition of the metals onto an electrode is a mass transport-based process. Usually, only a very thin interface between a sample and electrode participate in the reaction, so in flow through mode or under stirring conditions an increase of the signal can be observed.
3. Equilibration step: the role of this step is to allow the homogenization of the ion's concentrations within the electrode surface boundaries.
4. Stripping step: metals that were reduced onto electrode during the deposition step are now released (oxidized) as a square-wave is applied within the specific potential range. Oxidation for each metal occurs under the specific potential value, so the final voltammogram represents various peaks at different potentials and records electrical current proportional to the concentration of the metals. The voltammograms then need to be interpreted using software to measure the height or integrate the area under the peak, which is compared to standard concentrations, to calculate metal concentrations in the sample solution.

The steps of this method require a measuring system composed by a potentiostat, sensing electrode system (sensors), flow cell, peristaltic pump, software and a data processing system [3].

3. RESULTS AND DISCUSSION

3.1. Lake Koumoundourou

The Heavy Metals system was firstly tested in Lake Koumoundourou (28/05). The presentation was organized by Athens Water Supply and Sewerage Company (EYDAP S.A.) and the Institute of Marine Biological Resources and Inland Waters (IMBRIW) of the Hellenic Centre for Marine Research (HCMR). The outcome of the above deployment on demand was that EYDAP chose the Lake as a test area for the HM system. Therefore, on Tuesday, July 2nd, 2019, water samples collected from Lake Koumoundourou at three stations near the shore (demo, pumping and dam station). The HM system was tested successfully in the laboratory for Lake Koumoundourou and representative results are shown in Table 1, indicating the presence of free ions of Lead and Copper in low concentrations, close to the Limit of Quantification of SW-ASV method.

Table 1. Results of HM boat for Pb and Cu, Lake Koumoundourou 2/7/2019

No	Sample Name	Pb* (μg/L)	Cu** (μg/L)
1	koumoundourou demo station	8.06	< LOD
2		< LOD	< LOD
3	koumoundourou pumping station	< LOD	< LOD
4		20.0	26.6
5	koumoundourou dam station	12.3	8.83
6		8.09	< LOD

*Pb: LOD= 4 μg/L LOQ=14 μg/L **Cu LOD=7 μg/L LOQ=22 μg/L

3.2 Asopos River

On October 11th, a campaign was performed with the HM boat in Asopos river in collaboration with Laboratory of Environmental Chemistry of the National and Kapodistrian University of Athens (LEC-NKUA) (Figure 1). The calibration curves for Pb and Cu are shown in Figure 3. Measurements were conducted in real time in Asopos estuary with the results shown on Table 2.

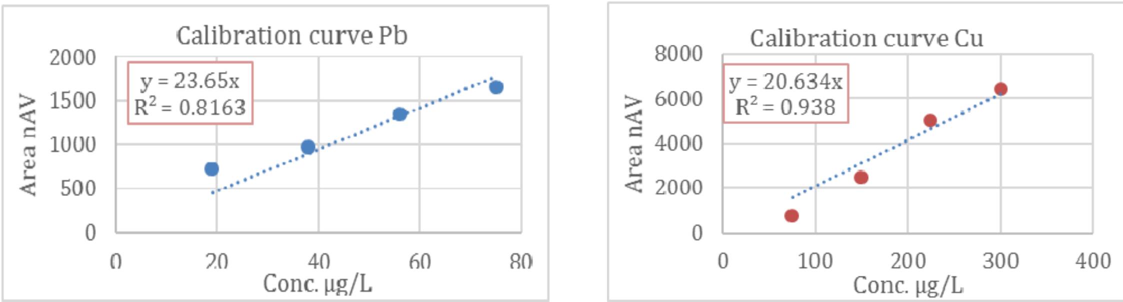

Figure 3. Calibration Curves for Pb and Cu, 11/10/2019

Table 2. Results of HM boat campaign for Pb and Cu, Asopos River 11/10/2019

No	Sample Name	*Pb^{2+} (μg/L)	**Cu^{2+} (μg/L)
1	Asopos river estuary (field campaign)	10.48	< LOD
2		<LOD	
3		7.63	
4		10.36	
5		10.81	

*Pb: LOD= 4 μg/L LOQ=14 μg/L **Cu LOD=7 μg/L LOQ=22 μg/L

4. CONCLUSION

The developed integrated system performs positively in terms of in-situ detection of concentration changes for Pb and Cu in surface water bodies in the range of several μg/L (4μg/L and 7μg/L respectively). This detection sensitivity can enable addressing certain INTCATCH challenges such as detection of point contamination from road runoffs, misconnections and cross connections, but it is not sufficient for measuring the accurate concentrations of these metals in aquatic environment [3]. The analytical method shows a lack of selectivity due to influences from various ingredients in water and from concentrations rate of other metals. Based on, the above observations further development work is ongoing between three project partners involved (ICN2, GOSYS and BOKU) towards the goal of enhancing sensitivity and minimizing/avoiding interferences, using the fingerprinting approach.

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