Sustainable Mediterranean

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"Environmental Perspectives of the Gulf of Elefsis A Mediterranean case study where Science meets the Society"

Elefsis, Greece, 11-12 September 2015

This issue of Sustainable Mediterranean is co-produced by the City of Elefsis, UNEP/MAP, the Ministry of Environment and Energy, the University of Athens and MIO-ECSDE.

UNEP

MAP

40 Years TOGETHER FOR A SUSTAINABLE MEDITERRANEAN

Environmental Chemistry Laboratory

United Nations Educational, Scientific and Cultural Organization

UNESCO Chair on Sustainable Development Management and Education in the Mediterranean
HELLENIC REPUBLIC
National and Kapodistrian University of Athens

ΔΗΜΟΣ ΕΛΕΥΣΙΝΑΣ

MINISTRY OF RECONSTRUCTION OF PRODUCTION, ENVIRONMENT & ENERGY

MIO-ECSDE

M. Pouqueville, Grèce, Paris, Firmin Didot Freres, Editeurs, M DCCC XXXV (1835).
L' Univers - Histoire et Description de tous les peuples.

EDITORIAL

This special issue of the "Sustainable Mediterranean" Journal of the Mediterranean Information Office for Environment, Culture and Sustainable Development (MIO-ECSDE) celebrates the 40 years of UNEP/MAP and is a contribution to the 19th Conference of the Parties to the Barcelona Convention. It is a concrete demonstration of partnership in action. The issues is co-produced by UNEP/MAP, Secretariat of the Barcelona Convention, the Ministry of Environment and Energy of Greece, the City of Elefsis, the University of Athens (UoA) and, of course, MIO-ECSDE. It is devoted to the case study of the Gulf of Elefsis.

The articles included, virtually encapsulate most of the elements one would like to see developed and combined in the interface between good science and meaningful public participation, when dealing with the protection of the environment and the sustainable development of the Mediterranean region. In fact, they are the outputs of the "*International Conference on the Environmental Prospects of the Gulf of Elefsis: A Mediterranean case study where Science meets Society*".

The Gulf of Elefsis (GoE) is a site of immense natural, archaeological/historic and economic value, but also a notorious pollution "hot spot" because of its rapid industrialization in the second half of the 20th century. In the northern coasts of the GoE and in a distance of few kilometers two of the major crude oil refineries of Greece, major steel mills, cement factories, harbours, shipyards, food processing and other manufacturing industries operate in a densely populated area. The western part of the Gulf hosts summer resorts, places for recreation and even thriving mussel growing farms. Despite the pressures and thanks to a series of favourable bio-geo-chemical characteristics, the area is still a biodiversity treasure house where even rare and threatened species exist (such as *Pinna nobilis, Pecten Jacobaeus*, etc.). Dolphins and even a sea turtle *Caretta caretta* (!!) were spotted there, last summer.

From the historic and cultural point of view, its eastern entrance was the place of the famous naval battle of Salamis in 480 BC between Greeks and Persians which shaped international history, while Elefsis was one of the most famous sites of the Mediterranean, because of the "Elefsinian Mysteries".

Although, undoubtedly a very special place, characteristics similar to those of the GoE are found in many other coastal embayments throughout the Mediterranean, making the GoE a "typical" Mediterranean example and a valuable "open" biogeochemical laboratory.
What is of particular importance in this case is the early interaction of science with public awareness, mobilisation and policies. Both the research and the efforts for the protection of the environment of the GoE were initiated in the early 1970s by committed Civil Society involvement. A lone student, first, with minimum support, then a young academic and his undergraduate students, supported for their first experiments by instrumentation bought by the Greek NGO Elliniki Etairia/The Hellenic Society for the Protection of the Environment and Cultural Heritage (which was also one of the founding members of MIO-ECSDE together with the EEB and RAED) were the first documented pioneers.

Significant innovative research in the GoE, concerning metals, magnetic parameters, etc., was continued and carried out also abroad (in the University of Liverpool). This experience was brought back and replicated not only in the GoE but throughout Greece. The results back in 1979-81 were publically announced, widely reported in the daily press and debated, stimulating a series of measures and further initiatives, while also shaping and "stamping" the character and career of a large number of post-graduate students and scientists who worked in the area and beyond, and participated in environmental management protection and/or educational initiatives, multiplying through the involvement of many other local actors, teachers and schools, the impact of the scientific work.

In this publication, among other important outputs, is an account of the work supported by the "Horizon 2020 Initiative to Depollute the Mediterranean", demonstrating through concrete findings, for the first time in the Mediterranean and beyond, the beneficial impact on the environment that has resulted from the introduction and implementation of environmental policies and legislation in combination with the adoption and employment of Best Available Techniques (BATs) by industry.

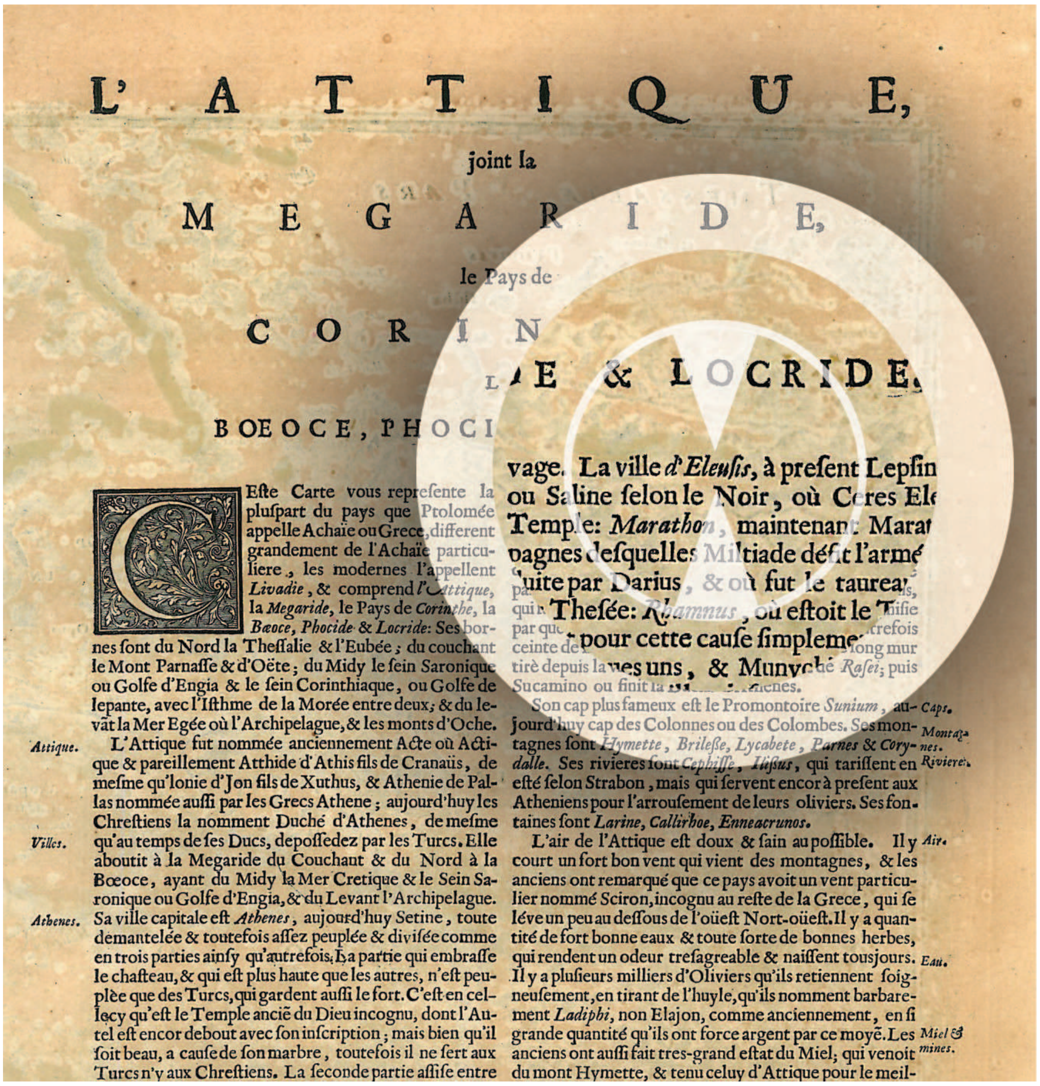
Since the 70s, the research and management work has been continued by the Laboratory of Environmental Chemistry and the UNESCO Chair and Network for Sustainable Development Management and Education of the University of Athens and resulted in more than 150 papers, mostly in peer reviewed journals and one of the best "time series" of data reported by Greece to UNEP/MAP. A major part of these studies was communicated to the Local Authorities of Elefsis, presented in public meetings and inspired or supported the activities and initiatives of local and national NGOs.

The publication also includes related significant results of the work of the Hellenic Centre for Marine Research and concludes with a preliminary proposal for Strategic Guidelines aiming at facilitating the creation of a Common Vision and the drafting of a truly Integrated Coastal Management Plan for the area, inspired by a similar procedure undertaken under the Horizon 2020 Initiative for Lake Bizerte (Tunisia). The Strategic Guidelines also take into consideration the Integrative Methodological Framework (IMF), recently published by UNEP/MAP-PAP/RAC, GWP-Med and UNESCO-IHP, hoping that the competent local and national authorities will follow it up.

The fact that the City of Elefsis not only graciously hosted the International Conference but also supported the publication of the present edition is a very promising sign for the commitment of the Mayor and the Council to this end. The Ministry for the Environment and Energy gave a positive signal, as well. The UoA, MIO-ECSDE and UNEP-MAP have already stated their willingness to further support the protection and sustainable development of the area.

All the elements mentioned above justify why this case study deserved a special edition of "Sustainable Mediterranean" to mark the 40th Anniversary of the Barcelona Convention and UNEP/MAP, the institutional and practical work of which has inspired, stimulated and framed the initiatives for the protection of the environment of the Mediterranean Sea and the sustainable development of the Region.

Prof. Michael J. Scoullos



L'ATTIQUE,
joint la
MEGARIDE,
le Pays de
CORIN
E & LOCRIDE,
BOEOCE, PHOCI

CEste Carte vous represente la plusspart du pays que Ptolomée appelle Achaïe ou Grece, different grandement de l'Achaïe particuliere, les modernes l'appellent *Livadie*, & comprend *l'Attique*, la *Megaride*, le Pays de *Corinthe*, la *Bæoce, Phocide & Locride*: Ses bornes sont du Nord la Thessalie & l'Eubée; du couchant le Mont Parnasse & d'Oëte; du Midy le sein Saronique ou Golfe d'Engia & le sein Corinthiaque, ou Golfe de lepante, avec l'Isthme de la Morée entre deux; & du levãt la Mer Egée où l'Archipelague, & les monts d'Oche.

Attique. L'Attique fut nommée anciennement Acte où Actique & pareillement Atthide d'Athis fils de Cranaüs, de mesme qu'lonie d'Jon fils de Xuthus, & Athenie de Pallas nommée aussi par les Grecs Athene; aujourd'huy les Chrestiens la nomment Duché d'Athenes, de mesme

Villes. qu'au temps de ses Ducs, depossedez par les Turcs. Elle aboutit à la Megaride du Couchant & du Nord à la Bœoce, ayant du Midy la Mer Cretique & le Sein Saronique ou Golfe d'Engia, & du Levant l'Archipelague.

Athenes. Sa ville capitale est *Athenes*, aujourd'huy Setine, toute demantelée & toutefois assez peuplée & divisée comme en trois parties ainsy qu'autrefois. La partie qui embrasse le chasteau, & qui est plus haute que les autres, n'est peuplèe que des Turcs, qui gardent aussi le fort. C'est en celle cy qu'est le Temple anciẽ du Dieu incognu, dont l'Autel est encor debout avec son inscription; mais bien qu'il soit beau, a cause de son marbre, toutefois il ne sert aux Turcs n'y aux Chrestiens. La seconde partie assise entre

vage. La ville *d'Eleusis*, à present Lepsin ou Saline selon le Noir, où Ceres El
Temple: *Marathon*, maintenant Marat
pagnes desquelles Miltiade défit l'armé
suite par Darius, & où fut le taureau
Thesée: *Rhamnus*, où estoit le
par que pour cette cause simplement
ceinte de long mur
tirè depuis la es uns, & Munychie *Rasei*; puis
Sucamino ou finit la

Caps. Son cap plus fameux est le Promontoire *Sunium*, aujourd'huy cap des Colonnes ou des Colombes.

Montagnes. Ses montagnes sont *Hymette*, *Brilesse*, *Lycabete*, *Parnes* & *Corydalle*.

Rivieres. Ses rivieres sont *Cephisse*, *Ilissus*, qui tarissent en esté selon Strabon, mais qui servent encor à present aux Atheniens pour l'arrousement de leurs oliviers. Ses fontaines sont *Larine*, *Callirhoe*, *Enneacrunos*.

Air. L'air de l'Attique est doux & sain au possible. Il y court un fort bon vent qui vient des montagnes, & les anciens ont remarqué que ce pays avoit un vent particulier nommé Sciron, incognu au reste de la Grece, qui se léve un peu au dessous de l'oüest Nort-oüest.

Eau. Il y a quantité de fort bonne eaux & toute sorte de bonnes herbes, qui rendent un odeur tresagreable & naissent tousjours. Il y a plusieurs milliers d'Oliviers qu'ils retiennent soigneusement, en tirant de l'huyle, qu'ils nomment barbarement *Ladiphi*, non Elajon, comme anciennement, en si grande quantité qu'ils ont force argent par ce moyẽ.

Miel & mines. Les anciens ont aussi fait tres-grand estat du Miel, qui venoit du mont Hymette, & tenu celuy d'Attique pour le meil-

Hendrik Hondius, "Attica, Megarica, Corinthiaca, Boeutia, Phocis Locri", Atlas Novus…, Amsterdam 1639.

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The publication is based on work largely financed by the European Union (European Social Fund) and National Funds (Hellenic General Secretariat for Research and Technology) in the framework of the project ARISTEIA I, 640 "Integrated Study of Trace Metals Biogeochemistry in the Coastal Marine Environment", within the "Lifelong Learning Programme".

Giorgos Tsoukalas

Mayor of Elefsis

The International Conference entitled *"The Environmental Perspectives of the Gulf of Elefsis - A Mediterranean case study where Science meets Society"*, held on 11 and 12 September in Elefsis, was a great success.

The Conference, jointly organized by the Municipality of Elefsis, the Laboratory of Environmental Chemistry and the UNESCO Chair & Network on Sustainable Development in the Mediterranean of the University of Athens, the Ministry of Environment and Energy and the United Nations Environment Programme/Mediterranean Action Plan (UNEP/MAP) within the framework of the *Aristeia I project "Integrated Study of Trace Metals Biogeochemistry in the Coastal Marine Environment"* of the University of Athens, took place at the City Hall of Elefsis.

In recognition of the significance of the works and findings of the Conference for Elefsis and the surrounding Thriassio Plain, the Municipality of Elefsis, gladly undertook the cost of producing the conference proceedings, aiming to reach out to as many interested parties as possible.

The main conclusion of the recent scientific studies (presented at the conference) is that the quality of the Gulf of Elefsis, which was dramatically degraded between 1960-1980 due to untreated industrial waste and urban wastewater, is already showing a major improvement. In fact, researchers and scientists are pleasantly surprised by the rate of recovery, which is beyond any expectation. The improvement is due to the reduction in inputs of fluid industrial waste (due to enforcement of measures, the shut-down of polluting industrial units and changes in the production processes of others), the improvement in the quality of industrial waste (installation of waste treatment systems), the reduction of decommissioned ships, the operation of the Psyttalia sewage treatment plant and the characterization of the Gulf of Elefsis as a sensitive area.

Crucial to the improvement were the efforts of the local residents and authorities of Elefsis and of the general Thriassio Plain. In recognition of the improvement of the Gulf of Elefsis, the Ministry of Health decided in 2003 to allow bathing in its waters. The classification of the Elefsis bathing waters as of "excellent quality" (as measured by the Ministry of Environment) from 2011 onwards, has been yet another major milestone. Nevertheless, the observed undeniable improvement, should not lead to complacency, but contribute to the continuation of efforts, so that there is an even greater and faster improvement of the gulf.

The conference also highlighted the connection between science and society: the results of scientific research can and should help to address environmental problems (as in the Gulf of Elefsis).

It is worth mentioning that at the end of the conference, Professor Michael Scoullos was proclaimed as Honorary Citizen of Elefsis, in recognition of his many years of scientific research and efforts in studying and protecting the environmental integrity of the gulf.

We hope that the conference proceedings will be useful to anyone interested in the environmental problems of our region and will encourage young scientists to contribute through their research to address these problems.

Jacques Ganoulis

Emeritus Professor AUTH, Special Secretary for Water, Ministry of Environment and Energy, Special Secretariat for Water

With great pleasure I welcome you to the International Conference on "Environmental Perspectives of the Gulf of Elefsis: A Mediterranean case study where Science meets Society".

My presence here today, in my capacity as Special Secretary for Water of the Ministry of Environment and Energy, Special Secretariat for Water, and as co-organizing partner, signifies the great importance attributed by the Greek Government for high level scientific research and knowledge as important prerequisites for the protection of the environment, management and sustainable Development of the Gulf of Elefsis.

The Gulf of Elefsis is one of the most well-known pollution hot spot areas and one of the best studied and monitored sites in the Mediterranean, thanks, to a large extent, to the continuous work of the Laboratory of Environmental Chemistry on various aspects of its environmental conditions, since the mid '70s. This resulted to the fact that today there is an extremely useful time-series of data available, able to demonstrate the evolution of the situation and even allow us to attribute some of the changes to the policies and strategies introduced at regional (Mediterranean), sub-regional (European) and national level.

It is very important that the Conference is co-organized through wider partnership including the City of Elefsis, the Laboratory of Environmental Chemistry and the UNESCO Chair & Network on Sustainable Development in the Mediterranean of the University of Athens, the United

Nations Environment Programme/Mediterranean Action Plan (UNEP/MAP) and the Mediterranean Information Office for Environment, Culture and Sustainable Development (MIO-ECSDE). Such partnerships should mark all aspects of modern governance from design and selection of priorities to planning and implementation of strategies policies and measures.

I am confident about the success of the Conference, which is guaranteed by the results of the project Aristeia (Integrated Study of Trace Metals Biogeochemistry in the Coastal Marine Environment) complemented with data from related programmes (e.g. Horizon 2020 for the De-pollution of the Mediterranean) and Institutes (e.g. HCMR). The results will help the development of measures and will enhance the hope of the wider society of Elefsis for the actual protection and an effective management of the marine and coastal environment of the Gulf.

With these thoughts I would like to welcome all the distinguished speakers of the Conference from Greece and abroad and I am sure that the results of their work will help the local authorities, society and the State to develop actions for a promising future.

Maria Peppa

Head of the Directorate of Studies and Projects for Urban Renewal Ministry of Environment and Energy

On behalf of the Ministry of Environment and Energy I would like to express my sincere thanks to the Municipal Authorities of the City of Elefsis and in particular to the Mayor, Mr. G. Tsoukalas for the hosting of such a significant event, directly linked to the protection of the environment and the sustainable development of Elefsis. I would also like to thank all the co-organizers of the International Conference and all those who have contributed with their presentations and interventions leading to useful conclusions which could benefit Elefsis and its ecologically and culturally significant region which faces long standing major environmental challenges. Special thanks are due to the University of Athens and the successful Aristeia/"Excellence" programme of the Laboratory of Environmental Chemistry which has produced valuable results presented during the Conference. In the same direction noteworthy are also the projects of the Hellenic Centre for Marine Research, which were also presented at the Conference.

The cooperation among all the co-organizers and participating institutions is exemplary and has contributed to the excellent results. I wish that such collaboration is continued and extended, if possible, to even more stakeholders in the future.

The results of the International Conference regarding the state of the Gulf of Elefsis are very optimistic in the sense that significant environmental improvement and recovery is shown. No doubt that the good results should not make us "relax". They should act as a stimulus to further action to eliminate the pollution, since significant pollution sources are still present.

In addressing pollution, a more efficient and coherent implementation and enforcement of the relevant legislation and policies is necessary, combined with application of the Best Available Techniques (BATs) according to the existing provisions and standards. The draft Strategic Plan for the Sustainable Management of the area of Elefsis and its gulf presented by Professor Scoullos is an excellent starting point for the Integrated Coastal Zone Management of the area. It acts in coplementarity with the scope of a set of projects and plans elaborated by the Ministry of Environment and Energy in the past few years, concerning the Master Plan of the Area of Attica focusing on the Sustainable Development of the Thriassion Plain of which Elefsis area constitutes the most significant part. Therefore, the Ministry welcomes the initiative.

Finally, let me also stress that under the current difficult economic circumstances of the country, the National Authorities hope and encourage combined, comprehensive initiatives of Local Authorities/ Municipalities, Universities and other Academic and research institutions as well as competent National, European and International Bodies (i.e. UNEP-MAP) and civil society. Joint initiatives by all stakeholders aiming at the protection of the environment, as well as achieving the sustainable development of ecologically sensitive areas, such as the Gulf of Elefsis, which are treasure houses for biodiversity, culture and history but also centers of dynamic industrial and commercial activities. All these activities need to remain in the epicenter of our interest, seeking for the achievement of an effective protection and restoration of the natural and human environment of Elefsis and the prosperity and well-being of the communities living in the region.

Thomas Sfikopoulos

Rector of the University of Athens

It is a great pleasure for the Rectorate of the National and Kapodistrian University of Athens, and for me personally, to participate in the International Conference entitled "The Environmental Perspectives of the Gulf of Elefsis - A Mediterranean case study where Science meets Society".

The great importance of the Conference derives from a four point combination.

1. The first point is the great scientific value of the research carried out under the "Aristeia I" project of the Laboratory of Environmental Chemistry (LEC) of the University of Athens. It must be stressed that LEC is internationally considered as one of the "State of the Art" laboratories working on environmental issues particularly aquatic and marine. Its connection with the UNESCO Chair & Network on Sustainable Development Management and Education in the Mediterranean provides a very useful scheme and

its cutting edge is recognized by a wide network of relevant International Institutions.

2. The second point focuses on the Gulf of Elefsis and the Thriassion Plain as an ecosystem and as the center of the industrial activity of the country, which connects the area and the research carried out within it, directly to the economy, both the positive and negative impacts of its fluctuations and, of course, to the crisis we are experiencing and the many different obstacles, which result from it and which we need to deal with and overcome. The research carried out at the University of Athens by the LEC, has effective and close collaboration with other high level research institutions (e.g. HCMR) and has successfully turned the scientific outcomes into public knowledge used for education, awareness and informed decision-making on environmental issues in order to benefit society.
3. The third point of particular importance, which is already stressed in the conference title, is the relationship between science and the role of Universities and other scientific institutions (such as HCMR) which cooperate closely with society in the field of research. Most of our work, or at least the majority of our studies, are not just based on scientific "curiosity". They derive from important issues (environmental, health, economic, legal, social, etc.) and the results and conclusions are communicated to the society for the identification of better solutions. The University of Athens is one of the very few institutions, that is an integral part of society.
4. The fourth important point is that the Conference is co-organized and supported by a wider partnership of agencies. From the extremely important local level, such as the Municipality of Elefsis, to the national level, with active participation of the Ministry of Environment and Energy and the International level, such as the United Nations Environment Programme/ Mediterranean Action Plan (UNEP/MAP) and the Mediterranean Information Office for Environment, Culture and Sustainable Development (MIO-ECSDE), a very important Federation of many Non-governmental Mediterranean organizations, with which UOA has a long and successful collaboration also through the Horizon 2020 Initiative for the De-Pollution of the Mediterranean.

Gaetano Leone

Coordinator, Mediterranean Action Plan of the United Nations Environment Programme / Barcelona Convention Secretariat

The beautiful, historic city of Elefsis, like many places in Greece, distils the essence of the unparalleled richness and of the profound challenges that the Mediterranean faces, especially along its shores. In a country like Greece, famed around the world for its extraordinary history and unique beauty, one sees it every day that the Mediterranean is a cradle of civilizations and a link among very diverse peoples and economies. But, looking beyond the perspective of the historian, the philosopher, the artist, the tourist, who passionately comes to Greece, one also sees that the Mediterranean, probably more than any other regional sea in the world, is a fundamental source of development, a vast set of coastal and marine ecosystems that deliver valuable benefits to all of its coastal inhabitants. Here the importance of ecosystems to people's livelihoods, their economic, social, physical and mental well-being, as well as their cultural heritage is under our eyes, it is an integral part of our identity as peoples of the Mediterranean.

Yet conditions around the Mediterranean region and ecosystems continue to be degraded. The pressures are heavy on such limited and vulnerable resources, coastal zones and the marine environment, caught in a vicious circle with the needs for growth and development that is hard to break and often difficult to understand.

The integrated management of coastal, marine and living resources that promotes conservation and sustainable use in an equitable way, and the monitoring and assessment of the environment of the Mediterranean Sea are at the centre of the mandate of the UNEP/MAP-Barcelona Convention – a Convention that celebrates this year its 40th anniversary. UNEP/MAP welcomes the scientific work presented at the International Conference in Elefsis and to be made available to the 19th Ordinary Meeting of the Contracting Parties to the Barcelona Convention (Athens, 9-12 February 2016). Work that provides a rigorous and clear view on the current state of the environment of the Gulf of Elefsis, developing the knowledge that is required for understanding environmental and socio-economic impacts. Most importantly, knowledge that is policy relevant and that, supporting the definition of appropriate concrete action and solutions, can turn the vicious circle mentioned above into a virtuous one.

It is because of this scientific assessment that the Gulf of Elefsis is one of the best studied and monitored sites in the Mediterranean, with its major pollution sources including the important industrial activity in the northern coastal zone of the Gulf and local municipal effluent, and its low rate of water exchange. We salute, therefore, the efforts of the many researchers, scientists and students over the years, compiling the monitoring of the most industrialized coastal areas of Greece since 1986. Their efforts have resulted in the most complete time series of trace metal levels in waters and sediments not only of the Gulf of Elefsis, but also of the Saronikos Gulf and South Evoikos Gulf. These data demonstrate the evolution of the situation and make it possible to attribute some of the changes to the policies and strategies introduced at regional, sub-regional and national level, successfully transforming those scientific outcomes into public knowledge used for education, awareness and informed decision-making on environmental issues to benefit society.

The United Nations Environment Programme Mediterranean Action Plan (UNEP/MAP) and the Barcelona Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean and its Protocols

Forty Years of Cooperation, Achievements and Challenges

The Mediterranean Action Plan and Barcelona Convention celebrate in 2015-2016 their 40th anniversary. For the last 40 years, they have provided a unique legally-binding regional instrument addressing the challenges faced by the Mediterranean coastal and marine ecosystems. The 21 countries bordering the Mediterranean Sea and the European Union are bound together through this advanced legal environmental framework comprised of the Convention and its seven Protocols aiming at:

- Preventing Dumping from ships and aircraft and incineration at sea.
- Preventing Pollution from ships and combating pollution in cases of Emergency.
- Protecting against Pollution from Land-based Sources and Activities.
- Establishing Specially Protected Areas and preserving Biodiversity.
- Protecting against Pollution Resulting from Offshore Exploration and Exploitation.
- Preventing Pollution from Transboundary movement of Hazardous Wastes.
- Establishing a common framework for the Integrated Management of the Coastal Zone.

MAP operates through its Coordinating Unit in Athens, Greece, the MED POL Programme, and Regional Activity Centers located in 6 different countries:

- Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea (REMPEC), Malta
- Plan Bleu Regional Activity Centre (PB/RAC), France
- Priority Actions Programme Regional Activity Centre (PAP/RAC), Croatia
- Specially Protected Areas Regional Activity Centre (SPA/RAC), Tunisia
- Regional Activity Centre for Sustainable Consumption and Production (SCP/RAC), Spain
- Regional Activity Centre for Information and Communication (INFO/RAC), Italy

The MAP-Barcelona Convention has been addressing the opportunities and challenges of the environment of the Mediterranean Sea and coasts, linking environmental sustainability with socio-economic development.
Over the past forty years, the main objectives of the Convention - assessment and control of marine pollution, protection of the marine environment and coastal zones, sustainable management of natural marine and coastal resources, strengthening solidarity among Mediterranean Coastal States - have spurred much progress:

- An advanced and comprehensive legal framework to achieve effective regional and sub-regional collaboration and national implementation.
- A transformative process to translate major sustainable development global milestones that are relevant to the MAP mandate to the regional level.
- A solid regional and national governance mechanism in place.
- A unique and efficient Trust Fund for the Protection of the Mediterranean environment.
- Progress towards a healthy Mediterranean with marine and coastal ecosystems that are productive and biologically diverse, contributing to sustainable development.
- Important policy, regulatory, technical and management measures are place: the number of waste water treatment plants and solid waste landfills in coastal cities, the use of BAT and BEP including in Small and Medium Enterprises, the number of marine protected areas and SPAMIs have substantively increased over the last 20 years, and the number of pollution hotspots has been reduced.
- Coordinated marine pollution monitoring programmes to be soon expanded to integrated biodiversity, hydrography, coastal protection and noise monitoring and assessment programmes to assess Good Environmental Status in an integrated manner.
- Several prestigious regional and subregional assessment reports have addressed the state, pressures, drivers and responses at regional and national levels, as well as the main challenges to protect the marine and coastal environment - taking into account environment and development interactions.

In conclusion, the MAP system has delivered remarkable achievements in areas of great importance, and development and application of transversal issues, such as: the implementation of the ecosystem approach (including biodiversity protection, natural resources management, combating pollution and litter); coastal and marine management (Integrated coastal zone management, marine spatial planning, integrated river basin management, marine and coastal protected areas); sustainable consumption and production; and climate change adaptation. Monitoring and assessment, research and knowledge development, provision of strategies, action plans, guidelines, management tools and capacity-building have been produced and have resulted in significant impact across the region. Most importantly, it has delivered successful cooperation among countries and stakeholders in a region characterized by its diversity and complexity.

Forty years since the MAP and the Barcelona Convention were signed off, the mission is still ambitious and exciting, the mandate is still most relevant, the opportunities for impact are still abundant and attainable, and the expectations are still high. This is one moment in a process of transition and change for UNEP/MAP that reflects a reality in the Mediterranean very different from 1975-1976, with new environmental challenges, tensions, and opportunities, where the situation of the marine and coastal environment continues to be under very difficult pressures, but where new instruments and approaches emerge to sustain our objectives.

Today's Responses

It is evident that conditions around the Mediterranean region and ecosystems continue to be degraded. The pressures are heavy on such limited and vulnerable resources, coastal zones and the marine environment, caught in a vicious circle with the needs for growth and development that is hard to break and often difficult to understand.

Problems should not define where we want to go. We are living a defining moment for global sustainable development and for the future of the Mediterranean region: integrating the agreed universal and transformative global goals and targets of the 2030 Agenda for Sustainable Development adopted at the UN Summit in September 2015, transitioning to a green and blue economy, implementing the new Paris climate change agreement, and striving to revive and boost stagnant economies are processes with a profound impact at all levels.

A number of strategic documents will be delivered at the 19th Ordinary Meeting of the Contracting Parties to the Barcelona Convention and its Protocols (COP 19, Athens, Greece, 9-12 February 2016):

- The UNEP/MAP Mid-Term Strategy 2016-2021;
- The Mediterranean Strategy for Sustainable Development 2016-2025, underpinned by the conviction that investment in the environment is a crucial way to secure long-term sustainable job creation and socio-economic development;
- The Mediterranean Offshore Action Plan;
- The Regional Strategy for Prevention of and Response to Marine Pollution from Ships 2016-2021;
- The Regional Action Plan on Sustainable Consumption and Production in the Mediterranean;
- The Regional Climate Change Adaptation Framework for the Mediterranean Marine and Coastal Areas;
- A very ambitious Integrated Monitoring and Assessment Programme of the Mediterranean Sea and Coast and Related Assessment Criteria;
- Several sets of Guidelines and Action Plans.

This is a package that will support and facilitate translation of global aspirations and goals expressed by the 2030 Agenda for Sustainable Development and its SDGs at regional level.

Relevance of the International Conference on the Environmental Perspectives of the Gulf of Elefsis - A Mediterranean case study where Science meets the Society (Elefsis, 11-12 September 2015)

This Conference and the research presented are linked to the entire agenda of UNEP/MAP but more closely to the MED POL programme and its main Protocol, namely the one on Land-Based Sources of Pollution, as well as to the one on Integrated Coastal Zone Management.

The MED POL programme assists Mediterranean countries in the formulation and implementation of pollution monitoring programmes, including pollution control measures and the drafting of action plans aiming to eliminate pollution from land-based sources, since it has been proven that 80% of the main sources of pollution for the marine environment originate from human activities on land. Moreover, the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources and Activities adopted in 1980 and amended in 1996 aims to prevent, abate, combat and eliminate to the fullest possible extent pollution caused by discharges from rivers, coastal establishments or outfalls, or emanating from any other land based sources and activities within their territories, giving priority to the phasing out of inputs of substances, that are toxic persistent and liable to bioaccumulate.

Over the past 20 years in particular, UNEP/MAP have developed and implemented regional policies and their national responses:

- 1997-2001: Overarching policy: SAP MED - the regional strategic policy to facilitate the implementation of the 1996 Land Based Sources (LBS) Protocol. 38 precise pollution regional targets and timetables aiming at a gradual pollution reduction in 2010, 2015 and elimination in 2025.
- 2002-2005: National Action Plans (NAPs) describing policy and priority pollution reduction/elimination projects. COP13, 2005 endorsed the NAPs.
- 2008 COP Almeria, Spain Decision IG 17/8: (i) continue

NAP implementation and support capacity building; (ii) foresee a revision of the NAPs in 2011; (iii) prepare legally binding pollution reduction/elimination measures and timeframes (Regional Plans) for selected pollutants and sectors.
- 2009-2013 COP 16, COP 17, COP 18 adopted 10 regional plans on BOD from WWTP, POPs, 10 additional POPs, BOD from food sector; Mercury from different sectors and RP on Marine litter; 3 regional plans in force since 2009; and approved Ecological Objectives for the Mediterranean.
- NAP update to achieve GES and take into account the legal commitments of the regional Plans.

Work on Monitoring and Assessing Marine Pollution is ongoing for 30 years. Over the last decades, monitoring data about the Gulf of Elefsis were being reported to MED POL, helping significantly the progress of its work. Despite the great complexity of the anthropogenic activities in the Gulf and its catchment area and the overlapping management competencies of various ministries and entities, the biogeochemical conditions in the Gulf, in combination with the legislation and its implementation through a series of measures, and the considerable technological improvements in environmental technologies, has resulted in visible reduction of the pollution loads and clear improvements in the state of the environment of the Gulf. In fact, although improvements are reported in many places, there are still very few attempts to study and demonstrate the correlation between policies and their impacts in the improvement of the environment.

For UNEP/MAP, but also for the other environmental Conventions, regional and international organizations, etc., this kind of work is needed and should be encouraged. It is because of this scientific assessment that the Gulf of Elefsis is one of the best studied and monitored sites in the Mediterranean, with its major pollution sources including the important industrial activity in the northern coastal zone of the Gulf and local municipal effluent, and its low rate of water exchange. The efforts of the many researchers, scientists and students over the years, compiling the monitoring of the most industrialized coastal areas of Greece since 1986 have resulted in the most complete time series of trace metal levels in waters and sediments not only of the Gulf of Elefsis, but also of the Saronikos Gulf and South Evoikos Gulf.

The Contracting Parties are aiming at reaching a good environmental status of the Mediterranean waters by 2020. Until this objective is met, the environment of the Mediterranean marine and coastal systems will continue to be threatened, and the delivery of important and valuable ecosystem services will be at risk. As a result, so will be the communities and countries that border the basin. The Integrated Coastal Zone Management Protocol adopted in 2008 is an innovative response to the challenges of sustainable development, considering that the development of coastal management systems can truly attain economic, social and environmental objectives if addressed in an integrated fashion while involving all the stakeholders who benefit and enjoy the services of the marine and coastal ecosystem.
The coastal zone is an area of intense activity, an area of interchange within and between physical, biological, social, cultural and economic processes. Changes, at any point in any part of the systems, can generate chain reactions far from their point of origin, and possibly in a totally different system whose environmental conditions will be subsequently altered. Integrated coastal zone management means a dynamic process for the sustainable management and use of coastal zones, taking into account at the same time the fragility of coastal ecosystems and landscapes, the diversity of activities and uses, their interactions, the maritime orientation of certain activities and uses and their impact on both the marine and land parts.

In 2008, the Contracting Parties expressed their conviction that as an irreplaceable ecological, economic and social resource, the planning and management of coastal zones with a view to their preservation and sustainable development requires a specific integrated approach at the level of the Mediterranean basin as a whole and of its coastal States, taking into account their diversity and in particular the specific needs of islands related to geomorphological characteristics.

The Integrated Coastal Zone Management Protocol was approved that same year. This is a pioneering Protocol and it constitutes crucial added value for the Barcelona Convention and the Mediterranean Action Plan. It is the first time that Integrated Coastal Zone Management is fully addressed by a legally-binding international instrument. On 24 March 2011, the ICZM Protocol entered into force. With this instrument, the Contracting Parties have committed to establish a common framework for the integrated management of the Mediterranean coastal zone and take the necessary measures to strengthen regional co-operation for this purpose.

In this context, the data available and presented at the International Conference in Elefsis demonstrate the evolution of the situation and make it possible to attribute some of the changes to the policies and strategies introduced at regional, sub-regional and national level, successfully transforming those scientific outcomes into public knowledge used for education, awareness and informed decision-making on environmental issues to benefit society and support the sustainable development of the region.

The Aristeia ("*Excellence*") Project for the "Integrated Study of Trace Metals Biogeochemistry in the Coastal Marine Environment"

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Abstract

Trace Metals have attracted significant scientific interest due to their wide dispersal in the environment, their provenance from a variety of natural and anthropogenic sources, and their toxicity to biota and humans. European environmental issues and related policies, such as, the Marine Strategy Framework Directive (MSFD), the Water Framework Directive (WFD), the Union for the Mediterranean's Horizon 2020 Initiative to De-Pollute the Mediterranean, the UNEP/MAP Integrated Coastal Zone Management (ICZM) protocol, etc., refer to trace metal distributions, speciation and behavior. The understanding of the environmental biogeochemical cycling of metals that includes their sources and sinks, as well as their transport and interaction patterns, requires sound knowledge of their chemical speciation, which is also useful for assessing the impacts of pollutants on the overall ecosystem functioning, including their toxicity and bioavilability. The *Aristeia* ("*Excellence*") project aimed to elucidate the trends in trace metal pollution of notorious hot spot coastal areas (The Gulf of Elefsis as well as the Evoikos Gulf) and evaluate the effectiveness of measures and policies that have been applied for the reduction/prevention of pollution of the coastal zone. Furthermore, we aimed to identify in detail the current environmental status of these areas including potential risks for the ecosystem and human health and compare them with past records. Finally, through the Dissemination Actions we aimed to communicate these results to local stakeholders and the general public.

Keywords: trace metals, biogeochemistry, coastal, *Aristeia*.

Introduction

The Laboratory of Environmental Chemistry (LEC) of the National and Kapodistrian University of Athens (NKUA) was established in 1982 by Prof. M. Scoullos who is considered to be a pioneer among Greek Academia in the field of Marine Chemistry and introduced the study of different chemical forms of metals in waters and sediments as early as the late seventies. Since then LEC - NKUA has a demonstrated excellence in trace metal analysis in a wide variety of environmental media and has used a large variety of speciation methodologies and techniques. During this time the staff of LEC-NKUA has published over 200 scientific papers, more than 300 other types of publications and a very long list of conference presentations. Furthermore, more than 160 doctorate and master degrees have been awarded based on research carried out in the LEC. LEC has also compiled the monitoring of the most industrialized coastal areas of Greece since 1986 and is now holding one of the most complete time series of trace metal levels in waters and sediments of the Gulf of Elefsis and Evoikos Gulf (Scoullos *et al.* 2015). LEC has effective close collaboration with other high level research institutions (e.g. HCMR) and is also working in Public Awareness, Environmental Education (EE) and Education for Sustainable Development (ESD) and has successfully transformed the produced scientific outcomes into public knowledge used for education (Koutalidi and Scoullos, 2015), awareness and informed decision making on environmental issues to benefit society.

Materials and methods

The *Aristeia* project aimed to undertake speciation studies combined with total trace metal analysis in water, sediment and biota samples with existing protocols used in our research efforts and with new protocols that were developed during the project by the scientific team (Scoullos *et al.*, 2015). In order to successfully undertake the above mentioned studies LEC purchased an analytical instrument (ICP-MS) through this project (Fig.1). Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is arguably the most versatile trace elemental analysis technique available today. Depending on the individual instrument configuration, sample types ranging from sea waters and rock digests to ultra-pure semiconductor grade chemicals can be routinely analysed, for almost all the elements in the Periodic Table, from low pg/mL (in most cases) to high µg/mL concentration levels.

The utilization of the highly sensitive, multi- elemental technique ICP-MS system with collision cell technology to remove interferences in conjunction with the existing infrastructure of LEC (a clean room, atomic absorption spectrometers, environmental sampling equipment) allowed the integrated study of trace metal distributions, exchange between phases and compartments, sources and sinks in polluted coastal marine environments and in special intermittently anoxic conditions (Kapetanaki *et al.*, 2015; Karavoltsos *et al.*, 2015a, 2015b; Katsouras *et al.*, 2015; Louropoulou *et al.*, 2015; Scoullos *et al.*, 2015).
LEC carried out in depth study of almost all aspects of distributions in the aquatic environment for the most common trace metals (Cd, Cr, Cu, Zn, Ni, Fe, Mn, Al, Pb) for which there was already extensive background research.

Fig.1: Inductively Coupled Plasma Mass Spectrometry (model iCAP-Qc)v

Furthermore, the utilization of the new ICP-MS gave LEC-NKUA the opportunity to measure for the first time a larger number of other trace elements i.e. As, Ga, Se, V, Rb, Sr, Cs and start research in Rare Earth Elements.
Since the ICP-MS was used for the first time in the LEC-NKUA one aspect of this research was to focus on analytical methodology i.e. to plan the analytical protocols and validate them.

The *Aristeia* project focused on two coastal areas of Greece that face increased environmental pressures and pollution problems. The first area (Gulf of Elefsis) is affected by significant industrial activities and increased ship traffic and suffers from intermittently anoxic conditions during summer (Scoullos *et al.*, 2015). The other one (Evoikos Gulf) is also under environmental pressure from industrial (Louropoulou *et al.*, 2015) and urban sources for several decades and it is also affected by a strong tidal current which is rare in the Mediterranean area. The research activities of the project included:

- In situ measurements of physicochemical and hydrological parameters.
- Samplings of seawater – sediments – particulate matter – organisms in all parts and depths of the selected areas.
- Determinations of total metal concentrations and various metal forms using speciation methodologies and measurements with ICP-MS.
- Use of statistical programmes for the handling of research results, as well as construction of specific databases.

The trace elements determined, represent four categories: a) elements of high priority in the Mediterranean Region (Pb, Cd, As), b) essential for organisms elements (Fe, Cu, Se, Zn), c) elements with high concentrations in the sediments of the studied areas due to geological singularity (Ni, Cr, Mn) and d) metals deriving from anthropogenic activities with little toxicity data (V, Rb, Sr).

The project assisted the staff of LEC to strengthen existing collaborations and form new ones in the areas of trace metal speciation and analysis. The collaborating researchers and institutes were: Ruder Boskovic Institute of Zagreb (Assoc. Prof., Dr. Marta Plavšić), Marine Environmental Studies Laboratory (MESL-IAEA, Director Dr. Agelidis, Dr. Emilia Vassileva), Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry (Assoc. Prof., Dr. Diana Rabadjieva), Priority Action Program/ Regional Activity Centre (PAP/RAC) (Split, Croatia) and Institute of Atmospheric Pollution Research of the National Research Council of Italy (CNR-IIA).

Scientific Team - Work packages

The proposed research carried out by the following scientific team members:

- Experienced Academic Staff – Steering Commitee: 1) Prof. M. Scoullos (Principal Investigator), 2) Prof. M. Dassenakis 3) Prof. Ath. Valavanidis.
- Experienced LEC - Researchers: 1) Dr. S. Karavoltsos, 2) Dr. A. Sakellari, 3) Dr. F. Botsou, 4) Dr. V.

Paraskevopoulou, 5) Dr. E. Stathopoulou.
- New members: 1) Dr. G. Katsouras (post doctorate researcher), 2) E. Louropoulou (doctorate candidate), 3) N. Kapetanaki (doctorate candidate), 4) O. Chalkiadaki (MSc student), 5) N. Mpoura (MSc student), 6) A. Andrioti (MSc student) and 7) V. Kalambokis (MSc student).

In order to achieve the project aims, the following working packages (WP) were implemented:

WP1 – Purchase and installation of scientific equipment - Set up of equipment - Analytical protocols - Test runs (Month 0-30): After setting the technical characteristics of the requested equipment and having an indication of the requirements and the costs, an ICP-MS and the Hg-fluxes modules were purchased. The development of analytical protocols took place by the experienced researchers of LEC in collaboration with all the new members of the scientific team and under the supervision of the Academic Staff of LEC.

WP2 – Samplings and Analysis (Month 13-36): This work package included the main part of the experimental work for this project, i.e samplings in the selected hot spot coastal areas (Gulf of Elefsis and Evoikos Gulf) and the analysis of samples. All LEC members (old and new) with their experience were involved in designing and carrying out sampling missions and finally did the neseccary analyses.

WP3 – Collaborations with other Institutes (Month 4-36): This work package covered the exchange visits of LEC staff to the other European Institutes mentioned above and the travel of their researchers to Athens.

WP4 – Dissemination actions (Month 18-36): The last package included the organization of the Final Conference of the *Aristeia* project as dissemination action, as well as the presentation of the research outcomes of the project in National and International conferences and scientific journals.

Conclusions

In conclusion, through all the measures mentioned above, the following specific objectives of the *Aristeia* project were achieved from 9/2012 to 9/2015:

a) The study of metal pollution trends and the evaluation of the effectiveness of measures and policies that have been applied for the reduction/prevention of pollution in the coastal zone of Elefsis and Evoikos Gulf.
b) The investigation of the biogeochemical cycles and speciation of metals that have newly emerged as pollutants, by means of new sophisticated methodologies and techniques (ICP-MS). The operation of the unique ICP-MS equipment in the NKUA alone, has already led to research collaborations with other departments of NKUA for biological, geological and medicinal applications.
c) The realisation of the vision of the Laboratory of Environmental Chemistry, to become a robust Centre of Excellence, able to contribute effectively to the improvement of the Mediterranean Coastal Environment by employing better environmental and analytical chemistry, improving inter-disciplinarity, and disseminating useful knowledge through collaborations with governmental and scientific bodies, education and public awareness.

During the same period (2012 – 2015) the research strategy of LEC/NKUA, linked to several current marine policy issues and research initiatives. The ones presenting greater synergy possibilities were: The *Marine Strategy Framework Directive*, the *Water Framework Directive*, the *UNEP/MAP ICZM* Protocol the *Strategic Action Program* (SAPMED of UNEP/MEDPOL), the *HORIZON 2020 Initiative* to De-Pollute the Mediterranean.

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The Scientific Team, 2015.

Snapshot from the International Conference, 2015

Trace metals in seawater and sediments of the Gulf of Elefsis: 1977 – 2015

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Abstract

For several decades the industrial activities in the enclosed gulf of Elefsis contributed with significant amounts of trace metals to the seawater and sediments. In recognition of the environmental problems related to pollution in Elefsis bay, monitoring campaigns have been undertaken by research teams of the Laboratory of Environmental Chemistry starting in 1977 by Prof. Scoullos and continue to this day. This study presents a compilation of all available data for some of the major trace metals from the 1977 until the current monitoring campaigns of 2015 organized for the project "*Aristeia* – Integrated Study of Trace Metals Biogeochemistry in the Coastal Marine Environment". The comparative study of trace metal levels in seawater (dissolved and particulate forms) during these last 38 years shows a significant decrease in all cases of the metals studied (Cd, Cu, Fe, Mn, Pb, Zn). In the sediments comparison of current concentration levels against sub-surface sediments as well as against older data showed in the case of Pb a decreasing trend in all stations and occasional decrease in the cases of Zn and Cu.

Keywords: cadmium, copper, nickel, lead, zinc, Saronikos

Introduction

Trace metals in the marine environment are known to play a dual role, either as essential micro-nutrients (e.g. Fe, Co, Zn, Cd, Cu) and/or as toxic agents especially when present in high concentrations (e.g. Cu, Pb, Cd, Ni, Cr, Hg, As). In such cases trace metals may cause degradation of the environment and pose a risk for serious damages through the processes of trophic transfer and bioaccumulation. In coastal waters and marginal seas trace metal concentrations are usually found higher than in open oceanic waters. The enrichment in metals is attributed to both natural and anthropogenic inputs. Among the natural ones are included the transport of weathered crust material via streams, surface runoff, submarine groundwater discharges (SGDs), emanation from sediments, atmospheric deposition and upwelling of deep waters. Anthropogenic sources include direct industrial emissions, emissions from roads and marine traffic, surface runoff from urbanized areas, sewage discharges, activities in ports, all of which impact trace metal levels and their biogeochemical cycling.

Saronikos Gulf and mostly the enclosed gulf of Elefsis on the northern coast are subjected to intense anthropogenic pressures since they are the marine border of the cities of Athens and Piraeus with ~4 million inhabitants. Saronikos and Elefsis are the only water bodies in Greece which have been systematically monitored from 1985 onwards in the framework of two projects: the 'National Monitoring Program for the Assessment and Control of Marine Pollution in the Mediterranean' MAP/UNEP MED-POL and the 'Monitoring of the Saronikos Gulf ecosystem under the influence of the Psittalia sewage outflow' supported by the Athens Water Supply and Sewerage Company.

Saronikos Gulf is situated in the central Aegean Sea (northeast Mediterranean) between 37.30′N - 38.00′N and 24.01′E - 23.00′E. The length of the coastline is ~ 270 km, the surface ~ 2.866 km^2 and the mean water depth is ~100m. To the north, a shallow (~30m depth) embayment is formed, the gulf of Elefsis, which is separated from the gulf by the island of Salamina, and it communicates with it through two narrow channels: the eastern Elefsis channel and western Elefsis channel. Two small urbanized rivers (Kifissos and Ilissos), discharge into Saronikos but due to obstructive heavy modifications of their flow their discharges become visible only during heavy rainfall (Paraskevopoulou *et al*., 2014).

Water circulation in the gulf of Elefsis is both thermohaline and wind driven. Surface waters enter the bay via both channels, mix with less saline waters and exit again via both channels. Most of the subsurface water exchange occurs through the eastern Elefsis channel which is much deeper (~25m) than the western one (~10m) (Scoullos and Riley, 1978). Due to its specific morphology and water circulation, the bay experiences hypoxic or intermittently anoxic conditions in its deeper part, during the stratification period (Pavlidou *et al*., 2010). During autumn and winter months however, episodic rainfalls provide freshwater into the bay through four ephemeral streams, the small Koumoundourou Lake (via a narrow channel) as well as via submarine groundwater discharges, resulting in lower salinity values in both surface and bottom waters (Dimitriou *et al*., 2008).

Several point and non-point pollution sources are present in the greater area of the Saronikos and Elefsis gulfs. Until 1994 the untreated effluents of Athens and Piraeus were discharged outside the gulf of Elefsis but a significant part of the mixed waste water - seawater mass was transported into Elefsis through the western channel due to the prevailing water circulation. After that time the Athens WWTP (waste water treatment plant) went into operation and this phenomenon stopped because the treated effluents are discharged into Eastern Saronikos and at increased depths (60m). Recently (2012) a new WWTP came into operation that discharges into Elefsis. Other point sources are spread along the coasts and include marinas, touristic facilities, fish farms and the treated or untreated effluents of smaller towns and settlements. The industrial zone of Athens, with numerous polluting activities, is situated at the Elefsis area. These activities include shipyards, oil refineries, food industries, iron steelworks, cement factories, cable manufacturing, waste recycling plants, landfills, military installations including a naval military base and an airport; some activities such as illegal waste dumping in wells have been also identified in the past. Most of them have direct input to the bay's waters while others contaminate the soils or the groundwater affecting the marine environment via runoff and/or SGDs. The non-point pollution sources for Saronikos Gulf include marine traffic, since the port of Piraeus is one of the largest in the Mediterranean, where approximately 5000 ships per year are recorded, and possibly the atmospheric deposition of metals from rainfall in the adjacent urban areas (Paraskevopoulou *et al* 2014).

Materials and methods

The trace metal data presented in this paper were compiled over 38years (1977-2015) and they correspond to 80 sampling campaigns in 3 - 5 stations across Elefsis Bay and 300-558 samples depending on the metal in question. Samplings were carried out either by rented boats or with the oceanographic vessels of HCMR (Hellenic Centre for Marine Research) "Aegaeo" and "R/V Philia". From 2001 until 2014 studies of metals in marine waters have not been funded in the various monitoring campaigns but we have continued to collect samples for trace metal analysis with the gracious assistance of HCMR research staff and technical staff. The map of stations is presented in Figure 1.

As soon as possible after collection the samples (~2L) were transferred to the laboratory where they were filtered through nitric cellulose Millipore membrane filters

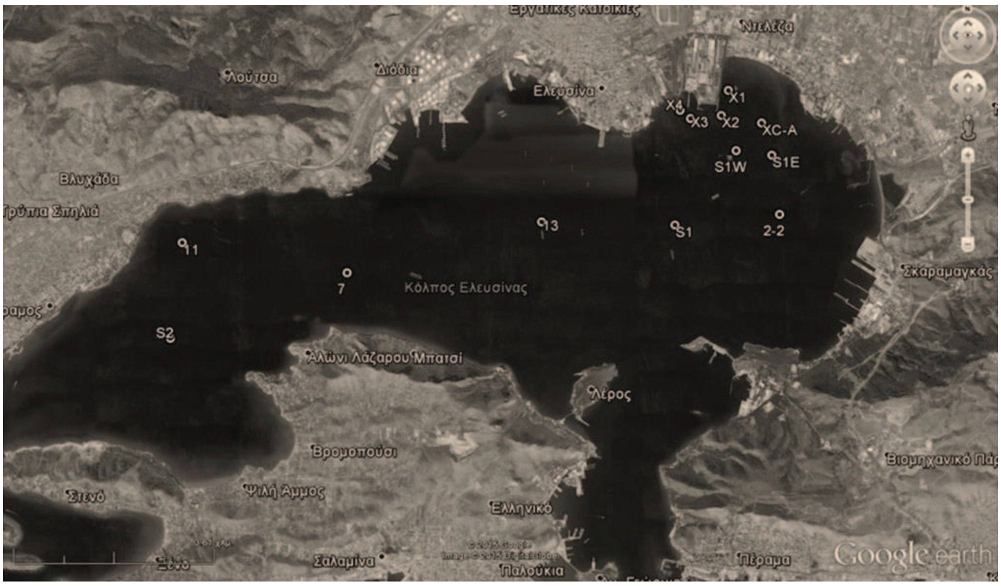


Fig.1: Map of stations in Elefsis Bay

(0.45 µm pore size). The filtered samples were acidified to pH 2 with HNO_3 65% s. p. and stored refrigerated until analysis. For the determination of dissolved trace metals (Cd, Cu, Ni, Pb, Zn, Fe, Mn), a preconcentration procedure was followed using Chelex-100 resin in a clean laminar hood (class 100 US Stds). This procedure is a slight modification (Scoullos *et al*., 2007) of that proposed by Riley and Taylor (1968) and Kingston *et al*. (1978). The metals retained on the resin were eluted with 1M HNO_3

s.p. The preconcentration factor was usually 50-100 but could be extended up to 250. The particulate matter retained on the filters was dried to constant weight and the filters were then digested with concentrated nitric acid in closed PTFE vessels on a hot plate or in a microwave oven (CEM-MarsXpress).

Surface and subsurface (15 cm depth) sediments were sampled on 31 March 2015 by a Birge-Ekman grab sampler from four central stations of the bay (S1, 13, 7, and S2; Figure 1). The samples were freeze-dried in a Lab Congo apparatus and the silt and clay fraction (<63 μm) was separated by sieving. Total element contents of the silt and clay fraction of sediments were determined after complete dissolution of sediment samples with an acid mixture of HNO_3-$HClO_4$-HF (ISO-14869-1:2000). The 0.5 N HCl extractable major elements and trace metals were determined after the method of Agemian and Chau (1976). Magnetic parameters, low-field magnetic susceptibility (xlf) and frequency dependent susceptibility (xld%) were measured on a mass specific basis by a Bartington susceptibility sensor. Further details are given in Scoullos *et al*. (2014).

Metal concentrations in the eluates and particulate matter / sediment digestion solutions were determined by atomic absorption spectrometry (flame and graphite furnace techniques). The same equipment has been used since 1996 (Varian SpectrAA 640Z with Zeeman background correction and Varian SpectrAA 200). All glassware and labware used was previously soaked in 10% nitric acid for 48 h and afterwards rinsed with ultrapure Milli-Q water. Precautions were taken during all stages in order to avoid contamination.

Results and Discussion

Seawater

All metals exhibit a decreasing trend during these last 38 years. In some cases the decrease was quite dramatic. This trend can be attributed to improvements in production processes in the industries, reduction of emissions and discharges due to legislation provisions and their implementation through the installation of filters and depolluting devices, shut-down of some industries and decrease in production levels of others, as well as changes to the fuels used (replacement of heavy oil by gas) and the use of unleaded gasoline for vehicles.

For each metal in particular more specific reasons and causes exist. The dramatic decrease of Cd concentration (Figure 2a) is probably attributed to the abandonment of the practice of dumping the phosphogypsum waste generated during phosphate fertilizers production. The fertilizer plant was closed down in the mid 1990s and demolished in 2003.

Considerable reduction of Fe (Figure 2b) but also of other metals such as Zn, Cu and Pb was caused by the installation of effective reduction technologies for the air and liquid emissions in large metallurgies of the area that are using considerable quantities of metal scrap for iron and steel production. The reduction of Pb concentrations may furthermore be attributed to the gradual replacement of leaded gasoline by lead-free fuels and more systematic recycling of lead batteries. Mn in Elefsis bay should be considered separately from the other trace metals because of the intermittently hypoxic and anoxic conditions. Dissolved Mn presents extreme concentrations in the bottom waters during the summer months (stratification period).

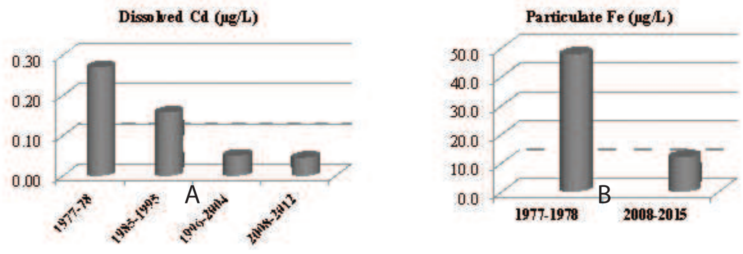
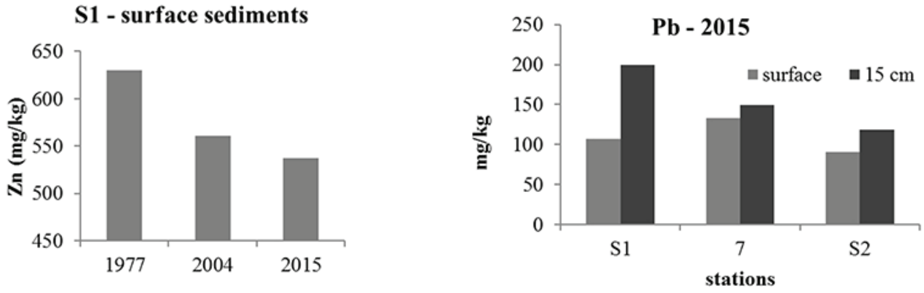


Fig.2: (a) Evolution of dissolved Cd concentrations, (b) evolution of particulate Fe concentrations

Sediments

Magnetic susceptibility χin of the sediments followed a decreasing trend from the western (χin=1.00 10-6 m^3 kg^{-1} at station S1) to the eastern part of the bay (χin=0.24 10-6 m^3 kg^{-1} at station S2) and correlated well with total Fe ($r=0.970$ $p<0.0005$). Early studies of Scoullos (1979; 1983) and Scoullos *et al*. (1979) by combining magnetic measurements and trace metals analyses on the SPM (Suspended particulate matter) on a seasonal basis had enlightened the origin of Fe in the bay: the strong, positive correlation between Fe in the particulate phase and the magnetic properties of the suspended solids, provided evidence that the magnetically active, rich in Fe oxyhydroxides particles, deriving from the steelmaking process, at the iron and steel making plant located on the NE coast of the bay, constituted a stable component of the particulate Fe population in the studied area (Scoullos *et al*., 2014).

Apart from Fe, Mn contents at the surface sediments exhibited maximum value at station S1. On the other hand, the highest values of Cu, Pb, and Zn were found at station 7 and the extractability of these metals by 0,5 N HCl was more than 75%. Trace metals levels of the surface sediments of the 2015 sampling were compared against older values of Scoullos (1977), and when available with the MED POL data of 2004, at the same stations, as well as against subsurface sediments obtained in 2015. Considering Cu and Zn (Fig 3a) a decreasing trend is observed at station S1, whereas no clear trend is observed at all other stations. Lead levels exhibited a clear decreasing trend at all stations (Fig. 3b). Finally, Zn surface levels also decreased at the central station 7 whereas no clear trend was observed at the other stations.



A B

Fig.3: (a) Evolution of Zn levels in surface sediments of station S1, (b) Concentrations of Pb in surface and sub-surface sediments of Elefsis Gulf

Conclusions

The trace metal dataset from the Gulf of Elefsis is quite extensive beginning in the late70s when the area was still heavily industrialized and the counter-pollution and environmental protection measures were scarce or nonexistent. Therefore we have observed a significant decrease in trace metal levels in seawater due to the implementation of emission reduction measures on one hand but also due to the negative economic climate that led to significant de-industrialization of the area. The decrease of metals in sediments is also apparent but less pronounced, thus their contribution as a secondary source to the overlying water column should continue to be a research priority. The case study of metals in Elefsis Gulf proves that when pollutant inputs are reduced even a severely polluted environment can be restored.

Acknowledgements

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Evolution over the last 30 years of the trophic conditions in the Gulf of Elefsis

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Abstract

In this work, long term biochemical data were evaluated to study the evolution of the trophic status in Elefsis Bay during the last thirty years, in phase with the anthropogenic and natural pressures in the study area. The overall trophic status of the Elefsis Bay ecosystem for the last decade (2005-today) is characterized as POOR. However, a significant improvement of the trophic status has been observed after 1995 till today, which possibly reflects the decrease of the nutrient pollution in the bay, mainly due to the operation of the Sewage Treatment Plant in Psitallia since the end of 1994.

Keywords: Trophic status, Elefsis bay, nutrients, eutrophication, eutrophication index (E.I.)

Introduction

Coastal marine environments are usually influenced by both human-induced and natural pressures, which may alter their functioning, and finally contribute to ecosystem degradation. The legislation developed and applied worldwide requires suitable methods to assess the ecosystems' quality in relation to anthropogenic impacts, using various elements of the ecosystem. In Europe, the umbrella regulations for addressing the ecological quality of the water systems are the Water Framework Directive (WFD; 2000/60/EC), and the Marine Strategy Framework Directive (MSFD; 2008/56/EC) (Pavlidou *et al*., 2015 and references therein).

Regarding eutrophication, several methods have been developed in the EU, in order to assess the eutrophication status and evaluate its trends. In Greece, a eutrophication scale has been developed (Ignatiades *et al*, 1992; Karydis, 1999; Pagou *et al*, 2002; Simboura *et al*, 2005) in the context of WFD. In addition, two multiparametric methods, Eutrophication Index (E.I.) and TRIX, were used for the assessment of the trophic conditions of the Greek coastal waters, according to the WFD requirements (Pavlidou *et al* 2015 and references therein).

This study was conducted in Elefsis Bay, a semi-enclosed marine area of the Aegean Sea in the East Mediterranean Sea, affected mainly by the industrial zone of Athens (oil refineries, shipyards, chemical plants, food, metal, cement industries, etc.) and the effluents from the Waste Water Treatment Plant (WWTP) of west Attica. The Elefsis Bay ecosystem is very complicated, variable and fragile, due to its morphology (enclosed), bathymetry (shallow, 33m max depth) and intense anthropogenic activity.

In the eastern reach of Elefsis Bay lies the city of Athens with a population of over five million. The eastern Keratsini channel (Fig. 1) is impacted by the industrial and shipyard area of Piraeus harbor, the largest harbor in Greece. Until 1994, the Keratsini channel was receiving the untreated domestic and industrial sewage of the Athens Metropolitan area, which was discharged into the surface water layer of the channel and enriched the Elefsis bay in metals, nutrients and organic matter. After 1994, the sewage of the Athens Metropolitan area was primarily treated in the Psitallia Sewage Treatment Plant and discharged into the inner Saronikos Gulf, whereas, by the end of 2004 the secondary stage of the Psittalia Sewage Plant was operating. During the last three years, the eastern part of the bay, with maximum depth 20m, receives the effluents from the Waste Water Treatment Plant (WWTP), discharging at 14m depth.

In this work, long term biochemical data were evaluated to study the evolution of the trophic status of Elefsis Bay over the last thirty years, in phase with the anthropogenic and natural pressures in the study area. A five-step methodological tool, the Eutrophication Index (E.I.), was used in order to assess the eutrophication status of Elefsis bay in the context of the WFD.

Materials and Methods

Elefsis Bay has been thoroughly studied since the 1960s by the National Research Center "Demokritos", the University of Athens and the Hellenic Center for Marine Resesarch (HCMR) (Pavlidou *et al*., 2010 and references therein). The data used in the present work were obtained from four to twelve cruises per year during 1987-2015 within the framework of monitoring programs realized by HCMR, on board of the research vessels «Aegaeo» and «Filia» of HCMR, or smaller rented boats. The data used herein are from two stations (S1, S2) in Elefsis bay and one in Keratsini (S3). During the last three years two more stations (S1e, S1w) are being monitored, in order to study the influence of the WWTP in the eastern part of the bay (Fig. 1). Seawater samples were collected from standard depths with Niskin bottles, either mounted on a rosette or individually on a hydro wire. Nutrient and chlorophyll-a data were measured using standard methods.

For the assessment of the trophic status of the water column the synthetic Eutrophication Index (E.I.) was used, which combines the concentrations of nutrients (phosphate, nitrate, nitrite, ammonia) and chlorophyll-*a* biomass into a single formula (Primpas *et al*., 2010):
$E.I.= 0.279^* C_{PO4} + 0.261^* C_{NO3} + 0.296^* C_{NO2} + 0.275^* C_{NH4} + 0.214^* C_{Chla}$

Where: C_{PO4} the concentration of phosphate (in mmol*m^{-3}); C_{NO3} the concentration of nitrate (in mmol*m^{-3}); C_{NO2} the concentration of nitrite (in mmol*m^{-3}); C_{NH4} the concentration of ammonium (in mmol*m^{-3}); C_{Chla} the concentration of phytoplankton chlorophyll-a (in mg*m^{-3}).

The E.I is divided into five classes: (a) less than 0.04; (b) 0.04-0.38; (c) 0.38-0.85; (d) 0.85-1.51; (e) greater than 1.51, corresponding to the High, Good, Moderate, Poor and Bad water qualities of the WFD.

Results/Discussion

Before the operation of the sewage treatment plant in Psittalia, the average concentrations of phosphate and ammonium at the surface layer of station S1 were 0.474 ± 0.448 μmol/L and 1.263 ± 1.392 μmol/L, respectively, whereas, after the primary sewage treatment (1995-2004) the average phosphate and ammonium concentrations at the surface layer decreased to 0.259 ± 0.292 μmol/L and 0.680 ± 0.814 μmol/L, respectively. Moreover, after the operation of the secondary phase of sewage treatment at the end of 2004, the average concentrations of phosphate and ammonium at the surface layer of station S1 showed further decrease (0.084 ± 0.065 μmol/L for phosphate and 0.525 ± 0.533 μmol/L for ammonium). This has led to the relative improvement of the trophic status in the eastern part of Elefsis Bay from 1997 till today (Fig. 2), which could be related to the drastic decrease of phosphate concentrations in the area since 2005 (Pavlidou, unpublished data). However, an increase in inorganic nitrogen has been observed since 2013 at station S1, but further investigation with more data is needed in order to confirm and explain this increase.

The application of the eutrophication index based on the annual nutrient and chlorophyll-a concentrations,

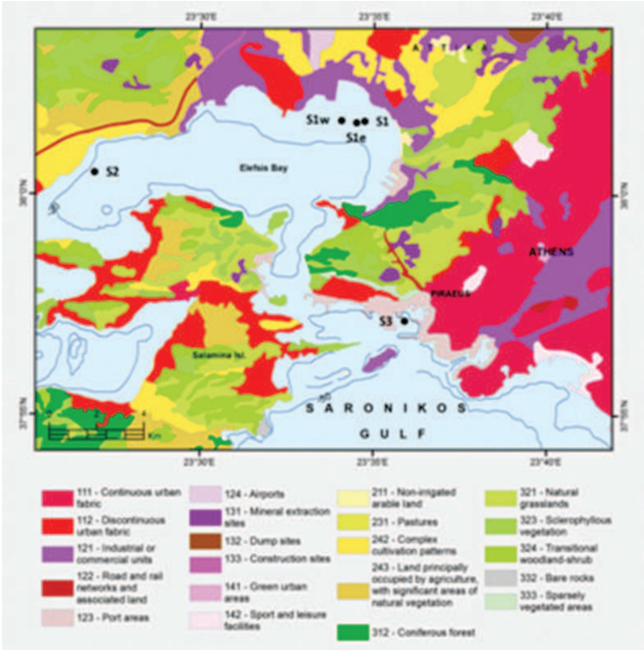

Fig.1: Map of the study area with the sampling stations and Corine Land Cover data.

also showed a significant improvement of the ecosystem quality in the western part of Elefsis after 1997 (Fig. 3), despite the hypoxic/anoxic conditions observed every year. At station S2, the development of a strong temperature-driven pycnocline during the warm period (May–late October) results in the isolation of the deeper part of the water column, which periodically remains hypoxic or even anoxic. Low DO values (<1.00 mL/L) have been observed from July to October near the bottom of Elefsis Bay, whereas, DO rise after October (Pavlidou *et al*., 2010). This situation retains nutrients and organic matter in the deeper layer of Elefsis bay and leads to high nutrient accumulation. Ammonium concentrations increase significantly with depth against nitrite and nitrate but in parallel with silicate and phosphate, suggesting the occurrence of organic matter remineralisation processes (Pavlidou *et al*., 2010). The chemical characteristics of the anoxic layer indicate that denitrification occurs, even though this has only been confirmed by measurements of sulfide concentrations (Pavlidou, unpublished data) and not by direct measurements of denitrification in the water column. Station S2 has been upgraded from BAD trophic status before the operation of the Wastewater Treatment Plant in Psittalia, to POOR trophic status.
The mean annual phosphate and ammonium concentrations showed a decreasing trend after 1998, whereas, the mean annual nitrate concentrations decreased after 2007. This situation has led also to the significant upgrade of the Keratsini ecosystem since 2008 (Fig.4).

The overall trophic status of the Elefsis Bay ecosystem for the last decade (2005-today) is characterized as POOR for both stations (S1, S2), whereas Keratsini Bay trophic status is characterized as MODERATE.

Conclusions

Elefsis bay is a very dynamic and fragile ecosystem. The overall trophic status of the Elefsis ecosystem for the last decade (2005-today) is characterized as POOR. A significant upgrade of the trophic status has been observed since 1995, which possibly reflects the decrease of the nutrient pollution in the bay, due mainly to the operation of the Sewage Treatment Plant in Psitallia since the end of 1994. The trophic status evolution in Elefsis bay during the last 20 years is the result of nutrient and primary production variability, depending on the point and non-point land based sources for nutrient enrichment, the changes in anthropogenic activity and the variability of intense anoxia, as well as the amount of the accumulated organic material in the deeper layer of the ecosystem.

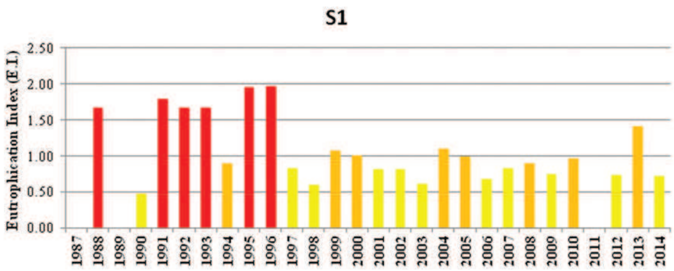

Fig.2: The Eutrophication Index (E.I.) according to nutrient and chlorophyll-a annual concentrations at station S1. The different colors of the bars indicate the eutrophication status of each area (Yellow for Moderate; Orange for Poor and Red for Bad eutrophication status).

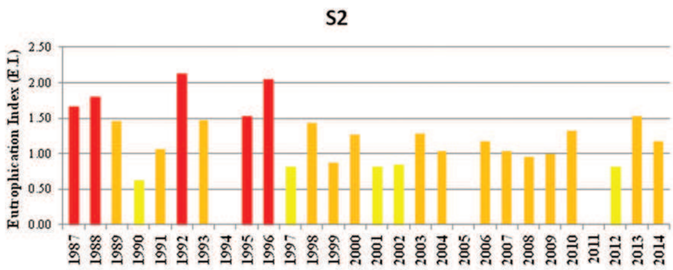

Fig.3: The Eutrophication Index (E.I.) according to nutrient and chlorophyll-a annual concentrations at station S2. The different colors of the bars indicate the eutrophication status of each area (Yellow for Moderate; Orange for Poor and Red for Bad eutrophication status).

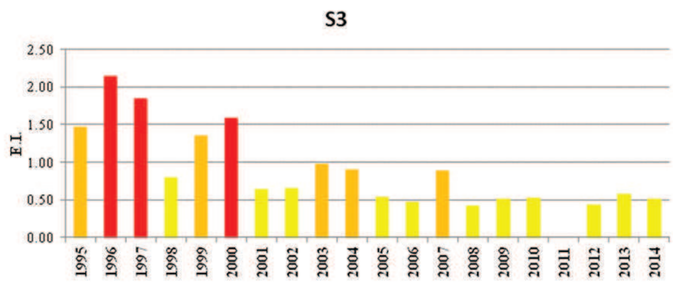

Fig.4: The Eutrophication Index (E.I.) according to nutrient and chlorophyll-a annual concentrations at station S3. The different colors of the bars indicate the eutrophication status of each area (Yellow for Moderate; Orange for Poor and Red for Bad eutrophication status).

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Pollutant levels and evidence of effects in biota from Elefsis bay

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Abstract

Heavy metal concentrations and a suite of biomarkers were measured in marine bioindicator species (the mussel *Mytilus galloprovincialis* and the fish *Mugil cephalus*) in order to monitor marine pollution along the Saronikos gulf coastline while a sediment transplantation experiment was conducted in Elefsis bay. A gradient along the geographical north-south axis was observed for the studied mussel metal concentrations in Saronikos gulf with higher values in Elefsis bay especially at the eastern part of the bay in the marine front of the industrial zone. Results from the sediment transplantation experiment showed that although sediment decontamination was evident by the improvement of the environmental conditions, the completion of the restoration was proved to be a slow and multidisciplinary procedure.

Keywords: *Mytilus galloprovincialis*; *Mugil cephalus*; heavy metals; biomarkers; sediment transplantation

Introduction

Marine pollution studies involve determination of contaminant levels in the different compartments of the marine ecosystem (seawater, sediment, organisms). Metal levels in marine bioindicator organisms represent an integration of bioavailable metal in the environment, reflecting metal concentrations over long periods of accumulation summed across all sources (Wang & Rainbow, 2008). Moreover, biological effects of pollution are elements of major importance for the assessment of environmental quality since by definition pollution implies hazards to living resources. Biomarkers reflect general stress or exposure to specific classes of environmental contaminants and can be used as early warning signals of environmental disturbance (Walker *et al*., 2006).

The Mediterranean blue mussel (*Mytilus galloprovincialis*) is commonly used as a sentinel of marine pollution within the framework of MED-POL (MAP/UNEP National Monitoring Program) since 1985. Mussels are considered suitable bioindicator species for biomonitoring studies due to their wide geographical distribution, their feeding behaviour (filter-feeders) and their ability to accumulate and tolerate high levels of contaminants including metals in relation to their bioavailability in the marine environment, while for the same purpose fishes are also used.

The main industrial zone of the greater Athens metropolitan area is located along the north coast of Saronikos gulf, mainly along the N–NE coastal area of Elefsis bay. At this industrial area (Thriassio Plain), at least 2200 large and small industrial plants operate with various industrial activities (Mavrakis *et al*., 2012). During the recent years, a wastewater treatment plant (WWTP) was constructed on the northern shores of the Elefsis bay, covering the Thriassio Plain needs (http://www.eydap.gr/), contributing to the elimination of domestic and industrial effluents discharged directly into the sea.

Maintenance of the good environmental status of the Saronikos gulf marine ecosystem is very important due to many anthropogenic pressures coming from the Athens metropolitan area (about 4 million inhabitants) and Piraeus harbour (one of the major harbours in the Eastern Mediterranean Sea). In order to protect and improve the marine environment and implement effective policies to sustain its quality, it is necessary to monitor not only pollutant levels and effects on marine organisms and their spatial variation, but also to employ appropriate tools for the detection of pollutants temporal trends. This paper aims to contribute in this direction combining and compiling levels of heavy metals and biomarkers in indicator marine organisms.

Materials and methods

A) Mussel metal concentrations

Pooled samples of mussels containing the soft tissues of 20 individuals each, were seasonally collected (spring, summer, autumn and winter) from 4 coastal sampling stations from Saronikos gulf within the framework of the MEDPOL programme (from 1985 to 2000 & from 2004 to 2006 and occasionally till 2010): **C3** (Elefsis bay-Salamis island), **C8A** (east coast of Salamis island), **C8B** (outer Saronikos gulf) and **C10** (Aigina island. Fig. 1). Cadmium, Cu, Cr, Ni, Zn, Fe, Mn, Pb were measured by atomic absorption spectroscopy (flame and/or graphite furnace, depending on concentrations and metals).

B) Biomarkers
The neurotoxicity marker acetylcholinesterase activity (AchE) and metallothionein (MT) content as biomarker of heavy metal exposure were measured in *M. galloprovincialis* seasonally over a two-year period (spring 2001-autumn 2002; Tsangaris *et al*, 2004). AchE was determined in gills and MTs in digestive gland pooled samples of mussels containing 6 individuals each, from stations **F** (shipyard) and **G** (musselfarm) within Elefsis bay and station **P** (Piraeus harbor, Fig. 1). In addition, MT levels in digestive gland and metals in the whole body tissue were measured monthly from December 2000 to January 2002 (Strogyloudi *et al*, 2012), from stations **F** (shipyard) and **D** (steelworks) at the eastern part of Elefsis bay and station **G** (musselfarm) at the western part of the bay (Fig 1).

Cellular antioxidant defenses, namely activities of the antioxidant enzymes catalase (CAT), selenium (Se)-dependent glutathione peroxidase (Se-GPX), glutathione-S-transferase (GST), and lipid peroxidation indicative of oxidative damage, were used as oxidative stress biomarkers while the micronucleus (MN) test indicating chromosome structural aberrations was applied as biomarker of genotoxicity in fish *Mugil cephalus*, seasonally collected from stations **K** (Perama bay) and **A** (Anavissos coastal area) during autumn 2006, spring 2007 and autumn 2007. Oxidative stress biomarkers were measured in the liver and the MN test was applied in erythrocytes of the fish (Tsangaris *et al*, 2011).

C) Sediment transplantation field experiment
A large scale field experiment was conducted within Elefsis bay (1986-1988), in order to investigate the decontamination and recolonization capability of heavily polluted and azoic marine sediments translocated to a clean environment (NCMR, 1992). The contaminated sediments from the eastern part of Elefsis bay (station L, Fig. 1) placed in experimental modules were transplanted to the moderated contaminated west part of the bay (station G) and monitored for 19 months. Sediments from the host site were equally put in modules. Every month metals and petroleum hydrocardons were determined in sediments and sediment pore water from the experimental modules while their colonization was examined by the study of benthic and meiobenthic communities.

Results

A) Mussel metal concentrations
Within the MED.POL monitoring program, approximately 1550 pooled mussel samples were prepared and Cd, Cu, Cr, Ni, Zn, Fe, Mn, Pb concentrations were measured for more than two decades in the Saronikos gulf. Results are showed in Figure 2 as mean values with 95% confidence intervals (μg/g dw).

MED POL results showed that Elefsis bay is the most metal polluted area followed by the east Salamis island coast (station C8A). However, high values were occasionally recorded at station C8B, located in the front of the old Athens Airport (north-east coast of Saronikos gulf) possibly due to sewage distribution from the Athens WWTP (Psyttalia island) without excluding non-continuous local land-based metal pollution source at that station (station C8B). However, metal pollution is restricted to the north coasts of Saronikos gulf, since at C10 station (Aigina island) mussel metal concentrations are not elevated.

Finally, the temporal variation of mussel metal concentrations during the 1985-2006 period showed increasing trends for Zn and Fe (to a lesser extent) while Ni, Cd and Mn presented, more or less, a decreasing tendency in relation to the decade of 1980 (Fig. 3).

B) Biomarkers
During the seasonal study from spring 2001 to autumn 2002, measurements of AChE and MTs levels in indigenous mussel populations did not reflect the expected pollution spatial gradient in Saronikos gulf (no significant differences among stations, Fig. 4). Both biochemical markers revealed a variation with respect to the season of sampling which may have masked the net response to pollutant exposure. However, mussels from station G (musselfarm, west Elefsis bay) were in a better condition than mussels collected from the shipyard (station F) and the Piraeus harbour (station P).
Spatial and monthly variability of mussel Cd, Cu, Cr, Ni, Zn, Fe and Mn and metallothionein (MTs) concentrations for the December 2000-January 2002 period, showed higher concentrations of both metal concentrations and MTs in mussels inhabiting industrial locations (steelworks and shipyard, Fig. 5). The pattern of the temporal variation of mussel metal concentrations and the MTs levels was similar among stations with higher values during the winter–spring season and lower during the summer–autumn period. The inverse relationship of the flesh condition index with mussel metal concentrations was attributed to the influence of the annual mussel reproductive cycle.

Antioxidant enzyme activities were lower in fish from station K (Perama bay) compared with fish from station A (Anavissos) which was used as a reference site. Low antioxidant enzyme activities suggest deficiency of the antioxidant system to compensate for oxidative stress which is further supported by the higher lipid peroxidation levels representing oxidative damage in fish from station K (Fig. 6). Micronuclei frequency was higher in fish from station K compared with fish from station A, indicating genotoxic effects. Correlations between biomarkers suggest that observed effects were due to contaminants exhibiting oxidative stress potential that can also induce genotoxicity.

Fig.1: Sampling stations

Conclusions

A gradient along the geographical north-south axis was observed for the studied mussel metal concentrations in Saronikos gulf for the period 1985-2006 with higher values within Elefsis bay and gradual depletion of the metal load to the south. Despite the considerable seasonal and inter-annual variations, the results of this study are generally comparable to values from other non polluted Greek, Mediterranean and/or Black Sea coastal areas and within the recommended international guidelines for shellfish intended for human consumption, except some maximum outlying values.

Mussel metal concentrations from the coastal marine environment within Elefsis bay were in accordance to land based anthropogenic activities. A spatial gradient along the east-west axis of Elefsis bay was observed with higher metal concentrations in mussels inhabiting industrial locations at the eastern part of the bay.

Oxidative stress and genotoxic effects as estimated by relative biomarkers in grey mullets from an area influenced by multiple pollution sources, showed that observed effects were due to contaminants exhibiting oxidative stress potential that can also induce genotoxicity.

C) Sediment transplantation field experiment

The results of the sediment transplantation experiment showed that the highly polluted sediments from the eastern part of Elefsis bay, within only a two month period, lost almost 50% of their metallic load of Cu, Cd, Zn and Pb (Figure 7; Catsiki *et al*, 1992). Despite variations, reduction was progressive and constant. According to the same experimental approach, although a slight increment of the abundance of meiobenthic species was detected, the ecological balance of meiobenthic communities was destroyed by the sediment disruption during modules filling. Meanwhile, the recolonization of the contaminated sediments by macrobenthic species was fully completed just within the 2 first months of the transplantation.

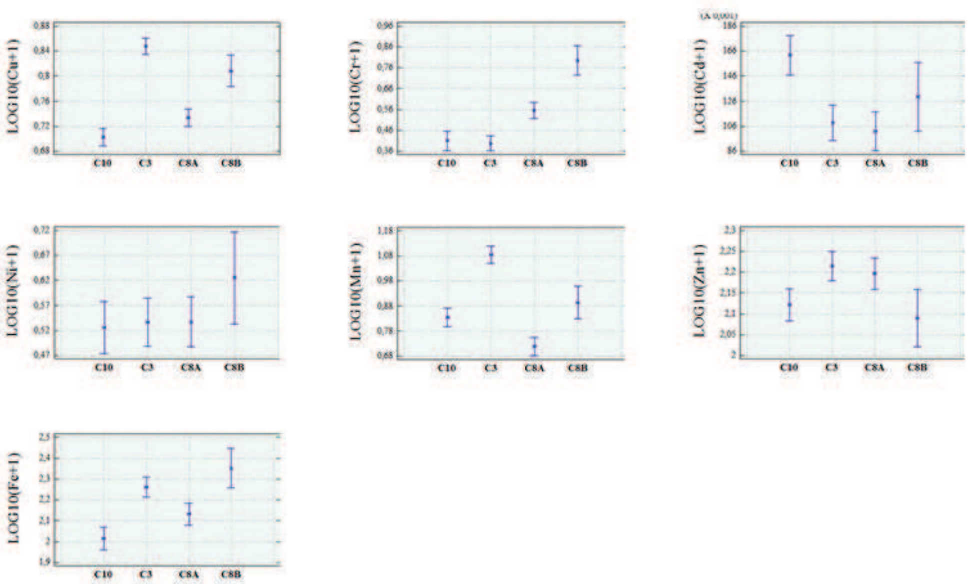

Fig.2: Mussel metal concentrations from the MED POL data base in Saronikos gulf (C3: Elefsis bay, C8A: north-east Salamis island coast, C8B: outer Saronikos gulf and C10: Aigina island). ANOVA, 95% LSD intervals

Finally, results from the sediment transplantation experiment showed that the disruption of the sediment structure within the experimental essays had negative effect in the recolonization of the sediments by meiobenthic species. The disturbance of the sediment had no effect on macrobenthic species as their colonization was completed within a bimonthly period. Although sediment decontamination was evident by the improvement of the environmental conditions, the completion of the restoration was proved to be a slow and multidisciplinary procedure.

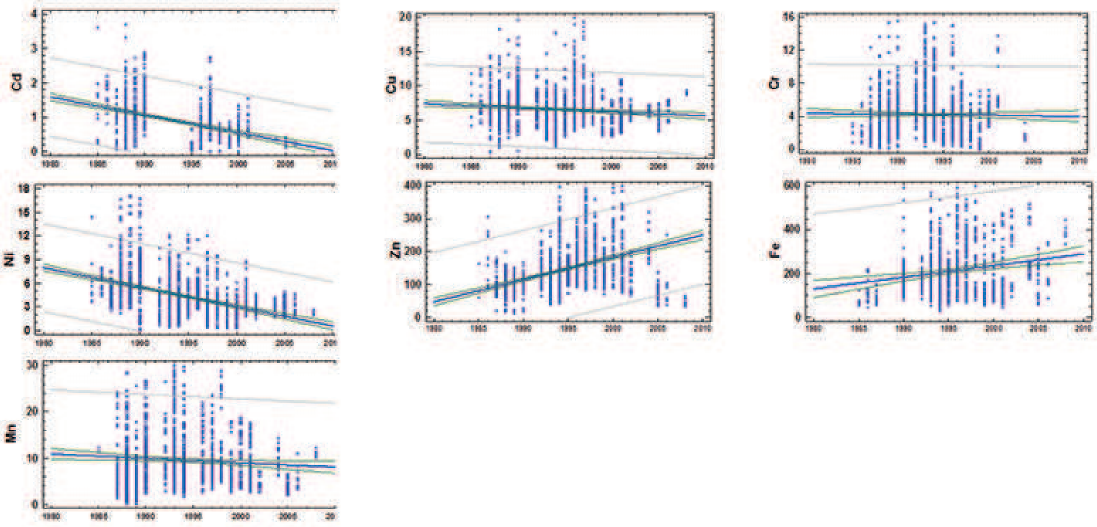

Fig.3: Temporal variation of mussel metal concentrations from 1985 to 2006 (HCMR Ecotoxicology Laboratory Data Base within MED POL Program)

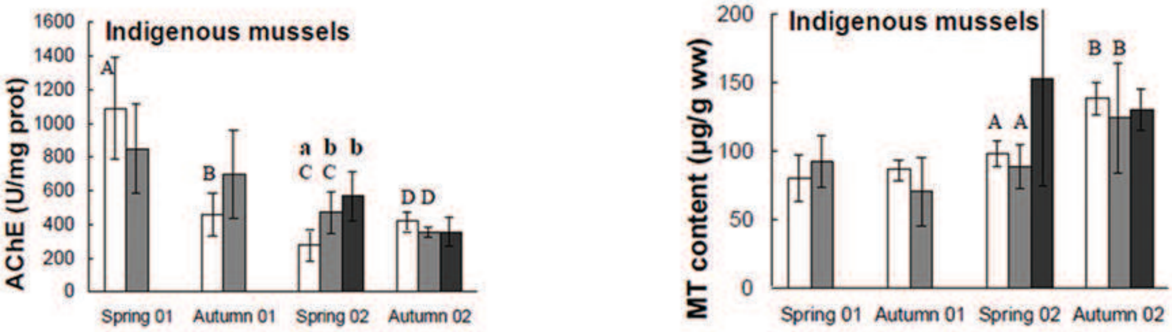

Fig.4: MT content (µg/g ww tissue) in the digestive gland and AChE activity (U/mg protein) in the gills of indigenous mussels at different stations in Saronikos gulf over a two-year period (2001-2002). Significant differences between stations represented by different small letters and significant differences between seasons displayed by different capital letters for p<0.05, *white bars: station* ***G****-musselfarm; grey bars: station* ***F****-shipyard; black bars: station* ***P****-Piraeus harbour*

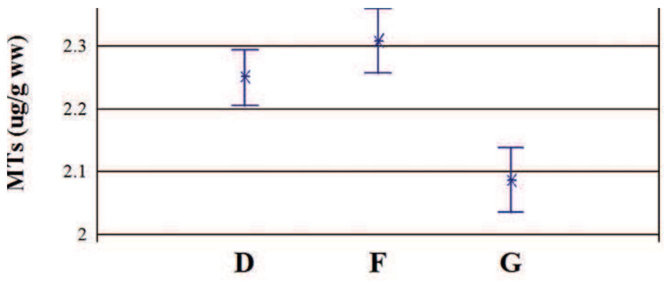

Fig.5: Spatial variation of metalothionein concentrations in the digestive gland of mussels from Elefsis bay (December 2000-January 2002, D: steelworks, F: shipyard, G: musselfarm). (ANOVA, 95% Tukey HSD intervals)

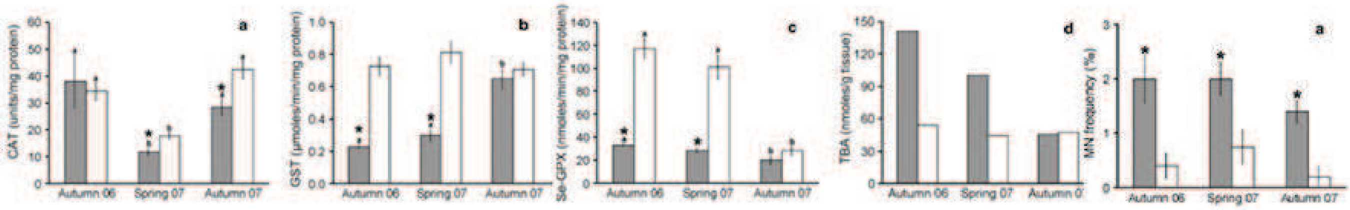

Fig.6: Antioxidant enzyme activities, lipid peroxidation and MN frequencies in grey mullets *M. cephalus* from two sites in Saronikos gulf. Asterisks indicate significant difference between the two sites within one sampling period, and different letters indicate significant differences between sampling periods for each site (t test for p<0.05), *grey bars: station* ***P****-Perama bay; white bars: station* ***A****-Anavissos-reference site*

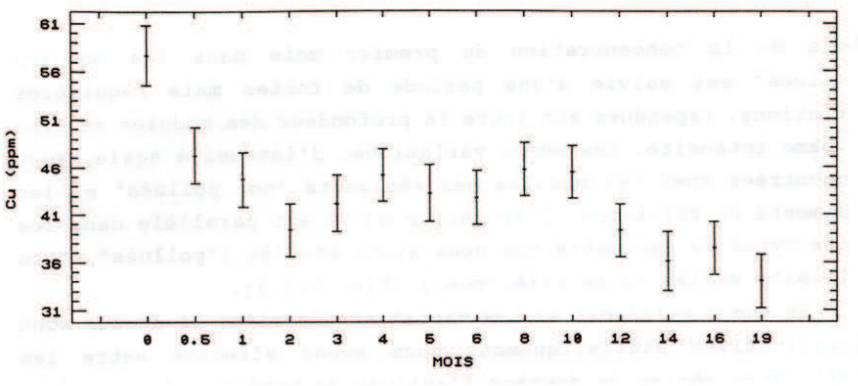

Fig.7: temporal (monthly) variation of Cu concentrations in sediments from Elefsis bay (station LOK, east Elefsis bay) transplanted in station G (west Elefsis bay) (ANOVA, 95% Tukey HSD intervals)

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The sea surface microlayer in the Gulf of Elefsis: trace metals and organic matter

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Abstract

Surface microlayer (SML) and underlying (ULW) water samples were collected in 3 sampling seasons from 3 coastal microenvironments within the gulf of Elefsis, Greece. The enrichment factors (EF) of the various parameters examined, calculated as the ratio of their concentration in the SML to that in the corresponding ULW, demonstrated significant enrichment of the SML in suspended particulate matter (SPM), in both dissolved and particulate trace metals such as Cr, Cu, Ni and Pb, as well as in dissolved organic carbon (DOC).

Keywords: Sea surface microlayer; trace metals; organic matter

Introduction

The sea surface microlayer (SML) constitutes the boundary layer between the atmosphere and the sea surface, with a typical thickness of tens to hundreds of μm (Zhang *et al*., 2003). As such it plays a vital role in the processes occurring between these two major environmental reservoirs. However, it has been understudied due to difficulties associated with its sampling.

The chemical composition of SML and the enrichment factors of individual substances vary widely in time and space. The SML is generally enriched in metal ions, affecting their residence time and biogeochemical cycling, organic substances, mainly surface active and microorganisms relative to the subsurface water (Marty *et al*., 1988).

In the present study trace metals determination and organic matter characterization were carried out in SML samples obtained from the Gulf of Elefsis in the Eastern Mediterranean for which such data do not exist. For the calculation of the enrichment of the parameters studied in the SML a comparison with the underlying water (ULW) was performed.

Materials and methods

Study area

Pairs of SML and ULW samples were collected in three sampling seasons, during October – November 2012, February 2013 and June – July 2013, from Loutropyrgos and Vourkari within the Gulf of Elefsis and Pahi located at the western entrance of the Elefsis Gulf. The sampling station of Loutropyrgos (approximate depth of 15–20 m) is located at a relatively small distance from the industrial zone of the Gulf of Elefsis (the nearest installations are 3.5 km away), whereas Vourkari is a particularly shallow area within the western part of the gulf with its depth varying between 1 and 3 m. The sampling site at Pahi is located outside the Gulf of Elefsis, in direct contact with the open waters of Saronikos Gulf and is the deepest one (approximately 50 m) among all sampling sites studied in the present work.

Sampling

SML samples were collected under calm conditions (wind speed <4 m s^{-1}) from a small rubber boat equipped with an electric engine which was stationary during sampling. Samples used for trace metals determination were obtained with the glass plate of Harvey and Burzell type (Harvey and Burzell, 1972). The thickness of the sampled microlayer was 50 μm. Following withdrawal of the samplers from seawater, the samples were drained immediately into a FEP-Teflon container for the case of trace metal measurements and a glass container for organic parameters measurements. ULW samples were collected by immersing an 1 L FEP-Teflon and glass container for trace metal and organic matter respectively, at a depth of 50 cm.

Samples were transported refrigerated immediately to the laboratory. For the determination of dissolved and particulate trace metals the samples were filtered, inside a laminar flow cabinet, through nitro-cellulose membrane filters (0.45 μm pore size; 47 mm diameter) (Millipore, Bedford, MA, USA), whereas for dissolved organic matter determination the samples were filtered through 0.4 μm nuclepore polycarbonate membrane filters (Whatman, Buckinghamshire, UK).

Seawater temperature, pH and salinity were measured *in situ* with a YSI 63 pH/conductivity meter (YSI, Brannan Lane, Ohio, USA), solar irradiation and air temperature with a DO9721 (probe LP9021) quantum photo-radiometer (Delta Ohm, Padova, Italia) and wind speed with a Testo 425 anemometer (Testo Inc., Sparta, NJ, USA).

Sample analysis

Total dissolved trace metals were determined using the solvent extraction technique described by Danielsson *et al*. (1982). Treatment of the samples was carried out inside a clean room with positive pressure. Metal measurements were performed by inductively coupled plasma – mass spectrometry (ICP-MS; Thermo Scientific ICAP Qc). Suspended particulate matter (SPM) was determined by filtration of samples through Millipore nitro-cellulose membrane filters (0.45 μm pore size; 47 mm diameter). After drying of the filters until a constant weight is reached, the particulate matter retained on the filters was weighed and then acid digested in a microwave oven (MARS Xpress, CEM, Matthews, USA). Determinations of Cd, Cr, Cu, Ni and Pb concentrations were carried out by graphite furnace atomic absorption spectrometry with Zeeman background correction (SpectrAA 640Z; Varian, Mulgrave, Victoria, Australia).

DOC and TOC were determined by the method of High Temperature Catalytic Oxidation employing a TOC-5000A Shimadzu analyzer (Shimadzu Scientific Instruments, Columbia, MD, USA). The particulate organic matter (POC) was calculated indirectly by subtracting the value of DOC from that of TOC.

Measurements of mono- and polysaccharides were performed in the dissolved fraction employing the method of Myklestadt *et al*. (1997).

Chl-α was determined spectrophotometrically by a UV/Vis spectrophotometer (CARY/1E; Varian, Mulgrave, Victoria, Australia), according to Strickland and Parsons (1968). Concentrations of Transparent Exopolymer Particles (TEP) were measured according to the colorimetric method of Passow and Alldredge (1995).

Results and discussion

An enrichment of the SML in various materials in relation to ULW generally occurs (Liss and Duce, 1997), with the enrichment factor ($EF=C_M/C_S$) calculated as the concentration (C_M) of any substance in the microlayer divided by its concentration (C_S) in the subsurface water. EF values >1.0 are termed enrichments, while EF values <1.0 are designated as depletions (Chen *et al*., 2013). However, considering the measurement uncertainty in the applied analytical techniques, it is safe to say that only EF values >2 indicate relatively significant enrichment of the studied parameter in the SML.

The SPM ranged from 9.5 to 34.0 mg L^{-1} in SML and 3.9 to 7.8 mg L^{-1} in ULW (Table 1). In all pairs of samples analysed an enrichment of the SML in SPM was found, with the mean EF (3.5 ± 2.8) being significantly higher than unity ($p = 0.017$). This enrichment is attributed to the formation, under calm meteorological conditions, of a gelatinous microlayer within the SML, where both atmospheric and marine SPM are accumulated (Cunliffe *et al*., 2013).

With the exception of Cd, in all dissolved trace metals examined an enrichment of the SML was recorded in relation to ULW (Table 1), with mean values and ranges of EFs calculated respectively equal to 1.0 (0.2-2.1) for Cd, 1.5 (0.3-3.2) for Cr, 5.2 (1.2-23.1) for Cu, 1.7 (1.2-3.0) for Ni and 3.8 (1.3-8.7) for Pb. The highest enrichment in dissolved metals was calculated for Cu ($p = 0.050$), followed by Pb ($p = 0.007$), Ni ($p = 0.003$) and Cr ($p = 0.049$). Particulate metals also demonstrate a similar trend, with mean values and ranges of EFs being 1.6 (0.04-5.7) for Cd, 12.5 (2.2-35.5) for Cr, 12.9 (1.4-33.0) for Cu, 7.6 (2.2-17.3) for Ni and 5.5 (1.4-12.1) for Pb. In the particulate phase the enrichment order is Cu ($p = 0.010$) > Cr ($p = 0.014$) > Ni ($p = 0.002$) > Pb ($p = 0.020$).

In all paired samples examined an enrichment of the SML in DOC was recorded, excluding those of Pahi in autumn and Loutropyrgos in summer (where the surface film was disrupted) (Table 3). The mean EF of DOC (1.3±0.4) was significantly higher than unity ($p = 0.037$) indicating a relatively low enrichment in SML. The slightly higher mean EF obtained for DOC during winter in comparison to autumn and summer may be attributed to the fact that phytoplankton blooms seasonally differentiate, with winter ones being characterized by large diatoms, contrary to those of summer ones where pico- and nanophytoplantkon species prevail (Kormas *et al*., 2002). The EF of POC in SML varies between 0.1 and 4 with a mean value of 1.3 (Table 2).

Carbohydrates represent a significant portion of the DOC pool. Total carbohydrates (TCHOs), calculated as the sum of dissolved mono- and polysaccharides (Table 2), varied from 10 to 76% in the SML and from 8 to 100% in the ULW. The mean percentages of total carbohydrates to DOC for the three samplings of autumn, winter and summer realized were respectively equal to 14, 75 and 36%, with the relatively higher determined for winter being attributed to the winter phytoplankton bloom. Chl-α concentrations ranged from 0.34 to 3.67 μg L^{-1} in SML and from 0.32 to 2.94 μg L^{-1} in ULW (Table 2).

		Dissolved					Particulate				
	SPM	Cd	Cr	Cu	Ni	Pb	Cd	Cr	Cu	Ni	Pb
Automn 2012											
Lourtopyrgos SML	-	27.4	0.09	0.86	0.64	0.19	-	-	-	-	-
Loutropyrgos ULW	-	14.8	0.04	0.30	0.46	0.06	-	-	-	-	-
		(1.8)	**(2.2)**	**(2.9)**	**(1.4)**	**(3.0)**					
Vourkari SML	34.0	9.9	0.05	0.85	0.80	0.34	4.6	3.3	2.0	3.2	0.83
Vourkari ULW	4.1	7.9	0.04	0.16	0.47	0.18	4.8	0.29	0.06	0.40	0.07
	(8.3)	**(1.2)**	**(1.2)**	**(5.4)**	**(1.7)**	**(1.9)**	**(1.0)**	**(11)**	**(33)**	**(8.1)**	**(12)**
Pahi SML	29.0	13.3	0.02	1.6	0.48	0.59	2.6	1.2	0.54	0.86	0.22
Pahi ULW	3.9	58.2	0.06	0.07	0.23	0.08	1.7	0.10	0.05	0.11	0.02
	(7.4)	**(0.2)**	**(0.3)**	**(23)**	**(2.0)**	**(7.8)**	**(1.5)**	**(12)**	**(11)**	**(7.8)**	**(11)**
Winter 2013											
Lourtopyrgos SML	9.5	66.6	0.08	0.93	1.1	0.41	0.61	0.75	0.62	0.46	0.42
Loutropyrgos ULW	7.2	52.9	0.06	0.50	0.37	0.12	0.48	0.03	0.18	0.05	0.16
	(1.3)	**(1.3)**	**(1.4)**	**(1.9)**	**(3.0)**	**(3.3)**	**(1.3)**	**(25)**	**(3.4)**	**(9.2)**	**(2.6)**
Vourkari SML	14.3	20.0	0.04	0.92	0.85	0.10	3.0	0.57	0.56	0.55	0.32
Vourkari ULW	7.3	66.7	0.01	0.38	0.56	0.01	2.7	0.08	0.12	0.25	0.23
	(2.0)	**(0.3)**	**(3.2)**	**(2.4)**	**(1.5)**	**(8.7)**	**(1.1)**	**(7.2)**	**(4.7)**	**(2.2)**	**(1.4)**
Pahi SML	13.5	1.0	0.01	0.35	0.27	0.66	0.84	1.9	0.71	0.83	1.21
Pahi ULW	4.5	24.5	0.01	0.09	0.20	0.14	0.41	0.05	0.03	0.05	0.10
	(3.0)	**(0.4)**	**(1.2)**	**(3.9)**	**(1.3)**	**(4.8)**	**(2.0)**	**(36)**	**(21)**	**(17)**	**(12)**
Summer 2013											
Lourtopyrgos SML	12.2	17.9	0.06	0.72	0.43	0.48	0.17	0.39	0.27	0.35	0.13
Loutropyrgos ULW	6.6	24.6	0.06	0.59	0.37	0.33	4.2	0.15	0.19	0.07	0.09
	(1.8)	**(0.7)**	**(1.0)**	**(1.2)**	**(1.2)**	**(1.5)**	**(0.04)**	**(2.6)**	**(1.4)**	**(5.2)**	**(1.4)**
Vourkari SML	20.8	12.4	0.01	1.1	0.60	0.13	3.1	0.50	4.1	0.60	0.16
Vourkari ULW	7.8	19.0	0.01	0.88	0.40	0.06	0.54	0.23	0.18	0.14	0.10
	(2.6)	**(0.6)**	**(1.1)**	**(1.2)**	**(1.5)**	**(2.3)**	**(5.7)**	**(2.2)**	**(23)**	**(4.3)**	**(1.6)**
Pahi SML	11.3	18.8	0.01	1.5	0.41	0.12	0.49	0.77	0.69	0.42	0.20
Pahi ULW	6.9	9.1	<0.01	0.28	0.26	0.09	1.1	0.19	0.11	0.06	0.09
	(1.6)	**(2.1)**	**(2.2)**	**(5.3)**	**(1.6)**	**(1.3)**	**(0.5)**	**(4.0)**	**(6.3)**	**(6.7)**	**(2.2)**

Table 1: SPM (mg L^{-1}) and dissolved and particulate Cd (ng L^{-1}), Cr (μg L^{-1}), Cu (μg L^{-1}), Ni (μg L^{-1}) and Pb (μg L^{-1}) in SML and ULW and their enrichment factors (EF) in SML in bold inside parenthesis.

In 8 of the 9 SML and ULW paired samples examined an enrichment of the SML in TEP was calculated (Table 2). TEP concentrations varied seasonally, decreasing during the winter sampling. The relative seasonal stability characterizing TEP concentrations in Pahi site derives from the fact that the specific station is the deepest among those studied and in direct contact with the open sea. Accumulation of TEP in the SML is slightly more pronounced than that of TCHOs (mean EF values 1.6 and 1.0, respectively), possibly because TCHOs can be readily assimilated into polymeric material, which acts as precursor for the formulation of TEP. It is therefore suggested that the polymerization process inhibits the enrichment of the SML in TCHOs) (Wurl and Holmes, 2008).

The fraction of MCHOs to PCHOs concentrations was determined varying between 0.6 and 5.8. According to Pakulski and Benner (1994) polysaccharides constitute a "fresh" and reactive part of DOC, with the percentage of MCHOs to PCHOs in surface waters varying between 0.6 and 2.2. The relatively low values of MCHOs to PCHOs fraction for the samplings in autumn and winter indicate excretion by healthy phytoplankton cells rather than degradation both inside the cells as well as in the natural environment (Borsheim *et al.*, 1999).

A time-series study of higher resolution may allow a better understanding of the SML and its dynamic interactions with marine biogeochemical and physical variables, particularly in the Mediterranean, where regional events such as phytoplankton blooms together with global scale processes including marine pollution or dry atmospheric deposition, may affect SML structure and function.

	DOC	POC	MCHOs	PCHOs	TCHOs	Chl-α	TEP
Automn 2012							
Lourtopyrgos SML	1.5	0.1	<0.10	0.15	0.15	3.67	1337
Loutropyrgos ULW	1.3	<0.1	<0.10	0.10	0.10	2.94	312
	(1.2)	**(2.0) ***	**(1.0)**	**(1.5)**	**(1.5)**	**(1.2)**	**(4.3)**
Vourkari SML	1.3	0.4	0.12	<0.10	0.12	1.18	710
Vourkari ULW	1.1	0.1	<0.10	0.14	0.14	1.13	566
	(1.2)	**(4.0)**	**(2.4)**	**(0.4)**	**(0.9)**	**(1.0)**	**(1.2)**
Pahi SML	1.2	0.2	<0.10	0.12	0.12	0.65	984
Pahi ULW	1.2	0.9	<0.10	0.24	0.24	0.81	741
	(1.0)	**(0.2)**	**(1.0)**	**(0.5)**	**(0.5)**	**(0.8)**	**(1.3)**
Winter 2013							
Lourtopyrgos SML	2.0	<0.1	0.60	0.93	1.53	0.34	248
Loutropyrgos ULW	1.3	0.1	0.57	0.68	1.25	0.40	186
	(1.5)	**(0.5)**	**(1.0)**	**(1.4)**	**(1.2)**	**(0.8)**	**(1.3)**
Vourkari SML	2.5	<0.1	0.78	0.63	1.41	2.90	294
Vourkari ULW	1.9	<0.1	0.73	0.68	1.41	1.17	130
	(1.3)	**1.0**	**(1.1)**	**(0.9)**	**(1.0)**	**(2.5)**	**(2.3)**
Pahi SML	2.5	0.4	0.71	0.45	1.16	0.76	883
Pahi ULW	1.4	0.5	0.68	0.72	1.40	0.70	553
	(1.8)	**(0.8)**	**(1.0)**	**(0.6)**	**(0.8)**	**(1.1)**	**(1.6)**
Summer 2013							
Lourtopyrgos SML	1.7	0.1	0.64	0.11	0.75	0.70	31
Loutropyrgos ULW	3.5	1.2	0.90	<0.10	0.90	0.66	485
	(0.5)	**(0.1)**	**(0.7)**	**(2.2)**	**(0.8)**	**(1.1)**	**(0.1)**
Vourkari SML	2.6	0.1	0.66	<0.10	0.66	1.06	1087
Vourkari ULW	1.9	<0.1	0.55	0.18	0.73	0.81	837
	(1.4)	**(2.0)**	**(1.2)**	**(0.3)**	**(0.9)**	**(1.3)**	**(1.3)**
Pahi SML	2.3	0.7	0.60	0.18	0.78	0.45	960
Pahi ULW	1.6	1.0	0.58	0.22	0.80	0.32	721
	(1.4)	**0.7**	**(1.0)**	**(0.8)**	**(1.0)**	**(1.4)**	**(1.3)**

Table 2: Dissolved and particulate organic carbon (DOC, POC) (mg L^{-1}), MCHOS, PCHOs and TCHOs (mg L^{-1}), Chl-α (μg L^{-1}) and TEP (μg Xeq L^{-1}) in SML and ULW and their enrichment factors (EF) in SML in bold inside parenthesis.
*In the calculation of EF, values below the limit of detection (LOD) where assigned the LOD divided by 2.

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Speciation studies of copper in the Gulf of Elefsis: the role of the macroalga *Ulva rigida*

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Abstract

The Gulf of Elefsis, situated in the vicinity of Athens, is a high productivity area regarding the biota. One of the most abundant algae existing there is *Ulva rigida*. Controlled laboratory simulation experiments, as well as field investigations indicated that copper is complexed to a high extent with organic substances. A significant part of these organic ligands exhibit surface active properties, i.e. accumulation on different phase boundaries. The complexing capacity values of samples collected from different microenvironments within the Gulf of Elefsis, determined by the electrochemical method of differential pulse anodic stripping voltammetry (DPASV), vary between 0.04 and 0.43 μM Cu^{2+}. At the same time, the complexing capacities of samples obtained from the laboratory tanks in which *U. rigida* has been placed under controlled conditions, show much higher complexing capacity values (up to13 μM Cu^{2+}). The svurface active substances (SAS) expressed in equivalents of the nonionic surfactant Triton-X-100 were determined by out of phase a.c. voltammetry. Higher amounts of SAS were detected in the tanks containing *U. rigida* (up to 0.70 mg L^{-1} eq. T-X-100), in comparison to samples originating from natural microenvironments in the Gulf of Elefsis which had values ranging between 0.10 and 0.17 mg L^{-1} eq.T-X-100. These results show that *U. rigida*, contributes considerably to the production of ligands with high metal complexing capacity and high surfactant activity.

Keywords: copper complexing capacity, Ulva rigida, Gulf of Elefsis, surface active substances

Introduction

The abundance of complexing ligands, which are part of dissolved organic carbon (DOC) in seawater, determines the complexing capacity for metal ions (Plavšić *et al*., 1982). Copper ions, especially, form very stable organic complexes and copper is an essential metal ion, so very often the copper complexing capacities are measured in natural waters. The electrochemical technique of choice in the present work is differential pulse anodic stripping voltammetry (DPASV) which is employed for the determination of the complexing capacity. Inert complex as for the applied method of DPASV is the one which does not dissociate under the time scale of the measurement.

Organic ligands present in natural waters consist of a pool of largely uncharacterized macromolecular organic material, resulting from a combination of biological (e.g. phytoplankton exudates and bacterial activity) and geochemical activities (humic and fulvic substances). The organic matter is partly identified and classified into particular groups of compounds such as carbohydrates, amino acids, proteins, fatty acids, lipids and hydrocarbons.

A large part of the dissolved organic matter in natural waters exhibits significant surface active properties. Such properties, i.e. the presence of hydrophobic and hydrophilic groups of organic molecules, may cause their accumulation on different interfaces (e.g. at the boundaries of seawater with the atmosphere, in bubbles, in turbulent intermixing layers, on living and nonliving dispersed particulates and sediments), creating a major part of the surface microlayer and organic coating on mineral particles. Clear evidence of surfactant production by marine phytoplankton cultures based on laboratory and field experiments is also available (Plavšić *et al*., 1990). Due to the specific reactivity of surface active substances (SAS) at natural phase boundaries, their distribution and fate in the sea could be different, compared to those of organic matter pool values, i.e. dissolved organic carbon (DOC). SAS could be determined by alternating current out-of-phase voltammetry (Plavšić *et al*., 1990) and expressed in equivalent concentration of model –calibrating substance, e.g. nonionic surfactant Triton-X-100.

The study area of the present work is the Gulf of Elefsis, a shallow (maximum depth of 33 m) embayment rich in primary productivity, in the vicinity of Athens (Fig. 1). The area has been thoroughly studied in the last 40 years by the University of Athens team (Scoullos and Riley, 1978; Scoullos, 1979, 1983, 1986; Kaberi and Scoullos, 1996; Scoullos and Pavlidou, 1997; etc.) and is characterized by a particularly rich biota, with *U. rigida* being for many years the most abundant alga, anchored on rocky substrates or floating in the water. The highest rate of alga *U. rigida* biomass decomposition has been observed during summer, when samplings took place.

Materials and methods

Water sampling from the field

Seawater samples were collected by scuba diving and placed in plastic bottles extensively prewashed by 10% nitric acid supra pure. The collection took place during the summer of 1999 from five coastal sampling stations located at the northern part of Saronikos Gulf. Four of them are from within the Gulf of Elefsis while the fifth one is from the area of Piraiki, near Piraeus, the largest port of Greece (Fig. 1). All of them were surface samples (0.5 m). At the sampling area of Loutropyrgos, within the Gulf of Elefsis, water samples were collected from two depths: the surface and the bottom near the seabed (maximum depth of 3.0 m), where most of the biomass of *U. rigida* was accumulated. After their collection, seawater samples were transferred within 1 or 2 h to the laboratory where they were filtered through nitric cellulose Millipore 0.45 μm filters.

Fig.1: Sampling sites

The laboratory simulation experiments

The experiments carried out in the laboratory aimed at the simulation of natural conditions with restricted unknown factors. This was obtained by the use of artificial seawater, enriched with dissolved organic substances originating entirely from the decomposition of *U. rigida* biomass, under various controlled conditions. For the preparation of artificial seawater, commercially available salt Instant Ocean (Aquarium Systems) and water purified by reverse osmosis (Milli-RO, Millipore) and ion-exchange (Milli-Q, Millipore) were used. In each tank, the salinity was adjusted at 36‰ with the addition of appropriate amounts of salt.

Three distinctive conditions, usually coexisting in nature, were reproduced:

- **Condition (1)**, decomposition of fresh biomass under aeration (aerobic conditions) and plenty of light,
- **Condition (2)**, decomposition of fresh biomass under naturally developed anaerobic conditions,
- **Condition (3)**, decomposition of dried biomass which was also observed to take place in nature.

The experiments were carried out by employing three glass tanks filled with 20 L of artificial water each. For each experiment, 630 g (wet weight) of thoroughly cleaned *U. rigida* were used. The cleaning of *Ulva* included careful removal of epiphytes and thorough rinsing with artificial seawater. The actual duration of the experiments was 73 days for (1), 67 days for (2), and 58 days for (3).

Fig.2: Alga *U. Rigida*, a common, cosmopolitan alga found in mesotrophic and eutrophic areas

Analysis

Electrochemical measurements were carried out by using an Eco Chemie (The Netherlands) voltammetric instrument μ- Autolab II, connected to a Metrohm three electrode cell (VA 663, Metrohm stand, Switzerland). The working electrode was static mercury drop electrode (SMDE).

Results

In the seawater of the Gulf of Elefsis copper is to a high extent bound to organic ligands. The values determined for the apparent complexing capacity for Cu are in the range of 0.04 to 0.43 μM. The concentrations of surface active substances (SAS) in the same waters fluctuate between 0.10 and 0.17 mg L^{-1} eq. T-X-100. Samples derived from simulation experiments in tanks, containing the macroalga *U. rigida* show much higher surfactant activities (up to 0.70 mg L^{-1} eq. Triton-X-100) and significantly higher CuL values (up to 13 μM) compared to samples collected from the field. The presence of sulfur species (S_2 +S^0) was detected in the non aerated tanks which contained *Ulva* and these contributed to the complexing capacities through the formation of Cu- sulfides. The aforementioned results show that *Ulva* *rigida* releases significant quantities of dissolved and colloidal ligands with high complexing affinity for copper influencing its behavior and bioavailability. At the same time part of the organic matter deriving from *Ulva rigida* has a high surfactant activity. Consequently, although the organic ligands originating from *Ulva* in the particular area are not the only or necessarily the main contributors to the determined organic ligands, it is obvious that they represent a very significant component of measured DOC.

Conclusions

Surfactant activity of the released organic matter is responsible for the fact that a significant part of the interaction of copper with organic ligands takes place at different phase boundaries. This influences directly the bioavailability, bioaccumulation, toxicity and transport of copper at these boundaries. The basic trends exhibited in this paper could be extrapolated to other nutrient impacted coastal regions hosting different algal species.

Acknowledgment

The authors, M.P. and S.K. thank Prof. Michael Scoullos, who had initiated this research of the speciation studies of copper in the Gulf of Elefsis from which a fruitful collaboration developed between UoA, Athens, Greece and RBI, Zagreb, Croatia.

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Nutrient benthic fluxes and porewater concentrations in the Gulf of Elefsis

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Abstract

The aim of the present work is to study the diagenetic processes occurring across the sediment water interface in a coastal area, Elefsis bay, receiving intense natural and anthropogenic pressures. Elefsis Bay, is a semi-enclosed marine area of the Eastern Mediterranean Sea, where periodically hypoxic/anoxic conditions occur every year in late summer. Results of incubation experiments of induced anoxia that took place in February and September 2012 are presented. The influence of dissolved oxygen on the benthic flux of nitrate is demonstrated, as well as the main processes involved. The sediment diagenetic pathways for the bio-limiting nutrients in shallow coastal ecosystems is important to be studied and quantified, as the benthic fluxes could be an important source to the overlying water column or a major sink.

Keywords: sediment-water interface, nitrate, dissolved oxygen

Introduction

Shallow bays are highly productive habitats and important sites for organic matter mineralization and nutrient cycling in coastal marine environments (Borum, 1996). Due to the shallow water column, key biogeochemical processes take place in the surface sediment (Engelsen, 2008). The transport of dissolved constituents across the sediment-water interface links the processes between the sediment and the water column. The processes responsible for this transport include simple molecular diffusion, physical processes as sediment resuspension and water advection, as well as more complex biologically mediated processes as bioturbation and bioirrigation (Burdige, 2006). Especially in shallow marine ecosystems, the sediment-water exchange is often an essential nutrient source for primary producers, as sediments play a key role due to their capacity to store or release different compounds from or to the water column (Zhang *et. al*., 2014).

Increased nutrient loads can lead to higher rates of algal production and labile organic matter delivery to the superficial sediments. Under these conditions, high mineralization rates can occur, changing biogeochemical cycling to reactions that favor the release of large quantities of inorganic nutrients into the water column (Berelson *et. al*., 1998). Conversely, sediments can also act as sinks with potential implications for nutrient limitation in the water column. Establishing the magnitude of benthic fluxes is important for understanding geochemical budgets and for determining the role of sediments diagenesis in nutrient recycling (Grenz *et. al*., and references therein, 2010).

The benthic flux/efflux of phosphorous and nitrogen is affected by both abiotic and biotic parameters. Hence, it is important to define the sediment diagenetic pathways for the bio-limiting nutrients in shallow coastal ecosystems and estimate solute exchange rates, transport mechanisms and temporal and geographic variability in these rates (Berelson *et. al*., 1998).

Elefsis Bay is a shallow (32m maximum depth), polluted, semi-enclosed marine area of the Eastern Mediterranean Sea, which is affected by important coastal pressures due to human activity. These pressures are related to the growth of coastal populations, the development of shipping and industrialization. Elefsis Bay became one of the most interesting cases of eutrophication in the generally oligotrophic context of the Aegean, since periodic hypoxic conditions occur in the area every year in late summer.

The aim of this work is to study nutrient fluxes across the sediment water interface and the diagenetic processes that occur into the sediments controlling nitrogen and phosphorous cycling. In the present study, we will focus on the bioavailable form of nitrogen and phosphorous and how their concentrations may alter due to abiotic parameters. It is generally considered that nitrogen availability is one of the major factors regulating primary production in coastal marine environments (Herbert, 1999).

Materials and methods

Surface sediments were collected from station S2 (Fig.2) in Elefsis bay during February and September 2012 and from station S1 in September 2012. At station S2 hypoxic or anoxic conditions occur at late summer. Ex situ incubations were utilized to measure the exchange rates of nutrients, as well as dissolved oxygen across the sediment–water interface. In order to estimate dissolved oxygen consumption at the sediment-water interface, ex situ incubation experiments were conducted where oxygen was driven to depletion. The incubations were made under anaerobic conditions, with the use of gas impermeable materials, in order to prevent oxygen contamination. Sediment cores were also collected and pore water samples were extracted under an inert atmosphere after centrifugation. Gas-impermeable materials were used in order to prevent oxygen contamination. Dissolved oxygen was determined immediately after sampling according to the Winkler method. Nutrients were determined colorimetrically using standard auto-analyzer techniques. Seawater samples for nutrients were frozen until the analysis.

Results

Porewater profiles of phosphates (Fig.3) and ammonia (Fig.4) at stations S1 and S2 show a rather common pattern during summer 2012. At both stations a distinct maximum of phosphates at the horizon 1.5 - 2 cm is observed. Ammonia concentrations increased downcore at both stations. In September, phosphate and ammonia concentrations were higher at station S2. The porewater profiles obtained in two samplings at station S2 demonstrate that in the upper layers of the core, phosphate concentrations vary significantly (Fig.3), indicating that seasonal fluctuation occurs. During summer, at station S2 phosphate concentrations were much higher than those in winter at the first 4 cm. Below 8 cm the concentrations followed a rather common pattern. Ammonia profiles (Fig.4) also demonstrate the seasonal effect. In the upper horizons, in winter the profile presents a minimum instead of a maximum which is observed during the sampling in summer. The common pattern that ammonia and phosphate followed at the first 4 cm during summer and winter might indicate the common processes that are involved and regulate their concentrations.

The seasonal variability observed is probably due to parameters such as temperature, dissolved oxygen concentration at the bottom layer, etc., as well as the diversity of benthic fauna. Ex situ incubations were carried out in two different seasons at station S2, under well oxygenated water column conditions (February 2012) and at hypoxic conditions (oxygen at the bottom layer 0.55 ml/L, September 2012). The incubations were conducted in order to estimate the benthic oxygen demand and

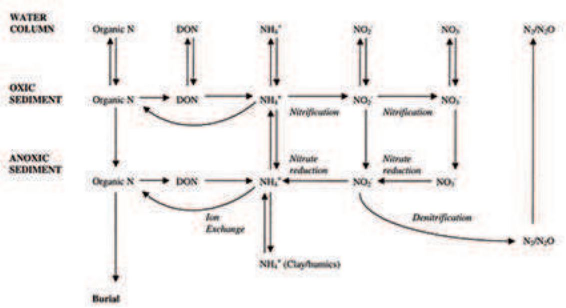

Fig.1: Nitrogen cycle in marine sediments

Fig.2: Map of the study area (Herbert, 1999)

to study the response of the sediment while dissolved oxygen concentration was decreasing in the overlying water column of the chamber. In February, at station S2 (Fig.5) dissolved oxygen (D.O.) was driven to depletion after 45 hours of incubation. At D.O. concentrations < 0.67 ml/L (Fig.3), nitrate concentration decreased, indicating that denitrification is possibly a process taking place when hypoxic conditions occur.

In September, at station S2, the chamber was inadvertently oxygenated (D.O. 2.55 ml/L) and then driven to hypoxic conditions (1.34 ml/L) in ~9 hours (Fig.6). Oxygen and nitrate concentrations followed a common distribution pattern. As D.O. increased, nitrate also increased, probably through nitrification process, followed by denitrification as the incubation continued and oxygen w asconsumed, implying that among others, oxygen concentration influences the potential nutrient flux of nitrogen from the sediments.

Dissolved oxygen concentration near the bottom water seems to influence the flux of nitrate from the sediment to the overlying water column. The flux experiments show that while the system was driven to anoxia/hypoxia, nitrate concentrations were decreasing in both seasons. There are many reasons that oxygen concentration in the water column affects the benthic flux of nutrients. First of all, the oxygen saturation near the bottom influences the oxygenated part of the surface sediment and thus the oxygen-sensitive processes that take place in the sediments. Oxygen represents the most favorable abundant electron donor available but this oxidant is soon depleted and generally only extends a few millimeters or centimeters into the sediments. After oxygen is depleted benthic carbon degradation is therefore mainly mediated anaerobically by microbes using nitrate, manganese oxides, iron oxides or sulfate as electron acceptors (Glud, 2008).

The correlations of nitrate to dissolved oxygen during the incubations showed that there is a significant correlation only in February at station S2, while no significant correlation was found during summer. It is possible that during summer denitrification is not the main process that controls their concentrations and that more processes are involved producing or consuming nitrates and oxygen.

Conclusions/Discussion

During the conducted incubations of induced anoxia, as dissolved oxygen depleted, nitrate also decreased, implying that processes of nitrogen removal occurr as oxygen is depleted (e.g. denitrification, DNRA). The response of the seafloor (meaning the processes occurring into the surface sediment) to bottom water oxygen concentration is believed to be really quick as illustrated by the incubation in September.

As far as the temporal distribution is concerned, the consumption rate of oxygen during winter and summer is estimated at about the same order of magnitude at station S2, while the negative flux of nitrate at station S2 during February is lower than that of September 2012. Several studies have demonstrated that the distribution and production rate of nutrients are strongly dependent on temperature (e.g. Magni & Montani, 2006) a factor not discussed in the present study, but one that influences the fluxes.

Summarizing, the conducted experiments can give us a lot of information concerning the seafloor nutrient processes that influence nutrient cycling. The experiments that took place at these stations in winter and summer and the porewater profiles demonstrate the seasonal variability of benthic nutrient dynamics, probably due to the different environmental parameters occurring, such as temperature and dissolved oxygen, as well as the pressures that each station receives and the seasonal variation of benthic fauna distribution which affects the processes involved.

Changes in abiotic parameters and anthropogenic pressures in the studied area could influence the benthic fluxes, thus the N:P ratio in the marine environment and so it could impact the functioning of the marine ecosystems.

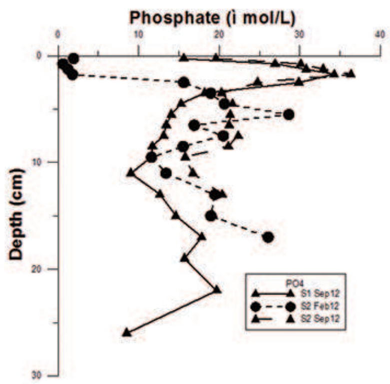

Fig.3: Porewater profiles of phosphates at stations S1 (September 2012) and S2 (February and September 2012)

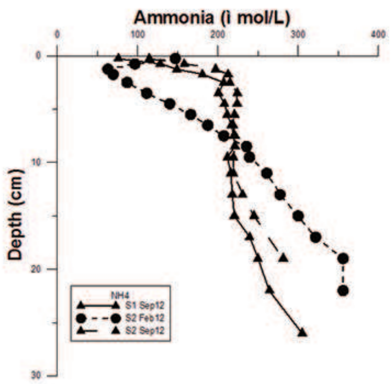

Fig.4: Porewater profiles of ammonia at stations S1 (September 2012) and S2 (February and September 2012)

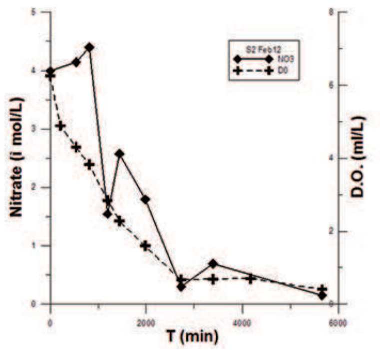

Fig.5: Dissolved oxygen and nitrate concentrations at station S2 during February 2012 (incubation of induced anoxia)

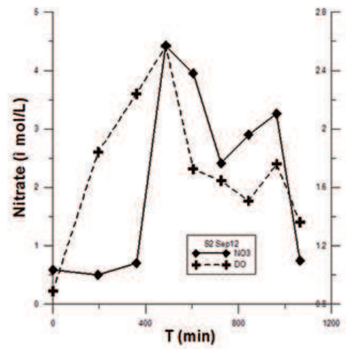

Fig.6: Dissolved oxygen and nitrate concentrations at station S2 during September 2012 (incubation of induced anoxia)

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Sampling in the Gulf of Elefsis in the 80s.

Nutrient cycle alterations in Elefsis Gulf under simulated ocean acidification conditions

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Abstract

Hypoxic coastal areas are considered as high-priority for Ocean Acidification (OA) research, because the co-occurrence and interaction of low oxygen with other environmental stressors, such as elevated pCO_2, warming and eutrophication, may put them at greater risk. In this work, a hypoxic coastal phenomenon exhibiting relatively reduced pH at the near bottom water layer was studied, combining in situ and microcosm experiment measurements. The results revealed that CO_2 content is not regulated by equilibrium with the atmosphere, but by CO_2 produced by organic matter decomposition at the bottom layers, and that acidification could spread towards shallower depths and neighboring less affected areas. The combination of hypoxia and OA was found to affect the nitrification/denitrification processes, inhibiting the consumption of N species, probably leading to nitrogen accumulation and eutrophication.

Keywords: experiment, microcosm, anoxia, nitrogen, phosphorus.

Introduction

Ocean uptake of anthropogenic CO_2 alters ocean chemistry, leading to more acidic conditions and lower chemical saturation states (Ω) for calcium carbonate ($CaCO_3$) minerals, a process commonly termed "ocean acidification" (OA) (e.g. Caldeira and Wickett, 2005). In coastal regions, the organic load input is usually high and the aerobic degradation of organic matter leads to a higher CO_2 production (Andersson *et al*., 2007). Hypoxic or anoxic systems are more acidic than normal marine environments, as the biochemical oxygen consumption is inextricably linked to the production of soluble inorganic carbon, including CO_2. In hypoxic coastal systems, the gas exchange balance with the atmosphere is not achieved, meeting extremely high pCO_2 levels (>1,000 μatm) (Feely *et al*., 2010), indicating that OA in such environments is already taking place and possibly spreading to adjacent systems.

Wallace *et al*. (2014) confirmed the hypothesis that the same processes promoting hypoxia also acidify the water column in coastal ecosystems. OA has direct impacts on carbon biogeochemistry, causing dissolution of existing sedimentary carbonates (Andersson *et al*., 2007) and alkalinity release in the supernatant water column, plus alterations on nutrient cycles, with decline in nitrification rates (Beman *et al*., 2011). Therefore, experiments combining acidification and low oxygen conditions are essential to fully understand and correlate the various observations in coastal environments.

The main scope of this experimental research was to investigate the nutrient cycle of an anoxic environment under acidification conditions. The aim of the experiment was to simulate the biogeochemistry and physicochemical conditions of the natural system including consideration of all vital parameters.

Methodologies

This research was conducted in Elefsis Gulf (Attica, Greece), a relatively shallow, semi-closed industrialised coastal system, which, due to the increased organic matter input and its hydromorphological characteristics, has intermittently anoxic conditions during summer (Scoullos, 1983). Field sampling took place in September 2014 with the R/V AEGAEO (HCMR). Hydrographical data were recorded through CTD measurements. Seawater and surface sediment from the deepest-anoxic-station (33m) was collected untreated and placed in four 25L Nalgene Polycarbonate containers (at a proportion 80% to 20%, respectively) in a thermostatic chamber (17.5°C). The seawater-sediment systems were left to equilibrate for a week in Ar atmosphere in order to maintain the anoxic field conditions. This was followed by the four week period of the experiment where CO_2 was also added to the microcosms.The stability of pH was maintained using a continuous flow system (IKS Aquastar, IKS Computer Systeme GmbH) which automatically adjusted CO_2 gas addition to the microcosms. The measured pH values by the IKS system were corrected with the parallel use of a laboratory pH meter (Jenway 3310) calibrated in NBS scale. The pH values selected for the experiment conditions were: (a) for the Control conditions (C), the pH value measured during sampling, and (b) for the Ocean Acidification conditions (OA), the pH value predicted for the year 2300 (6,80 NBS), for latitudes corresponding to the Mediterranean (Caldeira & Wickett, 2005). Each one of the two conditions was applied in two replicate tanks. Seawater from field (during the cruise) and microcosms (every 2 days) was sampled and filtered through 0.45μm pore size membranes, for the determination of ammonia, nitrite, nitrate phosphate, silicate, total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) (spectrophotometrically with a Varian Cary 1E UV-visible spectrophotometer; Grasshoff *et al*., 1999). Supplementary analyses included dissolved oxygen (DO; Winkler Method), dissolved organic carbon (DOC; High Temperature Catalytic Oxidation on a Shimadzu 5000 total organic carbon analyser), total alkalinity (A_T) (SMWW 2320), calculation of the rest of the carbonate system parameters based on pH_T and A_T values (in combination with PO_4^{3-} and SiO_4 determinations) through the R package seacarb, preconcentration method for the determination of trace metals with ICP-MS.

Results and Discussion

The near bottom physicochemical parameters shown in Table 1, indicate a reducing coastal environment of quite increased acidity. The value of 7,75 pH units corresponds approximately to the predicted pH levels for 2100 (Caldeira & Wickett, 2005), while the negative redox potential along with the minimum DO concentrations, reflect the anoxic conditions prevailing in the deeper parts of the area during summer. This enhanced CO_2 near-bottom content is not regulated by equilibrium with the atmosphere but by the decomposition of organic matter in the sediment and the lower parts of the stratified water column.

Nitrate and nitrite concentrations show moderate variations from surface to bottom, within the range of the time series values (Table 1). On the contrary, ammonium concentrations in the bottom were found significantly higher than at the surface, along with increased concentration and accumulation of phosphates and silicates. The main process affecting nitrogen species under low oxygen conditions in Elefsis is denitrification; in the absence of oxygen, nitrates become the most abundant respiratory oxidant in seawater, converting them to nitrogen gases released from the system. The ammonia, phosphates and silicates accumulation, resulting from organic matter oxidation are followed by nitrates, at first, and sulfates and MnO_2 reduction, then, leading to H_2S and dissolved Mn accumulation in the bottom water. For phosphorus, it seems that there is an increase in sediment-released phosphates from Fe-oxyhydroxides, to the pore water and subsequently to the water column via diffusion, resuspension or bio-irrigation mechanisms. This study, corroborates with previous findings (Scoullos, 1983, Pavlidou *et al*., 2013) regarding elevated $NH_4^{+,}$ PO_4^{3-} and SiO_4 near-bottom concentrations.

During the experiment, DO exhibited insignificant variations, as the anoxic conditions were maintained by supplying inert gas (Ar) to the system. Nitrates and nitrites show a similar trend in C conditions, during the experiment (not shown), with almost exponential rise till the 15th day (to 15 μmol/L and 12 μmol/L, respectively) followed by significant decline to values similar to the ones determined in the field after day 25. Contrariwise, in OA conditions, NO_3^- and NO_2^- appear to rise evenly throughout the duration of the experiment to final values of 5.1 μmol/L and 2.7 μmol/L, respectively. NH_4^+ concentrations, in C conditions, drop significantly to ~1μmol/L, while in OA conditions they decline less dramatically until they reach a medium value of 8 μmol/L. It seems that under enhanced OA conditions, even while anoxia prevails, nitrification is the dominant process taking place, consuming ammonia with subsequent production of nitrites followed by nitrites oxidation, to nitrates. Nitrite and nitrate concentrations, throughout the experiment, show that these are the main stable inorganic N species. PO_4^{3-} show similar gradually declining trends in both OA and C conditions, from 3 to 2 μmol/L and 2 to 1 μmol/L, respectively, which also indicates an elevated P reserve in the system under more acidified conditions. SiO_4 concentrations present minimum variations throughout the experiment for both conditions. Widdicombe *et al*. (2009) has reported that, in acidification experiments, in the presence of sandy sediments, pH decrease caused inhibition of NO_3^- and NO_2^- release from sediment to the water column, with parallel increase in NH_4^+ release and no impact in PO_4^{3-} and SiO_4 flux. In C conditions, sediments have been previously found to act as sources of NO_3^- and NO_2^-, having different pattern regarding nitrification-denitrification processes in relation to OA conditions. TDN appears to have the same gradually increasing trend for both OA and C conditions until the 12th day, followed by decreasing values with higher final values for OA conditions. TDP also presents the same behavior for both conditions until the 12th day, with higher final values for OA conditions.

It is noteworthy that the DIN:DIP ratio in Elefsis Bay (surface) varies between 20 in winter and 13.7 during summer, whereas it decreases in an anoxic bottom to 4.2 (Pavlidou *et al*., 2013). DIN in the water column appears to increase during summer, whereas in winter it decreases followed by elevated DON concentrations, indicating oxidation mechanisms of organic nitrogen to inorganic species during the warm period. (Pavlidou, 2013) In this

	pH	Redox	DO	PO4 3-	SiO4	NH4+	NO3-	NO2-	TDN	TDP	DIN:DIP
Elefsis - surface	8,16	112,9	4,62	0,011	0,797	0,331	0,322	0,100	12,247	2,938	66,40
Elefsis -bottom	7,75	-50,7	0,00	3,684	56,17	9,722	0,177	0,072	22,387	4,001	2,71
Ranges from Time series (1987-2008) in Elefsis bottom waters in September (Pavlidou et al. 2013)	-	-	0,00-2,00	1,00-7,00	14,5-43,5	8,00-18,00	0,00-2,50	0,50-0,60			0,17-6,44

Table 1: pH (in NBS scale), Redox Potential (mV) and Dissolved Oxygen (DO; in mL/L), PO_4^{3-} and TDP (μmol/L), NH_4^+, NO_3^- NO_2^- and TDN (μmol /L), SiO_4 (μmol /l) concentrations and DIN:DIP ratio for seawater field samples (absolute values).

experiment (Fig. 1), during C conditions, the DIN:DIP ratio varied between 10 and 18 until the 15th day, and after it decreased sharply to below 5. In OA conditions, the ratio is stabilized between 7.7-8.0 indicating a preserved elevated content of inorganic nitrogen species and phosphates in the water column in relation to C conditions. In parallel with phosphates release from the sediment, these two processes become the controlling factor of DIN:P ratios in the near-bottom waters. However, it becomes clear that under OA conditions, nitrites and nitrates are favored against ammonia throughout the experiment, indicating decreased denitrification mechanisms and probably enhanced nitrification processes, in the presence of more acidic environments. This dissolved N content preservation is also obvious through TDN and TDP determinations in OA conditions with elevated final values related to C conditions. From previous studies, in minimum oxygen conditions denitrification and anaerobic ammonia oxidation (anammox) take place having an additional indirect implication on the carbon reservoir, resulting in decreased N reserve and causing reduction of primary production along with limited CO_2 ocean sequestration (Paulmier *et al*., 2011). CO_2 increase, though, is known to cause inhibition of denitrification (Paulmier *et al*., 2011) and perhaps also in anammox rates that could result in build-up of N.

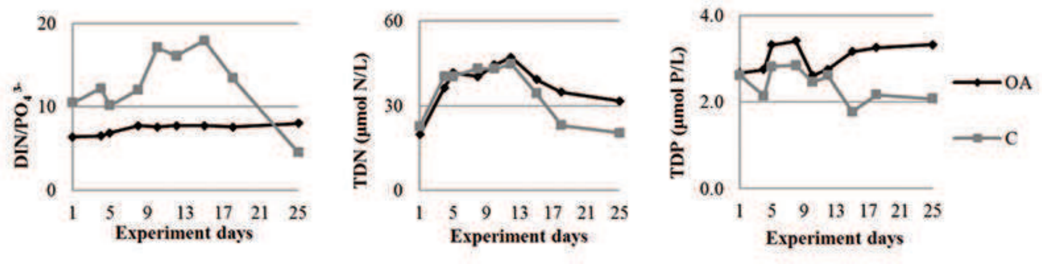

Fig.1: DIN:DIP ratio, TDN and TDP variations during the experiment for the OA and C conditions.

Conclusions

The results of this research showed that anoxic phenomena in coastal systems result in significantly decreased pH values in their deeper layers. This enhanced CO_2 near-bottom content is not regulated by an equilibrium with the atmosphere but by the decomposition of organic matter in the sediment and the lower parts of the stratified water column, a process that could lead to acidification spreading towards shallower depths and adjacent areas. While phosphates and silicates appear to be slightly affected or invariable, the combination of anoxia and OA conditions seem to increase nitrification processes against denitrification, preventing the consumption of inorganic N species, thus leading to nitrogen accumulation, possibly triggering and promoting eutrophication development after re-oxygenation and water mixing.

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Sampling in the Gulf of Elefsis in the 80s.

Sea bottom sediments of Elefsis Gulf: A potential secondary source of metals under simulated ocean acidification conditions

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Abstract

Hypoxic coastal areas are considered as high-priority systems for Ocean Acidification (OA) research, because the co-occurrence and interaction of low oxygen with other environmental stressors, such as elevated pCO_2, warming and eutrophication, may put them at greater risk. In this work, an anoxic coastal phenomenon exhibiting relatively reduced pH at the near bottom water layer was studied. *In-situ* and microcosm experiment measurements, simulating OA conditions, were conducted in order to assess the fate of dissolved trace metals that could either sink towards the sediment or be released towards the water column. OA conditions seem to induce the release of Al, Ni, Cd, Fe, Mn and As from the sediment while, in combination with anoxia, a restriction in this dissolution mechanism was found. Cr, Zn and Pb seem to follow a sink type mechanism under more acidified conditions while, in addition to anoxia, a source type mechanism is revealed. Hg seems to follow a source type mechanism under OA in any case. Regarding Fe species, it becomes evident that Fe (II) is the dominant species, indicating an increased stability as a result of acidified conditions.

Keywords: experiment, arsenic, iron, manganese, mercury, copper.

Introduction

Ocean uptake of anthropogenic CO_2 alters ocean chemistry, leading to more acidic conditions and lower chemical saturation states (Ω) for calcium carbonate ($CaCO_3$) minerals, a process commonly termed "ocean acidification" (OA). OA, especially when combined with hypoxic phenomena (Melzner, 2013), affects carbon and nutrient biogeochemistry, dissolved trace metal species and complexes' stability and sediment mineral phases, causing changes in benthic fluxes in the sediment-water interface (Ardelan *et al*., 2009, Atkinson *et al*. 2007, Scoullos, 1983) . Therefore, experiments combining acidification and low oxygen conditions are essential to fully understand and correlate the aforementioned observations in coastal environments (Melzner, 2013).

The aim of this project was to study the impacts of ocean acidification on a coastal industrialised system (Elefsis Gulf), affected by intermittent anoxic conditions, in order to distinguish if sediments act like a source or a sink for trace metals. Furthermore, it was evaluated, whether these sediment processes are imposed to alterations, as a result of acidification combined with intermittent anoxia.

Materials and methods

Elefsis Gulf is a small sized coastal system characterized by shallow depths (68 km^2, maximum depth 33 m) and limited communication with the wider Saronic (Scoullos, 1983). Due to the increased organic load and physiographic region, the inflow and the water exchange is restricted, resulting in the development of hypoxic/anoxic conditions during summer (intermittently anoxic) (Scoullos, 1983). Two laboratory experiments (I concerning only ocean acidification impact and II combining anoxia with ocean acidification) were conducted using experiment microcosms (25L), containing water and sediment from the greater depth (33 m) of the Gulf (at a proportion 80% to 20%, respectively). In both experiments, the stability of pH was maintained using a continuous flow system (IKS Aquastar, IKS Computer Systeme GmbH), which automatically adjusted CO_2 gas addition to the systems; in experiment II, the anoxic field conditions were also maintained by Ar supply. During exp. II, on the 25th day of the experiment, the Ar supply was ceased and the systems were left to re-oxygenate until day 33 in order to fully simulate the intermittent anoxic conditions of the study area. The pH values selected for the experiment conditions were (a) for the control conditions (C) the pH value measured during sampling

(7.85 for exp. I – 7.75 for exp. II), and (b) for the ocean acidification conditions (OA) the pH value predicted for the year 2300 (6.80) for latitudes corresponding to the Mediterranean (Caldeira and Wickett, 2005). Each one of the two conditions was applied in two replicate tanks. Water samples were collected daily during the four week period of the experiment; sediments were collected and treated according to EPA 3050 for final measurement with ICP-MS for As, Cr, Cu, Ni and Pb using the Collision Cell Technology (CCT) mode of the instrument, FAAS for Al, Fe, Mn and Zn, GFAAS for Cd and CVAAS for Hg. A colorimetric determination of Fe species was also applied for wet sediment samples (combined method of Bloom, 2004 and GEOMAR). All determinations were checked with Certified Reference Material treatment and analysis. Supplementary analyses included organic and inorganic carbon determinations (TOC and $CaCO_3$), nutrients' determinations (TP, TN) and mineral composition with XRF,XRD analyses.

Results

In exp. I, sedimentary Cr appears to decrease under OA conditions, whereas in exp. II, this process seemed to be restricted in OA along with anoxic conditions. This decrease in Cr particulate form, could be attributed to an increase in Cr solubility as a result of enhanced CO_2; in C conditions no such variation was observed indicating perhaps a restrictive mechanism in Cr solubilization.

Sedimentary Al appeared to slightly decrease in exp. I, under OA conditions, indicating perhaps release from the sediment but in the second experiment, a sharp increase was observed in both conditions. For Cr and Al, from previous experiments (Ardelan, 2009), it was found that under enhanced CO_2 concentrations, they are both effectively removed in dissolved forms as a result of increased solubility.

Ni also presented a similar trend to Cr, with a decrease in sedimentary concentrations in exp. I, under OA conditions; in exp. II, in OA conditions combined with anoxia, particulate Ni seemed to sink on sediment surface. From previous experiments, Ni has been found to dissociate more rapidly from the sediment into more labile phases towards the pore water and the supernatant seawater, which was confirmed in this study. Thus, the minimum oxygen conditions seem to restrain this solubilisation mechanism and preserve particulate Ni phases within the sediment. (Roberts *et al*., 2013)
In exp. I, Cu, Zn, Pb decrease to a lesser extent in OA conditions, in relation to C conditions; in exp. II, Cu decreased dramatically in both OA and C conditions. In anoxia, a direct extraction from the sediment with concomitant Cu dissolution from the suspended material became more effective within the first days of exp. II for both conditions, indicating that sediment acts as a source of Cu. From this study, sedimentary Zn and Cu, under OA conditions and OA combined with anoxia, seemed to act as a source for solubilised metals toward the water column, in contrast to previous results in the area (Prifti *et al*., 2015) that show that unaffected sediments act as a sink for these two metals under oxic conditions. A potential cause of this alteration could be the different redox conditions during our experiment, as acidified conditions were implemented along with minimum oxygen conditions, in contrast with oxic conditions implemented in the Prifti *et al*. (2015) study.

Cd appeared to decrease in exp. I, in both conditions, while in exp. II, an increase of Cd concentration was observed for both conditions. For Pb and Cd during OA conditions along with anoxia, a sink type mechanism of particulate phases precipitating on sediment surface was found; this is in agreement with the mechanism reported under oxic conditions for Pb and Cd (Prifti *et al*., 2015) while, a source type mechanism from the sediment toward the water column was observed for these two metals, when only acidified conditions prevail.

Hg presented a decrease in sediment concentration in both experiments; in exp. I, under OA conditions the decrease seems to be restricted in relation to C conditions. In exp. II, the Hg decrease was not affected by OA conditions, a distribution which seems to be affected only by the anoxia prevailing. Hg distribution, usually presents decreased surface values either because of its increased volatility or its precipitation in particulate phases. In stratified environments, an elevated content is found in the thermocline zone while it decreases below the thermocline. Hg is known to accumulate in deeper anoxic areas, removing dissolved Hg from the surface water. In reducing aquatic environments, Hg(0) is known to be the most stable Hg species, which is released as a gas towards the atmosphere. In this case, the sediment acts as a source but it is not clear to what extent Hg remains in the water column or it it eludes into the atmosphere (Colombo *et al*., 2013).

Fe seemed to slightly decrease during exp. I in OA conditions, while no changes were observed during C conditions; in exp. II a slight increase was observed for both conditions. Sedimentary Mn appeared to remain invariable in exp. I, during OA conditions, while in C conditions, a decrease was observed. In exp. II, both in OA and C conditions, an increase was observed. Under oxic conditions, it was previously found that sedimentary Fe acts as a source while Mn acts as a sink toward the sediment (Prifti *et al*., 2015). It has been shown (Ardelan *et al*., 2009) that CO_2 seepage is able to transform sedimentary Fe and Mn, leading to an enhanced release of these metals from the sediment to the overlying water, both as dissolved and suspended particulate forms.

As presented different trends during the two experiments. In exp. I, a decrease in both OA and C conditions was observed, leading to the assumption that sediment acts as a source of As towards the water column. In exp. II, an increase in As concentration was found, being more significant under acidified conditions; in this case, it appears that sediment act as a sink for As. From previous experiments, it was found that under anoxic conditions, As (III) being the major arsenic species, is mobilized from the upper sediment surface to the overlying water (Bennet, 2012). The mobility of As in sediments is known to be closely linked to Fe biochemistry. Fe(III) (hydr) oxide minerals strongly adsorb dissolved inorganic As via complexation. Reductive dissolution of these arsenic-bearing Fe(III) (hydr)oxides, under anoxic conditions, can release dissolved As into the porewater and result fluxes of As to the overlying water column. In this study, under OA conditions, a sharp decrease of sedimentary As was observed, while for Fe only slight alterations were detected. Moreover, in OA along with anoxia, although Fe remains invariable, Mn tends to precipitate to a larger extent leading to As accumulation (Bennet, 2012), a phenomenon that was verified in the present study as a significant increase of As concentration in the sediment was observed. It has been previously demonstrated, that metal release from metal-contaminated sediments is influenced by Fe and Mn redox chemistry (Atkinson *et al*., 2007). From previous experiments, the rate of oxidative precipitation of released Fe and Mn increases, as pH decreases, and appear to greatly influence the sequestration rate of released Pb and Zn. Released metals were sequestered less rapidly in waters with lower dissolved oxygen concentrations (Atkinson *et al*., 2007).

From the Fe ratio results (Fig. 1), it becomes obvious that, in both experiments Fe (II) is the dominant Fe species, even without anoxia prevailing. Under acidified conditions, Fe (II) is likely to show increased stability (Breitbarth *et al*., 2010), which is evident during the experiment, as Fe (II) remains high, even in ordinary oxic conditions. In exp. I, the Fe (II) ratio seems to decrease in OA conditions, while the Fe (III) ratio seems to increase. During exp. II, Fe (II) ratio seems to increase slightly for OA conditions, whereas a significant decrease was observed for C conditions after the re-oxygenation phase. The Fe (III) ratio presented the opposite trend, with a decrease in the OA conditions and an increase in C conditions. At the current pH of surface seawater, Fe (III) is at its minimum solubility and as pH decreases, solubility increases. A decrease in pH from 8.1 to 7.4 would increase the solubility of Fe (III) by approx. 40%, which could have a large impact on the biogeochemical cycles, because Fe is an important micronutrient (Millero *et al*., 2009). During this study, the increasing Fe (III) ratio in OA conditions in exp. I indicates an increase in the Fe oxidation rate that may also increase Fe(III) solubility towards the water column. In exp. II, the Fe (III) ratio decreased, as a result of the anoxic conditions, which indicates a reduction mechanism of Fe (III) to Fe (II), with possible restrictive Fe (III) solubilization mechanisms.

Conclusions

The results of this study revealed that under OA conditions, metals such as Al, Ni, Cd, Fe, Mn and As seem to follow a source type mechanism from sediments towards the water column. In contrast, in anoxic conditions, a diverse sink type mechanism for these metals was observed. Cr, Zn and Pb, followed a sink-type mechanism under enhanced CO_2, while in OA along with anoxic conditions, a source type mechanism from the sediment towards the water column was found. Hg seemed to act as a source type mechanism under acidification, regardless of the oxygen conditions but it remains unknown whether it is maintained in the dissolved form or it is released in the atmosphere. Regarding the Fe ratio, it became evident that in both experiments Fe (II) was the dominant Fe species, even without anoxic conditions prevailing, indicating the increased stability of Fe (II) as a result of increased CO_2.

Exp.	cond.	Exp. day	As	Fe	Mn	Cr	Cu	Ni	Pb	Zn	Cd	Al	Hg
	field	-1	12,6	2,04	330	117	63,2	130	108	414	0,37	3,50	0,29
	OA	25	10,9	1,93	335	101	26,4	118	79,1	301	0,30	3,05	0,20
I	C	25	9,79	2,05	302	124	8,3	156	54,0	206	0,26	3,30	0,16
	filed	-1	9,12	1,88	284	122	107	127	102	506	0,26	3,26	0,42
		18	12,6	1,95	324	112	33,0	130	106	411	0,42	3,48	0,22
	OA	33	12,1	2,12	350	112	33,4	138	111	408	0,39	3,57	0,21
		18	11,4	2,03	327	120	38,9	141	108	386	0,41	3,60	0,21
II	C		10,9	2,09	345	108	15,1	140	79,9	350	0,27	3,63	0,19

Table 2: Trace metal concentrations for field and experimental samples under the different conditions (cond.) and during the experiment days (Exp. day) [As, Mn, Cr, Cu, Ni, Pb, Zn, Cd and Hg in mg/kg, Fe and Al in %]

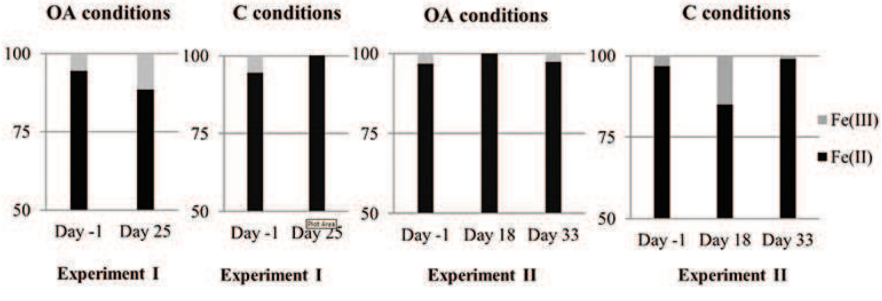

Fig.2: Fe species ratios in % (Fe(II)/Fe total and Fe(III)/Fe total) variation during the two experiments

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Metal fluxes in the bottom – water interface in Elefsis bay, Greece

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Abstract

The aim of this study was to estimate the mass flux of metals from sediments to the water column at two stations in Elefsis bay. The fluxes were estimated based on seawater concentrations of metals during ex situ incubation experiments. The results showed that the bottom sediments of Elefsis bay act as a sink for Fe and Mn and source for Zn and Ni. Cu, Cd and Pb were released from the sediment only at the western basin of Elefsis bay.

Keywords: metal fluxes, marine sediments, Elefsis bay

Introduction

The sea floor plays an important role in the regulation of the chemical composition of the overlying water. Processes in sediments, like organic matter degradation and early diagenesis, affect the mobility of substances like nutrients and metals. During mixing periods, the water column becomes homogeneous and oxic conditions occur in the bottom water, whereas during stratification periods the dissolved oxygen in the bottom layer is depleted. This periodic oscillation of the redox conditions of the bottom water has profound effects on the sediment geochemistry and in particular the role of sediments as a source or sink of metals. Thus, given the fact that bioavailable metals in the water column have negative impacts on epibenthic and pelagic biota, a quantitative assessment of the metal fluxes at the bottom-water interface is essential. This is commonly studied by *in situ* benthic chambers (Tenberg *et al*., 2004), by *ex situ* incubations of marine sediments or by calculating the metal flux from the pore water metal concentrations using Fick's First Law (Torres *et al*., 2013; Torres *et al*., 2014). The objective of this work was to evaluate the metal fluxes at the bottom-water interface at the eastern and western part of Elefsis bay under oxic conditions.

Materials and methods

Study area

Elefsis Bay is a closed, shallow, elongated sea basin, formed between the Attica coast and the Island of Salamis. It is connected to Saronikos Gulf through two narrow and shallow channels. The bay has a surface area of 67 km^2 and a volume of 1.3 billion m^3. Most of the bay has a depth of less than 18 m, while the greatest depth, 33 m, is observed near the center. Elefsis Bay is surrounded by one of the heaviest industrialized areas of Greece. Recently, in a report on the priorities for the Mediterranean environment, jointly issued by the European Environment Agency (EEA) and the United Nations Environment Programme /Mediterranean Action Plan (UNEP/MAP), Elefsis Bay was recognized as an area of major environmental concern (EEA & UNEP/MAP, 2005). The stations S1 and S2 represent the east and west Elefsis Bay, respectively (Figure 1).

Experimental procedure

Sediment cores about 10cm long were subsampled from a box corer collected from stations S1 and S2 in September 2012. The incubation experiments were conducted at the HCMR laboratory, after the cores had been transferred there, taking all precautions for the sediments to be undisturbed. The tubes were filled with bottom water, which was obtained from the bottom layer of the same sampling station. The incubation experiments lasted for approximately 17 hours (Figure 2). During this period, samples of the overlying water were taken every two hours for the determination of the metal concentrations. The volume of the overlying water was kept stable by replacing the sample volume with the same volume of bottom water; the total volume of all samples each time did not exceed 10% of the total volume of the overlying water. Aerated conditions were applied by a constant air supply to the water and a mixing valve that was regulated to the point that no disturbance was made to the sediment surface.

All samples were preconcentrated by the method described by Milne *et al* (2010) and analyzed with ICPQMS combined with the Collision Cell Technology (CCT) mode of the instrument.

Determination of metal fluxes

The metal fluxes through the water–sediment interface were estimated from the evolution of the metal concentrations in the overlying water through time:

$$F_{tank} = \frac{(Cf - Ci)V}{A\Delta t}$$

where Cf and Ci are the final and initial metal concentrations (mol/m^3) in the water tank, respectively, V is the water volume (m^3) in the tank, A is the total sediment–water surface area (m^2) and Δt is the duration (days) of each experimental step. Positive flux indicates the release of metals from the sediment, whereas, negative value indicates the flux from the water to the sediment.

Results

Metal fluxes showed significant differences between the two sampling stations and between metals (Table 1). Station S1 showed release from the sediment of Zn and Ni and transfer from the water to the sediment of Fe, Mn, Cu, Cd and Pb. This means that the sediment acts as a source of Zn and Ni, but it is a sink for the other metals. Mass fluxes at station S2 were negative for Fe and Mn, revealing a sink behavior of the sediments for these two metals while positive fluxes for all the other metals indicated that the sediment acts as a source of Zn, Cu, Ni, Cd and Pb.

The negative fluxes for Fe and Mn at both stations indicated that under oxic conditions the sediments of Elefsis bay can trap Fe and Mn. On the contrary, the positive Zn and Ni fluxes revealed a source behavior of Elefsis bay sediments for these metals.

Besides the different pollution sources, the grain size of the sediments at the two stations is different (<63μm fraction in S1: 35% and S2: 73%) and also the organic carbon content (S1: 2.29%, S2: 3.29%). The similar behavior of Fe, Mn, Zn and Ni at both stations suggests that these metals are not affected by the geochemical differences between the two stations. On the contrary, the opposing fluxes of Cu, Cd and Pb between the two stations implied that these metals are probably more sensitive to such differences.

Fig.1: Elefsis Bay, Greece

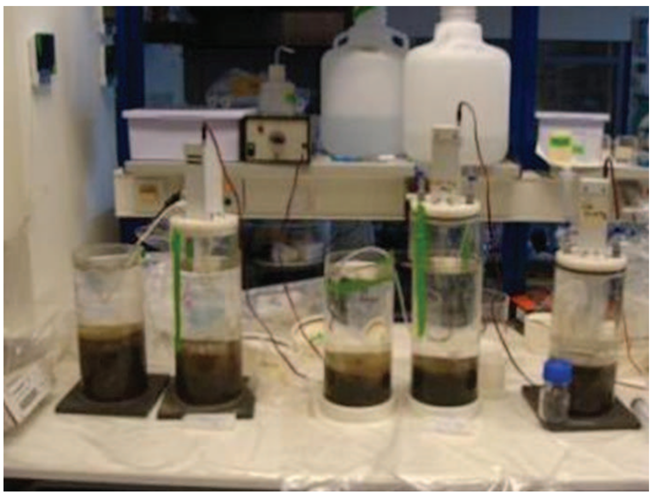

Fig.2: Incubation experiments

Flux μmol/(m^2*day)	Fe	Mn	Zn	Cu	Ni	Cd	Pb
S1	-27	-83	0.01	-0.26	1.25	-0.07	-1.79
S2	-26	-340	18	0.71	6.54	0.02	0.06

Table 1: Metal fluxes at Elefsis bay estimated from incubation experiments

Conclusions

The incubation experiments showed that, under aerated conditions, the bottom sediments of Elefsis Bay can act as a sink for Fe and Mn and as a source for Zn and Ni. At the western basin Cu, Cd and Pb were released from the sediment to the water column, whereas the sediments at the eastern part of the bay acted as a sink for Cu, Cd and Pb. The reverse behavior of Cu, Cd and Pb at the two stations of Elefsis bay is evidence for the complex dynamics that control the fate of these three metals.

Acknowledgements

We would like to thank the crew of the R/V AEGAEO and the colleagues who helped in the sampling and the analysis of the samples. This research was funded partly by the PERSEUS Project (EC Grant agreement no. 287600) and the MERMAID project (ERANET 12SEAS-12-C1).

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Rare earth elements in marine sediments of Elefsis Bay, Greece

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Abstract

The increasing economical importance of Rare Earth Elements (REEs) as well as the concern about their biological effects, which are least studied and understood, raise the need of an extended mapping of REEs concentrations in the environment. In this study, 14 REEs were determined in marine sediments from Elefsis Bay, an area which is of major environmental concern. This work showed that REEs concentrations in Elefsis Bay have no economic interest and no significant variations. Nevertheless, a more detailed study is needed in order to understand the geochemical processes that could explain the slightly higher REEs concentrations of the surface sediments at the eastern part of Elefsis Bay and to evaluate any potential risks that could originate from them.

Keywords: rare earth elements, marine sediments, Elefsis bay

Introduction

Rare Earth Elements (REEs) are increasingly important economic resources as they are critical in many developing "green technologies" and in the production of several of today's "high-tech" electronic devices, like permanent magnets, compact fluorescent lamps, catalysts, rechargeable batteries, etc. With China presently producing more than 90% of the global REEs output and its increasingly tight export quota, the rest of the world is confronted with a REEs supply risk. Thus, the European Union, in its landmark reports "Critical Raw Materials for the European Union" , considers REEs as the most critical raw materials group, with the highest supply risk, considering the fact that EU is 100% import dependent of REEs and has no active REEs mines (European Commission, 2010, 2014). The high importance of REEs for the European Union is also revealed in the extended report "Critical Metals in the Path towards the Decarbonisation of the EU Energy Sector" (Willis *et al*., 2013). Consequently, the European Union is funding a series of projects (ProMine, EuroGeoSource, EuRare, Minerals4EU) in an attempt to discover and map the potential REEs resources within its borders (Arvanitidis & Goodenough, 2014).

Greece is considered to have the most economically important deposits of the Mediterranean area in the form of bauxites existing mainly in the regions of Mt Parnassus, Mt Ghiona and Mt Helikon (central Greece) and on Evia Island (Deady *et el*., 2014).

In addition to the increasing interest for REEs concentrations due to their economic value, the potential health effects of REEs in organisms and their toxicity mechanisms have also sparked an increasing interest within the scientific community, given the fact that till today, information on REEs associated biological effects is very scarce (Pagano *et al*., 2015). Taking into account that these elements are used in the majority of electronic products, it is very important that their concentrations are studied not only as potential resources but also as potential pollutants.

In this study, we determined the REEs concentrations in the bottom sediments of Elefsis Bay, aiming at contributing to the effort of mapping natural REEs concentrations in the Greek marine environment and also to provide a background dataset for future monitoring of REEs concentrations in this heavily impacted area.

Materials and methods

Study area

Elefsis Bay is a closed, shallow, elongated sea basin, formed between the Attica coast and the Island of Salamis. It is connected to Saronikos Gulf through two narrow and shallow channels. The bay has a surface area of 67 km^2 and a volume of 1.3 billion m^3. Most of the bay has a depth of less than 18 m, while the greatest depth, 33 m, is observed near the center. Elefsis Bay is surrounded by one of the heaviest industrialized areas of Greece. Recently, in a report on the priorities for the Mediterranean environment, jointly issued by the European Environment Agency (EEA) and the United Nations Environment Programme / Mediterranean Action Plan (UNEP/MAP), Elefsis Bay was recognized as an area of major environmental concern (EEA & UNEP/MAP, 2005). The stations S1 and S2 represent the east and west Elefsis Bay, respectively (Figure 1).

Experimental procedure

Sediment cores from stations S1 and S2 were collected in September 2012. From station S1 (19m depth) a sediment core about 18cm long was acquired while the sediment core from station S2 (30m depth) was 28cm long. The sediments were sliced in layers of 1cm and each layer was analyzed for the concentration of 14 Rare Earth Elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu). The determination of REEs concentration was carried out by ICP-QMS combined with the Collision Cell Technology (CCT) mode of the instrument after a microwave induced acid digestion. Along with the samples, the Certified Reference Material BCR667 was analyzed with recoveries between 91% and 115%.

La 16-32	Ce 31-62	Pr 3.4-7.2	Nd 14-30	Sm 2.6-5.6	Eu 0.59-1.3	Gd 2.6-5.5
Tb 0.38-0.86	Dy 2.3-5.2	Ho 0.47-1.1	Er 1.4-3.2	Tm 0.20-0.45	Yb 1.4-3.2	Lu 0.19-0.49

Table 1: Concentration ranges (ppm) of REEs in sediments from stations S1 and S2

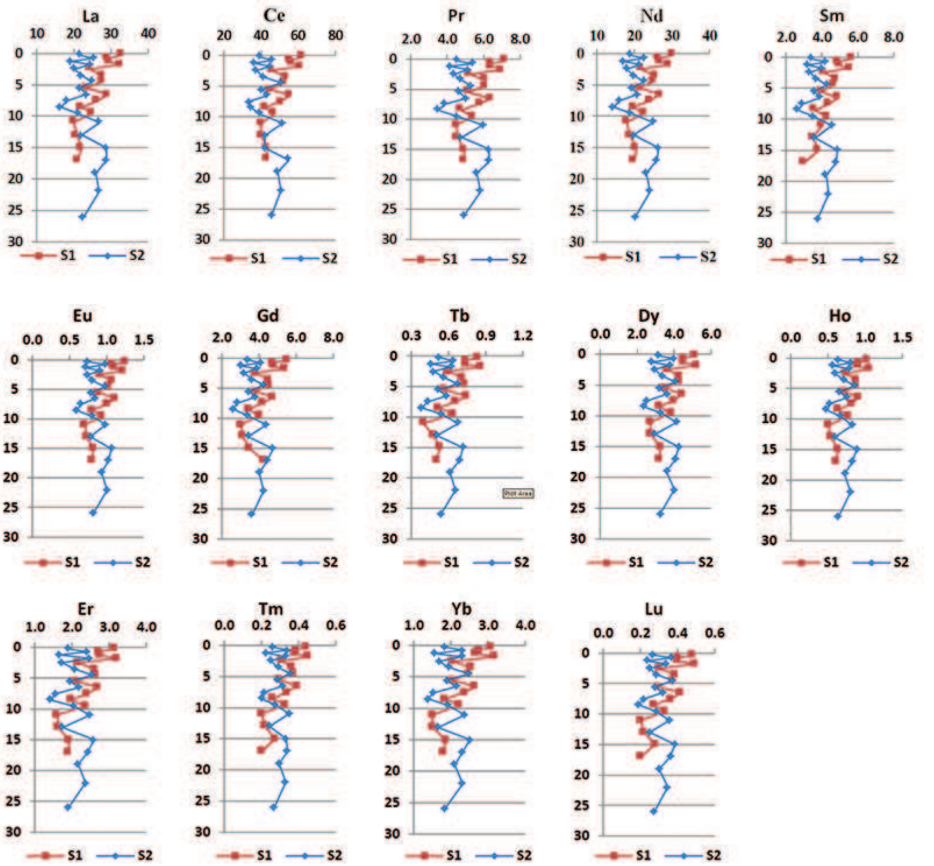

Fig 2: Vertical distribution of Rare Earth Elements in sediments of Elefsis Bay. Horizontal axis: Concentration (ppm) Vertical axis: depth (cm)

Fig.1: Elefsis Bay, Greece

Results

The ranges of the REEs concentrations are shown in Table 1. Vertical distributions of REEs do not show any significant variation, while all the elements that were determined, follow the same distribution pattern. At a depth of more than 10 cm the concentrations of the REEs are similar between the two sampling stations. On the contrary, at the 0-10cm sediment layer the concentrations of all the REEs are higher at the east station (S1) of Elefsis Bay (Figure 2). The concentrations of REEs found in the sediments of Elefsis Bay are much lower compared to the REEs values in the bauxites and lateritic bauxites of central Greece reported by Tsirambides and Filippidis (2012) (ΣREEs: 3275-6378ppm) and also lower than the ≈500ppm ΣREEs+Y reported by Deady *et al.* (2014) indicating that the area has no economic interest regarding REEs resources.

Conclusions

The determination of 14 REEs in the sediments of Elefsis bay showed that the total concentration of REEs in the area raises no economic interest. Although the concentrations of all elements are relatively stable in a depth of more than 10 cm, we clearly see slightly higher concentrations of all REEs in sediments from the East sampling station (S1). Further study of this difference is needed to evaluate whether the higher REEs concentrations of East Elefsis Bay are attributed to natural or anthropogenic processes.

Acknowledgements

We would like to thank the crew of the R/V AEGAEO and the colleagues who helped in the sampling and the analysis of the samples. This research was funded partly by the PERSEUS Project (EC Grant agreement no. 287600) and the MERMAID project (ERANET 12SEAS-12-C1).

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Mercury levels in Greek coastal areas

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Abstract

Mercury is recognized as a priority pollutant in the marine environment because of the severe toxicity associated with its species and the increased tendency to bioaccumulate. Humans are mainly exposed to mercury through marine foods. The complexity of the mercury biogeochemical cycle as well as the analytical difficulties in quantifying species at pM levels are the reasons for the relative scarcity of data compared to other metals. Selected mercury data for seawater, sediments and biota produced by the Laboratory of Environmental Chemistry from various Greek coastal marine areas are presented in this paper in comparison to other Greek and Mediterranean areas, European legislation and European and International quality guidelines.

Keywords: bioaccumulation, biomarkers, marine bivalves, detoxification, Efefsis.

Introduction

Among the toxic trace metals, mercury (Hg) is one of the most hazardous environmental pollutants. Hg exists in the form of highly toxic species (inorganic and methyl-mercury) and participates in a very complex biogeochemical cycle via both natural and anthropogenic sources.

Mercury can be found in the Earth's crust mostly in the form of cinnabar (HgS) which was traditionally mined for Hg production. This mineral is not very abundant but there are significant recorded deposits in several places around the world (USA, Mexico, Italy, the Balkan Peninsula and Turkey). Mining of cinnabar is largely abandoned and the demand for Hg is met by recovering it from industrial sources and existing stock piles.

Mercury is used in various industrial processes, such as the manufacturing of cells used in chlor-alkali plants, paints, batteries, fluorescent and energy-saving lamps, switches, electrical and electronic devices, thermometers and blood pressure gauges, pesticides, fungicides, medicines, and cosmetics.

The main natural sources of Hg in the environment are the continuous weathering of mercury-containing rocks, episodic volcanic events and on-going geothermal activity. Anthropogenic sources are divided in two categories. On one hand, Hg is emitted by coal burning, mining, industrial activities (e.g. cement, metallurgy). In these cases, because mercury is present as an impurity in the processed materials the emission or release is often referred to as 'by-product' or 'unintentional'. The second category of sources includes sectors where mercury is used intentionally. These are artisanal and small-scale gold mining (ASGM), waste from consumer products (including metal recycling), the chlor-alkali industry, and the production of vinyl-chloride monomer. Re-emissions constitute a third category of sources. Mercury previously deposited from the air onto soils, surface waters, and vegetation from past emissions can be emitted back to the air. Re-emission is a result of natural processes that convert inorganic and organic forms of mercury to elemental mercury, which is volatile and therefore readily returns to the air. Mercury deposited on plant surfaces can be re-emitted during forest fires or biomass burning (UNEP 2013).

Hg in natural waters can be found in 3 oxidative conditions Hg^0, Hg^{+1}, Hg^{+2}. In the marine environment Hg can be distinguished in the following species: Total Mercury (THg), Reactive Mercury (Hg_R), Ionic Mercury (Hg(II)), Elemental Mercury (Hg^0), Dissolved Gaseous Mercury (DGM), Methylmercury (MHg) and Dimethylmercury (DMHg). These species are interrelated: THg = Hg (II) + MeHg + DMHg + Hg^0

The pathways and fate of mercury in the aquatic environment are important because it is in waters, sediments, and wetland soils that inorganic mercury is converted into methylmercury through bacterial processes. Methylmercury, is highly toxic and concentrates (bioaccumulates and biomagnifies) in animals. The majority of human exposure to mercury, and the health risk that comes with mercury exposure, is from consumption of marine food. The evasion of mercury from aquatic surfaces to the atmosphere (Dissolved Gaseous Mercury – DGM) is a unique feature of the complex mercury biogeochemical cycle compared to other metals. The case of the mercury cycle, is of high significance in the Mediterranean region because of the combination of the known geochemical "anomaly" - large cinnabar deposits and high temperatures for many months of the year. An increased temperature due to climate change raises major concerns because with increased temperature the re-emission rate of Hg increases (UNEP 2013). Furthermore, warmer temperatures cause increased rates of organic productivity and bacterial activity that may lead to faster conversion of inorganic Hg to the neurotoxic methylmercury in fresh and marine water ecosystems and littoral sediments (UNEP, 2013; Verta *et al*., 2010).

The aforementioned aspects of mercury biogeochemistry are still poorly studied in the Mediterranean and there is still a relative scarcity of data, especially in Greece. It should be mentioned that although Hg was recognized as a priority pollutant in the MED POL programme and European legislation, the determination of total Hg concentrations in seawater was only recently included in the monitoring protocols of the Water Framework Directive (WFD) and it will also be included in the monitoring protocols for the implementation of the Marine Strategy Framework Directive (MSFD).

Selected mercury data for seawater, sediments and biota produced by the Laboratory of Environmental Chemistry from various Greek coastal marine areas are presented in this paper in comparison to other Greek and Mediterranean areas, European legislation and European and International quality guidelines.

Materials and methods

The quantification of Hg species in environmental media is quite challenging. Various instrumentation techniques can be used: Cold Vapor Atomic absorption spectrometry (CVAAS), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), and Atomic Fluorescence Spectrometry. Hg analysis is very difficult; since positive errors from sample contamination, as well as negative errors from the volatile nature of Hg can occur.

In this paper we present concentrations of Total Hg, i.e. all BrCl-oxidizable mercury forms and species found in an unfiltered seawater sample. These include, but are not limited to, Hg(II), Hg(0), strongly organo-complexed Hg(II) compounds, adsorbed particulate Hg, and several tested covalently bound organo-mercurials (e.g. CH_3HgCl, $(CH_3)_2Hg$, and $C_6H_5HgOOCCH_3$). The method of determination (EPA 1631) consists of oxidation of all species to Hg(II), purge and trap onto a gold trap, desorption and cold-vapor atomic fluorescence spectrometry (CVAFS) by a TEKRAN 2500 total mercury analyzer. It is the only technique that can directly measure the extremely low levels of Hg in seawater, which cannot be quantified by ICP-MS due to interferences by the saline matrix, or by HGAAS due to a much higher quantification limit. The original THg data presented here from the Project "*Aristeia* – Integrated Study of Trace Metals Biogeochemistry in the Coastal Marine Environment" are from seawater samples collected in North and Central Evoikos Gulf in 2014/ 2015 and in Elefsis Bay in 2015.

For the sake of comparison we also present data from samples analyzed by our research groups over the last few years. These are data from: a) Elefsis Bay, Saronikos Gulf, Central Aegean, Eastern Aegean and Ionian Sea samples that we were graciously allowed to collect during monitoring campaigns by HCMR (Hellenic Centre for Marine Research), b) selected samples from Elefsis, Saronikos, Evoikos, Thermaikos, Central Aegean, and Ionian Sea collected for the national Hellenic monitoring project for the implementation of WFD in which the Laboratory of Environmental Chemistry participates as the sub-contractor for THg analysis.

Furthermore, we present Hg levels in sediments from Elefis Gulf, Saronikos, North Evoikos and Maliakos gulf and biota samples (dog fish *Squalus acanthias* and smoothhound sharks *Mustelus mustelus*) digested in hermetically sealed vessels either using a microwave digestion system or on a hot plate and measured using CVAAS. The concern about Hg levels in these areas arises from several point and non point pollution sources, including steelworks, oil refineries, shipyards and cement factories (Scoullos *et al*., 2001, Paraskevopoulou *et al*., 2014).

Results

In Table 1 the legislation limits and quality guidelines for Hg in water, sediment and biota are presented, whereas Table 2 summarizes the results of Hg concentrations in seawater samples.

Two extreme values were measured in bottom samples in Elefsis (104 ng/L at S2/30m in September 2012) and Eastern Saronikos (187 at S7/70m in September 2012). These could be attributed to the hypoxia in the isolated bottom water of station S2 or the presence of wastewaters at the bottom of S7 (Athens WWTP discharge). Total Hg in water samples analyzed were far below the EU limit of 70ng/L.

A review of Hg levels in sediments has been published by Tzempelikou *et al*. in 2010. Some of these reviewed cases are also given here. The first group of sediments (Elefsis, West and East Saronikos and Korinthiakos) have been analyzed for Hg by members of the Laboratory of Environmental Chemistry. The lower values measured in sediments are near the reference value for the earth's crust. However, the maximum values often exceed the ERL limit and thus adverse effects to biota are possible. In two

Reference	Criteria – Limits - Guidelines		
EC/2013/39	Maximum allowable THg concentration in inland surface and other surface waters 70 ng/L	Environmental Quality Standard for fish 20μg/kg wet weight (ww)	
Anagonopoulos et al., 2012	GES marine waters 1μg/L	Background level 10ng/L	
	GES biota 150 μg/kg wet weight	Background level 10 μg/kg ww	
EC 1881/2006	Maximum in large fish 1000 μg/kg ww		
Long 1995, Rudnick and Gao 2003	ERL (effects range low) 150 μg/kg	ERM (effects range median) 710 μg/kg	Continental Crust 50 μg/kg

Table 1: Maximum permissible limits and quality guidelines for Hg in waters, sediments and biota.

Reference	Area	THg range (ng/L)	THg average (ng/L)
Current study (Aristeia project)	Central Evoikos	1,0 – 10,6	3,9
	Northern Evoikos	0,5 – 7,10	2,5
	Elefsis	2,7 – 14,5	9,4
	Elefsis - Steelworks stations	10,8 – 14,1	12,5
Tzempelikou 2010	Elefsis	3,1 – 8,1	6,5
	Eastern Saronikos	1,7 – 6,3	3,9
Bilias 2014	Elefsis	1,2 – 25,3	6,4
	Eastern Saronikos	0,2 – 36,9	7,2
	Central Aegean	3,7 – 44,3	-
	Eastern Aegean	0,4 – 21,4	-
	Ionian	0,5 – 17,2	-
WFD 2012-2015 (unpublished data)	Elefsis	2,9 – 23,9	10,5
	Eastern Saronikos	0,3 – 18,2	5,3
	West Saronikos	0,9 – 1,2	1,1
	Evoikos	0,4 – 20,2	4,3
	Thermaikos	1,0 – 36,9	5,3
	Laganas, Ionian Sea	0,4 – 18,2	4,4
	Kalogeroi Central Aegean	1,1 – 2,4	1,7
	Kastelorizo, Southern Aegean	0,87	0,87
Cossa et al., 1996	Gulf of Lion	0,4 – 1,3	-
Kotnik et al., 2007	Alboran Sea	0,1 – 0,5	-
Kotnik et al., 2007	Tyrrenian Sea	0,2 – 0,4	-
Kotnik et al., 2007	Ligurian Sea	0,2 – 0,3	-

Table 2: Total Hg concentration s in seawater samples

Reference	Area	Hg (μg/kg)	Reference	Area	Hg (μg/kg)
DEPPETH, 2006 Our Lab	Elefsis	100 - 510	Tzempelikou 2010	West Saronikos	67–327
	West Saronikos	180 - 230		Maliakos	158 – 340
	East Saronikos	40 - 50		North Evoikos, Larymna	144 – 536
	Korinthiakos	30 – 70	DEPPETH 2006	Patraikos Gulf	100 – 1360
DEPPETH 2006	Thermaikos Gulf	2900 - 8800	DEPPETH 2006	Pagasitikos Gulf	20 - 180

Table 3: Total Hg ranges in selected sediments

cases (Thermaikos and Patraikos) Hg levels exceed the ERM value of 710 μg/kg above which adverse effects to biota have been found to occur invariably.

The Hg levels in two large fish species caught in the Eastern Aegean Sea (Kousteni *et al*., 2006) were Mean THg 2070 μg/kg wet weight (range 0-5790) for *Squalus acanthias* and Mean THg 390 μg/kg wet weight (range 220-1830) for *Mustelus mustelus.* In the case of *S. Acanthias* the mean concentration was 2 times higher than the EC legislation limit of 1000μg/kg. for biota intended for human consumption.

Conclusions

In comparison to other trace metals the available Hg datasets in Greek coastal areas are quite limited. Our preliminary results indicate that since the concentrations in seawater are mostly low and below quality standards, monitoring efforts should emphasize on the study of sediments and biota. However, more detailed research is also needed in order to elucidate and quantify the biogeochemical cycling of Hg in various environmental compartments in Greece and the Eastern Mediterranean.

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Bioaccumulation of trace metals in marine mollusks from coastal areas affected by industrial activity

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Abstract

Various tissues of three marine bivalve species, *Mytilus galloprovincialis*, *Callista chione* and *Venus verrucosa*, collected from the Gulf of Elefsis (a moderately polluted area) were studied for Pb, Cd, Ni and Zn bioaccumulation as well as detoxification. Biomarkers' responses (metallothioneins, acetylcholinesterase, catalase and lipid peroxidation) were also measured. The present study reveals that the accumulation of heavy metals in different organisms is metal-organism-tissue and time dependent and detoxification is a slow procedure.

Keywords: bioaccumulation, biomarkers, marine bivalves, detoxification, Elefsis.

Introduction

The presence of heavy metals in aquatic environments and their accumulation in marine organisms has been widely investigated during recent years because of their possibly harmful effects in marine ecosystems and human health.

The use of bioindicator organisms is a useful tool for the study of these effects. The use of economically/commercially important bivalves as bioindicators is of high priority since it combines environmental monitoring with human health protection (Oertel and Salánki, 2003). In order to assess a complete aspect for the environmental quality of a polluted coastal area the measurement of the levels of pollutants in seawater, sediments and bioindicators must be combined with measurements of biomarkers indicating early effects of the exposure of marine organisms to toxic substances (Rainbow, 1995).

Common biomarkers are (Bennalia *et al*., 2015):

- Metallothioneins (MTs), which are metal binding proteins that regulate intracellular essential metals and can help in the detoxification process, since they bind free ions, making them less available for interaction with sensitive biomolecules.
- Acetylcholinesterase (AChE), which catalyses the hydrolysis of acetylcholine into choline and acetic acid, which is vital for normal functioning of sensory and neuromuscular system. Many pollutants, including heavy metals, are AChE inhibitors which lead to interruption of nervous transmission in aquatic organisms.
- Catalase, an antioxidant enzyme which dismutates two molecules of H_2O_2 to H_2O and O_2. Trace metals can enhance the formation of ROS (reactive oxygen species). To prevent the damage from ROS, cells possess antioxidant enzymes, such as catalase.
- Lipid peroxidation (LPO), which is a process initiated when ROS target lipids and lead to the formation of short-chain aldehydes and ketones, one of which is malondialdehyde (MDA), used as a marker for assessing the extent of lipid peroxidation.

In the present study we determined heavy metal concentrations in three bivalve species, *Mytilus galloprovincialis, Callista chione* and *Venus verrucosa*, which are common in the diet of many Mediterranean countries. We compared these concentrations with the limits set by the European Commission for certain contaminants in foodstuffs and the Marine Strategy framework Directive for the achievement of Good

Environmental Status (G.E.S.), as well as with values measured in the same area 10 years ago. Organisms collected from Elefsis gulf were also placed in aquaria with non polluted seawater for a period of one month to study the detoxifocation procedure; in terms of heavy metals concentrations as well as biomarkers levels.

Materials and methods

The bivalves were collected by scuba divers. After their arrival in the laboratory ("Day 0"), 10 bivalves of each species were dissected on ice and gills and mantle were separated from the remaining body. For *C. chione* and *V. verrucosa*, the digestive system was also separated from the remaining body. The other organisms were transferred to aquaria and acclimated to laboratory conditions in constantly aerated seawater. The organisms remained in pristine water for 30 days. Tissue samples were lyophilized and digested overnight with conc HNO_3 in closed PTFE beakers on a hot plate. Heavy metals concentrations were determined by Atomic Absorption Spectrometry. Metallothioneins were determined as described by Viarengo *et al*., 1997 and Ellman 1958 with small modifications. Catalase was determined using the Sigma-Aldrich method. Acetylcholinesterase was determined as described by Ellman *et al*., 1961 and lipid peroxidation using TBARS assay (Buege and Aust, 1978; Vlahogianni *et al*, 2007).

Results

The mean heavy metals levels measured in the Elefsis seawater were for Cd 0.04 μg/L, 0.70 μg/L for Ni, 0.14 μg/L for Pb and 8.70 μg/L for Zn. The corresponding concentrations from the non polluted seawater used in the aquaria were 0.009 μg/L for Cd, 0.201 μg/L for Ni, 0.10 μg/L for Pb and 0.90 μg/L for Zn.

As shown from Table 1, Cd concentration in *M. galloprovinciallis* was exactly at the maximum permissible content for edible bivalve mollusks set by the E.U. (Commission Regulation (EC) No 1881/2006), while Pb concentration in *C. chione* and *V. verrucosa* was higher. For the three species examined, both heavy metal concentrations were higher than the background values (from organisms from pristine areas).

Metal levels in all three species immediately after collection from the Gulf of Elefsis (Table 2, Day 0) represent initial concentrations from a polluted coastal area. The organisms that remained in unpolluted water for 30 days (Table 2, Day 30) showed decrease in accumulated metals in their tissues. The decrease in most cases was statistically significant ($p<0.05$).

For *M. galloprovincialis*, the results indicate that all metals had mostly accumulated in the gills. The same stands for *C. chione*, except for Ni, which had mainly accumulated in their body. Comparing *V. verrucosa* tissues, Pb had mainly accumulated in the mantle and body, but when the organisms were transferred to heavy-metal free seawater, higher Pb concentrations were measured in their gills ($p<0.05$). Cd was mainly accumulated in *V. verrucosa* gills ($p<0.05$), while Ni and Zn in their mantle ($p<0.05$).

M. galloprovincialis seems to accumulate more Pb, Cd and Zn in its gills. The trend for Pb in the gills of the three organisms was: *M. galloprovincialis*> *C. chione*> *V. verrucosa* ($p<0.05$). The Cd trend for the same tissue was: *M. galloprovincialis*> *C. chione*> *V. verrucosa* ($p<0.05$). For Zn was: *M. galloprovincialis*> *V. verrucosa*≈ *C. chione* and for Ni: *V. verrucosa*> *C. chione*> *M. galloprovincialis* ($p<0.05$).

The comparison of Cd and Zn levels in the tissues of the three bivalves collected in 2004 and 2014 (10 years interval) (Table 3), indicates that each metal exhibits a different pattern. Cd concentrations in all tissues of the three bivalves, except the gills of *C. chione* and *V. verrucosa* (the two sand burrowing organisms), has increased during the last 10 years. The higher increase is observed in *M. galloprovincialis* tissues, and especially in its mantle, where the value measured in 2014 is 8 times higher than the one measured in 2004 ($p<0.05$). Cd concentration in *C. chione* and *V. verrucosa* gills has decreased 30% and 42% respectively in the last decade ($p<0.05$). Zn concentrations in all tissues of the three species, except *M. galloprovincialis* gills, decreased in the last decade ($p<0.05$), probably due to the reduction of dissolved Zn which was observed in Elefsis gulf in the last decade.

MT content ($\mu molg^{-1}$ w. w.) in all tissues of the bivalves did not change during the 30 day experiment. MT levels in *M. galloprovincialis* control tissues were 0.045 in the gills, 0.046 in the mantle and 0.068 in the body. In *C. chione* tissues MTs were 0.059, 0.034 and 0.063 in the gills, body and digestive system respectively and between 0.034-0.059 in the mantle. Finally, in *V. verrucosa* tissues the MT levels were 0.016 (gills), 0.011 (mantle), 0.023 (body) and 0.010 (digestive system). It is interesting that although the highest heavy metal concentrations were measured in the gills of the organisms; the highest MT levels were found in other tissues depending on the species.

AChE activity measured in the control animal tissues ($\mu molmin^{-1}g^{-1}$ w.w.) was about 0.20, 0.71 and 0.45 for *M. galloprovincialis* gills, mantle and body respectively. For *C. chione* AChE levels were 0.084 (gills), 0.493 (mantle), 0.344 (body) and 0.561 (digestive tissue) and for *V. verrucosa* the values were 0.07 (gills), 0.06 (mantle), and 0.53 (body) and 0.46 (digestive system), respectively. AChE activity was lower in the gills of all species compared to the other tissues ($p<0.05$). As mentioned above, the gills of all species were the target organ for heavy metal accumulation and at the same time the MT content was low. So, it is obvious, that high concentrations of heavy metal in a tissue cause AChE inhibition as long as MTs are not overexpressed so the cells are not protected.

MDA levels in all tissues of the three test organisms slightly decreased during the 30 days of the experiment. MDA levels ($\mu molg^{-1}$ w.w.) in *M. galloprovincialis* control tissues were 4.5-4.7 in the gills, 2.8-3.2 in the mantle and 5.2-5.7 in the body. In all *C. chione* tissues MDA levels were lower than *M. galloprovincialis* and rather constant at 0.42-0.64 and in *V. verrucosa* tissues the MDA levels were about 0.17 (digestive system), 0.28 (mantle), 0.21 (body) and decreasing from 1.33 to 1.21 in the gills.

	measured values		E.C. regulation		Background values	
	Pb (mg/kg w.w.)	Cd (mg/kg w.w.)	Pb (mg/kg w.w.)	Cd (mg/kg w.w.)	Pb (mg/kg w.w.)	Cd (mg/kg w.w.)
M. galloprovincialis	1.1	1.05	1.5	1.0	0.16	0.12
C. chione	2.5	0.24	1.5	1.0	0.16	0.12
V. verrucosa	3	0.45	1.5	1.0	0.16	0.12

Table 1: Heavy metal concentrations in mollusks collected from Elefsis gulf compared to legislation and background

		Pb (mg/kg d.w.)		Cd (mg/kg d.w.)		Ni (mg/kg d.w.)		Zn (mg/kg d.w.)	
Elefsis gulf		**DAY 0**	**DAY 30**	**DAY 0**	**DAY 30**	**DAY 0**	**DAY 30**	**DAY 0**	**DAY 30**
M. galloprovincialis	gills	9.7	9.0	3.6	2.2	3.0	1.8	234	175
	mantle	1.3	0.7	2.2	0.6	0.69	0.3	44	51
	body	1.5	1.0	2.3	1.1	2	0.9	97	86
C. chione	gills	6.7	4.6	0.53	0.60	3.5	3.1	46	36
	mantle	3.3	2.6	0.52	0.31	6.3	4.9	26	22
	digestive system	3.5	2.2	0.43	0.30	7.8	8.0	39	26
	body	2.9	2.9	0.36	0.10	31.5	10.05	30	21
V. verrucosa	gills	1.6	2.1	1.1	0.86	9.6	8.8	47	30
	mantle	7.8	1.2	0.67	0.53	10.7	9.2	85	93
	digestive system	7.7	1.1	0.64	0.55	4.1	3.7	35	21
		0.90	0.70	0.55	0.71	1.4	0.94	28	20

Table 2: Heavy metal concentrations in tissues of M. galloprovincialis, C. chione and V. verrucosa immediately after their collection from Elefsis gulf (Day 0) and after 30 days in pristine water (Day 30)

species	**tissue**	Cd (mg/kg d.w.)		Zn (mg/kg d.w.)	
		2004	**2014**	**2004**	**2014**
M. galloprovincialis	gills	1.01	3.6	205	234
	mantle	0.28	2.2	60	44
	body	0.86	2.3	129	97
C. chione	gills	0.76	0.53	61	46
	mantle	0.34	0.52	35	26
	digestive system	0.35	0.43	64	39
	body	0.2	0.36	62	30
V. verrucosa	gills	1.85	1.07	71	47
	mantle	0.49	0.67	172	85
	digestive system	0.45	0.64	63	35
		0.09	0.55	45	28

Table 3: Comparative levels of Cd and Zn in mollusk tissues from Elefsis Gulf collected a decade apart (present study and Sakellari, 2006)

Catalase levels were rather constant in the gills and mantle of *C. chione* and *V. verrucosa*. In the body of the two bivalves, a slight decrease was observed (8% for each), while increase was observed in their digestive systems (24% for *C. chione* and 13% for *V. verrucosa*). In the *M. galloprovincialis* gills and mantle a slight increase of the enzyme activity was observed (18% and 4% respectively), while in the body, no change was observed.

Conclusions

- Pb concentration in *C. chione* and *V. verrucosa* from the Gulf of Elefis was higher than the maximum permissible content for edible bivalve mollusks set by the E.U. However when the mollusks remained in unpolluted water for 30 days (depuration experiment), Pb levels decreased below the legislation limits.
- Similarly, after the 30 day depuration experiment, a significant decrease was observed for Cd, Zn and Ni in the bivalve tissues compared to the initial field concentrations.
- From the above it is advisable that a depuration period is needed before the bivalves end up in the market.
- During the last decade, Cd concentration in bivalve tissues from the Gulf of Elefsis has increased by 22-686%, with the higher increase in *M. galloprovincialis*

tissues. On the contrary, Zn concentrations in all tissues and species, decreased in the last decade, probably due to the reduction of dissolved Zn. The decrease was 25-51%.
- Generally, all metals were preferably accumulated in the gills of the three bivalve species.
- Although the highest heavy metal concentrations were measured in the gills of the organisms; the highest MT levels were found in other tissues depending on the organism.
- AChE activity was lower in the gills of all species compared to the other tissues. As mentioned above, the gills of all species were the target organ for heavy metal accumulation and at the same time the MT content was low. So, high heavy metal concentrations in a tissue cause AChE inhibition as long as MTs are not overexpressed and the cells not adequately protected.
- MDA levels in all tissues of the three test organisms slightly decreased during the 30 days of the experiment.
- From the biomarkers examined in the present study, AChE and LPO are ones that respond faster to heavy metal pollution.

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Benthic communities in Elefsis Gulf

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Abstract

The present study focuses on the phytobenthic and macrozoobenthic communities of Elefsis Bay. In order to examine the phytobenthic communities, macroalgae and the marine angiosperm *Cymodocea nodosa* were sampled and EEI and CymoSkew indices were applied respectively. The ecological quality status was assessed as moderate at the station of Aspropyrgos in the eastern Gulf and as good at the station of Nea Peramos which is located in the western part of the Gulf. Regarding macrozoobenthic communities the application of diversity indices showed a considerably richer biodiversity in the Eastern station (S1). Ecological quality assessed by the Bentix index was evaluated as moderate in the eastern Gulf station S1 and poor in station S2 in the western opening of the Gulf. These differences or variations were attributed to the specific hydrological circulation favoring the accumulation of organic material in the deeper western station.

Keywords: phytobenthos, macrozoobenthos, Elefsis.

Introduction

Since 1980 the Hellenic Centre for Marine Research has been regularly monitoring the benthic communities of the Gulf of Elefsis in relation to the oceanographic characteristics (Friligos, 1982; HCMR, 1988; Friligos & Zenetos, 1988), initially in relation to the design and function of the sewage treatment plant of Psittalia, and recently in relation to the sewage treatment plant of Thriassio (HCMR, 2011).
In the present study the status and trends of the benthic communities in Elefsis Gulf are presented focusing on two main stations situated in the eastern and the western part of the gulf. After long term monitoring of the benthic communities in the area, significant differences between the two parts of the Gulf were noted, with the most significant of them attributed to seasonal hypoxia in the deeper western part.

Materials and methods

Phytobenthic samples were collected at two stations (Figure 1) by free diving along the upper infralittoral, 30-50 cm below the lowest water level. In Nea Peramos, samples of the marine angiosperm *Cymodocea nodosa* were collected in July 2013, while in Aspropyrgos macroalgal samples were taken in March and September 2014. The selected sites are considered representative of the phytobenthic communities of each area. Conventional sampling was carried out by removing the phytobenthic organisms from a quadrat of 400 cm^2 (20cm x 20cm). Samples were placed in labeled plastic bags, transferred to the laboratory and then stored at -20˚C until further processing. In the case of macroalgae, species were identified down to the lowest possible taxonomic level, and the abundance of each taxon was measured in order to apply the Ecological Evaluation Index (EEIc) (Orfanidis *et al*., 2011). In the case of the marine angiosperm *C. nodosa*, the biotic index CymoSkew was applied (Orfanidis *et al*., 2010).

Macrobenthic communities in the study area were sampled with the R/V "AEGAIO" in December 2013 using a Box corer benthic sampler with 0,1m^2 sampling surface. Two representative stations were sampled; S1 in the eastern gulf and S2 in the western gulf, and two replicate samples were sampled at each station. One additional sample was taken at each station for the measurement of organic carbon and nitrogen sediment content with a CHN analyzer. According to granulometric analysis the sediment was characterized as muddy sand and mud at stations S1 and S2 respectively.

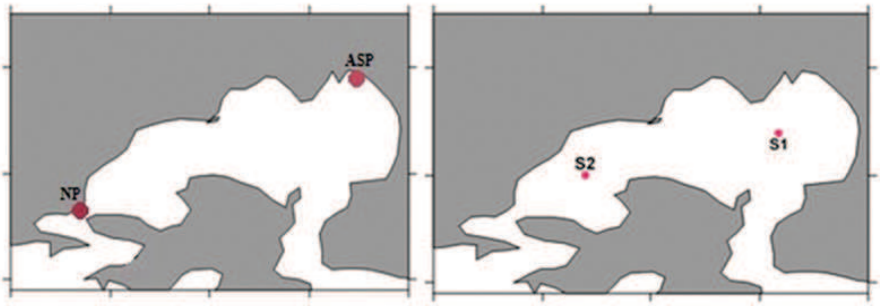

Fig. 1 and 2.
Maps with the sampling stations for phytobenthos (NP: Nea Peramos, ASP: Aspropyrgos) (left) and for macrozoobenthos (right).

After sieving with a 1mm mesh size sieve, samples were fixed and stored in 4 % formalin solution. In the lab, organisms were sorted out from the sediment and identified to species level. The following parameters and indicators were calculated: a) number of species per sampling surface (S/0.1 m2), b) number of individuals (N) or abundance of individuals expressed as number of individuals per square meter (N/m2), c) community diversity index (H) according to Shannon-Wiener (Shannon & Weaver, 1963), d) evenness of distribution (J) of individuals among species J (Pielou, 1969) and the biotic ecological status index Bentix (Simboura & Zenetos, 2002).

Results-Discussion

Dense *C. nodosa* meadows were recorded in Nea Peramos in a shallow, semi-enclosed bay with moderate hydrodynamic conditions. The aforementioned characteristics are favorable for the growth of the species *C. nodosa* (Pérez-Lioréns *et al*., 2014). The ecological quality of the area was assessed as "Good" (Table 1).

	Ecological quality status based on CymoSkew	Ecological quality status based on EEIc
NP (Nea Peramos)	Good	-
ASP (Aspropyrgos)	-	Moderate

Table 1: Ecological quality status at the sampling stations.

When it comes to macroalgae, 22 taxa in total were identified in Aspropyrgos during 2014. In the cold season, 14 taxa were recorded (5 Chlorophyta, 2 Ochrophyta, 7 Rhodophyta). Throughout the study area a common pattern of prevailing species was observed, including the brown seaweed *Dictyota dichotoma* var. *intricata*, the red alga *Corallina elongata* and the nitrophilous green alga *Ulva rigida*. Near the surface, macroalgal populations were frequently displaced by dense mussel populations. Deeper, mussel and oyster populations were dominant. During the warm season, 16 taxa were identified (3 Chlorophyta, 1 Ochrophyta, 12 Rhodophyta). The coralline red algae *Corallina elongata* and *Jania rubens* prevailed in the upper infralittoral zone, while the presence of nitrophilous algae was limited. Deeper, mussel and sea anemones populations were dominant.
During the cold season macroalgae sampling stations usually exhibit lower ecological quality values when compared with results obtained from the warm season (Panayotidis & Salomidi, 2004; Tsiamis *et al*., 2013) due to the natural seasonal cycle of nitrophilous species, which are typically known to thrive in early spring and decline again during summer (Scanlan *et al*., 2007).
Regarding macrobenthos, in all samples 1495 individuals/m^2 were identified belonging to a total of 42 species. Table 2 shows the values of the benthic indices per station in 2013. The ecological quality status was estimated as "Moderate" in the eastern Gulf station (S1) and as "Poor" in the western opening of the Gulf (S2). Moreover, the highest species richness and specimens' abundance was observed at station S1.

The benthic communities of the eastern gulf are very different from those at the western gulf and their status is determined from a) the type of the substrate (and depth) b) the anthopogenic pressures and c) the hydrological regime. In the eastern gulf, the sediment is coarse and heterogeneous (muddy sand), while at the deeper western part the sediment is fine (mud). Thus, the communities of the eastern gulf are richer in species number and more diverse than those of the western gulf. It is well documented that diversity indices are significantly influenced by the type of substrate and the habitat, by the sampling methodology, the seasonal variations and other factors (Reiss & Kröncke, 2005). Bionomically in the eastern gulf the community of the muddy sand in highly protected areas –SVMC- according to Peres & Picard (1964) is dominant, while in the western gulf the community of the coastal terrigenous muds (VTC) elevated in the infralittoral is predominant. The "Moderate" ecological quality of the eastern gulf is attributed to the anthropogenic pressures of the area (industries, the treatment plant of Thriassio, influences from the Psittalia treatment plant). However, the degrading of the status to "Poor" at the western opening of the Gulf is associated to the natural accumulation of organic material at the spot which is caused by the hydrological circulation. Indeed, the values of organic carbon and nitrogen sediment content were higher at station S2 (3,349 % and 1,193 % respectively).

Regarding the trends of the indices based on long time series of data (2000-2012) in the area of Elefsis and the Inner Saronikos gulf (Simboura *et al*., 2014), the diversity and species richness indices in the area of Elefsis show an increasing trend after 2004 when the secondary (biological) sewage treatment

	S/0,2 m2	N/m2	J	H	Bentix	Ecological quality status
S1	39	925	0,79	4,16	2,74	Moderate
S2	7	570	0,54	1,26	2,39	Poor

Table 2. Benthic indices values at sampling stations in 2013. *S: Species richness, N: Abundance of specimens, J: Pielou's Eveness, H: Shannon-Wiener Diversity.*

of Psittalia became operational, in contrast to the ecological quality index Bentix which has been decreasing after 2004. On the other hand, in the inner Saronikos Gulf all the indices show an increasing trend after 2004, especially close to Psittalia. These findings are indicative of the complex processes including the local hydrology and physiography as well as the local pressures that influence the condition of the benthic communities of the area.

In conclusion, both of the results obtained from the phytobenthic and zoobenthic communities in the examined sampling stations describe the ecological quality status of the eastern gulf as moderate, mainly due to the anthropogenic pressures located in the area. However, in the sampling stations of the western gulf the ecological quality varies, with the upper infralittoral rendered as good by the angiosperm *C. nodosa* and the deeper communities rendered as poor mostly due to the natural accumulation of organic material.

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Interannual changes and trends in the pelagic ecosystem of Elefsis bay

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Abstract

The aim of the present work is to study the variability of phytoplankton biomass, mesozooplankton biomass and particulate organic matter during the last 27 years (1987-2014) in Elefsis Bay. This Bay is a semi-enclosed, very complicated and variable system which receives a large volume of domestic and industrial effluents. Its variability over the last years can be attributed to the differences in dissolved oxygen distribution and the amount of the accumulated organic material.

Keywords: Chlorophyll α, mesozooplankton, particulate organic matter, Elefsis Bay

Introduction

Elefsis Bay is a small and shallow (ca. 68 m^2 with a mean and maximum depth of 20 m and ~35 m, respectively), enclosed embayment in the Aegean Sea (Eastern Mediterranean Sea). It is connected to the Saronikos Gulf by narrow and shallow channels on both of the eastern and western side (8 m minimum depth at the western and 12 m minimum depth at the eastern). The ecosystem of Elefsis Bay seems to be very complicated and variable. Its variability is probably related to the differences in hypoxia/anoxia events and the amount of the accumulated organic material.

In the last 40 years, Elefsis Bay has been studied by many research and academic institutions, because of environmental problems which are caused by intense urbanization and industrialization of its northern coastline. In addition, the morphology of Elefsis Bay and freshwater inflow result in limited water exchange with the open Saronikos Gulf resulting in hypoxic/anoxic conditions in the deeper layers, especially during the warm season (Pavlidou, *et al*., 2010). Therefore, the study of chlorophyll α concentrations as an indicator of phytoplankton biomass, mesozooplankton biomass and particulate organic carbon, which are involved in processes associated with the distribution of dissolved oxygen, is necessary to assess the situation of a marine ecosystem where anthropogenic effects are present, such as Elefsis Bay.

Materials and methods

Monitoring study of Elefsis Bay has been performed by HCMR over the last 27 years (1987, 1989, 1998, and from 2000 to 2014). Sampling was done monthly (in 1987, 1989, 1998, and from 2000-2007) or seasonally at the stations S1, S2 (Fig. 1). Chlorophyll α was measured in the laboratory with a fluorometer TURNER 00-AU-10 according to Holm-Hansen *et al*., 1965. Zooplankton was sampled by the use of a WP-2 net (200 μm mesh) and zooplankton biomass as dry weight was analyzed according to Omori and Ikeda (1984). The determination of organic carbon was performed with elemental analyzer CHNS FLASH 2000 Thermo Scientific according to Cutter and Radford-Knoery (1991) and Verardo *et al*. (1990).

Fig.1: Map of the study area and the location of the sampling stations (chlorophyll α, mesozooplankton biomass and Particulate Organic Carbon organic matter, POC) in Elefsis Bay.

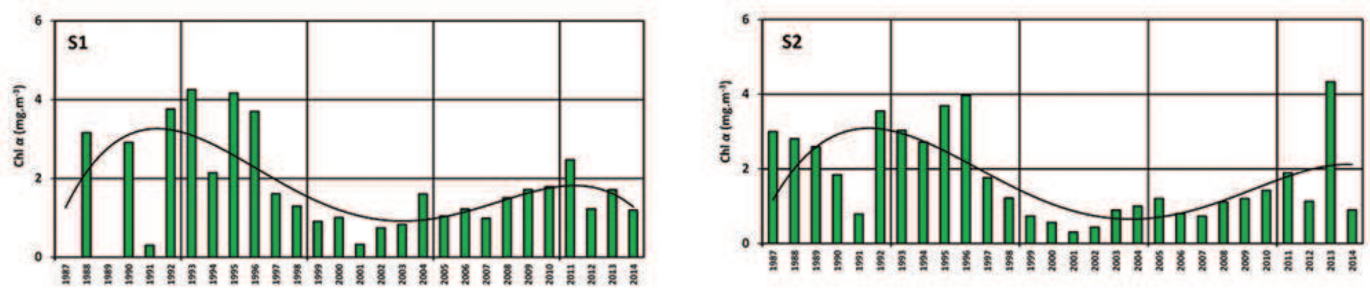

Fig.2: Annual mean phytoplankton biomass values (mg m^{-3}) at the stations S1, S2 (Elefsis Gulf) for the period 1987-2014.

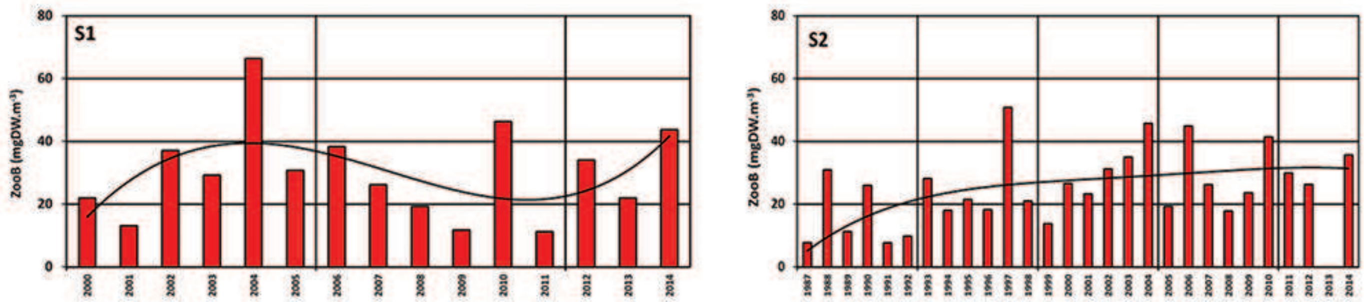

Fig.3: Annual mean mesozooplankton biomass values (mg m^{-3}) at the stations S1, S2 (Elefsis Gulf) for the period 1987-2014.

Results

In Fig. 2, 3 and 4 the average annual fluctuations of chlorophyll α, mesozooplankton biomass and particulate organic carbon (POC) are illustrated. The mean annual concentration of chlorophyll α in both stations ranged within the same levels (0.30 mg m^{-3} – 4.30 mg m^{-3}). Generally, a decreasing trend of chlorophyll α concentrations was observed until 2011, while in recent years an increasing trend was recorded (Fig. 2). Higher chlorophyll α values were recorded in the spring, whereas the lower values during summer.

The average mean values of mesozooplankton biomass at station S1 varied from 11.20 mg m^{-3} to 66.40 mg m^{-3} during the period 2000-2014, while at station S2 biomass ranged between 7.70 mg m^{-3} and 50.80 mg m^{-3} for the period from 1987 to 2014 (Fig. 3). Mesozooplankton biomass exhibited strong seasonal and temporal fluctuations. The maximum biomass values were recorded in spring (March to April) 1 or 2 months after the phytoplankton boost. The increasing trend of mesozooplankton was observed until 2004, then appears to decrease due to either the change in quality/quantity of phytoplankton or increase of small phytoplankton cells (<3.0 μm), which is not a good food source for mesozooplankton. Another possibility for the decreasing trend of mesozooplankton could be the increase of planktivorous fish due to the reduction of fishing activity in the area. The general decrease trend of chlorophyll α values, combined with the trend of increasing mesozooplankton biomass, indicates a fairly good top-down control of phytoplankton by mesozooplankton.

The concentrations of chlorophyll α and mesozooplankton biomass mentioned in this study represent patterns that are generally observed in other temperate coastal ecosystems (Ribera d'Alcala *et al.,* 2004; Fernandez de Puelles *et al.,* 2004). Regarding the seasonal variation of phytoplankton, the highest chlorophyll *α* concentrations were recorded during the spring period, which signaled the spring bloom of phytoplankton, due to the enrichment of the water column with nutrients and increase of temperature and light in temperate coastal ecosystems (Delgado, 1990; Estrada *et al.,* 1993).

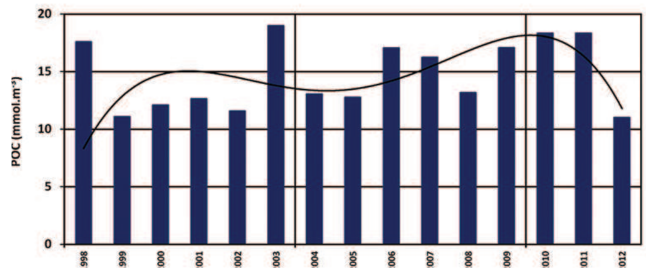

Fig.4: Annual mean values of Particulate Organic Carbon (POC, mmol m^{-3}) at the station S2 (Elefsis Bay) for the period 1998-2011.

The POC concentrations in Elefsis Bay were characterized by higher values (Fig. 4) compared to the Inner Saronikos gulf stations and can only be compared with those recorded near the WWTP sewage outfall (station S7, south of Psittalia) (Siokou-Frangou *et al.*, 1999; Siokou-Frangou *et al.*, 2004; Christou *et al.*, 2007; Krasakopoulou *et al.*, 2008; Krasakopoulou *et al.*, 2010).

Conclusions

Long-term accumulation of urban and industrial pollutants in combination with the geomorphology of the area has contributed to the formation of an isolated system with a distinct identity. A significant number of industries (oil refineries, shipyards, chemical plants, food, metal cement industries etc.) are located along the northern coastline of the Bay.

The results of this study showed that the area can be classified as mesotrophic with moderate to bad ecological quality, while the analysis of long-term time series data showed an increasing trend of quality indicators of the ecosystem. The study of abiotic and biotic parameters of Elefsis Bay can be used as a research tool to treat medium- and long-term issues, such as mechanisms of resistance of organisms to pollution, or the study of climate change, but should also be a driving force for the restoration of Elefsis Bay.

Acknowledgements

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Indicator bacteria concentrations in microenvironments of the Gulf of Elefsis (Greece)

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Abstract

This preliminary study demonstrates the water profile of the coastal area of the Gulf of Elefsis, with reference to microbiological parameters required by Directive 2006/7/EC, concerning the management of bathing water quality. In a grid of 14 coastal sampling sites, high mean levels of faecal contamination were found at the discharge of lake Koumoundouros. Faecal contamination around the outfall of the Psyttalia wastewater treatment plant was also evaluated.

Keywords: *Escherichia coli*; *Enterococci*; marine water quality

Introduction

Microbial contamination by pathogens of the surface waters of coastal areas has a significant impact on their commercial and recreational exploitation. Total coliforms, faecal coliforms and *Enterococci* are universally used as indicators of enteric pathogens in aquatic environments. Among the most important sources of surface waters contamination, untreated urban waste waters, industrial, agricultural and livestock farming wastes are included.

General degradation of water quality due to faecal contamination potentially results in increased hazards for public health (Kacar and Gungor, 2010). In bathing waters bacterial levels, considered as microbial indicators, are often found to be associated with health risks (Noble *et al*., 2003).

Directive 2006/7/EC (European Community, 2006) on the management of bathing water quality, resulted in a drastic reduction in the number of parameters employed: from 19 initial parameters (Directive 76/160/EEC on bathing waters) to only 2 key microbiological parameters (*Intestinal Enterococci* and *Escherichia coli*), providing the best match between faecal pollution and health impacts in recreational waters, according to available scientific evidence provided by epidemiological studies. Following contemporary patterns of bathing water use and of the state of scientific and technical knowledge, the purpose of the Directive is to preserve, protect and improve the quality of the environment and to protect human health. Studies have shown a reduction of total coliforms concentration in seawater, which may exceed 97% within 24-96 hours of their release, depending on water temperature, salinity and exposure to sunlight (Rovirosa *et al*., 2004). Since treated sewage is often discharged to the marine environment without being subjected to disinfection, questions may emerge on whether leaving a distance of few kilometers from the discharged sewage is sufficient for the protection of bathing areas against contamination (Christoulas and Andreadakis, 1995).

The fate of indicator microorganisms of Directive 2006/7/EC was studied in 14 coastal areas of the Gulf of Elefsis, characterized by various environmental pressures particularly near the discharges of runoff combined with fresh water streams, wastewater treatment plants (WWTPs), harbours/marinas, various discharges from industrial and commercial activities and bathing beaches. Furthermore, a preliminary field study was carried out examining the faecal contamination attributed to the outfall system of the central waste water treatment plant of Athens located at Psyttalia, where the treated effluents are discharged without disinfection.

Materials and methods

Sampling

Regarding the 14 coastal sampling sites (Fig. 1; *Schlitzer, R., Oean Data View, http://odv.awi.de, 2012*), two samplings were carried out on the coasts of Attica and Salamis island within the Gulf of Elefsis (28/9/2009; 23/11/2009). In order to evaluate the impact of the wastewater treatment plant of Psyttalia an additional sampling was realized on 7/12/2009 outside the Gulf of Elefsis and at the inner part of the gulf by the R/V Aegaeo, of the HCMR (Hellenic Centre for Marine Research), at stations S1, S2 (inner part of the gulf), at S3 station (Keratsini Bay) and at S7 station where the Psyttalia treated sewage outfall is located (Fig.1). In all cases surface samples were collected. During the first sampling moderately strong winds prevailed, leading to waving and water mixing. The second and third samplings were carried out under calm conditions without wave action.

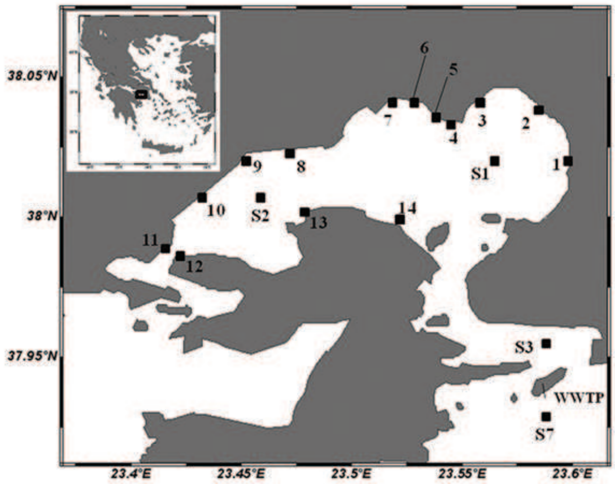

Fig.1: Sampling sites within Elefsis Gulf and around the WWT of Psyttalia

Immediately after their collection the samples were transported to the laboratory where the determinations of the examined microbiological parameters were directly carried out.

Analysis

For the determination of *Enterococci* the method ISO 7899-2 was employed and for *Escherichia coli* the method of membrane filtration with the use of the chromogen Hi Crome E. Coli Agar.

Results

The concentrations of faecal bacteria determined at the coastal zone of the Gulf of Elefsis are presented in Fig.2. The concentrations of *Enterococci* ranged from 3cfu/100 mL to 1231cfu/100 mL and their mean values from 15cfu/100 mL to 632cfu/100 mL. The highest concentration was detected at the "Blue lagoon" site (no.13) on the northern coast of Salamis island followed by that recorded at the site where the water of the shallow coastal Koumoundouros lake is discharged into the sea (no.1). Regarding *Escherichia coli* 3 and 9 positive samples were respectively determined during the first and second samplings. The highest concentrations of *Escherichia coli* were determined at lake Koumoundouros in both samplings and at Aspropyrgos (no.2) and Neraki (no.9) beaches only during the second sampling.

At all near shore sampling sites (S1, S2, S3, S7) Enterococci were detected, with the highest concentration measured at station S7 (188 cfu/100 mL), located close to the Psyttalia treated wastewater outfall (Table 1). In relation to *E. coli* the highest concentration was also determined at station S7 (37 cfu/100 mL), whereas at the rest of the examined sampling sites, excluding station S3 (1cfu/100mL), zero concentrations were measured.

Sampling station	Enterococci	E.coli
S1	71	0
S2	1	0
S3	84	1
S7	188	37

Table 1: Faecal bacteria concentrations (cfu/100 mL) in near shore sampling sites

Conclusions

In accordance with the Directive 2006/7/EC, only a few of the coastal areas studied within the Gulf of Elefsis are characterized as "poor" regarding the concentrations of Enterococci. These are areas where apparently contaminated fresh water enters the sea. The Koumoundouros lake/lagoon which constitutes a wetland for many bird species apparently receives poorly treated water from neighboring installations. This site should be considered as a significant hot spot. High concentrations of faecal contamination were measured at the sampling station near the outfall of the treated wastewaters released from the Psyttalia WWTP which, however, is

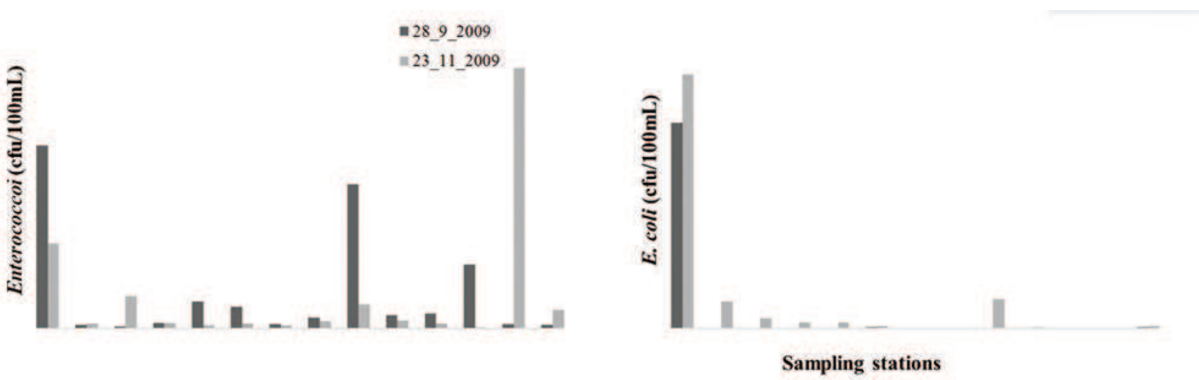

Fig.2: Faecal bacteria concentrations in the coastline of the Elefsis Gulf

located far from the coast. For robust conclusions in relation to the impact of the WWTP of Psyttalia in the inner Gulf of Elefsis, additionnal samplings are required, mainly in terms of Enterococci.

Acknowledgment

The co-authors cordially dedicate this work to Prof. Michael Scoullos who had initially inspired and encouraged them to devote a significant part of their research activities to the Gulf of Elefsis.

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Sampling in the Gulf of Elefsis in the 80s.

Assessment of Elefsis Bay Bathing Waters Based on their Microbiological Quality

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Abstract

In the present study, the main points of legislation for the classification and assessment of bathing waters and the assessment of two bathing beaches of Elefsis (i.e. "Fonias" and "Iris") according to the relevant legislation are presented. The official microbiological data set provided by the Ministry of Environment were used in order to calculate the upper 90^{th} and 95^{th} percentiles of the Escherichia Coli and Intestinal Enterococci values for years 2011 to 2014 and then the bathing waters of the two beaches were classified in one of the four quality categories (excellent, good, sufficient and poor quality). According to the percentiles calculated, the classification for the two bathing beaches is "good" for the year 2011 and then from 2012 to 2014 is "excellent". Finally, it is concluded that based on scientific-related and legislation-compliant methods of bathing water quality assessment, bathing water activities are no more prohibited in Fonias and Iris beaches in Elefsis since 2003, as recommended by the Ministry of Health (which is authorized as the responsible Ministry to make decisions with regards to bathing water prohibition).

Keywords: Elefsis Bay; bathing waters; microbiological quality; Escherichia Coli; Intestinal Enterococci; legislation

Introduction

Bathing beaches' quality is of main interest for the scientific community and constitutes a major concern for the majority of citizens for their recreational needs. Unfortunately, it is not uncommon for unauthorized and unofficial persons or groups confuse citizens by publishing several reports for bathing water quality which however are not relevant to the scientific-related and standardized methods of water quality evaluation. The present study focuses on bathing water quality assessment, highlighting the role of methods which are both scientific-related and in accordance to the relevant legislation, and presenting the results of the application of these methods in bathing beaches of Elefsis. Specifically, the classification and the assessment of bathing water quality will be presented according to the Joint Ministerial Decision no. H.P. 8600/416//E103/2009 "Quality and management measures of bathing waters", in compliance with European Directive No. 2006/7/EC "with regards to the management of bathing water quality and repealing Directive 76/160/EEC" of the European Parliament and the Council of 15 February 2006. In addition, the bathing water quality assessment is applied in two bathing beaches of Elefsis (1^{st} bathing beach "FONIAS" code: GRBW069229028101 and 2^{nd} bathing beach "IRIS" code: GRBW069229028101, respectively) based on the classification and evaluation from the above-mentioned Joint Ministerial Decision and official data from the Ministry of Environment.

Methodology

The assessment of the bathing water quality of the "Fonias" and "Iris" Elefsis beaches is based on the previous mentioned Joint Ministerial Decision, which is also in compliance with the current EU Directives. According to the Joint Ministerial Decision,

- the length of the bathing season is determined by the Ministry of Environment as a result of previous recommendation by the Central Water Agency.
- the minimum number of water samples per monitoring location is at least four for each bathing season (including one taken shortly before its launch) and the period between two water sample monitoring should not exceed a month.
- the microbiological examination of water samples includes Escherichia Coli and Intestinal Enterococci (cfu/100 ml).
- bathing waters are also visually inspected for signs of water pollution, i.e. tarry residues, glass, plastic, rubber or any other waste.
- for each bathing coast (or group of continuous coasts) a bathing water profile is established that includes several features for bathing water, i.e.

A	B	C	D	E
Parameter	**Excellent quality**	**Good quality**	**Sufficient quality**	**Poor quality**
Intestinal Enterococci (cfu/100 ml)	100(3)	200(3)	185(4)	ISO 7899-1 or ISO 7899-2
Escherichia Coli (cfu/100 ml)	250(3)	500(3)	500(4)	ISO 9308–3 or ISO 9308–1
[3] Based upon a 95 percentile evaluation. See Appendix II Joint Ministerial Decision				
[4] Based upon a 90 percentile evaluation. See Appendix II Joint Ministerial Decision				

Table 1: Standards for the classification of bathing waters

identification and assessment of causes of pollution that might affect bathing waters and affect bathers' health, assessment of the potential of cyanobacteria and evaluation of the potential for algae and / or phytoplankton.

The standards for the classification of bathing water quality as well as the relevant methods of assessment are presented in Appendix I of the Joint Ministerial Decision Standards for the classification of bathing water quality and reference methods of analysis are presented in Annex I of Joint Ministerial Decision and are summarized in Table 1.

According to the criteria presented in Appendix II of the Joint Ministerial Decision and after the end of the bathing season, the Central Water Agency classifies the bathing water using data of the last bathing season and the three preceding ones, as follows: a) poor quality, b) good quality, c) sufficient quality, or d) excellent quality.
The total measurements of the last four years (the last bathing season and the three preceding ones) are used for the assessment of the bathing waters. The 90^{th} ant 95^{th} percentiles are calculated for the total 4-year period values of Escherichia Coli and Intestinal Enterococci.

If the 90^{th} percentile is 'worse' (higher) than the standard (threshold) of sufficient quality (column D in Table 1), then the bathing water quality is classified as "poor".

If the 90^{th} percentile is "better" (equal or less) than the standard of sufficient quality (column D in Table 1), then the bathing water quality is classified as "sufficient".

If the 95^{th} percentile is "better" (equal or less) than the standard of good quality (column C in Table 1), then the bathing water quality is classified as "good".

Finally, if the 95^{th} percentile is "better" (equal or less) than the standard of excellent quality (column B in Table 1), then the bathing water quality is classified as "excellent".

Results

Using the set of measurements of the Ministry of Environment between 2008 and 2014 and applying the methodology of Annex II of the Joint Ministerial Decision, the upper 90^{th} ant 95^{th} percentiles are calculated for Escherichia Coli and Intestinal Enterococci for the bathing beaches "FONIAS" and "IRIS", as shown in Table 2.

Based on the previous data (Table 2) and according to the methodological points presented in the previous section, the classification of Elefsis bathing waters (i.e. "Fonias" and "Iris" beaches) is available as shown in Table 3. The classification for each year (i.e. result 2011; result 2012; result 2013; result 2014) is made from a 4-year period (i.e. period 2008-2011, 2009-2012, 2010-2013, and 2011-2014, respectively) as already described in Table 2.

Discussion and Concluding Remarks

Bathing water quality assessment in two specific Elefsis beaches (i.e. "Fonias" and "Iris", respectively) between

Elefsis beach	4-year period	Escherichia Coli		Intestinal Enterococci	
		90th Percentile	**95th Percentile**	**90th Percentile**	**95th Percentile**
Fonias	2008-2011	158,0	303,2	54,3	97,7
	2009-2012	69,4	129,1	36,5	67,0
	2010-2013	77,1	152,4	47,1	86,0
	2011-2014	68,6	137,1	53,8	97,3
Iris	2008-2011	158,3	298,5	52,3	95,2
	2009-2012	64,6	118,1	42,7	79,3
	2010-2013	59,6	107,7	41,7	75,0
	2011-2014	54,4	92,3	38,6	67,1

Table 2: Upper 90^{th} and 95^{th} Percentiles for Escherichia Coli and Intestinal Enterococci for Elefsis bathing beaches "Fonias" and "Iris"

Beach	Result 2011	Result 2012	Result 2013	Result 2014		Classification Legend
Fonias						Excellent quality
Iris						Good quality
						Sufficient quality
						Poor quality

Table 3: Elefsis bathing waters classification

2011-2014 reveals that water quality was already "good" in 2011 and "excellent" from 2012 until 2014. The previous classification is further supported by visual inspection of Fonias and Iris bathing waters, considering that there was no evidence of water pollution, such as tarry residues, glasses, plastics, rubbers or any other waste.

Furthermore, considering the results of measurements between 2007 and 2014 we observe that for "IRIS" coast only one value out of 79 for Escherihia Coli is greater than the limit value of 250 cfu/100 ml and only one value out of 79 is greater than the limit value of 100 cfu/100 ml for Intestinal Enterococci. With regards to "Fonias" coast, only one value out of 78 is greater than the limit value of 250 cfu/100ml for Escherichia Coli and only one value out of 78 are greater than the limit value of 100 cfu/100 ml for Intestinal Enterococci. It should also be mentioned that the first four measurements for the current year (May, June, July, August 2015) do not provide any evidence for Escherichia Coli and/or Intestinal Enterococci values that exceed the well-accepted standards. Specifically, the highest measured value for Escherichia Coli was 44 cfu/100 ml and the highest value for Intestinal Enterococci was 24 cfu/100 ml, with both of them being bellow the strict limit of 250 cfu/100 ml and 100 cfu/100 ml, respectively.

It is not surprising thus that based on the previous official data resulting from scientific-related and legislation-compliant methods of assessment, the Ministry of Health does not prohibit bathing activities in this area since 2003 (of note, the Ministry of Health is responsible for the relevant decision according to the Greek legislation).

Concluding, it should be noted that terms for bathing water quality other than the ones reported in the previous sections are not in accordance with the Greek legislation and thus, the classification system does not include terms such as "appropriate" or "inappropriate" which are usually found in newspapers or the web. The Ministry of Health and the local Regional Administrations are the only official bodies that are responsible for providing regulations prohibiting bathing in specific areas, based on official bathing water quality measurements. The public can be reliably informed with regards to the water quality of bathing beaches on the following website http://www.bathingwaterprofiles.gr/monitor_search provided by the Special Secretariat for Water of Ministry of Environment and Energy.

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http://www.bathingwaterprofiles.gr/monitor_search
http://www.bathingwaterprofiles.gr/monresrv/GRBW069229028101
http://www.bathingwaterprofiles.gr/monresrv/GRBW069229027101

Biogeochemical processes under anoxic conditions affecting Arsenic (As) distribution in Elefsis Gulf: possible alterations due to simulated ocean acidification conditions - a preliminary assessment

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Abstract

Arsenic (As) is a trace element well acknowledged for its toxicity. However, only few studies regarding its fate in marine environments have been conducted in Greece. The As cycle in the marine environment is closely linked to iron (Fe) and manganese (Mn) biogeochemistry, with direct adsorption on Fe-rich particulates and Mn particulate phases.

Hypoxic coastal areas are considered as high-priority for Ocean Acidification (OA) research, because the co-occurrence and interaction of low oxygen with other environmental stressors, such as elevated pCO_2, warming and eutrophication, may put them at greater risk. In this work, As distribution influenced by an intermittent anoxic coastal phenomenon, exhibiting already reduced pH at the near bottom water layer, was studied. In addition, a simulation of OA conditions was conducted in order to fully comprehend possible alterations of As. The results showed a nutrient-type As distribution, with depleted surface values and near-bottom accumulation, in full agreement with Fe and Mn near-bottom reductive dissolution from sediment surface, as a result of the prevailing anoxia. Regarding the OA experiment, As presented a decreased availability in dissolved forms, in contrast to both Fe and Mn, which could indicate a restrictive dissolution mechanism when anoxia and OA are both induced.

Keywords: iron, iron speciation, manganese, experiment, microcosm.

Introduction

Total dissolved As concentration in seawater is normally between 1.0-2.0 μg/l, while particulate As is negligible (Maher *et al*., 1988). Elevated As levels in sediments can be attributed to Fe-rich particulates settling and to direct adsorption on to the sediment surface. Although Fe may be crucial in the binding of As to sediments, there is a strong correlation between solid-phase As and Mn possibly because the two elements have similar geochemical mobilities. The prime mechanism for the release of As into porewaters is the dissolution of hydrous oxide phases to which the metalloid is adsorbed. Dissolution occurs by the reduction of Fe (III) and Mn (IV) to their soluble lower oxidation states, Fe (II) and Mn (II) (Bennet *et al*., 2012). Fe (III) (hydr)oxide minerals formed under oxic conditions, strongly adsorb dissolved inorganic arsenic via complexation and their dissolution can release dissolved As into the porewater and result in fluxes towards the overlying water column. Release of As from the decomposition of organic matter in sediments has not been demonstrated, even in anoxic sediments where ammonia and phosphate concentrations increased markedly with depth (Maher, 1988).

Ocean uptake of anthropogenic CO_2 alters ocean chemistry, leading to more acidic conditions and lower chemical saturation states (Ω) for calcium carbonate ($CaCO_3$) minerals, a process commonly termed "ocean acidification" (OA) (e.g. Caldeira & Wickett, 2005). In coastal regions, the organic load input is high and the aerobic degradation of organic matter leads to a higher CO_2 production. Anoxic systems are more acidic than normal marine environments, as the gas exchange balance with the atmosphere is not achieved, indicating that OA in such environments is already taking place and possibly spreading to adjacent systems. OA, especially when combined with hypoxic phenomena, affects carbon and nutrient biogeochemistry, dissolved trace metal species and complexes' stability and sediment mineral phases, causing changes in benthic fluxes in the sediment-water interface. OA is known to reduce both hydroxide (OH^-) and carbonate (CO_3^{2-}) concentrations in most natural waters (by 82% and 77% respectively). These anions form strong complexes in ocean water with divalent and trivalent metals, and such a decrease would influence trace metal speciation. Therefore, these metals would have a higher fraction in their free forms. In addition, the lower pH values will also affect trace metal adsorption on organic materials, with less available sites for adsorption. Finally, most metals are more soluble in waters of increased acidity, so their concentrations are expected to change as well (Millero, 2009). Therefore, experiments combining acidification and low oxygen conditions are essential to fully understand and correlate the various observations in coastal environments.

The main scope of this experimental research was to investigate As distribution in an intermittent anoxic environment and its possible alterations under simulated acidification conditions. The aim of the experiment was to simulate the biogeochemistry and physicochemical conditions of the natural system including consideration of all vital parameters.

Materials and Methods

This work was carried out in Elefsis Gulf (Attica, Greece), a relatively shallow, semi-closed industrialised coastal system, which, due to the increased organic matter input and its hydromorphological characteristics, result in intermittently anoxic conditions during summer (Scoullos, 1983). Field sampling took place in September 2014 with the R/V AEGAEO (HCMR). Hydrographical data were recorded through CTD measurements. Seawater and surface sediment from the deepest-anoxic-station (33m) were collected untreated and placed in four 25L Nalgene Polycarbonate containers (at a proportion 80% to 20% respectively) in a thermostatic chamber (17.5°C). The seawater-sediment systems were left to equilibrate for a week in Ar atmosphere in order to maintain the anoxic field conditions. This was followed by the four week period of the experiment where CO_2 was added to the microcosms; the stability of pH was maintained using a continuous flow system (IKS Aquastar, IKS Computer Systeme GmbH) which automatically adjusted CO_2 gas addition to the microcosms. The measured pH values by the IKS system were corrected with the parallel use of a laboratory pHmeter (Jenway 3310) calibrated in NBS scale. On the 25th day of the experiment, the Ar supply was ceased and the systems were left to re-oxygenate until day 33 in order to fully simulate the intermittent anoxic conditions of the study area. The pH values selected for the experiment conditions were (a) for the control conditions (C) the pH value measured during sampling, and (b) for the ocean acidification conditions (OA) the pH value predicted for the year 2300 (6,80 NBS), for latitudes corresponding to the Mediterranean (e.g. Caldeira & Wickett, 2005). Each one of the two conditions was applied in two replicate tanks. Seawater from the field (during the cruise, referred as day -1 in the experiment) and from the microcosms (every 2 days) was sampled for the determination of trace elements. For As, and Mn determination, the EPA methods 1640, 6020 were followed for preconcentration and final measurement with ICP-MS using the Collision Cell Technology (CCT) mode of the instrument; in order to evaluate the method performance Certified Reference Materials (CASS-5 and NASS-6, National Research Council Canada) were also treated and analysed the same as the samples. For total Fe and Fe(II), the colorimetric determination as described by Bloom (Bloom, 2004) was implemented while Fe(III) was calculated by substraction. It should be noted that all determinations refer to the total dissolvable metal content. Sediments were collected twice during the experiment and treated according to EPA 3050 for final measurement of As and Mn with ICP-MS and FAAS for Fe.

Results and Discussion

Results of the near bottom physicochemical parameters (pH=7.75) indicate a reducing coastal environment of quite increased acidity. This value corresponds approximately to the predicted pH levels for 2100, while the negative redox potential (-50.7 mV) along with the minimal DO concentrations (0.84 ml/L), reflect the anoxic conditions prevailing in the deeper parts of the area during summer.

The only available published data on dissolved As in Elefsis bay, are for near-coast areas with surface values between 2.9-3.6 μg/l (Ochsenkuhn-Petropulu *et al*., 1995); the results of the present study indicate that nowadays, the inner Elefsis bay, presents lower As concentrations despite the significant industrial activities dominating the surrounding area.

In this study, Fe low surface values were observed (2.24 μg/l) along with quite increased bottom values (110,0 μg/l) while Mn presents depleted surface values (2.74 μg/l) and significantly increased bottom values (234,7 μg/l).

The results show a vertical As distribution (Fig. 1) with low surface concentrations and an accumulation of As near the water-sediment interface, suggesting that it is taken up similarly to the nutrient elements by biological activity in the surface mixed layer and is partially regenerated at depth, especially near the anoxic interface (Maher, 1988).

Fe and Mn distribution (Fig. 1) consorts with previous findings, with higher dissolved forms in the bottom of Elefsis, as a result of their dissolution from sediment surface. Dissolution of sinking Fe particles and soluble Fe species formation could also be attributed to the specific profiles. Mn (IV) (present mainly as MnO_2 in the sediment) is reduced to dissolved Mn(II) eluding from the sediment to the overlying water; thus, this solubilised Mn is shortly re-precipitated at the oxic-anoxic layer which is found close to the bottom (Scoullos, 1983).

The increased bottom value of Fe and Mn is typical in anoxic environments (Scoullos, 1983), which explains the also elevated As bottom values. Particulate metals,

Fig.3: Total dissolvable As, Mn and Fe (ppb) for the water column of Elefsis Gulf

coprecipitated with Fe and Mn in oxic surface waters, sink downwards due to gravity, are deposited in the sediments and reduced in the suboxic or anoxic zone. Reductive dissolution of hydrated oxides of Fe (III) and Mn (III, IV) controls the supply of dissolved reduced forms of these metals in the anoxic zone. In Elefsis Gulf, the prevailing anoxia in summer, leads to reductive conditions with more soluble Fe and Mn forms and concomitant dissolution and accumulation of As near the water-sediment interface.

During the experiment, As showed the same trend both in OA and C conditions (Fig. 2), with elevated initial values in relation to field values (3.20-3.36 ppb and 1.61 ppb respectively), followed by small variations until the end of the experiment; in OA conditions the concentrations appear relatively lower than in C conditions, with no effect of the re-oxygenation phase. On the contrary, in C conditions the re-oxygenation phase resulted in As sediment release with concomitant elevated As values in the supernatant water (3.05 to 3.85 ppb, respectively). The total dissolved As concentration decreased with acidification has been previously reported in experiments conducted with CO_2. These results, which are in agreement with the results of this study, indicate that the total As in seawater would be less available to the marine biota under acidic conditions (Bassalote *et al*., 2015).

Mn concentrations (Fig. 2), also showed the same trend both in OA and C conditions, with significantly decreased values in relation to field values (5.98-10.20ppb and 234.7 ppb, respectively); in contrast to As, in OA conditions the total dissolvable Mn concentrations appeared higher than C conditions with lower final concentrations after the re-oxygenation (1.76 ppb and 1.46 ppb respectively).

For As, it appears that sediment oxygenation and irrigation leads to sediment release towards the water column with elevated initial values for the experiment in relation to field values; for Mn an opposite mechanism of water to sediment flux is found, which was also recently observed in benthic fluxes incubations for the specific area (Prifti *et al*., 2015). Apart from the decreased initial values, in OA conditions, Mn appears to prevail in more soluble forms and only after re-oxygenation, its particulate phase is favored leading to precipitation.

At the beginning of the experiment, total Fe showed decreased values (Fig. 3) for both OA and C conditions in relation to the field values (34.65 -30 ppb and 109.98, respectively), having the same trend until the 25th day. From day 5th, in OA conditions, total dissolvable Fe appear increased in relation to C conditions until the 25th day when re-oxygenation took place leading to approximate concentrations of 35,15 ppb and 45,78 ppb respectively. Fe (III) showed an increasing trend until the 5th day in both conditions; for C conditions Fe (III) decreased gradually until the re-oxygenation phase when it increased. In OA, Fe(III) increased more on the 11th day and decreases gradually till the end of the experiment. Fe (II) appeared to decrease from field values in relation to experiment initial values for both OA and C conditions (78,39 ppb and 1.96-1,82 ppb, respectively) which could be attributed to oxygenation of seawater during the transfer to the laboratory and experiment set-up. The re-oxygenation phase, in C conditions, appears to release Fe from the sediment to the overlying water in the Fe(III) form; in OA conditions this release is also evident but in both Fe(II) and Fe(III) forms. At the current surface pH of seawater, Fe (III) is at its minimum solubility; as pH decreases, solubility increases. A decrease in pH from 8.1 to 7.4 would increase the solubility of Fe (III) by about 40%, which could have a large impact on biogeochemical

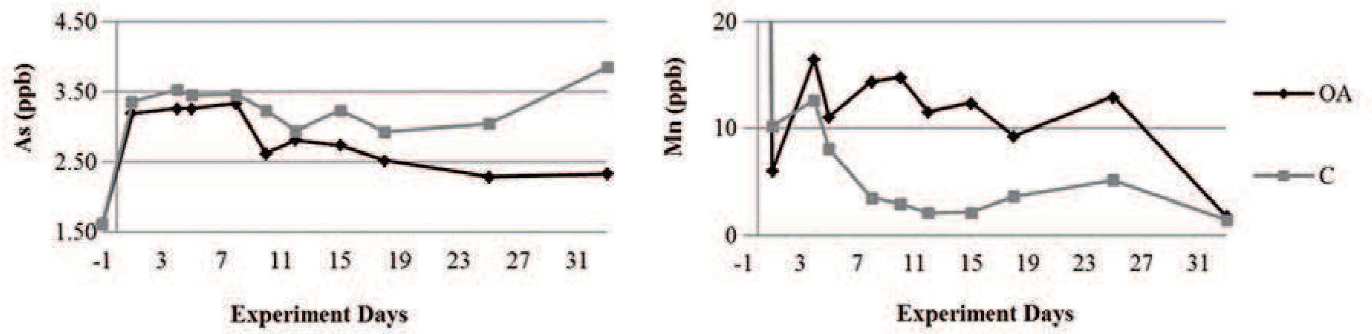

Fig.4: Total dissolvable As and Mn variation throughout the duration of the experiment

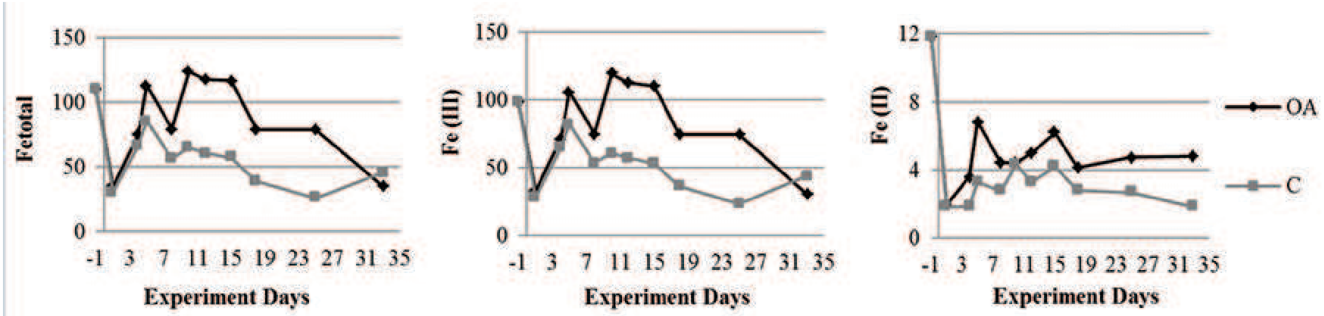

Fig.5: Total dissolvable Fe, Fe(II) and Fe(III) (in μg/l) variation throughout the duration of the experiment

cycles (Millero *et al*., 2009). Under acidified conditions, Fe (II) is likely to show increased stability that is evident during the experiment, from the 18th day until the end (OA conditions), with no oxidation to Fe (III) observed, despite re-oxygenation taking place (Breitbarth *et al*., 2010).

The low solubility plus the rapid oxidation rate of Fe could be responsible for its precipitation during the experimental time, and thus removing other metals by adsorption. Additionally, a disturbance in the Fe–Mn shuttle in the sediment could lead to increased concentrations of toxic metals. From previous experiments, Fe and Mn precipitation as hydroxides on the sediment surface can be disturbed by more acidic conditions leading to inhibited removal of dissolved Fe, Mn forms into the sediment which could result in increased concentrations in the seawater; this increase is evident during the first days of the experiment while, as the CO_2 supply continues, this increase is limited. This contrast could be attributed to the extraction of the easily leachable metal fractions from the sediment and suspended particles during the early phase of the experiment. The elevated dissolved values for these two trace metals during the OA conditions indicate an inhibited precipitation mechanism from the water to the sediment, preserving an elevated content in the water column. As on the contrary, during more acidic conditions appears slightly decreased in relation to C conditions with steady concentrations from day 18th till the end of the experiment, with no effect of the re-oxygenation phase. It appears that OA, in addition to anoxic conditions, acts as a restrictive factor for As dissolution in the water, maintaining slightly lower values in relation to C conditions. It could be presumed that for As, in acidic conditions, the sediment acts like a sink.

Conclusions

This study showed an As distribution with depleted surface values and near-bottom accumulation during summer; this trend indicates that the main process affecting As concentrations is coprecipitation with Fe and Mn (oxy)hydroxides in the oxic surface followed by their reductive dissolution in the anoxic zone, leading to solubilised forms of Fe and Mn along with extended release of dissolved As. Regarding the OA experiment, Fe and Mn precipitation as hydroxides seem to be disturbed by more acidic conditions leading to inhibited removal into sediment and elevated dissolved values for these two metals. On the contrary, OA, in addition to anoxic conditions, acts as a restrictive factor for As availability in dissolved forms, maintaining slightly lower As content in the water column in relation to less acidified conditions, probably leading to the assumption that, in such conditions, the sediment acts like a sink for As.

Acknowledgements

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Investigating the pollution from BTEX in the groundwater of the Thriassio Plain, W. Attica

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Abstract

The Thriassion Plain, a glorious cultural centre of antiquity, has been associated with unregulated development of various activities, since agriculture, heavy industry and port facilities coexist within three municipalities. The oil- relevant industries have strongly impacted the air, water and soil of their surroundings. The purpose of this paper is to investigate whether potential leakage of hydrocarbons, has polluted the two major aquifers of the study area, and to which extent. The target hydrocarbons are benzene, toluene, ethylbenzene and xylenes, known as BTEX. Sampling and laboratory identification were carried out in spring and autumn of the years 2003, 2004 and 2005. The Solid Phase Micro Extraction coupled with Gas Chromatography-Mass Spectrometry was applied to concentrate and identify, respectively, the target compounds. Spatio-temporal statistical analysis of the laboratory results was performed with GIS software. The results showed that concentrations of benzene exceeded the Maximum Contaminant Limit of the EU and USEPA in a few samples in autumn, whereas, the spring samples, when water level is maximum, had lower concentrations of all target compounds. An overall decrease was also noticed from 2003 to 2005. The fluctuation of the concentrations may lead to interesting discussion about the aquifer's "natural flushing" as well as the temporal character of the pollution.

Keywords: BTEX, aquifer pollution, Thriassio Plain.

Introduction

One of the most historical, cultural landmarks of Greece, the Thriassio Plain, has suffered severe environmental deterioration, because a number of polluting activities were placed there without proper programming and suitable infrastructure. As a result, multi-scale manufacturing operates in the vicinity of three municipalities, as well as agriculture. According to scientific documentation, the industrialization has affected the air (Mavrakis *et al*, 2014), the soil (Katsinis & Zannikos, 1990) and Saronikos Gulf which is the final receiver of human activity (Scoullos and Pavlidou, 2000; Stathopoulou *et al*., 2005; Scoullos *et al*., 2007). Heavy industries involved with oil refining, processing and transport, such as the Hellenic Refinery of Aspropyrgos (known as ELPE), the Refinery of Elefsis, an old petroleum recycling unit (CYCLON), along with the Military Airfield may potentially be responsible for hydrocarbon release in the groundwater, which is used in industries, or to irrigate agricultural land. Evidence of groundwater contamination from hydrocarbons has been reported by Kounis and Siemos (1987) and by Gidarakos and Aivalioti (2004).

This paper is the first effort to investigate whether pollution from BTEX (benzene, toluene, ethylbenzene and xylenes) has occurred within the two major aquifers of the Thriassio Plain. The target pollutants are volatile compounds basically found in gasoline and some jet fuels. Benzene is listed among the priority pollutants according to the U.S. Environmental Protection Agency (USEPA, 2002) and is regulated by the European Union Water Framework Directive (2000/60/EC).

Materials and methods

Sampling

Groundwater samples were collected from wells and boreholes of the two aquifers: A carbonate formation, located at the circumference of the Thriassio Plain, as well as at the north-eastern side of the Hellenic Refinery of Aspropyrgos (ELPE), and a granular formation which is made of transferred material, either loose or connected, in the centre of the study area (Dounas and Panayotidis, 1964; Parashoudis, 2002). Sampling of groundwater was carried out from 2003 to 2005, twice per year, in autumn and in spring, at the lowest and the highest water level respectively, covering a total surface of 75 km^2

approximately. At the beginning, thirty five (35) samples were collected but after the first laboratory results it was estimated that the sampling area should be expanded, thus another ten (10) samples were added.

Laboratory work

The chemical identification of the target analytes (benzene, toluene, ethylbenzene and xylenes) was carried out in the Laboratory of Environmental Chemistry, Department of Chemistry, University of Athens, according to the USEPA Analytical Method 524.2 (USEPA, 1992). The Solid Phase Microextraction was applied to concentrate BTEX before separation from the water column with Gas Chromatography and detection with a Mass Spectrometer. The detection limit of the method was 95 ng/l (ppt) for benzene, 67 ng/l for toluene, 78 ng/l for ethylbenzene, 67 ng/l for meta- and para-xylenes and 74 ng/l for ortho-xylene. The laboratory qualification (standard solutions, standard deviation, correlation coefficient, etc.) proved that the analytical method was reliable for all periods of characterization.

Results /Discussion

Termporal analysis: The results of the BTEX investigation were reported in tables and GIS contour maps (temporal-spatial analysis). The limit values above which immediate remediation is necessary (Maximum Contaminant Limit) were considered. The European Union, with the 2000/60/EC has regulated 0.001 mg/l (ppm) as benzene MCL. According to the National Drinking Water Standards of USEPA, the MCLs for ethylbenzene and xylenes, are 1 mg/l, 0.7 mg/lt and 10 mg/l respectively.

Table 1. demonstrates the benzene reported concentrations over the EU threshold. Figure 1 and figure 2 illustrate the spatial distribution of the benzene concentration in November 2004 and May 2005 respectively. In twenty three (23) out of forty five (45) groundwater samples the concentrations exceeded the MCL. For the rest of the samples, the values fluctuated from the detection limit up to 0,90 μg/l. Regarding the other three compounds, the concentrations of toluene fluctuated from the detection limit to 46 μg/l (ppb), of ethylbenzene, from the detection limit to 41μg/l and of xylenes, from the detection limit to 105 μg/l. All reported concentrations of toluene, ethylbenzene and xylenes were much lower than their respective MCLs.

Spatial analysis: Fig.1 and Fig.2 illustrate the spatial distribution of benzene. Toluene, ethylbenzene and xylenes concentrations follow similarly the contour shape of benzene.

By studying the spatial distribution, it becomes apparent that BTEX were found in four specific locations within the study area: a) northeast of ELPE b) at the eastern area of the town of Aspropyrgos, c) at the eastern boundary of the Military Airfield of Elefsis, and d) within the space of the "Pyrkal" installations where the maximum concentration of 57 ng/l was reported. This company, though not involved with oil products, is situated next to the Hellenic Refinery of Elefsis (ELPE), and very close to the coast. This finding strongly suggests a leakage from the refinery of Elefsis. The concentrations detected at the boundary of the Military Airfield, indicate that the Airfield is also a potential source of pollution. Another high concentration (29 μg/l) was reported in an abandoned area between ELPE and the town of Aspropyrgos (id 12).

This concentration seems not to decrease significantly from autumn to spring. It could be considered as "trapped" pollution within unconsolidated non-permeable deposits because no other high concentration

SampleID	**Nov2003**	**May2004**	**Nov2004**	**May2005**	**Nov2005**
3	2,96	nd	2,63	nd	1,96
8	10,99	0,85	9,98	1,01	7,30
12	29,03	13,89	24,30	9,99	25,21
20	No data	No data	2,46	0,48	0,34
27	No data	No data	3,08	0,54	2,07
32	No data	No data	1,18	nd	0,56
37	No data	No data	4,52	0,98	2,41
44	2,16	0,19	1,95	0,10	0,88
46	No data	No data	2,41	0,45	2,61
54	18,02	0,60	9,50	1,78	7,21
55	2,69	0,56	2,78	nd	1,30
58	No data	No data	2,00	0,23	1,03
63	1,60	nd	1,25	nd	0,10
98	1,60	0,17	1,48	0,10	0,65
136	1,02	0,32	0,90	0,10	0,40
3000	5,21	nd	3,19	0,56	3,42
5000	1,85	nd	1,65	nd	0,71
10300	No data	No data	5,67	5,10	No data
10400	No data	No data	2,77	1,45	No data
10500	No data	No data	57,20	15,80	No data

Table 1: Benzene groundwater samples with concentrations over the MCL.

was found near that location. The origin of this high concentration is not so clear, since there is no obvious polluting source in the vicinity of the location and it might be attributed to illegal dumping of waste.

As regards the area in the vicinity of the oil recycling unit, "CYCLON", low to negligible concentrations of all BTEX were recorded. Additionally, when comparing same seasons (e.g. November 2003 with November 2005) the concentrations seem to decline, with time. Even benzene values next to the Military Airfield, tend to decrease, a feature that cannot be fully explained. Nevertheless, the volatile character of the studied pollutants in combination with the high variability of the hydrological regime of the area could offer the answer.

Conclusions

The laboratory characterization demonstrated moderate to significant pollution, mainly from benzene within the aquifers of the study area. The concentrations of toluene, ethylbenzene and xylenes were much lower than their respective MCL, in general. Regarding benzene, concentrations exceeded the EU Maximum Contaminant Limit, basically in autumn in twenty out of forty five samples. The maximum reported concentration of benzene was 57 μg/l, at a location next to the Refinery of Elefsis. Another high value (29 μg/l) was found in an abandoned location, east of Aspropyrgos, which might indicate illegal dumping of wastes.

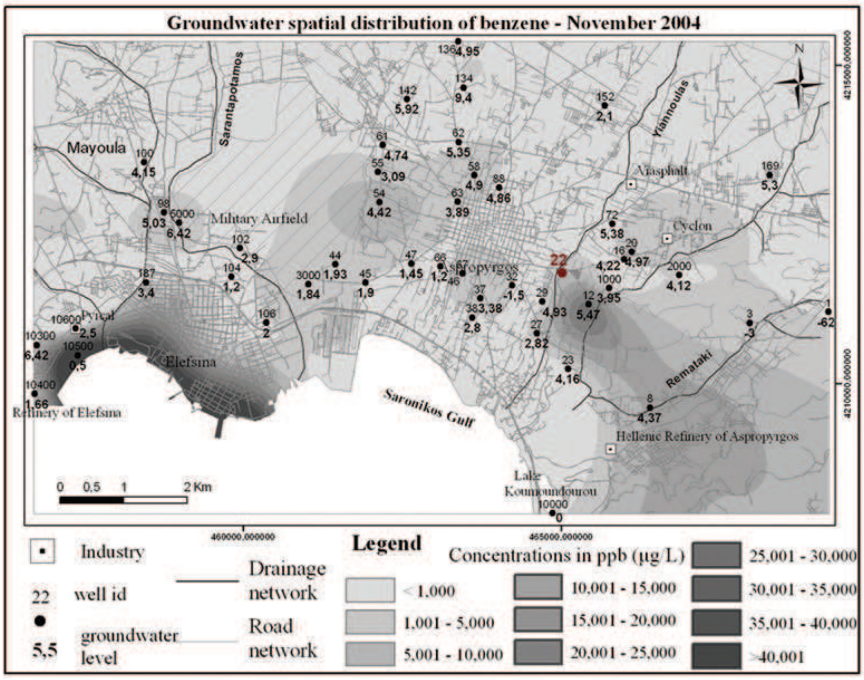

Fig.1: Benzene pollution contours in November 2004.

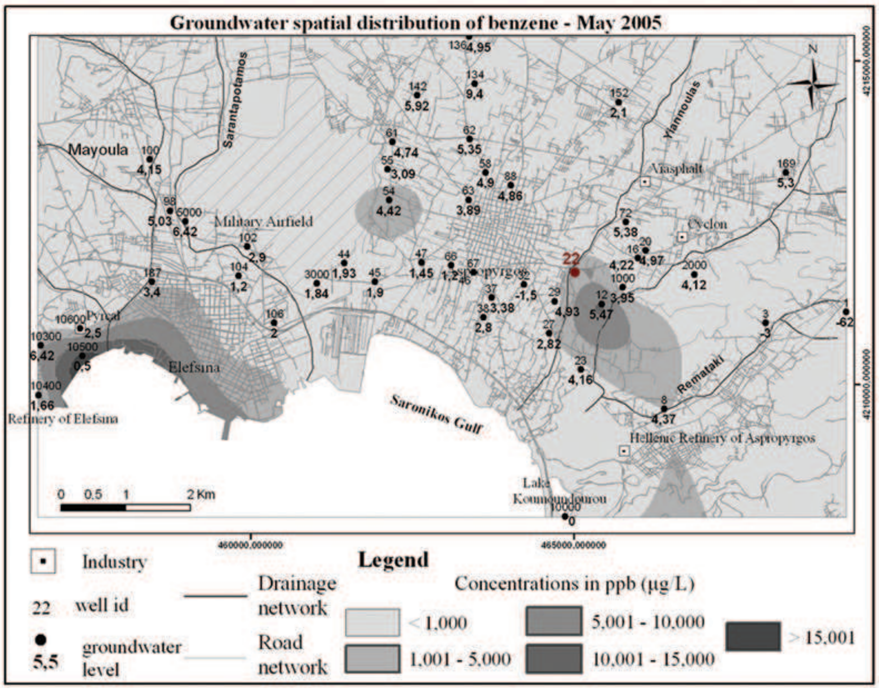

Fig.2: Benzene pollution contours in May 2005.

The spatial distribution of all compounds of BTEX was identified in four specific areas; in most of them, the source of hydrocarbon pollution becomes apparent. It is remarkable that BTEX concentrations drop significantly from November to May. It seems that concentrations are strongly influenced by the seasonal rise and fall of the water level, indicating active natural recharging flashing and self purification mechanisms.

When comparing same seasons (e.g. November 2003 with November 2004, and November 2005) the concentrations seem to decline. If no further diffusion of petroleum fractions occurs, it is possible that either the hydrological particularities, such as good aeration through the pores, or the aquifer remediation below ELPE installations, may have contributed in local or large scale identified recovery of the area.

Overall, it is advisable to monitor the VOCs concentrations, especially in locations a) with a view to confirm their occasional or permanent character, b) considering the active communication between the coastal aquifers and the seawater. In case that BTEX concentrations remain, it is suggested to study their origin with the Kaplan method and take the necessary measures to address the issue effectively.

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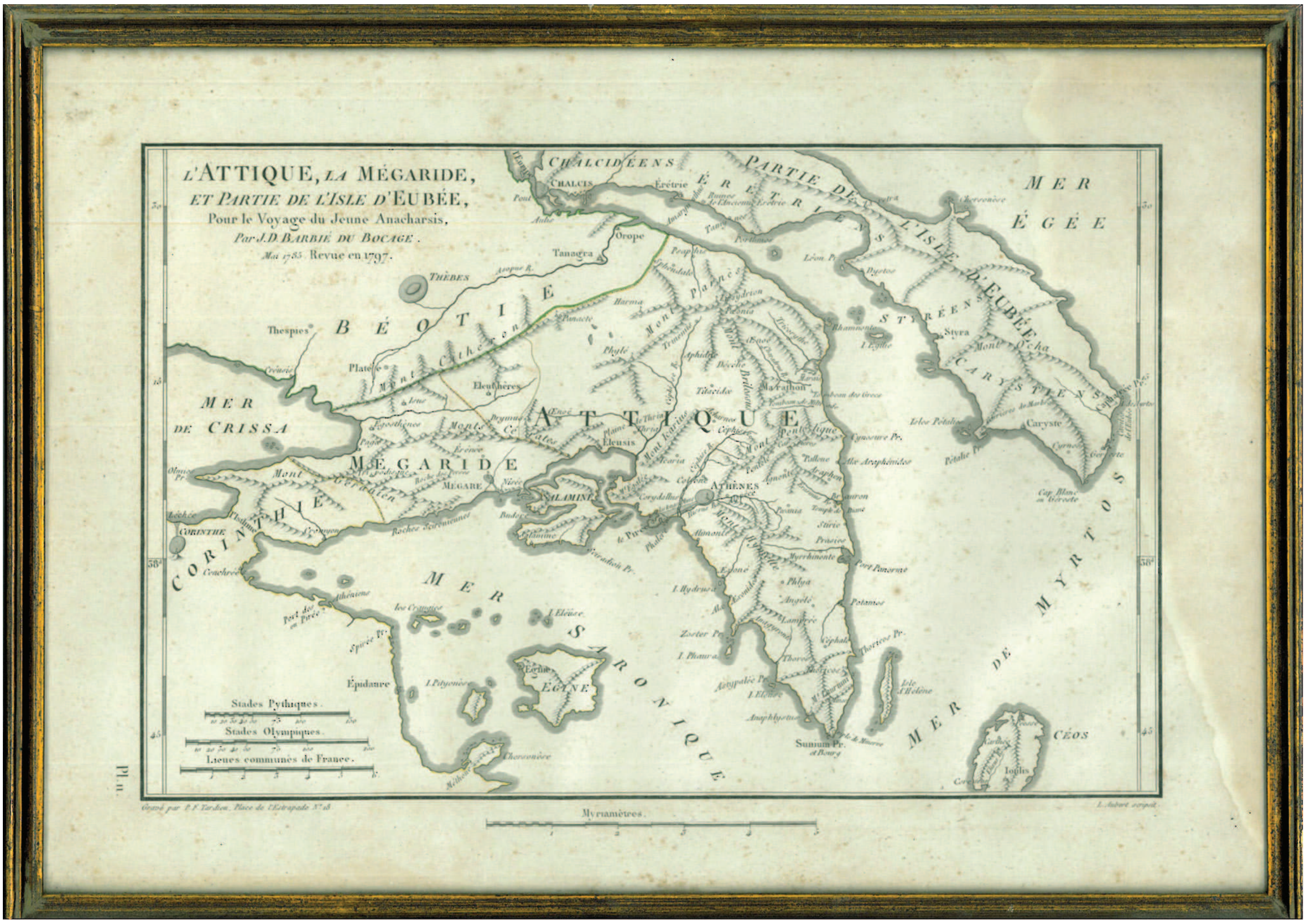

Voyage Du Jeune Anacharsis, Paris, 1797.

Trace metal pollution in the marine environment of Evripus Straits and Larymna Bay in Evoikos Gulf

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Abstract

The current study presents the levels and distribution of Zn, Cu, Pb and Ni in seawater and sediment samples obtained from the Larymna Bay and the Central Evoikos Gulf. In the water column of N. Evoikos Gulf, high concentrations of trace metals were determined inside the Larymna Bay (Ni, Zn), as well as the aquacultures (Cu), whereas in the Central Evoikos Gulf high concentrations are determined close to the shipyards and the town of Chalkida. It was found that dissolved Ni is transported and dispersed at long distances from the Fe-Ni smelter plant. In the Central Evoikos Gulf, trace metal concentrations in the water column decreased remarkably compared to previously published results.

Keywords: trace metals, seawater, sediments, Evoikos Gulf.

Introduction

Urban and industrial activities introduce large amounts of pollutants into the marine environment, causing significant and permanent disturbances in the marine systems and, consequently, environmental degradation. This phenomenon is especially significant in coastal zones (Dassenakis et al., 1996).

The Northern Evoikos Gulf receives domestic, industrial and agricultural wastes (Dassenakis et al., 2003), as well as the wastes of the ferronickel smelting plant LARCO since 1969. The smelter is located in the Larymna Bay and the by-products in the form of slag are disposed directly to the sea. Elevated trace metals contents in sediments have been determined in the past (Voutsinou-Taliadouri and Varnavas, 1993), whereas there are no published data concerning trace metal levels in the seawater.

The area near the Evripus Straits is significantly affected by anthropogenic pollution, as it receives large amounts of domestic and industrial wastes. The waste water treatment plant of the town of Chalkida is located on a small island and the treated effluents are disposed to the sea. Several industries such as cement, textile, paint, food, metal-forming and ceramic factories, shipyards, etc. are located near the coastal zone of the Evripus Straits. Shipping is another significant polluting source in the area, as well as the near shore national roads and some drainage channels (Dassenakis et al., 1998). Previous studies carried out in the study area, showed high concentrations of trace metals. However, some of these industries have closed (e.g. the cement plant), but since then no further studies have been conducted in the region.

The morphology of the area causes the development of a strong (about 12 km/h at the narrowest position) tidal current that changes its direction every 6 hours (Dassenakis et al., 1998) and causes the quick transport and dispersion of pollutants. There are also some small bays where the efficiency of the current in removing the pollutants is rather limited since its velocity is less than 10 cm/sec.

Despite the fact that the area of Evoikos Gulf is very important because of trace metal pollution, there is limited published data on the trace metals concentrations in the dissolved and particulate metals in seawater (Dassenakis et al., 1996; Scoullos and Dassenakis, 1983) and there is not a monitoring system for marine environmental quality. The purpose of this study was to investigate the levels of trace metals which are mostly related to the anthropogenic activities in Evoikos Gulf (Larymna Bay-Northern Evoikos and Central Evoikos Gulf).

Materials and Methods

Four water samplings took place for the present study; an autumn sampling for each region in October 2014, a spring sampling in March 2015 for the region of Chalkida/ Evripus Straits and one for the region of Larymna in the North Evoikos Gulf in June 2015 in which the network of stations was extended outside the bay of Larymna. Additionally, surface sediments were collected from both study areas in October 2014 (Fig.1).

Water samples were collected using Niskin bottles and stored in acid washed polypropylene containers. Upon arrival in the laboratory, the samples were filtered under vacuum through 0.45μm Millipore filters in a laminar flow bench in order to collect the suspended particles. The filters were digested with concentrated HNO_3, HF and $HClO_4$ in covered Teflon beakers for trace metal determination. Dissolved trace metals were preconcetrated on Chelex-100 resin columns and eluted by 2N HNO_3 (Scoullos and Dassenakis, 1983). Surface sediments were collected by a Birge-Ekman grab sampler, freeze dried and sieved in order to separate the silt and clay fraction (<63 μm) of the sediments. For the determination of total metals contents, sediments were digested with a mixture of acids (HNO_3-HF-$HClO_4$) on a hot plate. The analytical determinations of trace metals in all extracts were carried out with Flame (Varian SpectrAA-200) and Graphite Furnace AAS (Varian SpectrAA-640 Zeeman).The accuracy of the analytical procedures was checked using the certified reference material PACS-3 from the National Research Council of Canada. In some cases, ICP-MS was used in order to compare the results.

Results and Discussion

Water Column

Trace metal concentrations in seawater for both regions and all samplings are presented in Table 1. In the Northern Evoikos Gulf, during the autumn sampling, the maximum values of total Zn and Cu (the sum of the dissolved and the particulate phase expressed in μg/L) were determined in station NEV-5 where an aquaculture is located, while the maximum values of total Ni and Pb were measured in station NEV-3 which is located inside the Larymna Bay. During the spring sampling, the maximum concentrations of all studied trace metals were determined in station NEV-1, inside the Larymna Bay in very close vicinity to the Fe-Ni smelter plant.

Interestingly, whereas particulate Ni concentrations decreased from the inner stations of the Larymna Bay to the open stations of the Northern Evoikos Gulf, dissolved Ni concentrations did not differ significantly between the inner and the outer stations (Fig. 2B). This finding indicates a dispersion mechanism of Ni far away from the smelter plant. Nevertheless, the concentrations of total Ni in the Central Evoikos Gulf were significantly lower than in the Northern Evoikos Gulf. Copper also displayed higher concentrations inside the Larymna Bay that decreased southwards. However, there was no statistically significant difference between concentrations of Cu in the Northern and Central Evoikos. Furthermore, Fig. 2C presents the vertical distributions of dissolved, particulate and total Ni in central station N10 of 40 m depth. It is apparent that concentrations of Ni did not vary significantly with depth, indicating the mixing and homogenization of the water column.

In the Central Evoikos Gulf, during the autumn sampling, the maximum value of total Zn was determined in station CEV-1 near the urban area of Chalkida, while the maximum values of total Cu, Ni and Pb were determined in station CEV-9 located near the shipyards. During the spring sampling, the maximum concentrations of total Zn, Ni and Cu were determined in the northern stations CEV-1 and CEV-2 respectively, while total Pb exhibited the maximum value in station CEV-4 near the urban area of Chalkida.

With regard to the partitioning of trace metals between the dissolved and the particulate phase, it was observed that, both in the Larymna Bay and the Central Evoikos Gulf, Cu, Ni and Zn were predominantly found in the dissolved phase, which accounted for 64±13%, 82±11% and 70±28% of the total concentrations, respectively (Fig. 2). On the other hand, Pb was primarily bound to

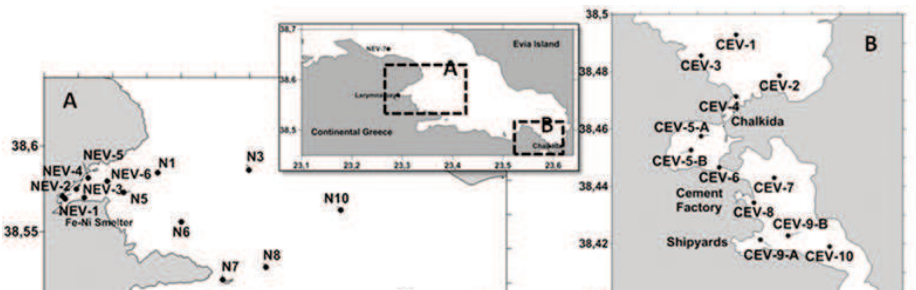

Fig.1: Sampling stations in **A)** Larymna Bay-Northern Evoikos, and **B)** Central Evoikos.

			Zn		Cu		Pb		Ni	
	AREA	Parameter	Dissolved	Particulate	Dissolved	Particulate	Dissolved	Particulate	Dissolved	Particulate
Seawater (μg/L)	**Northern Evoikos**									
	autumn sampling 10/2014	AVERAGE	3.61	1.13	0.27	0.18	0.09	0.15	1.53	0.73
		RANGE	0.03 - 11.94	0.43 - 3.58	0.03 - 0.63	0.03 - 0.35	0.03 - 0.24	0.05 - 0.46	0.02 - 2.60	0.03 - 2.28
	spring sampling 6/2015	AVERAGE	1.81	0.69	0.20	0.10	0.07	0.03	3.29	0.83
		RANGE	0.04 - 10.03	0.03 - 3.29	0.07 - 0.43	0.01 - 0.32	0.02 - 0.20	0.003 - 0.18	2.10 - 6.94	0.08 - 6.82
	Central Evoikos									
	autumn sampling 10/2015	AVERAGE	3.19	0.57	0.22	0.18	0.10	0.18	1.29	0.46
		RANGE	2.13 - 6.49	0.25 - 1.19	0.15 - 0.33	0.09 - 0.67	0.06 - 0.14	0.11 - 0.32	0.97 - 1.46	0.26 - 1.25
	spring sampling 03/2015	AVERAGE	2.40	0.27	0.22	0.24	0.09	0.05	1.03	0.21
		RANGE	0.97 - 4.95	0.01 - 0.88	0.13 - 0.31	0.05 - 1.47	0.04 - 0.23	0.02 - 0.11	0.28 - 1.96	0.14 - 0.36

Table 1: Concentrations of trace metals in seawater in the study areas

particles in the Central Evoikos Gulf in both samplings, as well as in the Northern Evoikos during the autumn sampling (52±17%), whereas during the spring sampling dissolved Pb prevailed (70±15% of total concentrations).

In Fig.3**,** average concentrations of both samplings of the current study were compared with previously published data for Central Evoikos Gulf (Scoullos and Dassenakis, 1983; Dassenakis et al., 1996; Dassenakis et al., 1998). It is evident that the concentration levels of all trace metals investigated in seawater decreased during the past years. This decline might be attributed to the shutdown of some industries (e.g. the cement industry) in the area.

NEV-3 (Larymna Bay), whereas the maximum Cu content was determined in station NEV-5 (aquaculture). In the Central Evoikos Gulf, the maximum Zn and Ni contents were detected in stations CEV-7 (waste water treatment), maximum Pb were determined in station CEV-5 (near the town of Chalkida), and Cu presented its maximum value in station CEV-9 (shipyards).

Independent t-test for statistically significant differences of trace metals contents between the two sampling areas showed that Ni and Zn contents were much higher in the sediments of the Northern, than in Central Evoikos Gulf, indicating the influence of the smelter's activity and the disposal of the slag. On the contrary, Pb contents

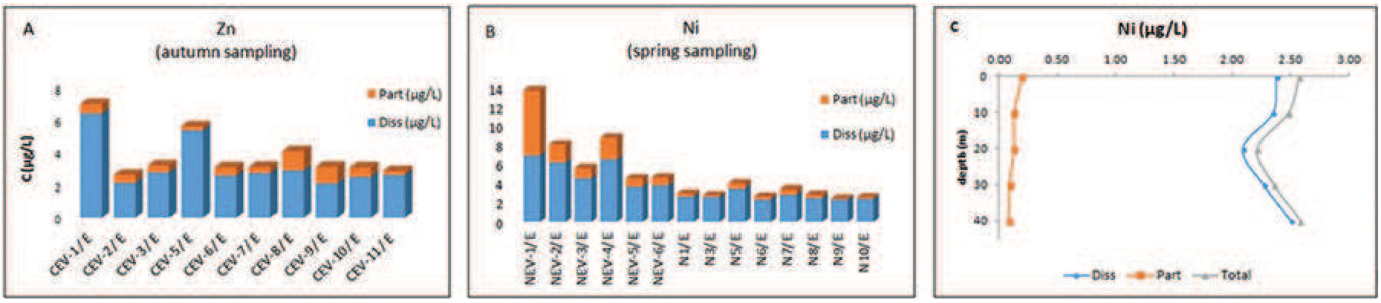

Fig.2: Distribution of dissolved and particulate form of **A)** Zn in Central Evoikos during the autumn sampling, **B)** Ni in Northern Evoikos during the spring sampling, and **C)** Ni in the water column of station N10 (40 m depth) in N. Evoikos Gulf

Compared to the Elefsis Gulf, where average concentrations of dissolved Zn, Cu, and Pb were 17.11 µg/L, 1.09 µg/L and 0.45 µg/L respectively (Scoullos et al., 2015) both study areas in the Evoikos Gulf exhibited lower concentrations of Zn, Cu and Pb.

Furthermore, data obtained from the current study of the Northern and Central Evoikos were compared with

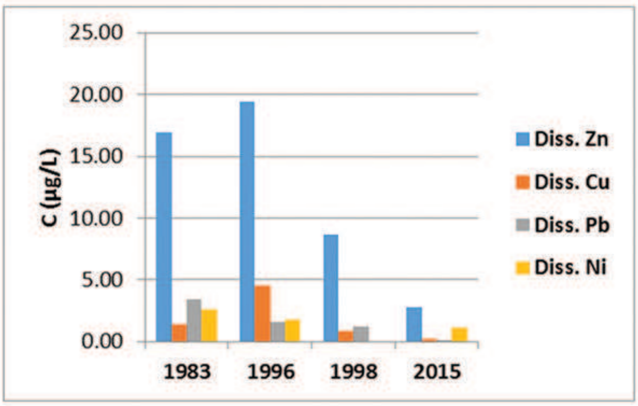

Fig.3: Comparison of average dissolved Zn, Cu, Ni, Pb in Central Evoikos with older data.v

Good Environmental Status Criteria - GES suggested in the framework of the Marine Strategy Framework Directive (Anagnopoulos et al., 2012). Concentrations of Zn, Cu and Pb do not exceed GES values (Zn=100 µg/L, Cu=10 µg/L, Pb=10 µg/L). There are no GES criteria suggested for Ni.

Sediments

In the Northern Evoikos Gulf, the higher Zn, Ni and Pb contents of the sediments were determined in station

were higher in the Central Evoikos Gulf sediments than in the Northern. Copper levels did not vary significantly between the two areas.

Previously published data for trace metal contents in sediments are presented in Table 2. In Northern Evoikos Zn, Cu and Ni concentrations ranged to similar levels. Concerning Pb, there are no available data for Northern Evoikos. In the Central Evoikos Gulf, Zn and Cu ranged within the same levels in comparison with previous studies (Karabela, 1999), whereas Pb and Ni decreased. Finally, trace metal contents of sediments were compared to the values of Effects Range Low - ERL and Effects Range Median - ERM suggested by Long *et al.* (1995). Levels below the ERL value suggest that adverse effects on benthic biota would be rarely observed, within ERL - ERM adverse effects would occasionally occur, whereas above ERM effects would frequently occur (Long *et al*., 1995). In both areas, Pb contents were below the ERL value, while Cu contents were between ERL - ERM values. Zinc exceeded the ERM value in the Northern Evoikos Gulf, whereas, in the Central Evoikos Gulf Zn contents were below the ERL value. As far as it concerns Ni, the ERL - ERM values are much lower than the respective background levels (Louropoulou et al., 2015), indicating that the SQGs are over-conservative for the studied areas.

Conclusions/Discussion

In the current study the levels of Zn, Cu, Pb and Ni were monitored in the Northern and Central Evoikos Gulf. Concerning the water column, it was generally observed that in the Northern Evoikos Gulf the concentrations of all metals were higher inside the Larymna Bay and decreased

AREA	Parameter	Zn	Cu	Pb	Ni	Reference
Northern Evoikos	RANGE	160 - 778	31.5 - 106	5.6 - 15.3	526 - 3207	Current study
	AVERAGE	393	56.8	9.3	1847	
Central Evoikos	RANGE	51.0 - 123	16.5 - 73.8	15.7 - 39.0	51.0 - 123	
	AVERAGE	96.8	35	26.5	96.8	
Northern Evoikos	RANGE	69 - 471	20.9 - 114	-	370 - 3610	Voutsinou-Taliadouri and Varnavas, 1993
Central Evoikos	RANGE	83.8 - 125	33.2 - 40.9	4.2 - 67.2	240 - 485	Karabela, 1999
SQGs (ERL - ERM)	ERL	150	34	46.7	20.9	Long et al., 1995
	ERM	410	270	218	51.6	

Table 2: Trace metals contents of sediments in the study area and SQGs (values in μg/g)

in the open stations. Between the Northern and the Central Evoikos Gulf, a statistically significant difference of total trace metals concentrations was observed only in the case of Ni.

In the sediments of the Northern Evoikos Gulf, the maximum Zn, Ni and Pb contents were determined in station NEV-3 near the Fe-Ni smelter, indicating the influence of the industry on the area. Lower Ni, Cu and Zn contents were determined in the Central Evoikos Gulf. On the contrary, statistically significant higher Pb contents were detected in the sediments of the Central Evoikos Gulf compared to the Northern.

The results of the current study were compared to previously published data for the area of Central Evoikos. It was generally observed that the concentrations of all trace metals in the water column decreased during the past years. This could be attributed to the shutdown of some industries located in the coastal zone of Central Evoikos.

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Chromium and Nickel distribution in sediments of a coastal area impacted from metallurgical activities: the case of the Larymna Bay

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Abstract

In the present study, the geochemistry and distribution of Cr and Ni was investigated in the surface sediments from Larymna Bay (Northern Evoikos Gulf), the metallurgical slag samples discharged in the marine environment, as well as the parent rocks that outcrop extensively in its basin. Furthermore, for comparison reasons, surface sediments from the Evripus Straits, located south of Larymna Bay, were also included in this study, in order to investigate the changes of Cr, Ni geochemical distribution in the less affected by metallurgical activities, adjacent sea. Elevated contents of Cr and Ni, as well as high values of magnetic susceptibility were determined in all samples. The distribution into grain-size fractions was differentiated for the two elements, with Cr showing a preferential accumulation into the sand fraction, whereas Ni was enriched in the silt/clay fraction. Magnetic susceptibility correlated well with Cr contents in all samples ascribing to the presence of Fe-Cr spinels and chromite identified by mineralogical analysis. Low leachability was determined for Cr, since chromite is the major crystalline phase of Cr in the samples analyzed, whereas higher leachability was observed for Ni.

Keywords: chromium, nickel, parent rocks, slag, sediments, Evoikos Gulf.

Introduction

Natural weathering, surface runoff, atmospheric transport, and direct discharges of waste materials of urban or industrial origin contribute to the enrichment of the marine environment in heavy metals. Marine sediments act as primary repositories of the transferred particles. However, in areas where local minerals contain high natural metal concentrations, the investigation of element geochemistry in marine sediments is not always straightforward (Angelidis & Aloupi, 2000).

The Northern Evoikos Gulf is surrounded by a variety of sedimentary, magmatic and metamorphic rocks containing naturally high amounts of Cr and Ni (Voutsinou-Taliadouri & Varnavas, 1993). Moreover, the daily discharge of a slag originating from a Fe-Ni smelter located in Larymna Bay, contributes significantly to sedimentation processes in the Northern Evoikos Gulf by forming an underwater bottom layer of 20 km^2 (Simboura et al., 2007). The only study reporting metal levels (extracted by 2N HCl) in the area is that of Voutsinou and Varnavas, and dates back to 1993. In the present study, the distribution of Cr and Ni was investigated in parent rocks, slag and marine sediments of Larymna Bay/Northern Evoikos, in order to study Cr and Ni geochemistry and to assess their mobility. For comparison reasons, the study of these two elements was also extended to the adjacent Evripus Straits/Southern Evoikos Gulf.

Materials and methods

Sampling of parent rocks from the catchment area of the Northern Evoikos took place in May 2013. Parent rocks included ophiolites, Ni -laterites and soil. These Ni-laterites are used as a feedstock in the Fe-Ni smelter located in Larymna Bay.

Sampling of surface sediments in the Northern Evoikos Gulf took place in October 2014 in Larymna Bay, where the ferro-nickel plant is located (Stations NEV-1 to NEV-6) (Fig.1B). NEV-8 sediment was collected from the underwater slag deposition area whereas station NEV-7 is located far from Larymna Bay in the Northern Evoikos Gulf (Fig.1A). Additionally, a slag sample was collected directly from the factory right before its discharge. Surface sediments were also collected from the Evripus Straits/Southern Evoikos Gulf in October 2014 (Stations CEV-2 to CEV-11) (Fig.1C). All sediments were immediately transferred to the laboratory and placed in deep freeze. Moreover, two sediment cores were collected in order to investigate the background levels of Cr and Ni; one from station NEV-12 in Northern Evoikos, and one from station CEV-10 in the Evripus Straits/Southern Evoikos.

	Fraction	Total Cr	% HCl extr. Cr	Total Ni	% HCl extr. Ni	$\chi lf\ 10^{-6}\ m^3/kg$
Parent Rocks		2176-21929	0.22-6.5	1845-6611	6.7-50.1	1.85 -25.8
Slag		17577	16,4	1623	75,6	4,08
Marine Sediments						
Slag deposit (NEV-8)	f<63	4017	35,8	2447	65,4	1,52
	f>63	19878	32,0	670	84,9	2,36
Larymna Bay	f<63	1726-10299	8.2-33.2	1180-3207	7.0-23.0	2.57-11.64
	f>63	72.8-18262	7.1-53.16	82.8-1362	29.7-58.6	0.302-5.48
NEV-7	f<63	529	3,3	526	12,9	0,265
	f>63	38,4	34,5	65,6	55,4	0,061
Evripus Straits	f<63	74.5 - 422	4.7 - 18.7	101 - 426	15.6 - 27.4	0.390 - 0.829

Table 1: Total Cr and Ni concentrations in (mg/kg) and percentage of HCl-extractable Cr and Ni in the analyzed samples.

Concerning the analysis of surface sediments from Larymna Bay, all analytical procedures were performed for both fractions <63 μm and >63 μm, since slag particles were visible in the fraction f>63μm. Analysis of sediments from the Evripus Straits/Southern Evoikos was performed in the <63 μm fraction only.

Magnetic parameters, low-field magnetic susceptibility (χlf) and frequency dependent susceptibility (χld%) were measured on a mass specific basis by a Bartington susceptibility sensor (Botsou et al., 2011; Scoullos et al., 2014).

The labile fraction of Cr and Ni was determined in the parent rocks, the slag and the freeze-dried sediments after a weak-acid digestion with 0.5N HCl (Agemian & Chau, 1977). Total Cr and Ni contents were determined by ultrasonic assisted digestion with a mixture of concentrated acids, including HF. Additionally, sequential extractions according to the BCR protocol were carried out in the parent rocks, the slag and the surface sediments from the Northern Evoikos Gulf in order to determine the different geochemical fractions of Cr and Ni (EUR report 19502EN). Chromium and Ni analysis in all extracts was carried out with Flame (Varian SpectrAA-200) and Graphite Furnace AAS (Varian SpectrAA-640 Zeeman).

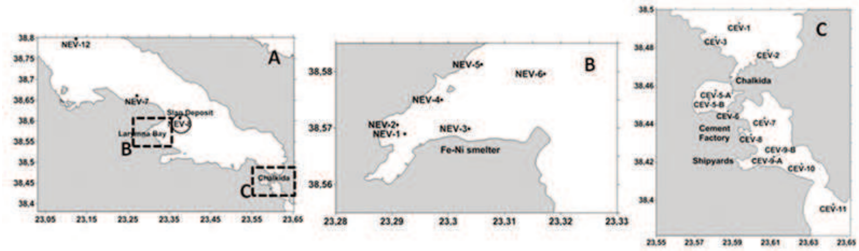

Fig.1: Surface sediment sampling stations in **A)** Northern Evoikos Gulf, **B)** Larymna Bay and **C)** Evripus Straits/Southern Evoikos Gulf.

Results

Concerning the granulometric composition of the sediments, in Larymna Bay most samples consisted of sand, whereas the silt/clay fraction ranged from 9% to 48%. Station NEV-4 consisted primarily of sand. Black grains of slag were detected during sieving in stations NEV-1, NEV-2, NEV-3 and NEV-6. The grains were visible in the fraction >63 μm. On the other hand, the silt/clay fraction was dominant in the sediments from the Evripus Straits ranging from 59 to 100% of the total sediment mass, with the exception of one station (CEV-2) where the silt/clay fraction was 16.2%.

Chromium contents of all samples analyzed are presented in Table 1. Elevated Cr contents were determined in all samples of N. Evoikos Gulf. The maximum value was determined in station NEV-8 in the slag underwater deposit. It was generally observed that in the stations where slag particles were detected (i.e. NEV-1, NEV-3, NEV-6, NEV-8), Cr contents were higher in the sand fraction, indicating the contribution of the coarse slag particles to the Cr-content of the sediment. Lower Cr contents were observed in the Evripus Straits where the maximum value of Cr was detected in stations CEV-2 and CEV-9, the stations near the town of Chalkida and the Shipyards, respectively.

Elevated Ni contents were also determined in all samples (Table 1). For example, in the underwater slag deposit area Ni contents were 2447 mg/kg and 670 mg/kg in the silt/clay and sand fraction respectively. The maximum Ni contents were determined in station NEV-3 located outside the smelter, while the lowest were observed in station NEV-4. Distribution of Ni between the two fractions exhibited different behavior compared to Cr. Higher Ni contents were determined in the silt/clay fraction in all stations, despite the presence of slag particles in the sand fraction. Lower Ni contents were observed in the Evripus Straits (101 - 426 mg/kg of total Ni) where, similarly to Cr, the maximum values were determined in stations CEV-2 and CEV-9.

Total Cr correlated well with total Ni using Spearman correlations for both the silt/clay ($r= 0.952$, $p<0.01$) and the sand fraction ($r= 0.833$, $p<0.05$) in Larymna Bay and for the silt/clay fraction in the Evripus Straits ($r=0.707$, $p<0.01$).

The extraction with 0.5N HCl gives an estimation of the more labile forms of an element. As shown in Table 1, the leachability of Cr in parent rocks ranged from 0.22 to 6.5% for Cr and from 6.65 to 50.1% for Ni. These percentages for both elements increased in the slag, in the slag deposit area, and in the marine sediments from Larymna Bay. The highest percentages were observed for both elements in station NEV-8 where the underwater slag deposit is located. Lower leachability was observed for Cr in the surface sediments of the Evripus Straits. On the contrary, the leachability of Ni in the Evripus Straits ranged within

(mg/kg) Fraction	Cr F1	Cr F2	Cr F3	Cr F4	Ni F1	Ni F2	Ni F3	Ni F4
Parent Rocks (Ni-Laterite)	5,0	16,7	65,4	17470	86,2	250	352	6680
Slag	103	215	357	15964	81,7	286	178	1159
Marine Sediments								
Larymna Bay	0.07-10.7	3.8-173	135-1139	1587-8975	5.3-58.7	8.1-142.8	28.0-127.3	1130-2901
Slag Deposit (NEV-8)	9,0	276	504	3227	216	554	552	1125
NEV-7	0,08	0,23	11,5	517	0,77	2,0	8,3	515

F1= Acid Soluble, F2=Reducible, F3=Oxidizable, F4=Residual

Table 2: Cr and Ni concentrations after BCR sequential extractions

similar levels compared to the surface sediments from Larymna Bay.

Sequential extractions performed on the parent rocks, the slag and the surface sediments from Larymna Bay showed that the maximum Cr contents were detected in the residual fraction in all samples (Table 2). However, significant amounts were detected in more labile fractions that might be mobilized and released to the environment under changes of environmental conditions. For example, in the slag deposit area the sum of fractions f1+f2+f3 accounted for 789 mg/kg of Cr. Concerning Ni, in the parent rocks and in most of the surface sediments from Larymna Bay, maximum contents were determined in the residual fraction. However, Ni contents increased in the f1, f2, f3 fractions of the pure slag and the underwater slag deposit, implying that Ni is more labile than Cr in these samples. For example, in the silt/clay fraction of the slag deposit sample the percentages of Ni accounted for f1=9%, f2=23%, f3=22% f4=46% of total Ni.

Mineralogical analysis performed with XRD and SEM in the parent rocks (i.e. Ni-laterites) and in the slag showed that chromite - $FeCr_2O_4$ was the major crystalline phase containing Cr, while the presence of other Fe-Cr spinels were also identified (Andrioti *et al,* 2014; Andrioti, 2015). Due to the low solubility of chromite occurring in the parent rocks and slag, the leachability of Cr after 0.5N HCl extraction and BCR sequential extraction was low in these samples. Thus, it was observed that the leachability of Cr increased in the following sequence: parent rocks < slag < marine sediments, indicating probably a transformation of Cr-bearing phases from the sources to the deposition area. On the other hand, the leachability of Ni was higher compared to Cr both in the parent rocks and the slag. This might be attributed to different and more soluble Ni-bearing mineral phases.

Regarding the magnetic susceptibility-χlf, high values were observed in parent rocks, pure slag and surface sediments from Larymna Bay, including the underwater slag deposit. In surface sediments, **χ**lf values were increased in the silt/clay fraction, whereas the lower values in the sand fraction are probably attributed to the presence of carbonates, which is a diamagnetic component and decreases the magnetic signal. Spatial distribution showed that the strong signals were observed in stations NEV-1, NEV-2, NEV-3 and NEV-6, where slag grains were present. The maximum value was determined in station NEV-3. Comparison of the sediments' and slag's **χ**lf values implies that apart from the slag there are other components of geologic origin that contribute to magnetic susceptibility. The presence of ferrimagnetic minerals (e.g. magnetite) in the parent rocks was verified by their high **χ**lf values. Lower values of magnetic susceptibility were observed in the surface sediments from the Southern Evoikos Gulf, since **χ**lf ranged from 0.390 to 0.829 10^{-6} m^3/kg. Magnetic susceptibility correlated well with total Cr both in the sand ($r= 0.952$, $p< 0.01$) and in silt/clay fraction ($r=0.833$, $p<0.05$) in Larymna Bay and the Evripus Straits ($r=0.717$, $p<0.05$). This positive correlation ascribes to the presence of Fe-Cr spinels and chromite that were identified by mineralogical analysis. Although chromite is among the "less common" magnetic minerals, it is one of the more resistant minerals in nature and together with other Fe-Cr spinels could represent

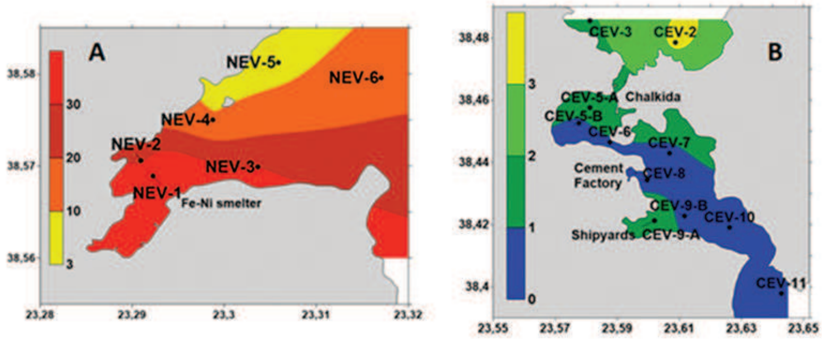

Fig. 2: Spatial Distributions of Enrichment Factor - EF for Cr in A) Larymna Bay, and B) Evripus Straits/Southern Evoikos

a significant proportion of relict magnetic assemblages (Scoullos *et al*., 2014).

Finally, Enrichment Factors (EFs) were calculated for the silt/clay fraction according to the formula $EF= (element/Al)_{sample} / (element/Al)_{reference\ value.}$ For the Northern Evoikos Gulf, a 200 cm sediment core (NEV-12; Fig. 1A) was analyzed in order to establish the reference values for Cr and Ni (Reference Values: Cr= 240 mg/kg, Ni= 510 mg/kg). Enrichment Factors in Larymna Bay ranged from 1.9 to 49.1 for Cr and from 1.0 to 6.1 for Ni. The maximum values were observed for both elements in stations associated with the smelter (NEV-1, NEV-3, NEV-6, NEV-8), implying that surface sediments are strongly affected by the smelter's activity and the slag's disposal. In the case of the Evripus Staits/Southern Evoikos Gulf, EFs were calculated using as reference values the lower parts of a sediment core obtained from Station CEV-10 (Fig. 1C; Reference values: Cr= 252 mg/kg, Ni= 355 mg/kg). Enrichment Factors in the Evripus Straits were lower compared to Larymna Bay and ranged from 0.21 to 3.16 for Cr and from 0.20 to 1.55 for Ni. The maximum values in the Evripus Straits for both elements were observed in stations CEV-2 and CEV-9.

Conclusions/Discussion

This study of Cr and Ni distribution in Larymna Bay showed that the area is strongly affected by the plant's activity and highly enriched in both Cr and Ni. Compared to Larymna Bay, the Evripus Straits/Southern Evoikos Gulf is less enriched in Cr and Ni. The grain size distribution of these two elements showed that Cr content in marine sediments was higher in the sand fraction in stations of the Northern Evoikos Gulf, where slag was detected. On the contrary Ni was always dominant in the silt/clay fraction in all stations, despite the presence of slag particles in the sand fraction.

Chromite was the prevailing crystalline phase of Cr both in the parent rocks that outcrop in the catchment area of N. Evoikos and in the slag deposited in the marine environment. However, the higher leachability of Cr both in the slag deposition area and in surface sediments indicates the increasing contribution of the more soluble, Cr-bearing phases. Sequential extractions performed in parent rocks, slag and marine sediments from Larymna Bay in the current study confirm this assumption. Furthermore, preliminary results indicate that minerals containing Ni are more soluble than those containing Cr. This explains the higher leachability of Ni in all samples analyzed.

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Lake Bizerte (Tunisia) and its 'Charter': A potentially useful example for the Management of the Gulf of Elefsis

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Lake Bizerte is one of the most important lagoons of Tunisia with many complex, accumulated problems deriving from poorly planned anthropogenic activities carried out in the entire catchment area for many years. In fact, the "Lake" is a semi-enclosed marine embayment of similar size with that of the Gulf of Elefsis, although it is less deep (its greater depth is around 15m compared to 33m of the Gulf of Elefsis), while it receives more fresh waters from the nearby Lake Ichkeul, than what the Gulf of Elefsis receives from the Koumoundourou Lake.
It has been identified by the Tunisian Government as a "hot spot", meaning a site of high concentration of pollution sources and severe environmental problems requiring urgent action. The site is included in both the list of the 'hotspots' under the NAPs (National Action Programmes) prepared by the Contracting Parties of the Barcelona Convention and compiled by UNEP/MAP and, also under the priority areas tackled by the Horizon 2020 Initiative to depollute the Mediterranean by the year 2020, a flagship programme of the Union for the Mediterranean (UfM). Within the latter, the Integrated Programme for the Protection of the Lake Bizerte against Pollution was developed and through the Mediterranean Hot Spots Investment Programme – Project Preparation and Implementation Facility (MeHSIP - PPIF), a state of environment/feasibility study was completed[1] based on a thorough review and synthesis of existing research (including both biogeochemical and socioeconomic aspects).

Fig 1. Map of Lake Bizerte

Figure 1 shows Lake Bizerte and its connection to the Mediterranean Sea and Lake Ichkeul. Figure 2 presents some results of this study showing the concentrations of Nitrates in the waters of the Lake, while Figure 3 demonstrates the distribution of Cadmium concentrations. It is noteworthy that for both parameters there was a considerable decrease of their levels, a feature similar to that observed also in the Gulf of Elefsis.

Using this study and other background information, an extensive dialogue with stakeholders took place, throughout the period 2011-2012, followed by a multi-stakeholder consultation meeting (7-8 June 2012) facilitated by the EU-funded Mediterranean Environment Programme (CB/MEP), under the supervision of its Team Leader, Prof. Scoullos. The consultation was concluded with the agreement by all stakeholders involved and the ceremonial signing a few months later (16 October 2012) of the so called *Lake Bizerte Charter (see Appendix 1*) for the sustainable future of the lake. The text of the Charter is a vision-setting document and a Memorandum of Understanding among all the key stakeholders in the region, including line Ministries, Local Authorities and international organisations, such as the European Investment Bank (EIB) and the Mediterranean Information Office for Environment, Culture and Sustainable Development (MIO-ECSDE), describing the major steps to be taken for the restoration of the environment and for the Sustainable Development of the region.

A commitment by the EIB was made to fund a series of projects/activities for the reduction of the pollution load deriving mostly from industrial activities. In parallel, the UfM, in recognition of the effort being a flagship project that could be an example for other promoters and institutions in the region, 'labelled' the Integrated

Programme for the Protection of the Lake Bizerte against Pollution on 3 October 2013 in order to stimulate investment for its implementation. To facilitate the overall management, the Tunisian Government established a locally based Unit ('Cellule') staffed by officials of the Ministry of the Environment and Sustainable Development and local actors, who are expected to implement decisions, coordinate, facilitate and improve the legal, institutional and operational frameworks for the smoother implementation of the specific actions/projects but also for ensuring and promoting a truly integrated management for the sustainable development of the entire Lake Bizerte region.

In obtaining the consensus agreement for the Charter as a strategic "vision" for the integrated management of Lake Bizerte and its catchment area, two frameworks for integrated management were considered and presented as particularly useful models, relevant to the specific character of the area: Integrated Coastal Zone Management (ICZM) and Integrated Water Resources Management (IWRM). Both ICZM, as described in the relevant Protocol of the Barcelona Convention, and IWRM are processes that strive to balance regional development while achieving wise environmental and natural resources stewardship. In both, similar methodological approaches are used, including, as an important component, the Ecosystem Approach (EcAp)/Ecosystem Based Approach (EBA). The same methodological approach was used also elsewhere and is described in detail in an important work that has been concluded, and will be circulated soon under the title "An Integrative Methodological Framework (IMF) for Coastal, River Basin and Aquifer Management"[2]. It is a joint publication by PAP-RAC of UNEP/MAP, UNESCO and GWP-Med. This approach could be easily replicated also in the case of the Gulf of Elefsis.

As a follow up, within the Horizon 2020 framework, in October 2014, an exercise involving also the DPSIR (Drivers, Pressures, State, Impacts, Responses) approach took place by (a) briefly reviewing a proposed set of projects considering them as a concrete response; (b) assessing them against the identified from previous steps problems (pressures, state, impacts); (c) comparing them with the 'ideal' set of provisions expected for a fully integrated ICZM-IWRM plan for the entire area and, finally, (d) Identifying what additional responses were necessary either as potential new activities/projects or as 'supporting' conditions and/or activities including funding.

The exercise described above was very useful since it was considered as the first monitoring/assessment of the progress of the Charter and its implementation. It also paved the road for some extension and enhancement of complementarity with other projects, while it identified and promoted milestones for an Action Plan for the elaboration and implementation of ICZM with full consideration of IWRM and application of the EcAp. Among the results/conclusions of the review, some were of particular importance able to guide further action. The most positive results that the review acknowledged were:

- The inclusion of the Ichkeul lake system in the planning.
- The creation of a dedicated administration unit (cellule), based in the area.
- The elaboration and inclusion of a series of new important interventions (addressing heavy polluting industries, waste water treatment plants, etc.) within the existing funding scheme.
- The clustering of a series of new and ongoing research studies on the state of environment of the region.
- The announcement, by the Government of Tunisia, of the Durability/Perennisation Fund and other relevant Funds to be used for the implementation of interventions.
- The implementation of a series of awareness raising and sensitization activities.
- The formal announcement of the intent of the Government to link the programme to an overall ICZM/IWRM plan of the county.

The review noted also that despite the indisputable progress, a series of issues and developments were still pending or needed further support, considering a number of sectors and "fronts" such as on:

- Fisheries and more specifically on overfishing, where designation of suitable sites for aquaculture was suggested, which required provisions for appropriate zoning.
- Solid waste, and in particular for three (3) types, namely household, demolition and industrial waste. Poorly managed waste from land based sources continues to be also the main source of marine litter, which is detrimental for the marine ecosystems, fisheries and the economy of the area. A close monitoring and elimination of uncontrolled dumping sites, planning of appropriate sites for new solid waste management facilities with emphasis on separation at source, recycling, valorisation and linking it to circular economy were suggested. The need for elaboration and implementation of the appropriate legal framework encouraging the involvement of private sector and new approaches, and the necessary systematic and efficient awareness campaigns towards a positive attitude and ownership by the local communities, were suggested as appropriate actions.
- The energy sector and its requirements including provisions for mitigation and adaptation to climate change were proposed as priorities to be considered in drafting the Action Plan. The use and the promotion of compatible renewable energies were suggested as a complementary activity for the area.
- Pollution. Apart from point source pollution, diffused pollution from agricultural activities and urban runoff was considered as important to be addressed.
- The cultural heritage of the area including significant archeological sites on the southern bank of the Lake was also considered as an integral part of its capital including its intangible heritage (traditional knowhow, etc.).The need to be protected and

provisions for them were suggested to be included in the Action Plan in order to allow for their protection, promotion so as to use them as a valuable element for the development of relevant quality tourism.
- Sound research was recognized as a pillar of the whole planning process and local academic and scientific institutions were proposed to be given the opportunity to contribute.

The review emphasized that the Governance schemes for the design, follow-up and implementation of the Action Plan for the Lake Bizerte Charter needs to be addressed carefully with provisions for decentralization and for an appropriate structure based in the region. The participatory process followed was exemplary, however additional support is needed with clarification of roles and institutionalization, including for instance, participation of local academia and other competent bodies, NGOs and Civil Society Organisations in the steering groups and/ or management bodies. It was suggested to consider the establishment of a new local entity for the Bizerte/Ichkeul Lakes system management with the participation of all relevant agencies and stakeholders, public and private. It was emphasized that improvement in the management plan should be firmly placed in the framework of ICZM/ IWRM. Monitoring of ecosystems, including the ecological, chemical and other parameters was considered necessary. It was stressed that monitoring should be viewed as an integral part for the design, the road map and the implementation of the Action Plan. The appropriate set of indicators and provisions for the free access to data and the dissemination and publishing of the result is lacking and needs to be developed.
Considering the similarity of both the geobiochemical and socioeconomic conditions between Lake Bizerte and the Gulf of Elefsis, the experiences and recommendations concerning the management of the former could be extremely valuable and useful for the latter. The fact that in both areas the University of Athens and MIO-ECSDE act as present key players may facilitate the transfer and feedback of this experience.

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Appendix 1: Joint Commitment of Lake Bizerte / Charter of Lake Bizerte / Memorandum of Understanding

In the framework of the H2020 consultations in view of the development of the project for the depollution of Lake Bizerte, the participants representing major stakeholders gathered on 7th and 8th June 2012, on an invitation by the Ministry of the Environment and the Horizon 2020 in a meeting facilitated by Horizon 2020 CB/MEP,
***Informed** about the development of the project and the results of the feasibility study carried out by MeSHIP/PPIF, informed about other relevant projects under development in the area, informed as well about the new tendencies in managing similar coastal systems in the Mediterranean Region and beyond, based on IWRM, ICZM, Ecosystem Approach (ECAP), MAB/UNESCO Biosphere Reserves,…*
***Recognizing** the acute pollution and degradation of the ecosystems of Lake Bizerte, the accumulated environmental problems leading to extremely high concentrations of contaminants in the atmosphere, waters, soils and sediments which have direct and indirect impacts on the health of people and the ecosystems,*
***Recognizing** that this pollution is coming from industrial point sources, diffuse pollution from agriculture and runoff, discharge of untreated waste waters, poorly managed solid waste, transport and other human activities,*
***Realizing** that the above mentioned pollution is linked either to lack of the appropriate institutional/regulatory framework and deficiencies of the implementation and enforcement of existent regulations, or inadequate infrastructures and mechanisms in place for the depollution and environmental management of the Lake.*
***Admitting** that for the necessary management there are insufficient data, analysis and monitoring,*
***Convinced** that one of the root causes of the problem is the lack of appropriate awareness among authorities/decision makers, producers, consumers and the wide public, in general, inadequate education for sustainable development and insufficient mechanisms of public participation,*
***We are calling** for an integrated management plan which will ensure the sustainable development of the region in the medium and long term (by the year 2020 and beyond). Such a management plan should fulfill, simultaneously, the requirements and provisions/objectives of IWRM, ICZM, ecosystem approach, etc. It should:*

- *cover the wider catchment area including Lake Ichkeul and the coastal marine section including Harbors.*
- *integrate all important sectoral programmes for land use management, industry, agriculture, fisheries and aquaculture, solid waste, etc.*
- *be linked with a systematic monitoring scheme, with the appropriate agreed indicators and associated with SEIS (Shared Environmental Information System). The system should be able to follow all key parameters including major physical chemical and biological ones, statistics on production and key socio-economic factors, and also act as an early warning system.*

We will try to accommodate, as much as possible, the needs and aspirations of all stakeholders in order to:

- *provide a substantial improvement of the life of the inhabitants of the region and welfare of the local communities,*
- *reduce significantly pollution from all sources and respect national and international standards for Good Environmental Status,*
- *move in a systematic and efficient way towards transforming the industry of the region to environmentally sound and "green",*
- *improve agricultural practices and reduce the use and accumulation of agrochemicals such as fertilizers and pesticides in the soils and aquatic systems of the region,*
- *promote the preservation and further sustainable development of fisheries and aquacultures within the carrying capacity of the lake Bizerte system and following the appropriate practices,*
- *safeguard and, whenever possible, restore the biodiversity of the region (protection of species under extinction, inhibition of the intrusion of alien species, enhancement of the biological stock,…) in designated and protected areas as well as in open green spaces and the coast line that will allow for the full development of the "ecological services" of the Bizerte ecosystem,*
- *protect and promote the cultural heritage of the region*
- *optimize the use of natural and cultural heritage of the region in view of development of environmentally compatible tourism and ecotourism.*
- *We commit to continue and strengthening our work together in a participatory way to elaborate an Action Plan that reflects our vision and through which we will make reality our aspiration through concrete action. This Action Plan should include provisions for adaptation to climate change helping to address extreme events.*
- *We commit to elaborate and implement a comprehensive public awareness and education for sustainable development programme to address local, national and global issues.*
- *We consider the necessary depollution investments proposed and agreed by the respective actors and stakeholders under the project H2020 as an important integral part of this Action Plan*
- *We encourage national authorities and international donors and organizations to supplement the above mentioned investments for the completion of the Action Plan and the activities needed for its implementation*
- *And we commit to work together in preparing and, further on, implementing such an Action Plan in the coming years.*

A record of industrial metal pollution reduction as a result of change of production route, implementation of legislation and the application of BAT's

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Abstract

Traditionally, the steel industry has been considered as one of the biggest polluters in the world, especially in coastal areas. Nowadays the steel industry has made drastic improvements in emission control and steel production has potential for achieving high level of pollution prevention and environmental protection. For the assessment of pollution from a representative iron and steel plant, sediment cores were collected from the coastal area affected by the plant. The degree of pollution and the effects on the aquatic environment were determined using enrichment factors and sediment quality guidelines respectively. The results show considerable improvement in the level of the contamination and the toxicity probability of biota despite the increased productivity during the last 10 years. This reduction is the result of the combined application of Best Available Techniques (BAT's) under European and national policy and regulation and the change of the production route.

Keywords: steel, sediments, pollution, techniques, regulations, route

Introduction

Steel is a widely used material and behind the name of steel hide several thousands of different alloys, and there are currently more than 3500 different grades with various properties – physical, chemical and environmental – which have been developed in the last 20 years (UKEA/IPPC, 2004).

The steel industrial sector is highly material and energy intensive and traditionally has caused significant air, water and soil pollution. Due to the nature of the process, large amounts of solid, liquid and gaseous waste is generated in the steel plant. More than half of the mass input becomes outputs in the form of off-gases and solid waste or by-products.

There are two main routes for the production of steel: production of primary steel using iron ore and scrap (integrated steelworks, primary route) and production of secondary steel using scrap only (mini-mills, secondary route). Integrated steelworks are plants where pig iron is made by reducing iron ore in blast furnaces. In mini-mills, scrap and ores are melted and converted into crude steel directly in electric arc furnaces. Steel recycling (mini-mills, secondary route) uses less energy, less virgin materials and less water; it also produces fewer water pollutants, fewer air pollutants and less mining waste.

Steel plant air emissions may occur as direct emissions (from stacks), and as indirect emissions (diffuse and fugitive from irregular operation, leakages, valves, pumps, flanges, vents and open parts, accidents, etc.) during all the steps of the process. Water pollution occurs from discharges of waste water sources (from off gas treatment, rainwater runoff, cooling water, etc.) to lakes, rivers or the sea. The pollution of the soil occurs from materials, products and waste management (incoming materials, additives, intermediate and finished products, solid and liquid waste) (EC, 2010; EC, 2001).

In the production of iron and steel, over 600 Best Available Techniques (BAT's) that have environmental benefits are generally identified. Best Available Techniques describe techniques which achieve a high level of environmental protection. Emissions can be controlled by end-of-pipe techniques or by process modification according to the principles of cleaner production and industrial ecology or symbiosis. These principles are: minimal use of raw materials (especially non-renewable), recycling of materials (water, by products), minimal use of energy, minimal production of waste and minimal emissions to all media (EC, 2010; EC, 2001).

The main changes that have been made in the last 40 years in relation to (EC, 2010; EC, 2001) are:

- shutdown of older and less efficient mills (replacing old and outdated plants)
- increase of steelmaking yield
- higher capacity utilization (near design capacity)
- reduced specific consumption of raw materials and energy
- increase of steel production by electric arc furnace route
- near total convection to continuous casting
- adoption of management systems
- improvement of environmental protection techniques
- increase of scrape use
- increase of the share of natural gas as energy source
- improved recycling of steel products
- improved use and recycling of by-products
- reduction of water usage and waste water discharge
- investment in process improvements and development of new and breakthrough technologies
- enhancement of the quality of input materials and logistics
- development of new steels (Advanced High Strength Steel) that improve the eco-efficiency of steel-using products

Marine sediments can be a sensitive indicator for monitoring of contaminants in the marine environment (Balls *et al*., 1997), and sediment analysis can reflect the current quality of the system and the pollution history of a certain area (Hallberg, 1992). For chemical analysis, sediment samples are preferable to seawater samples because pollutant concentrations are higher and indicate a lower variation with respect to time and space, allowing a more consistent assessment of contamination (Power and Chapman, 1992). Sediments show a great capacity to accumulate and integrate heavy metals and organic pollutants even from low concentrations in the overlying water column (Maher and Aislabie, 1992).

Materials and methods

The study area in this work is located in Elefsis bay, a small semi-enclosed, shallow elongated bay, which is the most industrialized, economically developed and polluted area in Greece. The bay represents an example of marine ecosystem whose contamination balances have been modified in relation to the anthropogenic development (in particular to industries located in the coastal area) and was recognized as an area of major environmental concern in a report on priorities for the Mediterranean environment (UNEP/MAP/WHO, 1999 ; UNEP/WHO, 2003). The bay receives the effluents of major industries like petroleum refineries, shipyards, steel works, foundries, cement factories and sewage outfall. For several decades, the industrial activity has contributed sizeable volumes of wastes to the water column and the sediment.

The steel industry since its establishment in the area, has changed the steel production method (from integrated route to secondary route), the technology facilities and in the last 10 years has adopted the Best Available Techniques and other social and economic tools for achieving a high level of environmental protection. The sampling stations were selected by considering the contamination sources of the iron and steel industry and were chosen to provide good area coverage of the industry.

In order to evaluate the level of pollution, sediment cores were collected using a pneumatic Mackereth minicorer (Mackereth, 1969). This method of sampling normally eliminates metal contamination and preserves the water-sediment interface undisturbed. Thereafter each core was sliced into sub-samples of 1 cm thickness each and the slices were stored in plastic vials. The sub-samples were frozen at -20°C until the analysis. In the laboratory, sediment sub-samples were defrosted at room temperature, dried at 40 °C up to a constant weight, sieved through a 1mm screen and then they were wet sieved through a 63 μm nylon screen in order to reduce the variance from different grain sizes (Ackerman, 1980; Mayer and Fink, 1980). Each sub-sample was dried at 40 °C, ground and very well homogenized to a fine powder in a swinging motorized mill with agate mortar and balls to reduce variability between replicates. The following analyses were performed in the sub-samples:

- Calculation of the actual sedimentation rate: estimated from the 210Pb vertical distribution (Vesterbacka and Ikäheimonen, 2005)
- Measurement of the magnetic susceptibility (xlf): it provides a simple, safe and rapid non-destructive method for monitoring of marine particulate pollution from iron facilities (Scoullos et al., 2014)
- Measurement of the minor and major elements by X-ray spectroscopy (Van Griegen and Markovitcz, 2002)
- Determination of the total organic carbon by the Walkey-Black method (Tanner and Leong, 1999)
- Geochemical normalization using Al, in order to reduce the variance from the different geochemical composition of the sediments (In this study aluminium is selected as a normalization element) (Salomons and Förstner, 1984)
- Calculation of the enrichment factors (EF, mCd) in order to distinguish the anthropogenic fraction of the metals from the background and to assess the degree of anthropogenic influence (Abrahim and Parker, 2008)
- Biological effects on the aquatic environment (m-ERM-Q): to predict biological effects on benthic organisms (Long et al., 2006)
- Statistical analysis: a) correlation analysis to ascertain similar vertical distribution among variables, b) cluster analysis to classify similar variables into groups, c) principal component analysis to identify the possible sources in the sediment samples, to

explain the maximum amount of variance with the fewest number of components (Loska and Wiechula, 2003).

Results

- The sedimentation rate was estimated between 0,3-0,4 cm/y for some cores and between 1-1,2 for others
- The cluster analysis showed a group for the variables xlf, C, Fe, Mg, S, Mn, As, Mo, Pb, Sb, Zn with a level of similarity over 90 %

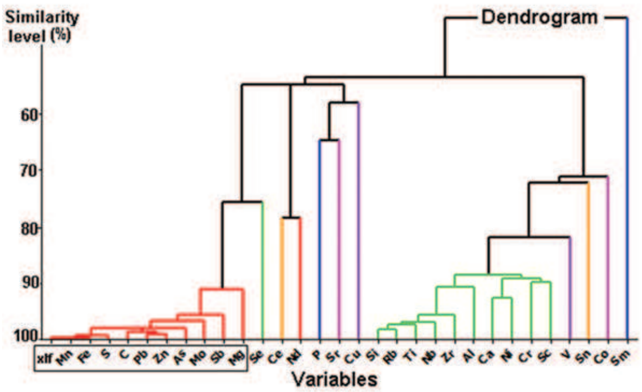

Fig.1: Cluster analysis of variables in sediments

- The correlation coefficient of these variables with iron (mark element from steel production) and the correlation coefficient between these variables were above 0,8 with a p-value less than 0,001

P.C.C$_R$ (p-value)	Variables
R > 0,80 (p < 0,001)	xlf, C, Fe, S, Mn, As, Mo, Pb, Sb, Zn, Mg

Table 1: correlation coefficient of variables in sediments (p-value)

- The vertical distribution of xlf, C, Fe, Mg, Mn, As, Mo, Pb, Sb and Zn was similar at all depths to the vertical distribution of steel production except for the last production period (2003-2014) (figure 2).
- The factor analysis shows that 4 of the factors explain most of the variability. The remaining factors explain a very small proportion of the variability and are likely unimportant. The first factor (PC1) that accounts for 62 % of the variance, exhibited high loadings of xlf, C, Fe, S, Mg, Mn, As, Mo, Pb, Sb and Zn, could be interpreted as iron and steel production since these elements are makers for steel production.
- The modified degree of contamination (mCd) for the three periods (2014-2003, 2002-1982 and 1981-1963) was low to high, high to very high and very high, respectively (figure 2).
- The toxicity probability for biota (m-ERM-Q) for the three periods (2014-2003, 2002-1982 and 1981-1963) was less than 49%, 49% and 76%, respectively (figure 2).
- The pollution reduction from the third period (1981-1963, production route: Blast Furnace) up to the first period (2014-2003, production route: Electric Arc Furnace in combination with Best Available Techniques) was more than 90% (figure 2).

Conclusions/ Discussion

Coastal sediment cores were collected in the vicinity of an Iron and Steel plant in order to evaluate the pollution history caused by this plant. For the determination of the pollution status of sediments, two approaches were used: (1) comparison of elemental concentrations in samples with those of samples from pre-industrial/background concentrations using Enrichment Factors, (2) comparison with Sediment Quality Guidelines for each contaminant and the cumulative effects of contaminants in sediments. The results of the present study indicated that the study area is significantly affected by the iron and steel industrial activity. The sediments have shown elevated total metal content in comparison to the background levels. The situation seems to have improved significantly during the last 10 years (the reduction of pollution was found to be more than 90 %) due to the change of the production route, the implementation of BATs and of appropriate environmental protection policies.

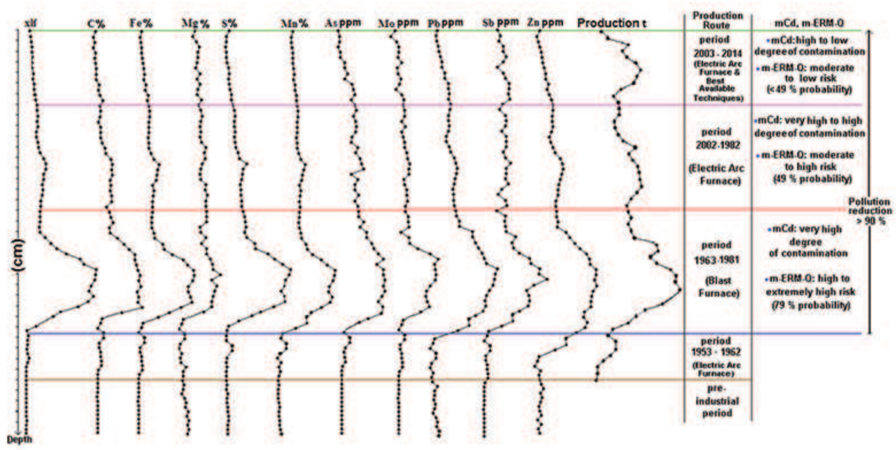

Fig.2: Vertical distribution of variables in sediments, the vertical distribution of steel production, the degree of contamination, the toxicity probability for biota and the pollution reduction during: 2014-2003, 2002-1982, 1981-1963.

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Addressing the growing threat of marine litter: MIO-ECSDE actions on the science-policy-society interface

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Abstract

The growing urgency and complexity of interconnected societal challenges demand that they be addressed through the strengthening of the science-policy-society interface so as to provide the necessary conditions for translating research-based knowledge into effective action. This paper showcases the actions of a regional NGO with member organisations in all Mediterranean countries, MIO-ECSDE, in addressing one such issue, marine litter, and is an account of the diversity, added value and particular strengths that the NGO community brings to environmental governance, such as leadership, creativity, flexibility, entrepreneurship and capacity for vision and long-term thinking.

Keywords: science-policy-society interface, marine litter, NGOs

Introduction

NGOs are essential partners in promoting environmental protection and achieving sustainable development. Their active participation at local, national and transboundary level in all phases of projects and processes, from their design, implementation in the field, operationalization, monitoring and evaluation, contributes not only to increased transparency, wide visibility and outreach of the project or process, but also to enhanced overall quality and increased ownership of the outcomes, as well as amplified possibilities for replication of its activities (Scoullos *et al.*, 2002).

Oftentimes, the role of NGOs in environmental protection processes is perceived less as an active one and more as a passive one, where NGOs are simply recipients of one-way flow of information (Roniotes *et al.*, 2015). This in fact facilitates only one part of what is termed as 'access to information', one of the prerequisites of public participation. However, NGOs have a more crucial role to play which includes their contribution to raising public awareness and building the capacities of different stakeholder groups on key environmental issues; promoting co-responsibility and building consensus via enhanced stakeholder participation and partnership building; strengthening decision making and policy implementation by providing analysis, expertise and commitment from the inception and policy dialogue phase to the implementation phase at different operational or administrative levels (regionally, nationally and locally) for more creative and dynamic solution identification and problem solving approaches; filling in the knowledge gaps that stand in the way of effective decision making through participatory science, including data collection, collective intelligence, grassroot activities, participatory experiments (Scoullos *et al.*, 2002; Gemmill & Bamidele-Izu, 2002; Roniotes *et al.*, 2015).

Fig 1. NGO contribution to tackling marine litter

In this respect, this article features a collection of concrete MIO-ECSDE actions on the science-policy-society interface that address the growing threat of marine litter in the Mediterranean (and beyond). Marine litter is globally acknowledged as a major societal challenge of our times, which negatively impacts coastal and marine ecosystems and the services they provide, ultimately affecting people's livelihoods and well being (Gall and Thompson, 2015). Unfortunately, the Gulf of Elefsis is no exception. How marine litter and its inherent environmental, economic, social, political and cultural dimensions have been tackled by MIO-ECSDE illustrates the broad extent of involvement and interventions required for the protection of the marine and coastal environment.

Main lines of action

In full acknowledgement of the prominent role of NGOs in the realm of environmental governance, MIO-ECSDE, a Federation of some 130 Mediterranean NGOs working on Environment and Sustainable Development, in fulfilling its vision and mission, has developed and implemented a number of actions with regards to tackling marine litter, ranging from the monitoring and influencing of relevant policy, all the way to hands on activities. A brief presentation follows:

- Scientific and technical expertise contribution to all stages (from development to implementation) of the main legislative marine litter related processes for the Mediterranean, namely the Marine Strategy Framework Directive (MSFD) and the UNEP/MAP Regional Plan for Marine Litter Management in the Mediterranean. MIO-ECSDE has contributed to the consultation process of UNEP/MAP for the management of marine litter in the Mediterranean (2008) and the elaboration of the corresponding Regional Plan on Marine Litter Management in the Mediterranean (adopted by the Contracting Parties of the Barcelona Convention in 2013). In cooperation with UNEP/MAP-MEDPOL, the Hellenic Marine Environment Protection Association (HELMEPA), and Clean up Greece, MIO-ECSDE prepared the first Assessment of the status of marine litter in the Mediterranean (2008). Currently it is actively involved in the implementation process of Regional Plan, which provides for programmes of measures, including the elaboration of monitoring programmes. At European level, MIO-ECSDE actively contributes to the work carried out by the Marine Strategy Framework Directive/Good Environmental Status Technical Sub-Group on Marine Litter (MSFD/GES TSG ML), set up to advise on the standardization of monitoring methods and provide a forum for exchange of principles and best practices on target setting and assessment methodologies. It has co-led the task on the development of an overarching strategy for monitoring marine litter at European level, while it has also contributed on the development of technical documents, such as the "Marine Litter, Technical Recommendations for the Implementation of MSFD Requirements" (Galgani et al., 2011) and the Guidance on Monitoring Marine Litter in European Seas (Galgani et al., 2013). MIO-ECSDE is currently involved in the elaboration of the upcoming MSFD Technical Group 10 report on marine litter sources expected to be published in 2016. Furthermore, within this context it encourages and supports marine litter monitoring activities (citizen science) in a harmonized manner by promoting the guidelines developed at EU level and thus ensuring public engagement in filling in the data gaps as an essential tool to addressing marine litter appropriately.
- Close monitoring of the on-going marine litter policy debates and enforcement of the MSFD and provision of support to its member and collaborating NGOs to effectively and constructively participate in the process at Member States level. In this respect, in 2012, MIO-ECSDE was involved in the implementation of an on-line survey aiming to take stock of the NGO experiences in the MSFD related public consultation processes and to get a first idea of the quality of the Member State reports. The results from this survey were presented in the Marine Strategy Coordination Group meeting. In 2014, MIO-ECSDE together with 13 other European NGOs developed a joint NGO paper on Priorities for Programmes of Measures within the MSFD process. The paper was presented at the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) Inter-sessional Correspondence Group-MSFD Meeting and the DG ENV workshop on public participation and it was well appreciated by the participating Member States.
- Filling in the knowledge gaps that stand in the way of effective decision making through participatory science and community-based data collection initiatives. Within this context, MIO-ECSDE was tasked by UNEP/MAP to conduct a survey based regional assessment on abandoned, lost or discarded fishing gear and ghost nets, relying on information collected mainly from fishermen in eleven Mediterranean countries: Albania, Algeria, Croatia, Egypt, Israel, Lebanon, Morocco (Atlantic and Mediterranean side), Palestine (Gaza), Syria, Tunisia and Turkey. The objective of this survey was to provide insight on the situation in the targeted countries given that relevant information is lacking, fragmented and inconsistent. The main vehicle for collecting the needed information from the eleven countries was a questionnaire and the survey was carried out by NGOs (UNEP/MAP, 2015).
- Strengthening the science-policy interface and facilitating the efforts of policy makers and stakeholders in effectively dealing with the issue of marine litter in the Adriatic MacroRegion through the IPA Adriatic funded project entitled DeFishGear (www.defishgear.net). Since 2013, MIO-ECSDE has been leading the work package on monitoring and assessment. More specifically, it has been coordinating the development and implementation of a harmonized marine litter monitoring methodologies towards a comprehensive assessment of the status (amounts, composition, impacts) of

marine macro-litter (macro-litter) in the Adriatic. Furthermore, it is developing with the DeFishGear partners recommendations and policy options based on sound-scientific evidence and knowledge to meet regional and national objectives regarding marine litter (Marine Strategy Framework Directive, Regional Action Plan on Marine Litter Management in the Mediterranean, Ecosystem Approach, etc.).

- Improving the understanding of the science-society interface in order to address the urgent and complex challenge of marine litter via effective use of knowledge towards sustainable and responsible individual and collective actions. Together with eighteen other organizations from the EU, MIO-ECSDE was a key partner the FP7 project entitled MARLISCO (www.marlisco.net). MIO-ECSDE led the Awareness Raising & Education related component of the project and was also the Regional Node Leader for the Mediterranean. MIO-ECSDE substantially contributed to a series of actions such as: formulating clear messages based on sound scientific evidence and findings; enhancing the understanding of the prevailing perceptions and attitudes of different stakeholders on marine litter; inspiring action through concrete examples; empowering society through national fora; developing effective awareness raising and educational tools for informed decisions and responsible behaviour (Veiga *et al*., 2015).
- Raising of public awareness and promotion of co-responsibility for marine litter in the Mediterranean via different initiatives, such as the aforementioned MARLISCO project and the "Keep the Mediterranean Litter-free Campaign". The latter was developed in 2006, with the support of the Regional Seas Programme of UNEP and UNEP/MAP-MEDPOL and it was implemented by MIO-ECSDE in collaboration with HELMEPA and Clean Up Greece. The objective was to educate the general public, as well as stakeholders, such as the maritime industry, the tourism sector, agriculture, regional and national authorities, NGOs, the media, etc. Numerous international organizations and NGOs have conducted surveys and beach cleanup campaigns yielding data and information on marine and coastal litter pollution of the Mediterranean Sea. These efforts, which remain ongoing, are considered to be reliable sources of data and information.
- Enhancement of participatory science initiatives via mainstreaming citizen science into existing schemes (cleanup and awareness raising actions, educational materials); promotion of relevant technologies (e.g. Marine Litter Watch) and participating and working collectively within a think tank on citizen science & marine litter.

a

b

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Fig 2. (a) MIO-ECSDE performing a marine litter survey in Thesprotia, Greece within the framework of the DeFishGear project; (b) MIO-ECSDE carrying out a capacity building workshop on marine litter monitoring at Gothenburg, Sweden within the framework of the H2020 CB/MEP project; (c) MIO-ECSDE at Let's Cleanup Europe event in Athens, Greece; (d) MIO-ECSDE organizes the launch of the MARLISCO exhibition in Athens, Greece.

Conclusions

As scientists call for more research on global environmental changes in an effort to gain a better understanding of the human induced implications for all of life on Earth, it remains an inconvenient truth that if the world had acted upon the knowledge that the scientific community already produced, the state of many ecosystems would be different today (Vlachogianni *et al.*, 2016). A better understanding of the science-policy-society nexus and a strengthened respective interface is what provides the enabling environment and creative power to address the complex challenges that society faces towards sustaining the vitality and integrity of socio-ecological systems. In this respect, the NGO community has an essential role to play and can also offer useful insights with regards to the barriers that hinder an effective response from society on the issue of marine litter and other societal challenges.

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Training actions and educational interventions in the Gulf of Elefsis

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Abstract

The purpose of this paper is to present the training actions and educational interventions of the Elefsis Environmental Education Centre and the Environmental Coordinators of the Primary and Secondary Education of West Attica Directorates concerning the Gulf of Elefsis and its coastal zone. Informing, raising awareness and developing sound educational practices for the coastal environment were the key design parameters of the training actions and educational interventions. The subject areas regard the structure, function and evolution of coastal areas and the need for their protection. The pedagogical approach is based on the principles and methods governing environmental education projects. Student environmental groups, through exploration, cooperative and experiential activities, discover the coastal area of Elefsis, view it critically, identify positive or negative practices, become aware of outlooks and attitudes and make proposals for action.

Keywords: Environmental Education, marine environment, training, environmental actions and interventions

Introduction

The Greek Ministry of Education supports Environmental Education through the institutions of the Environmental Education Centres (EECs) and the Environmental Education Coordinators of the Directorates of Primary and Secondary Education. The EECs' role is to inform and sensitize young people and local communities on environmental issues, to provide educators with in-service training on Environmental Education, to produce teaching material and to collaborate with bodies such as Universities, local councils, NGOs, etc.

The Local Directorates of Primary and Secondary Education propose 'innovative action projects' concerning the environment to both Primary and Secondary school teachers. These projects are undertaken on a voluntary basis by teachers and students every school year. Their implementation is achieved through lectures, literature research, experiential approaches, field work and visits, reporting and presentation of outcomes (Iliadis *et al*., 2012; Papavasileiou & Mavrakis, 2013; Pitoska & Lazarides, 2013; Economou *et al*., 2015a). Very often student environmental groups select environmental projects related to the marine environment. Coastal areas undoubtedly constitute an important environmental, social and economic resource, as well as sensitive ecosystems. Intensive exploitation of marine ecosystems and the overconcentration of activities and population have led to serious environmental issues and hazards that cause destruction and irreversible changes and threats to the health and quality of these ecosystems. The main problems noted in coastal areas are habitat destruction, loss of biological diversity, pollution of land-based and water resources, land use conflicts and cultural heritage destruction as a result of uncontrolled growth (Economou *et al*., 2015a). The primary underlying causes of environmental degradation are currently considered to be the lack of information and education of individuals, as well as false beliefs concerning individual and collective responsibility (Scoullos *et al*., 2008). Education should lead individuals to acquire knowledge that will allow them to grasp concepts and phenomena pertaining to various environmental issues, so that they become aware of the role and responsibility of their own but also of various bodies in the creation and resolution of these problems. Marine environment and water related issues are primary concerns in environmental education projects. Through these projects, students should learn about the major environmental and development issues (Scoullos, 1995; Scoullos, 2008; Scoullos *et al*., 2008; Papavasileiou & Mavrakis, 2013; Economou *et al*., 2015b).

The purpose of the present paper is to briefly present the training actions and educational interventions implemented by the Elefsis Environmental Education Centre (EEC) and the Environmental Coordinators of Primary and Secondary Education of West Attica Directorates, on the marine and coastal environment of the Gulf of Elefsis.

Materials and Methods

The materials used for the present paper were the evaluation reports of the Elefsis EEC and the Coordinators of Primary and Secondary Education of West Attica for the school years 2013-2014 and 2014-2015. These also include pedagogic proposals and recommended activities for teachers and their environmental groups, as material for the implementation of environmental education projects on the aforesaid issues.

Results

The basic principles in the design and implementation of the pedagogic activities are group work, an experiential approach, making use of learning tools (e.g. ICT, measuring instruments) and the students' active participation throughout the project (Vassala & Flogaiti, 2005). These all contribute to the effective implementation of an environmental project that involves the coastal and marine environment, providing the possibility to be informed and realise the importance of its preservation and protection. Thus, students get acquainted with the coastal environment of the area in its social, historical and environmental dimensions, discover its values, comprehend and evaluate human interventions, so that they become sensitised and their ability to seek solutions as future citizens who will contribute to a sustainable future is fostered. Likewise, teachers are trained in the exploitation of these techniques.

Elefsis Environmental Education Centre (EEC)

The Elefsis EEC runs the programme "Coastal Elefsis…A neighbourhood in the Saronikos Gulf", which focuses on the Gulf of Elefsis and its coastal zone and has been attended so far by 84 student environmental groups, with 1,990 students and 155 teachers.
The EEC provides in-service training for teachers by organising seminars on the marine environment and the sustainable management of urban and coastal areas. Such were the following: "Environmental routes from the Aigosthena castle to the Kithairon forest", "Environmental trail through the city of Elefsis", "Actions for the environment and sustainability in Western Attica", "The environment converses with History" and "Coastal Elefsis…A neighbourhood in the Saronikos Gulf". 306 teachers in total were trained in these seminars.
In addition, other actions are organised such as: participation in the "Researchers' Night" hosted by the NTUA (National Technological University of Athens), the School Activities Festival of the Directorates of Primary and Secondary Education of Western Attica, the debriefing workshop of the Network "The Sea" coordinated by the Argyroupolis EEC, the workshop "Environmental games in Marine Ecosystems", the presentation of the school activities projects of the Directorate of Primary Education of Western Attica at the site of the Aischyleia Festival, the MAREXPRESS showcase of the NKUA (National and Kapodistrian University of Athens) with workshops on the classification of marine organisms and marine biodiversity, the Vourkari wetland and Koumoundourou Lake for the protection of these areas.

The Elefsis EEC is a partner in the following Networks: "Corinthian Bay: our little sea", regionally coordinated by the Amfissa EEC, "The Sea", nationally coordinated by the Argyroupolis EEC, and "The Ports of Greece", nationally coordinated by the Drapetsona EEC.

The experience gained in all of the above is used for scientific output in the form of announcements in scientific conferences, such as, for example: the International Conference "Environmental Prospects of the Gulf of Elefsis", the 11th Panhellenic Symposium on Oceanography and Fisheries, the 7th Conference of P.A.T.E.E. [ΠΕΕΚΠΕ] (Panhellenic Association of Teachers for Environmental Education) and the 3rd Panhellenic Conference of HEL.P.S. (Hellenic Phycological Society).

Primary Education

The goals set for Primary Education include developing and cultivating eco-consciousness in children so that they become active citizens. Thus, the experiential projects designed for the pupils take into account all relevant pedagogic aspects. Design is targeted so that physical action is accompanied with knowledge, exercising mental skills, fostering critical thinking and exercising social skills like team spirit, participation and solidarity. We mainly aim at changing outlooks and attitudes, which will accompany pupils throughout their lives and later as adults. During all these actions, effort is made to involve scientific bodies, environmental organisations, local councils and voluntary citizens' organizations, with the aim of disseminating the experience gained. The following actions are indicative:
A) Cleaning up the Aspropyrgos beach, recording and separating the rubbish, followed by three pedagogic relay games, while exploiting cultural elements of the area. 100 pupils from four Primary schools took part in this.
B) With the pupils at Koumoundourou Lake: one more wetland of West Attica became the field of environmental action for 200 pupils from eight Primary schools. C) The children clean up Varea: as part of the campaign "Clean up the Mediterranean", the beach of Megara was cleaned up, with the contribution of local authorities and environmental organisations, by 90 pupils from three Primary schools. To help disseminate the experience from sea-and-shore related projects, a wiki has been created (http://aktofylakes.wikispaces.com/), where teachers and their pupils publicise their actions.

Secondary Education

From 2013 to 2015, 19 environmental education projects were implemented with the voluntary participation of 65 teachers and 450 students. Project activities comprise lectures, literature research, experiential approaches, field work, educational visits and presentation of outcomes. For secondary education, the pedagogic aims set are the following: for the students to develop attitudes that will allow their contribution to sustainable development, skills so that they can work in groups, a critical way of thinking, to recognise ecological problems and the reasons behind the degradation of the marine and coastal environment of the Gulf of Elefsis.

In the implementation stage, students make use of bibliographical and digital material, visit educational institutions like the HCMR (Hellenic Centre for Marine Research) and the EECs (Environmental Education Centres). Finally, project outcomes are presented within the school and at school activities festivals.

Conclusions

This paper presented the training actions and educational interventions of the Elefsis Environmental Education Centre and the Environmental Education Coordinators of Primary and Secondary Education of West Attica focusing on the Gulf of Elefsis and its coastal zone. The whole effort is characterised by a holistic approach towards the issues related to the coastal environment. Informing, sensitising and developing sound practices towards the coastal environment constitute key parameters in the design of training actions and educational interventions.

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Strategic Guidelines for the Integrated Coastal Zone Management and Sustainable Development of the area surrounding the Gulf of Elefsis

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Preamble

Major elements concerning the Gulf of Elefsis and the surrounding area, the evolution of anthropogenic pressures -mostly pollution and environmental degradation - the invested efforts for addressing the problems and some of the most important scientific and management results are considered herewith. They have been presented in previous works of my team and other colleagues, as well as in the articles included in the present publication.

It is outside the scope and ambition of the present document to provide thorough and detailed recommendations on the sustainable development of the area around the Gulf of Elefsis, a task that requires even more systematic work and coordinated input from many stakeholders and, ideally, an official mandate accompanied by a set of prerequisites and definition of the mission and the governance context for both the elaboration of the Management Plan and its implementation. Being in the exceptionally privileged position of working, on one hand, for more than 40 years in the region, assessing the pollution pressures and the overall evolution of the environment in the area, and on the other, being the principal author of the so called Integrative Methodological Framework (IMF) for coastal areas (see UNEP/MAP-PAP/RAC, GWP-Med, UNESCO-IHP (2015)), I took the initiative of describing in the present article the main Strategic Guidelines that need to be followed, in my point of view, for the drafting and adoption of the Integrated Management Plan of this area. In doing so, and for the purpose of this phase, many of the statements or judgments made in this work are not extensively supported with data or references, nevertheless they should be understood as "tested" and/or substantiated by a long series of observations, going beyond a simple "expert judgment".

What kind of management Plan?

It is clear that the area of the Gulf of Elefsis (GoE) needs a fully Integrated Management Plan which will combine basic physical planning requirements with coastal zone management, marine spatial management of the entire gulf and management of the catchment area surrounding the gulf. Such a plan should include provisions for water resources management, the management of biotopes and biodiversity, as well as the handling/maximization of the ecological services, based on an agreed by all key stakeholders, including civil society, **vision** defining the overall future and destiny of the region. For these Strategic Guidelines to become fully understood, some indicative examples and proposals have been included and briefly presented.

To whom is this document addressed?

The present document is meant to encourage and facilitate the start-up of the process of systematic planning and it is addressed to all decision makers, primarily the Authorities of the City of Elefsis, but also to those of the other cities of the region and the local stakeholders, public and private, the Prefectural, Regional (Periphery), National Authorities and all those who may influence directly or indirectly the state of the environment, the economy, the society and governance in the region, affecting each one and all the facets of the Sustainable Development "tetrahedron" of the region. (figure1).

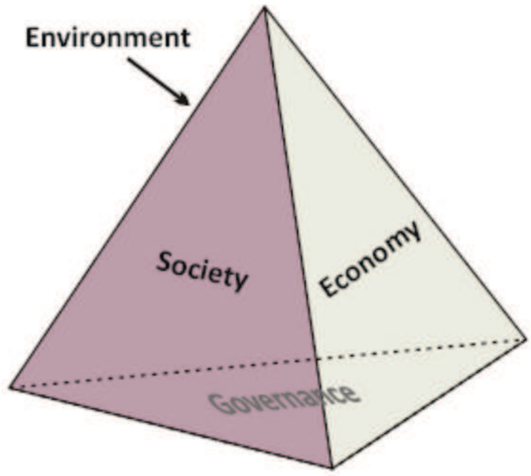

Fig 1. The tetrahedron of sustainable development, where Governance is considered as a fundamental facet for the achievement of Sustainable Development.

Where do we stand as it concerns the DPSIR Framework?

A very instructive depiction of the dynamic nature of the needed for the GoE planning and the close relationship of the integrated plan with governance and the policy cycle is the DPSIR (Driving Forces – Pressures – State – Impacts – Reactions) sequence or framework developed by the European Environment Agency (EEA, 1999). It is a descriptive, simple and flexible cause-consequence loop which illustrates the links between human activities and environmental processes. It has been widely used in environmental research and communication, as it helps stakeholders to understand the importance of natural systems, such as the area of the GoE in decision-making, as well as the repercussions of the various complex industrial, commercial, etc. economic activities which have developed in the area (Figure 2). The DPSIR framework, even if it might sometimes be disturbed by unexpected external parameters (such as political decisions concerning energy policy, placement or functioning of military installations, etc.), indicates that the initiation of an integrated plan corresponds to the responses phase of a well documented and communicated cycle where the pressures and impacts are adequately understood and, therefore, there is sufficient public support or even demand for a coherent strategy to address the problem.

The long standing scientific study of the area of the GoE and the public discussion triggered by the scientific results have contributed to such an understanding. Drivers, pressures, state and impact have been documented and analysed for many years and from different points of view.

Particular emphasis was given until now on the pressures, as well as the State of the environment and to some extent, to the impacts. A series of small or major gaps still exist. We have also analysed a series of policy responses and measures, several of which have been quite successful, while others were less effective. Other management responses, such as a series of plans, proposals, etc. have been abandoned even before any attempt to implement them as a result of fragmented sectoral approaches by specific Ministries or administrative departments and/or because of rapidly changing environmental, socioeconomic and political conditions.

In conclusion, as it concerns the GoE itself and the surrounding area, some aspects, sectors and issues are not fully clarified, and feedback, monitoring and appropriate adaptations are needed and should be considered as a necessary, integral part of the overall process of the plan preparation and implementation.

Furthermore, important limiting factors for the development of proper responses able to act as strong driving forces for the progressive improvement of the environment and development of the region are, on the one hand, the lack of a comprehensive and understandable, by the citizens, medium and long term management plan for the entire country (on which little can be done) and, on the other, the lack of a coherent, well defined and articulated **vision** for the future of the region that can be adopted by the widest possible spectrum of stakeholders. The latter is almost entirely in the hands of the local community, is part of the plan and its formulation requires the synthetic and practical integration of scientific knowledge and everyday practice. This is exactly the area to which the present document aims to contribute.

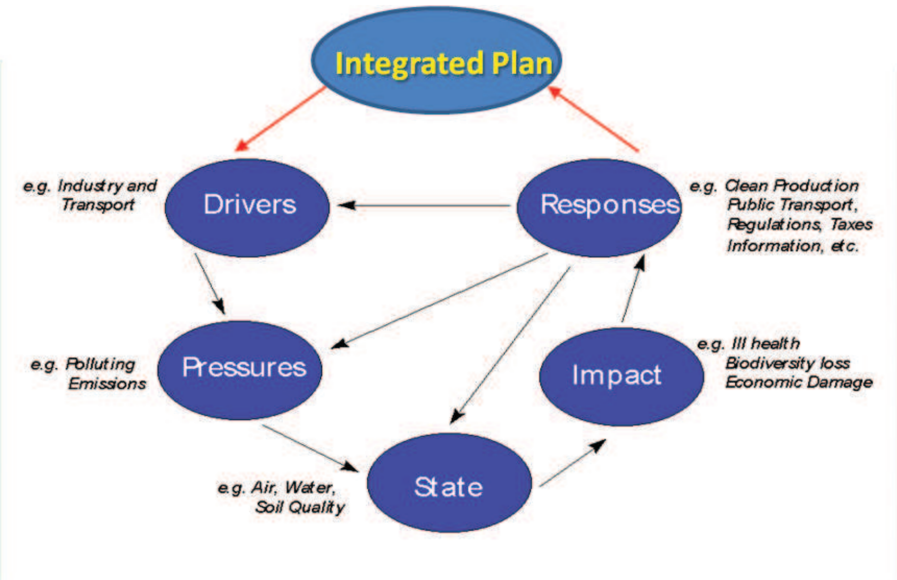

Fig 2. The DPSIR Framework informs the preparation of the Integrated Plan

Few practical suggestions to enhance the usefulness of the Plan to be prepared.

In elaborating and implementing truly integrated plans, which will also fulfill many conventional obligations of the countries, three clusters of actions should be considered:

1. Planning by keeping in mind that no plan is perfect from the very beginning and "adaptive management" is the way out in "correcting" and gradually improving the design through consultation and expert judgment during the implementation phases. In this respect the inclusion of "no regret measures", is advisable. Several of them are usually identified by local communities or scientists working for years in the region (e.g. by avoiding building infrastructures in vulnerable to flooding areas, by promoting non conventional water resources and waste recycling options, etc.).
2. Using nature, ecological services and natural capital in an appropriate way as capital and services by enhancing the functions of natural regulation systems (e.g. by re-naturalizing areas that could act as a natural buffer or water detention zones, such as transitional and intermittent wetlands for absorbing flood pressures, pollution). This is the main message of the Ecosystem Approach (EcAp).
3. Securing/preparing/providing both technical and human resources for adaptation to climate variability and change; and to increase the robustness and resilience of the systems involved to climate change and also to emergencies and extraordinary events of whatever nature. This also includes elaboration and testing of contingency plans, trainings and early warning systems, and also putting in place relevant facilities (e.g. high-capacity removable pumps), which could provide exceptionally useful services at difficult times and enhance the efficiency of the operation of an integrated plan even before it is made fully operational. All the above are also important in plans related to adaptation to climate change which Greece has agreed to prepare.

The planning process and its stages

In order to achieve the necessary integration in the area of GoE a planning process is suggested, according to the IMF, to guide the step-by-step preparation of the plan, and identify the issues for permanent and focused integration of coastal, catchment area and aquifer/groundwater management. The guidelines that follow are elaborated in a very "unbalanced" (as expected) way into the relevant sections representing the five stages of a planning process (see figure 3), within which the Integrated Coastal Zone Management (ICZM) ingredients are combined with those of Integrated Water Resources Management (IWRM), as implemented in Greece, through the EU Water Framework Directive (WFD), as well as with coastal aquifer and groundwater management, the EcAp principles and several other important inputs. More specifically, the planning takes into account the experience of several PAP/RAC Coastal Area Management Programme (CAMP) projects and a methodology, introduced under the EU-funded SUDECIR programme (Scoullos *et al.,* 1999). The aforementioned programme was implemented with emphasis on tourism on the island of Rhodes, Greece (Scoullos, 2004), and more recently in the Lake Bizerte area, in Tunisia, within the framework of Horizon 2020, obtaining an agreed plan/framework and a "Charter" *(www.h2020.net/news-andevents/news/107-ceremony-for-the-signature-andadoption-of-the-charter-for-the-sustainabledevelopment-of-lake-bizerte.html; and www.h2020.net/ news- and- events/news/95-the-lakebizerte-charter-a-step-towards-its-sustainabledevelopment-horizon-2020-enhances-stakeholderparticipation-for-the-integrated-management-of-lakebizerte-in-tunisia.html)* as well as a series of good practices on IWRM plans accumulated in the GWP Toolkit (*www.gwp.org/ToolBox*) and through the work of the EU FP7 PEGASO project (*www.pegasoproject.eu*).

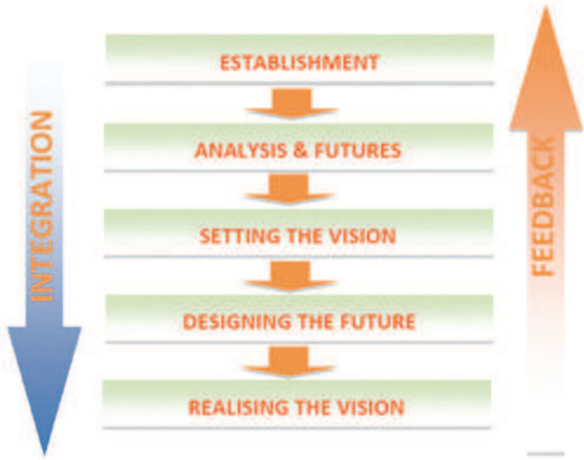

Fig 3. The proposed five stages Plan preparation and implementation process

Establishment

The overall aim and objectives of the establishment stage is to define/make known the intention by the competent GoE authorities for drafting the plan and identify the "convening" authority/the "initiator" authority often a "Champion" or body responsible and/or willing to take on the overall coordination of the planning.

All major parties who should be involved from the State, regional or local authorities and key stakeholders should be identified and effectively invited and involved, and an operational foundation should be established for the subsequent preparation of the plan and its implementation. A "Core Group" or "Task Team" is formed and this generates the process of understanding the challenges the area faces, including the differences in perceptions of those challenges. This "Core Group" which may also include committed experts and/or a "champion" university, begins building a constituency of support for the plan.

In the initiation step, efforts should be focused on clarifying what the mission context and mandate are.

Who is asking for the integrated plan? Which authority will lead and take the main responsibility for the plan and how is this going to be used? To what extent and how extensively can ICZM, IWRM, aquifers management, etc., be integrated? What statutory/conventional purposes or obligations towards international conventions will the plan serve or may cover? What are the likely driving forces to support the planning process? What are the available time and financial frameworks within which the plan should be delivered?

At a second step, the circle of those involved is extended. All partners interested in the plan's preparation should be identified, informed and they should agree in principle on the most appropriate/desirable final legal status of the plan. All relevant national, regional authorities should be aware and in principle, if possible, signed up to the preparation of the plan and help identify and agree on the body or bodies responsible for its adoption as soon as possible. All the above could eventually be put in a first document, a so-called "foundation statement", issued by the convening/initiator authority, sometimes co-signed by other key partners.

In the same step, coordination mechanisms for the planning process (steering group or committee, the core group or task team, the technical group and/or consultative group) could be established with provisions for amendments and inclusion/ cooperation/co-option/ employment of other parties, as necessary, conditional on the resources available. Depending on the site and scale of the undertaking, the steering committee and the core group /partners may or may not coincide. It is not the intention or purpose of this stage to achieve a fully detailed scientific analysis of the state of the plan area or the complex interrelationships between issues. Rather, the purpose is to specify the system, achieve a picture of the likely range of human and natural forces, the existing sectoral policies and plans, as well as their potential interrelationships to be used as a focus for discussion, challenges, opportunities, analysis and the identification of priorities in subsequent stages. At this early stage, effort should also be directed to creating tools for engaging stakeholders through good design of the process and supporting documents in a non-technical language by employing appropriate tools. The Core Group or Task Team should in the case of the GoE be led by, or at least include, the Authorities of the City of Elefsis and ideally all other cities and communities of the Thriassion Plain but also the northern part of the Salamis Island. The Port Authorities, key industries and/or their associations and associations/unions of workers, fishermen, farmers, the responsible of the military installations of the region, related "knowledge" generators (Universities, Research centers/Agencies, etc.) should also be involved.

Key tasks of this step are to clearly define the territorial boundaries of the Plan area, agree the governance context, review and agree on the stakeholders to be involved and at what level/degree elaborate mechanisms to enhance their involvement and start working on the potential vision.

In the case of the GoE, the entire catchment area, including the water body of the Gulf, should be considered. This is scientifically self-evident but not necessary desirable from the administrative point of view. Therefore, at this stage this could be decided and a convenient solution, if problems arise, is the differentiated intensity of management provisions in some of its parts. Furthermore, for the purpose of developing specific activities or projects for the Gulf or even for specific cities, such as Elefsis, the "boundaries" of the Plan area could be "expanded" in order to create the necessary "alliances" and "frameworks".

An example demonstrating this case may be the consideration of a wider area including even Piraeus with a minimum of "common" management provisions. Such an "expansion" will be necessary for facilitating the combination of the candidacy of Elefsis for the "Cultural Capital of Europe, 2021" with that of the city of Piraeus with one major "common" advantage (shared also by Salamis island): the inclusion in the candidacy portfolio as a main asset and justification of the proposal, of the world famous naval battle of Salamis which took place at the entrance of the GoE between Greeks and Persians in September of 480 BC. The year 2021 coincides with the 2500 year anniversary of this event which determined the history of humanity.

This is only one - but important - example of an "opportunity" that demonstrates that by adopting such an approach, significant aspects of timing and, eventually, of funding of the integrated planning, could automatically be introduced/secured.

Analysis and futures

The overall aim of the analysis and futures (alternative scenarios for the future) stage is to establish an operational foundation for the subsequent preparation of the plan and its implementation and engage stakeholders in the search for concrete results.

The objectives of the analysis and futures stage are:

1. 1. to substantiate the issues and problems through more rigorous analysis and review, describe the present state and likely future trends
2. 2. to evaluate the natural, technical, financial and managerial capacities in the plan area including future options resulting from climate change impacts
3. 3. to assess system change and effective response to external changes and opportunities
4. 4. to identify the strategic options of the plan area development for achieving its goals
5. 5. to identify carrying capacities and conditions for the allocation and use of the respective marine and land parts of the plan area in accordance with the identified expected changes
6. 6. to generate and test alternative views for the future through the use of tools and scenarios
7. 7. to lay the foundations of future cooperation and implementation through pilot actions and the identification of potential future funding sources.

Key tasks of this step include the:

- Building of the evidence: closer analysis of key issues whenever needed in completing the DPSIR policy cycle
- Identification of "futures" by elaborating alternative scenarios

As said already, the area is adequately **studied and analysed** although some identified gaps (on some missing statistical data, etc.) need to be filled in. Overall, the area hosts a very high percentage of the industrial activities not only of the wider metropolitan area of Athens with approximately 4.5 million inhabitants but also of the entire country. Therefore, it receives considerable loads of pollution which reached a maximum in the late 1970s and into the mid 80s. Since then the situation has improved significantly, as a result of three factors or rather their combination:

1. Improvements in industrial production processes and technology, following the adoption by major industrial complexes of BATs, reducing, therefore, wastage of raw materials and energy and pollution emissions too.
2. Important investments in pollution reduction/waste treatment technologies for the implementation of the advanced EU policies, strategies and legislation.
3. Closing-down of industries or reduction of their production/operation due to the prolonged economic crisis in Greece.

Recent research has shown that the contribution of factors 1 and 2 is significant and in some cases even greater than factor 3.

The environmental conditions that we have found through the "Aristeia" program of the University of Athens and a series of monitoring and research projects are, today, in general, good (results are given in the previous articles of the present issue). Still, many problems exist, particularly in parts of the eastern part of the gulf and in the operation of certain industrial installations (e.g. refineries) that must be urgently dealt within in an effective way.

The overall strategy that we had promoted persistently in the past was the preservation at any cost of a good natural environment with minimum industrialization in the western part of the Gulf and the northern coast of Salamis island. This strategy was followed by all governments and stakeholders throughout the last 40 years and has been proven very beneficial. As a result of it we allowed "pockets" of thriving biodiversity to be maintained and under improved environmental conditions they facilitated the natural reintroduction of benthic and other species, some of which are rare such as *Pinna nobilis* and *Pecten jacobaeus*; we have also seen, in the summer of 2015, dolphins playing in the gulfs' waters and even the appearance of a turtle *Caretta caretta* (!!) in the western part of the gulf.

Apart from the reduction of polluting industrial activities in the gulf, the installation of new de-polluting technologies, the improvements in production systems and legislation, we have also the very positive impact of the operation of the new waste water treatment plant for the sewage of Athens on Psitaleia islet and the closing down of the fertilizer factory in Drapetsona, both located just outside the GoE but directly influencing the quality of its waters because of the prevailing water circulation.
As for the **scenarios**, these are useful tools in linking e.g. the drivers, main characteristics or assets of a region to the aspirations of the society facilitating the building of the necessary common "Vision". There are many variations of scenario-producing processes, but they can be placed between two extremes:

1. A limited number of expert top-down scenarios generated formally by the planning team and subject to a formal consultation – often consisting of "high" and "low" intervention options.
2. A fully participatory process involving facilitated workshops, etc., at the end of which participants may come with their own "agreed" scenario based on aspirations and opportunities. It is important to note that scenario making is not, *per se*, a decision-making process.

In the GoE, although there was never a systematic discussion based on well-articulated alternative scenarios, several stakeholders have presented considerably diverging views for the future, from a region fully and exclusively devoted to industry, mostly a heavy one, to complete de-industrialization and "return" to agriculture with parallel rehabilitation and restoration of ecosystems targeting fisheries and tourism as key economic sectors.

Apparently, the majority of stakeholders' views, as expressed in a number of occasions (including during the presentation of a draft of the present document at the City Hall of Elefsis on 11-12th September 2015) indicate that neither of the two extremes could gain public support or offer tangible benefits for the majority of the stakeholders of the region, but rather follow a "mid-way" common sense. Therefore, the Vision to be elaborated should take seriously into account every single "strength" and "asset" or "capital" of the region and, even more importantly, their creative interaction and combination in a dynamic "sufficient whole" which has a "strength", interest, as well as a market and intrinsic value, greater than its individual components.

In the case of the GoE and the area around it, the major assets/capitals on which further scenarios and the "Vision" could be built are the following:

The **natural capital** represented by the Gulf of Elefsis itself and specific biotopes connected to it (such as the Koumoundourou Lake and the Vourkari wetland) as well as the mountainous ecosystems in the borders of the catchment area.

The Gulf is a true "treasure house" of extremely rich biodiversity and formidable resilience and capacity of natural recovery. It is a main production area of seafood, mussels (through mussel growing farms), and wild "kydonia" (*Venus verucosa*), oysters and several other species of seafood. We have recorded in the past both abrupt and/or gradual disappearance of species, some of them rare (such as *Hippocampus*, *Spondylus gaederopus*, *Arca noae*, different types of *Pectens,* etc.), as well as "explosions" of the populations of specific species, for instance, of Ulva macro-algae, jellyfish, aplysiae, etc. Today we have a rather balanced system with a natural reintroduction of indigenous species (e.g. *Pinna nobilis, Pecten jacobaeus,* etc.*)*, without forgetting that the gulf is a quite hospitable environment for alien species.

The second capital is linked to the fact that the area **is the heart of the industry** of the country. This heart is seriously injured and both the society and the State must help it to "detoxify", recover and function in a new framework that could act in a renewed fashion and can properly operate for the wellbeing of the whole body, the entire area, as it is supposed to supply it with adequate "clean blood".

The third capital is the great **cultural/archeological** linkage. Elefsis has not only a major Archeological site and an important Archeological Museum but also a big intangible capital that is linked with the above: the mythological, historical and spiritual significant "Elefsinian Mysteries" and their legacy.

Finally, there is a series of other assets/capitals related to its beaches, sport fishing, agriculture, religion tourism, recreation, cultural diversity, gastronomy, etc., all of which may contribute to the creation of an inspiring and powerful **vision** and trigger prosperity and sustainable development.

Setting the Vision

This is an extremely crucial step for the GoE area and therefore this document elaborates more on it, following also the previous part on scenarios and assets.
The overall objective of the setting of the vision stage is to engage stakeholders in the joint vision for the plan area, and to set the course for the eventual shape of the plan and its implementation. From a selected set of alternatives, that are proposed herewith, the Core Team, in agreement with stakeholders and based on the necessary trade-offs between different interest groups and uses, will propose the optimal long-term vision. A vision should be both rational and inventive: "Prospective is above all an attitude of mind (…) and a way of behaving (…) If it has no future direction the present is empty of meaning (…) The rational and the inventive trends of strategic planning are complementary, only *prima facie* they seem opposite" (Godet, 1987). The vision should include, or be complemented by, a set of goals so that we know what we want to accomplish, who are committed to this vision and eventually how each group will contribute. The "when" and the "what" will depend on how much it will cost and what the consequences and benefits will be. More detailed work elements of this stage include:

1. Building consensus – reaching agreement among stakeholders and the wider community on the key problems, issues and priorities for the plan area.
2. Preparing the vision statement (setting the direction) – observing the priorities and the consistency of the objectives of the plan.
3. Measuring success – selecting the necessary set of (at least preliminary "core") indicators to measure the success of both the planning process and its outcomes.

The common vision, in my point of view, should be of a plan that is innovative, tangible and implementable with the maximum public support and ownership for a really "model" region. A region of creative coexistence of natural, cultural and manmade/industrial environment, where other important activities such as aquaculture, fisheries, education, recreation, etc. will be integrated harmoniously.

A basic part of the Vision is to identify and remove first, all what the stakeholders consider unanimously as "unsustainable", "unacceptable" and "damaging".

One such issue concerns the pollution loads discharged in the coasts and waters of the Gulf in the form of "litter". This problem is serious and it is clearly linked to loss of any sense of responsibility and respect for the common goods and constitutes the true background of the crisis experienced not just in this area but in the entire country, at large. We are in need of a cleaning program for any type of litter ranging from urban waste to abandoned ships and by means of legal mechanisms that have been implemented in a number of European countries, this can be done, perhaps not immediately but within a few years, based on a specific timetable. These beaches can be cleaned and the collected solid waste and litter could be recycled either as scrap, or as alternative fuel in the cement industry, and therefore the whole coastline will be upgraded.

Some other unsustainable practices have to be addressed such as: industrial emissions, illegal or uncontrolled building, "occupation" of part of the sea-shore not allowing the public to have free access to the sea, illegal fishing, mechanical collection of benthic species or illegal mussel-growing farms. All the above should and could be regulated according to enforcement of existing legislation and should be accompanied with better patrolling and enhancing safety and security of the activities in both the terrestrial and the marine parts of the gulf.

It should be stressed that, because of the high density of sometimes incompatible activities in close vicinity to each other, accidents in the region might have extremely detrimental implications. Therefore, apart from strict and careful procedures for issuing permits for operations and new, or extension of, installations, contingency plans, capacity building and systematic awareness raising campaigns for the public should be in place.

Among the awareness raising and educational interventions it is necessary that at schools but also at all levels and for all age groups, to enhance the knowledge, understanding, familiarization, respect and "stimulation of pride" of the inhabitants, about the natural and cultural environment of their region. This requires systematic visits and *in situ* projects. There are already many extremely successful projects at the schools with the support of the Environmental Education and Education for Sustainable Development Center of Elefsis that needs to be further supported and expanded. Among them are projects carried out in the two special biotopes of the area namely Vourkari and Koumoundourou lake.

We should not forget that the whole coastline of the eastern part of the gulf was a major biotope and habitat, a wetland, until the end of the 19th century, gradually disappearing in the first half of the 20th century because of the construction of the military airport and the ensuing industrialization. If we help the system by using the excess amount of flood waters at a rather very low cost, certain parts of the old wetland could be revived (concrete evidence already exists in some parts) and we can have a triple benefit; apart from maintenance and reintroduction of wild life, a replenishing of the underground aquifer and, at the same time, protection from flooding. The coastal underwater sources of fresh water in Vlichada and at other points of the western part of the gulf constitute additional mechanisms of self-purification and renewal of the waters of the gulf, provided that we can ensure that this mechanism will be fully and continually operational.

A higher visibility and recognition of the importance of both the natural and cultural capitals may help. As an example, concerning the natural capital I believe that the GoE could be designated as a Biosphere Reserve under the UNESCO Man and the Biosphere Programme (MAB/UNESCO).

The Greek National Committee of MAB/UNESCO, is willing to assist the local actors, if they wish to characterize the area of the gulf as a "biosphere reserve", with a very small part of the gulf as a "core", where dredging, the use of divers and mechanical tools for the collection of clams, etc. should be strictly prohibited. A limited "buffer zone" and an extended "transition zone" with differentiated management provisions will be the model. This is an idea "stolen" from the Norwegians, who on a similar area, are trying to promote the co-existence of rich biosphere with an, in principle, "very polluting" human activity. They wanted to include a whole oil extraction platform in a biosphere reserve emphasizing that the sustainability model of the future requires "coexistence" and a high level of responsibility.

The protection and promotion of the natural capital is closely connected to the further improvement of the quality of the waters of the Gulf, the further reduction of industrial pollution and therefore the proper management of industrial activities so as to become sustainable ones. This transformation is in the spirit and according to the provisions of the "circular" and "green" economy provided by the European Union and the post 2015 Programme of the UN and the Sustainable Development Goals (SDGs) agreed by all countries, including Greece, in New York at the end of 2015.

The above should be linked with a vision where the industrial heart of the country is maintained and becomes sustainable, which is also the only "way forward" and "way out" of the current crisis. There are three basic principles being promoted in relation to the advancement of such a vision about industry, particularly useful for industrially "aged" areas such as the vicinity of Elefsis/Aspropyrgos:

1. Help, to a large extent morally, industries that are trying to become sustainable. Recognition of the positive efforts is equally or more important than mere criticism. This aspect needs to be introduced or strengthened in the region and it is not easy because of a very "charged" past. However, it is the necessary element of a new "era".
2. Reinforcement and encouragement, supported with incentives, for the installation in abandoned older industrial buildings or spaces, of new, modern, clean, green industries, which demand less space, are more specified and have lower energy, water, and raw material demand and minimal environmental footprint, while generating more income.
3. In all countries there are policies in place to protect and safeguard clean, unspoiled agricultural land by discouraging installation of industrial and commercial activities on them. Instead, spaces previously occupied by industry are "reused" for industry after proper clean-up actions. The "reuse" of industrial land maintains also their value. In the UK, for instance, there are legal provisions demanding that 60-80% of new industrial activities should be placed in old "brown" areas. Such examples need to be studied, properly adapted and introduced in the Thriassion Plain to allow for the revitalization and introduction of a new generation of enterprises (mostly SMEs) based on "new knowledge".

The incentives for such a shift must be sought in the pre-existing local know-how, the proximity of the area to major markets such as Athens, the pre-existing industrial activities and their modernization, as well as the encouragement of the use or valorization of their products and by-products and waste as raw materials for other industries ("circular economy approach"), further improvement and rational utilization of transport infrastructures (including highways, the Elefsis harbor, etc., always respecting and advancing a set of safety and quality prerequisites), etc.

It is important that the vision about the future of the industry in the region is shared by the widest possible part of stakeholders within and outside the industrial sector, including organized groups and individuals. An honest relationship between society and industry, based on realism, the mutual understanding for a need for harmonious coexistence and a cultivation of a new spirit of cooperation for identifying and implementing mutually beneficial solutions is critical. I do not suggest nor pretend that the building of mutual confidence will be easy or rapid and that all issues will be automatically settled after a long period of suspicion, conflictual relationships and mutual lack of understanding and trust between a large part of industry, on the one hand, and a large part of the society, on the other. However, the vision is needed by all parties and we have quite a long list of similar to the Elefsis sites where such an approach became not only possible but also very successful (see Barcelona, Liverpool, Manchester, Glasgow, Gothenburg, Hamburg, etc.). In most of these cases both the levels of industrial pollution and the relationships between industry and society were much more difficult to deal with than in the case of Elefsis.

As it concerns the cultural capital the vision is to "develop" and properly promote the importance of Elefsis as a "site of great interest". In antiquity, Elefsis was a destination equal to Olympia and Delphi. The prestige of the "Elefsinian Mysteries" was huge if we think of the awe with which Emperors (even Nero) approached it. Nero, despite his gifts to the temple, was never a participant in the Mysteries. He was excluded because a person who had committed a crime could never participate.
New signs with annotations could be put forth on many parts of the "Iera Odos", for instance at the sanctuary of Aphrodite, Koumoundouros Lake (where bloodless sacrifices and other ceremonies used to take place), etc., etc. The historical monasteries of the area could also be promoted, as well as many old agricultural (e.g. oil mills) and industrial buildings that could be restored, promoted and used, establishing in them new museums, artistic creation workshops (as in Hamburg, Johannesburg, etc.) "boutique" wineries and other activities. Through this transformation the area can soon acquire a powerful cultural stamp. If the necessary prerequisites for placement, guarding and security are fulfilled, a first class museum of African Art with more than 1000 exhibits is considering to be installed in the area, and others could follow.

Cultural activities could be combined with the creation and transmission of knowledge such as hosting Archeological and Scientific Conferences, University Campuses, experimental industrial plants and long-term projects (e.g. for decommissioning and rehabilitating industrial sites, etc.). We are examining already the closer connection of the Environmental Education and ESD Center of Elefsis with the UNESCO Chair and Network of the University of Athens and MEdIES.

Furthermore, an **alternative tourism** could very successfully be developed in the area, because of the attractions this area offers in combination to its close vicinity to Athens (i.e. daily excursions). Alternative tourism could be based on the aforementioned important cultural incentives if combined with a series of other advantages such as beautiful beaches for swimming and angling, especially if these beaches are increased and if they are kept clean and accessible to the public, connected also by boat. Gastronomic tourism could also be developed, based on already very many excellent places for seafood, roast meet, etc. to be further enhanced without too much effort, based on local products; the clams, mussels, etc., from the gulf, poultry and organically grown lamb and goat meat. The above, combined with a valorized multicultural "color" of Elefsis can promote the area as a gastronomic attraction pole in "the west of the city".

For special kinds of tourism activities, the military airport, under prerequisites that are very feasible using experience from other similar cases, could be developed to host model aircraft displays, flying clubs, etc. Finally, the many attractions (biodiversity, antiquity sites, food, nightlife), could make Elefsis a popular destination for secondary school tourism.

Designing the Future - Finalising the Plan

This is a very important stage of the planning process, particularly as it concerns the formal acceptance of the Plan. The ultimate aim of this stage is to lay the foundation for the management towards sustainable development. At this stage specific activities and an investment portfolio will be developed/secured.

The shaping of the proposed vision and its transformation into specific measures requires a powerful partnership of all the municipalities and settlements around the gulf in order to shape a joint win –win strategic development plan. The industry and trade sector must take initiatives; they owe it to the area. A series of tangible actions necessary to realize the vision should be based on will, inspiration and use of all available funding opportunities, national, EU regional funds and private investment, local and foreign. In the previous chapters a set of ideas for appropriate interventions have been mentioned and briefly described.

It should be stressed that the management plan must also make use of everything useful that has been done before. Nothing should be wasted, particularly plans that are stored in drawers. Everything should be considered and examined, not under the light of suspicion but in a spirit of synthesis and consensus. This will create trust, ownership and support.

Realising the Vision – Implementation

This is a very important and long-lasting (ongoing) stage, where decisions and policy design are implemented on the ground. It refers to a period that is suggested by the steering group or committee and agreed by the governance structure. It should be long enough to allow for proper feedback and adaptive management to make the necessary adjustments and improvements.

Characteristic activities of this phase include monitoring and review and supporting actions such as awareness raising, enhancement of partnerships and most importantly financing and investment. In this phase any missing elements and gaps will be filled in so that the plan fully responds to the principles of Integrated Coastal Zone Management and everything that was said before, that is the Marine Framework Strategy Directive, the Framework Directive on Maritime Spatial Planning, the Barcelona Protocols, the Water Framework Directive, the Ecosystem Approach and also the response of the country for climate change adaptation. All the above should be part of the one, single plan which should be able to ensure the sustainable development of the region for the benefit of the current and, most importantly, the future generations which come after us.

The overall process of drafting and agreeing the plan should become a "model process" for the GoE region and constitute for it a landmark. If such a plan becomes successful it will be used by many other areas in Greece, the rest of the Mediterranean and beyond, making Elefsis a genuine champion for sustainable development.

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The Mediterranean Information Office for Environment, Culture and Sustainable Development, is a Federation of Mediterranean Non-Governmental Organizations (NGOs) for the Environment and Development. MIO-ECSDE acts as a technical and political platform for the intervention of NGOs in the Mediterranean scene. In cooperation with Governments, International Organizations and other socio-economic partners, MIO-ECSDE plays an active role for the protection of the environment and the sustainable development of the Mediterranean Region.

Background

MIO-ECSDE became a federation of Mediterranean NGOs in March 1996. Its roots go back to the early 80s, when the expanding Mediterranean membership of the European Community encouraged the European Environmental Bureau (EEB) to form its Mediterranean Committee supported by Elliniki Etairia (The Hellenic Society for the Protection of the Environment and the Cultural Heritage). The Mediterranean Information Office (MIO) was established in 1990 as a network of NGOs, under a joint project of EEB and Elliniki Etairia and in close collaboration with the Arab Network of Environment and Development (RAED). The continuous expansion of MIO-ECSDE's Mediterranean NGO network and the increasing request for their representation in Mediterranean and International Fora, led to the transformation of MIO-ECSDE to its current NGO Federation status. Today it has a membership of 130 NGOs from 26 Mediterranean countries.

Our Mission

Our mission is to protect the Natural Environment (flora and fauna, biotopes, forests, coasts, natural resources, climate) and the Cultural Heritage (archaeological monuments, and traditional settlements, cities, etc.) of the Mediterranean Region. The ultimate goal of MIO-ECSDE is to promote Sustainable Development in a peaceful Mediterranean.

Major tools and methods

Major tools and methods used by MIO-ECSDE in order to achieve its objectives are the following:

- Promotion of the understanding and collaboration among the people of the Mediterranean, especially through their NGOs, between NGOs and Governments, Parliaments, Local Authorities, International Organizations and socio-economic actors of the Mediterranean Region.
- Assistance for the establishment, strengthening, cooperation and co-ordination of Mediterranean NGOs and facilitation of their efforts by ensuring the flow of information among relevant bodies.
- Promotion of education, research and study on Mediterranean issues, by facilitating collaboration between NGOs and Scientific and Academic Institutions.
- Raising of public awareness on crucial Mediterranean environmental issues, through campaigns, publications, exhibitions, public presentations, etc.

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