THALES atmospheric deposition and mediterannean sea water productivity

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THALES- ADAMANT FULL PROPOSAL

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STATE OF THE ART AND OBJECTIVES:

Many factors influence Earth's climate, however human activities have become dominant and are responsible for most of the warming observed over the past 50 years (IPCC, 2007). Recently it was widely recognized that we are now living in the anthropocene era where humans have drastically affected the environment (Steffen et al., 2007). The observed unprecedented increases in CO_2, CH_4 and other greenhouse gas levels in the atmosphere have been caused by societies' increasing need for energy and food production. In turn, CO_2 is naturally removed from the atmosphere by terrestrial vegetation as well by oceanic sequestration.

Atmospheric CO_2 is captured into the oceans via the biological pump that is associated with oceanic primary productivity; both are limited by the bioavailability of nutrients (Duce et al., 1991; Mills et al., 2004). In surface waters nutrients originate from i) atmospheric deposition into the ocean, ii) riverine inputs and iii) inputs of nutrient-rich waters from upwelling regions and lateral flows from continental margins (Jickells et al., 2005). Remarkably, the oceans present significant regional heterogeneity, experiencing different limiting nutrient conditions which vary on decadal or shorter timescales (Ruttenberg, 2003):

- Nitrogen (N) is a critical nutrient for ecosystems; large amounts of bioavailable nitrogen are supplied to the marine ecosystems by the anthropogenically increased atmospheric pool of nitrogen (Duce et al., 1991). There is increasing evidence that nitrogen is limiting net primary productivity in large parts of the oceans (Duce et al., 2008) and that oceanic nitrogen is controlled by atmospheric deposition.

- Phosphorus (P) has been suggested to be the limiting nutrient on geologic time-scales. There is increasing evidence that several oligotrophic oceanic regions such as the Eastern Mediterranean Sea and the oligotrophic gyres of both the western North Atlantic and subtropical North Pacific are P-limited (Ruttenberg, 2003; Krom et al., 2005).

- Iron (Fe) is an essential micronutrient for phytoplankton growth and is now recognized as a limiting factor for primary productivity in at least 30% of the oceans particularly in ''High Nutrient Low Chlorophyll'' regions (Jickells et al., 2005).

Despite the fact that atmospheric inputs (gases and aerosol deposition) have been proposed as a major source of nutrients to the marine environment (e.g. Duce et al., 1991; Jickells et al., 2005; Mahowald et al., 2005), their exact contribution to the oceanic nutrients budget and thus their impact on ocean productivity and subsequently to the climate is still under scientific debate. In addition the response of ocean productivity to the modification of atmospheric inputs in a changing climate has not been consistently evaluated yet. It remains an open question how marine productivity and the biological pump have been and will be affected due to human induced atmospheric inputs into the ocean and to the climate changes that we are experiencing.

The Mediterranean region (MS) is of interest for both its marine and atmospheric environment. The Mediterranean atmosphere with high photochemical activity is a cross road for air masses of distinct origin, affected by both natural and anthropogenic emissions that interact chemically, leading to the formation of nutrients such as nitrogen compounds (Vrekoussis et al., 2006; Finlayson-Pitts,2009). Dust aerosols from the African continent are also affecting the area as carriers of nutrients such as iron and phosphorus. Interaction of these aerosols with acid gases from anthropogenic sources causes reduced pH and increases the fraction of bioavailable Fe and P in the dust laden air-masses (Nenes et al., 2011).

The MS (Figure 1), and especially the Eastern basin where nutrient levels are very low, is globally one of the least productive seas (Azov, 1991; Bethoux et al., 1998; Krom et al., 2004; Krom et al., 1991; Thingstad and Rassoulzadegan, 1995; Van Wambeke et al., 2002). The circulation of the Mediterranean is complex with a number of basin-scale, sub-basin-scale and mesoscale structures where permanent recurrent and transient cyclonic and anticyclonic eddies are interconnected by jets and currents. The MS provides the ideal test case for hind-cast simulations and numerical process studies as it exhibits a wide range of variability scales from eutrophic in shallow coastal waters to extremely oligotrophic.
More specifically:

• Due to the limited extent of the continental shelf, the general circulation patterns (open ocean processes) significantly influence coastal processes and dominate the Mediterranean ecosystem.

• The open Mediterranean Sea ecosystem is regarded as primarily oligotrophic and P limited and presents unusually high N/P ratio with increasing P limitation from west to east.

• The nutrient availability for phytoplankton and bacteria is controlled hydrodynamically in the winter and through ecological processes for the rest of the year.

• In coastal areas the herbivorous food web is more important. However, the dominant carbon flux along the trophic web can seasonally shift from herbivorous to the microbial loop.

The Mediterranean Sea presents large diversity, which is a challenge in developing reliable models. These models must be able to properly simulate the ecosystem not only in space and time but rather to include appropriate mechanisms describing the system transition from one trophic status to another. These models, if properly combined (air - sea), can be used to investigate complex processes such as the impact of atmospheric deposition on the marine ecosystem.

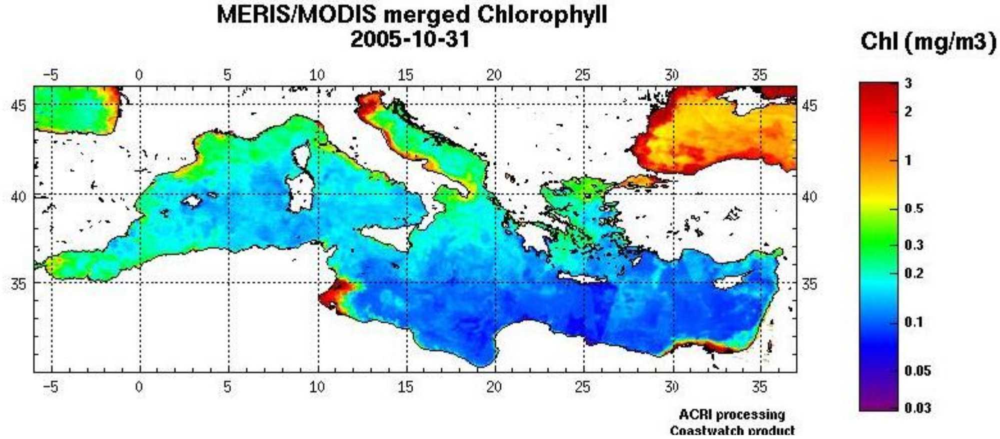

Figure 1: Satellite observations of chlorophyll-a in the Mediterranean Sea as a marine primary productivity marker.

The proposed project combines atmospheric and oceanographic models for the first time, with field measurements and experiments and aims to understand, describe, simulate and predict the effects of atmospheric deposition on marine productivity in the MS. Previous efforts based on mesoscale field studies and microcosms experiments in the Eastern Mediterranean (European Programs CYCLOPS (Thingstad et al., 2005) and ADIOS (Heussner and Charrière, 2003)), did not result in an accurate understanding of the fate of dust constituents in the water column, the ecosystem dynamics and the underlying biogeochemical processes.

Furthermore, the project has an innovative multidisciplinary approach (controlled laboratory experiments, field measurements and numerical simulations of marine and atmospheric environment) and a multidisciplinary expertise that characterizes the proposing team (chemists, physicists, geologists, biologists, ecologists, both experimental and theoretical).

The proposed study aims to assess the effect of atmospheric deposition of nutrients on primary production, population distribution and flows of carbon in the food chain over time; beginning from the preindustrial era up to future years (hind cast, present and forecast simulations). In order to achieve this objective it is necessary to understand the atmospheric and marine processes that regulate the effects of atmospheric deposition in the marine ecosystem and the N/P ratio as well as its temporal evolution in the Eastern Mediterranean. To this end, targeted marine mesocosm and chemical kinetics experiments, atmospheric and marine environmental measurements and numerical simulations will take place. A 3-d atmospheric model will be used to calculate the deposition of nutrients into the sea in synergy with a marine biogeochemical model. The effect of atmospheric deposition to the N/P ratio in the sea and the marine carbon and nutrients cycles will also be investigated.

METHODOLOGY:

The proposed project is divided into 4 work packages (Figure 2) which include:

WP1: Study of marine and atmospheric processes. This concerns: Targeted mesocosm experiments to study bioavailability and fluxes within the marine food web and their influence on organic and inorganic nutrient stocks. Kinetics experiments of heterogeneous reactions between aerosols and selected atmospheric compounds in order to understand atmospheric processes occurring in aerosols that cause changes in the physicochemical characteristics and their solubility in the marine environment.

WP2: Atmospheric deposition. This will be characterized by: Historical data collection of aerosols atmospheric deposition of nitrogen and phosphate, recording of the atmospheric conditions in the Mediterranean and field measurements at the atmospheric monitoring station at Finokalia, Lasithi. In addition, the three-dimensional atmospheric chemical-transport model will be improved for the nutrient atmospheric deposition simulations and will applied to simulate the present situation as well as past (1900) and future (2100) conditions.

WP3: Marine productivity. Historical data of the marine environment of the Mediterranean will be collected and additional field measurements at the observation station M3A will be performed. All important processes related to atmospheric deposition based on the mesocosm experiments results, will be integrated in the existing physico-chemical model. First, the 1-d marine model version will be calibrated and validated for the simulation of the M3A station area and the effect of atmospheric deposition on marine productivity will be evaluated. Significant effort will be put on the 3-d coupling of atmospheric deposition with the marine ecosystem model. Then, the present conditions and hind cast- forecast simulations of the marine ecosystem will be performed for the period between 1900-2100 using a combination of 1D and 3D modeling.

WP4: Project coordination and dissemination. Annual scientific meetings of the research team, creation of a website for the project and teleconference calls for project monitoring and problem solving are foreseen among the procedure supporting coordination and dissemination. Optimal dissemination of project outcome will be achieved via coordinated and co-authored high quality peer-reviewed publications, presentations or project results at International Conferences, targeted international workshops and the web-site of the project. The web-site (http://thales-adamant.hcmr.gr) will be appropriately modified within the first month of the project to increase project visibility and enhance participants interactions (data exchange etc). It will be continuously updated based on the flow of the innovative project results. A password protected area on the project web-site will enhance collaboration and will be a discussion forum for the project partners that show a strong complementary multidisciplinary expertise. Collaboration between partners and synthesis of the results will maximize via exchange visits between partners both of senior and of young scientists.

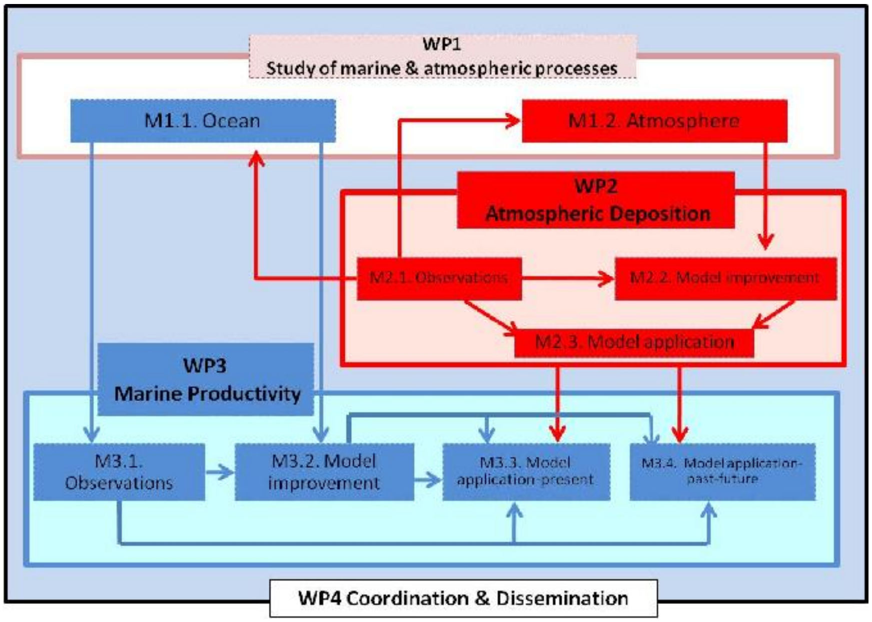

Figure 2: Management structure of the proposed project

More specifically the proposed project includes:

1. Experimental Work

<u>Kinetics experiments</u> of heterogeneous Reactions in the Atmosphere:

The majority of experimental studies currently available in the literature have been focused on uptake coefficients measurement of volatile organic compounds (VOC) on mineral dust-particles and on sea salt surfaces, but there are only a few experimental studies that measure the solubility of mineral dust-particles in sea water. However, it is well known that both processes are correlated; the adsorption of acidic and/or organic compounds in the sea water may alter the solubility of trace elements in it, e.g., iron (Fe) and phosphorous (P) on dust particles. Moreover, although the adsorption of HNO_3 on sea-salt and on mineral dust particles are competitive processes, the co-adsorption of acids and organic compounds on the surface of sea-salt and mineral dust particles may be synergist processes, representative to actual atmospheric conditions, which has not been investigated in past experimentally. Furthermore, the uptake of HNO_3 on sea-salt particles results in the emission of HCl from the surface, which subsequently interacts with mineral dust-particles and increases the solubility of Fe and P elements. Finally, most studies have been limited to the mineral dust-particles from the Sahara region (especially the ones related to solubility determination). It is well-known that mineral dust samples from various geographical regions have significantly different chemical composition, and particularly in the content in calcium carbonate ($CaCO_3$) that has the detection sensitivity and in silicon compounds that are less reactive towards acids (Usher et al., 2003). The proposed project will provide a thorough study about the heterogeneous interaction of mineral dust and sea salt particles with several acids and volatile organic compounds. Within this context it will include experiments to measure a) initial uptake coefficients and b) surfaces coverage of several acids and volatile organic compounds on different mineral dust and sea-salt particles, as well as on mineral dust/sea-salt mixtures. Experimental data will be analyzed using the appropriate adsorption isotherm model.

Mesocosm experiment: Simulating the Mediterranean marine ecosystem is a challenge that requires knowledge of the functioning of the euphotic zone microbial food web consisting of small unicellular phytoplankton, bacteria and protozoa. Phytoplankton growth is strictly related to the cellular constituents of carbon, nitrogen and phosphorus, and maximal growth rates of phytoplankton are reached when chemical composition of the cells is close to Redfield ratio. To our knowledge, in situ mesoscale additions in the E. Mediterranean have only twice been experimentally investigated during: a) a Lagrangian phosphate addition experiment in 2001 over the Cyprus eddy in the Levantine (CYCLOPS project, Thingstad et al. 2005) that yielded clear evidence of N and P co-limitation of autotrophs during summer and b) a fast response experiment (FRE) prior and during a pronounced natural dust deposition event over the Cretan Sea (ADIOS project) that provided unclear results with regard to the fate of the various dust constituents through the euphotic mixed layer and biochemical processes. Since then, various minor microcosm dust addition experiments have been performed but no explicit description of the fate and impact of dust constituents onto surface seawater layers biochemistry has been proposed for the area. Thus, to understand the fate of dust constituents through euphotic zone biochemical machinery we propose to study dust related mechanisms under well controlled conditions. Lagrangian experiments are expensive, can be hardly repeated and are subject to statistical problems related to the control samples taken in variable water masses outside the patch. In situ follow up of dust deposition events are also expensive lacking in the same time treatment availability. Therefore, in the present study, targeted mesocosm experiments will be carried out at the HCMR facilities (WP1) to understand the complex driving forces in the Mediterranean Sea and especially at the eastern basin (where the ambient seawater concentration of both dissolved inorganic P is exceptionally low), as well as the effect that atmospheric deposition has on these. The influence of different scale and composition nutrient additions on phytoplankton growth will be investigated and a method to estimate kinetic parameters of nutrient uptake and release by planktonic food web will be deduced. The main goal of these experiments is

i) to improve understanding of the complex relationship between nutrients and ecosystem response

ii) to precisely depict the nutrient cycles and particularly the removal pathways, improving thus parameterizations in the marine ecosystem model

iii) to understand how dust affects the system at different seasons. We now know that while in winter during the major plankton bloom the system is P Limited (Krom et al.,1991), in May it is N and P co-limited for plankton but P limited for bacteria and zooplankton (Thingstad et al., 2005) and in summer is seems to be N limited (Tanaka et al., 2011).

iv) to understand the role of trace metals such as Cu and others leached from natural and athropogenic aerosols on ecosystem health (Paytan et al., 2009).

Ambient in-situ samples of atmospheric dust with detailed chemical composition, obtained from the Finokalia station, will be added in a number of controlled tanks in the laboratory previously filled with water from the M3A station. From the addition of the primary limiting nutrients, in the form of environmental dust, and the comparison with control (blank) sea samples, the effect of the atmosphere on the Mediterranean marine system as well as the pathways that these nutrients follow in the marine ecosystem will be investigated.

2. Collection of historical data and new in-situ observations

The project will profit from available atmospheric and oceanic observational data from various stations covering the entire Mediterranean from 2000-2010 that will be compiled and used for model initiation or model evaluation purposes. Data available from earlier EU projects like EROS 2000, ADIOS, YOYO 2001 or being collated by ongoing projects like SESAME and CIRCE will be used. In particular, data on nutrients, chlorophyll, primary and bacterial productivity, stocks and zooplankton biomass will help in model tuning and validation. Several efforts have been carried out to compile historical oceanographic data in the Mediterranean Sea (MEDAR/MEDATLAS), including some of the nutrient and other relevant variables. However, much of the data relevant for modeling are still to be obtained from old and recent literature. In addition, in the frame of this proposal, significant effort will be put on assuring concurrent new observations of both oceanographic and atmospheric measurement station in the East Mediterranean (Figure 3).

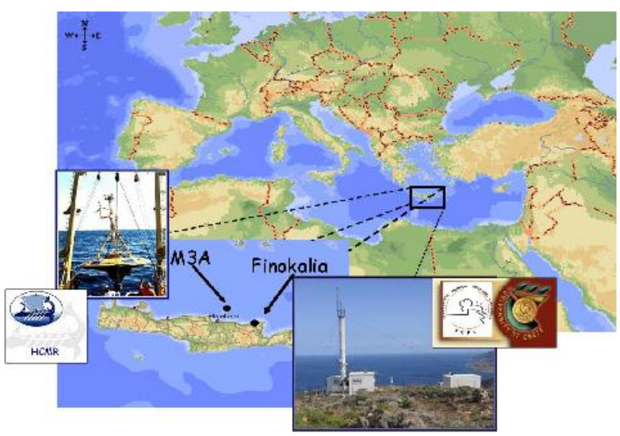

Figure 3: Oceanographic and Atmospheric measurement stations in East Mediterranean.

Atmospheric measurement Station: Finokalia atmospheric chemistry monitoring station of the University of Crete- ECPL (35^o 20' N, 25^o 40' E, 250 m asl) is operating since 1997 and is actually equipped for gas phase and aerosol and wet and dry deposition observations (http://finokalia.chemistry.uoc.gr). In addition meteorological data and radiation are continuously observed and recorded every 5 min. During the project N, P, Fe wet and dry deposition observations will be systematically performed.

Oceanographic Station: Since January 2000 HCMR operates a multi-sensor marine observing station for the continuous recording of open-ocean conditions in the East Mediterranean Sea (Petihakis et al, 2007c). The station is deployed 24 nm north of Crete at 35º39,627'N and 24º59,080'E at 1030m with three separate lines operating until 2006. In 2007 the buoy was incorporated into the POSEIDON system (http://www.poseidon.ncmr.gr) adopting a single line configuration with temperature, conductivity, pressure, transmissometer, fluorometer, PAR and dissolved oxygen sensors at 20, 50, 75 and 100m and with temperature and conductivity sensors at 250, 400, 600 and 1000m. The 3-hourly measurements are real-time transmitted through GSM to HCMR where they are stored in a data base. The observing capabilities of the M3A station have been expanded in the framework of EuroSITES project (2008 – 2011) with the addition of a subsurface CO2 sensor and the completion of meteorological sensors. Data from a sediment trap array (500 and 1000m) 10nm north of M3A and operated continuously since 1999 will be used for elements and nutrient analysis (Kouvarakis et al., 2001; Markaki et al., 2003). For the present project, the sediment traps will be deployed closer to the M3A station in order to minimize ship costs while discrete sampling for conventional analyses of stock variables (nutrients, chlorophyll a, microbial phytoplankton and zooplankton community structure) as well as basic rate measurements (primary, bacterial and zooplankton production) will be performed at the M3A site on a monthly basis with the HCMR R/V Philia and Iolkos.

Satellite observations are a powerful tool providing a clear global picture of the aerosol occurrence in the atmosphere as well as of the ocean productivity variability that is linked to chlorophyll-a observable from space. On the other hand sea-surface temperature anomalies can be used as indicators of upwelling motions in the ocean bringing nutrient rich deep water to the surface. Investigation of such satellite images together with the ground based observations of aerosol composition and deposition fluxes and atmospheric Chemistry Transport Model (CTM) and marine biogeochemistry model results will allow fast progress in our scientific understanding of the Earth system. Data from the MODIS, MERIS and SEAWIFS satellite sensors will be used for the present study.

3. Modelling

The atmospheric chemistry-transport model: TM4-ECPL The 3-dimensional atmospheric chemistry transport model TM4- ECPL will be applied for the present study to evaluate atmospheric deposition of nutrients into the ocean and its temporal evolution from preindustrial times to the future (WP2). TM4-ECPL is an off-line global model using ECMWF meteorology to drive transport in the troposphere and able to simulate gas phase chemistry (Myriokefalitakis et al., 2008), all major aerosol components, including the natural ones, like sea-salt and dust, and secondary organic aerosol (Tsigaridis et al., 2006; Myriokefalitakis et al., 2011). Gas-particle partitioning of inorganic species components is solved using the ISORROPIA II aerosol thermodynamics model that also calculates aerosol water content (Nenes et al., 1998). This will be further improved in the model to account for crustal elements. The model is running in several horizontal and vertical resolutions. Its actual high resolution version has a horizontal grid of 2.5^ox2.5^o and 31 vertical layers up to 0.01 hPa; whereas a finer resolution of 1ox1o is under development. For the hind cast and forecast studies in WP the model will be driven by daily/monthly meteorology, available at the GCM Data archive section of the Data Distribution Center (DDC) of the Intergovernmental Panel on Climate Change (IPCC) http://www.mad.zmaw.de/IPCC_DDC/ html/SRES_AR4/index.html and the SRES AR4 emission scenarios for research purposes. TM4-ECPL will be also improved for the deposition simulations by accounting the presence of P on the biomass burning and dust aerosols. Other combustion sources of P will be associated to the combustion sources of sulfur in the model. Fe in the model will be associated to the dust aerosol.

The hydrodynamic model is based on the Princeton Ocean Model (POM) (Blumberg and Mellor, 1987) that is widely used by the scientific community, and has been applied to the Mediterranean area in a number of studies both at basin, regional and local scales (e.g. Korres and Lascaratos, 2003; Baretta et al., 1995). POM is a primitive equation model that has a bottom–following vertical sigma coordinate system, a free surface and a split mode time step. This model is used both in 1-d and 3-d configuration in WP3.

The ecosystem model, ERSEM-2004, is the latest version of the European Regional Seas Ecosystem Model (Baretta et al., 1995; Varela et al., 1995) a generic model, which coupled to the physical model (POM), is capable of efficiently simulating the spatial pattern of ecological fluxes throughout the seasonal cycle and across eutrophic and oligotrophic gradients. Due to its generic character, the model has been already successfully applied in a range of different environments (e.g. Petihakis et al., 2007b and references therein). ERSEM describes both pelagic and benthic ecosystems and the coupling between them in terms of significant biogeochemical processes. ERSEM includes all those processes that may significantly influence ecosystem dynamics and resolves the ecosystem into sufficient functional groups so that those processes are sensibly defined.

The biota in the ecosystem is subdivided into three functional types, producers (phytoplankton), consumers (zooplankton and zoobenthos) and decomposers (pelagic and benthic bacteria), further sub-divided based on their trophic level to create a food web with a total of eight pelagic and five benthic functional groups. Carbon is the basic unit cycled in the system, followed by nutrients (N, P and Si), chlorophyll and oxygen, with variable carbon/nutrients and carbon/chla ratios. ERSEM-2004 gives a far better approximation to how nutrient limitation acts on cells allowing at the same time the production of significant pools of dissolved organic matter (DOM). The model includes the bacterial nutrient limitation, the resolution of detritus into a number of size based categories and the inclusion of labile and semi-labile DOM as explicit state variables. The detailed description of the bacterial model and treatment of DOM are essential for the simulation of the oligotrophic regions where bacterial growth is controlled by the availability of DOC (dissolved organic carbon) and the availability of inorganic and organic nutrients which allow them to assimilate DOC (Thingstad and Rassoulzadegan, 1995). Resolving DOM into labile and semi-labile provides a representation of the range of organic compounds in the dissolved fraction, some of which may be directly taken up by bacteria, some of which require further degradation before bacterial utilization. Dividing particulates into a number of size based categories, with bacterial utilization rates based on surface area to volume ratios and size dependent sedimentation rates, allows a more realistic treatment of carbon export.

The work packages, their milestones and their deliverables are presented in Table 1.

M.1.1 (mesocosm experiments) will be fed with information from the atmospheric deposition observations (M.2.1) and measurements of the marine environment (M.3.1). The results from this milestone will be used in improving the marine model (M.3.2). Kinetic experiments of the atmosphere (M.1.2) will use information from the M.2.1 (Compilation of atmospheric observations in the Mediterranean Sea) and the experimental results will be used to improve the atmospheric model (M.2.2). The improved atmospheric model will be used in three-dimensional application for the entire Mediterranean basin (M.2.3) to calculate past, present and future nutrient atmospheric deposition distributions. Results from the mesocosm experiments (M.1.1) with the marine environment measurements (M.3.1) will be used to improve the marine model (M.3.2). The improved marine model will be coupled with the atmospheric deposition model (M.2.3) and implemented in the Mediterranean basin (M.3.3) simulating the current state of the ecosystem. Hind cast and forecast marine ecosystem simulations for the period 1900 - 2100 (M.3.4), will be achieved by using atmospheric deposition data from M.2.3. WP4 involves the management of all deliverables, milestones and consequently all WPs, as well as the dissemination of the project results to the scientific community, the general public and relevant policy makers.

Table 1: Workpackages, Milestones and Deliverables of the proposed study.

WP 1 **Study of marine and atmospheric processes**	
Milestones	**Deliverables**
1.1 Understanding the marine processes – Mesocosm experiments Starting date (month) T1→ Ending date (month) T36	1.1.1 Protocol design of the mesocosm experiments (T1→ T24)
	1.1.2 Report of the experiments results (T1→ T24)
	1.1.3 Bioavailability of the atmospherically deposited nutrients on the marine ecosystem (T1→ T36)
	1.1.4 Food-web assimilation rates of the atmospherically deposited nutrients (T1→ T36)
1.2 Understanding the atmospheric processes Starting date (month) T1→ Ending date (month) T24	1.2.1. Initial uptake coefficient measurements, γ, for the heterogeneous interaction of HCl, HNO3 and SO2 with dust collected from various regions, sea salts and surfaces of dust and sea salt mixtures. (T1→ T18)
	1.2.2. Determination of surface coverages, θ and adsorption isotherms within temperature range that simulates atmospheric conditions. (T10→ T22)
	1.2.3. Volatile products (mass spectrometry and FT-IR spectroscopy) and compounds bound on the surface (Raman spectroscopy and optical microscopy) determination for the studied heterogeneous interactions. (T6→ T24)
	1.2.4. Solubility determination for the various dust mixtures, based on N, Fe and P, in pure and sea salt water. (T1→ T24)
WP 2 **Atmospheric Deposition**	
Milestones	**Deliverables**
2.1 Compilation of atmospheric observations in the Mediterranean Sea Starting date (month) T1→ Ending date (month) T36	2.1.1 Compilation of N & P atmospheric deposition data in the Mediterranean Sea (T1→ T12)
	2.1.2 New observational atmospheric data from Finokalia Station (Crete) (T1→ T36)
2.2 Improvement of the atmospheric chemistry transport model Starting date (month) T6→	2.2.1 TM4-ECPL coupled with the thermodynamic model ISORROPIA taking into account the impact of mineral dust on the calculation of particle composition (T6→ T18)

Ending date (month) T18	2.2.2 Updated description of the chemistry of the TM4-ECPL model based on the results of M1.2; presentation in a scientific conference (T6→ T18)
2.3 Atmospheric deposition simulations Starting date (month) T18→ Ending date (month) T36	2.3.1 Estimation of present day N and P deposition over the Mediterranean; presentation in a scientific conference (T18→ T24)
	2.3.2 Hindcast of nutrients atmospheric deposition over Mediterranean Sea; presentation in a scientific conference (T18→ T30)
	2.3.3 Forecast of nutrients atmospheric deposition over Mediterranean Sea; Publication (together with 2.3.2) (T24→ T36)
WP 3 **Marine Productivity**	
Milestones	**Deliverables**
3.1 Compilation of seawater observations in the Mediterranean Sea Starting date (month) T1→ Ending date (month) T36	3.1.1. Compilation of seawater observations in the Mediterranean (T1→ T12)
	3.1.2. New observations seawater data (satellite data and in-situ data from M3A) in the Mediterranean (T1→ T36)
3.2 Improvement of the marine ecosystem model – Simulation of the Cretan Sea ecosystem Starting date (month) T6→ Ending date (month) T30	3.2.1. Improvement of the marine biogeochemical model incorporating the necessary processes; presentation in a scientific conference (T6→ T18)
	3.2.2. Set –up of the modeling system for the Cretan Sea marine ecosystem, verification/validation of the results; presentation in a scientific conference (T18→ T22)
	3.2.3. Sensitivity tests results (T22→ T24)
	3.2.4. Impact of atmospheric deposition of N and P on the Cretan Sea productivity; Publication (T24→ T30)
3.3 3-d Marine ecosystem model for the Mediterranean Sea – Present Starting date (month) T16→ Ending date (month) T32	3.3.1. 3-D physical-biogeochemical model, present day simulations of the Mediterranean marine ecosystem and analysis of its dynamics; presentation in a scientific conference (T16→ T28)
	3.3.2. Impact of atmospheric deposition on the Mediterranean Sea productivity; Publication (T28→ T32)
3.4 3-d Marine ecosystem model for the Mediterranean Sea – Hindcast & Forecast Starting date (month) T32→	3.4.1. Simulation of the Mediterranean marine ecosystem before industrial revolution (1900 – 2000); Publication (T32→ T43)

Ending date (month) T43	3.4.2. Forecast the impact of the atmospheric deposition on the Mediterranean Sea productivity for the period 2000 – 2100; presentation in a scientific conference (T32→ T43)
WP 4 **Project coordination and dissemination**	
Milestones	**Deliverables**
4.1 Project coordination Starting date (month) T1→ Ending date (month) T27	4.1.1. Kick-off meeting
	4.1.2. Scientific meetings of the research team
	4.1.3. Website of the project
4.2 Dissemination of results Starting date (month) T1→ Ending date (month) T43	4.2.1 Project website with the main results
	4.2.2. Annual reports of the main results
	4.2.3. Dissemination of results

The proposed work will contribute to new knowledge into how nutrients enter the marine environment through atmospheric deposition, how they are uptaken by organisms and how this influences carbon and nutrient fluxes. Experimental work will be combined with atmospheric and marine models which will eventually be coupled. Important new knowledge will be obtained from mesocosm experiments into nutrient deposition and are uptake in marine systems through atmospheric deposition, and their effects on the marine carbon cycle and food chain. The overall contribution of deposition to marine productivity will also be evaluated. When the field and analytical work have been carried out this specific nutrient cycle will be described for the first time allowing the evaluation of effects of atmospheric deposition on marine productivity. The kinetics experiments will contribute to the understanding of atmospheric processes that change the properties and solubility of aerosols in the marine environment. It will be the first time that kinetic parameters of adsorption of acidic and organic volatile compounds in atmospheric samples of dust and marine salts will be estimated in conjunction with solubility of Fe, N and P in mixtures containing dust, in clean and marine water. The majority of laboratory experiments so far have focused either on evaluating the retention factors for volatile compounds in dust or marine salts or (to the dilution of particulate dust in marine waters with each process being examined separately. It is common knowledge that these processes are directly related. Although the proposed atmospheric and oceanographic models are being used by the contributing teams as operational tools they will be coupled for the first time to create a system that will be able to holistically deal with the effects of atmospheric deposition on the marine environment. Both research teams will upgrade their operational models through the work carried out. This will also consist of a model study that can be used in other locations globally. Moreover because of the flexibility of the models, their broad use by the scientific community and their open source nature, the upgrade achieved will be immediately available to the scientific community.

For the success of the project, the three research teams will collaborate substantially, with more than one group to participate in several activities and WPs.

1st Research Team– HCMR Modeling group/collaborators: RT1 expertise in simulation and prediction of dynamic conditions in the marine ecosystem and in operational oceanography, will coordinate and be responsible for WP3 and participate in all deliverables (D.3.1.1, D.3.1.2, D.3.2.1, D.3.2.2, D.3.2.3, D.3.2.4, D.3.3.1, D.3.3.2, D.3.4.1, D.3.4.2). RT1 will also coordinate WP4 and in collaboration with RT2 and RT3 will be responsible for all planed deliverables (D.4.1.1, D.4.1.2, D.4.1.3, D.4.2.1, D.4.2.2 and D.4.2.3). RT1 in collaboration with RT3 will also be involved in the design of the mesocosm experiments and the analysis of results (D.1.1.2, D.1.1.3 and D.1.1.4) that will be used for the improvement of the oceanographic model in WP3.

2nd Research Team – UoC / ECPL/collaborators: RT2 expertise in large-scale simulations of transport and chemical change, gaseous and particulate pollutants, interactions databases and atmospheric thermodynamics, will coordinate WP2 and be responsible for all deliverables (D.2.1.1, D.2.1.2, D.2.2.1, D.2.3.1., D.2.3.2., D.2.3.3). RT1 in collaboration with RT3 will also participate in WP1 with experimental studies on understanding atmospheric aerosol processes (D.1.2.1, D.1.2.2, D.1.2.3 and D.1.2.4). These results will be used for the improvement of the atmospheric model. Members of RT2 will participate in WP3 by providing atmospheric deposition data in the oceanographic model. The RT2 will collaborate with the other two research teams for WP4 and will participate in all planed actions (D.4.1.1, D.4.1.2, D.4.1.3, D.4.2.1 and D.4.2.2).

3rd Research team – HCMR Biological Oceanography group/collaborators: RT3 expertise in the pelagic microbial ecology and biogeochemistry will coordinate and participate in all planed actions of WP1. In collaboration with RT1 will be responsible for the deliverables: D.1.1.1, D.1.1.2, D.1.1.3 and D.1.1.4. RT3 will also collaborate with RT1 in WP3. RT3 will be involved in collecting historical of MS marine ecosystem (D.3.1.1 and D.3.1.2) and in transferring knowledge gained from the experiments (D.3.2.2 and D.3.3.2). RT3 will collaborate with the other two research teams for WP4 and will participate in all planed actions (D.4.1.1, D.4.1.2, D.4.1.3, D.4.2.1 and D.4.2.2).

CONSORTIUM EXPERTISE AND INFRASTRACTURE

The ADAMANT consortium is assembled based on the quality and range of expertise required to address the challenges of the particular scientific question. The three research teams together with their external collaborators have extensive previous experience of working at national and international level. The consortium comprises of highly committed scientists with international reputations for excellence from world-renowned institutes. The quality of the consortium is highlighted by the contributions of the project participants to major international programs. The partners have a strong scientific record and are highly experienced in modeling ecosystem dynamics, experimental facilities and monitoring programs. The consortium offers a wide range of complementary, disciplinary research skills, including: climatology, climate change impact and adaptation assessment, experimental and theoretical ecology, marine ecology, species and ecosystem modeling. This range of expertise and skills highlights the truly transdisciplinary nature of the consortium and demonstrates that the participants collectively constitute a consortium capable of achieving the project objectives. Moreover the work proposed is considered as low risk since all experiments will be carried out in controlled conditions from a team that has hands-on experience on this type of research.

The project structure is designed to integrate the different capacities in a straightforward and effective way to gain maximal synergy. Apart from its contribution with answers to key open scientific questions it will give the involved research teams a competitive advantage at international level.

It is therefore evident that the consortium has the scientific and technical capability to carry out the proposed work and also the impact to disseminate and exploit the results throughout the European community.

1st Research Team, HCMR - expertise in marine ecology, marine hydrodynamic and ecosystem modelling. In the field of operational oceanography the HCMR modeling group is an active member of EuroGOOS & MedGOOS and contributes by (a) developing a national monitoring / forecasting capacity through the POSEIDON program, and (b) participating in various EC and ESA funded research projects (MFSPP, MFSTEP, MERSEA_S1, ROSES, MERSEA_IP, MARCOAST, MEECE) for the development of the European capacity in Operational Oceanography under the GMES and GEOSS umbrella. By establishing a network of observation buoys and the creation of a specialized operational center for the processing of the data collected and the production of forecasts, POSEIDON system is an infrastructure at the leading edge of modern oceanography in Europe. The network of observation buoys records continuously the physical, biological and chemical parameters of the Greek seas. Those data are then transmitted to the operational center where they are sorted and fed into forecasting models. Furthermore during the last 16 years the team has developed a number of mathematical models and management tools, for a wide range of environments and applications. Fully coupled 3D biophysical models in Basin (Mediterranean) regional (East Med. – Aegean Sea) and coastal scales (Cretan Sea – N. Aegean) including state of the art assimilation schemes both in physical and biological parameters have placed the group at the forefront of operational oceanography. Modelling applications, include an oil spill prediction tool as well as a decision making management tool for aquacultures which provides valuable information on key parameters such as the location and size of the farm through a holistic environmental impact approach. Finally latest achievements are the development of end to end marine ecosystems models in the Aegean Sea incorporating all important components of the ecosystem from physics to fish through bacteria, phytoplankton, zooplankton, nutrients and organic material.

In order to support the computational part of work package 3, apart from a number of personal computers, printers etc. available in HCMR Crete and Anavyssos, 3 high performance modules have also been installed and will be available to the project:

1. 40 x Intel(R) Xeon(R) CPU X5570 @ 2.93GHz 64GB RAM (5 x 8 cores 1Gbps)
2. 96 x Intel(R) Xeon(R) CPU X5680 @ 3.33Ghz 428GB RAM (8 x 12 cores) 10Gps
3. Storage: SAN 10x2TB RAID10 + 8 x 500GB RAID1, Total: 14TB

These systems ensure the required computational power for performing the simulations.

The marine station M3A was designed and constructed during the Mediterranean Forecasting System (MFS) project (Pinardi and Flemming, 1998) as a novel permanent observatory for the continued logging of conditions in the open east Mediterranean Sea Μεσογείου (Nittis et al., 2007; Nittis et al., 2003; Petihakis et al., 2007). M3A started operating in January 2000, 24nm north of Crete at N35º39.627', E24º59.080' at a depth of 1440 m. This location has the characteristics of open sea conditions and is removed from coastal activities and is therefore ideal for feeding and calibrating biogeochemical models.

The systems basic operation is to log physical properties of the upper ocean layer (0-500m), of biochemical variables in the euphotic zone (0-100m) and meteorological parameters and air-sea interactions. The data transmission is done in near real-time which makes it usable for operational forecasting models. In the initial layout there were three separate arrays with the central one connected to the buyoy and the other two being sub-surface. The surface buoy hosted meteorological sensors (wind direction, speed and temperature, atmospheric pressure an humidity), marine sensors (temperature , conductivity, turbidity, dissolved oxygen and chlorophyll) as well as wave height and direction. On the buoy array there were temperature and conductivity sensors as 150, 250, 350 and 500m. On the neighboring arrays there was an ADCP to record current activity (0-500m) and four CTD’s at 40 65, 90 and 115 m recording temperature, conductivity dissolved oxygen turbidity, chlorophyll and photosynthetic active radiation. A nitrate analyser was also place at 35m. Data from each array were acoustically transmitted to the buoy and from the via satellite connection to HCMR. In 2007 M3A was integrated into the POSEIDON forecasting system (http://www.poseidon.ncmr.gr/) adopting the single array layout. To date there are measurements of temperature, conductivity pressure, turbidity fluorescence. Photosynthetic active radiation and dissolve oxygen at 20, 50, 75 and 100m depth. Additional temperature and conductivity sensors are placed at 250, 400, 600 and 1000m. Measurements are logged in real time every three hours and after transmission to HCMR where they are stored in a custom designed database. The observational capacity of M3A has been enhanced during the EuroSITES project with the addition of an underwater CO2 sensor. M3A is part of the global observational network OceanSITES (www.oceansites.org) and is a long term observational point of the marine environment in the eastern Mediterranean.

2nd Research Team, ECPL-UoC and Collaborators – expertise on atmospheric chemistry and biogeochemical cycles: The Department of Chemistry (DoC) was established in 1985 and from its inception placed particular emphasis on research excellence. DoC is now regarded as the leading chemical research establishment in Greece and has been recognized as an international centre of excellence in a number of key fields. The department has recently benefited by a high quality new building, which came complete with well-fitted and generous laboratory space. DoC attracted external funds and is classified as the first department within UoC in attracting funds and managing regional, national and EU projects (as expressed per faculty member). The following figures help to exemplify the department's recent accomplishments: active research faculty 24, post-docs national & international 16, postgraduate students 180, publications in prestigious peer-reviewed journals between 1999-2009, 848, citations 12588, h-index 49, citations per item 15.

The Environmental Chemical Processes Laboratory (ECPL) is legally an independent research unit of the Department of Chemistry of the University of Crete. ECPL focuses its research activity in Aquatic and Atmospheric Chemistry, Biogeochemistry, Exposure Assessment and Environmental Modeling. The four faculty members of ECPL demonstrated a prolific publication record in the most prestigious scientific journals of Environmental and Analytical Chemistry and the Earth Sciences (average IF>4.13). Between 2000-2010, ECPL faculty members (FM) published 224 refereed research articles, which received more than 5415 citations (6 papers/FM/year; 25 citations/article; 1354 citations/FM). According to Essential Science Indicators rankings, ECPL research record belongs to the top 1% for the fields of Environmental Sciences and Geosciences. The broader interest and significance of these publications was also demonstrated by their reference in both scientific magazines and prestigious international and national media. ECPL established close collaboration with prestigious European and USA Universities and research Centres. ECPL was successful in obtaining competitive European and National research grants.

The Environmental Chemical Processes Laboratory (ECPL http://ecpl.chemistry.uoc.gr) of the Chem. Dept. of the U. of Crete is actually running two Master Programs on environmental sciences with forty graduate and Ph.D. students. ECPL has up to date infrastructure for research in atmospheric sciences. The research team has more than 20 years of experience in the study of air quality and climate and is currently participating in the EUCAARI, ECLIPSE, EUSAAR, ACTRIS and PEGASOS projects.ECPL has four faculty members, three scientific collaborators, two technical staff members and forty graduate and Ph.D. students.

ECPL has up to date infrastructure to perform high level research relevant to the project: I) a state-of-the art sampling and analytical chemical instrumentation; II) a well-equipped air and aerosol background monitoring station in a central location of Eastern Mediterranean (Finokalia- Crete); III) Several workstations and linux Intel Xeon dual-Quadcore clustered computers. The ECPL modeling group of Prof Kanakidou uses a cluster of 8 nodes of total 30 CPUs, with 54 GB RAM, total storage space exceeding 20 TB, Gigabit Ethernet intra-nodes connections, Gigabit Ethernet connections of the cluster and operation system CentOS 64-bit. The cluster has the softwares required for the development of atmospheric chemistry and transport models and the analysis of their results. Like Intel Fortran, C, C++, Fortran 77/90/95 compilers and several libraries. A smaller cluster of 3 nodes with 6GB RAM and total storage of 2.29 TB. Γ) 3 additional Linux servers to support other network services (http, ftp, sharing).

Prof. Pilinis, member of this research team, benefits from the computing facilities at the Environmental Science Department of the University of Aegean: Environmental Science Department is equipped with two HP xw8600 Workstations. Each workstation has two Intel Xeon processors (E5410, 2.33 GHz) forming a total of 8 parallel CPU cores. The system chipset is the Intel 5400. Each workstation is equipped with 14 GB of RAM memory and a high - end 3D graphics card manufactured by NVIDIA (Quadro FX 3700). The installed internal hard disk drives have a total capacity of 1.75 TB. The chosen operating system is OpenSUSE Linux ver. 11.1 (64bit).

Laboratory of Photochemistry and Chemical kinetics (LAPKIN) of University of Crete (UoC) is directed by Prof. Papagiannakopoulos and has long and remarkable experience (~25 years) in National and European research programs implementation, in the field of Atmospheric Chemistry. Lab team is constituted from three excellent trained researchers with extended working experience in Atmospheric Chemistry issues. LAPKIN is equipped with four prototype and versatile experimental setups: (a) an Nd:YAG/Dye/BBOIII laser system, most commonly used as photolysis source to produce reactive species in relative rate kinetic measurements (Nd:YAG laser) and/or as reactive species detection technique, inducing electronic excitations and subsequently monitoring the fluorescence signal (Laser Induced Fluorescence, LIF). Laser system can be coupled with quadrupole mass spectrometry (QMS) and/or Fourier Transformed Infrared (FTIR) spectroscopy, improving quantitative detection for all volatile reactants, intermediates and products involved in the studied reaction systems and to measure optical properties of stable and transient species, (b) a modulated continuous flow molecular beam system (VLPR) coupled with quadrupole mass spectrometry (QMS). VLPR is equipped with specially designed retractable reaction cells, designated to be used in homogeneous gas phase and heterogeneous kinetic studies. (c) a thermostatted photochemical reactor equipped with Fourier Transformed Infrared (FTIR) and Reflection-Absorption Spectroscopy (RAS) techniques, that coupled with the laser system is used to perform gas and/or heterogeneous phase kinetic measurements in relevant to the atmosphere conditions and (d) A tunable CO2 laser system for IR multiphoton decomposition of polyatomic molecules, as well as laser ablation of solid metallic targets and/or chemical vapour deposition (CVD) experiments for the synthesis of novel materials. Moreover, a recent capability of the lab is related to surface characterization and analysis employing the reflection-absorption spectroscopy technique RAS/FTIR). Further, LAPKIN has extensive experience in molecular calculations employing Gaussian programme suites (Gaussian98 and Gaussian03) and the lab is equipped with a dedicated to that purpose multiple processors server PC running Fedora Core RedHat Linux operating system.

3rd Research Team, HCMR - expertise on marine ecosystem biology and dynamics: Hellenic Centre for Marine Research (HCMR) is the national laboratory of Greece for all aspects of marine research, physical oceanography, marine geology, wave prediction, coastal geomorphology, fisheries, aquaculture, marine biology, marine genetics and inland waters. HCMR operates the system Poseidon that provides real time forecasts for winds and waves in the Greek seas, through a network of deep ocean buoys. HCMR operates three oceanographic ships, one manned submarine and three remote operated vehicles. For the needs of the program the following units will be used:

The Mesocosm Facilities of Thalassocosmos Crete are part of a mesocosm network in the framework of the MESOAQUA project (Figure 4). The facilities have already been during the Nutritunnel project in September 2009. The experiment aimed at examining whether phosphate addition in phosphate limited areas results in zooplankton biomass increase through alternative pathways, bypassing the phytoplankton biomass increase. In September 2010 the tank was used again during the LIGHTMIX project looking at the function of mixotrophic grazers under a range of light conditions. Future plans include participation in mesocosm experiments on ocean acidification in the framework of the MedSeA project which will include CO_2 enrichment and temperature manipulation.

The Planktonic and Microbial Ecology Lab has participated in a number of European projects. To date, three MSc theses have been competed at the lab and three PhD's are ongoing. The laboratory is fully equipped with Different microscopes, inverted and epifluorescence, Image analysis system, Flow cytometer, several liquid N2 dewars, -80℃ freezer, • Radio-isotope lab for 14C and 3H measurements, cooled centrifuge, culture laboratory fully equipped with autoclave, laminar flow, incubator, milliQ water, laboratory washer, constant temperature room, analytical balance, vortex, baths.

The Biogeochemical Laboratory is fully equipped and follows Quality Control/Quality Assurance procedures and the accuracy of the analyses performed is confirmed through the participation in international intercalibration exercises. Recently the Biogeochemical laboratory has accredited by the Hellenic Accreditation System SA (ESYD) according to ELOT EN ISO/IEC 17025:2005 (Nr of certification: 366).

The Biogeochemical Laboratory consists of the following Laboratory Units: Nutrient Laboratory Unit, Organic Chemistry Laboratory Unit, Ecotoxicology Laboratory Unit, Plankton Laboratory Unit, Benthos Laboratoty Unit, Sedimentology - Geochemistry Laboratory Unit, Technical Geology Laboratory Unit, Electronic Microscope Laboratory Unit, Elemental analysis Laboratory Unit, Trace Metal and Dissolved Organic Carbon Laboratory Unit.

Figure 4: Mesocosm Facilities of Thalassocosmos Crete are part of a mesocosm network in the framework of the MESOAQUA project

EXPECTED BENEFITS AND IMPLEMENTATION POSSIBILITIES:

The project will highlight the biogeochemical functioning of the Mediterranean Sea and how this is influenced by human-enhanced atmospheric deposition of nutrients, and climatic change. Emphasis will be given on investigating the role of nutrients atmospheric deposition as driver of the oceanic biogeochemistry. This will be achieved through modeling and experimental work. With the completion of the project through a holistic and innovative studying approach of atmosphere-ocean as a single system we will have achieved to:

- Quantify the atmospheric deposition of N, P, Fe and Saharan dust and their long-term variability.
- Elucidate nutrient cycles in the marine environment and their role as drivers of the ocean productivity.
- Integrate and evaluate the associated parameterizations in the atmospheric and oceanographic models.
- Evaluate the response of the oceanic biogeochemistry to the nutrients atmospheric deposition and its evolution since preindustrial period and in the future (hind cast & forecast simulations).

The proposed project deals with the marine systems productivity and in particular the impact of atmospheric deposition on it, addressing the problem of eutrophication and thus, contributing to the implementation of Directives 2000/60/EC and 2008/56/EC of the European Parliament for the establishment of Community action in the field of water policy in the field of policy for the marine environment, respectively. Moreover, although MS is generally characterized as oligotrophic, coastal areas often present eutrophication phenomenons. These phenomenons lead to great social-economics problems related to tourism, fisheries and aquacultures. The proposed project due to better simulation of the marine ecosystem dynamics, through the integration of atmospheric deposition processes, will help to forecast extreme phenomena and contribute to their early treatment. Thus the proposed project contributes significantly to the protection and management of the marine environment, extremely important for the remote and less developed countries.

From the successful implementation of the project, several benefits in both local and international level will be achieved. As said before, Eastern Mediterranean is one of the most oligotrophic seas with an unusual eastward highly increasing N:P ratio and a phosphate limiting primary production. Understanding the sequestration of CO2 is necessary to understand climate change as described in the latest IPCC report (2007). The uptake processes balance the negative effects of increased CO2 emission. The decrease of emissions has been the subject of many international meetings from Kyoto (1997) to Copenhagen (2009). Moreover, nutrient input in the marine environment is another area of environmental interest related to eutrophication of marine areas and its impact on marine ecosystems.

This project looks at key questions the scientific community has yet to answer namely the role of atmospheric deposition on the function and dynamics of marine ecosystems, it’s possible relation to high N:P ratios and the future development of the Mediterranean system. This is mainly due to their complexity and limitations in resources and tools. The combination of the expertise of three Greek research teams enables the examination of interactions between atmospheric deposition and marine ecosystem in depth both in field and modeling.

Collaboration and involvement of outstanding scientists as Professor Krom and A. Baker ensures successful implementation of the project and international recognition.

Additional information related to the proposed project such as collaborating researchers CVs, web links to participating institutes previous project etc, can be found at the project's website:

http://thales-adamant.hcmr.gr/

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