ΕΛΛΗΝΙΚΗ ΔΗΜΟΚΡΑΤΙΑ

ΕΥΡΩΠΑΪΚΗ ΕΝΩΣΗ

ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ

«ΕΚΠΑΙΔΕΥΣΗ ΚΑΙ ΔΙΑ ΒΙΟΥ ΜΑΘΗΣΗ»

ΕΘΝΙΚΟ ΣΤΡΑΤΗΓΙΚΟ ΠΛΑΙΣΙΟ ΑΝΑΦΟΡΑΣ

ΕΣΠΑ 2007-2013

ΔΡΑΣΗ

«ΑΡΙΣΤΕΙΑ»

ABSTRACT

CHEMISAND-1346

ΑΚΡΩΝΥΜΙΟ/ΚΩΔΙΚΟΣ:	3680

ΚΥΡΙΟΣ ΕΡΕΥΝΗΤΗΣ:	Ευριπίδης Γ. Στεφάνου

ΦΟΡΕΑΣ ΥΠΟΔΟΧΗΣ:	ΠΑΝΕΠΙΣΤΗΜΙΟ ΚΡΗΤΗΣ

ΚΥΡΙΟΣ ΣΥΓΓΡΑΦΕΑΣ:	Ευριπίδης Γ. Στεφάνου

1.Synthesis and Dissemination of the Results

1.1. CHEMISAND website has created and activated during the first semester of the project. At the third year of the project the CHEMISAND website has been redesigned with an improved user interface and was constantly updated with the new data and information of the research progress [http://chemisand.chemistry.uoc.gr/].

1.2. The first planned paper reporting the results of the project is now published in the most prestigious scientific journal in the field of Environmental Science and Engineering, **"Environmental Science and Technology"**: T. Tziaras, S. A. Pergantis, and E. G. Stephanou, "Investigating the Occurrence and Environmental Significance of Methylated Arsenic Species in Atmospheric Particles by Overcoming Analytical Method Limitations", Environ. Sci. Technol., 2015, 49 (19), pp 11640–11648, DOI: 10.1021/acs.est.5b02328.

Furthermore, the following manuscripts are under preparation: *i) «Study of the Elemental Composition and Bacterial Communities Abundance of Atmospheric Fine Particles during African Dust Events in the Eastern Mediterranean». Authors: E.G. Stephanou, M. Iakovidis, S. Nikolaki, S. Pergantis, G. Tsiamis, T. Tziaras. ii) «Determination of Organochlorine Persistent Organic Pollutants in the Atmosphere Eastern Mediterranean during African Dust Events: Study of their Occurrence in Relation to Predominant Meteorological Regimes». Authors: M. Iakovidis, E.G. Stephanou, T. Tziaras. iii) «Occurrence of Polycyclic Aromatic Hydrocarbons in Fine Particles Collected during African and Middle East Dust Events in Crete and Cyprus". Authors: M. Iakovidis, E.G. Stephanou, S. Achilleos, P. Koutrakis. iv) «Assessment of Bacterial Diversity in Fine Atmospheric Particles by Use of High Density Microarray». Authors: S. Nikolaki, K. Zotou, K. Bourtzis, G. Tsiamis, M. Iakovidis, E.G. Stephanou.*

1.3. During the third year of the project, the Researchers of the project participated in several international conferences (funded by the "ARISTEIA-I_1346 action), to present the foremost research results of the project:

i) **European Winter Conference on Plasma Spectrochemistry** (EWCPS, 2015, Munster, February 22-26, 2015, Germany, https://www.ewcps2015.org/),

ii) **Gordon Research Conference in Atmospheric Chemistry 2015** (Waterville Valley, August 2-7, 2015, New Hamshire, USA, https://www.grc.org/programs.aspx?id=10915). The participation (travel expenses, housing and conference fees) was entirely funded by other sources and not by ARISTEIA-I),

iii) **Goldschmidt Conference 2015** (Prague, August 16-21, 2015, , http://goldschmidt.info/2015/program/programViewThemes),

iv) **3Rd International Congress in Bacteriology and Infectious Diseases 2015** (Valencia, August 4-6 2015, http://www.conferenceseries.com/Past_Reports/Bacteriology-2015-past/),

v) **18Th Edition of Euroanalysis in Analytical Chemistry-2015** (Bordeaux, September 6-10, 2015, http://www.euroanalysis2015.com/),

vi) **XV Symposium on Pesticide Chemistry "Environmental Risk Assessment and Management"** (Piacenza, September 2-4, 2015, http://www.symposiumpesticide.org/wp-content/uploads/2015/06/Proceedings-SPCXV_rev.pdf?e66407).

The conferences materials (abstract, oral presentation PPT files and poster files) are all included to the Deliverables Folder **"DISSEMINATION OF RESULTS-1346"** of the project repository and are available on the project website **[http://chemisand.chemistry.uoc.gr/dissemination-of-results].**

2.Sampling Network and Sampling

2.1. The implementation of the sampling network has been completed as foreseen at the first semester of the project, during which the sampling device(collection of particulate matter of aerodynamic diameter 10 micrometers (PM_{10}), particulate matter of aerodynamic diameter 2.5 micrometers ($PM_{2.5}$) and gas phase), was available and used.

2.2. The sampling campaign started six months (May 2012) before the foreseen formal launch of the project and has been completed one month before its formal completion (September 2015). 24-h samples were collected, including $PM_{2.5}$, PM_{10}, TSP (total suspended particles) and gas phase at the main study sampling station (semirural site). Further details on the number of the samples collected during the project and the physical, chemical and microbiological parameters studied, are reported in the **Database file** of the project repository **(DATA BASE 1346.xlsx, sheet "Workpackage_2.2")** and may also be displayed at the project website [http://chemisand.chemistry.uoc.gr].

3.Transport and Climatology of African Dust

3.1. The origin of the air masses was determined, for all the samples collected in this project, by using the HYSPLIT_4 transport and dispersion model, developed by NOAA (National Oceanic and Atmospheric Administration of USA). Back trajectories were traced for 3 days (72 h), using 8 h intervals, 4h after the initial setup of the daily sample, in 1000 m above sea level. The images archive of the air mass traces are all included in a separate folder **«Workpackage_3.1-back_trajectories»,** into the Deliverables Folder "**DISSEMINATION OF RESULTS-1346**" of the project repository.

3.2. Satellite data wwere obtained for the 65 sampling days.
For Aerosol Optical Depth (AOD) the data were acquired from MODIS (Moderate Resolution Imaging Spectroradiometer; NASA's Aqua and Terra satellites) in 550 nm projection. Additional data for AOD were available through the AERONET (Aerosol Robotics Network, NASA) database. The corresponding values ranged between 0.062 and 1.621, with an

average of 0.304±0.360. The whole dataset is located in the database file of the project repository **(DATA BASE 1346.xlsx, sheet "Workpackage_3.2")**.

It must be noticed that this period of time (reporting for ARISTEIA-I) satellite data linked to field measurements during the last sampling year (2015) could not be obtained. As soon the data will be available they will be uploaded to the website of the project and will be accessible.

4.Physical and Chemical Characterization of African Dust Particles

4.1. $PM_{2.5}$, PM_{10} and TSP concentrations for the whole dataset (71 atmospheric samples) including average, min, max, median and geo-mean concentration) are available in the database file of the project repository (**DATA BASE 1346.xlsx, sheet "Workpackage_4.1"**).

4.2. The first year of the project was devoted to sampling and to the development of a suitable and efficient analytical method for the geochemical-multielemental analysis of the airborne particulate matter of the African mineral dust. During the second and third year of the project, sampling continued and the collected samples were analysed using the analytical methodology established in the first year. In total 60 samples of suspended $PM_{2.5}$ particles were collected, of which 29 were strongly influenced by African dust (A.D.) Forty-six (46) elements were determined in elevated concentrations (e.g. ^{27}Al, ^{57}Fe, ^{55}Mn, ^{44}Ca and ^{24}Mg). Some trace elements (e.g. lanthanides ^{165}Ho, ^{159}Tb, ^{169}Tm, ^{175}Lu, ^{146}Nd, ^{153}Eu and ^{141}Pr) were determined in low concentration but their value as markers of A.D. is very important. A detailed report with the concentrations of the elements analysed are included in the project's database archive (**DATA BASE 1346.xlsx, "Workpackage_4.2"**.

4.3. The first year of the project was devoted to sampling and to the development of a suitable and efficient analytical method for the organic (OC), elemental (EC), total (TC) and carbonate (CC) carbon concentration. A total number of 83 samples ($PM_{2.5}$ and PM_{10}) was analysed. Average concentrations of these parameters and descriptive statistics are available in the database file of the project repository, which is attached along with the present report (**DATA BASE 1346.xlsx, "Workpackage_4.3"**).

4.4.a. In order to study the occurrence of several toxic organic compounds, transported from the upwind Sahara-Sahel savannah zone into the eastern Mediterranean, a reliable analytical procedure, which could combine the concurrent analysis of 36 Polycyclic Aromatic Hydrocarbon ($\Sigma_{36}PAH$) members, 48 Polychlorinated Biphenyl ($\Sigma_{48}PCBs$) congeners, along with 25 legacy and currently used Organochlorine Pesticides (OCPs), was developed and tested during the first year of the project, in conjunction with the implementation of the sampling campaign. Details and descriptive statistics on the toxic organic compound

concentrations are available via the database file of the project repository **(DATA BASE 1346.xlsx, "Workpackage_4.4.a.")**.

4.4.b. A <u>novel analytical method</u> has been developed for the determination of all <u>five arsenic (As) species</u> known to exist in atmospheric particulate matter (PM), i.e., the inorganic arsenite iAs(III) and arsenate iAs(V), and the methylated methylarsonate (MA), dimethylarsinate (DMA) and trimethylarsine oxide (TMAO). In the present study, an HPLC (with an anion and cation exchange column connected in series)-arsine generation-ICP-MS system provided complete separation of all five As species and limits of detection from 10 to 25 pg As mL^{-1}. This method was applied to analyze water extracts of the inhalable fraction of atmospheric PM (PM$_{10}$, PM$_{2.5}$ and PM$_{2.1}$). Eighty-one (81) samples were collected, most during Saharan dust events, from a semirural area, and analyzed. Details and descriptive statistics on the As species concentrations are available via the database file of the project repository **(DATA BASE 1346.xlsx, "Workpackage_4.4.b.")**

5. Microbial Analysis of African Dust

Within the frameworks of CHEMISAND the bacterial composition during several sandstorm events in the South of Greece that occurred from March 2015 until the July 2015 has been assessed using new generation sequencing technologies.

In total 22 samples (6 control samples and 16 event samples) with three biological replicates per sample have been characterized by Illumina amplicon sequencing using fusion primers U341F and 805R in order to amplify the V3-V4 region of the 16S rDNA gene. Fungal fragments of the nuclear ribosomal internal transcribed spacer region (ITS2), using primers ITS3F and ITS4R, failed to be amplified. In total 519,707 bacterial sequences were analyzed using Qiime, permutational multivariate analysis of variance (Permanova) and canonical analysis of principal coordinates (CAP) implemented in primer 6+ and PAST3.

Briefly, data analysis involved the following steps: i) filtering of low quality sequences, ii) detection and removal of chimeras using the GOLD database, iii) clustering sequences into OTUs with 97% sequence identity and iv) taxonomic assignment of OTUs using SILVA111. The resulting set of OTUs was used in alpha diversity analyses (rarefaction, microbial diversity indices) and beta diversity analyses (measure of distance between communities-ordination techniques and testing of significance).

Our results indicate distinct structure of the bacterial communities, with the samples collected during dust events forming a distinct cluster clearly separated from the control communities. There is also a clear separation between the dust events of 2013 and those of 2014 highlighting the unique bacterial profile of the sandstorms. Species richness estimators and community diversity indices for sandstorms are increased compared to controls. Rarefaction curves determine that sampling depth was sufficient to accurately characterize the bacterial community being studied. Analysis on the distribution of bacteria during the sandstorm events indicated that there is an increase in the relative abundance of

Alphaproteobacteria, a decrease for *Firmicutes, Actinobacteria and Bacterobacteria,* while *Cyanobacteria* are almost disappearing at the sandstorm of 2014.