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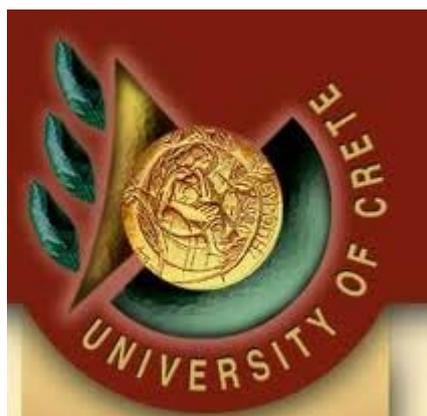
**HIGH RESOLUTION IONIC COMPOSITION
MEASUREMENTS OF FINE MODE AEROSOLS IN THE
EASTERN MEDITERRANEAN**

UNIVERSITY OF CRETE

DEPARTMENT OF CHEMISTRY

Environmental Chemical Processes Laboratory – ECPL

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EASTERN MEDITERRANEAN**



ALEXANDER VARDAVAS

THESIS SUPERVISOR: PROFESSOR N. MIHALOPOULOS

HERAKLEION

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ABSTRACT

A PILS-IC system was set up and modified in Crete to test its capability to measure anion concentrations arising from aerosols. The PILS of the experiment was based at the Environmental Chemical Process Laboratory (ECPL) of the Chemistry Department at the University of Crete. The location of the University of Crete is at Voutes located not more than 20 km from the city of Heraklion, with small populations close by and the main electricity power plant of the area is situated near the sea about 10 km away. However, because of the wind directions we are interested to see how accurately the PILS is able to rapidly sample air parcels from the wider geographical region.

Various anions were detected but their IC analysis was difficult due to low concentrations except for the sulfate. Although the IC was able to measure several anion concentrations (these included MSA, Cl^- , Br^- , NO_3^- , SO_4^- , HPO_4^- and oxalate anions) using a standard solution of high concentration, the PILS sample solution obtained from the air sample resulted in the detection and concentration measurement of only the sulfate anion by the IC.

Because of the importance of the concentration of SO_4^{2-} in the atmosphere and the location where the sampling was done, the main focus was the SO_4^{2-} anions. Sulfate concentrations were monitored approximately every 20 minutes for the period April-June 2011, which included a dust event and a major pollution event arising from the Athens Metropolitan area. Tests were also performed to ascertain the effects of operating the system with and without denuders on the measured sulphate concentrations using different IC eluents that demonstrated the effectiveness of the denuders in obtaining better concentration results.

1. INTRODUCTION

1.1. Aerosol measurements and the PILS system

Aerosol measurements have been made by a great variety of experimental methods in almost every possible location in the atmosphere during the last several decades. Much of the background data have been obtained with Aitken nuclei counters, which only sense the nuclei mode near sources of nuclei where nuclei dominate the number distribution, but are relatively more sensitive to the accumulation or fine mode for aged aerosols where the nucleation rate is small. On the other hand, most of the pollution-related concentration measurements have been of mass concentration using filter or impactor samples having variable and often uncertain large particle cutoffs. Only in the last decade have enough complete size distribution measurements been made so that the relative concentrations of the different modes in the distribution under various conditions can be determined.

The determination of anions and cations in atmospheric aerosols yields essential information concerning transport and atmospheric transformation processes as well as emission sources. Traditionally, off-line sampling methods have been used for the characterization of atmospheric aerosol, with the most common method of measuring aerosol composition involving the analysis of particulate matter collected onto a filter substrate (McMurray, 2000).

There are significant disadvantages associated with the use of filter samples, including sampling artifacts (Chow, 1995; Fan et al., 2003), but the most important disadvantage is the inherently low-time resolution. The latest developments in aerosol sampling involve the on-line, and almost real-time, collection of aerosol concentration information. These techniques provide the advantage of being able to observe highly time-resolved variations in aerosol composition and concentration. This has important implications for the understanding of atmospheric chemistry processes and the identification of the contributing aerosol sources.

The study of adverse effects of air pollution requires semi-continuous, rapid and accurate measurements of inorganic species in aerosols and their gas phase components in ambient air. The most promising instruments, often referred to as steam collecting devices, are the Particle-Into-Liquid-Sampler (PILS) coupled to wet-chemical analyzers such as a cation and/or anion chromatograph (IC).

The PILS is a type of “steam collection” device. Every study using such devices perform configurations and modifications to improve the effectiveness of the sampling. Steam collection devices are capable of being connected to other scientific instruments, such as an Ion Chromatograph (IC), in a line so that more and different results can be analyzed. Application areas for PILS–IC systems include the monitoring of pollutants inside buildings, emission control at the workplace for worker protection, monitoring of outside air,

measurements of tunnel air, determination of stack emissions and mobile use for example in monitoring aircraft trips.

1.2. Objectives of study and scope

The purpose of this study was to obtain concentrations of high resolution ionic compositions of fine mode aerosols in the Eastern Mediterranean region using an on-line system comprising a particle into liquid sampler (PILS) and an ion chromatograph. The PILS is regarded as a high temporal resolution sampling device because of its capability of almost real-time collection of aerosol information compared to the filter sampling technique with its main disadvantage being the inherently low temporal resolution. The PILS system is the first such high resolution system to be set up for fine aerosol composition and concentration analysis in Crete.

Amongst the advantages of the PILS-IC system are the determination of ions in aerosols with high temporal resolution, simple interfacing to an ion chromatography system, high sampling rate, diurnal variation analysis with high time resolution, direct on-site sample analysis, contamination-free aerosol collection techniques, no sample storage required and no sample preparation required.

Objectives of the study included:

- High temporal resolution sampling of fine mode aerosols every 20 minutes
- Anion concentration measurements using the PILS-IC system
- Validation of PILS measurements against off-line filter extracts
- Testing of denuder efficiency in removing spurious sources of anions
- Standard sample tests to ascertain IC correct performance
- Evaluation of PILS-IC operation for future field studies

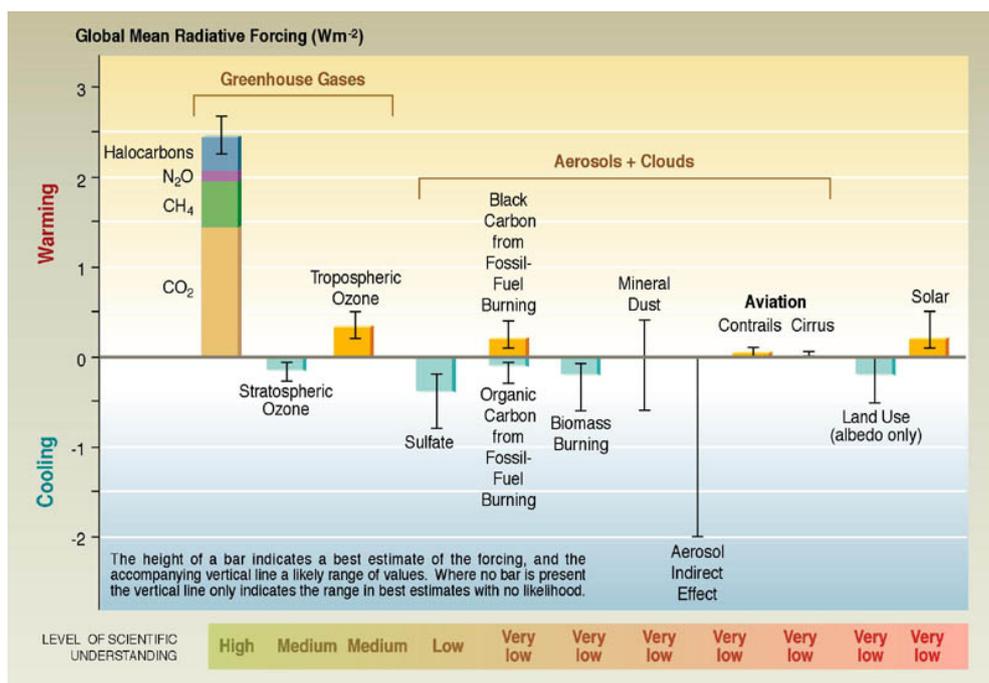
The scope of the study in order to test our PILS-IC system included high resolution measurements over a period from April to June, to obtain sulfate concentrations from the fine mode to monitor sulfate concentrations and track air pollution arriving in Crete to its sources that include nearby large cities of Athens, Istanbul, amongst others, and from the Sahara during dust events. For this we employed the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) program to obtain the backward trajectories and identify the sources of air pollution.

2. AEROSOLS AND SULFATE CONCENTRATION

2.1. Sulfate aerosol radiative forcing and climatic effects

Aerosols can influence climatic change through the absorption and scattering of solar radiation and to a smaller extent absorption of the Earth's infrared radiation.

Sulfate particles, both solid (mostly ammonium sulfate) and aqueous (containing sulfuric acid and sea salt) primarily tend to scatter solar radiation back to space and hence result in planetary cooling, as can be seen in Figures 1a and b. Globally these contribute a radiation forcing of about 0.6 Wm^{-2} compared to the greenhouse warming of 2.4 Wm^{-2} . On the other hand fine dust from deserts and soot particles from fires and combustion processes tend to be more absorbing and hence contribute to atmospheric warming with ramifications on cloud production. Both absorption and scattering primarily lead to the cooling of the Earth's surface and hence reduce oceanic evaporation.



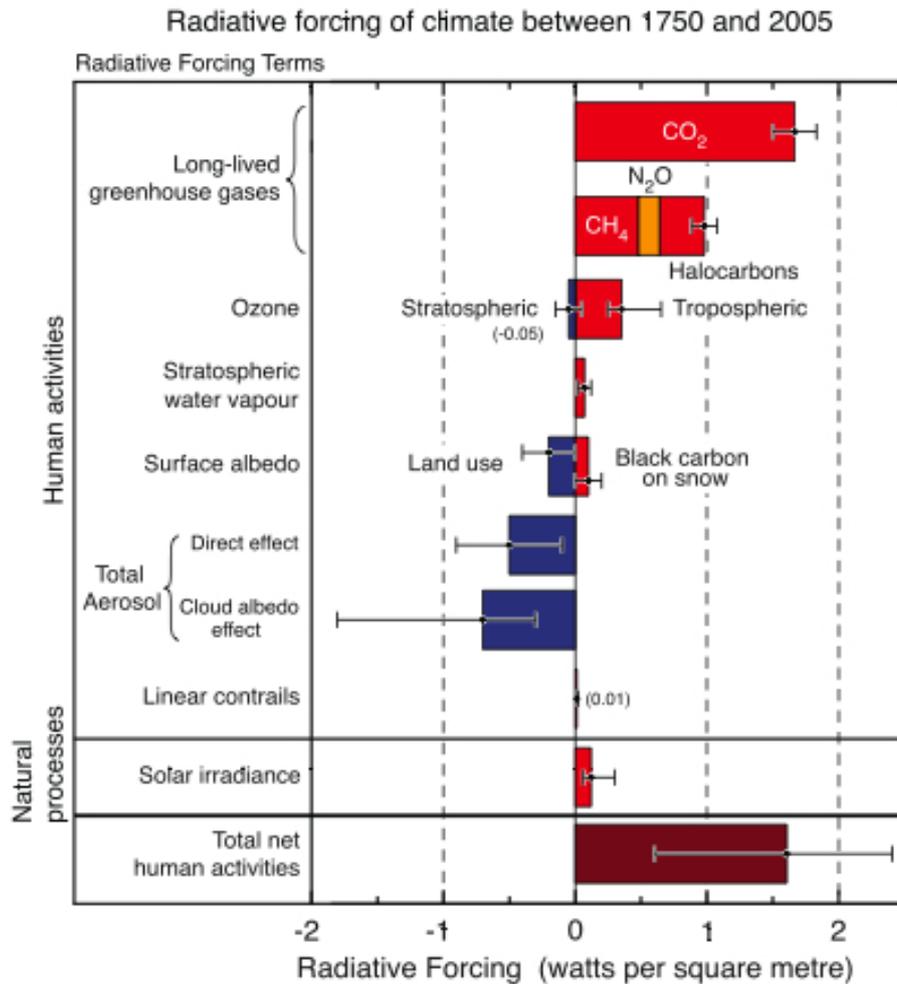


Figure 1. Global radiative forcing showing a) sulfate cooling b) total aerosol cooling (IPCC 2001, 2007)

2.2. The sulfur cycle and natural sources of atmospheric sulfur

Large quantities of sulfur dioxide enter the atmosphere each year from anthropogenic sources, mainly from the combustion of fossil fuels and industry. It is produced from the burning of fossil fuels (coal and oil) and the smelting of mineral ores (aluminum, copper, zinc, lead and iron) that contain sulfur. Most of the sulfur dioxide released into the environment comes from electricity power stations, especially those that burn coal. Some other sources of sulfur dioxide include petroleum refineries, cement manufacturing, paper pulp manufacturing and metal smelting and processing facilities. Locomotives, large ships, and some non-road diesel equipment currently burn high sulfur fuel and release sulfur dioxide into the air.

Sulfur dioxide dissolves easily in water to form sulfuric acid. Sulfuric acid is a major component of acid rain. Acid rain can damage forests and crops, change the acidity of soils, and make lakes and streams acidic and unsuitable for fish. Sulfur dioxide also contributes to the decay of building materials and paints, including monuments and statues.

The existence of natural sources of atmospheric sulfur include geothermal emissions mainly as volcanic emissions, mainly as SO₂ and some H₂S, wind generation of particulate sulfate (SO₄²⁻) in the form of sea salt (in sea spray), and emissions of reduced sulfur compounds such as H₂S (hydrogen sulfide), COS (carbonyl sulfide), CS₂ (carbon disulfide), CH₃SCH₃ (dimethyl sulfide, DMS) from the biosphere.

Sulfur is a relatively abundant element which plays an essential part in the environmental cycle. On land, it is found mainly as sulfide and sulfate ores and in the oceans it is present predominantly as dissolved sulfate. In the atmosphere, however, the principal sulfur compounds are hydrogen sulfide (probably together with other reduced sulfur species), sulfur dioxide and sulfate aerosols and mists. Sulfur compounds are not accumulating in the atmosphere. A cycle operates whereby sulfur is continuously transported between the different phases; and there is a delicate balance between the release of sulfur into the atmosphere and its return to the Earth's surface, although over the last 100 y or so, the increasing amounts of atmospheric sulfur generated by man may have shifted the balance point. This is shown by recent changes in the sulfur content of polar ice, which had previously remained constant over the centuries.

Removal of sulfur from the atmosphere takes place by precipitation processes (involving mainly sulfate) and by dry deposition (principally of sulfur dioxide). However, the overall sulfur cycle is complicated by transfers of sulfur from land to oceans, and vice-versa, and indeed also between the various land phases.

2.2.1. Geothermal emissions

Various sources of geothermal activity such as sulfur springs are responsible for the emission of sulfur compounds into the atmosphere. However, by far the greatest amount of sulfur generated in this way is derived from volcanoes. Volcanic emissions contain sulfur in the form of SO₂ which is converted via oxidation reactions to sulfuric acid (H₂SO₄) and H₂S which is oxidized to SO₂. Volcanism has been found to affect significantly the sulfate concentration in polar ice, especially as a result of precipitation following stratospheric transport. Nevertheless, it must be concluded that the amount of sulfur released into the atmosphere by volcanoes is unlikely to be significantly greater than 10 Tg(S)/yr and is thus small in comparison with that from other sources (see Table 1 taken from Seinfeld and Pandis 1998).

Table 1 Sulfur sources

Source	H ₂ S	DMS	CS ₂	OCS ^d	SO ₂	SO ₄	Total ^a
Fossil-fuel combustion + industry		Total reduced S: 2.2			70	2.2	71–77 (mid-1980s) (68/6)
Biomass burning	<0.01?	—	<0.01?	0.075	2.8	0.1	2.2–3.0 (1.4/1.1)
Oceans	<0.3	15–25	0.08	0.08	—	40–320	15–25 (8.4/11.6) ^b
Wetlands	0.006–1.1	0.003–0.68	0.0003–0.06	—	—	—	0.01–2 (0.8/0.2)
Plants + soils	0.17–0.53	0.05–0.16	0.02–0.05	—	—	2–4	0.25–0.78 (0.3/0.2) ^c
Volcanoes	0.5–1.5	—	—	0.01	7–8	2–4	9.3–11.8 (7.6/3.0)
Anthropogenic (total)							73–80
Natural (total, without sea salt and soil dust)							25–40
Total							98–120

^aNumbers in parentheses are fluxes from Northern Hemisphere/Southern Hemisphere.

^bExcluding sea-salt contributions.

^cExcluding soil dust contributions.

^dAndreae and Crutzen (1997)

Source: Berresheim et al. (1995).

2.2.2. Sea spray

A more important source of atmospheric sulfur is the fine spray, formed above the oceans, the individual droplets in which evaporate to leave even smaller solid particles. Sodium sulfate is the second most abundant constituent of sea water, the SO₄²⁻/Cl⁻ ratio being about 0.14. The amount of sulfur emitted into the atmosphere depends on the sulfate content of seawater (known to be reasonably constant at 0.27 %) and on the extent to which sulfate ions (SO₄²⁻) are enriched relative to sodium and chloride ions by fractionation during spray formation. The major part of the emission is returned to the oceans as a result of sedimentation (gravitational settling onto the Earth's surface) and precipitation scavenging but about 10% of the spray-generated sulfate is carried over and deposited on land surfaces.

2.2.3. Biogenic sources

The most important reduced sulfur gases in the air are H₂S (hydrogen sulfide), COS (carbonyl sulfide), CS₂ (carbon disulfide), CH₃SCH₃ (dimethyl sulfide, DMS). Their main natural sources on land are biogenic reactions in soils, marshlands, and plants (for H₂S, COS, CS₂, DMS), also biogenic reactions in the ocean due primarily to phytoplankton (COS, CS₂, primarily DMS, see Table 1). The biological reduction of sulfur compounds constitutes by far the most important natural source of atmospheric sulfur. Such reduction occurs most readily in the presence of organic matter and under oxygen-deficient conditions. The sulfur compounds entering the atmosphere are derived from the nonspecific reduction of sulfur in marine algae, soils and decaying vegetation and from bacteria, which specifically reduce various types of sulfur compounds predominantly sulfate-reducing bacteria, such as *Sporovibrio desulfuricans*, present in fine-grained mud).

When these gases are released into the oxygen-rich atmosphere they are oxidized to SO₂, and then over 65% of the SO₂ is oxidized to SO₄²⁻, through reactions with O₂, OH and catalytic (presence of Mn²⁺ and Fe³⁺) aqueous-

phase reactions in cloud droplets, and the remainder is removed by dry deposition on the Earth's surface. From Table 1 it can be seen that DMS dominates the emissions from oceans. An enormous amount of sulfate is ejected into the air from the oceans in sea spray but these relatively large particles are quickly recycled back to the ocean.

Hydrogen sulfide reacts only slowly with oxygen in the absence of catalysts but is oxidized photochemically. There are differing views as to its rate of interaction with ozone, which may diffuse down into the troposphere (lower atmosphere). The latter reaction may be quite rapid, especially in the presence of aerosols or take place only at a negligible rate under normal atmospheric conditions.

2.3. Anthropogenic sources of atmospheric sulfur

The total sulfur emitted by man into the atmosphere, and indeed also the percentage effect of his activities has been increasing markedly throughout the past 100 years. The main industrial sources of atmospheric sulfur remain the combustion of coal and petroleum, petroleum refining and the smelting of non-ferrous ores, although their relative weightings have been changing considerably.

2.3.1. Coal

The most abundant source of atmospheric sulfur is still the burning of coal and its by-products (about 60%). Unfortunately, the almost infinite variety of coals makes it difficult to quantify exactly the sulfur content of emissions from this source. Nevertheless, there are precise data regarding the amounts both of total hard coal and of lignite (or brown coal) consumed per year. Fossil fuels contain sulfur primarily in the form of organic sulfur compounds (those containing carbon). Combustion converts them to SO₂.

2.3.2. Petroleum

The next most important source of atmospheric sulfur is petroleum products. The proportion of sulfur generated from petroleum is still increasing. Although the rate of growth of petroleum consumption has been higher than that of coal, the amount of sulfur emitted by all activities of the petroleum industry has increased less rapidly than the total consumption of petroleum. Thus, even though the crude material contains, overall, progressively more sulfur, emission factors are lower and, in fact, the amount of sulfur emitted per ton of petroleum consumed has decreased after reaching a maximum in 1965. The major source of SO₂ from petroleum is the combustion of heavy residual fuel oils.

2.3.3. Non-ferrous ores

The next source of sulfur emissions, in quantitative terms, is the smelting of non-ferrous ores (mainly as pyrites). Here, copper is the main contributor, and

lead and zinc are the other, less important, ones. The emission of sulfur compounds from smelting has been steadily declining in comparison with that associated with petroleum products, but is gaining ground relative to coal. The large emission factors associated with nonferrous metal production derive from the fact that sulfur contained in the ores escapes mostly as SO_2 .

2.3.4. Other sources

The only other significant contribution is from the manufacture of sulfuric acid. The conversion of pulp to paper leads to H_2S and organic sulfide emissions but their magnitude is comparatively small.

(References used include the books: Seinfeld and Pandis 1998, Warneck 1988 and Hobbs 2000)

2.4. Sulfur uptake by aerosols

It is now well established that a significant fraction of sulfur emitted into the atmosphere either as a primary aerosol or as the product of gas-to-particle conversion, ends up in the atmosphere as a quite stable submicron aerosol. It is also increasingly clear that the fraction of the total fine particle mass aerosol of sulfur containing, or what are more generally called sulfate aerosols is increasing over and downwind of industrialized areas.

Atmospheric aerosols can be divided into water-soluble inorganic salts minerals from the Earth's crust that are insoluble in water or organic solvents, and organics some water soluble. The amount of water-soluble material increases with decreasing particle size at the expense of the mineral component.

Except for marine aerosols, the mass concentrations of which are dominated by sodium chloride, sulfate is one of the prime contributors to the mass concentration of atmospheric aerosols. The mass fraction of SO_4^{2-} ranges from about 20% to 40% for continental aerosols to about 70% for polar aerosols. Since the sulfate content of the Earth's crust is too low to explain the large percentage of sulfate in aerosols, most of it must derive from gas-to-particle conversion (GTPC) of SO_2 . The sulfate is contained mainly in submicron aerosols with a peak in the accumulation mode with a diameter D near $D=0.6$ microns as shown in Figure 2 (from Seinfeld and Pandis 1998).

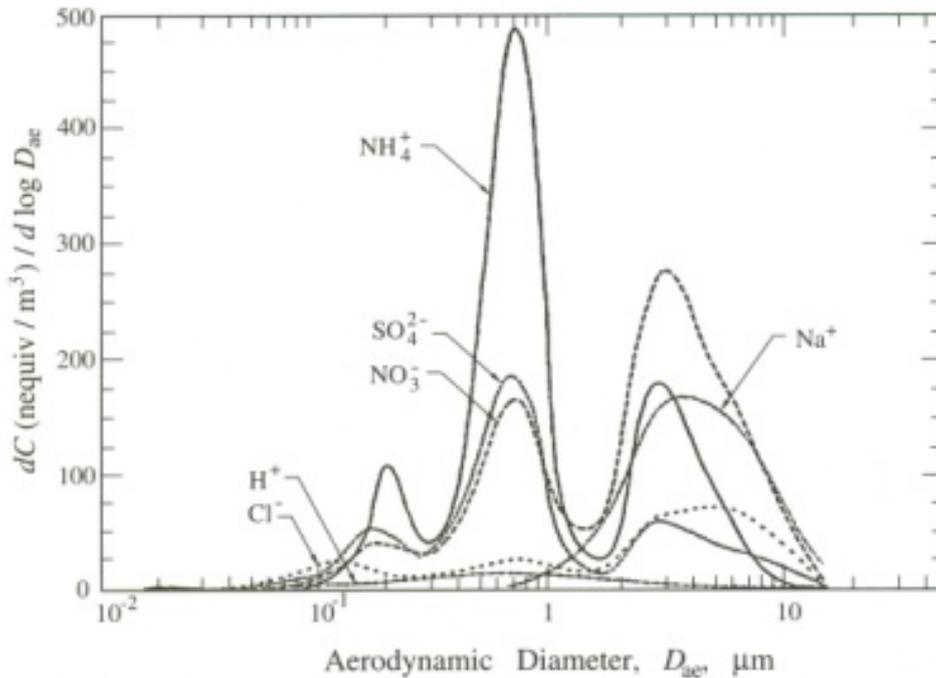


Figure 2. Sulfate in the accumulation mode

In marine air the main contributors to the mass concentration of aerosols are Na^+ , Cl^- , Mg^{2+} , SO_4^{2-} , K^+ and Ca^{2+} . Apart from SO_4^{2-} , these compounds are mainly in the coarse-particle mode because they originate from sea salt derived from bubble bursting. Sulfate mass concentrations peak in both the coarse-particle and accumulation modes; the latter is due to GTPC of SO_2 that derives primarily from biogenic gases such as DMS.

2.5. Gas-to-particle conversion

Although the mass concentration of aerosols peaks above 10 microns, i.e. large particles, as can be seen in Figure 3 (from Vardavas and Taylor 2011), the accumulation mode (0.1-1.0 micron) important to the modification of solar UV-Visible radiation (0.3-0.7 microns) in the atmosphere, has a number density that peaks at about 0.6 microns. The small particles referred to as Aitken nuclei (<0.1 microns), although have a higher number density do not play an important role on UV-Visible radiation, as we shall see in a later section.

The main process of sulfate aerosol production in the accumulation mode is through the dissolution of H_2SO_4 in water droplets in the atmosphere or its condensation onto existing particles. Reduced sulfur species such as H_2S (hydrogen sulfide), COS (carbonyl sulfide), CS_2 (carbon disulfide), CH_3SCH_3 (dimethyl sulfide, DMS) from the biosphere are oxidized to SO_2 which is then oxidized to H_2SO_4 via reaction with OH. Thus accumulation mode aerosols

contain a significant amount of sulfate over oceanic areas. Continental aerosols on the other hand can also contain insoluble ammonium sulfate.

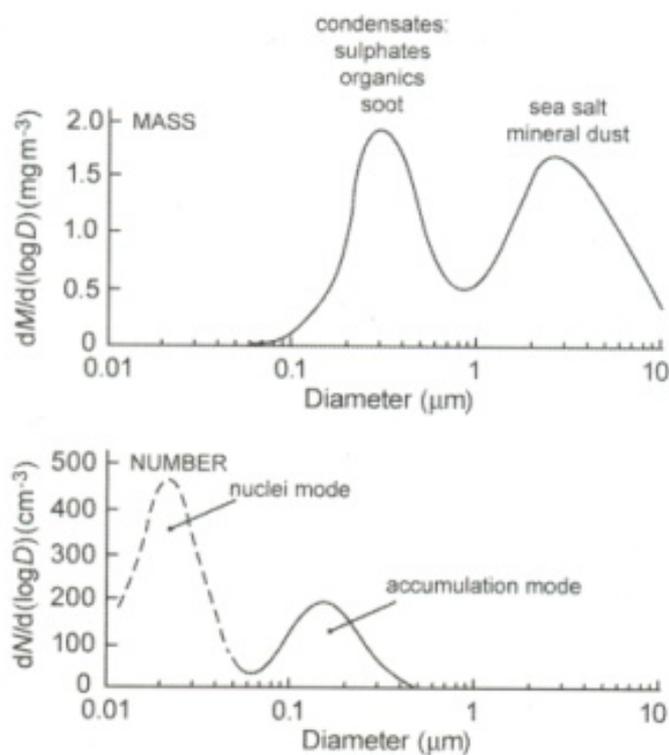


Figure 3. Sulfate number density peak between 0.1 and 1.0 micron.

Chemical reactivity of atmospheric sulfur compounds is inversely related to their sulfur oxidation state. The solubility of sulfur compounds also depends on their oxidation state. The high solubility of SO_4^{2-} is due to the sulfur high oxidation S(+6). The reduced sulfur compounds have a low oxidation state S(-2) and thus exist as gases in the atmosphere but are rapidly oxidized by OH so their lifetime in the atmosphere is small about a few days. The oxidized products SO_2 S(+4), SO_3^{2-} S(+4) and SO_4^{2-} (S+6) are in aqueous form and constitute a key component of aerosols shown in Table 2 (from Seinfeld and Pandis 1998).

Table 2 Sulfur compounds and their oxidation states

Oxidation State	Compound		Chemical Structure	Usual Atmospheric State
	Name	Formula		
-2	Hydrogen sulfide	H ₂ S	H—S—H	Gas
	Dimethyl sulfide (DMS)	CH ₃ SCH ₃	CH ₃ —S—CH ₃	Gas
	Carbon disulfide	CS ₂	S=C=S	Gas
	Carbonyl sulfide	OCS	O=C=S	Gas
	Methyl mercaptan	CH ₃ SH	CH ₃ —S—H	Gas
-1	Dimethyl disulfide	CH ₃ SSCH ₃	CH ₃ —S—S—CH ₃	Gas
0	Dimethyl sulfoxide	CH ₃ SOCH ₃	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{—S—CH}_3 \end{array}$	Gas
4	Sulfur dioxide	SO ₂	O=S=O	Gas
	Bisulfite ion	SO ₃ · H ₂ O		Aqueous
	Sulfite ion	HSO ₃ ⁻		Aqueous
6	Sulfuric acid	H ₂ SO ₄	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO—S—OH} \\ \parallel \\ \text{O} \end{array}$	Gas aqueous/aerosol
	Bisulfate ion	HSO ₄ ⁻	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO—S—O}^- \\ \parallel \\ \text{O} \end{array}$	Aqueous/aerosol
	Sulfate ion	SO ₄ ²⁻	$\begin{array}{c} \text{O} \\ \parallel \\ \text{O—S—O}^- \\ \parallel \\ \text{O} \end{array}$	Aqueous/aerosol

Over oceans aerosols also show a deficit of Cl and a surplus of sulfate. For example, sodium chloride in sea spray reacts with sulfuric acid vapor to produce sodium sulfate and HCl vapor leading to an apparent chloride deficit in marine aerosol.

2.6. Sulfur aerosol size distribution

It can be seen that the complete aerosol size distribution in the atmosphere is composed of three modes: the nucleus (or nucleation mode) which peaks near 0.01 microns, the accumulation mode that peaks near 0.1 microns and the coarse particle mode that peaks near 1 micron. The nucleation mode is produced by the condensation of gases such as H₂SO₄ and is thus prominent near sources of pollution. The accumulation mode is due to coagulation of small particles, the condensation of gases onto the existing particles and from the particles left from the evaporation of cloud drops.

Whether or not the sulfur converted from the gaseous state to the low vapor pressure state forms new nuclei (less than 0.1 microns) or condenses directly on existing aerosol particles, most of it ends up in the submicron size range and, in fact, is found in the accumulation mode.

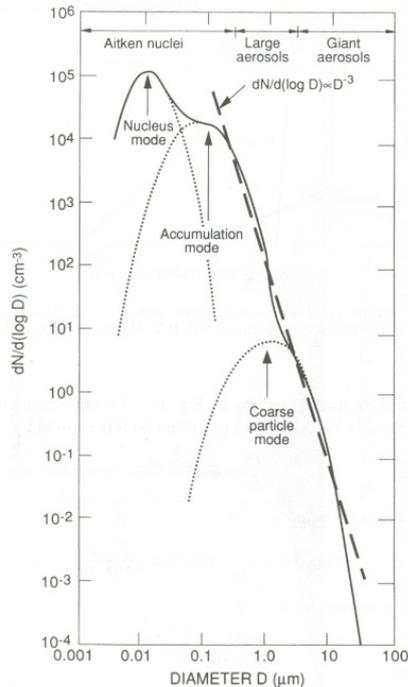


Figure 4. Aerosol diameter size for nuclei, accumulation and coarse modes.

2.7. Aerosol residence time

The residence time of aerosols depends on the sources and sinks in a complex way resulting in large spatial and temporal variability in aerosol concentration, especially near aerosol sources.

The Aitken or nucleation mode ($D < 0.1$ micron) lifetime is less than about 1 day due to coagulation into larger particles and diffusion into cloud particles. The large aerosol particles ($1 < D < 10$ microns) the lifetime is also about 1 day due to removal from the atmosphere by sedimentation (gravity settling), while accumulation mode ($0.1 < D < 1$ micron) results from the strong sources of coagulation of Aitken particles and evaporation of cloud droplets so their lifetime is about 10 days near the Earth's surface. Removal of the accumulation mode is by precipitation scavenging which leads to acid rain.

2.8. Climatic effects of sulfate aerosols

Aerosols can influence climatic change through the absorption and scattering of solar radiation and to a smaller extent absorption of the Earth's infrared radiation.

Sulfate particles, both solid (mostly ammonium sulfate) and aqueous (containing sulfuric acid and sea salt) primarily tend to scatter solar radiation back to space and hence result in planetary cooling, as can be seen in Figure 1a. Globally these contribute a radiation forcing of about 0.6 Wm^{-2} compared to the greenhouse warming of 2.4 Wm^{-2} . On the other hand fine dust from deserts and soot particles from fires and combustion processes tend to be more absorbing and hence contribute to atmospheric warming with

ramifications on cloud production. Both absorption and scattering primarily lead to the cooling of the Earth's surface and hence reduce oceanic evaporation.

As we have seen, sulfate aerosols are an important component of the accumulation mode aerosol particles (0.1-1.0 microns) based on their number density which is the important climatic parameter as these particles efficiency to interact with solar radiation depends on their number population. This interaction depends crucially on the relative size of the aerosol particle compared to the wavelength of the radiation. When the wavelength λ is about the size of the aerosol diameter D , radiation scattering processes such as refraction through water-containing particles and diffraction around such particles becomes important, referred to as MIE scattering. The sulfate aerosols size distribution peaks within the accumulation mode (Figure 2) thus within the peak of the solar UV-Visible radiation between 0.3-0.7 microns. Thus accumulation mode aerosol particles have sizes comparable to the UV-Visible radiation where MIE scattering becomes very important. These region of the spectrum corresponds to a value of the particle size parameter $x=D/\lambda$ of about 1. We see in Figure 5 (from Hobbs 2000) that the effect of aerosols on radiation is in the accumulation mode.

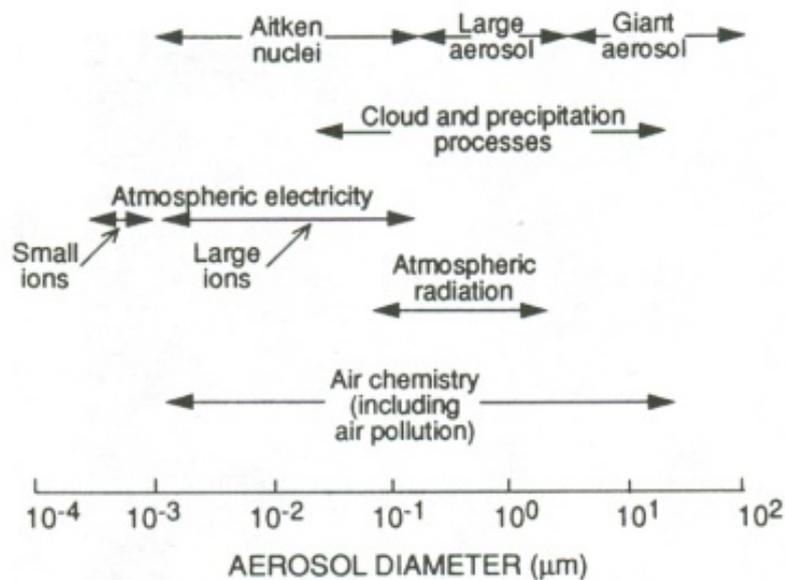


Figure 5. Aerosol diameter size and important atmospheric processes.

Thus sulfate aerosols play a crucial role in cooling the planet as we saw in Figure 1. On the other hand the very small Aitken nuclei that typically have high number densities contribute insignificantly to Rayleigh scattering ($x=0$) of the atmosphere since such scattering is dominated by the very high number densities of the molecules of N_2 and O_2 that constitute the Earth's atmosphere. The large aerosol particles have a considerable mass but their number density is not significant for them to play an important role in radiation scattering, except during major dust events.

3. THE PARTICLE-INTO-LIQUID SAMPLER (PILS)

The Particle-into-Liquid Sampler, or PILS for short, samples aerosol particles from an airstream and transfers them to the aqueous phase. Subsequently, they are analyzed by Ion Chromatography.

3.1. Introduction

The determination of anions and cations in atmospheric aerosols yields essential information concerning transport and atmospheric transformation processes as well as emission sources. Up to now these determinations have been carried out using filters that collect the aerosol particles over a long period of time, usually 24 hours. Prior to Ion Chromatographic analysis, the particles are removed from the filters and dissolved in water. However, this batch method only allows one to determine averages over a time span of 24 hours or more. Additionally, this method is very labour-intensive, temporal resolution is poor and semi-continuous on-line measurements are not possible. In addition, the results can be falsified by desorption processes and chemical transformations. The reliability of the results thus obtained is therefore questionable. In contrast to the above, the particle samplers to be described allow semi-continuous sampling of aerosols downstream from two different denuder systems. Changes in the ionic composition of the aerosols can be sensitively monitored.

3.2. Mode of operation

PILS puts aerosols into a supersaturated water vapor phase, where they quickly grow into droplets. These droplets are separated on the basis of their inertia and pumped on with a carrier fluid, which contains an internal standard to allow simple quantification. Air bubbles that are present are removed in a so-called debubbler, and the aqueous phase is transferred to an Ion Chromatograph for analysis. The size of the aerosol particles to be determined is limited by a cyclone or an impactor at the intake. This makes it possible, for example, to analyze particles smaller than 1 μm , 2.5 μm , or 10 μm (PM1, PM2.5, PM10), depending on requirements. To prevent interferences, the gases are absorbed by denuder systems. A vacuum pump produces an airstream in the system with a flow rate of about 1 m^3/h that ensures the intake of PM1 (fine mode) particles only.

3.3. The PILS method compared to the Filter Sampling method

Traditionally, off-line sampling methods have been used for the characterization of atmospheric aerosol, with the most common method of measuring aerosol composition involving the analysis of particulate matter collected onto a filter substrate (McMurray, 2000).

There are significant disadvantages associated with the use of filter samples, including sampling artefacts (Chow, 1995; Fan et al., 2003), but the most important disadvantage is the inherently low time resolution. The latest developments in aerosol sampling involve the online, and almost real-time, collection of aerosol concentration information. These techniques provide the advantage of being able to observe highly time-resolved variations in aerosol composition and concentration. This has important implications for the understanding of atmospheric chemistry processes and the identification of the contributing aerosol sources.

3.4. Application areas

PILS can be directly coupled with various analysis techniques. With Ion Chromatography, water-soluble anions and cations can be determined simultaneously. PILS can also be used for offline sampling with an autosampler. Other examples are the determination of total organic carbon (TOC Analyzer) or coupling with ICP techniques.

Application areas for PILS–IC:

- ✓ Monitoring of pollutants inside buildings
- ✓ Emission control at the workplace for worker protection
- ✓ Monitoring of outside air
- ✓ Measurements of tunnel air
- ✓ Determination of stack emissions
- ✓ Mobile use for example on aircraft

3.5. Advantages of PILS at a glance

- ✓ Determination of ions in aerosols with high temporal resolution
- ✓ Simple interfacing to an ion chromatography system
- ✓ High sampling rate
- ✓ Diurnal variation analysis with high time resolution
- ✓ Direct on-site sample analysis
- ✓ Contamination-free aerosol collection technique (Particles PM1, PM2.5, PM10)
- ✓ No sample storage required
- ✓ No sample preparation required

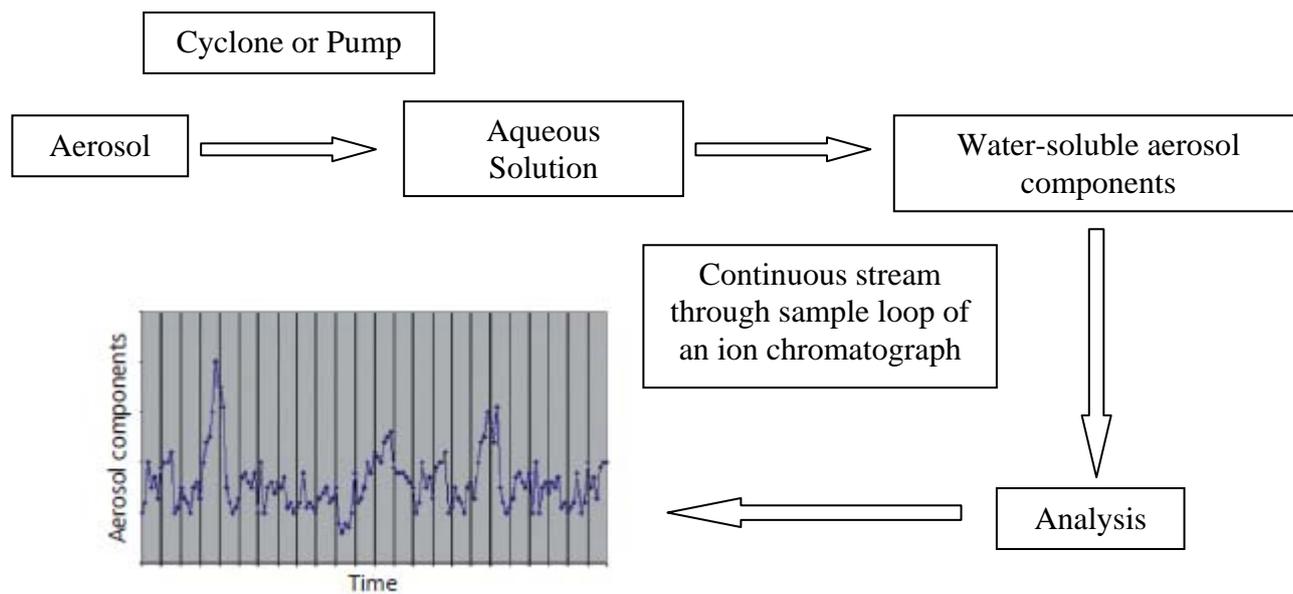


Figure 6. Flow diagram of the PILS system.

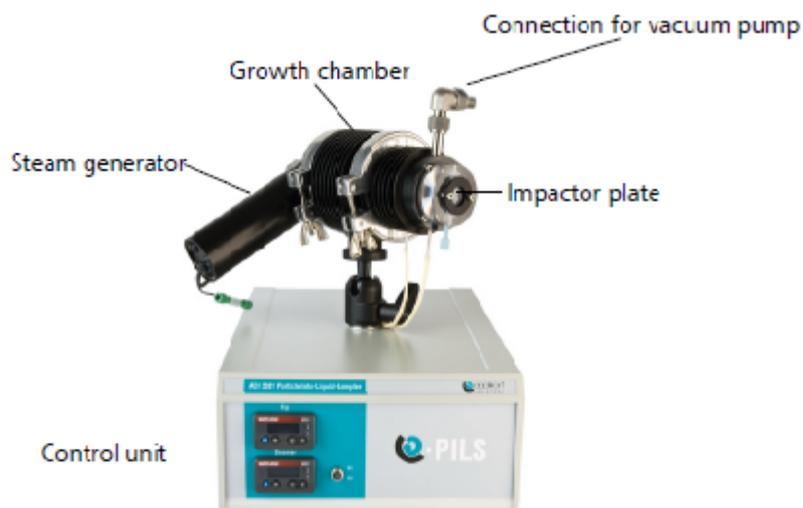


Figure 7. The main unit of the PILS in the current experiment.

3.6. Determination of anions and cations in aerosols by Ion

Chromatography

The study of adverse effects of air pollution requires semi-continuous, rapid and accurate measurements of inorganic species in aerosols and their gas phase components in ambient air. The most promising instruments, often referred to as steam collecting devices, are the Particle-Into-Liquid-Sampler (PILS) coupled to wet-chemical analyzers such as a cation and/or anion chromatograph (IC), shown in Figures 6 and 7. Instruments comprise gas denuders, a condensation particle growth sampler as well as pump and control devices. While PILS uses two consecutive fixed denuders (Figure 8) and a downstream growth chamber. The technique of growing aerosol particles into droplets in a supersaturated water vapor environment. Previously mixed with carrier water, the collected droplets are continuously fed into sample loops or pre-concentration columns for on-line IC analysis. Proper selection of the ion chromatographic conditions of PILS-IC allows for a precise determination, within 4 to 5 minutes, of seven major inorganic species (Na^+ , K^+ , Ca_2^+ , Mg_2^+ , Cl^- , NO_3^- and SO_4^{2-}) in fine aerosol particles (accumulation mode). With longer analysis times (10-15 minutes) even airborne low-molecular-weight organic acids, such as acetate, formate and oxalate can be analyzed.

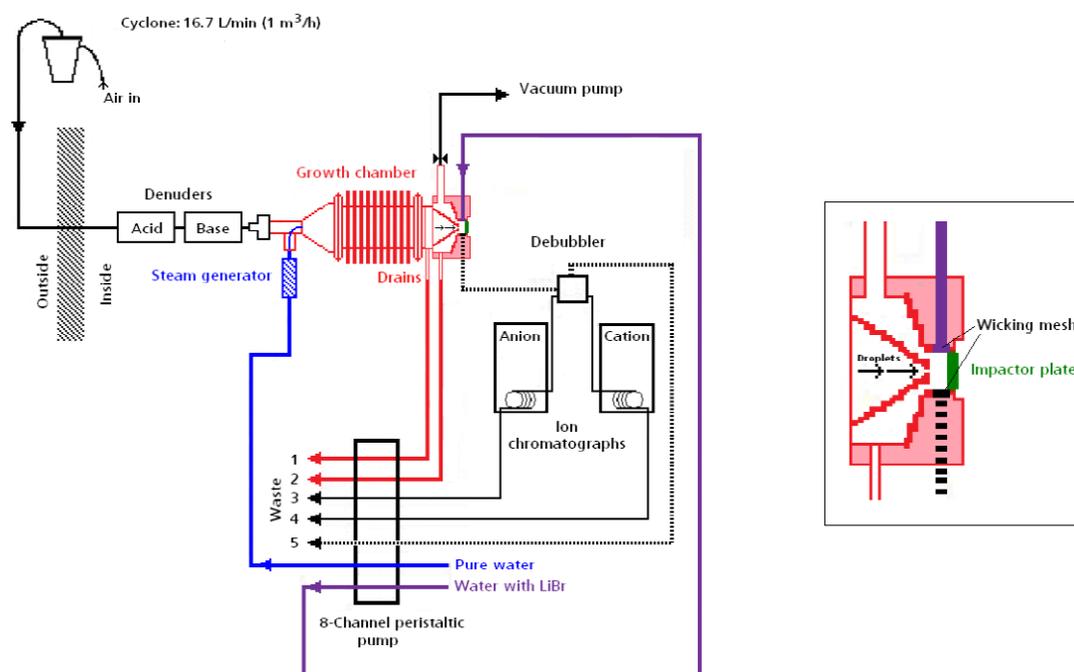


Figure 8. Schematic of a PILS-IC system.

3.7. The ECPL Particle-into-Liquid Sampler

The PILS of the experiment was based at the Environmental Chemical Process Laboratory (ECPL) of the Chemistry Department at the University of Crete. The location of the University of Crete is at Voutes located not more than 20 km from the city of Heraklion, with small populations close by and the main power plant of the county near the sea about 10 km away. However, because of the wind direction we are interested to see how well the PILS is able to sample such air samples with concentrations of the main ions.

The PILS was used to determine the SO_4^{2-} concentrations in the air. The PILS system consisted of the air pipe that was set outside the laboratory connected then to two denuders until the airstream reached using a cyclone (pump) the main control unit where the gaseous phase turns to the aqueous phase. For the main unit to work it needs continuous line feed of nanopure water and the help of two peristaltic pumps in order for the flow of the different liquids to continue to the next stage. Once the sample is in aqueous phase it continues to the Ion chromatography system where continuous injections of samples occur.

The IC is also connected to a continuous feed of nanopure water and the eluent that it needs to help the separation of the ions captured in the sample. Air samples were continuously sampled and analyzed throughout a two month run after many previous months of observations and settings that had been modified for correct operation of the PILS, and hence for correct results, due to the sensitivity of the PILS system.

Many of the modifications that were done to the Particle-into-Liquid Sampler were:

- Flow tests of all the pipes needed for in-takes and out-takes of the samples
- Flow tests for the standard feed line including the main air stream
- Speed tests of the two peristaltic pumps for a correct liquid flow
- IC intake of the liquid samples at the injection point, with different filter sizes or no filter at all installed
- Tests of different guard columns as of main columns
- Tests of different currents from the suppressor
- Tests of different sample times and injection times
- Tests of different eluents for the Ion chromatogram system
- Tests with and without the installment of the denuders

Table 3 Flow rates needed for the PILS system.

	Liquid Nanopure Flow to Steam Chamber	Liquid Nanopure Flow for Rinsing the Impactor	Liquid Flow to IC System	Air flow from Cyclone
Optimum Flow rate	1,2 - 1,6 (ml/min)	0,25 (ml/min)	0,17 (ml/min)	16 – 16,7 (L/min)
Repetition Time	5 min	5 min	10 min	1 min

Many maintenance procedures done to the PILS system were:

- Change of the flow pipes needed for the transfer of the liquids for the main feed for the sample in aqueous phase to reach the IC
- Fresh eluents and nanopure water for the system and for the IC
- Cleaning the guard column and main column of the IC
- Change of new loops and injection parts of the IC
- Often cleaning the impactor plate of the main control unit of the PILS
- Running tests with known standards
- Refreshing the denuders with new solution

Further information about the modification and maintenance procedures are explained further on.

3.8. Steam collection devices

The PILS is a type of “steam collection” device. Every study using such devices perform configurations and modifications to improve the effectiveness of the sampling. Steam collection devices are capable of being connected to other scientific instruments in a line so that more and different results can be analyzed. Some studies using “steam collecting devices” have been accomplished throughout the previous years, starting with the Atlanta Supersite experiment where the semi-continuous instruments chemically speciated ubiquitous short-lived fine particulate matter (Weber et al. 2003). As part of the 1999 Atlanta Supersite Experiment, a prototype particle-into-liquid sampler (PILS) was coupled to a dual channel ion chromatogram system and then concentrations of the major soluble inorganic ions were measured. Online collection of the impacted droplets was possible by adding an adjustable transport flow to the impactor (0.05–0.1 ml/min), which continually washed the droplets from the surface and filled sample loops for online IC analysis. These measurements were every 7 min and the LOD for the detected ion species was 0.1 mg/m³. The positive results from this study encouraged further development of the PILS system.

One of the first instruments of mixing steam with aerosol particles was achieved using in a 10 l/min sample flow. Then the particles were further

grown in a cooled stainless steel maze and finally collected from the air in a gas/liquid separator. The system was coupled to a concentrator column and ion chromatography (IC) and a sulfate LOD of $B2 \text{ ng/m}^3$ was attained for an 8 min sampling time (Simon and Dasgupta et al. 1995).

A system used in Europe named the Steam Jet Aerosol Collector (SJAC) (Khlystov et al. 1995; Slanina et al. 2001) collects grown droplets and condensed water vapor in a cyclone for online IC-analysis using a pre-concentrator column. Using a sample flow rate of 20–60 l/min, the LOD of the SJAC ranges from 20 to 50 ng/m^3 . Another system, developed by Kidwell and Ondov (2001), grows particles in a high aerosol sample flow (170 l/min) followed by droplet concentration using a combination of a virtual/real impactor. This technique allows for increased lower detection limits (LOD) ($B1 \text{ ng/m}^3$) and for online analysis of trace metals in aerosols using Graphite Furnace Atomic Absorption Spectroscopy.

Further analysis techniques have been applied to collect grown droplets in a system called the condensational-growth and impaction system (C-GIS) (Sierau et al., 2002). Here the instrument has a 1.5–2 l/min of an aerosol sample flow which is saturated with water vapor that further condenses on the particles in a laminar flow tube. The different techniques of offline analysis applied to the impacted droplets included capillary electrophoresis combined with UV-detection (CE-UV) and CE combined with electrospray (ion trap) mass spectrometry (CE-ESI-MS). Speciation of organic PM is possible in sampling times less than 10 min.

3.9. Other experiments and studies on the PILS system

An improved particle-into-liquid sampler (PILS) has been successful in both ground-based and aircraft experiments for rapid measurements of soluble aerosol chemical compositions. Modifications were made to the prototype PILS (Weber et al. 2001) to improve particle collection at higher sample flow (15–17 l/min) while maintaining minimal sample dilution.

Collection efficiency for particle diameters D_p between 0.03 and 10 μm are greater than 97%. In addition, the instrument now samples at low pressures as well (0.3 atmosphere) necessary for airborne measurements up to approximately 8 km in altitude. An ion chromatograph (IC) was coupled to the PILS for direct on-line analysis of the collected samples. Correct choice of columns and eluents allowed for a 3.5–4 min separation of 8 major inorganic species (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-}), while acetate, formate, and oxalate, are also possible in a 15 min separation (Orsini et al. 2003).

Another study focused on secondary organic aerosols that were created from the photooxidation of a mixture of isoprene and dimethyl sulfide (DMS). Different NO_x concentrations and humidities (12%, 42% and 80%) using a Teflon film indoor chamber were also studied. The effect of isoprene on DMS products, the major DMS photooxidation products, such as sulfuric acid, methanesulfonic acid (MSA) and methanesulfinic acid (MSIA), were quantified in both the presence and the absence of isoprene using a Particle-Into Liquid-Sampler coupled with an Ion Chromatography. The data showed that the

DMS aerosol yield significantly decreased due to the photooxidation of isoprene. The particle into liquid sampler was a Metrohm 761 Compact . All samples were collected at the end of each chamber experiment. The specific PILS-IC had a detection limit of 0.2 mg/m^3 and an associated error of 6%. Using a flow rate of 13 l/ min and the liquid flow rate in the anion column was set to 0.7 ml/ min. The denuders used for gas phase removal were coated with 1% glycerol and 2% K_2CO_3 in ethanol-water (1:1) (Chen and Jang 2012) .

At the SMEARII station in Finland atmospheric aerosol particles were collected with the particle-into-liquid sampler for analyses of biogenic acids. A PILS system for the collection of aerosol samples for the determination of α -pinene and its oxidation products was used. The sampling system, like ours, consists of an ADI2081 particle-into-liquid sampler (Applikon Analytical, Schiedam in The Netherlands) coupled with an eight-channel peristaltic pump (Watson Marlow 205S, Wilmington, USA). Direct Q-UV water was used as a working liquid and for transport flow. To remove gas phase compounds, three channel annular denuders (242mm length, Teflon coated, stainless steel sheath, URG, Chapel Hill, USA) with different coatings (XAD, phosphoric acid, potassium iodide) were used. Aerosols were size separated before the denuder line with a cyclone (PM_{2.5}, URG, Chapel Hill, USA). After two-hour sampling the collected samples were put into screw-capped vials and stored in a refrigerator until sample pretreatment. The volume of samples varied from 20 to 40 ml. The volume of PILS samples varied significantly from sample to sample thus the tubing used in the peristaltic pump did not provide a constant flow due to the deformation that takes place over time, also humidity and temperature of the sampled air may have affected the volume of samples. The inventors of PILS added lithium fluoride to the sample flow to correct for differences in sample volume during the on-line analysis (Parshintseva et al. 2010).

The application of a Multilinear Engine (ME) to a highly time-resolved aerosol concentration data set took part from 20 August to 25 September 2003 in Toronto, Ont., Canada for aerosol concentration, ambient gas and meteorological data. A suite of instruments was incorporated into the study, which produced a diverse air quality data set. The instrumentation included an aerosol mass spectrometer (AMS) , an aethalometer and a PILS-IC system. Aerosol particles were collected in water with the PILS and analysed for their major water-soluble inorganic chemical components with two ICs immediately following collection. Trace gases were denuded prior to entering the PILS-IC as well. Aerosol particles are grown to super-micron size droplets under supersaturated conditions created by mixing the sample air with steam. Particles larger than 30 nm diameter that enter the PILS are activated with a 497% CE at a sample flow rate of 15 l/ min. The droplets are impacted onto a surface that is washed off with a steady stream of de-ionized water. The water is delivered to the trace concentrator columns of the IC. During this study, each sample was accumulated over 15 min to coincide with the other measurements (Buset et al. 2003).

4. EXPERIMENTAL DESIGN

4.1. Stages of PILS System

The PILS system of the University of Crete (Figure 9) consists of the following stages.



Figure 9. Overview of the ECPL PILS system.

4.1.1. The aerosol sampling flow

The aerosol sampling flow is acquired via a cyclone that has a PM1 impactor that will only allow particles through the inlet that are smaller than 1 μm . A continuous air flow is caused because of an air pump and is measured many times to find the optimum flow rate which is around 16 L of air/min. Without obtaining a correct flow rate of air the next steps of the PILS system will not be possible.

4.1.2. The denuders

The air pipe transferring the air sample is connected to two denuders (Figure 10) that are coated with a solution of glycerol (2% in methanol) and a solution of sodium carbonate (2% in water) so as to prevent interferences from gases that are not wanted and removed before going into the growth chamber. The

denuders were multi-channel denuders that feature multiple channels to provide more surface area to expand the capacity of the denuder, combined with etched glass surfaces to provide maximum area for coating and collection. Also the denuders via both ends allow direct connection to cyclones, filter packs and other components, in this experiment the two denuders were connected to the air inlet and finally to the main PILS system.

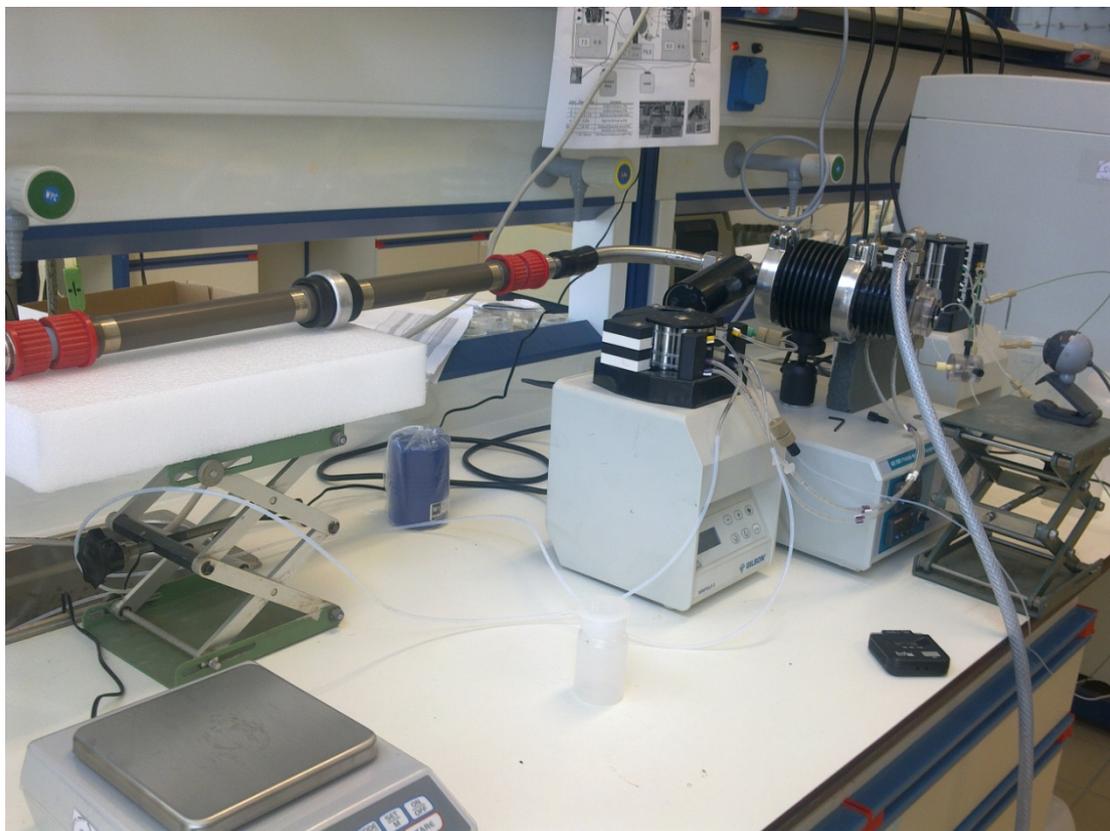


Figure 10. The denuder system of the ECPL PILS.

4.1.3. The main control unit AD2081 PILS

The main control unit was an AD2081 Particle-into-Liquid sampler engineered by Applicon Analytical from Metrohm. It consists of:

- ✓ A control cabinet, including temperature controller for the steam generator and read-out of the tip temperature
- ✓ A PILS cell including steam generator, air inlet connector, air outlet connector, impactor plate and a tubing set to connect water supply, drains , and internal standard feed line
- ✓ A debubbler unit including connectors and tubing set to connect the system to analytical instruments in this case the IC 1500 from Dionex.

The PILS main control system unit consists of the connection from the vacuum pump, the steam generator, the growth chamber and the impactor.

For the control unit to work it has to be connected to two peristaltic pumps used for water inlet for steam production, rinsing the PILS part of the impactor (draining), debubbling the liquid sample, sending the liquid sample to two different pipes, one to the drainage system again and second to the main pipe for the IC intake. The peristaltic pumps were Minipuls 3 by Gilson. They are specifically designed to meet process laboratory liquid handling needs. They combine microprocessor speed control with a high-torque stepper motor. Chemical resistant pump heads equipped with 10 stainless steel rollers set the performance standard in producing smooth low pulse flow and reproducible flow rates at higher pressures. The head speeds are adjustable from 0-48 rpm by increments of 0.01 rpm up to 9.99 rpm and by 0.1 rpm at above 10 rpm. For the current experiment we used two minipulse peristaltic pumps that were configured to +8.00 for the steam generator pipes, the drainage pipes and the feed line and for the debbubler and the intake for the IC it was set to +8.30 rpm.

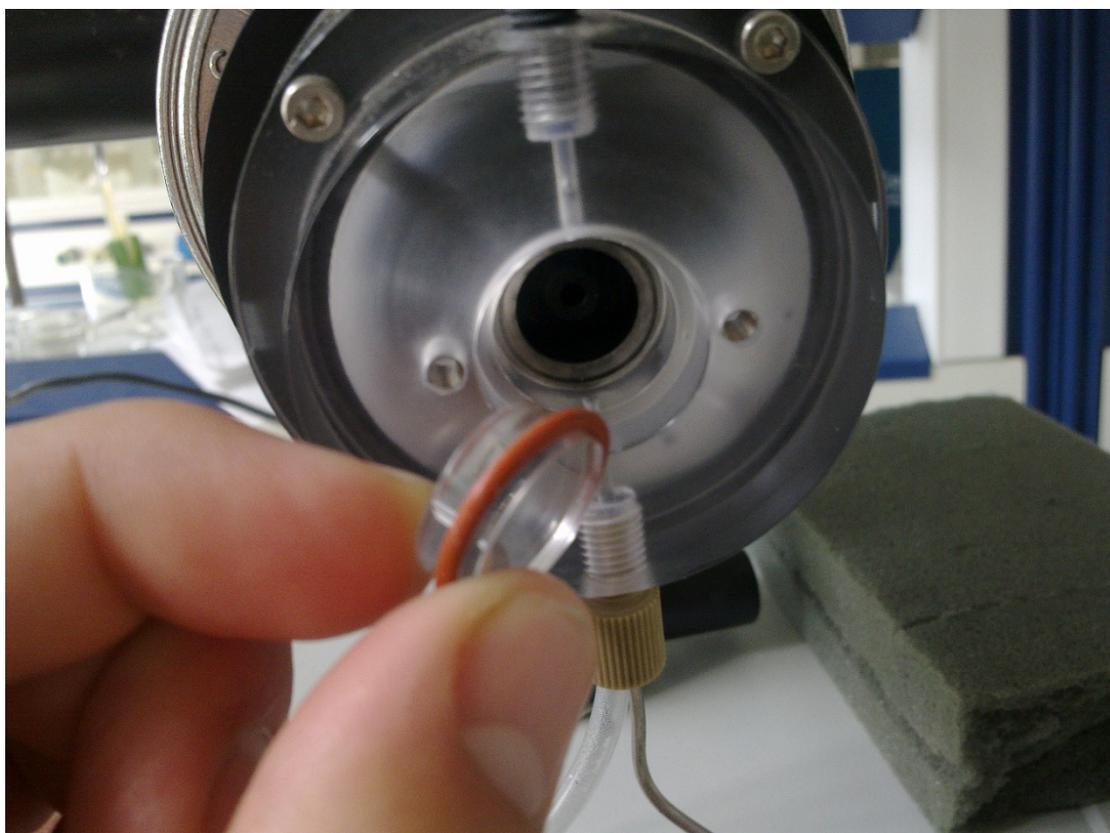


Figure 11. View of the Impactor plate of the AD2081 PILS.



Figure 12. View of the Impactor plate with the asterisk-like pattern.

A crucial check of the correct functioning of the PILS system is the formation of an asterisk-like pattern on the impactor plate that indicates that the flows of the system are corrected and that the sampling is then reliable. This can be seen in the view of the impactor plate in Figure 12.

4.2. The Dionex ICS-1500 Ion Chromatography System

The ion chromatography used was a Dionex ICS-1500 Ion Chromatography System. It performs ion analyses using suppressed or non-suppressed conductivity detection. An ion chromatography system typically consists of a liquid eluent, a high-pressure pump, a sample injector, a guard and separator column, a chemical suppressor, a conductivity cell and a data collection system (Figure 15). Before running samples the ion chromatography system is calibrated using a standard solution. By comparing the data obtained from the sample to that obtained from the known standard, sample ion can be identified and quantified. In this case the anions that we were sampling were Cl^- , NO_3^- and SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ but the experiment aimed mainly at SO_4^{2-} anions. The data collection system typically a computer running chromatography software produces a chromatogram that is a plot of the detector output vs time. The chromatography software converts each peak in

the chromatogram to a sample concentration and produces a printout of the results.

A typical IC analysis consists of six stages (see Figure 13):

1. **Eluent delivery**, a liquid that helps to separate the sample ions, carries the sample through the ion chromatography system. The ICS-1500 used is a isocratic delivery system that means that the eluent composition and concentration remain constant throughout the run.
2. Chromatography management system **sample injection**, the liquid sample is loaded into a sample loop either manually or automatically (Figure 16), in which case the samples come from a PILS so it is automatically done. When the injection time occurs it injects the sample into the eluent stream. The pump pushes the eluent and sample through the guard that was a Dionex Ion Pac AG11 4mm (10-32) and through to the separator column (chemically-inert tubes packed with a polymeric resin) that was a Dionex Ion Pac AS11 4mm (10-32) at first and finally a Dionex Ion Pac AS11HC 4mm (10-32) was used. The guard column removes contaminants that might poison the separator column thus called guard.
3. **Separation**, the separation is called ion exchange for the ICS-1500. The different sample ions migrate through the IC column at different rates depending upon their interaction with the ion exchange sites.
4. **Suppression**, once the eluent and sample ions leave the column they flow through a suppressor that selectively enhances detection of the sample ion while suppressing the conductivity of the eluent. Our suppressor currents were test with changes of the mA current from 50-70 mA.
5. **Detection**, a conductivity cell measures the electrical conductance of the sample ions as they emerge from the suppressor and produce a signal based on a chemical or physical property of the analyte.
6. **Data analysis**, were the conductivity cell transmits the signal to a data collection system in this case a Chromeleon ver. 6.80 was used to identify the ions based on retention time and quantifies each analyte by integrating the peak area or peak height. The data is quantified by comparing the sample peaks in a chromatogram to those produced from a standard solution (Figures 17-19). The results are displayed as a chromatogram and the concentrations of ionic analytes can be automatically determined and tabulated. Conversion of peak area ($\mu\text{S}\cdot\text{min}$) to concentration (ppb) can be achieved through a linear regression equation, as shown in Figure 19.

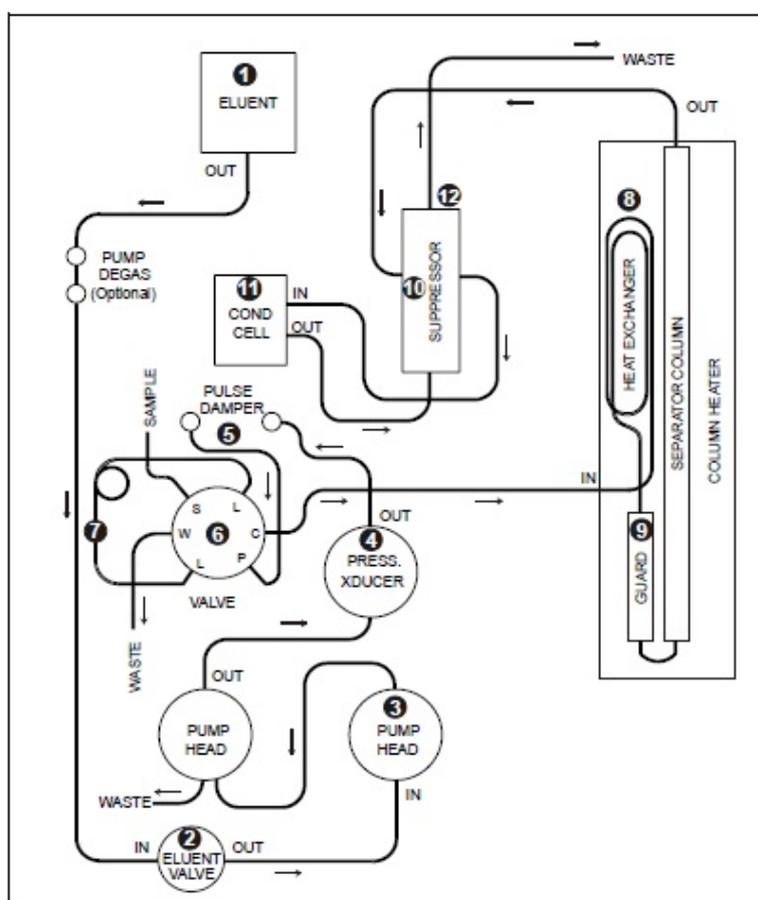
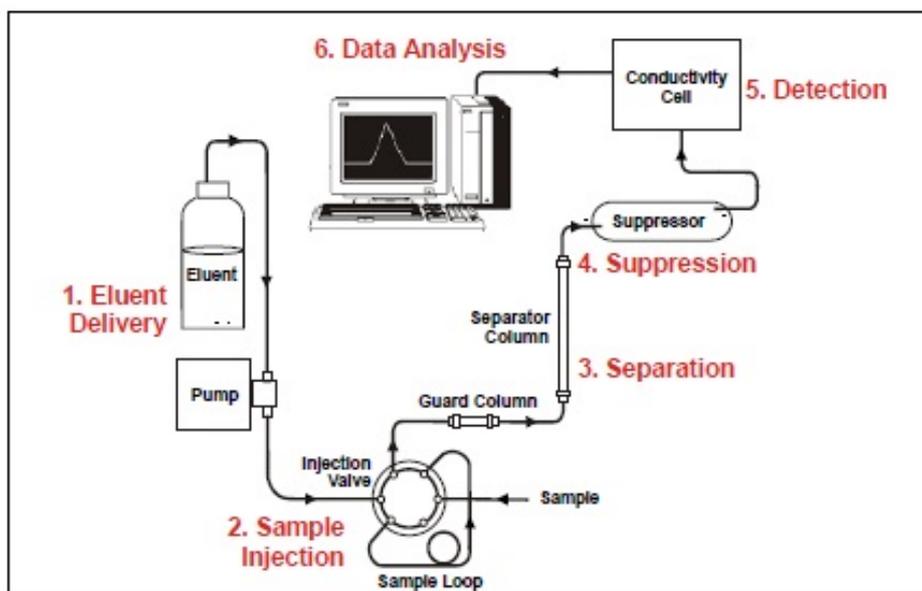


Figure 13. Sample processing steps and flow schematic of an IC analysis.

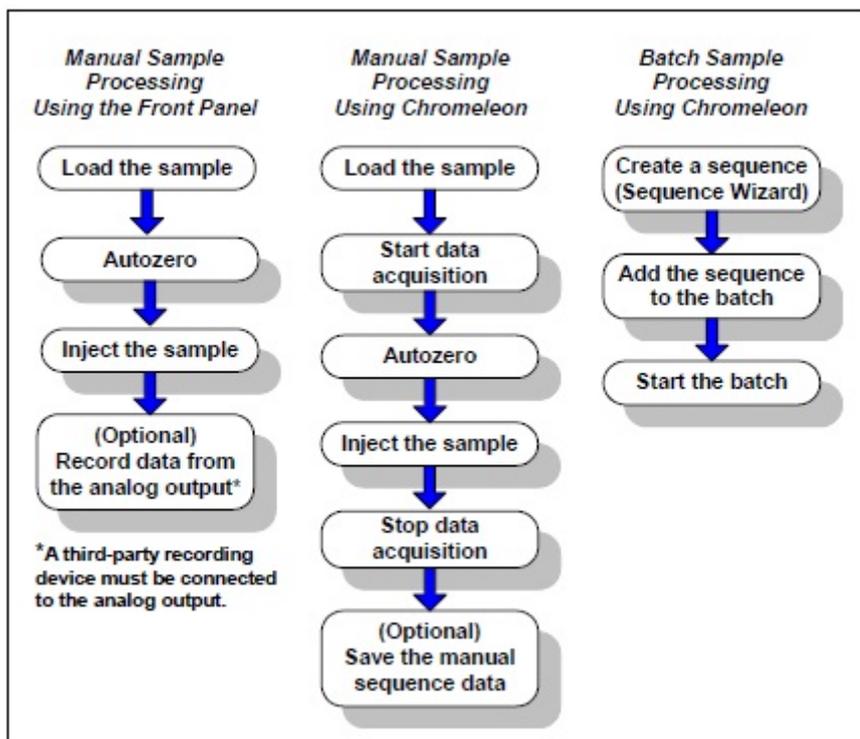


Figure 14. Sample processing overview of an IC Analysis.

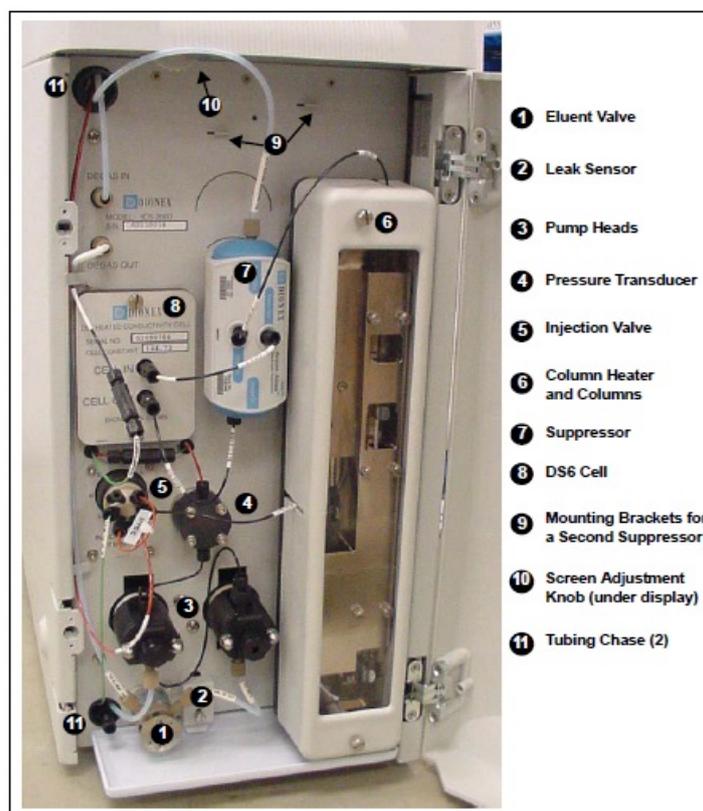


Figure 15. Panel of components of the ICS-1500 system.

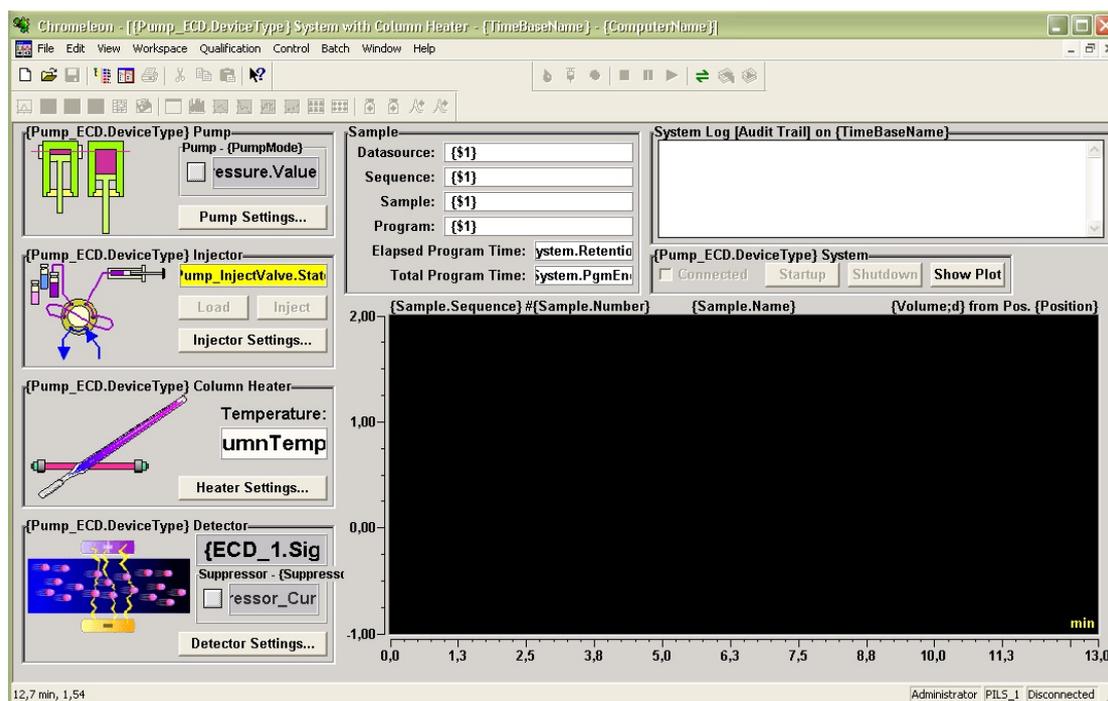


Figure 16. Chromeleon system control panel of ICS-1500.

4.3. Effectiveness of the IC in detecting anions

After the many PILS procedures and modifications that were performed to ensure that it sampled correctly the air for the various anions, the only anion detected whose concentration was sufficient to be measured subsequently by the IC was that of sulfate, as shown in Figure 17a. The anions MSA (methylsulfite, CH_3SO_3^-) and oxalate ($\text{C}_2\text{O}_4^{2-}$), were detected in less than 5% of the sampling, but with such low concentrations not to be measured by the PILS-IC system. This is in agreement with the findings of Bardouki et al. (2003), as shown in Figure 17b were only the sulfate anion was detected in the fine mode (sub-micron: $< 1 \mu\text{m}$).

In their summer campaign Bardouki et al. found MSA concentrations below $0.05 \mu\text{g}/\text{m}^3$ with the peak in the fine mode and less than $0.2 \mu\text{g}/\text{m}^3$ for the oxalate both in fine and coarse modes. Concentrations too low to be detected by the PM1 PILS-IC system, shown to have a precision of $0.4 \mu\text{g}/\text{m}^3$, as will be discussed later. The anions Cl^- and NO_3^- have been identified as the main components of the coarse mode (super-micron: $> 1 \mu\text{m}$).

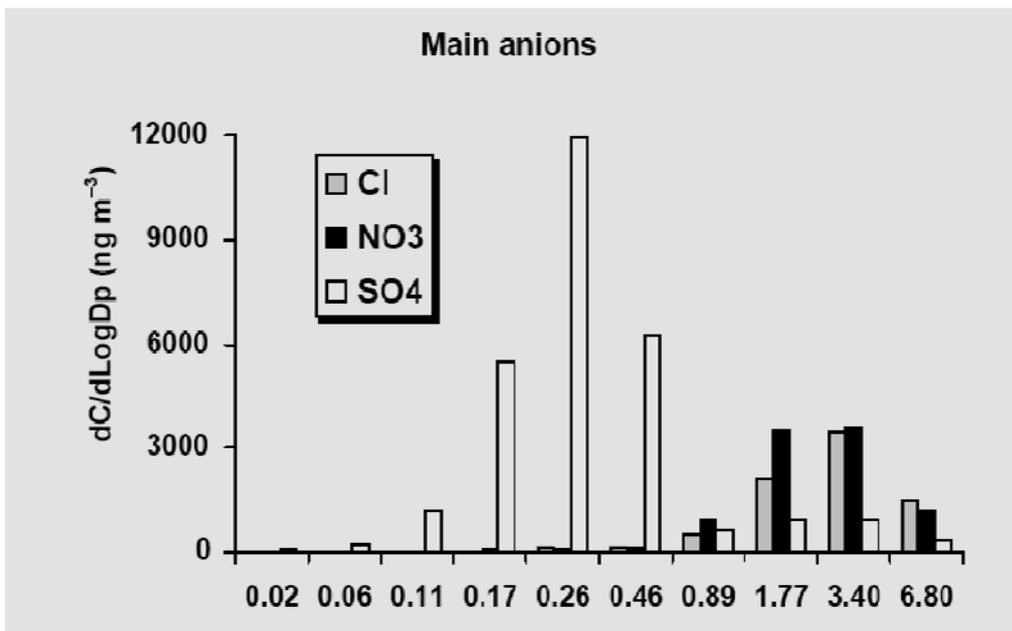
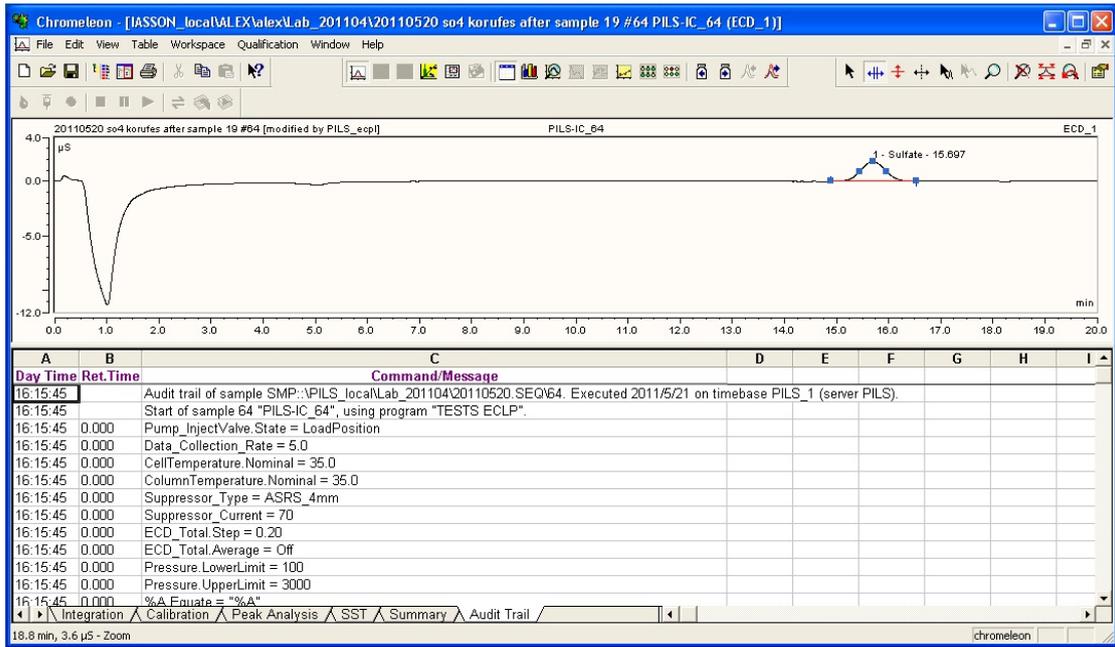


Figure 17. a) Chromeleon showing only sulfate peak. b) Particle size distribution of anions during summer in Crete.

It can be seen in Figure 18 that the IC was able to detect various anions in a standard high concentration solution, these included MSA, Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, HPO₄⁻, and oxalate anions. The results for each anion in a series of standard solutions of increasing concentration are shown in Figures 19 to 25. Although the PILS does pick up other anions the peak levels are too low to be countable. For this reason from now on all results will refer only to the sulfate anions.

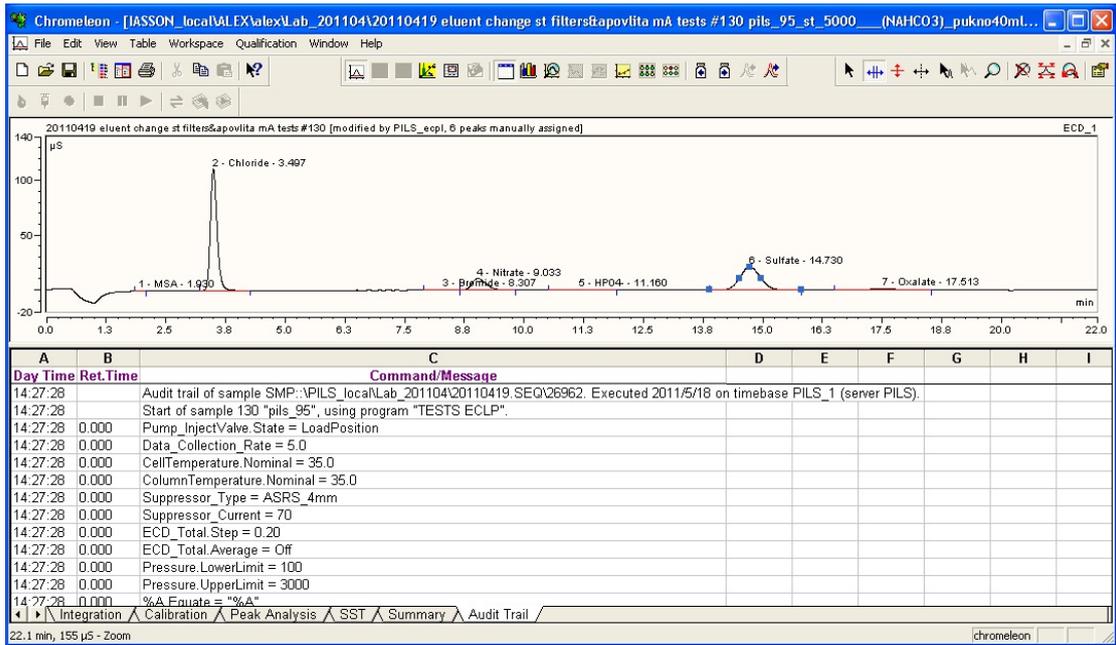


Figure 18. Output for a standard solution from the Chromeleon showing anions detected.

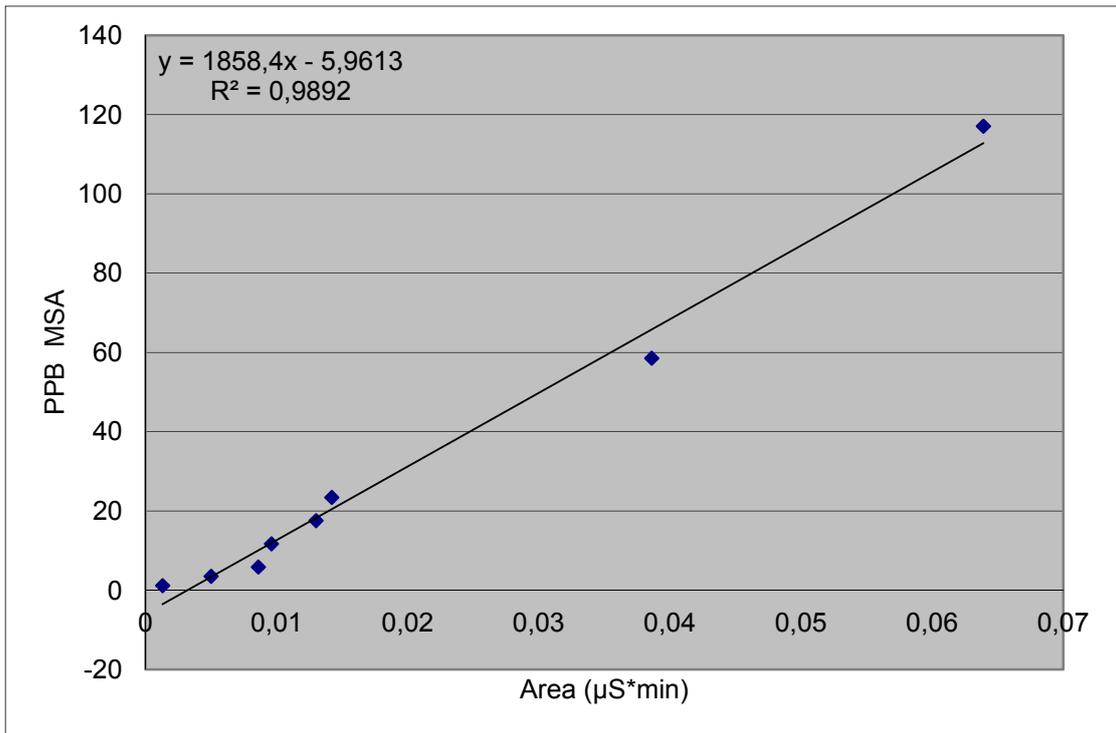


Figure 19. Concentration of a standard solution of MSA anions vs peak area generated by Chromeleon.

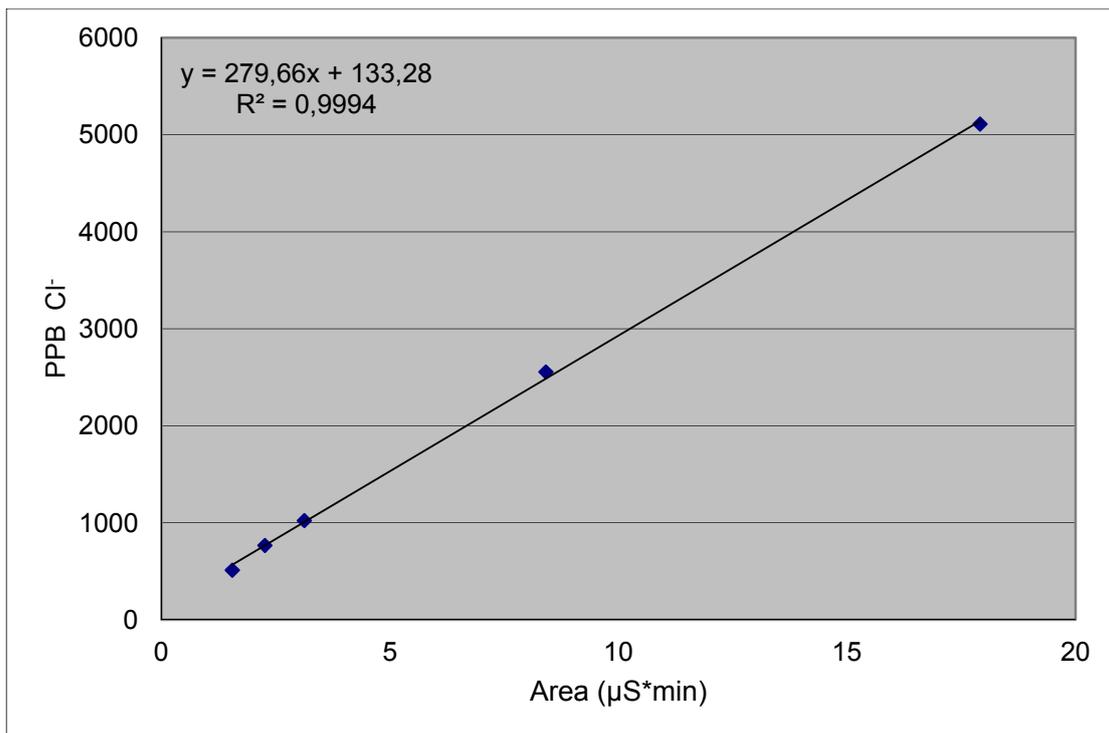


Figure 20. Concentration of a standard solution of Cl⁻ anions vs peak area generated by Chromeleon.

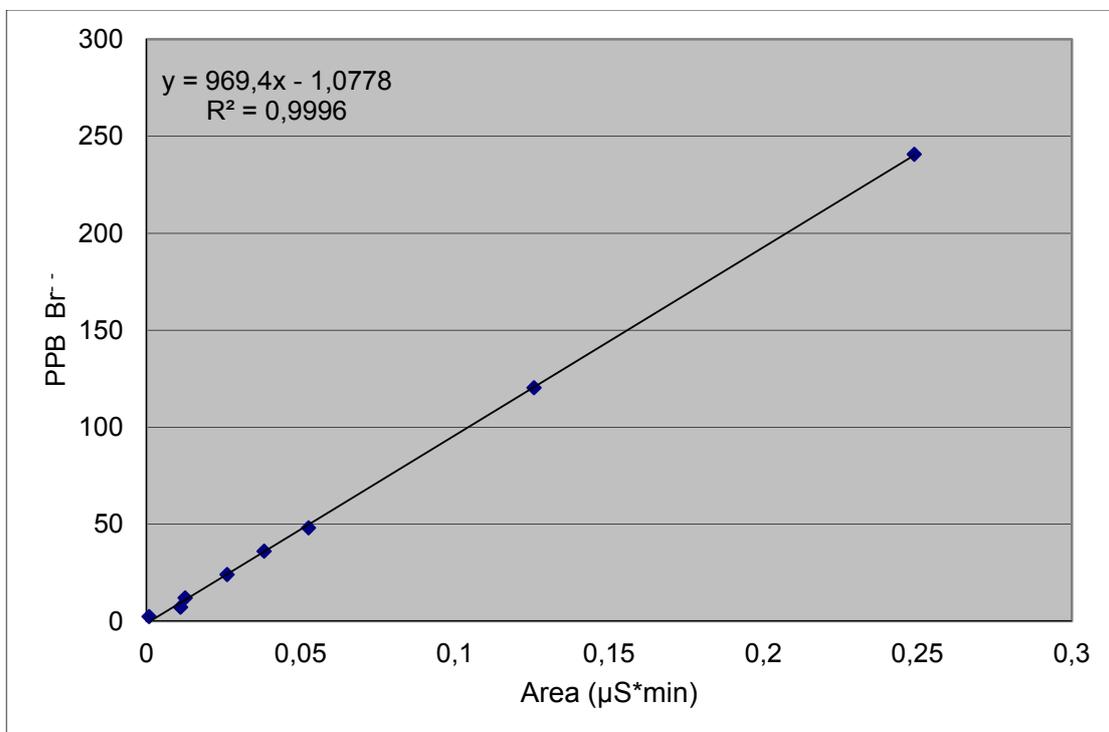


Figure 21. Concentration of a standard solution of Br⁻ anions vs peak area generated by Chromeleon.

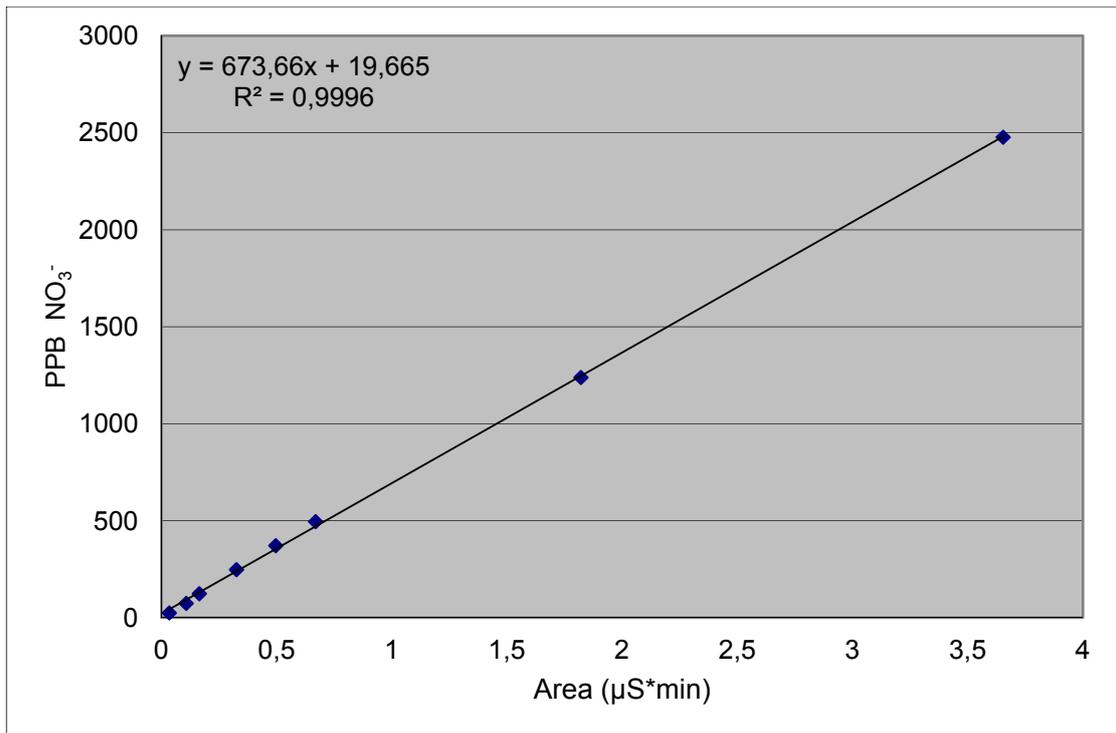


Figure 22. Concentration of a standard solution of NO_3^- anions vs peak area generated by Chromeleon.

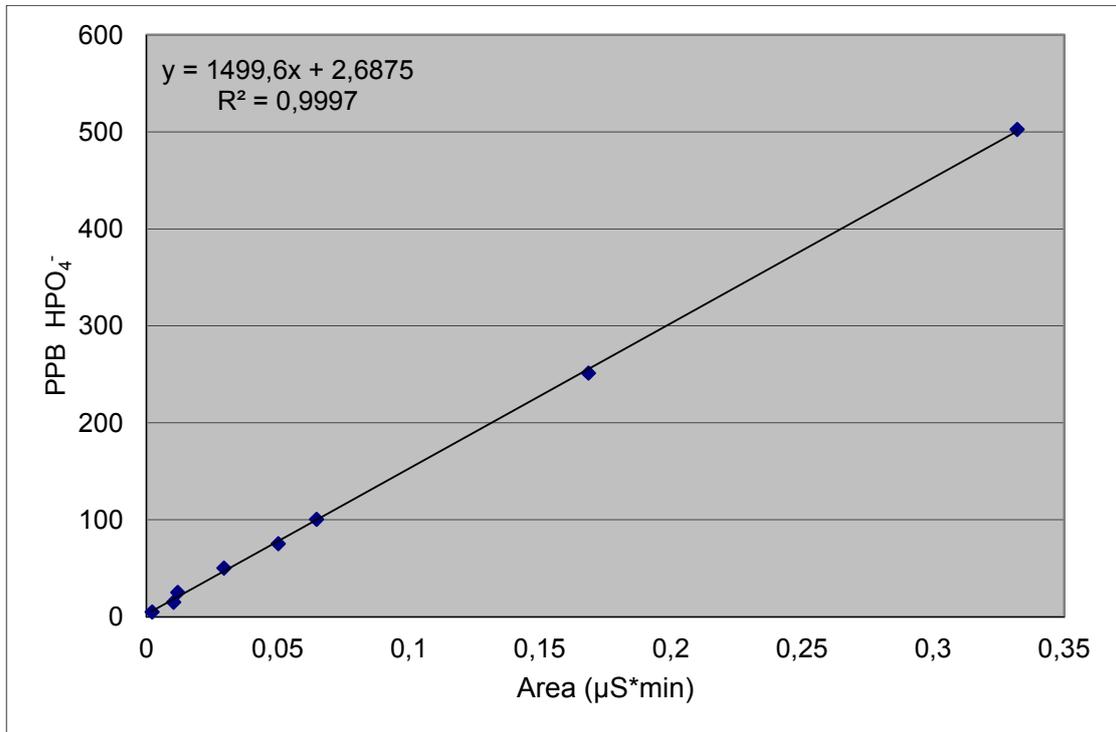


Figure 23. Concentration of a standard solution of HPO_4^- anions vs peak area generated by Chromeleon.

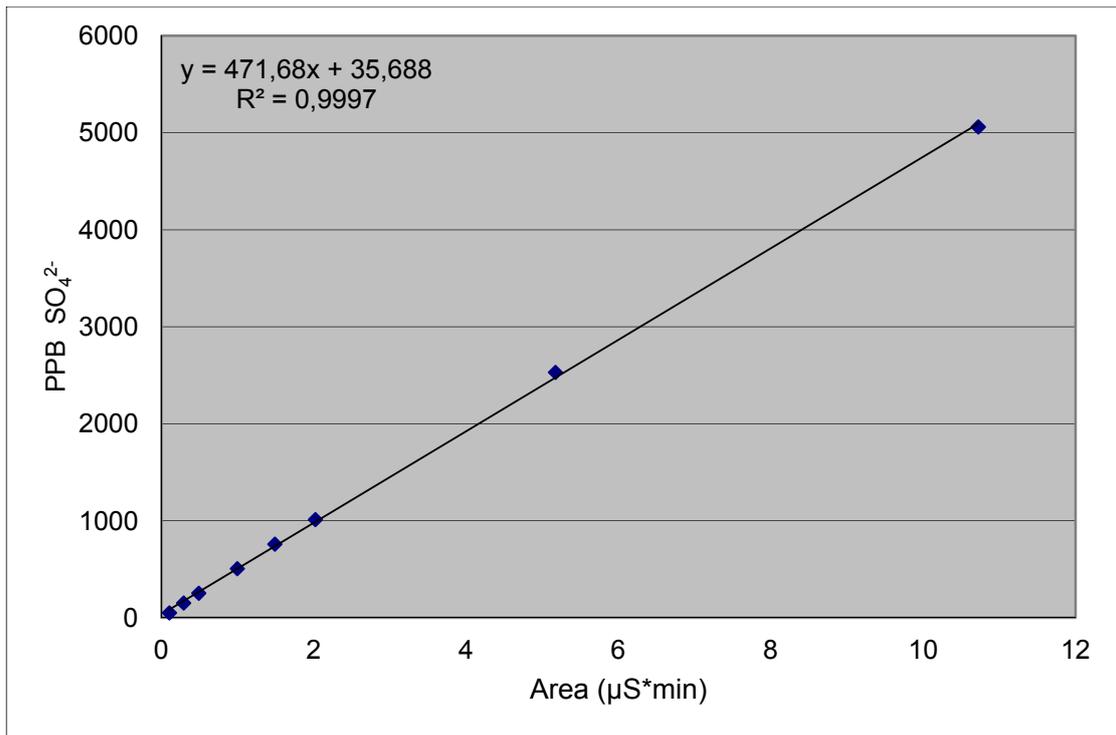


Figure 24. Concentration of a standard solution of SO_4^{2-} anions vs peak area generated by Chromeleon.

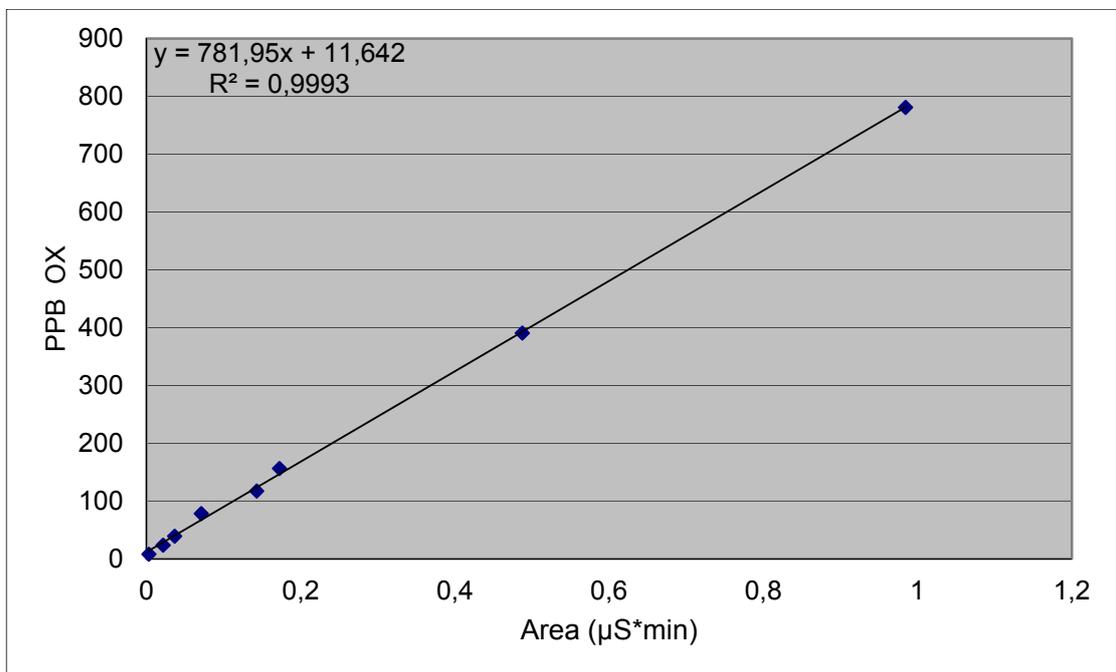


Figure 25. Concentration of a standard solution of OX anions vs peak area generated by Chromeleon.

5. EXPERIMENTAL PROCEDURES AND CONFIGURATIONS

5.1. Procedures and tests of the PILS System

After many runs and checks during the first days of April 2011 the PILS was started up to see its capability for tracking correctly anions in the air samples. The PILS worked normally, but due to the sensitivity that it has, rearrangements to the setting up of the PILS or small modifications had to be done. Running the IC and the software needed to plot the chromatogram, the main anions showed up as peaks. Before the operation of the PILS for each sampling sequence or change of tubing, various tests were performed listed and outlined below.

EXPERIMENTAL TESTS
1. Standard tests
2. Anion tests
3. Pipe tests
4. Flow tests
5. Glass impactor tests
6. Sampling time tests
7. Eluent tests
8. Suppressor current tests
9. Filter tests
10. Denuder tests

5.1.1. Standard samples tests

Standard samples of known concentration were injected manually into the Dionex 1500 ion chromatogram. The results give an equation that is used to find the ppbv of each separate anion in a sample and this is then converted into $\mu\text{g}/\text{m}^3$ concentration. The correct operation of the IC is demonstrated in Figures 19-25, which show excellent linear fits of anion concentration versus peak area generated by the Chromeleon.

5.1.2. Anion tests

Different samples of specific anions or samples consisting of multiple anion together were injected manually into the Dionex 1500 ion chromatogram to establish when they would appear during the sampling time to distinguish the different anion peaks.

5.1.3. Pipe tests

The peristaltic pumps that were used to create a flow of the different liquids distort and damage the plastic pipes after a period of time. This damage results in incorrect flows and hence unreliable results. Therefore the different size pipes were always checked before sampling and replaced when needed.

5.1.4. Flow tests

For the PILS to work correctly specific flow rates are needed. The flow rates that were always checked were for flows to the steam chamber, for rinsing the glass impactor, flows of the PILS system to the IC and last the air flow from the cyclone. These flow rates need to be kept within specified limits to ensure correct sampling and hence reliable concentrations.

5.1.5. Glass impactor tests

For the correct functioning of the PILS system a formation of an asterisk-like pattern on the impactor plate has to appear. To ensure this, modifications have to be made to the placement of the glass impactor such as tightening or loosening it and also all flow rates have to be correct.

5.1.6. Sampling time tests

Different sampling times were run in order to see when each peak will show up. The sampling times were from 13 minutes to a maximum of 20 minutes. Injection points were 2 minutes before the sampling time. The temporal resolution was kept at 20 minutes as this allowed all the various anion peaks to clearly appear.

5.1.7. Eluent tests

The two main eluents used for the separation process were NaOH and NaHCO₃. At first NaOH eluent was used with a concentration of 0.75ml/L but then reduced to 0.66ml/L for better results. This was then changed to NaHCO₃. Different concentrations of NaHCO₃ were used ranging from 25ml/L to 40ml/L. The reason for the eluent changes and their different concentrations were to see which eluent shows better peaks. The NaOH is a standard eluent that is used that gave clear oxalate peaks but was found to produce anion peaks that overlapped in time. On the other hand, the use of 40ml/L NaHCO₃ eluent produced more distinct anion peaks without overlapping.

5.1.8. Suppressor current tests

The suppressor selectively enhances detection of the sample ion while suppressing the conductivity of the eluent. The suppressor current tests varied from 50 mA to 70 mA. At 70 mA it was found that the baseline was devoid of noise.

5.1.9. Filter tests

As validation of the PILS sulfate concentration obtained, off-line method extract analysis was performed using outside filters connected to a pump with a flow meter that created a flow through the filter so that any anion will be absorbed. After the filter runs, the concentration of the extracts were obtained using the amount of air that passed through the filter and the amount of nanopure water used for the extraction of the filter.

The filter and PILS sampling were performed over the same time period and hence under the same atmospheric conditions of pollution and their variability. So one expects to measure the same concentrations of sulfates using the two methods. In Figure 26 the x-axis represents the filter extract measurements while the y-axis represents the results using the PILS system. As can be seen there is a linear relationship between the concentrations of the two methods verified by the $R^2=0.973$. Also we see that the slope 0.94 of the line fit is close to unity. The filter method is an established technique of ECPL so that the filter results obtained during the sampling period of the experiment are expected to be reliable. Hence, the PILS system can be used in future work to monitor sulfate levels.

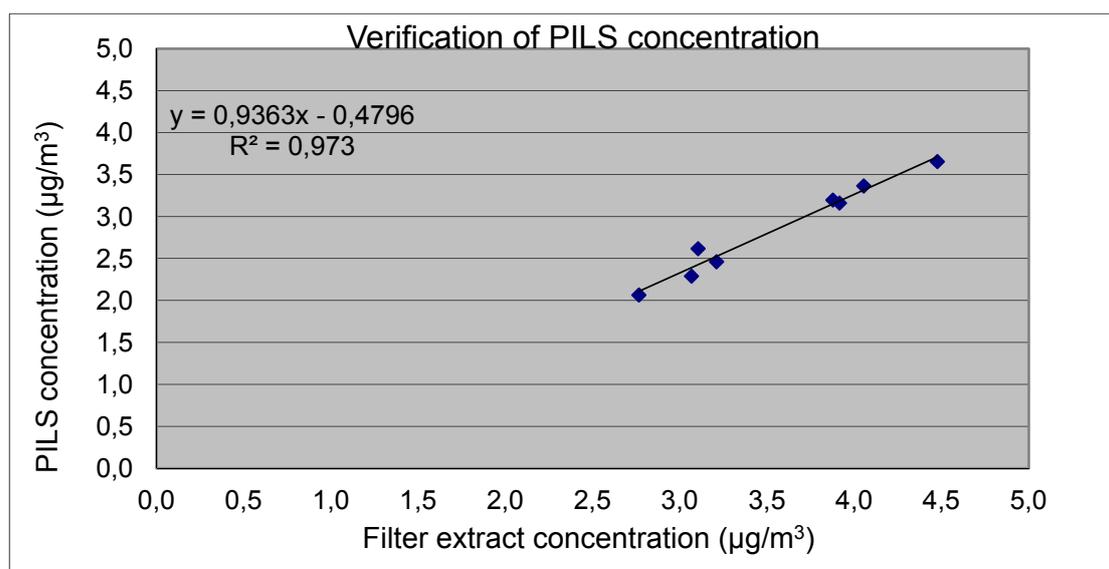


Figure 26. Comparison of sulfate concentration from off-line filter samples and PILS.

5.1.10. Denuder tests

Tests performed to ascertain the effects of operating the system with and without the denuders on the measured sulfate concentrations using different IC eluents. As can be seen from Figures 27 and 28, the effect of the denuders is to remove acidic gasses which contribute on average about $0.5 \mu\text{g}/\text{m}^3$ to the sulphate concentration obtained from the fine mode aerosols. Thus when

the denuders are removed the sulfate concentration rises and then stabilizes to a certain value, corresponding to the steps in the concentration with time.

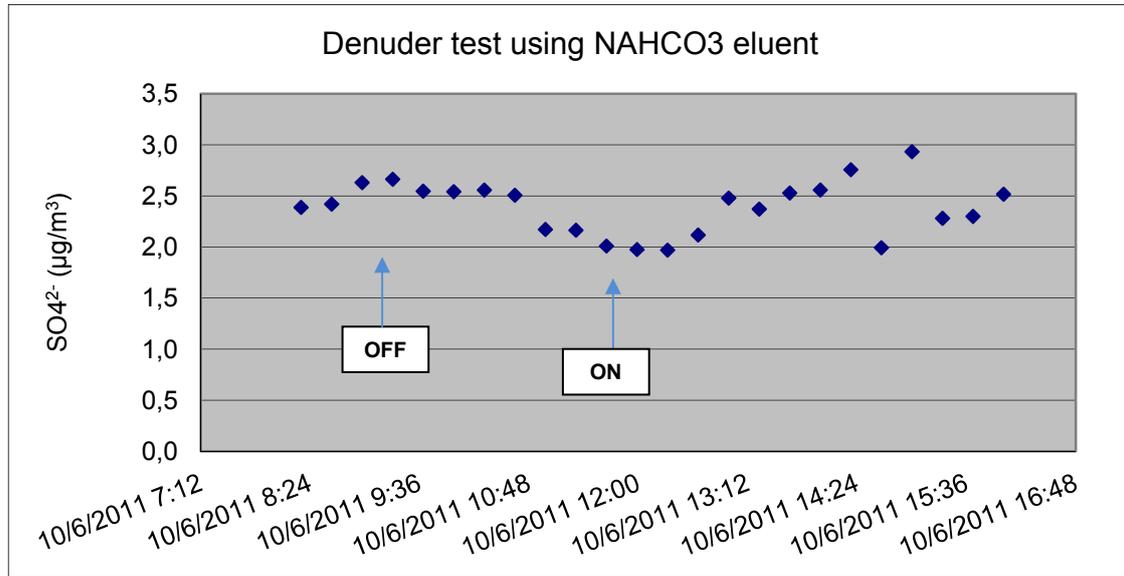


Figure 27. Sulfate concentration with and without denuders during June 2011 sampling with NaHCO₃ eluent.

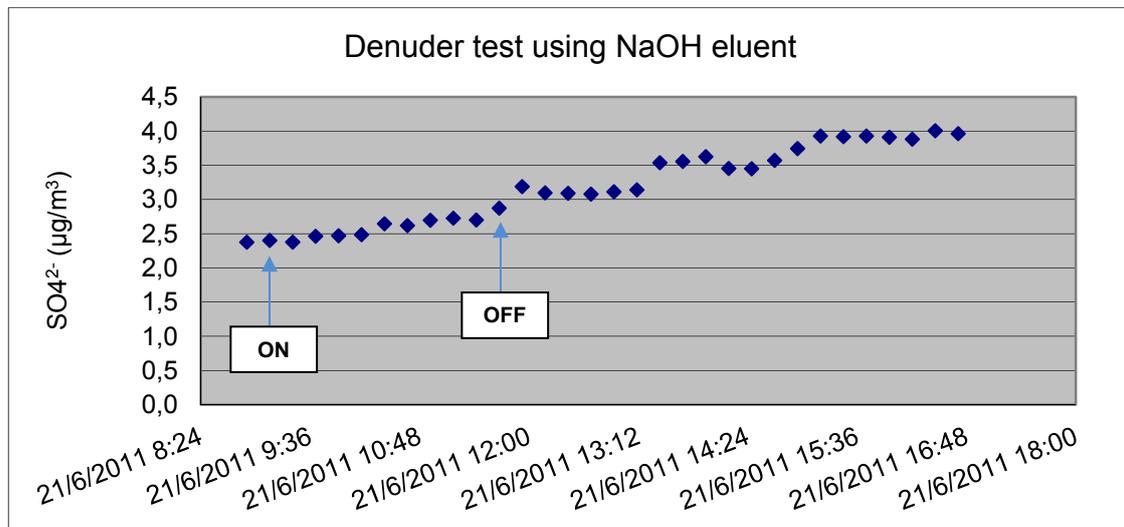


Figure 28. Sulfate concentration with and without denuders during June 2011 sampling with NaOH eluent.

6. FIELD APPLICATIONS

Having ensured the optimum operation of the PILS-IC system, we conducted PM1 measurements of anion concentrations in the field. The system was set up in the University of Crete campus at Voutes.

The anions that were monitored in the fine mode (sub-micron: $<1 \mu\text{m}$) were SO_4^{2-} , MSA and oxalate ($\text{C}_2\text{O}_4^{2-}$). The anions Cl^- and NO_3^- have been identified as the main components of the coarse mode (super-micron: $> 1 \mu\text{m}$) as demonstrated in the size-resolved study of Bardouki et al. (2003) who examined the chemical composition of aerosols in the east Mediterranean during summer and winter. Thus, the concentrations of the coarse mode anions were not measured while the MSA (mainly in fine mode) and oxalate (about 50% in fine and coarse modes) concentrations were too low to be measured by the PILS-IC system.

We converted the peak area given by chromeleon to sulphate concentration in ppbv using the linear regression equation based on the standard solution. The concentration in $\mu\text{g}/\text{m}^3$ was then obtained via the expression:

$$\text{Sulfate } (\mu\text{g}/\text{m}^3) = \rho * \text{sulfate (ppbv)} * \text{PILS flow (ml/min)} / \text{airflow (l/min)}$$

where ρ is the density of water in $10^6 \text{ g}/\text{m}^3$. Due to the dilution arising from the water vapour in the steam chamber, a correction to the above expression for the sulphate concentration was required by multiplying the concentration by a factor of 1.25.

The sulphate concentrations and associated backward trajectories for the sampling period April-June 2011 are shown in Figures 20-26.

6.1. Pollution Effects

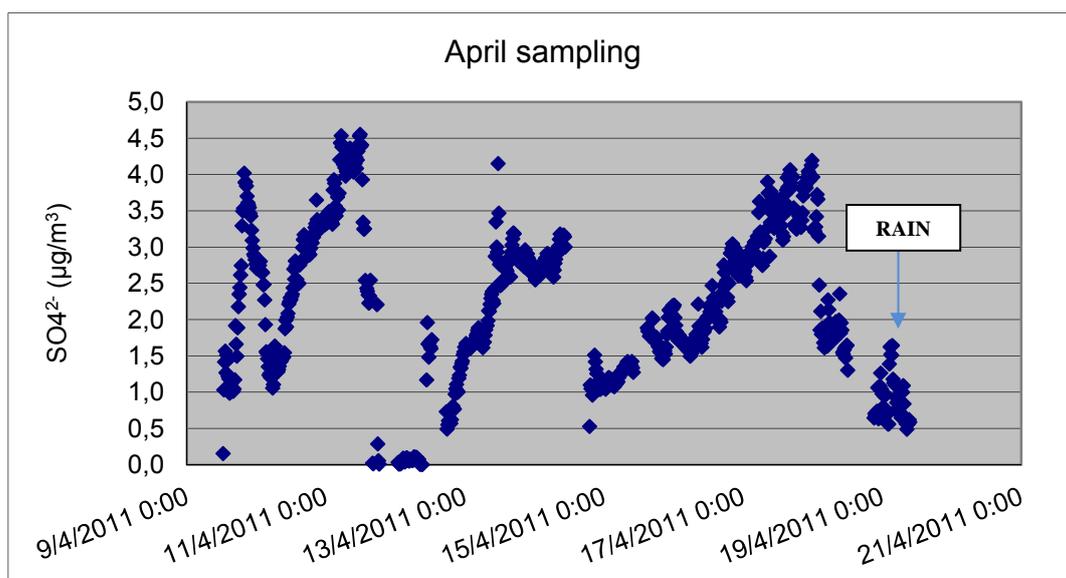


Figure 29. Sulfate concentration during April 2011 sampling.

During the April sampling period the sulfate concentration varied between generally lows of $0.5 \mu\text{g}/\text{m}^3$ to high values of about $4.5 \mu\text{g}/\text{m}^3$ as shown in Figure 29. As can be seen from the backward trajectory the source of the peak value of $4.6 \mu\text{g}/\text{m}^3$ on April 11 is Athens decreasing to $1.5 \mu\text{g}/\text{m}^3$ on April 13 when the wind direction changed to a more north westerly direction, shown in Figure 30. On April 19 there was substantial rain in Heraklion that is consistent with the low sulphate values detected due to the precipitation scavenging of the fine mode. The impact of the Istanbul source is more pronounced in the May sampling where on May 21 the sulfate concentration rose to the highest sampled value of $7.6 \mu\text{g}/\text{m}^3$, shown in Figure 31. The backward trajectory in Figure 32 clearly shows the Istanbul source on May 21 whilst on May 22 when the wind direction changed to a more north westerly but after passing through Istanbul giving rise to the double peaks of the concentration of $5.5 \mu\text{g}/\text{m}^3$.

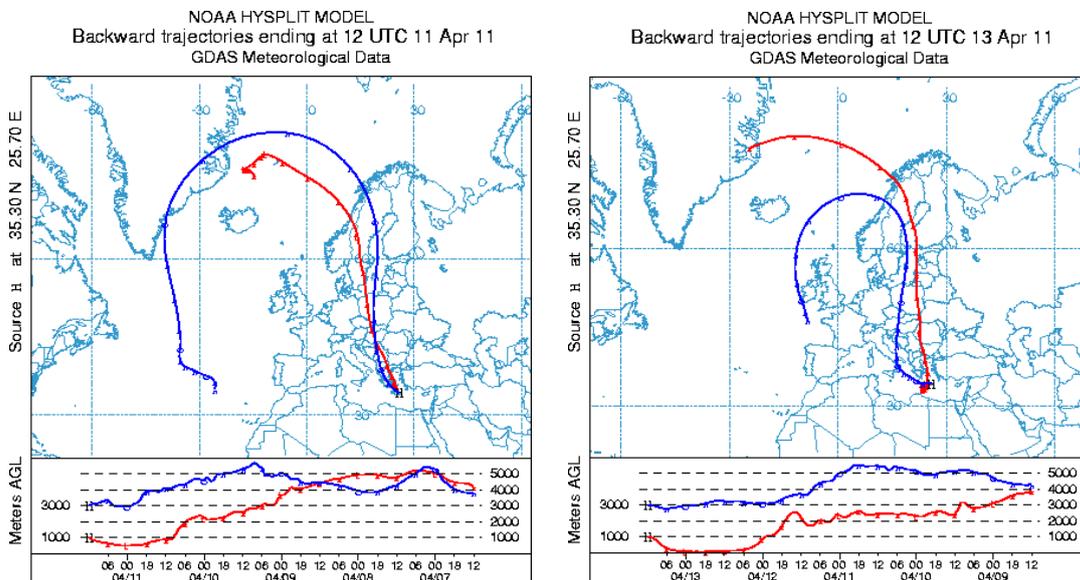


Figure 30. Backward trajectories showing Athens source of sulfate April 11.

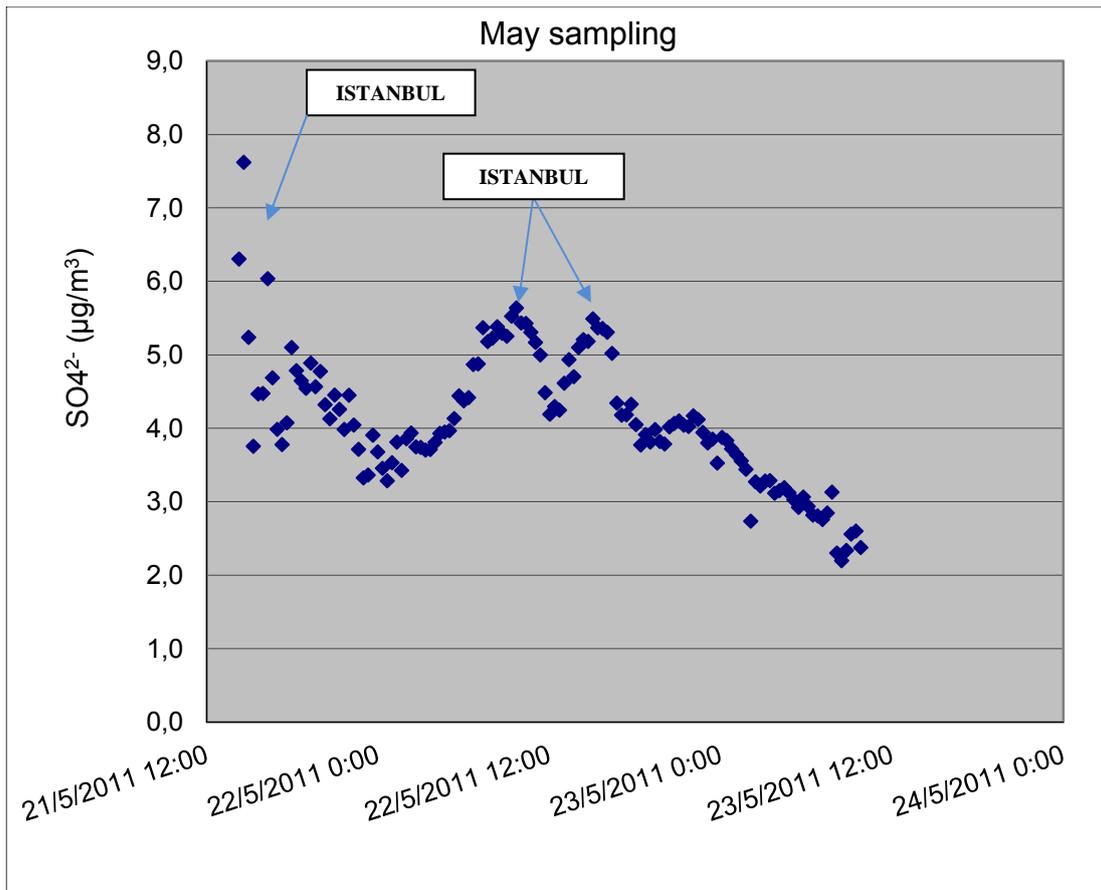


Figure 31. Sulfate concentration during May 2011 sampling.

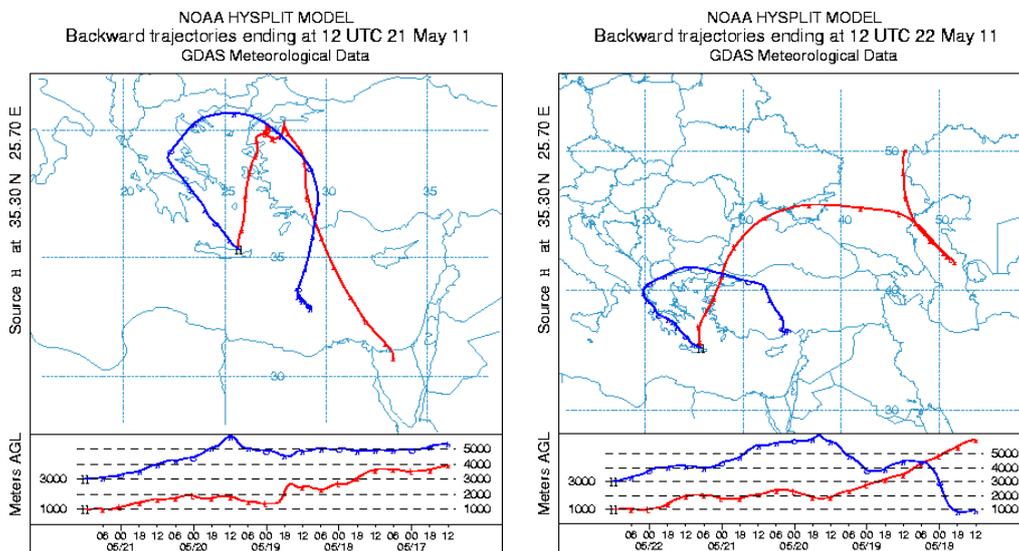


Figure 32. Backward trajectories showing Athens source of sulfate May 21.

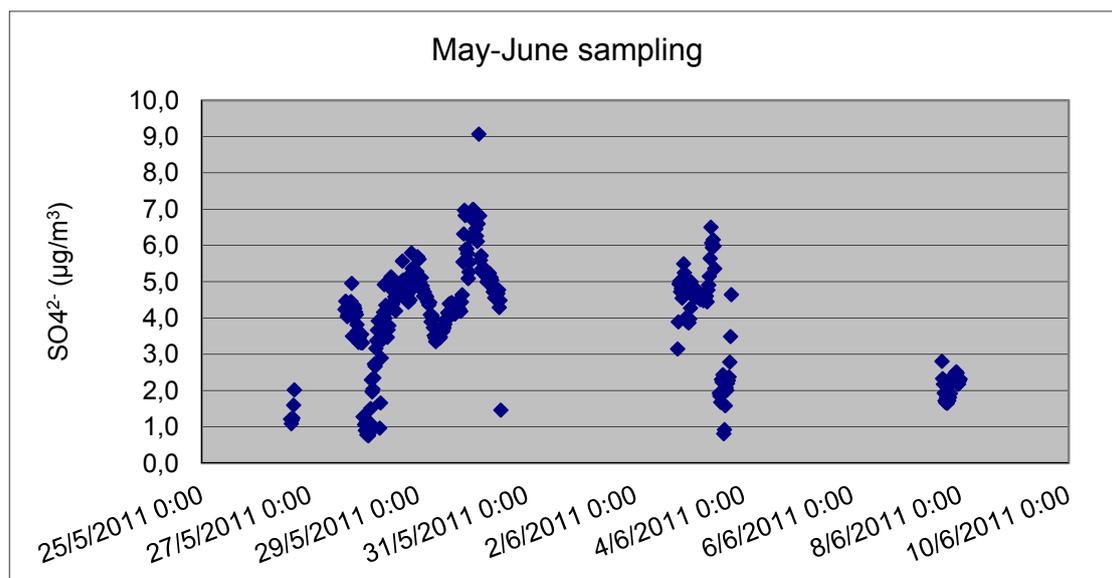


Figure 33. Sulfate concentration during May-June 2011 sampling.

In Figure 33 the peaks on May 29 and June 3 of concentration $7 \mu\text{g}/\text{m}^3$ correspond to air masses which originated from the Sahara, as shown in the backward trajectories in Figure 34. On May 28 there was heavy rain in Heraklion corresponding to a quite low concentration of $1 \mu\text{g}/\text{m}^3$. On June 7 low values of about $2 \mu\text{g}/\text{m}^3$ were also detected preceding the dust event of June 8.

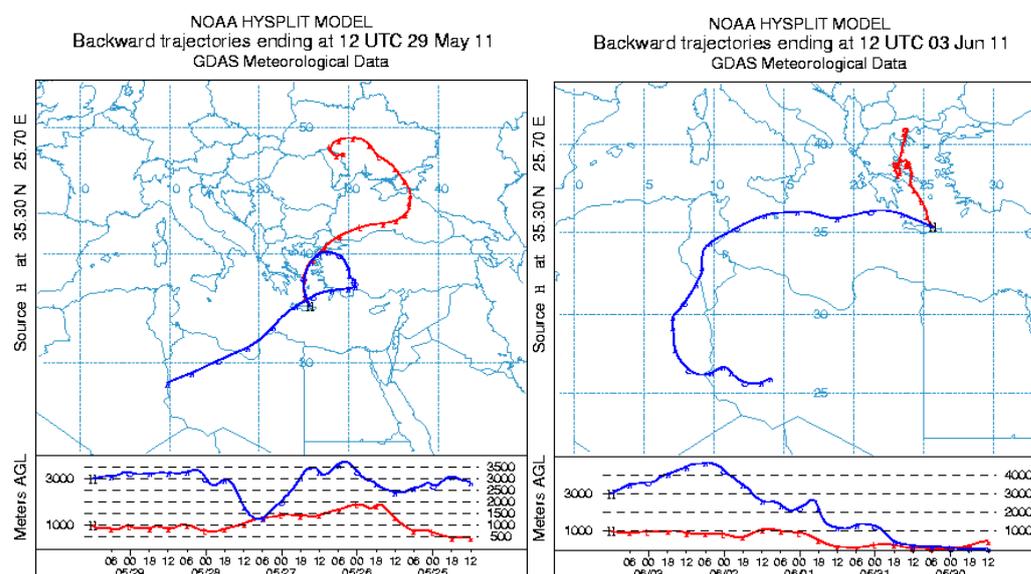


Figure 34. Backward trajectories with Sahara source of sulfate May 29 and June 3.

6.2. Dust Event

From June 8 to June 10 a dust event developed from Sahara as can be seen in Figure 36. The effect on the sulfate concentration can be seen in Figure 35

where the concentration rose to a peak value of $4.6 \mu\text{g}/\text{m}^3$ on June 8 starting from a value of $2.6 \mu\text{g}/\text{m}^3$ on the first day of the event June 7 and decreasing to $2.1 \mu\text{g}/\text{m}^3$ after the event on June 10.

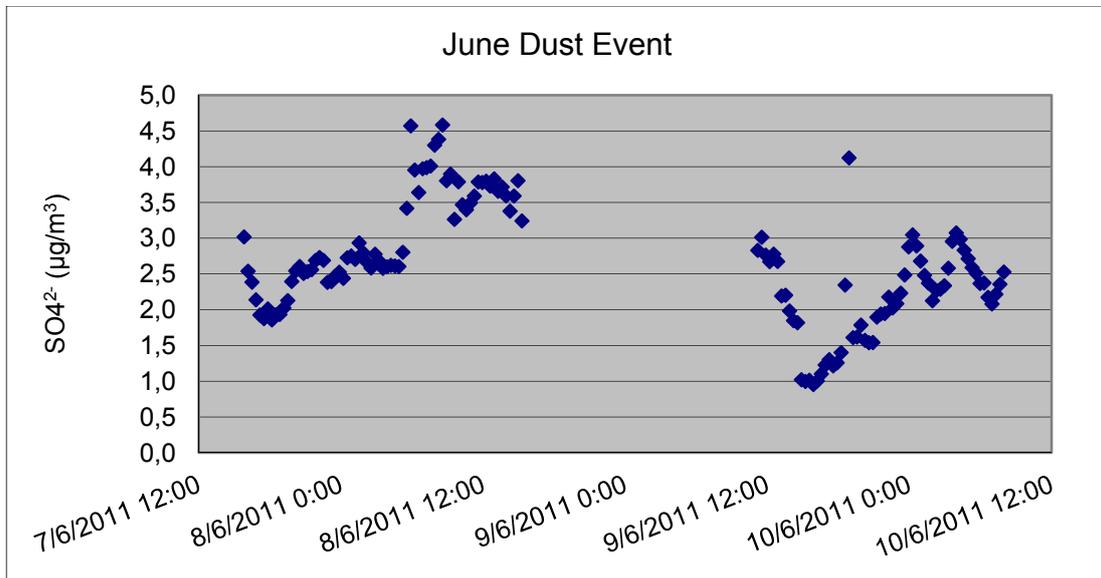
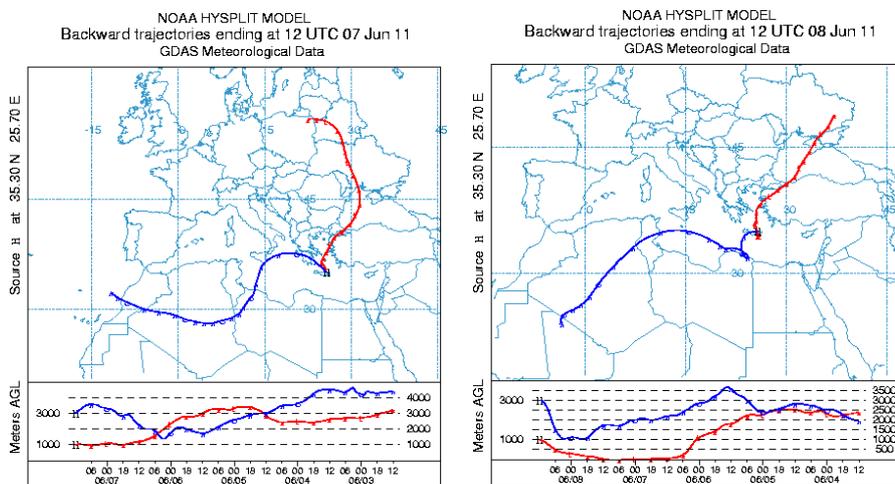


Figure 35. Sulfate concentration during June 2011 dust event sampling.



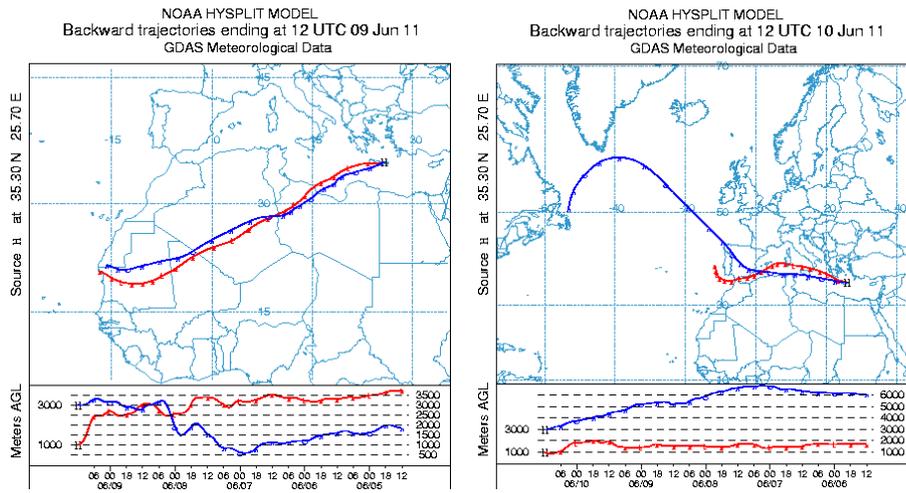


Figure 36. Backward trajectories showing Sahara dust event June 7-9.

7. CONCLUSIONS AND RECOMMENDATIONS

The high temporal (about 20 minutes) resolution PILS-IC system for monitoring and tracking atmospheric pollution on fine mode (PM₁) aerosols exhibit variations in anion concentrations not observable in data sets provided by the off-line standard method of filters that have long-averaging times (several hours or more).

Inter-comparison between the PILS results with those of the filter method is necessary to validate the high resolution results. In the present work 8 filters were used to perform long-time (12 hours on average) sampling concurrently with the PILS sampling. The two sets of results agreed very well giving a slope of 0.94 ($R^2=0.97$) in the linear fit of the scatter diagram of PILS versus Filter SO_4^{2-} concentration. This agreement is comparable to a similar validation performed under the AEROBIPOLAR Program by Sciare and Sarda-Esteve over a ten day period in 2008. Their slope was 0.87 ($R^2=0.90$) using 32 filters averaged over 3 hourly intervals. Further, in their work with the PILS system, Orsini et al. (2003) performed a two PILS side-by-side inter-comparison to ascertain the precision of the PILS system and found this to be $0.4 \mu\text{g}/\text{m}^3$ at the 99% confidence level. A value comparable to the differences between the PILS results in the present work and the filter measurements. This demonstrates the usefulness of the PILS high resolution system in fast tracking of pollution and the reliability of its measurements.

In this study the sub-micron anion detected and whose concentration was measured accurately was SO_4^{2-} in the range $1\text{-}10 \mu\text{g}/\text{m}^3$ over the period April-June 2011. This is in agreement with the findings of Bardouki et al. (2003). The anions MSA and oxalate, were detected in less than 5% of the sampling, but with such low concentrations not to be measured by the PILS system. In their summer campaign Bardouki et al. found MSA concentrations below $0.05 \mu\text{g}/\text{m}^3$ with the peak in the fine mode and less than $0.2 \mu\text{g}/\text{m}^3$ for the oxalate both in fine and coarse modes.

The air was sampled at the Voutes campus of the University of Crete about 20 km west of Herakleion and 10 km south-east of the electricity power station. High temporal variability was exhibited by the sulfate concentration and back trajectories were examined to analyze the origin of significant peaks. Three important sources were detected Athens, Istanbul and the Sahara during a dust event, verifying that Crete is in the crossroads of regional pollution sources. During rain events low concentrations were seen as a result of precipitation scavenging and sedimentation. The development of the accumulation or fine mode of aerosols takes about 1 day for growth from the Aitken nuclei stage and the lifetime of this fine mode can be about 10 days before transport or sedimentation removal. Thus, the contribution to the sulfate concentration from local sources is expected to be not important as diurnal wind changes on the island assure that the residence time is much smaller than 1 day.

The PILS system is thus tracking accurately sulfate in large regional air masses and is now ready for long-term measurements with a temporal resolution of 20 minutes.

The PILS-IC system used can undergo some modifications to improve its operation for future work. These improvements include:

- The installation of electronic flowmeters to monitor both the air and liquid flow rates so that the correct flows are maintained.
- The replacement of the peristaltic pumps by electronic pumps for setting flow rates and reducing damage to the plastic tubing. This will avoid the large time needed to adjust the peristaltic pump to obtain the correct flow rate and the replacement of the tubing.
- Upgrade of the IC unit to detect both anions and cations to allow the extra dilution due to condensation in the steam chamber to be better estimated using for example the Li^+ tracers as suggested by the work of Orsini et al. (2003).

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10. APENDIX

10.1 April Sampling Data

Date and Time	ppbv	$\mu\text{g}/\text{m}^3 \cdot 1,25$
9/4/2011 12:26	7,61	0,15
9/4/2011 12:41	50,80	1,03
9/4/2011 12:57	69,75	1,42
9/4/2011 13:12	77,11	1,57
9/4/2011 13:27	62,45	1,27
9/4/2011 13:42	74,49	1,51
9/4/2011 13:57	70,82	1,44
9/4/2011 14:12	59,88	1,22
9/4/2011 14:27	58,33	1,18
9/4/2011 14:42	48,49	0,99
9/4/2011 14:57	51,95	1,06
9/4/2011 15:12	56,47	1,15
9/4/2011 15:28	55,71	1,13
9/4/2011 15:43	51,64	1,05
9/4/2011 15:58	49,87	1,01
9/4/2011 16:13	51,42	1,04
9/4/2011 16:28	57,71	1,17
9/4/2011 16:43	94,42	1,92
9/4/2011 16:58	81,80	1,66
9/4/2011 17:13	73,65	1,50
9/4/2011 17:28	92,96	1,89
9/4/2011 17:44	107,27	2,18
9/4/2011 17:59	115,73	2,35
9/4/2011 18:14	120,29	2,44
9/4/2011 18:29	128,70	2,61
9/4/2011 18:44	135,13	2,74
9/4/2011 18:59	162,14	3,29
9/4/2011 19:14	172,11	3,50
9/4/2011 19:29	173,97	3,53
9/4/2011 19:44	197,89	4,02
9/4/2011 19:59	191,51	3,89
9/4/2011 20:15	191,91	3,90
9/4/2011 20:30	189,12	3,84
9/4/2011 20:45	182,16	3,70
9/4/2011 21:00	177,73	3,61
9/4/2011 21:15	176,27	3,58
9/4/2011 21:30	174,50	3,54
9/4/2011 21:45	170,47	3,46
9/4/2011 22:00	168,65	3,43
9/4/2011 22:15	159,18	3,23
9/4/2011 22:30	152,22	3,09
9/4/2011 22:46	147,00	2,99
9/4/2011 23:01	142,74	2,90
9/4/2011 23:16	141,64	2,88
9/4/2011 23:31	139,20	2,83
9/4/2011 23:46	136,10	2,76
10/4/2011 0:01	133,13	2,70
10/4/2011 0:16	135,30	2,75
10/4/2011 0:31	135,04	2,74
10/4/2011 0:46	132,51	2,69
10/4/2011 1:01	135,26	2,75
10/4/2011 1:17	138,05	2,80

10/4/2011 1:32	130,83	2,66
10/4/2011 1:47	130,96	2,66
10/4/2011 2:02	130,30	2,65
10/4/2011 2:17	122,06	2,48
10/4/2011 2:32	122,28	2,48
10/4/2011 2:47	111,83	2,27
10/4/2011 3:02	95,09	1,93
10/4/2011 3:17	76,71	1,56
10/4/2011 3:33	75,69	1,54
10/4/2011 3:48	71,92	1,46
10/4/2011 4:03	66,52	1,35
10/4/2011 4:18	60,81	1,24
10/4/2011 4:33	61,96	1,26
10/4/2011 4:48	59,35	1,21
10/4/2011 5:03	62,49	1,27
10/4/2011 5:18	59,30	1,20
10/4/2011 5:33	52,04	1,06
10/4/2011 5:48	54,43	1,11
10/4/2011 6:04	61,07	1,24
10/4/2011 6:19	80,56	1,64
10/4/2011 6:34	77,15	1,57
10/4/2011 6:49	69,98	1,42
10/4/2011 7:04	64,13	1,30
10/4/2011 7:19	63,11	1,28
10/4/2011 7:34	64,57	1,31
10/4/2011 7:49	66,87	1,36
10/4/2011 8:04	71,39	1,45
10/4/2011 8:19	70,02	1,42
10/4/2011 8:35	70,82	1,44
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10/4/2011 9:20	72,99	1,48
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16/4/2011 6:27	77,99	1,58
16/4/2011 6:42	82,82	1,68
16/4/2011 6:57	85,39	1,73
16/4/2011 7:12	80,52	1,64
16/4/2011 7:27	83,09	1,69
16/4/2011 7:42	88,49	1,80
16/4/2011 7:57	83,75	1,70
16/4/2011 8:12	83,53	1,70
16/4/2011 8:27	109,04	2,21
16/4/2011 8:42	94,02	1,91
16/4/2011 8:58	90,92	1,85
16/4/2011 9:13	86,94	1,77
16/4/2011 9:28	82,33	1,67
16/4/2011 9:43	79,72	1,62
16/4/2011 9:58	85,03	1,73
16/4/2011 10:13	89,73	1,82
16/4/2011 10:28	90,35	1,84
16/4/2011 10:43	96,90	1,97
16/4/2011 10:58	92,47	1,88
16/4/2011 11:14	98,90	2,01
16/4/2011 11:29	100,00	2,03
16/4/2011 11:44	100,40	2,04
16/4/2011 11:59	99,07	2,01
16/4/2011 12:14	108,02	2,19
16/4/2011 12:29	103,77	2,11
16/4/2011 12:44	106,60	2,17
16/4/2011 12:59	102,04	2,07
16/4/2011 13:14	121,62	2,47
16/4/2011 13:29	104,26	2,12
16/4/2011 13:45	113,11	2,30
16/4/2011 14:00	100,09	2,03
16/4/2011 14:15	108,69	2,21
16/4/2011 14:30	103,86	2,11
16/4/2011 14:45	111,52	2,27
16/4/2011 15:00	112,49	2,29
16/4/2011 15:15	99,61	2,02
16/4/2011 15:30	97,57	1,98
16/4/2011 15:45	93,49	1,90
16/4/2011 16:00	98,63	2,00
16/4/2011 16:16	96,86	1,97
16/4/2011 16:31	110,90	2,25
16/4/2011 16:46	116,97	2,38

16/4/2011 17:01	121,62	2,47
16/4/2011 17:16	135,66	2,76
16/4/2011 17:31	130,39	2,65
16/4/2011 17:46	130,61	2,65
16/4/2011 18:01	134,02	2,72
16/4/2011 18:16	125,07	2,54
16/4/2011 18:31	113,65	2,31
16/4/2011 18:47	110,68	2,25
16/4/2011 19:02	123,12	2,50
16/4/2011 19:17	134,55	2,73
16/4/2011 19:32	143,54	2,92
16/4/2011 19:47	142,97	2,90
16/4/2011 20:02	146,51	2,98
16/4/2011 20:17	149,92	3,05
16/4/2011 20:32	147,97	3,01
16/4/2011 20:47	147,75	3,00
16/4/2011 21:03	144,78	2,94
16/4/2011 21:18	140,22	2,85
16/4/2011 21:33	139,25	2,83
16/4/2011 21:48	132,51	2,69
16/4/2011 22:03	129,59	2,63
16/4/2011 22:18	128,31	2,61
16/4/2011 22:33	135,04	2,74
16/4/2011 22:48	137,08	2,78
16/4/2011 23:03	142,74	2,90
16/4/2011 23:18	139,38	2,83
16/4/2011 23:34	138,76	2,82
16/4/2011 23:49	140,26	2,85
17/4/2011 0:04	134,77	2,74
17/4/2011 0:19	130,30	2,65
17/4/2011 0:34	131,72	2,68
17/4/2011 0:49	127,20	2,58
17/4/2011 1:04	124,90	2,54
17/4/2011 1:19	137,87	2,80
17/4/2011 1:34	139,73	2,84
17/4/2011 1:49	136,59	2,77
17/4/2011 2:05	140,00	2,84
17/4/2011 2:20	144,21	2,93
17/4/2011 2:35	144,47	2,93
17/4/2011 2:50	145,71	2,96
17/4/2011 3:05	147,93	3,00
17/4/2011 3:20	147,71	3,00
17/4/2011 3:35	144,43	2,93
17/4/2011 3:50	150,89	3,07
17/4/2011 4:05	151,07	3,07
17/4/2011 4:20	152,00	3,09
17/4/2011 4:36	140,44	2,85
17/4/2011 4:51	154,97	3,15
17/4/2011 5:06	153,33	3,11
17/4/2011 5:21	171,13	3,48
17/4/2011 5:36	178,66	3,63
17/4/2011 5:51	158,02	3,21
17/4/2011 6:06	152,44	3,10
17/4/2011 6:21	137,12	2,79
17/4/2011 6:36	135,22	2,75
17/4/2011 6:52	140,04	2,84
17/4/2011 7:07	150,76	3,06
17/4/2011 7:22	152,75	3,10

17/4/2011 7:37	153,46	3,12
17/4/2011 7:52	159,62	3,24
17/4/2011 8:07	175,79	3,57
17/4/2011 8:22	192,04	3,90
17/4/2011 8:37	184,38	3,75
17/4/2011 8:52	172,91	3,51
17/4/2011 9:07	141,46	2,87
17/4/2011 9:23	164,31	3,34
17/4/2011 9:38	185,22	3,76
17/4/2011 9:53	181,63	3,69
17/4/2011 10:08	182,69	3,71
17/4/2011 10:23	178,35	3,62
17/4/2011 10:38	160,46	3,26
17/4/2011 10:53	177,51	3,61
17/4/2011 11:08	178,84	3,63
17/4/2011 11:23	169,32	3,44
17/4/2011 11:38	172,64	3,51
17/4/2011 11:54	166,57	3,38
17/4/2011 12:09	162,81	3,31
17/4/2011 12:24	178,22	3,62
17/4/2011 12:39	175,34	3,56
17/4/2011 12:54	179,06	3,64
17/4/2011 13:09	162,32	3,30
17/4/2011 13:24	157,18	3,19
17/4/2011 13:39	152,36	3,09
17/4/2011 13:54	154,84	3,15
17/4/2011 14:09	178,40	3,62
17/4/2011 14:25	170,65	3,47
17/4/2011 14:40	183,93	3,74
17/4/2011 14:55	186,42	3,79
17/4/2011 15:10	194,74	3,96
17/4/2011 15:25	188,36	3,83
17/4/2011 15:40	194,83	3,96
17/4/2011 15:55	197,18	4,01
17/4/2011 16:10	200,19	4,07
17/4/2011 16:25	191,29	3,89
17/4/2011 16:41	196,38	3,99
17/4/2011 16:56	188,41	3,83
17/4/2011 17:11	195,10	3,96
17/4/2011 17:26	174,37	3,54
17/4/2011 17:41	163,07	3,31
17/4/2011 17:56	161,79	3,29
17/4/2011 18:11	160,28	3,26
17/4/2011 18:26	159,89	3,25
17/4/2011 18:41	161,79	3,29
17/4/2011 18:56	170,51	3,46
17/4/2011 19:12	168,79	3,43
17/4/2011 19:27	166,31	3,38
17/4/2011 19:42	169,10	3,43
17/4/2011 19:57	161,04	3,27
17/4/2011 20:12	165,82	3,37
17/4/2011 20:27	171,05	3,47
17/4/2011 20:42	182,34	3,70
17/4/2011 20:57	186,42	3,79
17/4/2011 21:12	191,07	3,88
17/4/2011 21:27	189,38	3,85
17/4/2011 21:43	187,88	3,82
17/4/2011 21:58	194,74	3,96

17/4/2011 22:13	192,35	3,91
17/4/2011 22:28	199,04	4,04
17/4/2011 22:43	197,89	4,02
17/4/2011 22:58	193,06	3,92
17/4/2011 23:13	195,14	3,96
17/4/2011 23:28	203,20	4,13
17/4/2011 23:43	206,52	4,20
17/4/2011 23:58	195,23	3,97
18/4/2011 0:14	160,11	3,25
18/4/2011 0:29	159,35	3,24
18/4/2011 0:44	158,29	3,22
18/4/2011 0:59	161,44	3,28
18/4/2011 1:14	168,34	3,42
18/4/2011 1:29	183,36	3,72
18/4/2011 1:44	180,13	3,66
18/4/2011 1:59	155,01	3,15
18/4/2011 2:14	121,97	2,48
18/4/2011 2:30	91,41	1,86
18/4/2011 2:45	104,17	2,12
18/4/2011 3:00	88,53	1,80
18/4/2011 3:15	92,74	1,88
18/4/2011 3:30	89,02	1,81
18/4/2011 3:45	82,78	1,68
18/4/2011 4:00	79,36	1,61
18/4/2011 4:15	79,85	1,62
18/4/2011 4:30	86,76	1,76
18/4/2011 4:45	84,10	1,71
18/4/2011 5:01	80,43	1,63
18/4/2011 5:16	111,92	2,27
18/4/2011 5:31	105,19	2,14
18/4/2011 5:46	96,59	1,96
18/4/2011 6:01	95,53	1,94
18/4/2011 6:16	86,45	1,76
18/4/2011 6:31	86,63	1,76
18/4/2011 6:46	84,24	1,71
18/4/2011 7:01	88,53	1,80
18/4/2011 7:16	86,10	1,75
18/4/2011 7:32	85,43	1,74
18/4/2011 7:47	94,38	1,92
18/4/2011 8:02	97,17	1,97
18/4/2011 8:17	94,96	1,93
18/4/2011 8:32	95,40	1,94
18/4/2011 8:47	95,31	1,94
18/4/2011 9:02	98,19	1,99
18/4/2011 9:17	115,99	2,36
18/4/2011 9:32	89,33	1,81
18/4/2011 9:47	96,28	1,96
18/4/2011 10:03	91,37	1,86
18/4/2011 10:18	76,31	1,55
18/4/2011 10:33	74,89	1,52
18/4/2011 10:48	77,90	1,58
18/4/2011 11:03	79,23	1,61
18/4/2011 11:18	72,46	1,47
18/4/2011 11:33	80,56	1,64
18/4/2011 11:48	81,09	1,65
18/4/2011 12:03	64,13	1,30
18/4/2011 21:09	31,80	0,65
18/4/2011 21:24	34,76	0,71

18/4/2011 21:39	33,21	0,67
18/4/2011 21:55	33,61	0,68
18/4/2011 22:10	36,40	0,74
18/4/2011 22:25	52,35	1,06
18/4/2011 22:40	31,18	0,63
18/4/2011 22:55	32,46	0,66
18/4/2011 23:10	53,45	1,09
18/4/2011 23:25	62,18	1,26
18/4/2011 23:40	51,37	1,04
18/4/2011 23:55	48,14	0,98
19/4/2011 0:10	39,06	0,79
19/4/2011 0:26	36,45	0,74
19/4/2011 0:41	46,55	0,95
19/4/2011 0:56	34,23	0,70
19/4/2011 1:11	47,61	0,97
19/4/2011 1:26	37,11	0,75
19/4/2011 1:41	34,28	0,70
19/4/2011 1:56	27,68	0,56
19/4/2011 2:11	27,59	0,56
19/4/2011 2:26	68,34	1,39
19/4/2011 2:41	80,03	1,63
19/4/2011 2:57	74,89	1,52
19/4/2011 3:12	74,27	1,51
19/4/2011 3:27	80,91	1,64
19/4/2011 3:42	58,11	1,18
19/4/2011 3:57	55,45	1,13
19/4/2011 4:12	55,45	1,13
19/4/2011 4:27	54,03	1,10
19/4/2011 4:42	45,79	0,93
19/4/2011 4:57	42,20	0,86
19/4/2011 5:12	38,35	0,78
19/4/2011 5:28	41,50	0,84
19/4/2011 5:43	38,09	0,77
19/4/2011 5:58	34,76	0,71
19/4/2011 6:13	35,61	0,72
19/4/2011 6:28	32,02	0,65
19/4/2011 6:43	40,21	0,82
19/4/2011 6:58	49,25	1,00
19/4/2011 7:13	53,72	1,09
19/4/2011 7:28	41,36	0,84
19/4/2011 7:44	30,29	0,62
19/4/2011 7:59	29,45	0,60
19/4/2011 8:14	27,85	0,57
19/4/2011 8:29	24,09	0,49
19/4/2011 8:44	29,85	0,61
19/4/2011 8:59	27,72	0,56
19/4/2011 9:14	30,65	0,62
19/4/2011 9:29	28,96	0,59

10.2 May Sampling Data

Date and Time	ppbv	$\mu\text{g}/\text{m}^3 \cdot 1,25$
21/5/2011 1:57	28,06	0,6
21/5/2011 2:17	33,97	0,7
21/5/2011 2:37	30,06	0,6

21/5/2011 2:57	23,08	0,5
21/5/2011 3:18	24,72	0,5
21/5/2011 3:38	24,40	0,5
21/5/2011 3:58	24,43	0,5
21/5/2011 4:18	25,00	0,5
21/5/2011 4:38	25,15	0,5
21/5/2011 4:58	25,04	0,5
21/5/2011 5:18	23,51	0,5
21/5/2011 5:38	22,55	0,5
21/5/2011 5:58	24,08	0,5
21/5/2011 6:18	26,57	0,5
21/5/2011 6:39	24,86	0,5
21/5/2011 6:59	23,33	0,5
21/5/2011 7:19	24,90	0,5
21/5/2011 7:39	26,82	0,5
21/5/2011 7:59	29,77	0,6
21/5/2011 8:19	29,70	0,6
21/5/2011 8:39	32,15	0,7
21/5/2011 8:59	34,50	0,7
21/5/2011 9:19	30,91	0,6
21/5/2011 9:39	30,34	0,6
21/5/2011 10:00	35,39	0,7
21/5/2011 10:20	36,28	0,7
21/5/2011 10:40	43,50	0,9
21/5/2011 14:15	310,38	6,3
21/5/2011 14:35	375,17	7,6
21/5/2011 14:55	257,90	5,2
21/5/2011 15:15	184,93	3,8
21/5/2011 15:35	219,94	4,5
21/5/2011 15:55	220,33	4,5
21/5/2011 16:15	297,22	6,0
21/5/2011 16:35	230,79	4,7
21/5/2011 16:55	196,25	4,0
21/5/2011 17:16	186,03	3,8
21/5/2011 17:36	200,66	4,1
21/5/2011 17:56	251,11	5,1
21/5/2011 18:16	235,63	4,8
21/5/2011 18:36	228,77	4,6
21/5/2011 18:56	223,78	4,5
21/5/2011 19:16	240,65	4,9
21/5/2011 19:36	224,82	4,6
21/5/2011 19:56	235,10	4,8
21/5/2011 20:16	212,79	4,3
21/5/2011 20:37	203,33	4,1
21/5/2011 20:57	219,23	4,5
21/5/2011 21:17	209,66	4,3
21/5/2011 21:37	196,17	4,0
21/5/2011 21:57	219,09	4,5
21/5/2011 22:17	199,16	4,0
21/5/2011 22:37	182,83	3,7
21/5/2011 22:57	163,73	3,3
21/5/2011 23:17	165,61	3,4
21/5/2011 23:38	192,33	3,9
21/5/2011 23:58	181,12	3,7
22/5/2011 0:18	170,17	3,5
22/5/2011 0:38	161,77	3,3
22/5/2011 0:58	173,87	3,5
22/5/2011 1:18	187,67	3,8

22/5/2011 1:38	168,71	3,4
22/5/2011 1:58	189,88	3,9
22/5/2011 2:18	193,79	3,9
22/5/2011 2:38	184,47	3,7
22/5/2011 2:59	184,11	3,7
22/5/2011 3:19	182,33	3,7
22/5/2011 3:39	182,80	3,7
22/5/2011 3:59	187,49	3,8
22/5/2011 4:19	193,54	3,9
22/5/2011 4:39	194,43	3,9
22/5/2011 4:59	195,36	4,0
22/5/2011 5:19	203,54	4,1
22/5/2011 5:39	218,70	4,4
22/5/2011 5:59	215,35	4,4
22/5/2011 6:20	217,52	4,4
22/5/2011 6:40	239,69	4,9
22/5/2011 7:00	240,11	4,9
22/5/2011 7:20	264,38	5,4
22/5/2011 7:40	255,06	5,2
22/5/2011 8:00	257,37	5,2
22/5/2011 8:20	264,98	5,4
22/5/2011 8:40	260,64	5,3
22/5/2011 9:00	258,62	5,3
22/5/2011 9:20	272,06	5,5
22/5/2011 9:41	277,58	5,6
22/5/2011 10:01	267,51	5,4
22/5/2011 10:21	267,23	5,4
22/5/2011 10:41	261,36	5,3
22/5/2011 11:01	254,52	5,2
22/5/2011 11:21	246,09	5,0
22/5/2011 11:41	220,83	4,5
22/5/2011 12:01	206,39	4,2
22/5/2011 12:21	211,54	4,3
22/5/2011 12:42	209,09	4,2
22/5/2011 13:02	227,16	4,6
22/5/2011 13:22	242,96	4,9
22/5/2011 13:42	231,58	4,7
22/5/2011 14:02	251,11	5,1
22/5/2011 14:22	256,37	5,2
22/5/2011 14:42	255,20	5,2
22/5/2011 15:02	270,32	5,5
22/5/2011 15:22	264,31	5,4
22/5/2011 15:42	263,85	5,4
22/5/2011 16:03	261,28	5,3
22/5/2011 16:23	247,20	5,0
22/5/2011 16:43	213,86	4,3
22/5/2011 17:03	205,78	4,2
22/5/2011 17:23	205,96	4,2
22/5/2011 17:43	213,04	4,3
22/5/2011 18:03	199,41	4,1
22/5/2011 18:23	185,79	3,8
22/5/2011 18:43	192,79	3,9
22/5/2011 19:03	187,71	3,8
22/5/2011 19:24	196,07	4,0
22/5/2011 19:44	188,06	3,8
22/5/2011 20:04	186,39	3,8
22/5/2011 20:24	197,85	4,0
22/5/2011 20:44	200,23	4,1

22/5/2011 21:04	201,90	4,1
22/5/2011 21:24	199,06	4,0
22/5/2011 21:44	198,17	4,0
22/5/2011 22:04	205,32	4,2
22/5/2011 22:24	202,83	4,1
22/5/2011 22:45	194,15	3,9
22/5/2011 23:05	187,10	3,8
22/5/2011 23:25	189,66	3,9
22/5/2011 23:45	173,62	3,5
23/5/2011 0:05	190,84	3,9
23/5/2011 0:25	188,74	3,8
23/5/2011 0:45	183,15	3,7
23/5/2011 1:05	179,31	3,6
23/5/2011 1:25	175,15	3,6
23/5/2011 1:45	169,45	3,4
23/5/2011 2:06	134,69	2,7
23/5/2011 2:26	161,09	3,3
23/5/2011 2:46	158,28	3,2
23/5/2011 3:06	161,56	3,3
23/5/2011 3:26	161,91	3,3
23/5/2011 3:46	153,48	3,1
23/5/2011 4:06	155,19	3,2
23/5/2011 4:26	157,14	3,2
23/5/2011 4:46	153,73	3,1
23/5/2011 5:07	149,07	3,0
23/5/2011 5:27	143,98	2,9
23/5/2011 5:47	150,92	3,1
23/5/2011 6:07	144,66	2,9
23/5/2011 6:27	138,75	2,8
23/5/2011 6:47	138,25	2,8
23/5/2011 7:07	135,80	2,8
23/5/2011 7:27	140,17	2,8
23/5/2011 7:47	154,16	3,1
23/5/2011 8:07	113,35	2,3
23/5/2011 8:28	108,22	2,2
23/5/2011 8:48	115,09	2,3
23/5/2011 9:08	126,01	2,6
23/5/2011 9:28	128,08	2,6
23/5/2011 9:48	117,05	2,4

Date and Time	ppbv	$\mu\text{g}/\text{m}^3 \cdot 1,25$
26/5/2011 15:19	51,72	1,2
26/5/2011 15:39	46,39	1,1
26/5/2011 15:59	50,69	1,2
26/5/2011 16:19	53,04	1,2
26/5/2011 16:39	68,16	1,6
26/5/2011 16:59	86,13	2,0
27/5/2011 15:24	180,77	4,2
27/5/2011 15:44	190,48	4,5
27/5/2011 16:04	182,48	4,3
27/5/2011 16:25	172,37	4,0
27/5/2011 16:45	174,61	4,1
27/5/2011 17:05	179,77	4,2
27/5/2011 17:25	175,72	4,1
27/5/2011 17:45	178,78	4,2
27/5/2011 18:05	190,02	4,5
27/5/2011 18:25	211,44	5,0

27/5/2011 18:45	149,32	3,5
27/5/2011 19:05	170,74	4,0
27/5/2011 19:25	185,18	4,3
27/5/2011 19:46	181,94	4,3
27/5/2011 20:06	177,74	4,2
27/5/2011 20:26	174,61	4,1
27/5/2011 20:46	162,94	3,8
27/5/2011 21:06	155,83	3,7
27/5/2011 21:26	142,02	3,3
27/5/2011 21:46	147,57	3,5
27/5/2011 22:06	143,41	3,4
27/5/2011 22:26	141,77	3,3
27/5/2011 22:47	151,52	3,6
27/5/2011 23:07	141,42	3,3
27/5/2011 23:27	54,64	1,3
27/5/2011 23:47	54,75	1,3
28/5/2011 0:07	45,28	1,1
28/5/2011 0:27	38,42	0,9
28/5/2011 0:47	47,70	1,1
28/5/2011 1:07	33,40	0,8
28/5/2011 1:27	36,85	0,9
28/5/2011 1:47	32,23	0,8
28/5/2011 2:08	35,25	0,8
28/5/2011 2:28	47,31	1,1
28/5/2011 2:48	64,25	1,5
28/5/2011 3:08	97,98	2,3
28/5/2011 3:28	83,82	2,0
28/5/2011 3:48	86,98	2,0
28/5/2011 4:08	100,22	2,3
28/5/2011 4:28	116,58	2,7
28/5/2011 4:48	113,84	2,7
28/5/2011 5:09	134,94	3,2
28/5/2011 5:29	144,02	3,4
28/5/2011 5:49	156,36	3,7
28/5/2011 6:09	167,28	3,9
28/5/2011 6:29	141,20	3,3
28/5/2011 6:49	41,19	1,0
28/5/2011 7:09	70,86	1,7
28/5/2011 7:29	123,56	2,9
28/5/2011 7:49	158,28	3,7
28/5/2011 8:09	151,20	3,5
28/5/2011 8:30	177,42	4,2
28/5/2011 8:50	209,94	4,9
28/5/2011 9:10	170,49	4,0
28/5/2011 9:30	185,71	4,4
28/5/2011 9:50	162,62	3,8
28/5/2011 10:10	147,96	3,5
28/5/2011 10:30	156,90	3,7
28/5/2011 10:50	161,66	3,8
28/5/2011 11:10	181,27	4,2
28/5/2011 11:30	186,14	4,4
28/5/2011 11:51	219,12	5,1
28/5/2011 12:11	205,89	4,8
28/5/2011 12:31	186,64	4,4
28/5/2011 12:51	202,19	4,7
28/5/2011 13:11	203,40	4,8
28/5/2011 13:31	195,53	4,6
28/5/2011 13:51	179,03	4,2

28/5/2011 14:11	193,93	4,5
28/5/2011 14:31	206,53	4,8
28/5/2011 14:52	194,68	4,6
28/5/2011 15:12	204,93	4,8
28/5/2011 15:32	209,41	4,9
28/5/2011 15:52	206,56	4,8
28/5/2011 16:12	198,31	4,6
28/5/2011 16:32	213,72	5,0
28/5/2011 16:52	237,62	5,6
28/5/2011 17:12	215,28	5,0
28/5/2011 17:32	203,22	4,8
28/5/2011 17:52	200,91	4,7
28/5/2011 18:13	213,18	5,0
28/5/2011 18:33	195,82	4,6
28/5/2011 18:53	197,78	4,6
28/5/2011 19:13	218,84	5,1
28/5/2011 19:33	189,17	4,4
28/5/2011 19:53	192,30	4,5
28/5/2011 20:13	191,83	4,5
28/5/2011 20:33	203,18	4,8
28/5/2011 20:53	247,23	5,8
28/5/2011 21:13	228,87	5,4
28/5/2011 21:34	214,75	5,0
28/5/2011 21:54	208,09	4,9
28/5/2011 22:14	209,09	4,9
28/5/2011 22:34	222,40	5,2
28/5/2011 22:54	208,81	4,9
28/5/2011 23:14	225,42	5,3
28/5/2011 23:34	242,75	5,7
28/5/2011 23:54	239,90	5,6
29/5/2011 0:14	240,01	5,6
29/5/2011 0:35	212,43	5,0
29/5/2011 0:55	206,07	4,8
29/5/2011 1:15	218,02	5,1
29/5/2011 1:35	208,52	4,9
29/5/2011 1:55	204,75	4,8
29/5/2011 2:15	196,35	4,6
29/5/2011 2:35	201,30	4,7
29/5/2011 2:55	196,64	4,6
29/5/2011 3:15	197,24	4,6
29/5/2011 3:35	195,53	4,6
29/5/2011 3:56	190,34	4,5
29/5/2011 4:16	189,27	4,4
29/5/2011 4:36	186,18	4,4
29/5/2011 4:56	189,09	4,4
29/5/2011 5:16	174,44	4,1
29/5/2011 5:36	166,18	3,9
29/5/2011 5:56	173,76	4,1
29/5/2011 6:16	170,84	4,0
29/5/2011 6:36	159,24	3,7
29/5/2011 6:56	149,99	3,5
29/5/2011 7:17	147,43	3,5
29/5/2011 7:37	142,91	3,3
29/5/2011 7:57	145,51	3,4
29/5/2011 8:17	146,58	3,4
29/5/2011 8:37	145,76	3,4
29/5/2011 8:57	147,47	3,5
29/5/2011 9:17	146,76	3,4

29/5/2011 9:37	148,25	3,5
29/5/2011 9:57	156,82	3,7
29/5/2011 10:18	155,61	3,6
29/5/2011 10:38	154,87	3,6
29/5/2011 10:58	157,00	3,7
29/5/2011 11:18	159,28	3,7
29/5/2011 11:38	163,41	3,8
29/5/2011 11:58	167,82	3,9
29/5/2011 12:18	168,60	4,0
29/5/2011 12:38	170,56	4,0
29/5/2011 12:58	176,78	4,1
29/5/2011 13:18	176,25	4,1
29/5/2011 13:39	187,46	4,4
29/5/2011 13:59	176,78	4,1
29/5/2011 14:19	176,86	4,1
29/5/2011 14:39	188,77	4,4
29/5/2011 14:59	183,37	4,3
29/5/2011 15:19	180,56	4,2
29/5/2011 15:39	176,53	4,1
29/5/2011 15:59	175,43	4,1
29/5/2011 16:19	175,97	4,1
29/5/2011 16:39	177,82	4,2
29/5/2011 17:00	183,40	4,3
29/5/2011 17:20	179,63	4,2
29/5/2011 17:40	191,05	4,5
29/5/2011 18:00	181,44	4,3
29/5/2011 18:20	179,38	4,2

10.3 June Sampling Data

Date and Time	ppbv	$\mu\text{g}/\text{m}^3 \cdot 1,25$
7/6/2011 15:49	128,78	3,0
7/6/2011 16:09	108,34	2,5
7/6/2011 16:29	101,77	2,4
7/6/2011 16:49	91,28	2,1
7/6/2011 17:09	82,18	1,9
7/6/2011 17:30	80,08	1,9
7/6/2011 17:50	85,82	2,0
7/6/2011 18:10	79,26	1,9
7/6/2011 18:30	82,36	1,9
7/6/2011 18:50	82,51	1,9
7/6/2011 19:10	86,36	2,0
7/6/2011 19:30	90,82	2,1
7/6/2011 19:50	102,20	2,4
7/6/2011 20:10	108,52	2,5
7/6/2011 20:30	111,16	2,6
7/6/2011 20:51	107,02	2,5
7/6/2011 21:11	108,16	2,5
7/6/2011 21:31	109,23	2,6
7/6/2011 21:51	114,72	2,7
7/6/2011 22:11	116,47	2,7
7/6/2011 22:31	114,76	2,7
7/6/2011 22:51	101,66	2,4
7/6/2011 23:11	102,09	2,4
7/6/2011 23:31	105,48	2,5

7/6/2011 23:52	107,77	2,5
8/6/2011 0:12	104,06	2,4
8/6/2011 0:32	116,33	2,7
8/6/2011 0:52	117,43	2,8
8/6/2011 1:12	115,33	2,7
8/6/2011 1:32	125,21	2,9
8/6/2011 1:52	119,43	2,8
8/6/2011 2:12	113,55	2,7
8/6/2011 2:32	110,19	2,6
8/6/2011 2:52	118,47	2,8
8/6/2011 3:13	114,44	2,7
8/6/2011 3:33	110,05	2,6
8/6/2011 3:53	110,94	2,6
8/6/2011 4:13	111,87	2,6
8/6/2011 4:33	111,48	2,6
8/6/2011 4:53	111,12	2,6
8/6/2011 5:13	119,61	2,8
8/6/2011 5:33	145,80	3,4
8/6/2011 5:53	195,00	4,6
8/6/2011 6:13	168,67	4,0
8/6/2011 6:34	155,29	3,6
8/6/2011 6:54	169,42	4,0
8/6/2011 7:14	170,13	4,0
8/6/2011 7:34	171,02	4,0
8/6/2011 7:54	183,44	4,3
8/6/2011 8:14	186,97	4,4
8/6/2011 8:34	195,54	4,6
8/6/2011 8:54	162,28	3,8
8/6/2011 9:14	166,28	3,9
8/6/2011 9:35	139,23	3,3
8/6/2011 9:55	161,64	3,8
8/6/2011 10:15	147,98	3,5
8/6/2011 10:35	145,01	3,4
8/6/2011 10:55	149,01	3,5
8/6/2011 11:15	153,15	3,6
8/6/2011 11:35	161,57	3,8
8/6/2011 11:55	161,21	3,8
8/6/2011 12:15	162,03	3,8
8/6/2011 12:36	159,11	3,7
8/6/2011 12:56	163,39	3,8
8/6/2011 13:16	156,00	3,7
8/6/2011 13:36	158,57	3,7
8/6/2011 13:56	153,22	3,6
8/6/2011 14:16	144,16	3,4
8/6/2011 14:36	153,19	3,6
8/6/2011 14:56	162,32	3,8
8/6/2011 15:16	138,31	3,2
9/6/2011 11:11	120,75	2,8
9/6/2011 11:31	128,57	3,0
9/6/2011 11:51	117,97	2,8
9/6/2011 12:11	114,01	2,7
9/6/2011 12:31	118,54	2,8
9/6/2011 12:51	114,12	2,7
9/6/2011 13:12	93,53	2,2
9/6/2011 13:32	93,99	2,2
9/6/2011 13:52	84,65	2,0
9/6/2011 14:12	78,83	1,8
9/6/2011 14:32	77,62	1,8

9/6/2011 14:52	43,61	1,0
9/6/2011 15:12	42,51	1,0
9/6/2011 15:32	43,29	1,0
9/6/2011 15:52	40,69	1,0
9/6/2011 16:12	42,90	1,0
9/6/2011 16:33	47,04	1,1
9/6/2011 16:53	52,39	1,2
9/6/2011 17:13	55,60	1,3
9/6/2011 17:33	51,86	1,2
9/6/2011 17:53	53,71	1,3
9/6/2011 18:13	59,78	1,4
9/6/2011 18:33	100,06	2,3
9/6/2011 18:53	175,91	4,1
9/6/2011 19:13	68,73	1,6
9/6/2011 19:34	69,09	1,6
9/6/2011 19:54	76,19	1,8
9/6/2011 20:14	67,13	1,6
9/6/2011 20:34	65,70	1,5
9/6/2011 20:54	65,81	1,5
9/6/2011 21:14	80,90	1,9
9/6/2011 21:34	82,79	1,9
9/6/2011 21:54	83,08	1,9
9/6/2011 22:14	92,92	2,2
9/6/2011 22:34	86,43	2,0
9/6/2011 22:55	89,00	2,1
9/6/2011 23:15	95,24	2,2
9/6/2011 23:35	106,09	2,5
9/6/2011 23:55	122,79	2,9
10/6/2011 0:15	130,03	3,0
10/6/2011 0:35	123,39	2,9
10/6/2011 0:55	114,37	2,7
10/6/2011 1:15	105,84	2,5
10/6/2011 1:35	101,20	2,4
10/6/2011 1:56	90,71	2,1
10/6/2011 2:16	96,81	2,3
10/6/2011 2:36	97,60	2,3
10/6/2011 2:56	99,67	2,3
10/6/2011 3:16	110,12	2,6
10/6/2011 3:36	126,10	3,0
10/6/2011 3:56	131,17	3,1
10/6/2011 4:16	127,39	3,0
10/6/2011 4:36	120,86	2,8
10/6/2011 4:56	115,83	2,7
10/6/2011 5:17	110,48	2,6
10/6/2011 5:37	107,12	2,5
10/6/2011 5:57	100,99	2,4
10/6/2011 6:17	101,31	2,4
10/6/2011 6:37	92,74	2,2
10/6/2011 6:57	88,78	2,1
10/6/2011 7:17	94,60	2,2
10/6/2011 7:37	100,52	2,4
10/6/2011 7:57	107,87	2,5

10.4 Denuders Sampling Data

Date and Time	ppbv	$\mu\text{g}/\text{m}^3 \cdot 1,25$
10/6/2011 8:18	109,15	2,4
10/6/2011 8:38	110,61	2,4
10/6/2011 8:58	120,25	2,6
10/6/2011 9:18	121,74	2,7
10/6/2011 9:38	116,41	2,5
10/6/2011 9:58	116,19	2,5
10/6/2011 10:18	116,90	2,6
10/6/2011 10:38	114,59	2,5
10/6/2011 10:58	99,29	2,2
10/6/2011 11:18	98,94	2,2
10/6/2011 11:39	91,86	2,0
10/6/2011 11:59	90,29	2,0
10/6/2011 12:19	90,04	2,0
10/6/2011 12:39	96,80	2,1
10/6/2011 12:59	113,31	2,5
10/6/2011 13:19	108,40	2,4
10/6/2011 13:39	115,59	2,5
10/6/2011 13:59	116,94	2,6
10/6/2011 14:19	126,01	2,8
10/6/2011 14:40	91,11	2,0
10/6/2011 15:00	134,05	2,9
10/6/2011 15:20	104,27	2,3
10/6/2011 15:40	105,13	2,3
10/6/2011 16:00	115,05	2,5

Date and Time	ppbv	$\mu\text{g}/\text{m}^3 \cdot 1,25$
21/6/2011 8:54	108,60	2,4
21/6/2011 9:09	109,77	2,4
21/6/2011 9:24	108,64	2,4
21/6/2011 9:39	112,60	2,5
21/6/2011 9:54	112,93	2,5
21/6/2011 10:09	113,63	2,5
21/6/2011 10:24	120,93	2,6
21/6/2011 10:40	119,71	2,6
21/6/2011 10:55	123,27	2,7
21/6/2011 11:10	124,62	2,7
21/6/2011 11:25	123,45	2,7
21/6/2011 11:40	131,34	2,9
21/6/2011 11:55	145,78	3,2
21/6/2011 12:10	141,59	3,1
21/6/2011 12:25	141,28	3,1
21/6/2011 12:40	140,77	3,1
21/6/2011 12:55	142,31	3,1
21/6/2011 13:11	143,60	3,1
21/6/2011 13:26	161,71	3,5
21/6/2011 13:41	162,58	3,6
21/6/2011 13:56	165,76	3,6
21/6/2011 14:11	157,87	3,5
21/6/2011 14:26	157,73	3,5
21/6/2011 14:41	163,30	3,6
21/6/2011 14:56	171,19	3,7
21/6/2011 15:11	179,57	3,9
21/6/2011 15:27	179,12	3,9
21/6/2011 15:42	179,57	3,9

21/6/2011 15:57	178,77	3,9
21/6/2011 16:12	177,44	3,9
21/6/2011 16:27	183,12	4,0
21/6/2011 16:42	181,13	4,0

10.5 Procedures

Preview of the procedures:

From 8-4-2011 to 19-4-2011

- Attempts to separate peaks of HCO_3^- και NO_3^- using samples consisting of these anions.
- Also samples with SO_4^{2-} as well as mixtures containing the other compounds were used.
- Sample times were 15min while injection times were 13min.
- A full sequence with a standard and some single standards fed to the IC to check for peak matching.

From 28-4-2011 to 20-5-2011

- Change of eluent from NaOH to NaHCO_3 in order to separate the peaks.
- Comprehensive tests with different concentrations of NaHCO_3 .
- Comprehensive tests with different flows to the suppressor.
- Comprehensive tests with different times.
- The main measurements begun from 8-4-2011 to 18-4-2011 (the SO_4^{2-} concentrations were computed in $\mu\text{g}/\text{m}^3$)
- Filter results (8 filters) and corresponding extracts were conducted between 12-4-2011 and 18-4-2011.
- A whole sequence of a standard with only MSA to identify the peak.
- Three complete sequences of a standard and samples consisting only of HCO_3^- , NO_3^- και SO_4^{2-} .

From 20-5-2011 to 10-6-2011

- PILS detects the peaks of SO_4^{2-} .
- Dust event measurements of SO_4^{2-} in $\mu\text{g}/\text{m}^3$.
- Experiments with and without the denuders with eluent NaHCO_3 .
- A whole sequence with a standard.

From 15-6-2011 and afterwards

- Return to eluent NaOH to see OX peaks.
- Experiments with and without denuders
- A complete sequence of standard solutions.

One of the key features of the chromeleon software used is that all samples that were running are placed in sequence files. In each sequence you have information of the main settings of the IC and the main configurations chosen. Some configurations that can be noticed in the control panel of each sequence can be:

- Pump injection valve state (loading the sample or injecting the sample)
- Data collection rate (set to 5hz)
- Cell temperature nominal (set to 35°C)
- Column temperature nominal
- Suppressor type (in this case ASRS_4mm)
- Pump ECD. carbonate
- Pump ECD. bicarbonate
- Pump ECD. tetraborate
- Pump ECD. Other eluent
- Suppressor current (varied from 50 mA to 70 mA)
- ECD _Total Stop
- ECD_ Total Average
- Pressure lower limit
- Pressure upper limit
- A. equate
- Pump ECD. hydroxide
- Pump ECD. Recommended , current (25)
- Flow (set to 1.00ml/min)
- Sampling time (separation)
- Injection time (automatically or manually)

In case of use of such

The main and most important configurations are the sample time, meaning how long the separation takes, the injection time of the sample in the loop and the different currents of the suppressor.

Modifications to procedures done due to sensitivity factors:

Sequence 20110408:

- starting samples
- eluent used is NaOH
- suppressor current set to 50mA
- injection time set to 13min and sample time 15min

Sequence 20110409:

- SO_4^{2-} peaks showing up
- eluent used is NaOH

- suppressor current set to 50mA
- injection time set to 13min and sample time 15min

Sequence 20110410:

- SO_4^{2-} peaks showing up until sample No.59
- Running water samples
- Running sample of a standard 10 (new)
- Rest of samples from PILS without SO_4^{2-} peaks
- eluent used is NaOH
- suppressor current set to 50mA
- injection time set to 13min and sample time 15min

Sequence 20110412:

- small SO_4^{2-} peaks showing up
- running a series of standards
- running combined samples containing NO_3^- , SO_4^{2-} , OX
- SO_4^{2-} peaks back to normal levels
- eluent used is NaOH
- suppressor current set to 50mA
- injection time set to 13min and sample time 15min

Sequence 20110413:

- SO_4^{2-} peaks showing up
- eluent used is NaOH
- suppressor current set to 50mA
- injection time set to 13min and sample time 15min

Sequence 20110414:

- SO_4^{2-} peaks showing up
- running combined samples containing NO_3^- , SO_4^{2-} , OX
- eluent used is NaOH
- suppressor current set to 50mA
- injection time set to 13min and sample time 15min

Sequence 20110414b:

- SO_4^{2-} peaks showing up
- testing old and new eluent concentrations
- running combined samples containing NO_3^- , SO_4^{2-} , OX
- eluent used is NaOH
- suppressor current set to 50mA
- injection time set to 13min and sample time 15min

Sequence 20110415:

- SO_4^{2-} peaks showing up
- running samples containing HCO_3

- eluent used is NaOH
- suppressor current set to 50mA
- injection time set to 13min and sample time 15min

Sequence 20110416:

- SO_4^{2-} peaks showing up
- eluent used is NaOH
- suppressor current set to 50mA
- injection time set to 13min and sample time 15min

Sequence 20110417:

- SO_4^{2-} peaks
- eluent used is NaOH
- suppressor current set to 50mA
- injection time set to 13min and sample time 15min

Sequence 20110418:

- running samples containing HCO_3^- and NO_3^- combined and separately because their peaks show up in the same running time
- eluent used is NaOH
- suppressor current set to 50mA
- injection time set to 13min and sample time 15min

Sequence 20110419:

- eluent change from NaOH to NaHCO_3
- running series of standards with different eluent concentrations
- running samples of MSA
- running samples from the extraction of the filters (8) and the simultaneously collected samples from PILS (8)
- eluent used is NaHCO_3
- suppressor current varied
- injection time set to 18min and sample time 20min

Sequence 20110420:

- SO_4^{2-} peaks after sample 19
- eluent used is NaHCO_3
- suppressor current set to 70mA
- injection time set to 18min and sample time 20min

Sequence 20110421:

- SO_4^{2-} peaks showing up
- running samples without a filter at the injection point
- eluent used is NaHCO_3
- suppressor current set to 70mA
- injection time set to 18min and sample time 20min

Sequence 20110422:

- SO_4^{2-} peaks “dropped”
- running bypass , loop and standard tests
- eluent used is NaHCO_3
- suppressor current set to 70mA
- injection time set to 18min and sample time 20min

Sequence 20110427:

- SO_4^{2-} peaks back to normal
- eluent used is NaHCO_3
- suppressor current set to 70mA
- injection time set to 18min and sample time 20min

Sequence 20110428:

- SO_4^{2-} peaks showing up
- eluent used is NaHCO_3
- suppressor current set to 70mA
- injection time set to 18min and sample time 20min

Sequence 20110602:

- “refreshing” the denuders for the upcoming dust event
- running samples for the dust effect
- running tests with and without the denuders
- running a series of standards
- eluent used is NaHCO_3
- suppressor current set to 70mA
- injection time set to 18min and sample time 20min
- after the tests the eluent was changed to NaOH the suppressor current remained at 70mA and the injection time changed to 13min and sample time to 15min

Sequence 20110603:

- different peaks
- eluent used is NaOH
- suppressor current set to 70mA
- injection time set to 13min and sample time 15min

Sequence 20110604:

- running tests with and without denuders
- eluent used is NaOH
- suppressor current set to 70mA
- injection time set to 13min and sample time 15min