Environ Monit Assess (2009) 152:231–244
DOI 10.1007/s10661-008-0311-9

Characterisation of gaseous and particulate atmospheric pollutants in the East Mediterranean by diffusion denuder sampling lines

C. Perrino · M. Catrambone · G. Esposito · D. Lahav · Y. Mamane

Received: 23 July 2007 / Accepted: 9 April 2008 / Published online: 6 June 2008

Abstract A field study aimed to characterize atmospheric pollutants in the gaseous and the particulate phases was conducted during the fall–winter of 2004 and the summer of 2005 in the Ashdod area, Israel. The site is influenced by both anthropogenic sources (power plants, refineries, chemical and metal industries, a cargo port, road traffic) and natural sources (sea-spray and desert dust). The use of diffusion lines—a series of annular diffusion denuders for sampling gaseous compounds followed by a cyclone and a filter pack for determining $PM_{2.5}$ composition—allowed a good daily characterization of the main inorganic compounds in both the gaseous (HCl, HNO_3, SO_2, NH_3) and the particulate phase (Cl^-, NO_3^-, $SO_4^=$, NH_4^+, and base cations). During the summer campaign two other activities were added: an intensive 3-h sampling period and the determination of $PM_{2.5}$ bulk composition. The results were interpreted on the basis of meteorological condition, especially the mixing properties of the lower atmosphere as determined by monitoring the natural radioactivity due to Radon progeny, a good proxy of the atmospheric ability to dilute pollutants. Several pollution episodes were identified and the predominance of different sources was highlighted (sea-spray, desert dust, secondary photochemical pollutants). During the summer period a considerable increase of nitric acid and particulate sulphate was observed. Secondary inorganic pollutants (nitrate, sulphate and ammonium) constituted, on the average, 57% of the fine particle fraction, organic compounds 20%, primary anthropogenic compounds 14%, natural components (sea-spray and crustal elements) 9%. The advantages of the diffusion lines in determining gaseous and particulate N− and S− inorganic compounds are discussed.

Keywords Air pollution · Diffusion denuder · East Mediterranean · Particulate matter · Pollution sources · Sampling artefacts

Introduction

A field study was carried out in the city of Ashdod, Central Israel, on the south–east Mediterranean coast, during the fall–winter of 2004 and the summer of 2005, in the framework of the research project “Modelling system for urban air pollution”, funded

C. Perrino (✉) · M. Catrambone · G. Esposito
C.N.R. Institute of Atmospheric Pollution,
Via Salaria km. 29,300 Monterotondo Stazione,
00015 Rome, Italy
e-mail: perrino@iia.cnr.it

D. Lahav
Ashdod-Yavne Regional Association
for Environmental Protection,
P.O. Box 12402, Ashdod, Israel

Y. Mamane
Environmental and Water Resources Engineering,
Technion,
Haifa 32000, Israel

by the Italian Ministry of Environment and Territory. The study was addressed to collect air pollution data during specific field campaigns carried out in Central Israel, to be subsequently used for testing a high-resolution integrated mesoscale modelling system for urban air pollution.

The field campaigns were scheduled for 3 weeks during the autumn–winter (from November 14th to December 4th 2004) and 2 weeks during the summer (from July 7th to 21st 2005) and were addressed to studying the influence of the mixing properties of the lower atmosphere on atmospheric pollution events, with special emphasis on N− and S− inorganic compounds in both the gaseous and the particulate phase; during the summer campaign, the bulk composition of $PM_{2.5}$ was also determined. Although some aerosol characterisation studies had been already carried out in Israel (Graham et al. 2004 and cited therein), this study constitutes the first attempt to characterise gaseous and particulate pollutants, especially nitric acid and nitrates, using denuder lines.

The experimental set-up relied on the continuous monitoring of natural radioactivity, aimed to trace the evolution of the dilution properties of the lower atmosphere, and on the use of diffusion denuder lines to determine the main inorganic components in the gaseous and the particulate phase minimizing the mutual interferences during the sampling stage.

Natural radioactivity can be used as a reliable tracer of the dilution properties of the lower atmosphere. The emission of Radon from the ground can be considered as constant in the time and space scale of our observation (a few weeks, a few kilometres) and the main parameter determining the concentration of Radon daughters in the atmosphere is the height of the mixing layer (Shery et al. 1984; Porstendorfer et al. 1991; Shweikani et al. 1995). So the behaviour of Radon daughters can be assimilated to the fate of a non-reactive pollutant having a constant emission rate. The determination of natural radioactivity due to Radon daughters allows discriminating between the variations in pollutants concentration due to changes in their emission/transformation rate, and those that are due to changes in the dilution properties of the atmosphere (Perrino et al. 2001a, 2008; Sesana et al. 2003; Vecchi et al. 2007).

Diffusion lines, composed of five annular denuders set in series, a cyclone and triple filter-pack, allow the selective removal and collection of the gaseous compounds (HCl, HNO_3, SO_2, HONO, NH_3) on the denuders and the subsequent collection of the particulate phase in the cyclone and on the filter pack. The configuration of the filter pack, with one Teflon filter and two back-up filters, allows the recovery of the gaseous species evolved during the sampling from unstable particulate compounds such as ammonium nitrate, and thus the unbiased determination of ammonium salts (Perrino et al. 2001b, 2008; Allegrini et al. 1994).

In addition, during one week of the summer campaign the determinations were extended to the measurement of the bulk chemical composition of fine particles: in addition to the determination of ions by IC, the metal content of $PM_{2.5}$ was determined by XRF and the elemental and organic carbon content by thermo-optical analysis (Astolfi et al. 2006; Perrino et al. 2007).

Experimental

Sampling site

The measurements were carried out in the city of Ashdod, about 200,000 inhabitants, on the Israeli coast, 40 km south of Tel Aviv. The sampling site was on the roof of the Ashdod-Yavne Municipal Association for the Environment, about 20 m above the ground level. The site is about 2 km east of the sea. Both the main Israeli cargo port, and the industrial area that includes a 1,300 mW power plant, refineries and chemical plants, are sited north–west of the sampling location. More details about the sampling site are reported in the paper of Mamane et al. (2008).

Natural radioactivity

Natural radioactivity was measured by means of an automatic stability monitor (PBL Mixing Monitor, FAI Instruments, Fontenuova, Italy), schematically consisting of a sampler for the collection of particulate matter on filter membranes and a Geiger–Muller counter for determining the total beta activity of the short-lived Radon progeny attached to particles. The instrument operates on two filters at the same time: sampling is performed on the first filter for a 1-h sampling duration, then this filter undergoes the beta measurement phase while a second one undergoes the sampling phase. These instrumental features assure that the short-lived beta activity of the particles is determined continuously over an integration time of 1 h and that the beta measurement period is long enough to guarantee a good accuracy of the results. Residual radioactivity is also taken into account. The accuracy of the determination is improved by the automatic subtraction of the background radiation (such as cosmic rays), the continuous monitoring of the stability of the high voltage supplied to the Geiger detector and the normalisation of this value to a reference value (Perrino et al. 2000).

Sampling method

Inorganic N− and S− compounds were collected by means of diffusion lines consisting of five annular denuders, one cyclone and a triple filter pack set in series. These devices allow the selective collection of gaseous species on the denuder section, where gaseous molecules diffuse towards the wall of the denuders and are collected on a suitable coating layer. Particles, on the other hand, thanks to their much lower diffusion coefficient, proceed unaffected along the denuder section and can be collected in the cyclone and on the downstream filters without any bias due to the interference of gaseous species.

Denuders were made of frosted Pyrex glass, 20 cm in length, 3.3 and 3.0 cm in outside and inside diameters, respectively. Coatings were sodium chloride (summer/fall campaign) or sodium fluoride (summer campaign) for the first two denuders, sodium carbonate plus glycerin for the third and fourth denuders, phosphorous acid for the fifth one. Details about the coating solutions, coating and extracting procedure and about the theoretical basis of the annular denuder technique are reported in Febo et al. 1989; Perrino et al. 2001b, 2008; Allegrini et al. 1994. The cyclone had an aerodynamic cut size of 2.5 μm at the operative flow rate of 15 l min^{-1}; the filter pack was constituted of a Teflon filter (Gelman, 47 mm, 1 μm pore size) for the collection of fine particles, a back-up Nylon filter (Gelman, 47 mm, 1 μm pore size) for the recovery of evolved nitric acid and a back-up H_3PO_3-impregnated paper filter for the recovery of evolved ammonia.

Sampling was carried out by means of a sequential sampler able to control the fluid-dynamic conditions of the sampling in real time (Sequair 92A, D.A.S., Palombara Sabina, Italy); the diffusion lines were hosted into a temperature-controlled housing directly operated by the sequential sampler.

Collection efficiency was better than 97% for all the gaseous species (HCl, HNO_3, SO_2, HONO, NH_3). The small interference in the measurement of HNO_3 due to NO_2 and particles collection was taken into account by applying a differential technique: the small nitrate amount collected on the second denuder (back-up NaCl denuder), due to NO_2 and particulate nitrate interference, was subtracted from the amount detected on the first one (main NaCl denuder) where nitric acid is efficiently collected and where the same amount of interference is expected. Similarly, for the accurate determination of SO_2, the sulphate amount collected on the fourth denuder (back-up Na_2CO_3 denuder), due to particulate sulphate interference, was subtracted from the amount detected on the third one (main Na_2CO_3 denuder) where sulphur dioxide is efficiently collected; adsorption of SO_2 on the NaCl denuders was also taken into account (Febo et al. 1989; Perrino et al. 1990). No correction is required for ammonia. The described sampling line is able to quantitatively retain HONO but the determination of this species in urban areas may be biased by the interference of NO_2 in conditions of high SO_2 concentration, as discussed in Febo et al. (1992). For this reason, HONO data obtained by the diffusion lines are not discussed in this paper. The use of NaCl coating prevented the determination of HCl during the first campaign; only results gathered during the summer campaign, when NaF coating was used, are reported. Also in this case, the differential technique was used to take into account the small interference of particles.

At the operative conditions of the study (sampling time of 24 h; sampling flow rate of 15 l/min) the detection limit ranged between 4.5 and 20 ng/m^3 for the gaseous species and between 1.5 and 7.5 ng/m^3 for the particulate species. The overall precision of the measurements was better than 5% for all the compounds. The QA/QC program reported in Perrino et al. (2001b, 2008) was applied to the denuder measurements during the whole study.

Three days of the summer campaign were devoted to an intensive measurement program, with five 3-h determinations during the day (from 6 A.M. to 9 P.M.) and one 9-h determination during the night.

Ozone and sulphur dioxide concentrations were continuously monitored at the Ashdod-Yavne Municipal Association for the Environment by means of a UV Photometric Ozone Analyzer and a UV Fluorescence Sulfur Dioxide Analyzer (Thermo Electron Model 43C and Model 49C, respectively).

Side-by-side to the diffusion line, during 1 week of the summer campaign additional daily samplings were carried out on a single Teflon filter (Gelman, 47 mm, 1 μm pore size) and on a filter pack made of two pre-fired quartz filters (QF20 Schleicher and Schuell). Both systems were preceded by polyethylene cyclones exactly alike the ones placed in the diffusion lines. These samplings were devoted to the determination of the bulk composition of $PM_{2.5}$ (mass closure experiment) measuring, in addition to ions, all particulate components typically present at concentration higher than 1%: Al, Si, Fe, elemental carbon, organic carbon.

Chemical analyses

Denuders, cyclones and filters from the diffusion lines were extracted by means of appropriate water solutions and analysed for their anionic (Cl^-, NO_3^-, $SO_4^=$) and cationic (Na^+, NH_4^+, K^+, $Mg^{++}Ca^{++}$) content by ion chromatography (IC, DX100, Dionex Corporation, CA, USA).

Single Teflon filters were first analysed by energy-dispersion X-ray fluorescence (EPD-XRF, X-Lab 2000, SPECTRO) for determining major elements (Al, Fe, K, Mg, Ca, Ti, S, Si). Then they were water-extracted and analysed by ion chromatography with the same procedure and instrument used for analysing the filters from the diffusion lines.

Quartz filter were analysed for their elemental carbon and organic carbon content (EC/OC) by means of a thermo-optical analyser (OCEC Carbon Aerosol Analyser, Sunset Laboratory, OR, USA). The filter is first heated in He atmosphere up to 870°C (evolution of organic carbon compounds) and then heated again up to 900°C in $He+O_2$ atmosphere (evolution of elemental carbon compounds); carbon compounds are converted from CO_2 to CH_4 and determined by a flame ionisation detector. Pyrolytic conversion is taken into account through laser monitoring.

Results and discussion

Atmospheric mixing

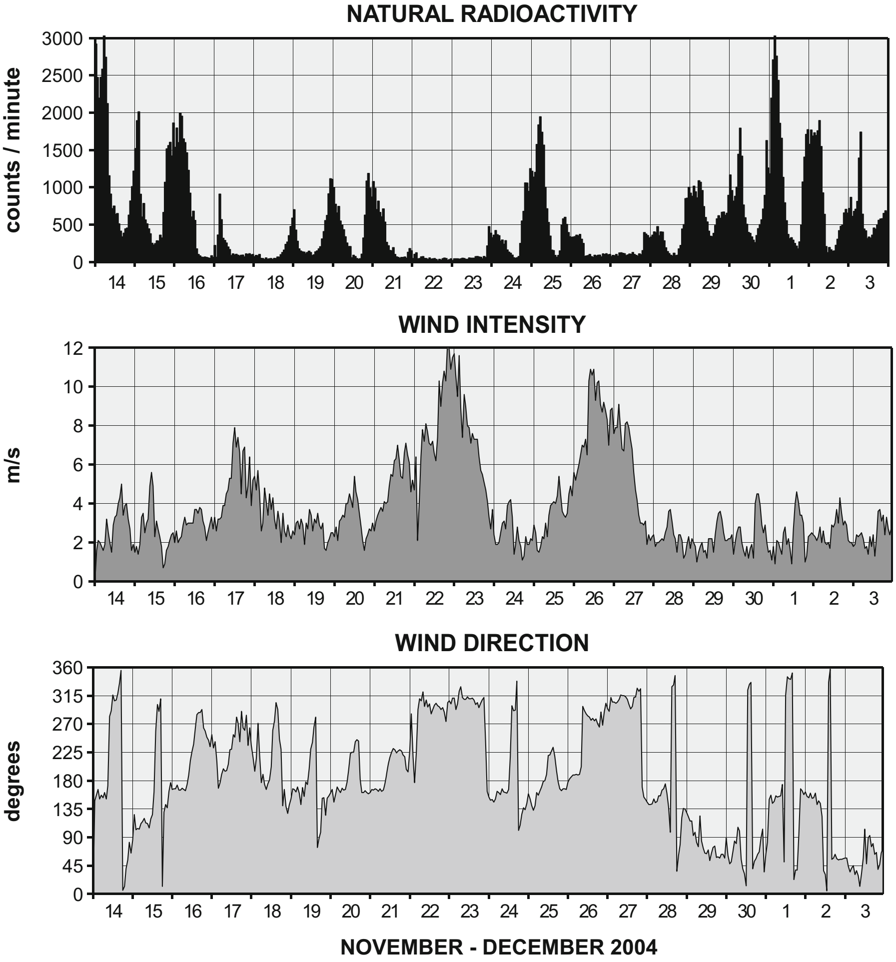
Natural radioactivity data provided an accurate description of the mixing properties of the atmosphere during the two campaigns. During the fall–winter period (Fig. 1) the pattern of natural radioactivity indicated an alternation between atmospheric stability and advection: atmospheric stability can be detected by high night-time radioactivity values and daytime minima of a few hundreds counts per minute, advection can be identified by steady low radioactivity values. Examples of atmospheric stability conditions can be found during the first 3 days and the last 5 days of the campaign: the formation of a nocturnal surface-based inversion layer is detected by the fast increase of natural radioactivity values (accumulation of Radon) while at sunrise, when the heating of the ground surface causes the dissipation of the inversion layer and the turbulent mixing of increasingly high atmospheric layers, the progressive dilution of Radon is immediately shown by the decrease of natural radioactivity values. Examples of advection are during the periods 17th–18th, 22nd–23rd and 26th–27th, November 2004: the emitted Radon is immediately diluted and natural radioactivity values are constantly low. The time patterns of the wind intensity and wind direction (Fig. 1) showed, as expected, a sharp increase of the wind intensity during the periods of constantly low natural radioactivity values. Rain events were recorded on November 17th, 22nd (the main one: 24 mm) and 26th–27th.

During the summer period (Fig. 2) natural radioactivity pattern showed a well-modulated pattern, with high night time values (always occurring after midnight) and low values from early morning to late evening (convective mixing of the atmosphere). The intensity and direction of the wind (Fig. 2) showed a very uniform pattern: southerly winds late at night and north-westerly winds during the day; the intensity was always between 2 and 6 m s^{-1}, with a maximum around 2.00 P.M.

High concentration pollution events are generally associated with high atmospheric stability: in particular, photochemical pollution is triggered by multi-day summer stability periods, while particulate pollution events are favoured by weak daytime atmospheric mixing. It is therefore expected that poor air quality will occur during high-stability periods of the autumn–winter, while the summer intense daytime mixing of the atmosphere should limit accumulation of particulate pollutants.

The time pattern of natural radioactivity constitutes a very reliable key for the interpretation of ozone

Fig. 1 Time pattern of natural radioactivity, wind intensity and wind direction during the fall–winter (2004) campaign



variations. The time pattern of ozone during the fall–winter campaign, reported in Fig. 3, shows the usual alternation between very low values at night and high values during daylight hours, with the exception of the nights of November 16th, 17th, 21st, 22nd and 26th. During these nights, ozone keeps the same value reached during the middle-hours of the day, that is, the background concentration that is typical for this season and latitude (around 40 ppb). These data can be explained by persistence of the atmospheric mixing also during the night (advection), highlighted by the flat pattern of natural radioactivity. In these situations, the transport of background ozone from the upper layers prevails over the chemical losses at the ground (NO titration). During the rest of the period, mechanical mixing occurs during mid-day (convection), while during the night the lower atmospheric layer is uncoupled from the upper layer and the removal reactions cause the decrease of ozone concentration.

Inorganic pollutants

Nitric acid concentrations during the two campaigns are reported in Fig. 4. During the first period, nitric acid concentrations were quite low, with the lowest values recorded during the rainy and windy days of November 2004 (17th–18th, 22nd–23rd, 26th–27th). During the summer, nitric acid concentrations were distinctly higher, as is expected from a photochemical pollutant. The time pattern of HNO_3 during the intensive 3-h campaign, shown in Fig. 5, shows that the highest values were recorded around noon, with a maximum concentration of 4.1 μg/m^3 recorded on July 13th between noon and 3 P.M.. During the night, HNO_3 concentration was very low, around 0.1 μg/m^3.

Fig. 2 Time pattern of natural radioactivity, wind intensity and wind direction during the summer (2005) campaign

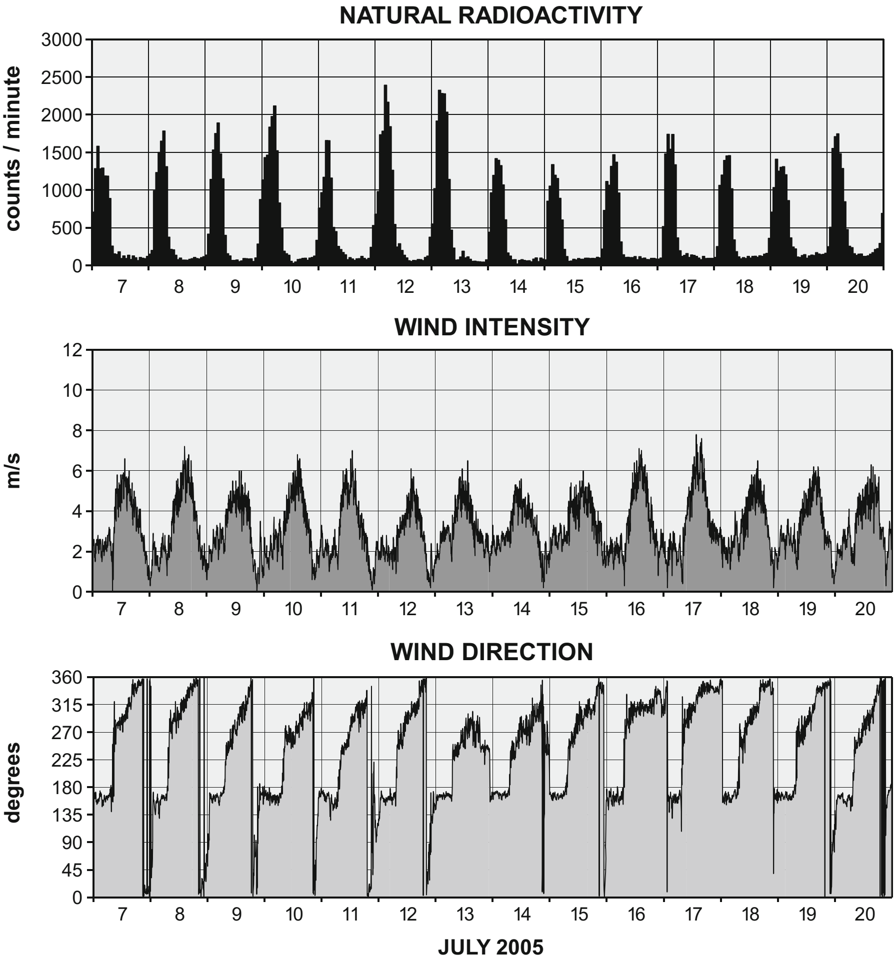
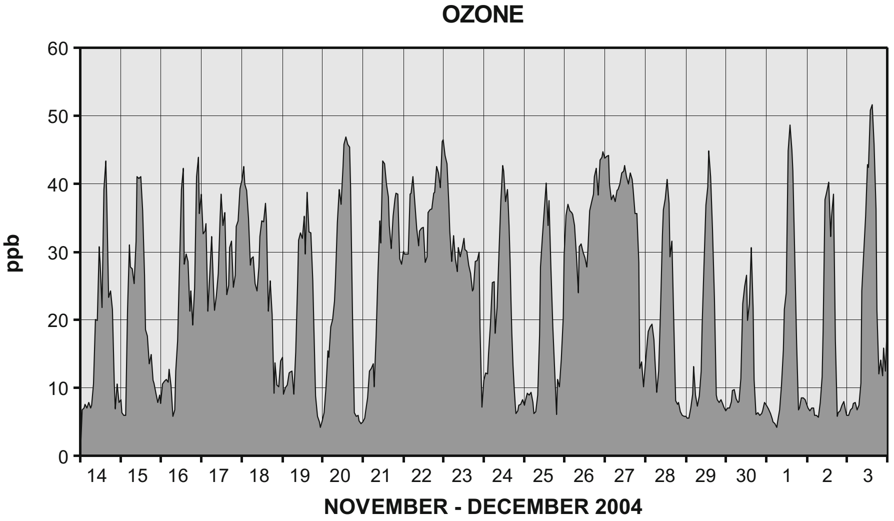


Fig. 3 Time pattern of ozone concentration during the fall–winter (2004) campaign



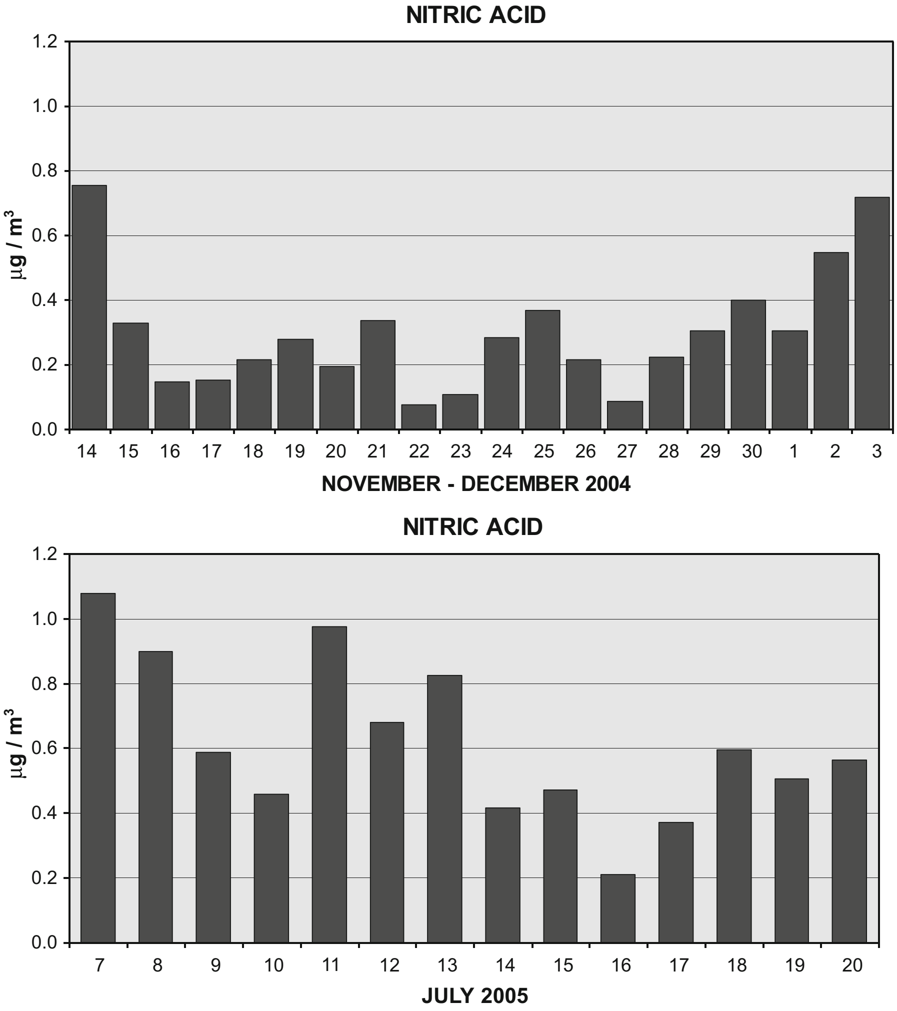


Fig. 4 Time pattern of nitric acid during the fall–winter and the summer (2005) campaign

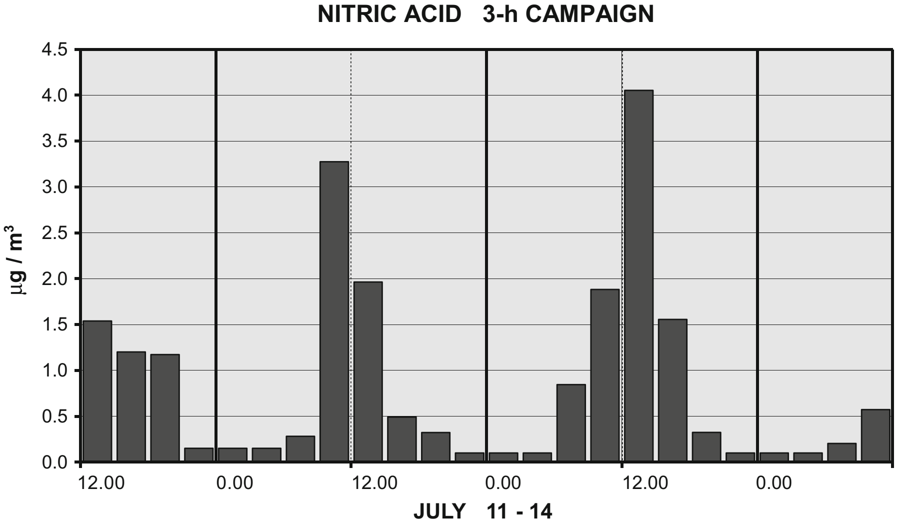


Fig. 5 Time pattern of nitric acid during the intensive 3-h summer (2005) campaign

Table 1 Average concentration, standard deviation and maximum concentration of all the species determined by the diffusion lines during two campaigns

	Fall–winter (µg m^{-3})			Summer (µg m^{-3})		
	Average	SD	Maximum	Average	SD	Maximum
HCl	–	–	–	0.52	0.17	0.80
HNO_3	0.30	0.19	0.76	0.61	0.25	1.08
SO_2	19.56	19.77	85.56	17.97	13.49	51.27
NH_3	11.27	5.22	20.09	12.91	2.53	16.39
Cl^-	3.11	2.52	8.50	2.79	1.50	6.37
NO_3^-	3.11	1.95	8.84	4.02	1.09	6.00
$SO_4^=$	4.71	2.11	8.63	11.08	2.84	16.93
NH_4^+	2.31	1.24	5.20	3.70	1.45	6.95
K^+	0.38	0.31	1.26	0.50	0.27	1.08
Mg^{++}	0.35	0.15	0.74	0.36	0.15	0.76
Ca^{++}	3.99	3.41	11.62	1.54	0.68	2.82

A comparison of the average values, standard deviation and maximum values during the fall–winter and summer period for all the species determined by the diffusion lines is reported in Table 1. Nitric acid and particulate sulphate, both of photochemical origin, were clearly higher during the summer period. For all the other compounds, the average concentrations were comparable but the standard deviations were generally higher during the fall–winter, due to the less homogeneous meteorological conditions recorded during this period of the year (see Fig. 2).

The highest concentrations were recorded for SO_2, which reached 85.5 µg/m^3 on November 17th. SO_2 concentrations determined by the diffusion lines agreed very well with the continuous monitor data. The two data sets, shown, for the first campaign, in Fig. 6, were highly correlated (R^2=0.986). The high SO_2 concentrations are the result of north-westerly winds, afternoon strong convective mixing and emissions from the stacks of the power plant and refinery sited upwind of the sampling location.

The daily and average chemical composition of the ionic fraction in $PM_{2.5}$ and in $PM_{10-2.5}$ is reported as concentration values and mass percent composition in Figs. 7 and 8 for the fall–winter and the summer campaign, respectively.

The fine fraction was always dominated by sulphate, which constituted 63% of the ionic content of $PM_{2.5}$ during the summer campaign and 43% during the fall–winter period. Nitrate was an important constituent of $PM_{2.5}$ only during the fall–winter campaign (15%). The ionic balance shows that both fine sulphate and fine nitrate were mostly associated with ammonium, which was the main alkaline

Fig. 6 Comparison of SO_2 determination by the diffusion lines and the automatic analyser. Fall–winter 2004

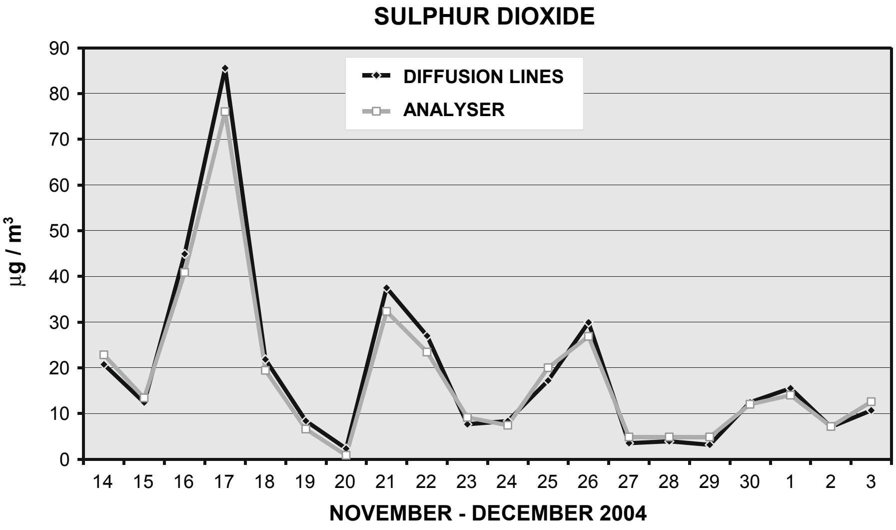
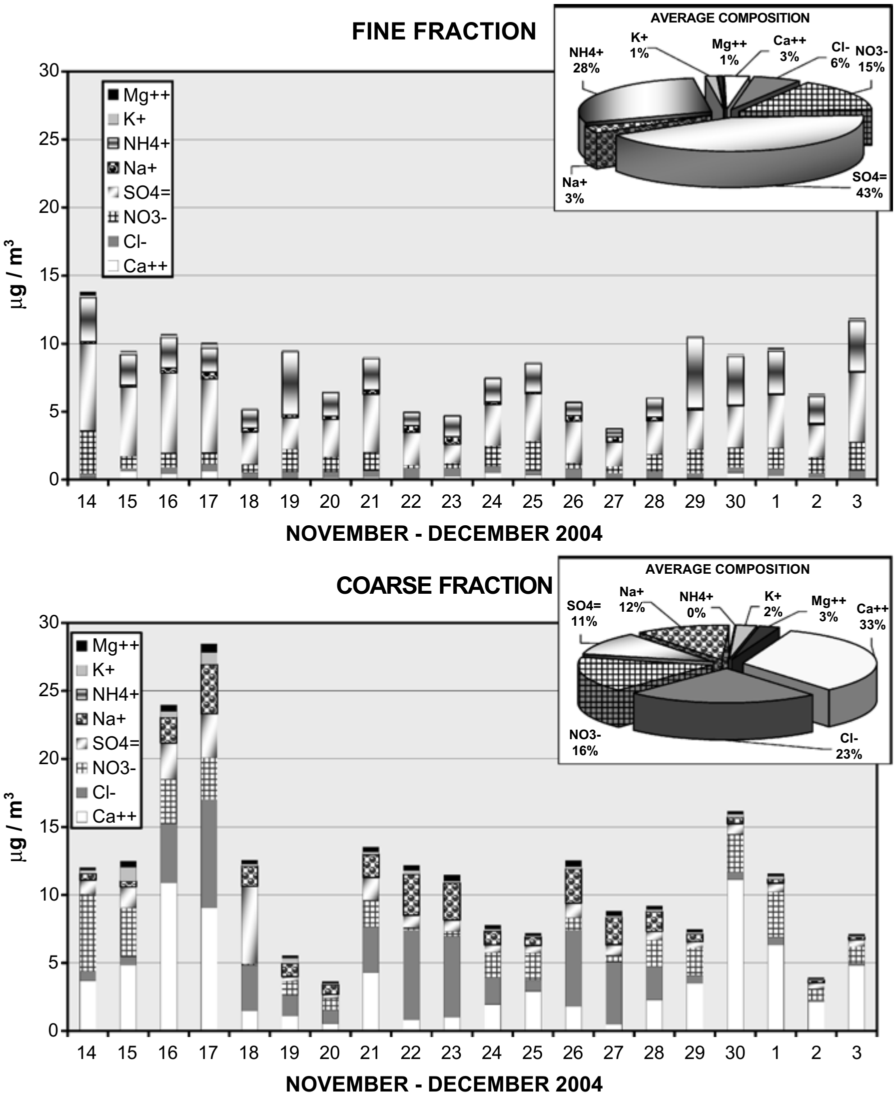


Fig. 7 Daily and average ionic composition of the fine and the coarse fraction during the fall–winter (2004) campaign. *Pie diagrams* are in mass percentage



constituent of the fine fraction. Earlier studies in Israel had shown that during the summer sulphates are transported from the eastern part of Europe (Luria et al. 1996; Wanger et al. 2000)

During both periods particulate chloride, nitrate, magnesium, calcium and, at a less extent, potassium, were mostly distributed in the coarse fraction. Ammonium in the coarse fraction was always below the detection limit.

The widest variations in the concentration and composition of the coarse fraction were recorded during the fall–winter period. In particular, on November 22–23 and 26–27, two sea-spray events caused a relevant increase in the concentration of sodium chloride, which, on November 22nd, constituted 82% of the total amount of inorganic ions. During these episodes, characterised by flat natural radioactivity pattern, wind direction from NW and wind intensity up to 12 m/s (see Fig. 1), a significant increase in magnesium concentration was also recorded and the concentration ratios Cl/Na and Mg/Na were close to the values typical of sea-water.

It is worth noting that most of the fine nitrate (61–98%) was detected on the back-up nylon filter; this indicates that a relevant release of ammonium nitrate from the Teflon filter occurred during the sampling. The evolution of volatile ammonium salts from the Teflon filter and, at a minor extent, the adsorption of gaseous species on the collected particles and on the collection medium are common drawbacks of the

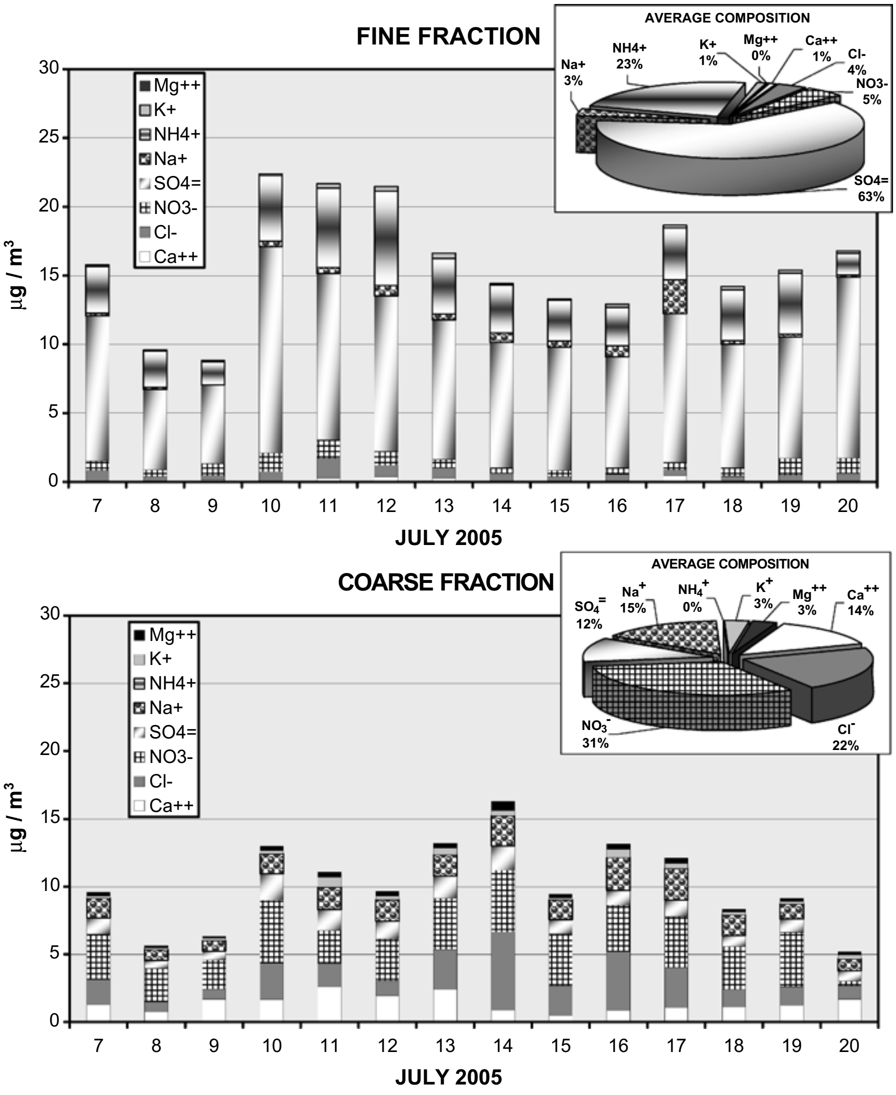
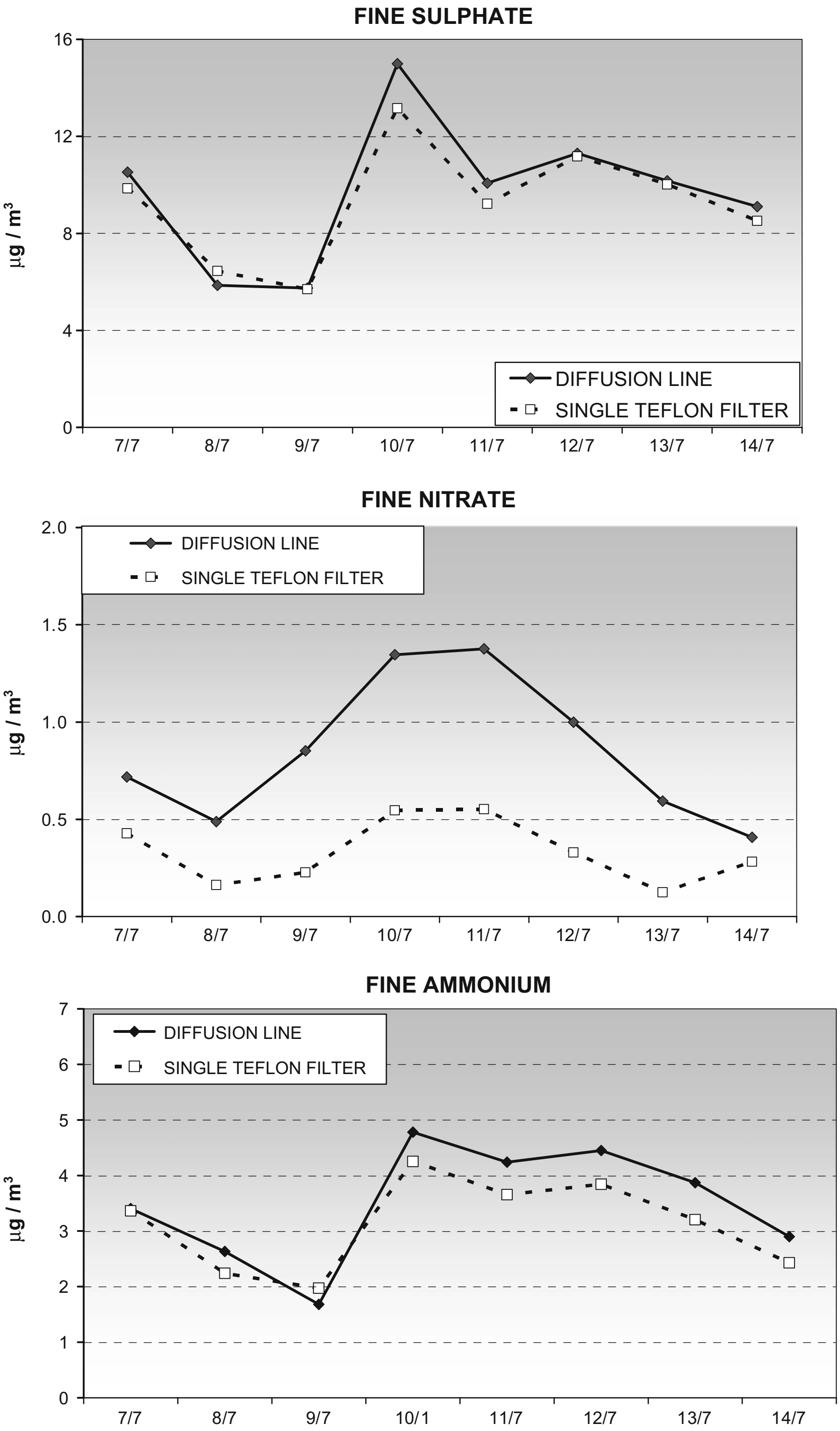


Fig. 8 Daily and average ionic composition of the fine and the coarse fraction during the summer (2005) campaign. *Pie diagrams* are in mass percentage

single-filter sampling technique, which can be successfully avoided by adopting the diffusion line technique. The comparison between the amounts recovered on a single-filter run side-by-side to the diffusion lines during 1 week of the summer campaign and the amounts recovered on the filter pack of the diffusion lines is shown, for sulphate, nitrate and ammonium, in Fig. 9. One can clearly see that the two techniques gave the same sulphate values; instead, up to 60% of the fine nitrate amount was lost when the single-filter technique was used. A small difference is recorded for ammonium. This is consistent with the observation that during the campaign most of the ammonium ion was in the form of ammonium sulphate, while ammonium nitrate constituted only a small fraction (5–10%) of the total NH_4^+. During the winter period, when ammonium sulphate and ammonium nitrate concentration are of the same order of magnitude, the difference in the determination of ammonium by the diffusion lines and the single filter would be more apparent.

This drawback, which concerns also ammonium chloride determinations, constitutes an important limitation not only for the manual single-filter sampling technique but also for all automatic analysers devoted to the measurement of particulate matter concentration, particularly in environments where ammonium nitrate is a main component of atmospheric PM.



FINE SULPHATE

FINE NITRATE

FINE AMMONIUM

Fig. 9 Sulphate, nitrate and ammonium content of $PM_{2.5}$ as determined by the diffusion lines and by the single filter technique

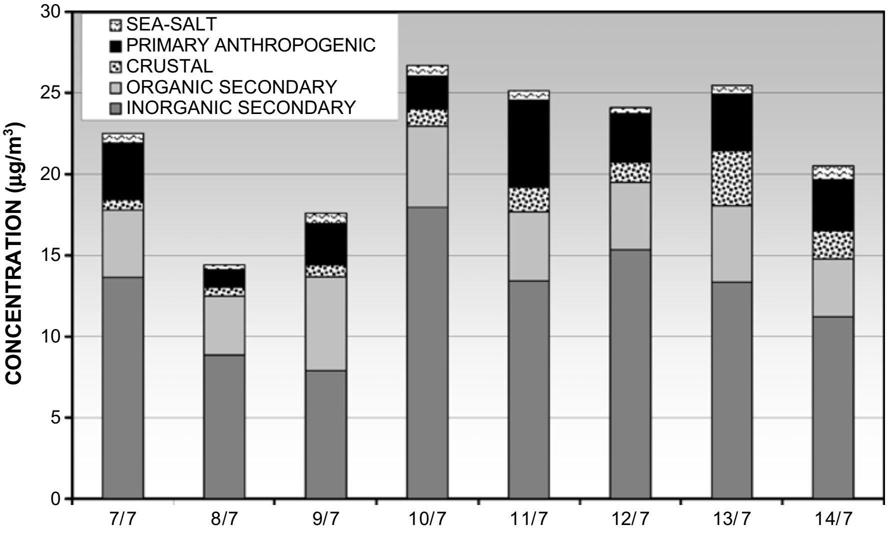


Fig. 10 Daily variation of $PM_{2.5}$ bulk composition, summer 2005

Mass closure

During the first week of the summer campaign the bulk composition of $PM_{2.5}$ was also determined by XRF (elements), IC (ions) and thermo-optical analysis (EC/OC). The total mass concentration was reconstructed considering five main components:

- Crustal matter, calculated as the sum of the main oxides of crustal elements (Al, Si, Fe, Ca, K) and multiplied by 1.12 to take into account the minor constituents (Mg, Na, Ti; Chan et al. 1997);
- Sea-spray, calculated as the sum of sodium and chloride concentration multiplied by 1.176 to take into account the minor constituents (S, Mg, Ca, K);
- Primary anthropogenic compounds, calculated as the sum of elemental carbon concentration and an equal concentration of organic carbon (Viidanoja et al. 2002);
- Inorganic secondary pollutants, calculated as the sum of sulphate, nitrate and ammonium concentration;
- Organic pollutants, calculated by multiplying the remaining amount of organic carbon by a conversion factor that takes into account the non-carbon components of organic molecules: for urban atmospheres this factor can be set to 1.6 (Turpin and Lim 2001).

With these approximations, the difference between the gravimetric determination of PM concentration and the reconstructed mass concentration was, on average, 1 µg/m^3, with a maximum difference of 6 µg/m^3. The scatter plot of the two data series gave a Pearson coefficient R^2=0.668 and a slope of 1.05.

The time pattern of $PM_{2.5}$ bulk composition, reported in Fig. 10, indicates that secondary inorganic matter was by far the main PM component (57% on average), while organic material, mostly of secondary origin, accounted for another 20%; primary anthropogenic compounds was responsible for 14%, and crustal matter and sea-spray for 6% and 3%, respectively. The low contribution of natural particles (crustal matter and sea-spray) is typical of fine particle composition since these components are found mainly in the coarse size range. These first results highlight the relevance of secondary pollution and of medium- and long-range transport as a main source of particulate pollution in Israel.

It is worth noting that the accuracy in the determination of PM mass on a single filter suffers from at least two important drawbacks: the above discussed release of ammonium salts and the possible positive and negative artefacts in the collection of organic carbon compounds. The analysis of the quartz-quartz filter pack devoted to the determination of EC and OC showed, in fact, that on the back-up filter the amount of EC was, as expected, always below the detection limits, while the amount of OC was generally proportional to the amounts detected on the front filter (about one third). This organic carbon amount can be attributed to the adsorption of organic vapours on the filter medium (Kirchstetter et al. 2001; Wittmaack and Keck 2004).

In addition to this positive artefact, which can be easily taken into account by subtracting the OC content of the back-up filter from the content of the main one, a negative artefact due to the release of the more volatile organic species from the collected material has to be considered. Similarly to the release of ammonium salts, particularly during the summer period and in the Mediterranean regions this artefact can be quantitatively relevant and difficult to be predicted. The loss of volatile organics and of ammonium salts can be reduced by keeping the filters at room temperature during the sampling and at a few degrees centigrade until the analyses are carried out.

Conclusions

The joint use of a natural radioactivity monitor for evaluating the dilution properties of the atmosphere, of diffusion lines and IC for the reliable determination of inorganic pollutants in both the gaseous and the particulate phase and of a method based on XRF, IC and thermo-optical analysis for the determination of the main PM components allowed us to obtain a reliable and detailed picture of pollution episodes in the city of Ashdod, Israel. Sea-salt episodes were experienced during the fall-winter period, while photochemical pollutants increased in concentration during the summer campaign. $PM_{2.5}$ composition was dominated by inorganic secondary compounds, of secondary origin, mostly medium-range/long-range transported. The difficulties in obtaining a reliable picture of PM composition by using a simple single-filter technique have been highlighted.

Acknowledgements This study was within the framework of the research project “Modelling system for urban air pollution”, funded by the Italian Ministry of Environment and Territory, 2004–2006. The authors acknowledge the Ashdod-Yavne Municipal Association for the Environment for their invaluable assistance during the study, and particularly Dr. Anat Rozen, general manager, Dr. Hana Shimoni, laboratory director, and Dr. Karolin Soudri, air monitoring coordinator.

The authors want to thank T. Sargolini, S. Dalla Torre and E. Rantica, who were precious in the preparation of the sampling campaigns.

References

Allegrini, I., Febo, A., Perrino, C., & Masia, P. (1994). Measurement of atmospheric nitric acid in gas phase and nitrate in particulate matter by means of annular denuders. *International Journal of Environmental Analytical Chemistry*, *54*, 183–201.

Astolfi, M. L., Canepari, S., Catrambone, M., Perrino, C., & Pietrodangelo, A. (2006). Improved characterisation of inorganic components in airborne particulate matter. *Environmental Chemistry Letters*, *3*, 186–191.

Chan, Y. C., Simpson, R. W., McTainsh, G. H., & Vowles, P. D. (1997). Characterisation of chemical species in PM2.5 and PM10 aerosols in Brisbane, Australia. *Atmospheric Environment*, *31*, 3773–3785.

Febo, A., De Santis, F., Perrino, C., & Giusto, M. (1989). Evaluation of laboratory and field performance of denuder tubes: A theoretical approach. *Atmospheric Environment*, *23*, 1517–1530.

Febo, A., Perrino, C., & Cortiello, M. (1992). A denuders technique for the measurement of nitrous acid in urban environments. *Atmospheric Environment*, *27A*, 1721–1728.

Graham, B., Falkovich, A. H., Rudich, Y., Maenhaut, W., Guyon, P., & Andreae, M. O. (2004). Local and regional contributions to the atmospheric aerosol over Tel Aviv, Israel: A case study using elemental, ionic and organic tracers. *Atmospheric Environment*, *38*, 1593–1604.

Kirchstetter, T. W., Corrigan, C. E., & Novakov, T. (2001). Laboratory and field investigation of the adsorption of gaseous organic compounds onto quartz filters. *Atmospheric Environment*, *35*, 1663–1671.

Luria, M., Peleg, M., Sharf, G., TovAlper, D. S., Spitz, N., BenAmi, Y., et al. (1996). Atmospheric sulfur over the east Mediterranean region. *Journal of Geophysical Research Atmospheres*, *101*(D20), 25917–25930.

Mamane, Y., Perrino, C., Yossaf, O., & Catrambone, M. (2008). Source characterization of fine and coarse particles in the East Mediterranean coast. *Atmospheric Environment*, (in press).

Perrino, C., De Santis, F., & Febo, A. (1990). Criteria for the choice of a denuder sampling technique devoted to the measurement of atmospheric nitric and nitrous acids. *Atmospheric Environment*, *24A*, 617–626.

Perrino, C., Febo, A., & Allegrini, I. (2000). A new beta gauge monitor for the measurement of PM10 air concentration. In J. E. Hanssen, R. Ballaman, R. Gehrig (Eds.), Proceedings of the EMEP-WMO workshop on fine particles—emissions, modelling and measurements, EMEP/CCC Report 9/2000 (pp. 147–152).

Perrino, C., Pietrodangelo, A., & Febo, A. (2001a). An atmospheric stability index based on radon progeny measurements for the evaluation of primary urban pollution. *Atmospheric Environment*, *35*, 5235–5244.

Perrino, C., Ramirez, D., & Allegrini, I. (2001b). Monitoring of acidic air pollutants by means of diffusion lines: Development of a specific quality control procedure. *Atmospheric Environment*, *35*, 331–341.

Perrino, C., Canepari, S., Cardarelli, E., Catrambone, M., & Sargolini, T. (2007). Inorganic constituents of urban air pollution in the Lazio region (Central Italy). *Environmental Monitoring and Assessment*, *128*, 133–151.

Perrino, C., Catrambone, M., & Pietrodangelo, A. (2008). Influence of atmospheric stability on the mass concentration and chemical composition of atmospheric particles: A case study in Rome, Italy. *Environment International,* DOI 10.1016/j.envint.2007.12.006.

Porstendorfer, J., Butterweck, G., & Reineking, A. (1991). Diurnal variation of the concentrations of radon and its short-lived daughters in the atmosphere near the ground. *Atmospheric Environment*, *25*, 709–713.

Sesana, L., Caprioli, E., & Marcazzan, G. M. (2003). Long period study of outdoor radon concentration in Milan and correlation between its temporal variations and dispersion properties of atmosphere. *Journal of Environmental Radioactivity*, *65*, 147–160.

Shery, S. D., Gaeddert, D. H., & Wilkening, M. H. (1984). Factors affecting exhalation of radon from a gravelly sandy loam. *Journal of Geophysical Research*, *89*(D5), 7299–7309.

Shweikani, R., Giadutt, T. G., & Durrani, S. A. (1995). The effect of soil parameters on radon concentration values in the environment. *Radiation Measurements*, *25*, 581–584.

Turpin, B. J., & Lim, H. (2001). Species contribution to PM2.5 mass concentration: Revisiting common assumptions for estimating organic mass. *Aerosol Science and Technology*, *35*, 602–610.

Vecchi, R., Marcazzan, G., & Valli, G. (2007). A study on nighttime–daytime PM10 concentration and elemental composition in relation to atmospheric dispersion in the urban area of Milan (Italy). *Atmospheric Environment*, *41*, 2136–2144.

Viidanoja, J., Sillanpaa, M., Laakia, J., Kerminen, V. M., Hillamo, R., Aarnio, P., et al. (2002). Organic and black carbon in PM2.5 and PM10: 1 year of data from an urban site in Helsinki, Finland. *Atmospheric Environment*, *36*, 3183–3193.

Wanger, A., Peleg, M., Sharf, G., Mahrer, Y., Dayan, U., Kallos, G., et al. (2000). Some observational and modeling evidence of long-range transport of air pollutants from Europe toward the Israeli coast. *Journal of Geophysical Research—Atmospheres*, *105*(D6), 7177–7186.

Wittmaack, K., & Keck, L. (2004). Thermodesorption of aerosol matter on multiple filters of different materials for a more detailed evaluation of sampling artifacts. *Atmospheric Environment*, *38*, 5205–5215.