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ORIGINAL PAPER

SO_2 in Beirut: air quality implication and effects of local emissions and long-range transport

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Abstract While sulfur dioxide (SO_2) emissions have been dramatically restricted in the past few decades, some cities in developing countries still encounter high pollution levels. This makes it essential to implement an air quality monitoring network in these sensitive regions. Results from a program of measuring ground-level concentration of SO_2 (from December 2004 till July 2006) at 22 curbside and background sites within the city of Beirut (Lebanon) are presented for the first time. Four-week sampling period measurements were made over 20 periods for all sites by passive sampling. Low SO_2 concentrations were observed (3.1 parts per billion on average for the whole period). This value is among the lowest observed in urban areas worldwide. Thus, Beirut is not polluted by SO_2 on an annual basis. Highest concentrations were measured in winter time, resulting from low height of the boundary layer and higher emissions of SO_2 (e.g., heating). Cluster analysis revealed two different SO_2 variation patterns over the city (high- and low-level patterns), highlighting the effects of local sources location and wind direction variability on SO_2 distribution. Analysis of seasonal variations pointed out a springtime SO_2 maximum in 2005. Beside local sources, long-range transport can account for an important source of SO_2 in Beirut, explaining around 50% of SO_2 levels within the city.

Keywords Passive sampler · Air quality · Beirut · Long-range transport · Sulfur dioxide

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Introduction

Effects of sulfur dioxide (SO_2) on ecosystems and human heath are now well recognized. On one hand, SO_2 oxidation by OH radicals in the gas-phase and by O_3 and H_2O_2 in the aqueous phase contributes to acid deposition and to sulfate formation, which scatter sunlight resulting in cooling of the troposphere (Finlayson-Pitts and Pitts 2000; USEPA 2008). On the other hand, long-term exposure to high concentrations of SO_2 can contribute to respiratory illness, particularly for children and the elderly, and aggravate existing heart and lung diseases (USEPA 2008). The World Health Organization (WHO) indicates that peak concentrations over short averaging periods, of the order of 10 min, can reach 350–700 parts per billion (ppb) in some circumstances, such as the grounding of plumes from major point sources or during peak dispersion conditions in urban areas with multiple sources (WHO 2000). The health effects observed include indices of ventilatory capacity increases in specific airway resistance and symptoms such as wheezing or shortness of

breath. Such effects are enhanced by exercise, which increases the volume of air inspired, thereby allowing sulfur dioxide to penetrate further into the respiratory tract. Whereas, averaged exposure over a 24-h period involving the mixed industrial and vehicular sources have demonstrated effects on mortality (total, cardiovascular, and respiratory) and hospital emergency admissions for total respiratory causes and chronic obstructive pulmonary disease at lower levels of exposure (WHO 2000). In addition to that, sulfur dioxide reacts with other chemicals in the atmosphere to form sulfate particles. When these are breathed, they gather in the lungs and are associated with increased respiratory symptoms and disease, difficulty in breathing, and premature death (USEPA 2008). As a consequence, many industrialized countries have stringently regulated SO_2 anthropogenic emissions to protect human health and ecosystems (Dutkiewicz et al. 2000). SO_2 is emitted into the atmosphere by natural sources (volcanoes, plant decomposition) and by anthropogenic sources. The major source of SO_2 is the combustion of fossil fuels containing sulfur, in particular from power stations burning coal and heavy fuel oil. Reducing SO_2 emissions has consisted in switching fuels by low sulfur content fuels (e.g., natural gas, petrol, and diesel fuels), as well as in replacing fossil fuels by electricity. In the past, the main source of SO_2 was the burning of coal in homes, factories, offices, schools, and other buildings. Today, in most Western cities, buildings are heated by natural gas and electricity, the latter being generated in large power stations typically situated in rural areas rather than close to towns. However, coal and heating oil remain important sources of space and water heating in a few cities in Western Europe where there are no supplies of natural gas (Holgate et al. 1999). Industrial combustion, especially for the generation of electricity, is the dominant source in all areas. Although road transport is a minor source of SO_2 at the national level, it can be important in some urban areas, especially alongside busy roads (Holgate et al. 1999). However, as a result of controls on the permitted sulfur levels in automotive fuels introduced in the mid-1990s both in the USA and the EU, it is likely that these elevated concentrations at the roadside will decrease. In the EU, further limits on the sulfur content of diesel and petrol were agreed on in the year 2000. These restrictions were not primarily introduced to reduce emissions of SO_2 from road transport but to facilitate the reduction in emissions of other pollutants.

While SO_2 maintains a downward trend throughout the world, great problems are still encountered in developing countries. The guideline from WHO (2000) recommends daily levels below 17.5 ppb as an annual mean. In some Asian and Central America cities, these levels are overpassed (Baldasano et al. 2003). Thus, it is essential to maintain SO_2 air quality monitoring in these regions and to implement SO_2 monitoring programs in potentially sensitive regions lacking in data. The Middle East is one critical region especially when looking at the few available data (e.g., Teheran, Iran) that indicate high pollution levels of SO_2. In Lebanon, two preliminary studies were conducted to determine SO_2 concentrations. The first one consisted in studying the diffusion and dispersion of pollutants of a smoke stack emission of a cement factory in North Lebanon. The aim was to assess the actual and potential health hazards to which the local population is exposed to Karam and Tabbara (2004). Results show concentrations up to 2,000 ppb as 3-h average depending on location and period (Karam and Tabbara 2004). The second study examined the temporal variation of SO_2 near a busy road in Beirut, showing generally hourly averaged concentrations less than 11 ppb (Saliba et al. 2006). The maximum permissible limit for SO_2 has been fixed at 30 ppb (MOE 1996). This threshold underscored the need to implement a more comprehensive and continuous air quality SO_2 monitoring in Beirut, the Lebanese capital. From December 2004 to June 2006, a passive sampling network of SO_2 covering the whole city was set up, in cooperation with the municipality of Beirut. Based on these new collected data, the purpose of this paper is (1) to assess the spatial and temporal distribution of SO_2 in Beirut, (2) to assess the importance of SO_2 on Beirut air quality, and (3) to characterize factors controlling SO_2 distribution. This is the first study that gathers temporal and spatial characterization of SO_2 in the country since a similar monitoring network has never been established in Lebanon.

Experimental section

SO_2 passive sampling

Several techniques exist for measuring SO_2, including ultraviolet fluorescence, differential optical absorption spectroscopy, wet chemical (pararosaniline) technique, gas chromatography with flame photometric or mass spectrometric detection, chemiluminescence method using reaction with $KMnO_4$, and filter method with either the $KMnO_4$ chemiluminescence or ion chromatographic detection (Finlayson-Pitts and Pitts 2000). Their advantages are measurement frequency and low detection limit. However, for long-term monitoring,

pollutant concentrations (including SO_2) are measured with fluorescence analyzers or passive samplers (Bush et al. 2001; Carmichael et al. 1995). Being low-cost and flexible, the passive samplers are widely used to assess SO_2 temporal and spatial distributions.

Their main disadvantage is that the measurement gives mean concentration over several days. The first application of passive samplers was the monitoring of human exposure at workplace atmospheres (Palmes et al. 1976). The average atmospheric concentration is calculated by Fick's first law, using the exposure period (Palmes and Lindenboom 1979). Several passive samplers have been developed since Palmes and Gunnison published the principles of passive sampling (Palmes and Gunnison 1973). Passive monitoring for SO_2 goes back to 1945 in the UK, where lead peroxide candles were used (Cox 2003). This method cannot be used for short-term SO_2 monitoring, such as several hours. The method was improved by using an inverted Petri dish that held a glass fiber filter covered with a lead peroxide layer (Huey 1968). Other absorbents were used for the passive sampling of SO_2 like tetrachloromercurate solution, potassium carbonate. Examples of absorbents are summarized in Table 1.

Different studies were carried out to evaluate the influence of environmental factors on SO_2 sampling. Cruz et al. (2005) and Krochmal and Kalina (1997) conducted several experiments with the purpose of studying face velocity, temperature dependance, relative humidity, exposure time, and concentration of interferent pollutants. Passam specified a working range for each influencing factor within which no influence is observed. Sampling time should vary between 2 and 4 weeks, temperature range varies between 10 and 30°C and humidity varies between 20% and 80%. Influence of wind speed is less than 10% when wind velocity is below 4.5 m s^{-1} (Passam 2007).

For this study, measurements were carried out with Passam passive samplers (provided by Passam ag). The passive samplers are composed of a polypropylene housing with an opening of 20 mm diameter. To reduce wind disturbance, a glass fibre membrane is attached, supported by a wire net. The Passam passive sampler for measuring SO_2 is based on the principle that SO_2 diffuses across the diffusive body toward a mix of sodium carbonate and glycerol, where it is trapped.

As passive samplers were at first designed to assess the quality of indoor air, it is advisable to protect them with a rain/wind shelter when sampling outdoors. Even in the absence of rain, the shelter is required to minimize dust contamination and the effects of advection on the diffusive samplers (Roadman et al. 2003). Here, shelters supplied by Fondazione Salvatore Maugeri were employed. The shelter was fixed by means of a cable tie. Special care was taken at all times when handling the passive samplers. Except during sampling, all samplers were kept in an airtight bag. After exposure, the sampler's cartridges were transferred to a plastic tube until preparation for analysis. Analysis was performed by Passam ag. by ion chromatography. The expanded uncertainty is 23.4% at concentration levels of 7.5–15 ppb.

Area of study

Beirut, a 32-km^2 city, is located at 33°52′10″N 35°30′40″E, on the eastern coast of the Mediterranean Sea. The north and west sides of the city are opened to the sea while the east side is surrounded by Mount Lebanon. The city population density is about 20,167 inhabitants per square kilometer. Beirut harbor is located on the north side of the city. An international coach station is located right next to the harbor with buses operated on diesel fuel. The main sources of pollution are vehicle traffic, the industrial activity being little developed in the surrounding city. The number of registered vehicles in Lebanon is greater than one million, with an average age for the vehicle fleet of more than 10 years (El-Zein et al. 2007). Fuel is imported, with little effective control by the government over its quality (El-Zein et al. 2007). In 15 July 2002, a law had been in effect finally banning diesel fuel for light- and medium-duty engines. The main thermal power station of the country is located 13 km northeast of the city

Table 1 Examples of sulfur dioxide passives samplers

Absorbent	Sampler type	Reference
Lead peroxide	Badge	Huey (1968)
Sodium tetracholomercurate	Permeation device	Reiszner and West (1973)
Potassium carbonate	Badge or candle	Orr et al. (1987), Syrek et al. (1997)
Sodium hydroxide	Badge or tube	Ayers et al. (1998), Carmichael et al. (1995), Ferm and Svanberg (1997)
Triethanolamine	Badge or tube	Krochmal and Kalina (1997), Radiello (2006)
Sodium carbonate and glycerol	Badge	Passam (2007)

(Fig. 1), while the airport is located 7 km southwest of the city.

Periods and sampling sites

The implementation of the sampling sites relied on the criteria of the *Agence De l'Environnement et de la Matrise de l'Energie* (2002). Since the objective of this program was to monitor the population's average exposure to the phenomena of atmospheric pollution known as "background" in urban centers and the maximum level of exposure to which the population located near a road network is likely to be exposed to, two types of sampling stations were selected: traffic sites and urban background sites. Two traffic sampling sites (S1 and S2) were selected. The site should be under the direct influence of the linear source without any obstacles. It is recommended to avoid obstacles such as hedgerows or walls that might disturb measurements. This type of site should be located either near a roadway with an annual daily traffic average (ADTA) in both directions greater than 10,000 vehicles per day or a canyon-type roadway with a risk of pollution accumulation. The sampler must be located at most 5 m from the road side. The recommended height is between 1.5 and 3 m above the ground (ADEME 2002; Vardoulakis et al. 2003). In this study, S1 is implemented at 3 m above the ground, but S2 is at 5.5 m above the ground for logistic reasons. For the background sites, 20 locations (S3–S22) were selected. Minimal distance of the site to the nearest road depends on the ADTA and varies from 10 m for ADTA less than 1,000 vehicles/day to over 200 m for ADTA greater than 70,000 vehicles/day. Samplers were located at about 3 m above the ground for these sites. Figure 1 shows the location of the experimental sites within Beirut.

The measurement campaign was carried out from December 2004 till June 2006 over the 22 sites. Four-week sampling periods were adopted for both types of site. The results presented in this paper were thus obtained from 20 periods of measurements, resulting in 440 determinations of SO_2 concentrations.

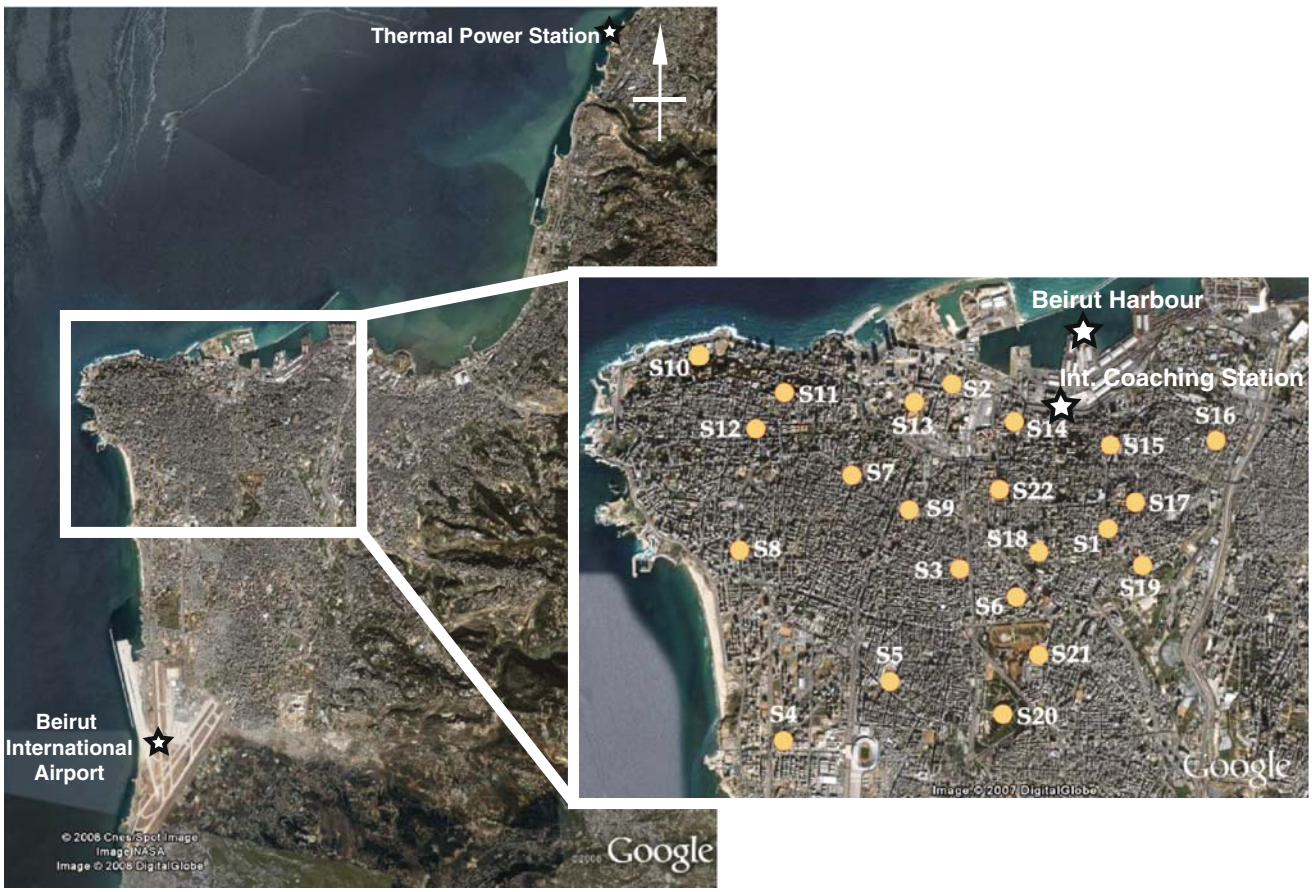

Fig. 1 Map of the sampling sites in Beirut. *S1* and *S2* are curbside sites. *S3* to *S22* are background sites

Results

Air quality and SO_2 in Beirut

SO_2 pollution levels are known to vary under diverse environmental settings. We gathered and pooled data sets of SO_2 measured at different station types from different countries (including this study) in order to assess the pollution level in Beirut compared to other cities (Table 2). Comparison of the different data sets indicates that concentrations measured from similar environmental types are fairly compatible within the

Table 2 Sulfur dioxide concentrations collected from different studies

Region	Description	Mean concentration (ppb)	Periods	References
Korea (Major cities)	Urban	8.15	1998–2003	Nguyen and Kim (2006)
Lithuania (Vilnius)	Urban	4.98	1995–1996	Perkauskas and Mikelinskiene (1998)
China (Chongqing Guiyang and Chengdu)	Urban	114	1985–1989	Lei et al. (1997)
Beirut	Urban	3.1	December 2004–July 2006	This study
Indonesia			1996	Gillett et al. (2000)
(Jakarta)	Urban	4.4		
(Bukit Koto Tabang)	Rural	1.3		
India (Rampur)	Rural	1.39	Winter and summer	Gupta et al. (2003)
Turkey (Antalya)	East Mediterranean coast	7.63	August, September, October 1995 February, March and April 1996	Erduran and Tuncel (2001)
Beirut (Lebanon)	Traffic	4.9	Summer 2004	Saliba et al. (2006)
		9.4	Winter 2004–2005	
North Lebanon	Industrial urban area	Reached 1800 (24-h average)	2003	Karam and Tabbara (2004)
Hong Kong	Urban sites (different floor height beginning at 6 m) Comparison Indoor/Outdoor	2.37 Indoor vs. 3.05 Outdoor	Summer (May to June) 1997	Chao (2001)
Rome (Italy)	Urban	5.6	1991	Avino and Manigrasso (2008)
		1.5	2000	
Pamplona (Spain)	Urban	2.6	2002	Zabalza et al. (2007)
		3.4	2003	
Alsasua (Spain)	Urban	1.5	2002	Zabalza et al. (2007)
		1.9	2003	
Ile-de-France (France)	Urban	2.3	2005	AIRPARIF (2006)
Southend-on-Sea (UK)	Urban	2.3	2005	UK Air Quality Archive (2008)
Thurrock (UK)	Urban	1.8	2005	UK Air Quality Archive (2008)
Burbank (California, USA)	Urban	2	2005	USEPA (2008)
Lompoc (California, USA)	Urban	1	2005	USEPA (2008)
Rubidoux (California, USA)	Suburban	4	2005	USEPA (2008)
New York (New York, USA)	Urban	9	2005	USEPA (2008)
Buffalo (New York, USA)	Urban	4	2005	USEPA (2008)
Texas City (Texas, USA)	Urban	4	2005	USEPA (2008)
Houston (Texas, USA)	Suburban	2	2005	USEPA (2008)
Mexico City (Mexico)	Urban	17.7	1990–2001[a]	Gurjar et al. (2008)
Sao Paolo (Brazil)	Urban	6.8	1990–2001[a]	Gurjar et al. (2008)
Buenos Aires (Argentina)	Urban	7.5	1990–2001[a]	Gurjar et al. (2008)
Dhaka (Bangladesh)	Urban	45	1990–2001[a]	Gurjar et al. (2008)

[a]Out of 54 observations, sample sizes for different years were as follows: 1990 ($n = 1$), 1992–1994 ($n = 3$), 1995 ($n = 7$), 1998–1999 ($n = 13$), 2000–2001 ($n = 30$) (Gurjar et al. 2008)

relatively narrow range. Urban data vary from 1 ppb (Lompoc, USA) to 45 ppb (Dhaka, Bangladesh). Dhaka is the most polluted megacity with SO_2 (Gurjar et al. 2008). The average concentration in Beirut for the whole period of measurement is 3.1 ppb. The annual average concentration for the 20 background sites in Beirut for 2005 is also 3.1 ppb, while the level recommended by the WHO is 17.5 ppb. This result indicates that the city does not suffer from SO_2 pollution and, thus, the population health is not under severe SO_2 threat.

In developed countries, data referring to last two decades have clearly shown a steadily decreasing trend for some important primary pollutants, especially SO_2 (e.g., Rome, Paris…). However, there is an exceptional case in that the SO_2 data from urban areas of China record exceedingly large values. The SO_2 values for the three urban sites in Southwest China (Chongqing, Guiyang, and Chengdu) ranged from 32 to 159 ppb, with a mean of 114 ppb (Lei et al. 1997). Measurements conducted by Karam and Tabbara in North Lebanon (2004), in an industrialized area with cement factories, showed concentrations reaching 10 times the maximum observed by Lei et al. in China.

Except for such unusual data sets, most studied results showed that SO_2 concentration levels in urban areas do not exceed a 10-ppb range. In fact, the lowest SO_2 value in urban areas was seen from Lompoc (USA) (Table 2).

Traffic site results from Saliba et al. (2006) are in concordance with the results obtained by S1 (7.15 ppb as a mean value during the whole measurement period), while, surprisingly, S2 showed a lower concentration (4.5 ppb as a mean value during the whole measurement period). The case of the S2 site will be detailed in the section "SO_2 spatial behavior." For the comparison between the relatively clean environments (rural), the SO_2 data from different studies can be compared against each other with concentrations less than 2 ppb.

The overall results of this comparison clearly show that the occurrences of the highest SO_2 values tend to center mainly in the urbanized areas affected by the industrial activities, while rural or suburban areas tend to record the fairly low SO_2 values. The observed background concentrations in Beirut are low and do not seriously affect human health. Furthermore, since no major SO_2 sources are present in the indoor environment in the developed countries, the indoor SO_2 level is usually much lower than the outdoor level (Gupta et al. 2003).

SO_2 temporal variation

The examination of seasonal variation patterns can provide valuable information on factors controlling SO_2 variability. The temporal variation (period mean and standard deviation) for all of the 20 background sites are presented in Fig. 2. SO_2 concentrations during the entire period of observation ranged from a minimum value of 1.6 ppb in October 2005 to a maximum value of 7.5 ppb in April 2005. The standard deviation of these measurements ranges from 0.82 to 3.60 ppb. As expected, SO_2 shows seasonal variations. The period of measurement between 2 December 2004 and 15 June 2006 was divided into groups corresponding to the four seasons: winter, spring, summer, and autumn. The average concentrations of SO_2 from all 20 background sites were found to be 3.31 ppb (winter 2005), 4.32 ppb (spring 2005), 2.12 ppb (summer 2005), 2.61 ppb (autumn 2005), 2.85 ppb (winter 2006), and 2.72 ppb (spring 2006). The lowest value is observed during the summer period, followed by fall and spring months. Except for spring 2005, the higher values are observed for winter periods. This can be attributed to meteorological conditions initiating the formation of a lower inversion layer during winter than in summer in addition to a combination of factors such as the slow rate of SO_2 oxidation during winter, diesel-operating vehicles, and the usage of central-heating burners. The SO_2 emission

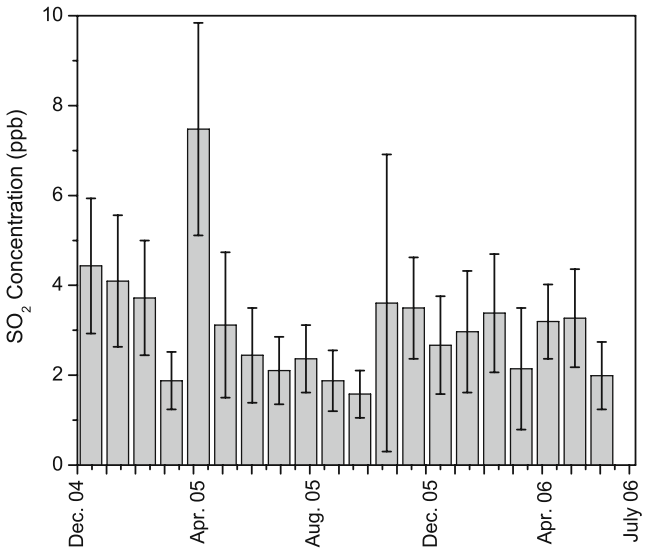

Fig. 2 Temporal variation of mean SO_2 concentration for the 20 periods of observation at the background sites from 2 December 2004 to 30 June 2006 in Beirut. *Vertical bars*: standard deviation for each period

can be enhanced by such source activities as industrial and vehicular emissions (Streets et al. 1997).

The spring 2005 value is higher than all other seasons since the fifth period of measurements was taken into account. This period (24 March 2005 until 21 April 2005) seems to have an atypical trend with very high values observed over the whole city with a mean concentration greater than 7 ppb. The analysis of this episode will be detailed in the section "The springtime SO_2 maximum."

SO_2 spatial behavior

Cluster analysis (CA) is one of a number of multivariate techniques that can be used to classify variables into homogeneous groups and identify their features in order to enhance understanding the studied phenomena. The objective of CA is to uncover the complex nature of multivariate relationships (by searching for natural groupings or types) among the data under investigation, so as to foster hypothesis development about the phenomena being studied. This multivariate method has come to be recognized as an effective statistical tool to deal with tasks as grouping time series, climatological regions, weather events, etc. (Fovell and Fovell 1993; Gramsch et al. 2006; Pires et al. 2008a, b). For a detailed description, see Wilks (2006).

Practically, according to the observed concentrations, the spatial distribution of SO_2 concentration levels varies within the city. CA was used to identify sites of similar behavior towards SO_2 in the city. The CA was carried out by using XLSTAT 2007 software from AddinSoft. It describes the nearness between objects (i.e., site concentrations). A dissimilarity matrix was built using the autoscaled data. The elements of this matrix are the squared Euclidean distances of one object from the rest. To obtain clusters, the Ward method was used (Ward 1963). In each step, this agglomerative method considers the heterogeneity or deviance (the sum of the square of the distance of an object from the centroid of the cluster) of every possible cluster that can be created by linking two existing clusters. Figure 3 shows the dendrogram resulting from the application of CA to the SO_2 concentrations. The results show that the 22 monitoring sites of the network can be grouped into three clusters: class 1 (C1), class 2 (C2), and class 3 (C3). The dotted line represents the truncation, leading to three interhomogeneous classes (C1, C2, and C3). C2 is more homogeneous than C3 since the higher homogeneity is indicated by the lower value of within-class variance (121 for C2 and 192 for C3). Class 1 contains only the S1 site. This can be explained by taking into account that S1 is a curbside site under direct influence of direct emissions resulting in higher concentration of SO_2. An interesting case is the one of

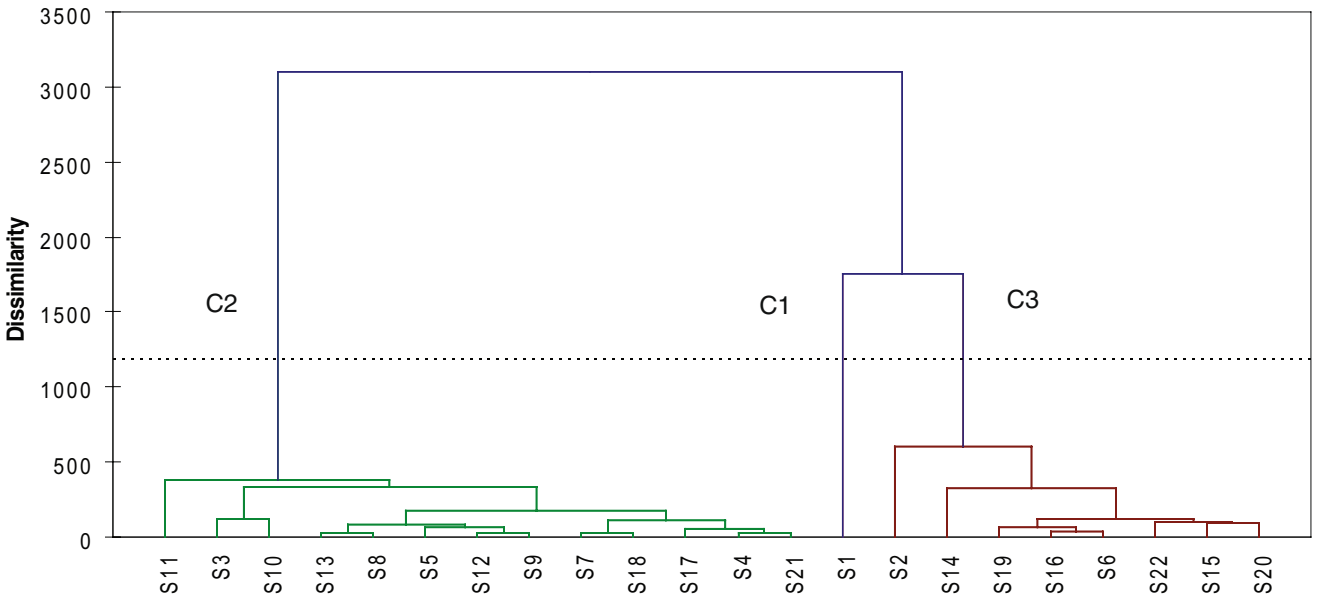

Fig. 3 Dendrogram presenting the results of the AHC analysis for the data classified by site (Si) with the different sites within each class. The *dotted line* represents the truncation level

S2, the second curbside site, which is classified within class C3. This classification is due to the different height of the samplers on this site (5.5 m from the ground for S2 compared to 3 m for S1). Since S2 is higher in height, SO_2 is more dispersed at 5.5 m than it is at 3 m of height. Consequently, the measured concentrations at 5.5 m are lower and tend to be comparable to concentrations at background sites. This result is in accordance with the recommendation of ADEME (2002) and Vardoulakis et al. (2003). Therefore, traffic sites should be implemented between 1.5 and 3 m of height to be representative of curbside transport emissions.

Practically, this classification results in two SO_2 background concentration areas (Fig. 4). Class 3 is more polluted than class 2. This difference in air pollution behaviors can be explained by the geographical location of the main pollutant sources and by the variability of wind directions across the region. According to the 2005 wind rose (Fig. 5), the southwest wind brings clean air masses from the sea and disperses the emitted SO_2 from the limited diesel-operating vehicles into the land. The sea breeze brings the SO_2 emitted from the harbor and the coaching station to the land. This combination results in the east side of the city having higher concentrations than the west side.

Surprisingly, S17, S18, and S21 are sorted within class 2 (east side of Beirut with lower concentrations) showing the importance of local wind circulation. The local wind circulation plays an important role: sites 17 and 18 are located on a small hill (190 m above sea level), resulting in SO_2 concentrations lower than the ones on the surrounding sites. Categorization of site 21 in class 2 is also attributed to local wind effects, resulting in lower SO_2 concentrations. The CA results imply that the network can be optimized by reducing the number of measurement sites for a future monitoring program.

Fig. 4 Map of Beirut presenting the geographical distribution of the different sites according to their classification based on CA

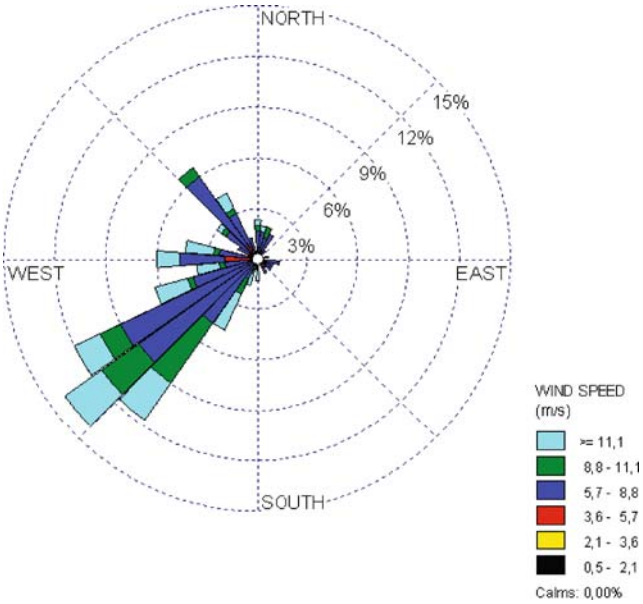

Fig. 5 Wind rose for Beirut for the year 2005 (location: Beirut International Airport)

The springtime SO_2 maximum

The HYSPLIT model uses a different technique in running a trajectory cluster analysis from the CA applied to the sites classification (Draxler et al. 2006). The

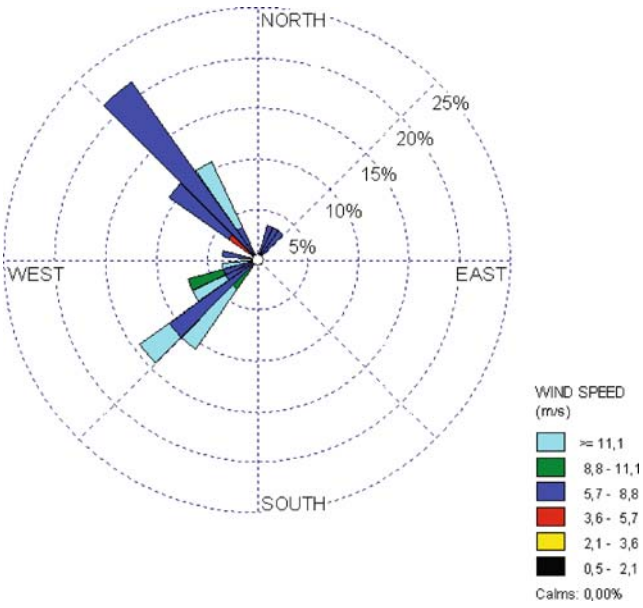

Fig. 6 Wind rose for Beirut for the fifth period of measurements (24 March 2005 till 21 April 2005, location: Beirut International Airport)

analysis gives clusters containing trajectories beginning at one location. At the beginning of the analysis, N clusters exist for the N trajectories. For combining two trajectories in a new cluster, the cluster spatial variance (SPV) is calculated. SPV is the sum of the squared distances between the endpoints of the trajectories and the mean of the trajectory in that cluster. The total spatial variance (TSV) is then calculated. TSV is the sum of all the cluster spatial variances. The two clusters with the lowest increase in TSP are combined, giving $N-1$ clusters. This iteration procedure continues until one cluster is formed containing the N trajectories. In the first iterations, the TSP increases greatly. Then, it rises at a small rate before increasing again at some point rapidly. The latter great increase indicates that the clusters being combined are not very similar.

Beirut data are situated in the lower part of the urban range with concentrations varying between 1.5 and 4.5 ppb and an exceptional value of 7 ppb for the fifth period of measurements. This last period (24 March 2005 until 21 April 2005) indicates a very high SO_2 concentration compared to the mean of the different measurement periods. This result might have different causes, such as (1) greater emissions of SO_2, (2) meteorological factors (like height of boundary layer, wind direction, or combination of land and sea breezes), or (3) long-range transport.

1. The increase of SO_2 emission might be due to an increase of the number of sources (e.g., vehicles, industries) or the quantity of SO_2 emitted by this source. This can be practically translated by a high increase of the number of diesel-operating vehicles during this period or a poorer quality of diesel with high sulfur concentration. None of these two hypotheses stand since NO_x emissions are significantly higher in diesel fuel than in gasoline (Colls 1997; Holgate et al. 1999), and Afif (unpublished data) did not observe any unusual increase of nitrogen dioxide concentrations (NO_2) in Beirut in that period of time.
2. The formation of an inversion layer increases the concentration of all the pollutants. However, since no effect was observed on the NO_2 concentrations in that period (Afif, unpublished data), this second assumption has been excluded. Another hypothesis relayed on a possible contribution of the thermal power station to the global concentration of SO_2 in Beirut. Figures 5 and 6 show the wind roses for 2005 and for the fifth period of measurement, respectively. Even though prevalent wind for 2005 is blowing from the southwest sector, the April 2005 air masses of marine origin (northwest and southwest) dominate. These air masses come from over the sea. The northeast direction (direction of the thermal power plant) does not account for more than 3% to 4% during this period. This assumption cannot explain the observed values. Moreover, thermal power plant emissions are known to include NO_x, SO_2 in considerable quantities. The relative contributions of these compounds to the total emissions of the facility are generally high. If the power plant emissions were brought over the city by the influence of land and sea breezes, this will result in higher SO_2 and NO_2 concentrations over the city. Since NO_2 in that period (Afif, unpublished data) did not show any unusual increase, this possibility might be excluded. We therefore conclude that this unusual increase was caused by neither local emissions nor meteorological factors.
3. The third hypothesis is the long-range transport of air masses enriched by SO_2. Many studies indicate that long-range transport of air masses originating from Eastern and Central Europe enrich the air with SO_2 (Lelieveld et al. 2002; Luria et al. 1996; Sciare et al. 2003; Zerefos et al. 2000). Since the lifetime of SO_2 varies from a few days to weeks (Wayne 2000), the HYSPLIT model was used to establish the 48-h backward trajectories of air masses ending in Beirut for the whole period of the measurements. Afterwards, the trajectories were clustered for each period using the same model. Since the number of clusters for the minimum TSP was three for most of the cases, we therefore adopted this number of clusters in order to compare the results. This analysis will give an idea on the regional origin of the air masses and whether long-range transport may be a possible explanation for the high observed concentration during the fifth period of measurement. Figure 7 shows the cluster mean for the 48-h backward trajectories for the whole period of measurement. It shows that 25% of air masses originate from Eastern to Central Europe (cluster 1), 63% from the Mediterranean Sea (cluster 2), and 13% from the Middle East (cluster 3). The individual CA for the fifth period indicates that 54% of air masses come from Eastern to Central Europe (Fig. 8), while other periods varied between 4% and 39% for the same direction. Emissions of SO_2 in Eastern and Central Europe are estimated to 28 Tg year^{-1} (SO_2 emissions map and data are available from the EDGAR web site; http://www.mnp.nl/edgar), while the Middle East emits 6 Tg year^{-1} (SO_2 emissions map and data are available from the EDGAR web site;

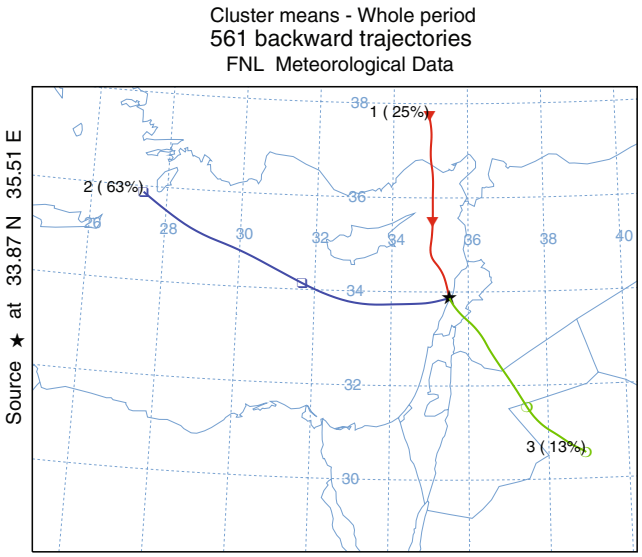

Fig. 7 HYSPLIT cluster means for the whole period of measurement (500 m AGL, Meteo Data: FNL, 48-h backward trajectories)

http://www.mnp.nl/edgar) and 1.2 Tg year^{-1} for the Mediterranean Sea (Marmer and Langmann 2005). The emissions of SO_2 from Mediterranean Sea consist essentially of international shipping. This result suggests that long-range transport from Central and Eastern Europe (80% of SO_2 emissions from the three cluster regions) may boost the pollutant concentration, and SO_2 in particular, over the east of the Mediterranean Sea, thus, over Beirut.

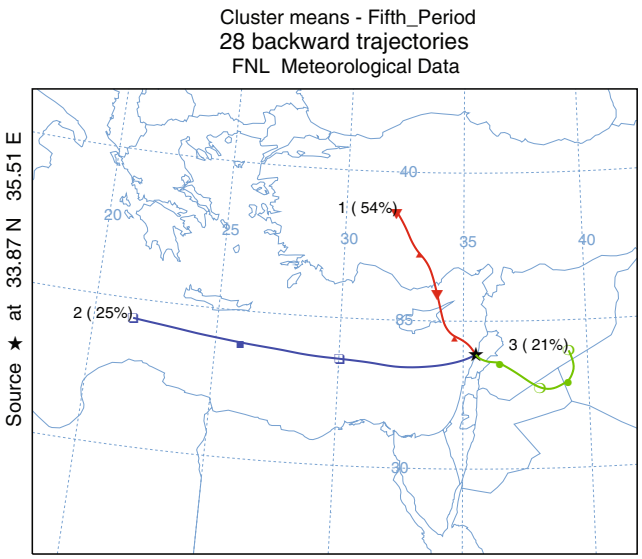

Fig. 8 HYSPLIT cluster means for the fifth period of measurement (24 March 2005 till 21 April 2005) (500 m AGL, Meteo Data: FNL, 48-h backward trajectories)

The variation of the values of SO_2 concentration during 2005 with the percentage of air masses coming from the European sector is reported in Fig. 8. The contribution of the clusters having their 48-h source point at the Mediterranean Sea were considered as null since cluster 2 accounted, in our case, for only 3% of the total emissions categorized by the clusters. Figure 9 shows that the total concentration of sulfur dioxide increases with the percentage of air masses coming from Central and Eastern Europe. The Pearson's correlation coefficient ($R(12) = 0.59$, $p < 0.05$) indicates that a moderate statistical relationship exists between the two variables. Thus, it is possible to consider that the SO_2 in Beirut has a dependent long-range transport contribution (full line) and an independent long-range transport contribution. The latter one can be considered as the local contribution due to local sources (e.g., harbor, traffic). The low value of the correlation coefficient can be attributed to meteorological (e.g., height of boundary layer) and chemical processes undergone by the SO_2 molecules that are different during the year. SO_2 reacts with OH to give H_2SO_4 in the presence of water vapor. OH concentration is a function of solar radiation and the concentration of its precursors, thus depending on the season. Moreover, SO_2 is also removed physically via dry and wet depositions, which are variable in space and time. This result indicates that an annual average of around 1.5 ppb (value of the y intercept) is due to local sources, while the contribution of long-range transport plays an important role by increasing the SO_2 concentration. For the mean value of 3.1 ppb for 2005, 26% of air masses arriving in Beirut originated from Eastern and Central Europe. This result indicates

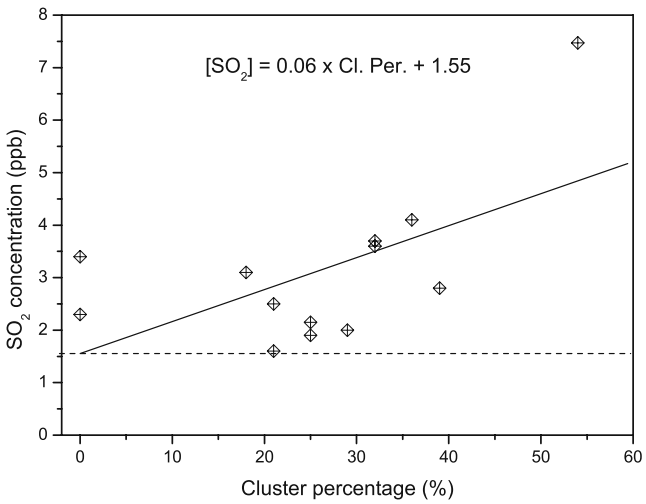

Fig. 9 Variation of sulfur dioxide concentration in 2005 with cluster percentage of air masses coming from Europe

that 50% of the mean concentration observed over the year is due to long-range transport emissions. It is worth reporting that no significant correlation was found in 2005 between the concentration of SO_2 and the percentage of air masses coming from the Mediterranean Sea or the Middle East.

Conclusion

First measurements of sulfur dioxide over 18 months in Beirut by means of passive samplers have been presented for the first time. SO_2 concentrations showed a seasonal variation. The concentration reaches a maximum value in winter and a minimal one in summer. The values observed were well under the WHO recommended value, indicating that the city does not suffer from pollution due to SO_2. Short-term measurements should me made in the future to assess short-term impact on population health. The harbor and the coaching station present the main sources of SO_2 in the city. Due to meteorological and geographical factors and source distribution, the city presents two areas of similar SO_2 behavior compared to the background concentration of SO_2. The east side of the city is the most polluted one. The local sources accounted for a mean concentration of about 1.5 ppb in 2005, while higher observed concentrations indicated a contribution of long-range transport of air masses. Long-range transport accounts for about 50% of SO_2 concentrations within Beirut, which is significant and should be taken into account when considering SO_2 emission reduction. Indeed, SO_2 emission reduction will be limited by this component.

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