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Air quality and deposition of trace elements in Didouche Mourad, Algeria

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Abstract Total suspended particulate matter and deposition fluxes of particles were investigated in the town of Didouche Mourad which is located 13 km north of Constantine. Samples of air particulate matter were collected at one site located in the heart of the town and situated 3 km north of a cement plant. Samples were collected from 2 November 2002 to 28 April 2003 every 3 days using a high volume air sampler. Sampling intervals were 24 h in all cases. During the same period, samples of dust fallout were collected at the same site. Samples were collected at 30-day intervals. Lead, chromium, manganese, nickel, copper, cobalt and cadmium deposition fluxes were measured and both the soluble and insoluble fractions were determined. Furthermore, the information gathered by this study was correlated with the corresponding hourly weather data provided by a weather station installed at the study station. The possible sources for dust and trace metals were analyzed by comparing average contributions of wind aspects to the concentrations and depositions of mass and chemical species with the average frequencies of wind direction. The mean concentration was 300 μg/m^3. The average dust deposition rate through the period of study was 221 mg/(m^2.day). Results indicate that anthropogenic sources contribute greatly to trace elements. An exposure assessment to the heavy metals taking into account the inhalation route and soil dust ingestion was carried out and allowed direct comparison of trace metal intakes via these routes.

Keywords Trace metals · Wind aspects · TSP · Deposition · Exposure assessment

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Introduction

The area of toxic air pollutants has been the subject of interest and concern for many years. The assessment of human health and environmental impacts resulting in major decisions on control actions by national and local authorities is based on such data as the quantity of airborne particulate material and deposited dust. Accurate measures of toxic air pollutants at trace levels are essential to proper assessments.

No previous investigations of airborne particulate and trace metal analysis have been undertaken in the area surrounding the cement plant located in the vicinity of the town of Didouche Mourad. The impact of this plant, despite nearby traffic and open air waste incineration, has been the subject of much controversy since the agricultural vocation of this region has been greatly disturbed since its construction more

than two decades ago. Data related to suspended matter would therefore be very useful and informative. Hourly cement production rates were recorded throughout the study period in order to appreciate the plant effect. Total suspended particulate matter and dust deposition were investigated at a residential area of Didouche Mourad which is the closest town to the plant. This town with a population of 36,500 is located 550 m above sea level and north of the city of Constantine. It has been suspected of having an air pollution problem originating from the cement plant situated 3 km only south of it. A quarry is situated 1.2 km south of the cement plant. Motor vehicles commuting past the town limits, industrial activities concentrated in the south and nearby refuse incineration constitute other major local sources of air pollution.

In various studies (Koçak et al. 2004; Kubilay et al. 1997; Bem et al. 2003; Hassanien 2001; Shakour et al. 2001), authors give only time series of TSP and trace elements. No attempt has been made to link these pollutants to the potential health risks incurred by the population based on the recommended soil intake rates.

When strategies to protect public health are under consideration, the air quality guidelines need to be placed in the perspective of total chemical exposure. It is believed that inhalation of an air pollutant in concentrations and for exposure times below a guideline value will not have adverse effects on health. Nevertheless, compliance with recommendations regarding guideline values does not guarantee the absolute exclusion of effects at levels below such values. Health effects at or below guideline values may also result from combined exposure to various chemicals or from exposure to the same chemical by multiple routes. The results presented here highlight the latter point.

In areas where PM10 measurements do not exist and in the absence of an agreed value, the World Bank Group will classify an airshed as moderately degraded if the annual and 24-h average levels of TSP are above 80 and 300 $\mu g/m^3$ respectively (World Bank Group 1998). When these recommended trigger values are exceeded, environmental mitigation alternatives should be sought. Guidelines of 0.5 $\mu g/m^3$ for Pb, 5 ng/m^3 for Cd, 0.15 $\mu g/m^3$ for Mn (WHO 2000), 20 ng/m^3 for Cu and 5 ng/m^3 for Co (California Environmental Protection Agency 1997) have been established for an averaging time of 1 year. The incremental unit risks based on lung cancer resulting from a lifetime exposure to chromium(VI) and nickel at a concentration of 1 μ/m^3 are 4×10^{-2} and 3.8×10^{-2} respectively (WHO 2000). The German TA-Luft (1986, 2002) established criteria for heavy metals deposition rates as follows: 100 $\mu g/(m^2.day)$ for Pb, 15 $\mu g/(m^2.day)$ for Ni, 2 $\mu g/(m^2.day)$ for Cd and 250 $\mu g/(m^2.day)$ for Mn, Cr and Cu.

Experiment

TSP measurement

Samples of air particulate matter were collected at one site in the heart of the town (Fig. 1). This site was selected for security reasons and because of the high population density surrounding it. Furthermore, this area is in the vicinity of heavy traffic pollution and a refuse incineration site. Samples were collected from 2 November 2002 to 28 April 2003 every 3 days. Sampling times were 24 h in all cases. The filters were changed at 1400 h. Midday was avoided so that the peak hours would not be missed. Midnight was also avoided for security reasons. A portable tripod high volume air sampler Model GT 22001 (Andersen,

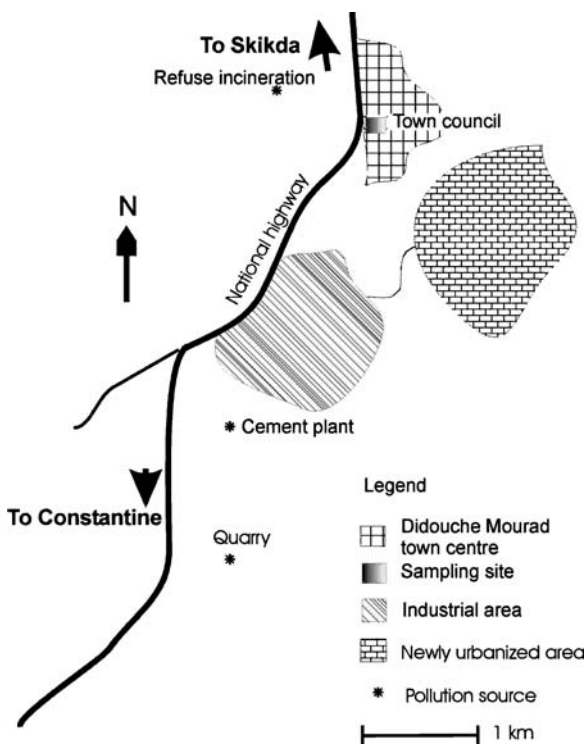

Fig. 1 TSP and dust fallout sampling site in an urban area of Didouche Mourad

Smyrna, GA, USA) was used to collect airborne particulate. It was situated 7 m above ground level on the top of the local council. The sampler consists of a motor especially housed in a durable plastic housing and a filter holder consisting of a cone-shaped stainless steel filter-support screen. The collection media utilized consisted of binderless hygroscopic 10×8 in. (25×20 cm) glass fiber collection filters supported by a cast aluminum face plate sealed with a neoprene sponge rubber gasket attached to the sampler with a threaded ring for easy assembly. In operation, the TSP sampler draws ambient air through the air inlet gap between the cover and the sampler housing walls. The gable roof design of the sampler allows the sampled air to be evenly distributed over the surface of the downstream filter where TSP is collected. Particles of 100 μm size and less enter the sampling inlet and are collected on the downstream filter. Flow rates were measured in the field using a 30 in. slack tube manometer which sensed the pressure drop across the sampler. The sampler calibration was carried out at least once every three months in the field using a top-loading orifice calibration kit and five resistance plates and after each time the blower motor brushes were replaced. After each sampling interval, the collection media were returned to the weighing laboratory and allowed to equilibrate for 24 h in a dessicator before weighing to a precision less than ± 0.1 mg using a Sartorius balance (model BP61). The mass of the sample on each filter was calculated by subtracting the initial weight from the final weight.

Proper care in handling the fiber glass filters was observed in order to avoid contamination problems. After the gravimetric analysis, the filters were stored until the atomic absorption spectrometry (AAS) elemental analysis could be performed. Before analysis, three 1 in.-wide strips were cut and were used to analyze metal elements.

Pye Unicam SP9 AAS supporting an acetylene flame was used to analyze the composition of heavy metal elements in TSP and deposited dust (Pb, Mn, Cr, Ni, Cu, Co and Cd). Method IO-3.2 was used for the determination of metals in ambient particulate matter (U.S. Environmental Protection Agency 1999). Three blank were subjected to the same procedure to prepare the blank samples. The results of the analysis of blank samples were used to estimate the element concentration produced by the filter and sample preparation.

The concentrations of metal elements in the sample solution were very low. Linear calibration technique was used in the AAS analysis. Three standard solutions with equally spaced concentrations ranging from zero to the maximum concentration were used to calibrate the instrument for each metal element. To eliminate the matrix interference, all standard solutions were prepared using a solution with the same proportion of acid and deionized water as the sampled solutions.

Dust deposition measurements

A dust deposition gauge constructed according to the French standard AFNOR NF X43-006 with a 10 cm radius was collocated with the high volume sampler and the meteorological station. To sample dust deposition, the gauge is filled with 10 l of distilled water and left exposed to settling dust and rain for a period of 30 days. Rinsing of the internal surface of the sampler with distilled water is carried out after each sampling period to detach deposited particles. The sampling solution is then poured in a clean propylene container and then taken to the laboratory to perform the different analyses. The sample volume is measured and the solution is then divided into sub-samples to determine dust mass, Pb, Mn, Cr, Ni, Cu, Co and Cd. Two sample types were prepared in order to distinguish dissolved and insoluble metal fractions. The sample solution is filtered through a mixed cellulose ester membrane (MCE 0.4 μm, ∅=25 mm). Then, 200 ml of the filtrate are dried at 105°C. The remaining solid deposit is solubilized in a 2 N nitric acid solution to allow for the analysis of the soluble trace elements. Once dried, the membrane material is weighed and allowed to stand for 48 h in a beaker containing 50 ml of 2 N HCl and 50 ml of 2 N HNO_3. The acid-extraction solution is filtered to remove any insoluble material and then placed in an oven at 80°C to reduce its volume down to 40 ml. After dilution to a volume of 50 ml with deionized water, the sample is ready for analysis of the insoluble fractions of the metals.

Blank filters were subjected to the same preparation procedure to estimate the elemental concentration produced by field handling, the filter and sample preparation.

Meteorological data

The information gathered by this study was correlated with the corresponding weather data. Hourly observations of wind speed, wind direction, temperature,

atmospheric pressure, precipitation and relative humidity that may affect the degree of pollution at the study area were obtained from an automatic weather station installed on the city council roof a few meters away from the high-volume collector.

Identification of possible source directions

An investigation into the contribution of each wind sector on measured concentrations and deposition fluxes of trace elements may show possible source direction. Qin and Oduyemi (2003) identified roughly the possible source direction that affects PM_{10} data in Dundee by comparing average contributions of wind sectors to the concentrations of mass and chemical species with the average frequencies of wind direction. This permits to identify the directions where sources contribute strongly to a given species. When the average contribution of the wind sector to a chemical species is higher than the wind direction frequency, it means the contribution of the source from this direction to this species is higher than the average level and the sources contribute strongly to this species in this direction. Conversely, in case the average contribution of the wind sector to a chemical species is lower than the wind direction frequency, it means the contribution of the source from this direction to this species is lower than the average level and the sources contribution to this species is weak in this direction.

Average contributions of wind sectors to concentrations or deposition fluxes of masses and trace elements can be calculated by using (Qin and Oduyemi 2003):

$$E_{jk} = \sum_{i=1}^{N} C_{ik} P_{ij} \Big/ \sum_{i=1}^{N} C_{ik} \qquad \text{(i)}$$

Where E_{jk} (%) is the average contribution of j wind direction on k chemical species, C_{ik} is the concentration or deposition flux of k chemical species in i sample, P_{ij} (%) is the frequency of j wind direction during i sampling period. N is the sample number.

Human health risk assessment

The exposure routes considered are inhalation of the metal elements and their ingestion as soil dust. We assume that all of these elements are attached to particles of inhalable size. Dietary intake, ingestion of water and contribution from other exposure pathways have not been considered due to a lack of data. The uptake of contaminants from dermal contact accounts for only a tiny fraction of the administered dose and has not been taken into account. This study focuses on exposures of adults and 2-year old children to the trace elements Pb, Mn, Cr, Ni, Cu, Co and Cd.

In order to assess chronic health hazard for non carcinogenic effects, screening tools such as RfDs and MRLs will be used, when available, to assess dose for chronic inhalation and/or oral exposure or minimum risk levels to metal elements that may pose risk to the exposed populations (Barnes and Dourson 1998; LaGrega et al. 1994). Minimum risk levels (MRLs) are derived using a modified version of the risk assessment methodology the US Environmental Protection Agency (EPA) provides to determine reference doses for lifetime exposure (RfDs) (Barnes and Dourson 1998). They provide valuable guidelines to protect public health but cannot be enforced by law. Carcinogenicity assessment for lifetime exposure from inhalation and/or oral exposure is based on air risk units.

Results and discussion

Meteorological data

According to statistical results of the analysis of meteorological factors measured at the automatic weather station, the major prevailing wind directions are westerly and north-westerly. During the period of study (2/11/2002-28/4/2003), the average frequency for westerly to northerly (WSW to N) winds is 46.31%. The frequency of calms was relatively high (31.73%). The average wind speed was 2.55 m/s. The average temperature was 10.6°C. Temperatures ranged from 1 to 27°C. Total rainfall was 629 mm.

A data analysis summary

A summary of the results of the analysis of TSP and deposited dust mass as well as seven chemical species are shown in Tables 1 and 2.

The elements exist mainly in dissolved form excepted for Ni and Cu. Ratios of dissolved to particulate fractions over the whole period of study

Table 1 TSP (μg/m^{-3}) and metal concentrations (ng m^{-3})

	Number of samples	Mass	Pb	Mn	Cr	Ni	Cu	Co	Cd
Min	53	11	1	2	8	0	5	2	0
Max		9,591	187	1093	73	109	65	90	18
Average		300	46	50	16	11	24	14	1
SD		1,316	97	616	36	60	31	47	10

are lowest for Mn, Pb (2 for both) and highest for Co, Cd and Cr (19, 11 and 5 respectively).

In comparison with the results measured at other sites and with the exception of Cu and Co, ambient concentrations of trace elements are high (Koçak et al. 2004; Kubilay et al. 1997; Bem et al. 2003; Hassanien 2001; Shakour et al. 2001). Concentrations of dust laden metals are high for Pb, Mn, Cu and Cd.

TSP concentrations and dust fallout

Temporal variations of mass and chemical species of TSP are shown in Figs. 2, 3. The mass concentration, shown in Fig. 2 fluctuates with time. It varies between 11 and 9,591 μg/m^3. The latter value represents the highest mass concentration of TSP which occurred on 15 November 2002. This corresponds to a sample taken when a sand storm raged in northern Algeria for two consecutive days on 14–15 November 2002. The very low concentration of 11 μg/m^3 was due to the absence of south to south westerly winds likely to carry TSP from the industrial area and to the predominance of calm winds. The mean concentration was 300 μg/m^3. If we exclude the value from data, we obtain a mean of 117 μg/m^3 which is well above the trigger value recommended by the World Bank.

Changes in pollution levels could be explained by marked changes in precipitation and wind speed for the periods 2/11/2002–11/01/2003 and 13/01/2002–28/4/2003 which show two obvious patterns of TSP and trace metal concentrations. The average wind speeds were 3.84 m/s and 1.15 m/s for these periods while precipitation levels were 260 and 369 mm respectively. Concentrations of TSP and trace metals increase with wind speed. These metal particulates are deposited on the ground surface and then blown by the wind while precipitation leads to atmospheric washing and soil wetting preventing direct suspension of soil particulates. Therefore the latter period (13/01/2002–28/4/2003) coïncided with decreasing trends in both TSP and trace metals (Figs. 2 and 3). If we ignore the exceptionnaly high concentration of 9,591 μg/m^3 recorded during the sand storm event, the average TSP concentrations measured for the above mentioned periods were 162 and 87 μg/m^3 respectively. Il was not surprising that trace metal concentrations followed the same trend as TSP.

The daily average dust fallout (221 mg/(m^2.day)) exceeds the British "custom and practice" limit of 200 mg/(m^2.day), but is lower than the Australian standard for "unacceptable reduction in air quality" of 333 mg/(m^2.day), and the German TA-Luft criteria for "possible nuisance" of 350 mg/(m^2.day) for all monthly periods (Environment Agency 2003).

Contributions of wind aspects to concentrations and depositions of mass and trace elements

Average contributions of wind directions (sectors from 1 to 16) to concentrations and deposition fluxes of masses and trace elements that were calculated according to Eq. 1 are shown in Tables 3 and 4 respectively. The average frequency distribution of wind direction measured at the study station is also shown in the tables.

Hourly average wind speeds and frequencies of winds blowing from 16 directions taking into account only the 53 days of TSP sampling and the total period of dust deposition measurements are graphically represented in Figs. 4 and 5 respectively. Seven

Table 2 Dust (mg/m^{-2}.day^{-1}) and metal depositions (μg m^{-2}.day^{-1})

	Number of samples	Mass	Pb	Mn	Cr	Ni	Cu	Co	Cd
Min	06	50	47	36	1	0	144	25	1
Max		544	696	485	38	21	735	874	42
Average		221	384	202	17	11	395	339	15
Average dust content (μg/g)		–	1280	914	77	50	1787	1534	50
SD		173	256	186	14	9	201	353	15

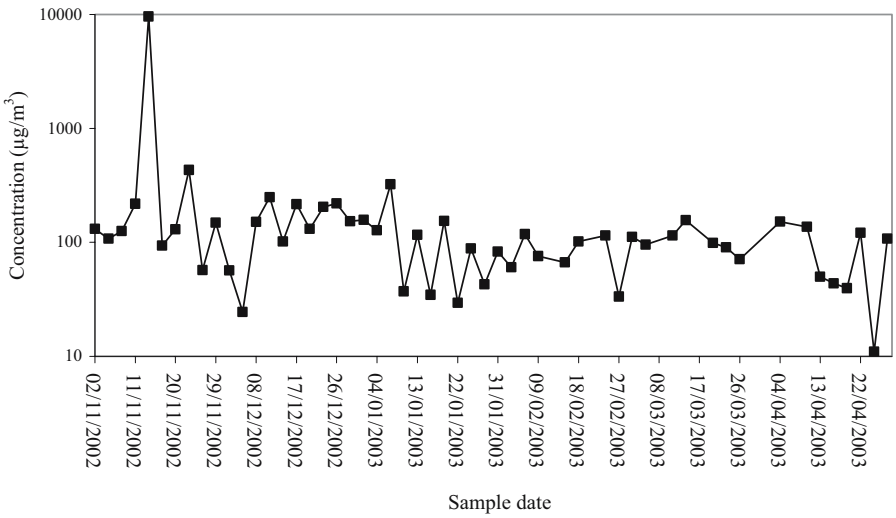

Fig. 2 Temporal variations of TSP from 2-11-2002 to 28-4-2003 in Didouche Mourad

samples could not be validated because of power cuts. The prevailing winds observed exclusively during TSP sampling are westerly (15.87%) and west-southwesterly (15.70%). The average contribution of these wind aspects to the TSP mass is 2.95% which is lower than the average value of the wind frequency in these directions. The average contribution of south to southwest winds (S to SW) to TSP mass is 69.15%. This is much higher than the average value of the wind frequency in this direction (8.97%). This comparison of the wind direction contribution and wind frequency indicates that the sources of TSP measured in Didouche Mourad are much stronger in the south to southwesterly direction and reflect the major impact of the cement plant, the quarry and the industrial area which are situated south-southwesterly of the sampling site.

Contributions of wind direction to each of the trace elements in TSP do not differ markedly from those affecting TSP mass concentration. The contributions of the southerly winds (SE to SW) to Pb, Mn, Cr, Ni, Cu, Co and Cd are 47.99, 57.59, 49.43, 49.08, 48.16, 52.85 and 20.23% respectively. These contributions are above the wind frequency in this direction (12.79%) and reflect the influence of the anthropogenic sources already mentioned in the case of TSP and the impact of traffic

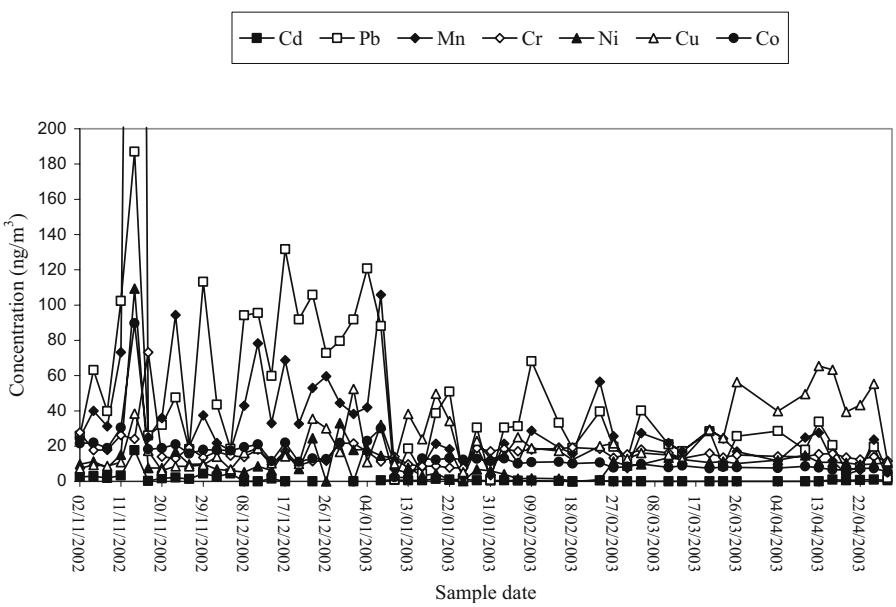

Fig. 3 Temporal variations of trace metals in TSP from 11-2-2002 to 4-28-2003 in Didouche Mourad

Table 3 Average percentage contributions of wind aspects to mass and chemical species of TSP

	AWF	Mass	Pb	Mn	Cr	Ni	Cu	Co	Cd
C	31.73	4.04	0.00	0.00	0.00	0.00	0.00	0.00	14.52
N	3.94	0.00	0.95	1.04	0.33	0.67	0.00	0.91	0.90
NNE	0.98	2.76	0.80	0.50	0.49	0.76	0.60	0.47	0.00
NE	1.11	1.49	1.43	0.61	0.99	0.32	1.75	0.69	0.79
ENE	1.11	4.20	0.00	0.00	0.00	0.00	0.19	0.00	0.53
E	1.97	1.80	0.41	0.12	0.39	0.54	0.00	0.10	0.06
ESE	2.21	1.66	2.08	9.28	0.96	4.34	1.01	2.54	0.00
SE	1.97	2.39	3.60	17.37	2.08	8.38	1.97	4.96	0.38
SSE	1.85	5.32	7.68	14.72	10.28	10.03	11.52	9.37	4.47
S	3.81	34.52	9.22	8.20	10.07	10.34	17.11	7.54	7.20
SSW	1.35	2.56	14.36	9.23	14.70	10.41	7.46	16.55	4.85
SW	3.81	32.07	13.13	8.07	12.30	9.92	10.10	14.43	3.33
WSW	10.70	1.53	1.04	0.85	2.09	2.40	7.80	1.77	19.64
W	15.87	1.42	7.11	4.26	7.97	6.45	5.96	9.36	20.97
WNW	3.44	0.73	4.73	3.03	5.05	4.36	5.09	4.58	1.98
NW	4.80	0.62	21.80	12.96	12.64	15.04	4.60	15.21	9.98
NNW	9.35	2.89	14.83	20.73	16.27	20.19	18.27	14.19	3.30

related pollution in the newly urbanized area. In addition, the contributions of west-northwesterly to north-northwesterly winds (WNW to NNW) to Pb, Mn, Cr, Ni, Cu and Co are 41.36, 36.72, 33.96, 39.59, 27.96 and 33.98%. They are higher than the wind frequency in these directions (17.59%) and they probably reflect the impact of the open air refuse incineration and vehicular emissions from the highway both located North West of the sampling site. The contributions of west-southwest to northwest winds (WSW to NW) to cadmium (52.57%) exceed the wind frequency in this direction (34.81%). Cd may be released from the application of phosphate fertilizers to vast arable lands situated west of the study station as well as waste incineration.

Contributions of wind direction to dust and trace elements deposition differ markedly from those affecting their atmospheric counterparts. The average

Table 4 Average percentage contributions of wind aspects to mass and chemical species of total fallout

	AWF	Mass	Pb	Mn	Cr	Ni	Cu	Co	Cd
C	11.87	17.55	13.05	22.58	6.17	4.55	8.53	23.81	22.39
N	6.97	4.77	5.29	3.13	8.15	7.51	6.65	2.76	2.96
NNE	3.63	2.74	2.7	1.65	3.83	3.52	3.07	1.43	1.57
NE	3.53	2.37	2.2	1.29	3.51	3.2	2.7	1.11	1.25
ENE	3.41	2.24	2.45	1.4	3.98	3.6	3.17	1.22	1.33
E	6.41	4.23	5.39	2.71	7.72	7.9	6.81	2.33	2.62
ESE	4.92	3.16	3.12	2.05	5.48	4.87	4.23	1.89	2.07
SE	4.87	3.36	3.75	2.39	5.52	5.65	4.82	2.28	2.59
SSE	4.68	3.77	5.39	2.97	5.69	7.58	6.3	2.82	3.4
S	4.65	4.02	4.25	3.67	5.42	5.59	5.03	3.72	4.04
SSW	2.61	3.7	3.15	3.72	2.66	2.83	2.76	3.9	4.18
SW	3.12	4.25	3.43	4.78	2.75	2.35	2.82	4.99	4.95
WSW	6.34	8.41	7.46	10.98	3.7	4.06	5.63	11.47	10.81
W	9.31	10.9	10.61	12.9	7.38	7.7	9.05	13.14	12.48
WNW	5.58	5.95	6.67	7.11	5.67	5.64	6.37	7.11	6.66
NW	6.12	6.69	7.89	7.26	6.96	7.62	7.75	7.18	7.14
NNW	11.99	9.87	11.6	7.45	14.11	14.57	13.03	6.82	7.4

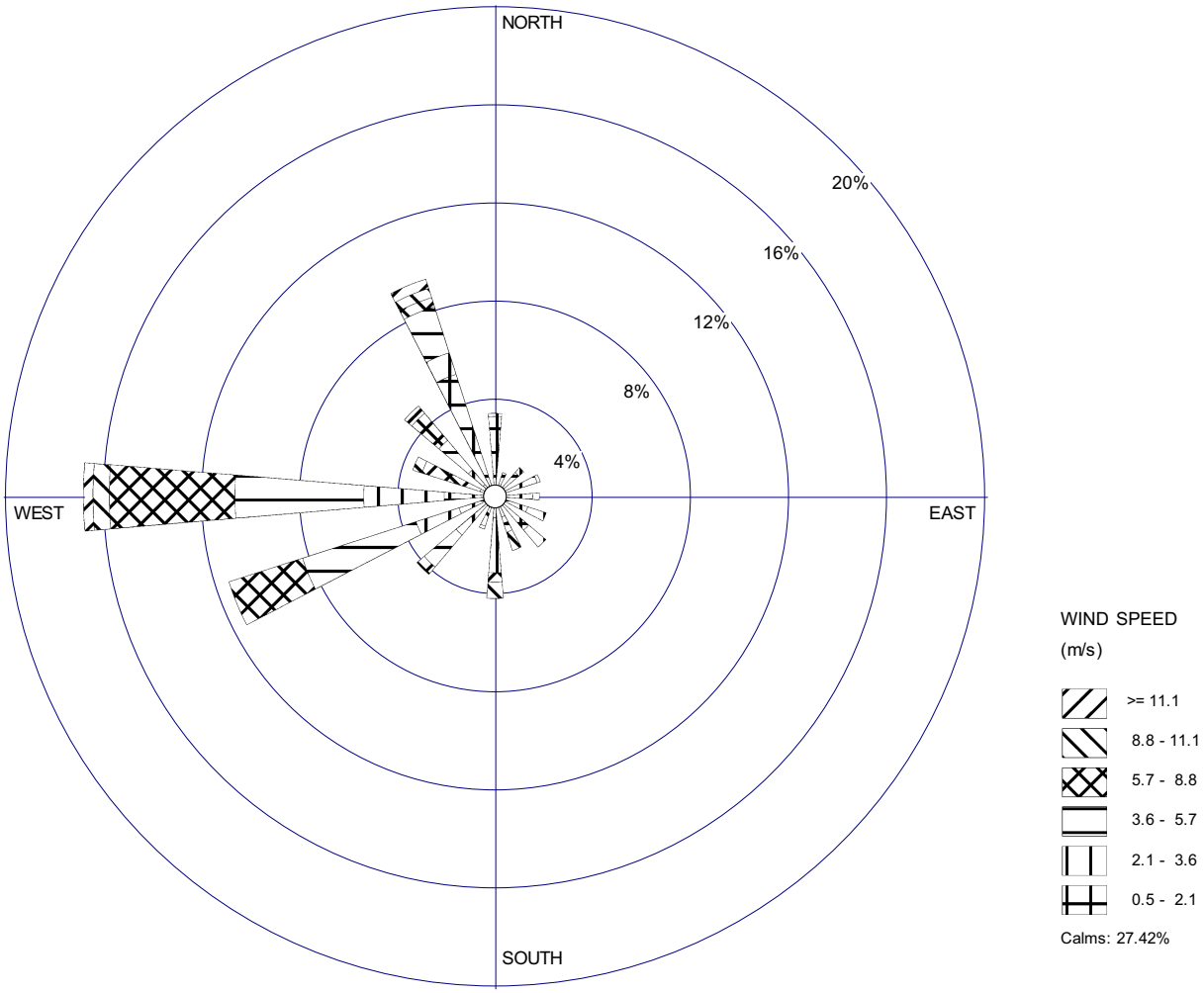

Fig. 4 Wind rose taking into account the 53 days of TSP sampling

contribution of westerly winds to the dust fallout, Pb, Mn, Co and Cd in the sectors SSW to NW are 39.9, 39.21, 46.75, 47.79 and 46.22% which are all higher than the average value of the wind frequency in this direction (33.08%). The average contribution of southerly wind (SSE to SSW) to the dust fallout is 11.49% (Table 4). Conversely, this is lower than the average value of the wind frequency in the southerly direction (11.94%). These results thus show that the sources for dust fallout in Didouche Mourad are stronger in the westerly direction than in the southerly direction. This suggests that surface soil contributes more than industrial processes in dust deposition. Surface particulates are disturbed by wind and soon become in suspension when a certain wind speed limit is achieved. Mn, Co and Cd may originate from the use of fertilizers and phytosanitary products widely used in the vast agricultural lands located west of the town of Didouche Mourad while lead originates mainly from the national highway leading to the coastal city of Skikda. Moreover, the contributions of southerly winds (SSE-SSW) to Cr, Ni and Cu are 13.77, 16 and 14.09% respectively and are higher than the wind frequency in the southerly direction (11.94%) and reflect the impact of industrial activities south of the sampling site.

Heavy metals

The average metal element concentrations and deposition fluxes are compared with the appropriate established standards. Daily ventilation rates of 20 m^3/day for adults and 6 m^3/day for 2-year old children are

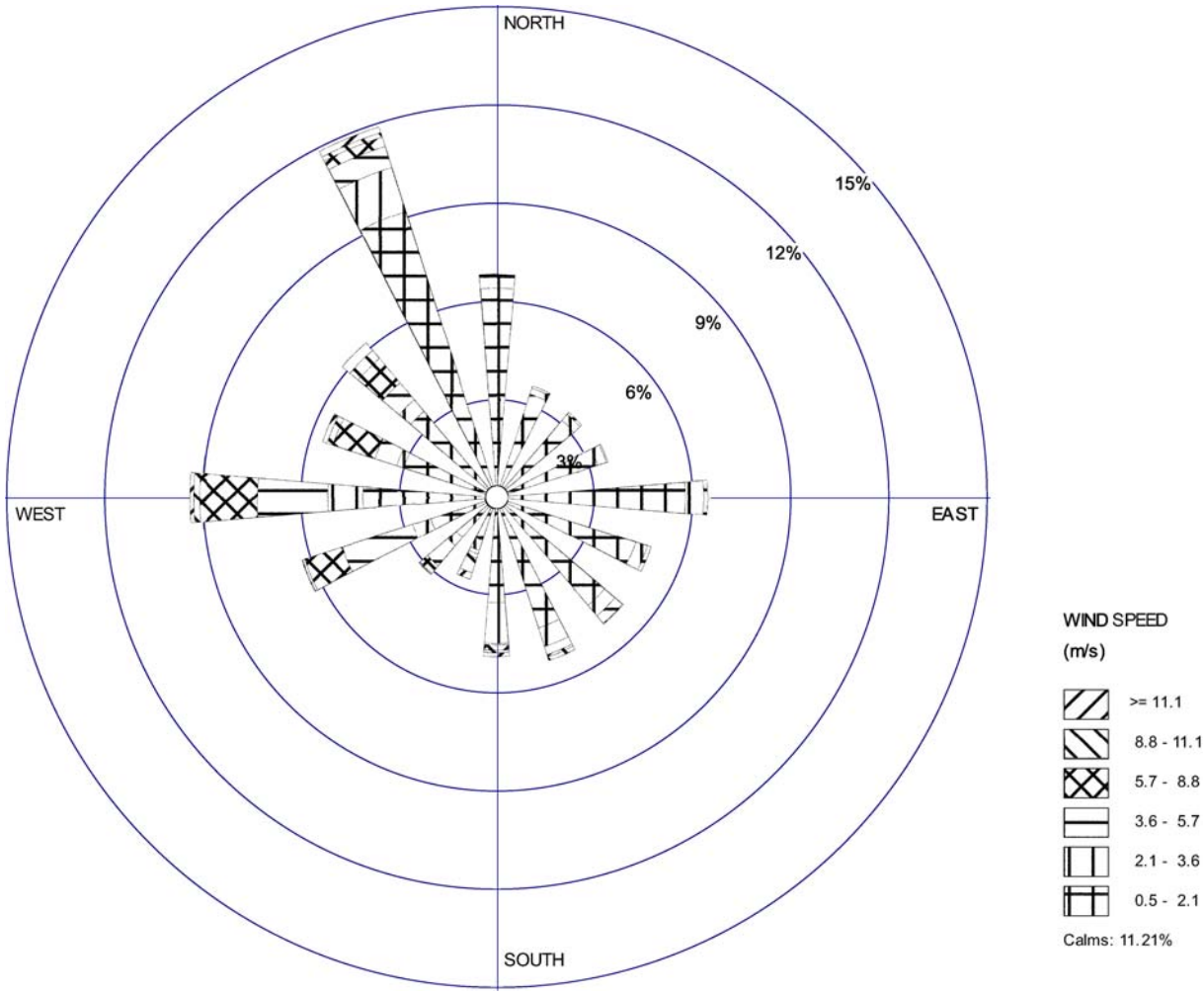

Fig. 5 Wind rose taking into account the total period of dust deposition (2-11-2002 to 28-4-2003)

used in the human health risk characterization (LaGrega et al. 1994). In all cases, we assume two exposure scenarios. The first one assumes that 20 mg/day of dirt is ingested by adults and 80 mg/day by children (Binder et al. 1986; Clausing et al. 1987). The second scenario assumes that the ingestion rates are 100 and 200 mg/day respectively (LaGrega et al. 1994). The received doses are indicated in Table 5.

Lead

The average Pb concentration was 46 ng/m^3. This value was lower than the annual standard of 500 ng/m^3 (WHO 2000) or the quarterly EPA standard of 1.5 μg/m^3 (Agency for Toxic Substances and Disease Registry (ATSDR) 1999a). However, Pb deposition was 384 μg/(m^2.day) which is exceeds by a factor of 3.84 the German TA-Luft annual standard of 100 μg/(m^2.day) (TA-Luft 2002). Such dust is then an important Pb carrier for young children (U.S. Environmental Protection Agency 1986; Drill et al. 1979). The average dust deposition through the period of study was 221 mg/(m^2.day). It follows that the average dust content of Pb was 1738 μg/g. Assuming daily ventilation rates of 20 m^3/day for adults and 6 m^3/day for 2-year old children (LaGrega et al. 1994), the administered Pb dose originating from TSP for adults and children was 0.92 and 0.28 μg respectively. Furthermore, supposing that 20 mg/day of dirt is ingested by adults and 80 mg/day by children (Binder et al. 1986; Clausing et al. 1987), the expected daily amounts of Pb ingested this way were 34.76 and

Table 5 Daily intake of metal elements from TSP and soil dust

Metal element	Media	Concentration	Adults (70 kg)		2-year old children (13,6 kg)		Standards	Ref.
			intake		intake			
			µg/day	µg/(kg. day)	µg/day	µg/(kg. day)		
Pb	Air ng/m^3	46	0.92	0.01	0.28	0.02	Tolerable daily intakes= 7.14 and 3.57 µg/(kg.day) for adults/ and children respectively	Organisation Mondiale de la Santé (OMS) 1987
	Soil dust µg/g	1280	34.76[a] 173.8[b]	0.5[a] 2.48[b]	139.04[a] 347.6[b]	**10.22**[a] **25.56**[b]		
Mn	Air ng/m^3	50	1,00	**0,014**	0,3	**0,022**	RfD for chronic inhalation and oral exposures=0.0114 and 10 µg/(kg.day) respectively	LaGrega et al. 1994
	Soil dust µg/g	914	18.28[a] 91.4[b]	0,26[a] 1,31[b]	73.12[a] 182.8[b]	5.38[a] **13.44**[b]		
Cr	Air ng/m^3	16	0.34	0.005	0.1	0.008	RfD for chronic oral exposure= 3 µg/(kg.day)	Agency for Toxic Substances and Disease Registry (ATSDR) 2000
	Soil dust µg/g	77	1.54[a] 7.7[b]	0.022[a] 0.11[b]	6.16[a] 15.4[b]	0.45[a] 1.13[b]		
Ni	Air ng/m^3	11	0.22	0,003	0.066	0,005	RfD for chronic oral exposure= 20 µg/(kg.day)	IRIS 1996
	Soil dust µg/g	50	1[a] 5[b]	0.014[a] 0.07[b]	4[a] 10[b]	0.29[a] 0.74[b]		
Cu	Air ng/m^3	24	0.48	0.007	0.14	0.011	Intermediate-duration oral MRL (14–365 days)=20 µg/(kg.day)	Agency for Toxic Substances and Disease RegistryATSDR 2002
	Soil dust µg/g	1787	35.74[a] 178.7[b]	0.51[a] 2.55[b]	142.96[a] 357.4[b]	10.51[a] **26.30**[b]		
Co	Air ng/m^3	14	0.28	0.004	0.08	0.006	Intermediate-duration oral MRL (14–365 days)=0.1 µg/(kg.day)	Agency for Toxic Substances and Disease Registry (ATSDR) 2001
	Soil dust µg/g	1534	30.68[a] 153.4[b]	**0.44**[a] **2.19**[b]	122.72[a] 306.8[b]	**9.02**[a] **22.56**[b]		
Cd	Air ng/m^3	5	0.06	0.9 10^{-3}	0.02	1.32 10^{-3}	Tolerable weekly cadmium intake=400–500 µg for an adult and chronic oral MRL (>365 days)=0.2 µg/(kg.day)	WHO 1989; Agency for Toxic Substances and Disease Registry (ATSDR) 1999b
	Soil dust µg/g	68	1.36[a] 6.8[b]	0.019[a] 0.097[b]	5.44[a] 13.6[b]	**0.4**[a] **1.0**[b]		

[a] Scenario 1: Computed values are for an ingestion rate of 20 mg/day for adults and 80 mg/day for children less than 2 years.

[b] Scenario 2: Computed values are for an ingestion rate of 100 mg/day for adults and 200 mg/day for children less than 2 years.

Intakes exceeding the corresponding standards are emboldened.

139.04 µg respectively. The total calculated intake of Pb was 35.68 and 139.32 µg respectively.

Dust represents the main source of Pb contamination. If the ingestion rates of soil dust are assumed to be 100 and 200 mg/day for adults and 2-year old children (LaGrega et al. 1994), then the daily dosages of lead are 173.8 and 347.6 µg/day respectively. The total calculated dosages of Pb would be 174.72 and

347.88 μg/day respectively (Table 5). These estimated values are minimal since Pb exposure from canned food and water contaminated from contact with plumbing has not been taken into account.

Provisional maximum tolerable weekly intakes of Pb are 50 μg/kg body weight for adults and 25 μg/kg body weight for children (Organisation Mondiale de la Santé (OMS 1987) corresponding to 7.14 and 3.57 μg/(kg.day) respectively. There exists a potential risk of exposure in both scenarios for children.

Manganese

The arithmetic mean over the period of study was 50 ng/m^3. This value is acceptable compared to the annual average guide value of 0.15 μg/m^3 set by the (WHO 2000).

The average Mn fallout was 202 μg/(m^2.day) which is lower than the German TA luft standard of 250 μg/(m^2.day) (TA-Luft 1986). The daily intake of Mn from ambient air is 0,022 μg/(kg.day). The latter exceeds the reference dose for chronic inhalation exposure (RfD) of 0.0114 μg/(kg.day) set up by the US EPA (LaGrega et al. 1994). The mass of Mn ingested from soil dust is 0.26 and 5.38 μg/(kg.day) respectively which is less than the oral RfD of 10 μg/(kg.day) (LaGrega et al. 1994). The latter is exceeded in the case of an oral ingestion of 200 mg/day of dust by a 2-year-old child since a calculated intake of 13.44 μg/(kg.day) is obtained (Table 5).

Chromium

In the absence of better information, a conservative approach would assume Cr in the air is predominantly hexavalent. It should be noted that Cr concentration in air is often expressed as total Cr and not Cr(VI).

The average ambient air concentration of Cr was 16 ng/m^3 during the period of study (Fig. 3). At an air concentration of Cr(VI) of 1 μg/m^3, the lifetime risk is estimated to be 4×10^{-2}. An excess lifetime risk of about 64: 100,000 can then be associated to the measured concentration.

In terms of fallout to the ground, the deposition rate was 17 μg/(m^2.day). This value is in conformity with the German annual standard of 250 μg/(m^2.day) (TA-Luft 1986). The inhalation and ingestion intake doses of Cr by adults and children in Didouche Mourad are shown in Table 5. These results indicate that the maximum ingested Cr dose was 1.13 μg/(kg.day) which is less than the oral RfD of 3 μg/(kg.day) suggested by the USEPA (Agency for Toxic Substances and Disease Registry (ATSDR) 2000). The inhalation intake was negligible.

Nickel

Ni compounds are human carcinogens by inhalation exposure. On the basis of the most recent information of exposure and risk estimated in industrial populations, an incremental risk of 3.8×10^{-4} can be given for a concentration of Ni in air of 1 μg/m^3 (WHO 2000).

The average daily Ni concentration was 11 ng/m^3 in the city of Didouche Mourad (Fig. 3). This is less than the MRL of 0.2 μg Ni/m^3 which has been derived for intermediate-duration exposure to Ni (15–364 days) (Agency for Toxic Substances and Disease Registry (ATSDR) 2003). On the basis of the WHO's unit risk, an excess lifetime risk of 4:1,000,000 can be calculated.

The amount of Ni deposition was 11 μg/(m^2.day). This value is less than the annual guideline value of 15 μg/(m^2.day) applicable in Germany as an annual average (TA-Luft 2002). The reference dose for chronic oral exposure (RfD) to Ni being equal to 20 μg/(kg day) (IRIS 1996), there is no potential risk associated with chronic exposure to soil dust in the case of both scenarios for adults and 2-year old children (Table 5).

Copper

Concentrations of Cu determined in 53 samples of ambient air in the city of Didouche Mourad over the period 2/11/2002–28/4/2003 averaged 24 ng/m^3 (Fig. 3). It is close to the reference concentration for inhalation of 20 ng/m^3 (California Environmental Protection Agency 1997). Cu deposition rate was estimated at 395 μg/(m^2.day). It exceeds the German TA-Luft annual standard of 250 μg/(m^2.day) (TA-Luft 1986).

An MRL of 20 μg/(kg.day) has been derived for acute-duration oral exposure (1–14 days) to Cu and has also been adopted as the intermediate-duration oral MRL (14–365 days) (Agency for Toxic Sub-

stances and Disease Registry (ATSDR) 2002). The calculated intakes of Cu from soil dust are all well below the minimum risk level excepted in the case of the worst exposure scenario for children (Table 5).

Cobalt

In this study, the mean measured ambient air concentration of Co was 14 ng/m^3. It is higher than the reference concentration for inhalation of 5 ng/m^3 (California Environmental Protection Agency 1997). An MRL of 0.1 μg cobalt/(kg.day) has been derived for intermediate-duration oral exposure (<365 days) and for chronic inhalation exposure to Co (Agency for Toxic Substances and Disease Registry (ATSDR) 2001). The oral exposure MRL was largely exceeded for adults and children for both exposure scenarios (Table 5).

Cadmium

The mean level of measured daily concentrations of Cd was 1 ng/m^3. It is less than the annual WHO guideline of 5 ng/m^3 (WHO 2000). The deposition rate of this metal was 15 μg/(m^2.day). This value is 7.5-fold the German TA-luft annual standard of 2 μg/(m^2.day) (TA-Luft 2002).

The provisional tolerable weekly Cd intake of 400–500 μg for an adult should not be exceeded (WHO 1989). The intake value of 6.8 μg/day is in conformity with such a guideline. Moreover, an MRL of 0.2 μg Cd/(kg.day) has been derived for chronic oral exposure (>365 days) (Agency for Toxic Substances and Disease Registry (ATSDR) 1999b). Such a level was exceeded for children for both scenarios (Table 5).

Conclusion

The concentration of total suspended particulates is generally high in the town of Didouche Mourad with a mean value of 117 μg/m^3 over the test period if we exclude the exceptional sand storm which led to a daily TSP concentration of 9,193 μg/m^3. High average daily dust deposition rates with high Pb, Cu and Cd fluxes exceeding the German TA-Luft criteria were also observed despite the fact that the measurements were taken during the cold season.

Ambient air concentrations of Pb, Mn and Cd were relatively small compared to the WHO guideline values, while those of Cu and Co pose a threat to health since their daily oral intakes are higher than the corresponding MRLs. Moreover, daily intake of Mn exceeded the reference dose for chronic inhalation for both adults and children. Carcinogenic elements Cr and Ni lead to lifetime risks exceeding 10^{-6}. Quantification of the human health risks indicated that direct ingestion of contaminated particles represents a much more important pathway of exposure to trace metals than the inhalation route. Intakes via the latter route represent only 0.07 to 1.78% of those resulting from the oral route in the case of the first exposure scenario and 0.03 to 0.71% in the case of the second scenario for children, while they represent 0.91 to 22.73% and 0.18 to 4.55% respectively for adults. Furthermore, the potential for adverse effects is greater for children than for adults. Deposition of metal elements leads to concentrations in soil dust that present, in terms of non carcinogenic effects, a potential risk to children exposed via the oral route to Pb, Mn, Cu, Co and Cd for at least one of the exposure scenarios considered while the adult population is exposed to such a risk only when exposed to Mn and Co.

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