

High Airborne Chlorine Concentrations in Micro or Sub-micrometer Particles

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Abstract. During standard analysis of airborne particle samples, a strange condition of extremely high dead-time was observed in a PM_{2.5} sample. The reason was promptly determined as an overwhelming amount of chlorine. Corresponding airborne concentration (which refers to a week average) was calculated to be of 14000 ng/m³ of chlorine carried in particles of aerodynamic diameter below 2.5 μm. Since then, care has been taken to properly identify cases such as this. The study of a 12 years series of airborne samples shows that several similar chlorine concentrations above 1000 ng/m³ did occur since 1995 in the Lisbon area or nearby. Maxima values for these cases show an average tendency for growing since 1995 up to present. Additional studies, including nuclear microprobe studies showed strange chlorine containing structures in the samples. These analysis also showed that chlorine containing particles have micrometer or even sub-micrometer sizes, and therefore should be seen as potentially harmful for Man. Elemental correlation studies point to a marine signature that is not compatible to the estimated size of the particles, at least if sea salt spray is assumed to be the origin. XRD studies showed no NaCl signature, which nevertheless corroborates a non-sea salt spray possibility. Finally, recent data that came to be available on the increase of the incidence of diabetes mellitus in Portugal in the years of 2004 and 2005 rises important questions.

Keywords: Airborne particles, PM_{2.5}, health impact, chlorine.

INTRODUCTION

The common atmospheric Cl species are Cl, Cl₂, Cl₂O, HOCl, HCl, BrCl and ClONO [1] and sea salt spray, which are either gases or particles having an aerodynamic diameter (A.D.) larger than 2.5 μm. In particles having A.D. below this, Cl is normally absent or present in low amounts. On the other side, the lungs of an adult man have about 300 millions of alveoli [2], which are small interconnected bubbles of 0.2 mm in diameter and less than 0.5 μm in wall thickness. Considering the whole area concerned, the alveolar system corresponds to roughly 80 m² and is therefore the greatest contact area of the human body with the outside environment [3].

The alveoli are covered from the inside (the side exposed to the atmosphere) with a fine layer of a special phospholipid surfactant, fundamental for the lungs functionality [4], which is synthesized in the alveolar type II cell. One of the main physical properties of the lung surfactant is its surface tension, which suffers variations in the normal alveoli expansion-compression during respiration. In this process, some surfactant molecules leave the alveoli surface, during compression and form micelles. During the alveoli expansion surfactant molecules return to the alveoli surface. It is therefore reasonable to assume that if particles having physical diameters less than 1 μm reach the alveoli (PM_{2.5} particles can easily have physical diameters less than that) can be trapped in these micelles and thus gain favouring conditions for

crossing of the blood-gas interface and reach the blood vessels. Consequences of these processes for toxicology of nanoparticles (assumed to have less than 100 nm in diameter) have been recently addressed in detail by Wallace et al. [5] in respect to diesel soot and silicate dust particles. The results there presented can nevertheless be easily expectable to be applicable to other cases such as the present one relating chlorine containing particles. Furthermore, Oberdöster[6] has shown recently that nanometer sized particles can also diffuse within the animal body in very complex ways, and as it is pointed by Dos Reys [7] some chlorine compounds, once in the body, may strongly affect the endocrine system. In this paper we present a set of observations which we feel deserve the attention of the scientific community as they may be present in other databases and may configure an elusive expression of an environmental hazard.

MATERIAL AND METHODS

Airborne PM10 particles were collected in dual mode (separate PM2.5 or fine mode, and PM10-2.5 or coarse mode) in the Lisbon and vicinity area from January 1995 up to December 2006, using Gent samplers [8] or a home made (ITN) prototype sampler derived from the Gent samplers. Samples collected since 1995 up to 1998 were sampled at Faralhão, about 40 km South from Lisbon using a Gent sampler and a week base filter replacement procedure already described in detail in previous publications [9,10]. The ones collected from 1999 up to 2003 were sampled at the ITN Campus, in the North-East Lisbon outskirts, using a Gent sampler, in a twice a week 24 hours continuous sampling methodology, also described in detail in Alves(1998) [9]. A comparison between the twice a week sampling procedures and the intermittent collection method, was also made by Alves in 1998 [9]. There, it is shown that apart from details, the two methods are essentially equivalent, the intermittent collection being potentially capable of a better full time representativity, at the same time as it allows for a reduction of the number of collected samples.

Since January 2004, up to the present, samples have been collected at the ITN Campus using an ITN prototype sampler derived from the Gent sampler. In this case a weekly-based sampling methodology (the same as used at Faralhão from 1995 to 1998) was used. The ITN design system, although essentially identical to the Gent samplers, contains some improvements and is described in detail in another communication at this conference[11].

All filters were weighed, before and after sampling, on a 10 µg sensitivity balance up to 2000, and since then on a 0.1 µg sensitive micro-scale. After weighing,

used filters were kept at -30°C until they were prepared for PIXE analysis. Proton beam energies of 1.22 MeV and 2.12 MeV were used for determination of elements with $Z \leq 20$ (Ca) and $Z \geq 20$, respectively, and all spectra were analysed using AXIL[13] and DATTPIXE [14] codes. Results for Ca were compared for control purposes. Data thus obtained for the temporal series of PM2.5 and PM10-2.5 fraction was handled using the SYSTAT® v11 commercial code, to determine the correlation matrices for the elements concentrations time series for: Al, Si, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn and Pb, without any prior standardization. SYSTAT® v11 was also further used to perform factor analysis on these more than 700 data points and identify the main sources present in the Lisbon and surrounding areas.

In the special case of the two 2004 samples presenting overwhelming chlorine concentrations, nuclear microprobe and XRD analysis were also carried out.

RESULTS AND DISCUSSION

TABLE 1: Factor loadings for each of the 4 factors found in PM2.5 data.

	<i>a</i> <i>Dust</i>	<i>b</i> <i>Fuel</i>	<i>c</i> <i>Industry</i>	<i>d</i> <i>Chlorine</i>
Al	0.9	0.1	0.0	-0.0
Si	0.9	0.1	-0.0	0.0
S	0.4	0.6	-0.1	0.0
Cl	-0.1	-0.2	0.1	0.6
K	0.4	0.3	0.4	0.4
Ca	0.4	0.3	0.4	0.4
Ti	0.1	0.2	-0.2	0.7
V	0.1	0.9	0.3	0.1
Mn	0.7	0.2	0.4	0.0
Fe	0.7	0.1	0.5	0.1
Ni	0.2	0.8	0.4	0.0
Cu	0.1	0.1	0.8	0.1
Zn	0.1	0.2	0.7	-0.0
Pb	-0.1	0.5	0.4	-0.1

In Fig. 1 the results for the time series of chlorine concentrations in the PM2.5 fraction determined since January 1995 up to December of 2006 are presented. It becomes clear that before the year 2000 (1827 to 2192

days of experiment), very few measurements reported values above $1 \mu\text{g}/\text{m}^3$.

In Fig. 1, the time series of the factor scores of the factor classified as the chlorine factor in the sequence of the factor analysis made using the full data sets, is also presented. It is interesting to note that the most intense factor score found occurs in the 29th of June of 2000 (just before day 2000 of the experiment), although in this day, a well below $1 \mu\text{g}/\text{m}^3$ concentration of chlorine was found (see Fig. 2 also).

The complete factor analysis of the PM2.5 data yield four factors, which factor loadings are presented in Table 1 and is discussed elsewhere [15]. Fig. 2, shows the factors scores for these four factors against the measured Cl concentration in PM2.5.

FIGURE 1. Time series for Cl concentration in PM2.5 airborne particles and the factor scores of the Cl factor for the whole 1995 to 2006 period. Day 0 of the experiment is the 15th of January of 1995.

Based on the factors composition in the correlation space, the following interpretation was made: factor *a*) associated with Al and Si, Saharan dust contribution (see ref [12]), factor *b*) associated with Ni and V, fuel powered industries contribution, factor *c*) associated with Cu, Zn and Pb, general industry, mainly coal powered. contribution, and finally, factor *d*) associated with chlorine, could not be interpreted in any specific way and was therefore named the chlorine factor. It is interesting to realise here that a chlorine factor has already been identified in two previous works related to a biomonitoring survey carried out in Portugal in 1993 [16,17]. In Fig. 2 it can be seen that while no significant correlation is obvious for concentration values below $1 \mu\text{g}/\text{m}^3$, above this value it can be seen that both the chlorine and the general industry factor present a positive correlation while there is a negative correlation for the fuel powered industries factor and no correlation what so ever for the Saharan factor.

In Fig. 3, nuclear microprobe scan images from one of the samples showing the very high and most important registered events is presented. In this case the Na-Cl correlation is well identified pointing to a marine signature associated to this events, also seen in the composition of the chlorine factor.

FIGURE 2. Factors scores as function of Cl concentration in PM2.5 airborne particles for the whole 1995 to 2006 period.

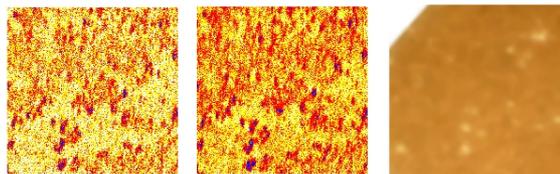


FIGURE 3. Left and middle $200 \times 200 \mu\text{m}$ nuclear microprobe scan results for Na and Cl. Right, Optical microscope image of the scanned region. Mismatch is not total as the optical photograph was not obtained in the irradiation chamber. The sample was collected on the week starting in the 13th December 2004.

Still, the XRD analysis of this sample did not confirm the presence of sodium chloride and the spectra could only be understood if complex chlorine containing compounds were present, (an organic compound containing Na and Cl being a possible candidate) as a single intense x-ray scattering line was observed.

In the case of the highest concentration other high chlorine concentration samples observed in the nuclear microprobe, no structures could even be found, thus pointing to even smaller dimensions of the chlorine containing particles.

In Fig. 4 a comparison between the maxima concentrations of chlorine measured for each year and the registered incidence of diabetes mellitus in Portugal is made. A striking similarity that can be found between both results raises a very important question about the possibility that there might exist a cause-effect relation behind these results. It should be stressed that these are annual data and therefore the time coincidence observed occurs within one full year.

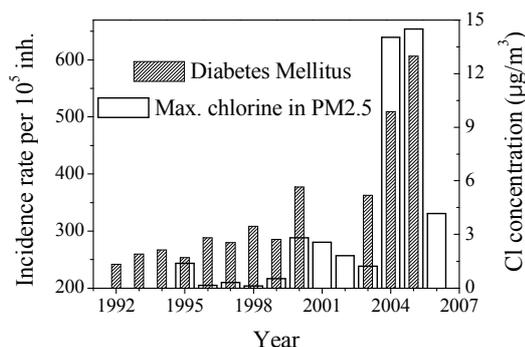


FIGURE 4. Comparison between the numbers of incidence of diabetes mellitus in Portugal per 100000 inhabitants and the year maxima value of either daily (between 1999 and 2003) or week averages of concentration of chlorine in PM2.5 fraction of airborne particles. Incidence data from refs [17].

CONCLUSIONS

Although it refers to just a very small number of data points and therefore, statistical inference cannot be made, an increase of more than 100 cases per 100000 in the incidence of diabetes mellitus in Portugal registered in 2004 and 2005 (30% increase in the case of 2004) [17,18], cannot be easily understandable. This whole sequence of fact strongly points to a problematic possibility that the high chlorine concentrations in PM_{2.5} events may be having a strong negative health impact in the population, whether this is indeed true or not, requires further investigation, but should definitely be carried out.

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