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Physical and chemical properties of particulate air pollution in major cities by portable sensors

Large Nanoparticle Air Pollution in Madrid

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Abstract

Nanoparticles act like vehicles of transport for dangerous substances toward the lung. In this poster we present measurements of nanostructures which are in suspension in the air of Madrid, with special emphasis on combustion generated particles on which Polycyclic Aromatic Hydrocarbons are adsorbed.

Introduction

Nanoparticles are susceptible of being caught in our lungs when we inhale them, because due to their reduced size, they are scarcely filtered in the nose. Therefore, it is important to know the amount of damage that these minuscule particles can cause to human health. Consequently we have to know the quantity of such particles in the air we breathe.

An important adverse health effect (lung cancer) is caused by Polycyclic Aromatic Hydrocarbons (PAHs), which are formed in any incomplete combustion of organic material [1]. A significant source for PAHs in the environment are combustion engines, especially diesel-powered vehicles (the amount of PAHs produced depends considerably on the fuel and the combustion conditions). These large and flat molecules are hydrophobic and are adsorbed at the surface of suspended soot particles. The carbonaceous soot particles are also formed in combustion. Those nanoparticles act as transport vehicles for PAHs into the lung. There, the cells try to get rid of the PAHs by making them water-soluble. In this oxidation process the ultimate carcinogen is formed which irreversibly binds to the DNA. This is a first step in cancer genesis [2].

We have carried out the two following nanoparticle measurements:

- Total particle surface determination by Diffusion Charging (DC): We measure the current of nanoparticles which have previously been charged by a glow discharge. For particles with diameters less than 100 nm (because of the mean free path of the ions in the gas is sufficiently large for this size of particles), this measure yields the total effective cross section of the particles (the "active surface"), independent of their surface chemistry.
- Surface coverage with PAHs, determined by Photoelectric Charging (PC): In the PC device, the aerosol is irradiated with ultraviolet light, ionizing the nanoparticles carrying PAHs (this charging is not effective for the larger microparticles). The measured current of the charged particles is proportional to the total mass of adsorbed PAHs. At ambient temperature only the PAHs with more than four rings are adsorbed on the nanoparticles.

The values obtained with PC are strongly related with the amount of PAHs in the air. Concretely, the measures given by PC are proportional to the total mass of nanoparticles which carry adsorbed PAHs with 4 or more rings [3], because the presence of these flat molecules causes a strong increase in photoelectric yield. On the other hand, the measures obtained by DC are independent of nanoparticle surface chemistry [4].

The ratio between the PC and DC signal allows one to determine the source of the combustion particles [3]. This ratio gives us a value proportional to the photoelectric yield per unit surface (active surface) of the soot particles. For example, we can distinguish between particles stemming from diesel combustion with particles from cigarette smoke by their different active surface.

PC is sensitive only to particles having PAHs adsorbed, that is, combustion aerosol, whereas DC will also measure other nanoparticles [5].

PAHs are very stable molecules, therefore they are resistant to oxidation by air. On the other hand, ultraviolet light (on a sunny day for example) together with oxygen will degrade the PAHs so that they lose their hydrophobic character and become water-soluble. Nevertheless, the meteorological influence to our measurements is small, since the detection is immediate, carried out in the vicinities of the sources (that is, urban highways). Because of the low temperatures in November (when the presented measurements were carried out) less PAHs will thermally desorb from the particles than on a hot summer day.

Measurements

We present measurements carried out using two portable sensors who measure nanoparticles in gas suspension by diffusion charging (DC) and by photoelectric charging (PC).

The calibration of the DC- and PC-sensors was carried out in Zurich in a street tunnel (Gubrist tunnel). The aim was to compare the data from Madrid with those obtained in other large cities around the globe.

The Zurich- and the Madrid-measurements have been carried out inside of a car with open windows. The sample inlet was located inside of the vehicle. The car was travelling on the main highways trough the capital of Spain (Madrid). The DC-and the PC-sensor recorded data every 10 seconds.

The day when the measurements were carried out was sunny and clear, but cold (temperatures about 14°C). There were no traffic jams except in the main shopping street ("Gran Vía").

Graphic 1 shows the route which was taken, leading through downtown (drawn in clear grey). It was the 25th November 1999 between 4 and 5 p.m. We attach typical photos. In the graph, some peaks can be observed where the value of PC exceeds the value of DC in an approximate factor of 1.5. This ratio is typical for diesel engines [3]. Certainly, at those moments, we circulated in the vicinity of a truck or a bus, like it is shown in the corresponding pictures (see photos 2, 4, 6, ...). In general, the average PC and DC values were 1325 ng/m^3 and 1430 a.u. respectively.

Graphic 2 shows a journey around downtown (itinerary in dark grey on the map), carried out at the same day, between 1:30 and 2:15 p.m.. Here also, we have reached high average values of PC and DC of 996 ng/m^3 and of 1194 a.u., respectively.

Graphic 3 (without photos) corresponds to the journey drawn in white on the map (University City). Those measurements were carried out the following day in the evening (between 7:47 and 8:00 p.m.). The itinerary was a round trip on the same road. Here also, the average values of PC and DC are very high.

Conclusion

The measurements carried out in Madrid on November 25. and 26., 1999 give an average value for PC of 1075 ng/m^3. Those carried out in Paris in September 1997 give an average value for PC of 659 ng/m^3. The measurements from Tokyo give an average value for PC of 926 ng/m^3 [3].

It is surprising and worrying that such high values are obtained in Madrid, especially concerning the PC case. We inculpate this high value in PC to the large number of automobiles with diesel engines (The registered diesel-using vehicles in Spain increased from 21,79% in 1987 to 46,20 in 1996 [*]), as well as to the antiquity of the automobile park. Another important factor is the combustion of coal for heating purposes, which is still used in many old buildings.

Finally, we want to point out that there are fuel additives available, such as $Fe(C_5H_5)_2$ (ferrocene), which facilitate the burnout of the particles trapped in an additional filter [6] (placed in the exhaust pipe) at exhaust temperatures. In fact, such a system is already in use, allowing a reduction of 99% in emitted soot particles and PAH [**]. We hope that such systems become mandatory in order to have clean air for breathing.

References

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[2] M.F.Denissenko, A. Pao, M.S. Tang and G.P. Pfeiffer, *Science* **274** (1996) 430.
[3] K. Siegmann and H.C. Siegmann. "Nanostructure in gas suspension", *Rev. Mex. Fis.* **45** (2)(1999) 182-188.
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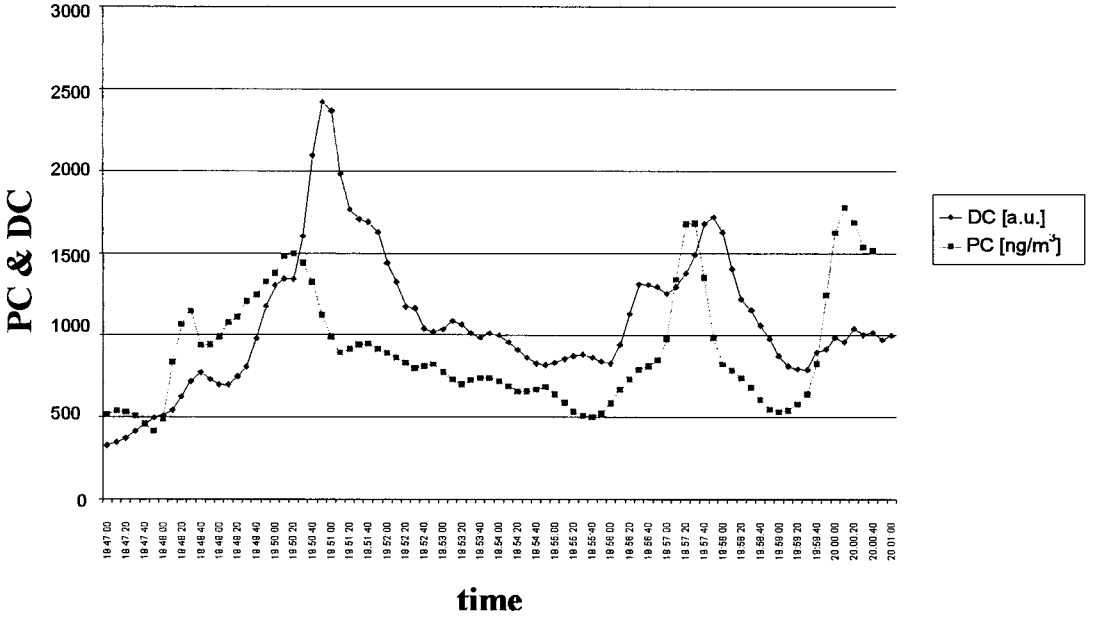
[5] M. Ammann et al., *Geophys. Res. Lett.* **19** (1992) 1387.
[6] A.Mayer *et al.*, *SAE International* **980539** (1998) 127.
[*] Information obtained by *http:/www.dgt.es/iboletin/vehiculos/matric6.html*
[**] "Un filtre à particules diesel en série dès le début 2000", *Ingénieurs de l'Automobile*, Avril 1999, Page 14.

Itineraries through Madrid where we carried out the measures

Graphic 3: University way 3 (UCM), 26.11.99

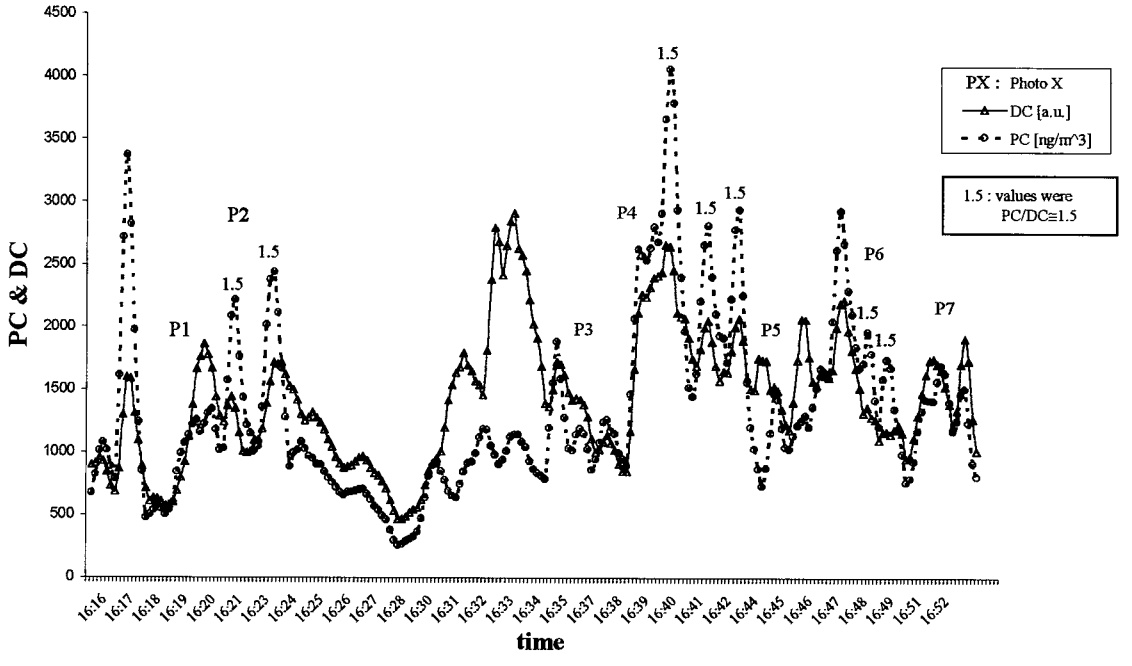
PC average : 905 ng/m^3, DC average : 1078 a.u.

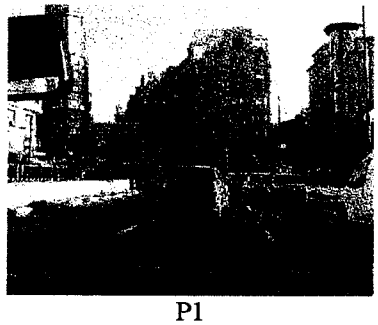


Graphic 3 : Also in the University City (UCM) there are very high concentrations of nanostructures in suspension in the air we breath.

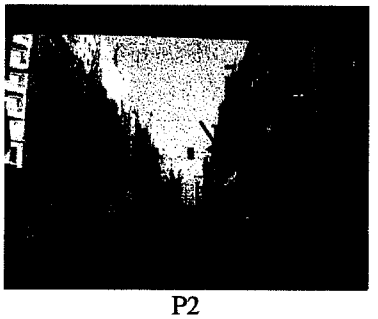
Graphic 1: Center way 1 through Madrid, 25.11.99

PC average : 1325 ng/m^3, DC average : 1430 a.u.

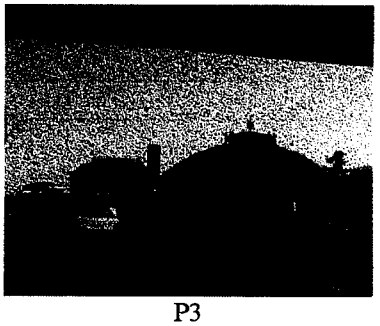




P1



P2



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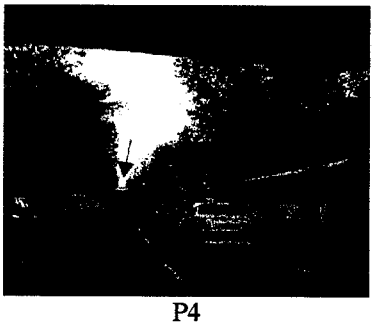

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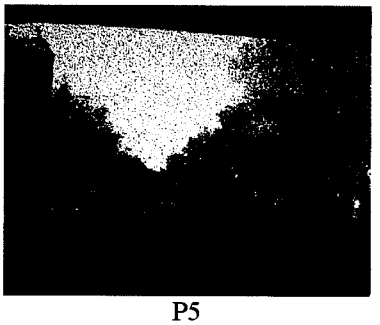

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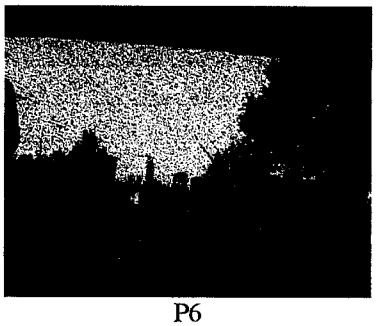
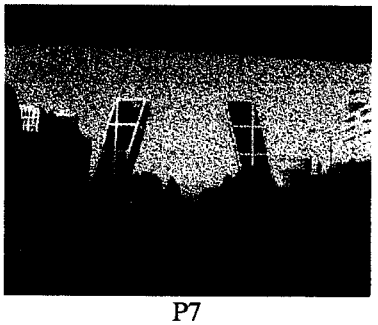


P6

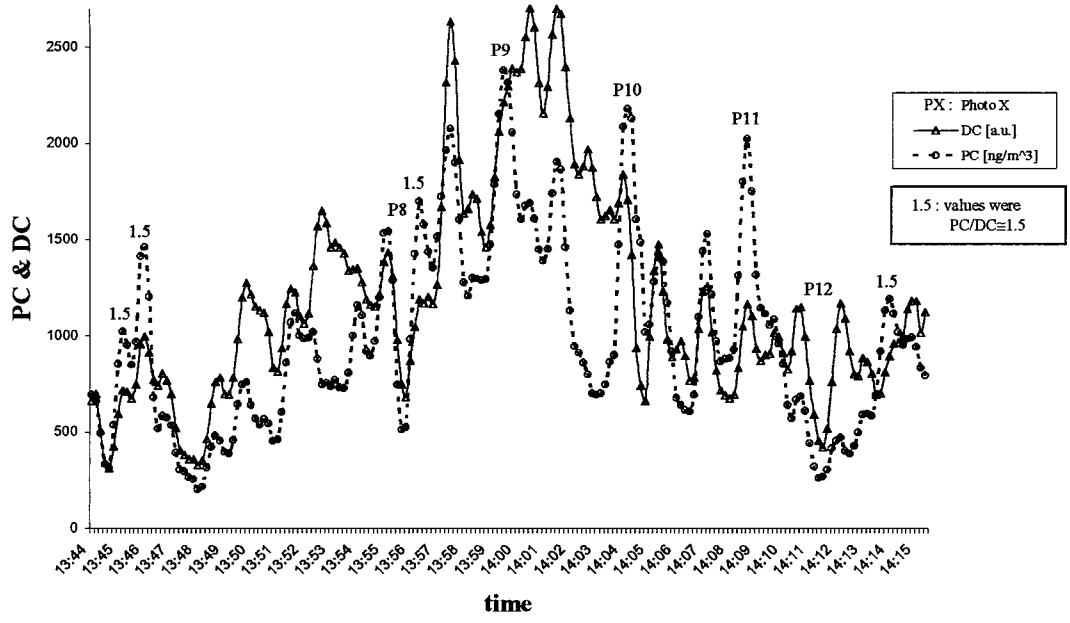


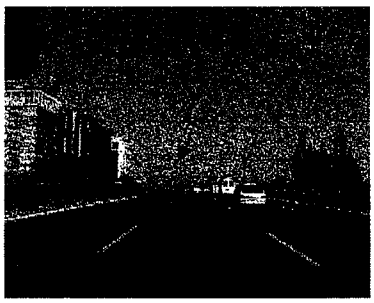
P7

Photos to graphic 1: In the photos P2, P3 and P4 we have indicated the vehicle (bus or truck) where have produced a value of PC who exceeds the value of DC in an approximate factor of 1.5. In P1, P3, P5 and P7 de levels of PC was smaller bad also high.

Graphic 2: Round way 2 around the dowtown of Madrid, 25.11.99

PC average : 996 ng/m^3, DC average : 1194 a.u.

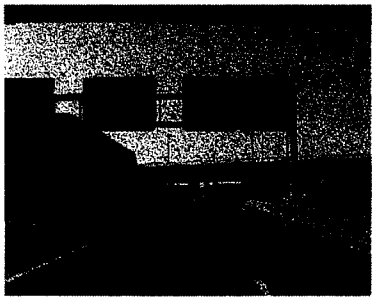




P8

P9

P10



P11

P12

Photos to graphic 2: In the photos P8, P9, P10 and P11 we can see the vehicle (bus or truck) where have produced a value of PC who exceeds the value of DC.