THE REDMAAS 2014 INTERCOMPARISON CAMPAIGN: CPC, SMPS, UFPM AND NEUTRALIZERS

F. J. Gómez-Moreno[1], E. Alonso[1], B. Artíñano[1], S. Iglesias Samitier[2], M. Piñeiro Iglesias[2], P. López Mahía[2], N. Pérez[3], A. Alastuey[3], B. A. De La Morena[4], M. I. García[5], S. Rodríguez[5], M. Sorribas[6,7], G. Titos[6,7], H. Lyamani[6,7], L. Alados-Arboledas[6,7], E. Filimundi[8] and E. Latorre Tarrasa[9]

Abstract —The Spanish network on environmental DMAs (Red Española de DMAs Ambientales, REDMAAS), working since 2010, is currently formed by six groups involved in the measurement of atmospheric aerosol size distributions by means of Differential Mobility Analyzers (DMAs). One of its activities is an annual intercomparison of mobility size spectrometers (SMPS and UFPM). In this work we show the results obtained in the 2014 campaign: the verification of DMA calibrations with latex, the results of the CPC and SMPS + UFPM intercomparisons, and a comparison of the new TSI 3087 X-ray and the former TSI 3077 ^{85}Kr neutralizers. The concentrations measured by different types of CPC were within the range of 10% of the average value. CPCs working at higher flow rates measured slightly higher concentrations, probably related to the smaller losses in the lines. All the SMPS worked at the same sampling and sheath flow rates (1:10 lpm). Four of the SMPS gave very good results for particles larger than 20 nm. The UFPM measured particle number concentrations in the average +/-10% band measured by the SMPS. Instruments working with the X-ray neutralizer measured higher concentrations than with the ^{85}Kr neutralizers. This could mean that particle losses are smaller inside this neutralizer.

Keywords — Atmospheric aerosols, Particle size distribution, SMPS, UFPM, X-ray neutralizer

1 INTRODUCTION

Atmospheric particle size affects the particle behavior and provides information about its origin and history. Size distributions are a key parameter in those processes where the atmospheric aerosol is involved. For example, a critical point in health effect studies is to obtain the fraction of particles deposited in the lungs and the respiratory system in general, as well as those able to penetrate into the bloodstream. These effects are mainly dependent of the particle size distribution. Some studies have shown that the particle toxicity per mass unit increases as the particle size decreases [1, 2], and therefore, an important goal is to study the smaller particles or ultrafine particles.

The radiation-matter interaction processes known as scattering and absorption also depend on the particle size. Atmospheric particles play a key role in the Earth's radiative balance and thus influence climate change [3]. Some climate models indicate that aerosols are delaying the expected warming due to the greenhouse gases. Sulfate and organic particles have a particular influence on this delay and both kinds of particles are mainly found in the ultrafine range.

In addition to those works focused on particle formation by nucleation [4], the origin and distribution of ultrafine particles has been studied in different kinds of stations: rural [5], regional background [6, 7], arctic and coastal background [8], tropospheric background in Antarctica [9] ... but mainly in urban sites in some European and American cities, e.g. Birmingham [10], Helsinki [11], Pittsburgh [12], Barcelona [13].

The Spanish network on environmental DMAs (Red Española de DMAs Ambientales, REDMAAS) is currently formed by six groups involved in the measurement of atmospheric aerosol size distributions by means of Differential Mobility Analyzers (DMAs). These groups are: IUMA-UDC, IDÆA-CSIC, INTA, IARC-AEMET, University of Granada and CIEMAT. This network has been working since 2010. Its objective is to promote the exchange and transfer of knowledge between the

1. *Department of Environment, CIEMAT, Madrid, E-28040, Spain, First Author E-mail: FJ.Gomez@ciemat.es*
2. *Grupo Química Analítica Aplicada, Instituto Universitario de Medio Ambiente (IUMA), Departamento de Química Analítica, Facultade de Ciencias,Universidade da Coruña, Campus de A Coruña, 15071 A Coruña, Spain*
3. *Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, E-08034, Spain*
4. *Atmospheric Sounding Station 'El Arenosillo', INTA, Mazagón-Huelva, E-21130, Spain*
5. *Izaña Atmospheric Research Centre, (IARC/CIAI), AEMet, Santa Cruz de Tenerife, E-38001, Spain*
6. *Andalusian Institute for Earth System Research, IISTA-CEAMA, University of Granada, Granada, E-18071, Spain*
7. *Applied Physics Department, University of Granada, Granada, E-18071, Spain*
8. *TSI GmbH, Aachen, D-52068, Germany*
9. *Álava Ingenieros, Madrid, E-28037, Spain*

groups and to optimize the use of instrumentation such as the Scanning Mobility Particle Sizers (SMPS). This is reached through a series of activities to ensure the quality of the measurements and the cooperation between the groups. One of the activities of the REDMAAS is an annual campaign where DMA calibration checks, and Condensation Particle Counters (CPC), UltraFine Particle Monitor (UFPM) and SMPS intercomparisons are performed. In this paper we introduce the results obtained during the 2014 campaign.

2 CAMPAIGN LOCATION AND INSTRUMENTATION

2.1 Location

The intercomparison campaign was held in the Atmospheric Sounding Station El Arenosillo (37.10°N, 6.73°W, 40 m a.s.l.) belonging to Instituto Nacional de Técnica Aeroespacial (INTA) (www.inta.es/atmosfera) [14]. The observatory is located on the Atlantic coast of Andalusia, in the province of Huelva and within the Natural Area of the Doñana National Park. Around the observatory, from W to SE and clockwise over several tens of kilometers, it is possible to find a tree forest with predominance of pine. The Atlantic Ocean is in the SE-W clockwise area and less than 1 km from the observatory. The closest large population is the City of Huelva (160 000 inhabitants), 35 km to the northwest. This location allows the research of wide and different kinds of particle size distributions, covering several orders of magnitude for the particle concentration (from marine aerosols to secondary formation from industrial and natural precursors).

2.2 Instrumentation

In the 2014 intercomparison campaign, all the groups except AEMET participated. TSI and their Spanish representatives, Álava Ingenieros, were also involved with the new electrostatic classifier TSI 3082. During the campaign 7 CPCs (3x3772, 2x3776, 1x3785 and 1x3775), 5 SMPSs (4x3080 and 1x3082) and 1 UFPM (3031) were deployed, all of them manufactured by TSI. At the same time a new TSI 3087 X-ray and the former TSI 3077 ^{85}Kr neutralizers were used.

This campaign was performed from February 17th to 21th, 2014. The instrument deployment used during the campaign can be found in Fig. 1.

Fig. 1. In this figure it is possible to see the five SMPSs used during the instrument intercomparison.

3 RESULTS

3.1 DMA calibration checks

As in other REDMAAS campaigns, previously to the intercomparisons, a general routine maintenance was performed to ensure proper operation of the different instruments. A Gilian Gilibrator-2 just calibrated was used as primary standard for the calibration of air flows. The difference in the flow rates among the different CPCs was less than 5% and among the SMPS systems the sheath flow rate difference was less than 4%.

The high voltage sources were checked using a HV probe and all the instruments showed a deviation smaller than 0.3% in the calibration.

After these verifications, the DMAs calibrations were checked by using latex particles of 80 and 190 nm suspended in water and aerosolized using a Collinson atomizer [15].

During this campaign, the deviations obtained were higher than during the previous ones, reaching an average value of 6.3% for the 80 nm particles and 5.4% for the 190 nm ones. It is remarkable that the deviation among the instruments were very small, indicating that the problem could be in the generating system, not in the instruments.

3.2 CPC intercomparison

The second activity was the CPC intercomparison. All used butanol as condensation liquid, with the exception of one water-based CPC (TSI 3785). Ambient air was sampled from a common flow splitter, which was connected to an external probe. The results have been classified into two groups, depending on the CPC flow rates. The first group corresponds to the CPCs working at 1 lpm and the second one with those running at 0.3 or 1.5 lpm. During this intercomparison both flow rates were checked for this second group showing lower concentrations than the first group for 0.3 lpm and higher ones for 1.5 lpm. The reason for these differences is the diffusional losses in the lines,

smaller as the resident time is shorter (higher flow rates). The differences among the CPCs inside each group are smaller than 10% as can be seen in fig. 2.

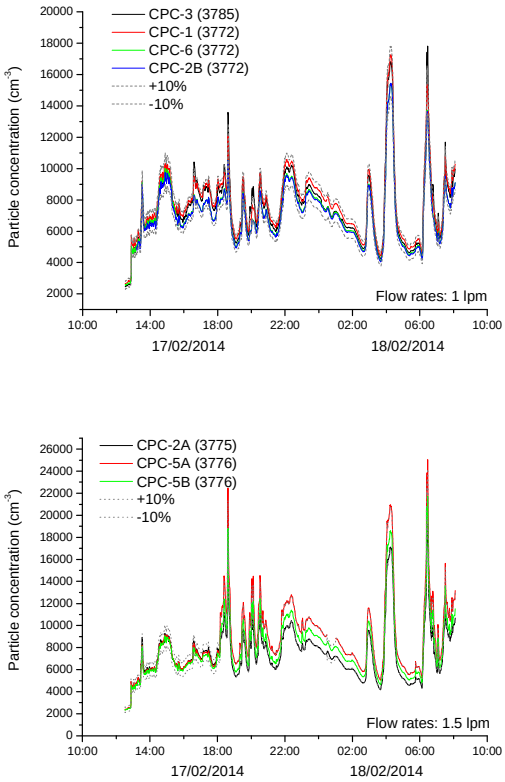


Fig. 2. CPC intercomparison during the campaign. They have been classified by their working flow rates.

3.3 SMPS and UFPM intercomparison

The SMPS intercomparison for a selected period is shown in Fig. 3. All SMPS systems worked at the same sampling and sheath flow rates (1:10 lpm).

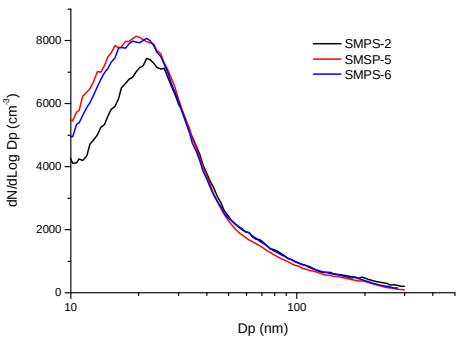


Fig. 3. SMPS measurement comparison for systems 2, 5 and 6. The results obtained are very good for particle sizes larger than 20nm. Below this size, it is very usual to find important differences among the instruments.

In this figure, SMPS-1 is not included as it worked with the new TSI X-Ray neutralizer (see next section). SMPS-3 is also not included because of a leak observed during the measurements. The differences between the three systems shown in the graph are important below 20 nm, a size range where the differences among the instruments have shown to be very large [16]. Above this particle diameter, the differences are very small. SMPS-1 is compared with SMPS-6 in figure 5a, where, again, the differences are small for particles bigger than 10 nm. The four systems have shown to have a good behavior.

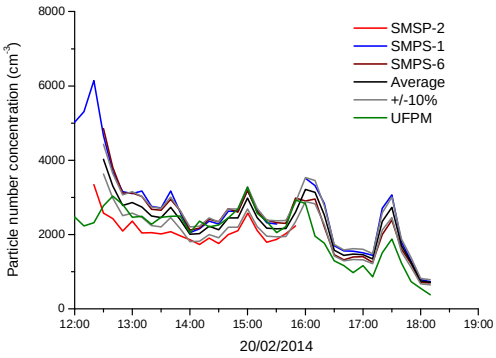


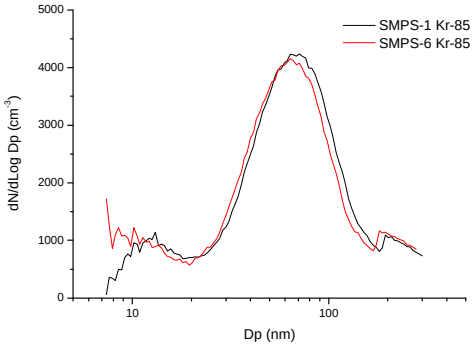
Fig. 4. Comparison of particle concentrations measured by the SMPSs and the UFPM.

The UFPM was also compared with the SMPSs. The period covered with these instruments can be found in figure 4. This figure shows the total particle number concentration measured by the 4 systems, the SMPS average values and the average +/- 10% band for these values. During the first period, before 16h, the UFPM measured properly the number concentration. SMPS-2 measured a lower concentration. This could be caused by a distribution with high concentrations of particles below 20 nm, where this SMPS measured smaller concentrations. After 16h, concentrations measured with SMPS-2 are within the average +/- 10% band, but the UFPM is below that band. The matrix selected in the UFPM was the factory calibration with ammonium sulfate.

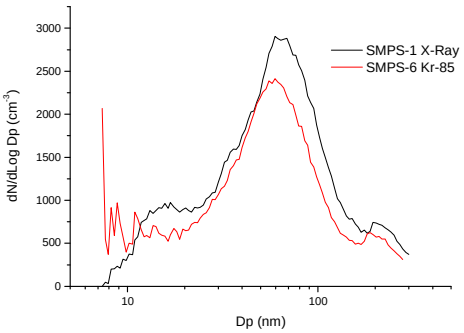
3.4 Neutralizer intercomparison

In order to check the new TSI X-ray neutralizer model 3087 (< 9.5 keV), the Kr-85 source was removed from the SMPS-1 and the X-ray neutralizer was installed. This SMPS was previously compared with SMPS-6 proving to measure very similar distributions when using both instruments the Kr-85 neutralizer, as it can be observed in fig. 5a. Subsequently, both systems were working during 16 hours with the different neutralizers and the average distributions obtained are shown in fig. 5b and 5c. The first and second graphs reflect to periods with

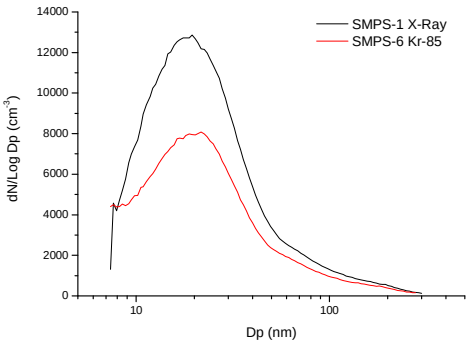
low and high particle concentrations, respectively. It is possible that the new X-ray neutralizer has lower particle losses than the Kr-85 one. The differences between the neutralizers seem to depend on the particle concentration, as they were more evident as the number concentration increased. At the moment, in the TSI AIM software there is no option to indicate which neutralizer is in use, so when applying correction for diffusion losses it considers the same losses in both cases.



(a)



(b)



(c)

Fig. 5. Comparison of SMPS-1 and SMPS-6 measurements when: a) both had a Kr-85 neutralizer; b) SMPS-1 had an X-Ray neutralizer and the particle concentration was low; c) as b, with high particle concentration.

8 Conclusions

The instruments belonging to the Spanish network on environmental DMAs (REDMAAS) had shown similar behaviors during the 2014 campaign. CPCs working at higher flow rates measured slightly higher concentrations, probably related to the smaller losses in the lines. Taking this into account, particle concentrations measured by the different types of CPC were within the range of 10% of the average value. Four SMPSs have given good results for particle sizes above 20 nm. The X-ray neutralizer has shown to have smaller losses than the traditional Kr-85 source. The total number concentration measured with the UFPM was also within the average +/- 10% band measured by the SMPSs.

This kind of campaign is very useful as it allows detecting instrumental problems that are difficult to detect during routine operation of the instrumentation at the stations.

Acknowledgment

This work has been financed by the Ministry of Science and Innovation (CGL2011-15008-E, CGL2010-1777, CGL2011-27020 & CGL2011-26259). E. Alonso acknowledges the FPI grant to carry out the doctoral thesis/PhD at the Energy, Environment and Technology Research Centre (CIEMAT). P. Esperon is acknowledged for her technical support. M. I. García acknowledges the grant of the Canarian Agency for Research, Innovation and Information Society co-funded by the European Social Funds.

References

[1] J.J.N Lingard, A.S. Tomlin, A.G. Clarke, K. Healey, A. Hay and C.P. Wild, “A study of trace metal concentration of urban airborne particulate matter and its role in free radical activity as measured by plasmidstrand break assay,” Atmos. Environ., 39, pp. 2377-2384, 2005.

[2] G. Oberdorster, “Toxicology of ultrafine particles: in vivo studies,” Phil. Trans. R. Soc. A, 358, 2719-2740, 2000.

[3] Climate change 2007: synthesis report. In: Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, R.K Pachauri, A. Reisinger, eds. IPCC, Geneva, Switzerland, 2007.

[4] M. Kulmala, H. Vehkamäki, T. Petäjä, M. Dal Maso, A. Lauri, V.-M. Kerminen, W. Birmili and P.H. McMurry, “Formation and growth rates of ultrafine atmospheric particles: a review of observations,” J. Aerosol Sci., 35, pp. 143–176, 2004.

[5] J.M. Mäkelä, P. Aalto, V. Jokinen, T. Pohja, A. Nissinen, S. Palmroth, T. Markkanen, K. Seitsonen, H. Lihavainen and

M. Kulmala, "Observations of ultrafine aerosol particle formation and growth in boreal forest," Geophys. Res. Lett., 24, pp. 1219-1222, 1997.

[6] M. Cusack, N. Pérez, J. Pey, A. Alastuey and X. Querol. "Source apportionment of fine PM and sub-micron particle number concentrations at a regional background site in the western Mediterranean: a 2.5 yr study," Atmos. Chem. Phys. Discuss. 13, pp. 3915-3955, 2013, submitted for publication in ACP.

[7] M. Cusack, N. Pérez, J. Pey, A. Wiedensohler, A.Alastuey and X. Querol, "Variability of sub-micrometer particle number size distributions and concentrations in the Western Mediterranean regional background," Tellus B, 65, pp. 19243, 2013.

[8] M. Sorribas, V.E. Cachorro, J.A. Adame, B. Wehner, W. Birmili, A. Wiedensohler, A.M. De Frutos and B.A. de la Morena, "Sub-micrometric aerosol size distributions in Southwestern Spain: Relation with meteorological parameter". ICNAA. Galway (Irlanda), 2007.

[9] J. L. Gras, "Condensation nucleus size distribution at Mawson, Antarctica: micro-physics and chemistry," Atmos. Environ., 27, Part A, pp. 1417-1425, 1993.

[10] R.M. Harrison, M. Jones and G. Collins, "Measurements of the physical properties of particles in the urban atmosphere", Atmos. Environ., 33, pp. 309-321, 1999.

[11] T. Hussein,, A. Puustinen, P.P. Aalto, J.M. Mäkelä, K. Hämeri and M.Kulmala, "Urban aerosol number size distributions," Atmos. Chem. Phys., 4, pp. 391-411, 2004.

[12] C.O. Stanier, A.Y. Khlystov and S.N. Pandis, "Ambient aerosol size distributions and number concentrations measured during the Pittsburgh Air Quality Study (PAQS)," Atmos. Environ., 38, pp. 3275-3284, 2004.

[13] J. Pey, S. Rodríguez, X. Querol, A. Alastuey, T. Moreno, J. P. Putaud and R. Van Dingenen, "Variations of urban aerosols in the western Mediterranean," Atmos. Environ., 42, pp. 9052-9062, 2008.

[14] M. Sorribas, B. A. de la Morena, B. Wehner, J. F. López, N. Prats, S. Mogo, A. Wiedensohler, and V. E. Cachorro, 2011. On the sub-micron aerosol size distribution in a coastal-rural site at El Arenosillo Station (SW – Spain). Atmospheric Chemistry and Physics, 11, 11185–11206.

[15] K.R. May, "The Collison Nebulizer. Description, Performance & Application," *J. Aerosol Sci*., 4, pp. 235-243 1973.

[16] A. Wiedensohler, W. Birmili, A. Nowak, A. Sonntag, K. Weinhold, M. Merkel, B. Wehner, T. Tuch, S. Pfeifer, M. Fiebig, A. M. Fjäraa, E. Asmi, K. Sellegri, R. Depuy, H. Venzac, P. Villani, P. Laj, P. Aalto, J. A. Ogren, E. Swietlicki, P. Williams, P. Roldin, P. Quincey, C. Hüglin, R. Fierz-Schmidhauser, M. Gysel, E. Weingartner, F. Riccobono, S. Santos, C. Grüning, K. Faloon, D. Beddows, R. Harrison, C. Monahan, S. G. Jennings, C. D. O'Dowd, A. Marinoni, H.-G. Horn, L. Keck, J. Jiang, J. Scheckman, P. H. McMurry, Z. Deng, C. S. Zhao, M. Moerman, B. Henzing, G. de Leeuw, G. Löschau, and S. Bastian: Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions, Atmos. Meas. Tech., 5, 657-685, 2012.