CSCanada
Advances in Natural Science
Vol. 6, No. 4, 2013, pp. 27-34
DOI:10.3968/j.ans.1715787020130604.9026

ISSN 1715-7862 [PRINT]
ISSN 1715-7870 [ONLINE]
www.cscanada.net
www.cscanada.org

Vertical Profiles of Airborne PM in Po Valley During Wheat Harvest Activities

C. Telloli[a],*; F. Coren[b]; E. Marrocchino[c]; C. Vaccaro[d]

[a]PhD. Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Technical Unit for Environmental Assessment Models, Methods and Technologies (UTVALAMB), Air Quality Laboratory, Bologna, Italy.
[b]Professor. National Institute of Oceanography and Experimental Geophysics, (OGS), Trieste, Italy.
[c]Researcher. Department of Earth Science, Ferrara University, Ferrara, Italy.
[d]Professor. Department of Earth Science, Ferrara University, Ferrara, Italy.
*Corresponding author.

Received 6 August 2013; accepted 4 November 2013

Abstract

Po Valley and Friuli Plain in Italy and Belgian Plain in Europe, are areas with the highest concentration of solid particulate matter in all the world (European Space Agency, 2004). This implies that those areas does not respect the limits imposed by European Parliament in 2008.[1] Aim of this study is the characterization of the particulate matter, through direct sampling in atmosphere to define physical properties and source of this particulate. A first campaign has been carried out in June-July 2009 in the Po Valley during farming activities of threshing, by means of a small aircraft (Cessna172P), that has been used as platform for collecting measure particles. Particle concentration has been measured for five aerodynamic equivalent diameters (0.5, 1.0, 2.5, 5.0, 10.0μm) using a laser counter (LIGHTHOUSE HH3016). The acquisition has been carried out vertically profiling the atmosphere from 150 to 2400m. SEM, as well as SEM-EDS analysis on single particles, have been carried out with the aim to obtain detailed dimensional and morphological information to define origin, toxicity and the nature of organic matter (Germani & Buseck, 1991; Grassi, Narducci, & Tognotti, 2004).

[1] European Parliament legislative resolution of 11 December 2007 on the Council common position for adopting a directive of the European Parliament and of the Council on ambient air quality and cleaner air for Europe (16477/1/2006—C6-0260/2007—2005/0183(COD)).

Key words: Air quality; PM_{10}; $PM_{2.5}$; SEM; Particle counter

C. Telloli, F. Coren, E. Marrocchino, C. Vaccaro (2013). Vertical Profiles of Airborne PM in Po Valley During Wheat Harvest Activities. *Advances in Natural Science*, *6*(4), 27-34. Available from: http://www.cscanada.net/index.php/ans/article/view/j.ans.1715787020130604.9026
DOI: http://dx.doi.org/10.3968/j.ans.1715787020130604.9026

INTRODUCTION

In the total PM concentration the natural sources contribute up to 94%, leaving the human factor less than 10% (Chabas & Lefèvr, 2000; Brewer & Belzer, 2001; Querol et al., 2002; Ryall et al., 2002; Bernabé& Carretero, 2003; Bogo et al., 2003; Almeida, Pio, Freitas, Reis, & Trancoso, 2005; Salvador, Artíñano, Querol, Alastuey, & Costoya, 2007). Scientific studies have shown a positive correlation between increased natural particles with increase in anthropogenic particles, but there is no information on the causes of this correlation. Most data relate to exposure in urban and industrial areas, while contributions related to agricultural practices are rarely investigated. The relationship between natural and anthropogenic factors is strongly site depending (Scientific Committee., 2005; Scientific Committee., 2006). The rise of human and industrial activities, especially in big cities, has led to the increased production of aerosols released to the atmosphere. In the lower troposphere, they cause visibility degradation, especially when these aerosols are located in the boundary layer, this is commonly experienced during the dust events (Husar et al., 2001; Reis et al., 2002; Vanderstraeten et al., 2008). In addition, highly concentrated aerosols, also known as suspended particulate matters (SPM), give rise to health problems. Epidemiological and environmental studies (Pope 3rd et al., 1995; Schwartz, Dockery, & Neas, 1996) have shown that exposure to fine particles, especially particulate

matter smaller than 2.5 μm ($PM_{2.5}$), can result in serious respiratory disorders as cardiovascular and respiratory diseases (Abbey, Ostro, & Peterson, 1995; Pope 3rd, 2000; Pope 3rd et al., 2002; Laden, Schwartz, Speizer, & Dockery, 2006; Hopke, 2008; Kelly, 2008), but also to the reduction of light (Vasconcelos, Macias, & White, 1994) to the change of biodiversity and the deterioration of monuments (Sabbioni, 1995; Torfs & Van Grieken, 1997; Maravelaki-Kalaitzaki & Biscontin, 1999; Brimblecombe & Grossi, 2009).

From several European publications between 1987 and 2009, it can be identifies four main sources of PM: locally from vehicles (Amodio, Caselli, Gennaro, & Tutino, 2009) and industrial fuel anthropogenic (Ragosta et al., 2006) and from widely crustal and sea spray of natural origin (Viana et al., 2008). Many of these publications are devoted both to the description of their spatial-temporal behaviour (Chow, Watson, & Lowenthal, 1999; Viana, Querol, Alastuey, Gangoiti, & Menéndez, 2003; Rodriguez et al., 2004) and to the analysis of their chemical composition (Marcazzan, Vaccaio, Valli, & Vecchi, 2001; Mazzei, D'Alessandro, Lucarelli, & Marengo, 2006; Amodio et al., 2008; Takahashi, Minoura, & Sakamoto, 2008; Samek, 2009). In situ concentration of atmospheric particulate, its size distribution and its chemical characteristics depend on emission sources, local meteorology and geographical features (Ragosta et al., 2006). For this reason, it is important to study the behaviour of particulate in zones with specific geomorphologic or anthropogenic characteristics where only few data are available. The scientific community is focusing hazard assessment of pollutants through the establishment of procedures for sampling and analysis and characterization of sources. Such information are generally available for the first meters of the troposphere, while rare are the information on chemical, particle size and morphology in the lower troposphere (from 0 to 2500 m).

This work, through an aircraft, aims to define the particulate before and after the threshing, to know the impact that this agricultural activity produce in the low troposphere behind the boundary layer, using a particle counter. Different studies from the literature concern he use of particle counters to assess air pollution concentration (Tuch, Brand, Wichmann, & Heyder, 1997; Weijers, Khlystov, Kos, & Erisman, 2004) and to investigate the relationship between particle number and particle mass (Harrison, Jones, & Collins, 1999; Hoek et al., 2008). In particular we investigated the nature of particulates in a rural area in the lower Po Valley and see if the major contribution is given either by natural or anthropogenic sources.

1. MATERIALS AND METHODS

The Po Valley is located in the northern of Italy, a flat region surrounded by the Alpine chain in the north and northwest, by the Apennine Hills in the south and by the Adriatic Sea on the eastern boundary. It is a flat plain mostly composed by terrigenous sediments transported and deposited by the river Po. There is a dominant presence of debris, clays impermeable or poorly permeable in the eastern areas proximal to the mouth. The outcropping sediments can be easily eroded an resuspended by wind action and contribute to particulate nature. Two measurements campaigns were carried out during the summer 2009 in an agricultural land in the east part of Po Valley of the Agricultural Cooperative SORGEVA near Argenta (Ferrara, Italy) (Figure 1). The sampling area is one of the greater agricultural area of the Emilia Romagna region, located near the sea in the Comacchio Valleys (44°36'40.79" N—12°04'10.52'' E, -1m). The soil is a silt clay soil, made from terrigenous sediments transported and deposited by the river Po (Bianchini, Laviano, Lovo, & Vaccaro, 2001). The rural area is far enough from the Adriatic Sea and from main and secondary roads, and therefore the contribution of particulate matter from sea spray and anthropogenic pollution from vehicular traffic and other combustion sources is negligible. The area is also far from factories or industries. The power plant Polesine Camerini in Porto Tolle 2640 Mw (RO) (44°56' N—12°19' E, 1m), the only significant source in the area was closed during the campaign. The aerosol background monitoring stations of ARPA Emilia-Romagna[2] "Ostellato", have measured an averaged mean $PM_{2.5}$ concentration of 8±2.6μg/m^3 during threshing operation. The contributions of biomass burning are also zero because there was no combustion event in the nearby area (information from MODIS fire/area burnt) during the sampling.

Figure 1
Map of Sampling Site

[2] ARPA Emilia Romagna—Stazione meteo di Cervia—mese di giugno 2009

In Italy, the wheat is the main grown product and it is farmed in extended fields (AGRIT, 2008). Therefore, the aerosol was sampled during wheat harvest threshing in summer, plowing and wheat sowing in autumn within the emitted plume behind the agricultural machine. The sampling periods were chosen such as to minimize the contribution of anthropogenic sources, therefore they were not affected by strong thermal inversions.

1.1 Sampling and Sample Analysis

The field experiment was performed on June 09 2009 from 11 a.m. to 12 a.m. (GMT+1), before wheat harvesting operations, and on July 14 2009 from 11 a.m. to 12 a.m. (GMT+1) during wheat harvesting operations. In the area, standard meteorological parameters including wind speed and direction, air temperature, relative humidity and others were routinely measured by the meteorological station of the Regional Agency for Prevention and Environment (ARPA) Emilia Romagna (44˚36'01.2'' N 12˚04'37.7'' E). The experiment consisted of two parts. The first part measured the vertical variations of PM in the lower boundary layer of Po Valley, and the second part collected particle aerosol to analyse by SEM. The mission has been conducted in an altitude interval between 150 and 2400m, counting the number of particles of different particle sizes have also been estimated temperature and relative humidity at different altitudes (Tittarelli et al., 2008). The device we used was a particle counter LIGHTHOUSE model HH3016IAQ series #: 080544003, which employs a laser diode optical sensor to detect and count particles in five size ranges: $PM_{0.5}$—PM_1—$PM_{2.5}$—PM_5—PM_{10}. Particles under 0.5μm diameter cannot be detected by the instrument. The particle counter continuously samples air form 150 m to 2400m. The average number of particles counted per litre per minute in each channel is recorded by the data acquisition system. The device was installed on a small airplane CESSNA172P owned by OGS of Trieste, which, starting from Ferrara flew over the study area; here a constant rate spiral climb with a constant vertical speed of almost 500ft/min (2m/s), was performed to profile the air column; the forward velocity component of the aircraft was maintained around 90kts (175km/h). We used also a particular impactor to collect particulate samples. An adduction plastic air tube of 2mm inner diameter was located in the ram air intake on the right wing leading hedge; the tube was exposed off the wing itself to intake undisturbed air; the air flow has then been conducted into a plastic box where the particle counter system was operated. The particle counter such the air by means of a depression constant flow pump that enable the system to operate following the collection protocols for monitoring air particles. The collection of the particles has whereas conducted using the direct flux of ram air because we did not have a suction pump, we assume in this case that because the speed of the aircraft has been maintained steely fixed, this causes the entrance of the ram air in the filter at a constant flow, so you can know the quantity of air passing through the filter. Sampling interval for the particle counter was set to 1 second therefore we acquired a full count on the device we used was a particle counter the six diameters every 2m (vertically). Teflon filters (TEFLO W/RING R2PL047) with a diameter of 47mm and porosity PM_{10} and $PM_{2.5}$ were used for SEM-EDS analysis to characterize the shape and morphology and the elemental composition of aerosol particles collected on the filters. The filters were pre-heated at 800°C for 3 hours before use and were placed in clean polyethylene petri dishes and wrapped with Teflon tape before and after field measurements. After collection, all samples were transported in a refrigerated cooler to UniFe laboratory in Ferrara and stored under refrigeration until microscopy analysis was performed (Hiranuma, Brooks, Auvermann, & Littleton, 2008).

The morphological observations and semi-quantitative chemical analysis were performed at the Centre for Electron Microscopy of University of Ferrara using a Scanning Electron Microscope (SEM) (ZEISS EVO40) equipped with an Energy Dispersive X-ray Spectrometer (EDS) (INCA 300 OXFORD) for X-ray microanalysis. The particle size and the surface morphology of sampled aerosol particles were investigated in high resolution mode (up to 20.000X) with a working voltage of 20kV which correspond to the detection limit of 1μm particle size. The analyses were qualitative and were performed in the manually mode. In EDS, the X-ray detector measures the number of emitted X-rays as a function of their energy. Since elements have a characteristic energy, the EDS spectrum can be used to identify the quantity of elements present (Frankel & Aitken, 1970). EDS technique is able to characterize the chemical composition of particles whose diameter is greater than 1μm (Wilkinson, Lundkvist, Seisenbaeva, & Kessler, 2011). The Scanning Electron Microscopy is a technique employed in numerous atmospherically studies (Goodarzi, 2006; De La Campa, De La Rosa, Querol, Alastuey, & Mantilla, 2007; Fromme et al., 2008; Hiranuma, Brooks, Auvermann, & Littleton, 2008; Campos-Ramos, Aragón-Piña, Galindo-Estrada, Querol, & Alastuey, 2009; Wilkinson, Lundkvist, Seisenbaeva, & Kessler, 2011). With the ability to operate both in conventional high vacuum, that in variable pressure (XVP SEM), with a maximum pressure 6 torr, it was possible to obtain more detailed information on chemistry, but also on the nature of the organic particles (Macias et al., 1981; Tombach, Seigneur, McDade, & Heisler, 1996). Portions of the filters were mounted on aluminium support (stubs) with double-sided tape which had a conductive graphite-based. The samples were then coated with a thin layer of carbon films, while others, with metallic gold, by electric arc high vacuum method and then analyzed by SEM. It is important to know that chemical and physical characterization of individual particles by SEM-EDS instrument can reveal source

information which cannot be determined through bulk chemical characterization.

2. RESULTS AND DISCUSSION

2.1 Vertical Profiles (150 to 2400 m) to the Size and Meteorological Parameters Measured With a Particle Counter

The particle counter LIGHTHOUSE HHIAQ3016 is an analysis system capable of counting and measuring the size of particulates on the basis of Fraunhofer diffraction of a laser beam. With this instrument tool it was possible to create vertical profiles describing the concentration of different sizes of the particles; also some basic meteorological parameters, such as temperature and relative humidity are contemporary measured.

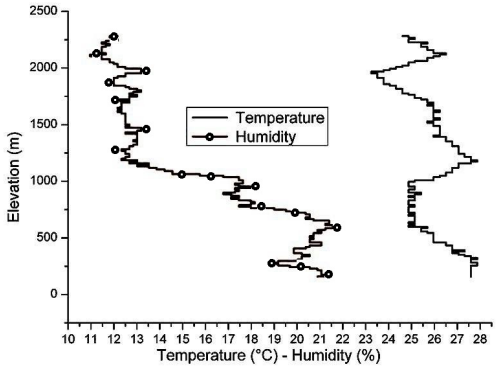


Figure 2
Graph on Temperature (°C) **and Relative Humidity** (%) **in Relation With Increasing Share in the Po Valley** (2009, June)

Figure 2 shows the relationship between temperature (°C: black line) and relative humidity (%: red line) with the altitude (m). Relative humidity shows a strong lowering around 1000m which coincides with an increase in temperature, in the closeness of the boundary layer. The clouds support the condensation of humidity and the increase of the temperature, creating a barrier for the particles of particulate that remain below the boundary layer.

In the period of acquisition, adverse weather conditions have produced a delay in harvesting activities, for which it was possible to detect a report to compare air quality data collected during activities of wheat harvest. On 9 June 2009 (pre-activities of threshing) conditions on the ground, recorded by the meteorological station of the ARPA Emilia Romagna "Ostellato", marked warm climate with temperatures ranging between 19°C and 25°C during the hottest hours, no precipitation, relative humidity 81% and a wind speed of 8km/h [2]. On 14 July 2009 (activities of threshing) conditions on the ground, recorded always by the meteorological station of the ARPA Emilia Romagna "Ostellato", marked warmer climate with temperatures ranging between 25°C and 30°C during the hottest hours, no precipitation, relative humidity 80% and a wind speed of 9km/h [2]. Meteorological variables are very important during the sampling. Relative humidity had a major influence: when relative humidity was high, PM_{10} particles were high, whereas $PM_{2.5}$ were significantly low. A likely explanation is that particles are hygroscopic (Witting et al., 2004) and increase in size on absorbing water (Wilson & Suh, 1997).

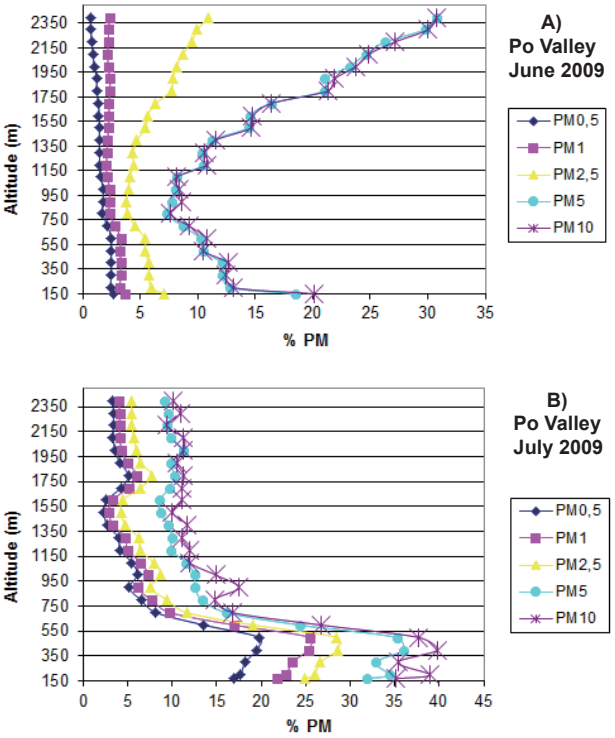


Figure 3
Graph on Percentage Particles in Relation With Increasing Share in the Po Valley: A) June 2009 Before Threshing; B) July 2009 After Threshing

Sampling in air allowed to discriminate the concentration of different size classes: $PM_{0.5}$—PM_1—$PM_{2.5}$—PM_5—PM_{10}, both in the pre-activities of wheat harvest (June 2009), that during wheat harvest activity (July 2009). The comparison gives indications of changes in distributions of different size classes of particles with altitude, due to the operation of activities of wheat and characterized by a significant increase in all classes up to 550m and a rapid decrease at higher altitudes. In the detail the monitoring of particulate, collected before the start of campaigns wheat harvest (Figure 3A), shows up to an altitude of 750m a constant decrease in concentration of all size classes of particles, although much more pronounced for the classes of coarse particles and especially PM_5, PM_{10}, probably at the inversion layer (Atmospheric Boundary Layer). With increasing altitude, about 1000m,

there is a difference in behaviour between the ultra-fine ($PM_{0.5,}$ PM_1), fine particles ($PM_{2.5}$) and coarse particles ($PM_{5,}$ PM_{10}) that, whereas the ultra-fine and the fine particles have a less pronounced but significant decrease increasing the share, the coarse particles are characterized by a gradual increase, which is more pronounced for bigger particles. It can be assumed that the reduction in ultra-fine and fine particles above 1000m is due to phenomena of nucleation, leading the small particles to join together creating thus bigger particles.

The second sampling (Figure 3B), performed in the same area, 14 July 2009 during the activities of wheat harvest, shows a percentage increase of all particle size classes with significant increases for both the ultra-fine, fine and coarse particulate. Again there is a strong reduction of the share at between 550 and 700m (inversion layer), which seems to indicate a tendency for the accumulation of particulate matter in the lower troposphere below the inversion layer. The rapid decrease of the number of particles affects all size classes. Unlike the pre-harvest period at altitudes above 750m the increase in concentration is not observed for coarse particles, probably because the organic component released into the atmosphere by the operation of harvesting (pollen, fungi and bacteria), consisting of cohesive walls and characterized by low bulk density, tend to congregate with other inorganic particles, favouring an increase in size and weight and consequently killing gravitational phenomena.

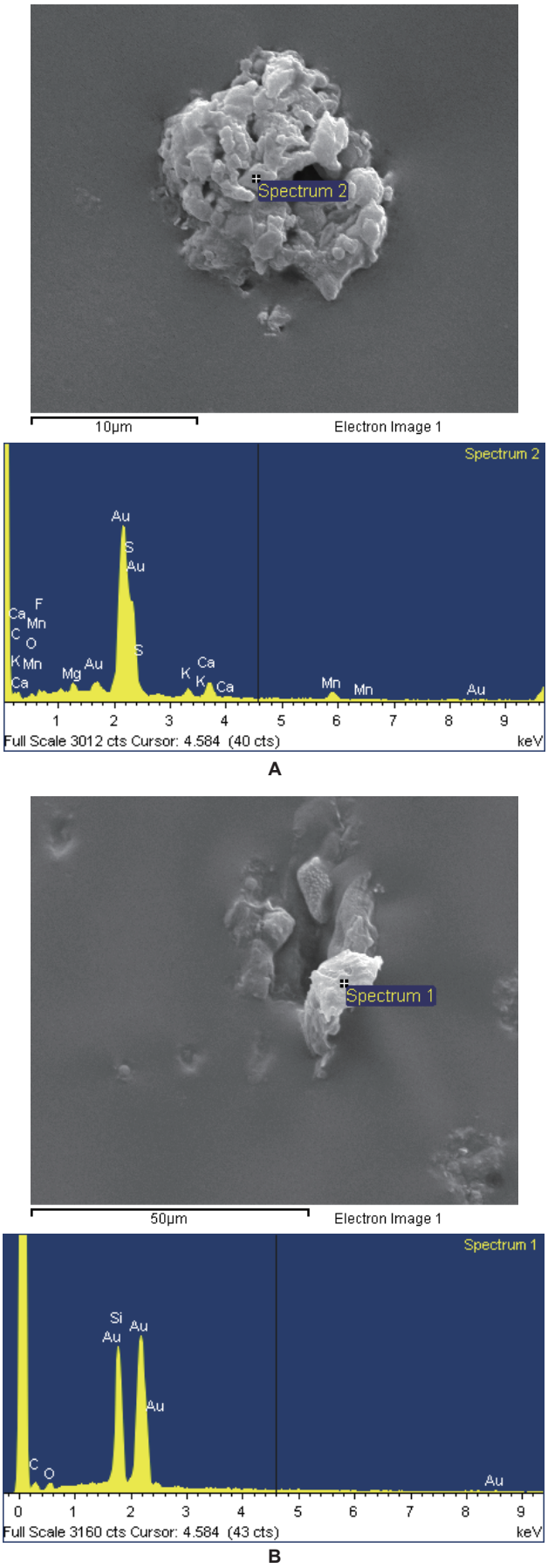
2.2 SEM Analysis

The choice of the manual impactor has been demonstrated very effective for collecting particulates that further have been observed by SEM, especially because the particles have been not disturbed. Chemical analysis and SEM observations showed the presence of three types of cluster, mainly microliths of calcite, quartz and subordinate silicate clay particles.

• The chemical composition of **calcite** crystals can incorporate these particles into the category of predominantly carbonates with calcite, have well-formed prismatic habitus despite the modest size (Figure 4A). These particles are derived mainly from erosion of soil and surrounding rocks and they are present at a rate of 35%.

• For **silicate** particles are distinguished those formed with silica granules more or less rounded likely source of cross-border and other silicate consisting of alkali feldspar (Si, Al, Ca or Si, Al, K), plagioclase and clay minerals (Si, Al or Si, Al, Fe) (Figs. 4B and 4C). The low percentage of clay minerals, the main constituents of soil, are assumed only from local contributions and a low prevalence of cross-border contributions. These particles are present at a rate of 60%.

• The **organic** particulate is present in very small quantities (≈ 5%), despite the monitoring was made during collection activities of wheat.



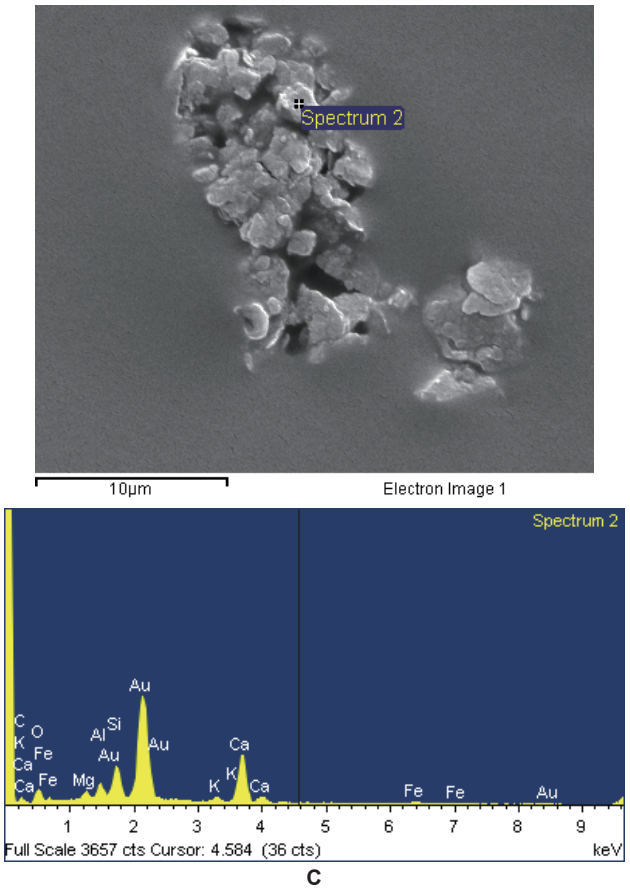


Figure 4
A) Calcite; B) Quartz; C) Feldspar

Figures 5 show, for both samplings, the averages abundances (percentages) of the three main components of particulate matter observed by SEM. Threshing activity produces coarse particulate (< 10µm), which is affected by the gravity and falls to the ground. For this reason, the contribution of particulate recorded at high altitude is modest.

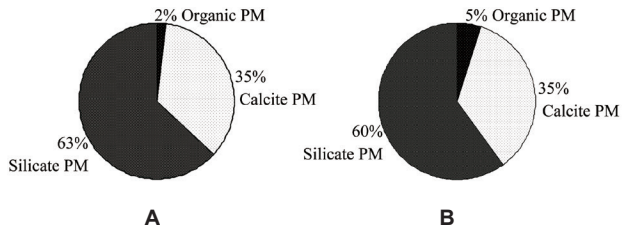


Figure 5
Average Abundances (Percentages) **of the Main Components of Particulate Matter: A) Before Harvest activity; B) During Harvest Activity**

CONCLUSION

This preliminary study was aimed at evaluating the contributions of the agricultural practice of threshing in the troposphere, characterized by a propensity for the accumulation of particulates below the inversion layer. The dynamics of spread of particulates in the troposphere, hypothesized on the basis of data, can be confirmed by the results obtained by SEM observation of samples taken during the flight.

The agricultural practice of threshing produces the issue close to the ground to airborne particulate matter, which produces a significant increase in all size classes. This increase is pronounced in the first 500m, especially for organic particles, while at higher altitudes the decrease interested in the bigger particles, which, from the SEM study, seem to be affected by gravitational aggregation. Indeed at higher altitudes to 550m are not detected significant amounts of organic particles. At high altitudes the prevalence of particles of natural origin, with carbonate composition and quartz and only less of clayey nature, is consistent with scientific works that define a major long range contribution to particulate inorganic solid. The threshing is carried out during June and July, which is the most favourable period for the contributions to long range particulate linked to current African from south-west. This is consistent with the composition found. The very low percentage of clay particles is probably due to vegetation cover, which limits the phenomena of resuspension of clay soil, typical of the area, and therefore very low contribution of inorganic particles of local origin.

AKNOWLEDGEMENTS

The authors wish to thank M.R. Bovolenta from Centre for Electron Microscopy Ferrara University for their assistance in the sampling and analysis.

REFERENCES

Abbey, D. E., Ostro, B. E., & Peterson, F. (1995). Chronic respiratory symptoms associated with estimated long-term ambient concentrations of fine particulates less than 2.5 micron in aerodynamic diameter ($PM_{2.5}$) and other air pollutants. *Journal of Exposure Analysis and Environmental Epidemiology, 5*, 137-159.

AGRIT. (2008). Indagine sull'occupazione territoriale delle coltivazioni a cereali in autunno-inverno in Italia.

Almeida, S. M., Pio, C. A., Freitas, M. C., Reis, M. A., & Trancoso, M. A. (2005). Source apportionment of fine and coarse PM in a sub-urban area at the Western European Coast. *Atmospheric Environment, 39*, 3127-3138.

Amodio, M., Bruno, P., Caselli, M., De Gennaro, G., Dambruoso, P. R., Daresta, B. E., ..., Tutino, M. (2008). Chemical characterization of fine PM during peak PM_{10} episodes in Apulia (South Italy). *Atmospheric Research, 90*, 313-325.

Amodio, M., Caselli, M., Gennaro, G., & Tutino, M. (2009). Particulate PAH sin two urban areas of Southern Italy: Impact of the sources, meteorological and background conditions on air quality. *Environmental Research, 109*, 812-820.

Bernabé, J. M., & Carretero, M. I. (2003). *Boletín de Sociedad Española de Mineralogía* [Spanish Society Bulletin of Mineralogy], *26*, 167.

Bianchini, G., Laviano, R., Lovo, S., & Vaccaro, C. (2001). Chemical mineralogical characterisation of clay sediments around Ferrara: a tool for an environmental analysis. *Applied Clay Sciences, 21*, 165-176. doi: 10.1016/S0169-1317(01)00086-2

Bogo, H., Otero, M., Castro, P., Ozafrán, M. J., Kreiner, A., Calvo, E. J., & Negri, R. M. (2003). Study of atmospheric PM in Buenos Aires city. *Atmospheric Environment, 37*, 1135-1147.

Brewer, X. R., & Belzer, W. (2001). Assessment of metal concentrations in atmospheric particles from Burnaby Lake, British Columbia, Canada. *Atmospheric Environment, 35*, 5223-5233. doi: 10.1016/S1352-2310(01)00343-0

Brimblecombe, P. & Grossi, C. M. (2009). Millennium-long damage to building materials in London. *Science of the Total Environment, 407*, 1354-1361. doi: 10.1016/j.scitotenv.2008.09.037

Campos-Ramos, A., Aragón-Piña, A., Galindo-Estrada, I., Querol, X., & Alastuey, A. (2009). Characterization of atmospheric aerosols by SEM in a rural area in the western part of México and ist relation with different pollution sources. *Atmospheric Environment, 43*, 6159-6167. doi: 10.1016/j.atmosenv.2009.09.004

Chabas, A., & Lefèvr, R. A. (2000). Chemistry and microscopy of atmospheric particulates at Delos (Cyclades – Greece). *Atmospheric Environment, 34*, 225-238. doi: 10.1016/S1352-2310(99)00255-1

Chow, J. C., Watson, J. G., & Lowenthal, D. H. (1999). Temporal variations of $PM_{2.5}$, PM_{10}, and gaseous precursors during the 1995 integrated monitoring study in central California. *Journal of the Air & Waste Management Association, 49*, 16-24. doi: 10.1080/10473289.1999.10463909

De La Campa, A. M. S., De La Rosa, J., Querol, X., Alastuey, A., & Mantilla, E. (2007). Geochemistry and origin of PM_{10} in the Huelva region, Southwestern Spain. *Environmental Research, 103*, 305-316. doi: 10.1016/j.envres.2006.06.011

European Space Agency. (2004). Global air pollution map. *Envisat's SCIAMACHY*. Retrieved from http://www.esa.int/esaCP/SEM340NKPZD_Protecting_1.html

Frankel, R. S., & Aitken, D. W. (1970). Energy dispersive X-ray emission spectroscopy. *Applied Spectroscopy, 24*, 557-566. doi: 10.1039/b817048g

Fromme, H., Diemer, J., Dietrich, S., Cyrys, J., Heinrich, J., Lang, W., …, Twardella, D. (2008). Chemical and morphological properties of PM_{10} and $PM_{2.5}$ in school classrooms and outdoor air. *Atmospheric Environment, 42*, 6597-6605.

Germani, M. S., & Buseck, P. R. (1991). Automated scanning electron microscopy for atmospheric particles analysis. *Analytical Chemistry, 63*, 2232-2237. doi: 10.1021/ac00020a008

Goodarzi, F. (2006). Morphology and chemistry of fine particles emitted from a Canadian coal-fired power plant. *Fuel, 85*, 273-280. doi: 10.1016/j.fuel.2005.07.004

Grassi, C., Narducci, P., & Tognotti, L. (2004). Atmospheric PM by SEM-EDX. World Clean Air and Environmental Protection Congress.

Harrison, R. M., Jones, M., & Collins, G. (1999). Measurements of the physical properties of particles in the urban atmosphere. *Atmospheric Environment, 33*, 309-321.

Hiranuma, N., Brooks, S. D., Auvermann, B. W., & Littleton, R. (2008). Using environmental scanning electron microscopy to determine the hygroscopic properties of agricultural aerosols. *Atmospheric Environment, 42*, 1983-1994. doi: 10.1016/j.atmosenv.2007.12.003

Hoek, G., Kos, G., Harrison, R. M., De Hartog, J., Meliefste, K., Ten Brink, H., …, Hameri, K. (2008). Indoor-outdoor relationship of particle number and mass in four European cities. *Atmospheric Environment, 42*, 156-169. doi: 10.1016/j.atmosenv.2007.09.026

Hopke, P. K. (2008). The use of source apportionment for air quality management and health assessment. *Journal of Toxicology and Environmental Health, 71*, 555-563. doi: 10.1080/15287390801997500

Husar, R. B., Tratt, D. M., Schichtel, B. A., Falke, S. R., Li, F., Jaffe, D., …, Malm, W. C. (2001). Asian dust events of April 1998. *Journal of Geophysical Research, 106*, 18317-18330. doi: 10.1029/2000JD900788

Kelly, R. J. (2008). Occupational medicine implications of engineered nanoscale PM. *Division of Chemical Health and Safety of the American Chemical Society,* 1-42.

Laden, F., Schwartz, J., Speizer, F. E., & Dockery, D. W. (2006). Reduction in fine particulate air pollution and mortality: Extended follow-up of the Harvard six cities study. *American Journal of Respiratory and Critical Care Medicine, 173*, 667-672. doi: 10.1164/rccm.200503-443OC

Macias, E. S., Zwicker, J. O., Ouimette, J. R., Hering, S. V., Friedlander, S. K., Cahill, T .A., ..., Richards, L. W. (1981). Regional haze case studies in the south western U.S. – I. Aerosol chemical composition. *Atmospheric Environment, 15*, 1971-1986.

Maravelaki-Kalaitzaki, P., & Biscontin, G. (1999). Origin, characteristics and morphology of weathering crusts on Istria stone in Venice. *Atmospheric Environment, 33*, 1699-1709. doi: 10.1016/S1352-2310(98)00263

Marcazzan, G. M., Vaccaio, S., Valli, G., & Vecchi, R. (2001). Characterisation of PM_{10} and $PM_{2.5}$ in the ambient air of Milan (Italy). *Atmospheric Environment, 35*, 4639-4650.

Mazzei, F., D'Alessandro, A., Lucarelli, F., & Marengo, F. (2006). Elemental composition and source apportionment of PM near a steel plant in Genoa (Italy). *Nuclear Instruments and Methods in Physics Research B, 249*, 548-551.

Pope 3rd, C. A. (2000). Epidemiology of fine particulate air pollution and human health: Biological mechanisms and who's at risk? *Environmental Health Perspectives, 108*, 713-723. doi: 10.2307/3454408

Pope 3rd, C. A., Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., & Ito, K. (2002). Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *JAMA, 287*, 1132-1141. doi: 10.1001/jama.287.9.1132

Pope 3rd, C. A., Thun, M. J., Namboodiri, M. M., Dockery, D. W., Evans, J. S., Speizer, F. E., & Heath, C. W. (1995). Particulate air pollution as a predictor of mortality in a prospective study of US adults. *American Journal of Respiratory Critical and Care Medicine, 151*, 669-674. doi: 10.1164/ajrccm.151.3.7881654

Querol, X., Alastuey, A., De La Rosa, J., Sánchez De La Campa, A., Plana, F., & Ruiz, C. R. (2002). Source apportionment analysis of atmospheric particulates in an industrialised urban site in south western Spain. *Atmospheric Environment, 36*, 3113-3125. doi: 10.1016/S1352-2310(02)00257-1

Ragosta, M., Caggiano, R., D'Emilio, M., Sabia, S., Trippetta, S., & Macchiato, M. (2006). PM_{10} and heavy metal measurements in an industrial area of southern Italy. *Atmospheric Research, 81*, 304-319. doi: 10.1016/j.atmosres.2006.01.006

Reis, M. A., Oliveira, O. R., Alves, L. C., Rita, E. M. C., Rodrigues, F., Fialho, P., ..., Soares, J. C. (2002). Comparison of continental Portugal and Azores Islands aerosol during a Sahara dust storm. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 189*, 272-278. doi: 10.1016/S0168-583X(01)01056-4

Rodriguez, S., Querol, X., Alastuey, A., Viana, M., Alarcon, M., Mantilla, E., & Ruiz, C. R. (2004). Comparative PM_{10}–$PM_{2.5}$ source contribution study at rural urban and industrial sites during PM episodes in eastern Spain. *Science of the Total Environment, 328*, 95-113. doi: 10.1016/S0048-9697(03)00411-X

Ryall, D. B., Derwent, R. G., Manning, A. J., Redington, A. L., Corden, J., Millington, W., …, Fuller, G. W. (2002). The origin of high particulate concentrations over the United Kingdom, March 2000. *Atmospheric Environment, 36*, 1363-1378. doi: 10.1016/S1352-2310(01)00522-2

Sabbioni, C. (1995). Contribution of atmospheric deposition to the formation of damage layers. *Science of the Total Environment, 167*, 49-55. doi: 10.1016/0048-9697(95)04568-L

Salvador, P., Artíñano, B., Querol, X., Alastuey, A., & Costoya, M. (2007). Characterisation of local and external contributions of atmospheric PM at a background coastal site. *Atmospheric Environment, 41*, 1-17. doi: 10.1016/j.atmosenv.2006.08.007

Samek, L. (2009). Chemical characterization of selected metals by X-ray fluorescence method in PM collected in the area of Krakow, Poland. *Microchemical Journal, 92*, 140-144. doi: 10.1016/j.microc.2009.02.007

Schwartz, J., Dockery, D. W., & Neas, L. M. (1996). Mortality Associated Specifically With Fine Particles. *Journal of Air and Waste Management Association, 46*, 927-939.

Scientific Committee on Emerging and Newly Identified Health Risks. (2005). New evidence of air pollution effects on human health and the environment. *SCHER*.

Scientific Committee on Emerging and Newly Identified Health Risks. (2006). The appropriateness of existing methodologies to assess the potential risks associated with engineered and adventitious products of nanotechnologies. *SCHER*.

Takahashi, K., Minoura, H., & Sakamoto, K. (2008). Chemical composition of atmospheric aerosols in the general environment and around a trunk road in the Tokyo metropolitan area. *Atmospheric Environment, 42*, 113-125. doi: 10.1016/j.atmosenv.2007.09.009

Tittarelli, A., Borgini, A., Bertoldi, M., De Saeger, E., Ruprecht, A., Stefanoni, R., ..., Crosignani, P. (2008). Estimation of particle mass concentration in ambient air using a particle counter. *Atmospheric Environment, 42*, 8543-8548. doi: 10.1016/j.atmosenv.2008.07.056

Tombach, I., Seigneur, C., McDade, C., & Heisler, S. (1996). Dallas-Fort Worth winter haze project. In: EPRI TR-106775-V3 Vol. 3, 1996—Electric Power Research Institute, Palo Alto, CA.

Torfs, K., & Van Grieken, R. (1997). Chemical relations between atmospheric aerosols, deposition and stone decay layers on historic buildings at the Mediterranean coast. *Atmospheric Environment, 31*, 2179-2192. doi: 10.1016/S1352-2310(97)00038-1

Tuch, T., Brand, P., Wichmann, H. E., & Heyder, J. (1997). Variation of particle number and mass concentration in various size ranges of ambient aerosol in Eastern Germany. *Atmospheric Environment, 31*, 4193-4197. doi: 10.1016/S1352-2310(97)00260-4

Vanderstraeten, P., Lénelle, Y., Meurrens, A., Carati, D., Brenig, L., Delcloo, A., …, Zaady, E. (2008). Dust storm originate from Sahara covering Western Europe: A case study. *Atmospheric Environment, 42*, 5489-5493. doi: 10.1016/j.atmosenv.2008.02.063

Vasconcelos, L. A., Macias, E. S., & White, W. H. (1994). Aerosol composition as a function of haze and humidity levels in the south western US. *Atmospheric Environment, 28*, 3679-3691. doi: 10.1016/1352-2310(94)00187-P

Viana, M., Kuhlbusch, T. A. J., Querol, X., Alastuey, A., Harrison, R. M., Hopke, P. K., …, Hitzenberger, R. (2008). Source Apportionment of PM in Europe: A Review of Methods and Results. *Journal of Aerosol Science, 39*, 827-849.

Viana, M., Querol, X., Alastuey, A., Gangoiti, G., & Menéndez, M. (2003). PM levels in the Basque Country (northern Spain): analysis of 5-year data record and interpretation of seasonal variations. *Atmospheric Environment, 37*, 2879-2891.

Weijers, E. P., Khlystov, A. Y., Kos, G. P. A., & Erisman, J. W. (2004). Variability of PM concentrations along roads and motorways determined by a moving measurement unit. *Atmospheric Environment, 38*, 2993-3002.

Wilkinson, K., Lundkvist, J., Seisenbaeva, G., & Kessler, V. (2011). New tabletop SEM-EDS-based approach for cost-efficient monitoring of airborne particulate matter. *Environmental Pollution, 159*, 311-318.

Wilson, W. E., & Suh, H. H. (1997). Fine particles and coarse particles: concentrations relationship relevant to epidemiologic studies. *Journal of Air and Waste Management Association, 47*, 1238-1249.

Witting, A. E., Anderson, N., Khlystov, A. Y., Pandis, S. N., Davidson, C., & Robinson, A. L. (2004). Pittsburgh air quality study overview. *Atmospheric Environment, 38*, 3107-3125.

