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Urban dew and rain in Paris, France: Occurrence and physico-chemical characteristics

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ABSTRACT

This paper summarizes one year (April 2011 to March 2012) measurements on planar condensing surfaces of dew and rain events and related physico-chemical characteristics in the urban environment of Paris (city center). Yearly collected water was 3.48 mm for dew (63 events) and 593 mm for rain (146 events). The latter value compares well with rain data (547 mm and 107 events) collected within 12 km at Paris-Orly airport. An estimation of dew yield based on meteo data gives 2.35 mm and 74 events, to be compared with 17.11 mm and 196 events at Paris-Orly. These differences highlight the large reduction in dew events and dew yields in an urban area as compared to a close rural-like area. This reduction is not due to a sky view reduction but to heat island that increases air temperature and decreases relative humidity.

Analysis of dew (34) and rain (77) samples were done concerning pH, electrical conductivity (EC), major anions and cations as well as selected trace metals and other minor ions. Mean pH values are found similar for both, dew (6.5) and rain (6.1), rain being slightly more acidic than dew. The mean dew total ionic content (TIC 1.8 meq/l) and EC value (124 μS/cm) are about four times that of rain (0.45 meq/l; 35 μS/cm), meaning that total dissolved solids in dew is nearly four times that in rain. Sulfate and nitrate are the most acidifying components, calcium the most neutralizing constituent with ratio of mean total acidity/total alkalinity comparable for dew and rain (~0.9). Sulfate and nitrate have mainly anthropogenic sources, whereas chloride and magnesium are mostly connected with marine air masses. Dew is a considerable factor of wet deposition of pollutants; dew and rain ion concentrations, however, meet the WHO requirements for drinking water.

1. Introduction

Dew is the result of passive condensation of atmospheric water vapor into liquid. The necessary cooling power is provided by the radiation deficit between atmosphere and the condensing support. Dew has not to be confused with fog or rain, constituted of already condensed liquid droplets. With typically <70 Wm^{-2} radiative power available, the maximum yield cannot exceed 0.7–0.8 lm^{-2} (Monteith and Unsworth, 1990; Beysens, 1995, 2006; Berkowicz et al., 2004). This low yield, however, can be a welcome and useful contribution to the biosphere (Zangvil, 1996; Agam and Berliner, 2006; Jacobs et al., 2006; Kidron et al., 2011; Uclés et al., 2013) and to potable water in arid or semi-arid climates (Nilsson, 1996; Beysens and Milimouk, 2000; Kidron, 2000; Beysens et al., 2006a; Lekouch et al., 2012; Tomaszkiewicz et al., 2015; Khalil et al., 2016; Mylymuk-Melnytchouk and Beysens, 2016), provided that water chemical and biological quality is acceptable (Beysens et al., 2006b; Muselli et al., 2006; Lekouch et al., 2011; Tomaszkiewicz et al., 2015). It can be also the source of plant disease (Luo and Goudriaan, 2000) and, in urban areas, cause degradation to roofs, cars and generally to any inorganic matter that can be corroded (Rubio et al., 2001, 2002; Xu et al., 2001). Dew formation is a local phenomenon. The steps governing dew chemical composition are formation on dry deposition solids, dissolution of the soluble portion of the dry deposition by dew water, and sorption of gases into the dew solution.

For any precipitation to fall there is a need for a cloud. Clouds are formed when the relative humidity reaches 100% and with enough hygroscopic nuclei in air so that condensation can take place. Cloud droplets initially grow quickly but to eventually produce precipitation collision/coalescence processes are needed. When drops become heavy enough to overcome air resistance they fall as rain. The chemical composition of precipitation is a result of three different processes: nucleation scavenging (chemical configuration of nuclei determines initial cloud composition), in-cloud scavenging (take up of non-activated particles and trace gases (major important) including chemical reactions within droplets), sub-cloud scavenging (absorption of gases and take

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up of particles). Not every cloud brings rain and on average a condensation nuclei may undergo many cloud cycling processes including chemical transformation before it comes back to earth surface, often far away from its primary source.

Carbon dioxide plays a special role in the formation of acidity in the atmospheric liquid phase because of its high and constant concentration. An important pathway in alkalinity (carbonate) formation goes via condensation nuclei (nucleation and droplet formation) as well as aerosol scavenging. The last process contributes significantly to subcloud scavenging into falling raindrops. The ability to capture particulates is very relevant for dew chemical composition and is strong at the beginning and weakened at the end of the condensation process. The acidity from dissolved CO_2, SO_2, and NO_x is mostly neutralized by Mg^{2+}, Ca^{2+} and NH_4^+; sometimes a slight alkaline character is observed in dew samples. Dew events with the higher ionic concentration occur following long periods without rain.

Uptake of high soluble gases on atmospheric water is very fast and not a question of time. Cloud cycling processes, microphysical conditions and heterogeneous reactions will influence dew and rain chemistry. When in equilibrium with atmospheric CO_2, the HCO_3^- concentration is an exponential function of the pH-value. When the pH solutions is higher than 6.35 (pKa1 of H_2CO_3) [HCO_3^-] can become important. But samples of the atmospheric multiphase system are most probably not in equilibrium with atmospheric CO_2 due to complex chemical compositions, microphysical processes and heterogeneous interactions and [HCO_3^-] can only be obtained by analytical estimation and not deriving Henry's law. A possible high contribution of bicarbonate to the ionic balance implies "errors" in the quality check between measured conductivity (where HCO_3^- is included) and the analyzed ions (where HCO_3^- is excluded). An observed difference between measured and calculated conductivity can also be caused by other not analyzed ions (e.g. formate, acetate, phosphate and in our study also ammonium).

In urban environment dew water composition is thus a function of both long range convected atmosphere and locally produced gas and aerosols. Several studies during the last decades have been concerned with dew chemistry in urban areas, in Santiago, Chile (Ortiz et al., 2000; Rubio et al., 2002, 2006, 2008), in Japan (Yokohama, Osaka, Tokyo) (Okochi et al., 1996, 2008; Takeuchi et al., 2001; Takenaka et al., 2003). Research were also carried out in Poland (Gdansk, Krakow, Wroclaw) (Polkowska et al., 2008), Jordan (Amman) (Jiries, 2001), Israel (Jerusalem) (Berkowicz et al., 2004), Bordeaux (France) (Beysens et al., 2006b), Zadar (Croatia) (Lekouch et al., 2010) and New Delhi (India) (Yadav and Kumar, 2014). The physico-chemical analysis of dew gives information about atmosphere from where it was condensed. The obvious sources of aerosols deposited on the collectors are (i) emissions of hydrocarbons and nitrogen oxides coming from the road traffic, (ii) greenhouse gases and sulfur dioxide coming from nearby industries and house heating in winter, (iii) solid particles coming from the close environment (limestone, ashes of open fires, etc.). Analyses of urban dew usually indicate higher concentration levels of Ca^{2+}, SO_4^{2-} and NO_3^- than in rural areas.

The aim of this study is then to determine in the urban environment of the historical center of Paris the volume and occurrence of dew as compared to rain and characterize the main chemicals present in dew and rain water. Such studies have not been performed so far to our knowledge in Paris and appear to be a good starting point to compare with further evolution in relation with air quality improvement and urban heat island.

2. Measurements and methods

2.1. Measurement site

The measurement site is located on an open terrace of the Ecole Supérieure de Physique et Chimie Industrielles ParisTech, 6.8 m above the ground, with large sky view factor. The site is in the historical center of Paris at the top of a small hill "Montagne Sainte Geneviève" at latitude 48° 50′ 28.24″ N, longitude 2°20′49.16″ E and 80 m above sea level (asl). Data have been collected during one year, from 01/04/2011–31/03/2012.

Paris metropolitan area presents a relatively flat relief with low elevation (from 28 to 130 m asl). The climate is temperate and mainly under oceanic influences (Köppen–Geiger climate classification: Cfb), with rainy and windy conditions, only infrequently continental. Dispersion of atmospheric pollutants is thus favored. However, the density of population and activities is quite high. Paris and its neighboring agglomeration concentrate about 90% of the regional population on a little >20% of the region area. According to Air Quality in Europe (2016), the metropolitan area is responsible for >75% of the regional NO_x emissions, 70% of the hydrocarbons (volatile organic compounds VOC) and 50% of the particles. The NOx emissions of the region represent 10% of the national emissions. The principal sources of pollution are transportation, building heating and industry. Road transportation is responsible for 53% of the nitrogen oxides (NO_x) emissions of the Paris agglomeration, 15% of the VOC and 25% of the particles produced by an important fleet of diesel vehicles. Sulfur dioxide seems to be no longer an issue, due to the emission decrease of industrial activities in the region.

2.2. Dew and rain evaluation

In the present study, dew is collected on three planar condensers with about same yield at 1 m above the floor of the terrace, facing approximatively SW (220° direction, see Fig. 1). Two reference condensers A and A′ are dedicated to automatic volumetric measurements with A′ as a spare condenser. Another condenser B is used for chemical sampling. All condensers are tilted with an angle of 30° with respect to horizontal to collect water by gravity. As noted by Gałek et al. (2015a), dew collected on plain radiative condensers effectively simulates artificial surfaces found commonly in urban areas, the latter being characterized by low thermal capacity and fast cooling during radiative nights.

Condenser A is made of a steel sheet of 1.0 mm thickness, 0.96×0.96 m^2 surface area covered with a commercial white painting (ITI Trimetal Steloxine Galva Protect by Akzo Nobel) designed for outdoor use where was added a few % of radiative hydrophilic mineral additives (0.2–2 μm diameter aluminosilicate powder) distributed by OPUR (2016). The sheet is thermally insulated beneath by 22 mm thickness Styrofam. Water is collected by gravity in a PVC gutter and flow is measured by a pluviometer connected to a weather station. Measurements are taken every min. Air temperature (T_a) was measured with an accuracy of 0.5 °C with 0.1 °C resolution; relative humidity (RH) accuracy was 5% with 1% resolution, corresponding to 0.9 °C accuracy and 0.2 °C resolution in dew point temperature T_d; wind speed (V) accuracy was 5% with 0.5 m/s stalling speed; wind direction accuracy was 7° with 1° resolution. The measurements were performed close to the edge of the building, 7.5 m above the ground level and about 2 m above the terrace (Fig. 1).

The calibration of the rain gauge was performed to convert the data in lm^{-2} (mm) of collected water. The pluviometer was calibrated by gently pouring different volumes of water and measuring the response of the weather station. The conversion ratio mm-condenser/mm-station is 8.51×10^{-3}. The resolution of water collection is 0.014 mm. Only little dew water remains pinned at the condenser surface (<5% according to Beysens et al., 2007), then the yield is close to a scraped surface.

Condenser A', dedicated to another study, is used as a spare condenser when technical problems occur with condenser A. It is made with 7.5 mm thick corrugated fibrocement, with surface area 1.52×0.92 m^2. Dew water is collected by gravity in a gutter and the corresponding volume is measured by a pluviometer. The resolution of water collection is 0.023 lm^{-2}. The measurements are taken every 15 min. The pluviometer was calibrated by pouring water. The