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Discussions

Classification of clouds sampled at the puy de Dôme (France) from 10 yr monitoring: mean features of their physico-chemical properties

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Abstract

Long-term monitoring of the chemical composition of clouds (73 cloud events representing 199 individual samples) sampled at the puy de Dôme (pdD) station (France) was performed between 2001 and 2011. Physico-chemical parameters, as well as the concentrations of the major organic and inorganic constituents, were measured and analyzed by multi-component statistical analysis. Along with the corresponding back-trajectory plots, this allowed distinguishing four different categories of air masses reaching the summit of the pdD: polluted, continental, marine and highly marine. This statistical tool leads to the determination of criteria (concentration of inorganic compounds, pH) that differentiate each categories of air masses. Highly marine clouds exhibited high concentrations of Na^+ and Cl^-; the marine category presented lower concentration of ions but more elevated pH. Finally, the two remaining clusters were classified as "continental" and "polluted" with increasing concentrations of NH_4^+, NO_3^-, SO_4^{2-}. This unique dataset of cloud chemical composition is then discussed as a function of this classification; this will allow the creation of "standard chemical scenarios" that can serve for modeling purposes on multiphase cloud chemistry.

1 Introduction

The atmospheric system is a complex dynamical and multiphase medium where chemical species can be transformed (Monks et al., 2009). Different phases (solid, gas, liquid and ice) are in permanent interactions; in this frame, the multiphase cloud system represents a medium of interest. They contain both organic and inorganic species that result from the mass transfer of soluble gases in the liquid phase and also from the dissolution of the soluble fraction of aerosol particles (Fuzzi et al., 2002; Sellegri et al., 2003). Modeling studies (e.g., Barth, 2006; Leriche et al., 2007; Lim et al., 2005; Tilgner and Herrmann, 2010; Tost et al., 2007), in situ measurements (e.g., Laj et al., 1997b; Möller et al., 1996; Moore et al., 2004) and laboratory investigations (e.g., Altieri

et al., 2006; Vione et al., 2006) highlighted the fact that chemical reactions in clouds play an important role in atmospheric chemistry and strongly affect the homogeneous and heterogeneous gas phase chemistry (Lelieveld and Crutzen, 1991). Depending on the physical and chemical characteristics of the cloud droplets, aqueous-phase reac-
5   tions potentially represent either a sink or a source for atmospheric trace compounds. In turn, the chemical transformations in the liquid phase control the fate of gaseous species and/or their reaction products upon cloud dissipation. Transport, distribution and removal of chemical species from the atmosphere are clearly influenced by physical and chemical processes in clouds.
10   The role of clouds in the atmospheric cycle of inorganic substances has been discussed in many papers in the past (see recent reviews from Fowler et al., 2009; Monks et al., 2009) focusing on the oxidation/transformation of sulfur and nitrogen compounds (Barth, 2006; Cape et al., 1997; Seinfeld and Pandis, 2006; Wells et al., 1997). The importance of the atmospheric liquid phase has been investigated for organic substances
15   (Fuzzi et al., 2002; Herckes et al., 2013), in particular for the formation/transformation of carboxylic acids (Chebbi and Carlier, 1996; Laj et al., 1997a; Monod and Carlier, 1999) or more recently for the formation of secondary organic aerosol (SOA) after cloud evaporation (Blando and Turpin, 2000; Hallquist et al., 2009; Lee et al., 2012; Lim et al., 2010; Loeffler et al., 2006). Actually, the formation of SOA has been largely
20   studied in the gas phase but the contribution of clouds is still uncertain (Ervens et al., 2011). Complex chemical reactions can occur in aerosol water forming accretion products such as oligomers. Recent laboratory studies demonstrated that small oxygenated compounds undergo these processes such as methylglyoxal (Altieri et al., 2008; Tan et al., 2010), hydroxyacetaldehyde (Perri et al., 2009) or glyoxal (Carlton et al., 2007; De
25   Haan et al., 2009; Ervens and Volkamer, 2010); these alternative chemical pathways are assumed to represent an efficient process to transform volatile organic compounds into SOA (Haddad et al., 2009).

Chemical reactions in clouds are driven by efficient oxidation processes due to the presence of photo-chemically produced oxidants such as hydroxyl and nitrate radicals

(respectively HO$^\bullet$ and NO$_3^\bullet$) as well as oxidants such as ozone (O$_3$) and hydrogen peroxide (H$_2$O$_2$). Reactivity is also influenced by the partitioning between droplets and the other phases (particle, gas, ice) and is catalyzed by photochemical processes (Barth, 2006; Hoigné, 1994; Minero et al., 2007; Ruggaber et al., 1997; Vione et al., 2006). Recently, a number of studies also suggested biological processes as potentially involved in the transformation of soluble organic material in cloud droplets, even at low temperatures (Deguillaume et al., 2008; Husárová et al., 2011; Vaïtilingom et al., 2010, 2011, 2013). An additional complexity derives from the presence of ice, which interferes with liquid/gas phase partitioning and modifies the photochemical equilibrium through feedbacks between ice, radiation and reactivity pathways (Long et al., 2010; Marécal et al., 2010; Voisin et al., 2000).

It is therefore crucial to study the chemical composition and reactivity of chemical species in clouds to understand and quantify their mechanisms of degradation in the atmosphere. Several in situ investigations of cloud chemistry are reported so far and most of them are based on specific single campaigns (Bower et al., 2000; Choularton et al., 1997; Collett Jr. et al., 1990; Decesari et al., 2005; Elbert et al., 2000; Ghauri et al., 2001; Gioda et al., 2009; Hegg et al., 2002; Hutchings et al., 2009; Kim et al., 2006a; Löflund et al., 2002; Moore et al., 2004; Sedlak et al., 1997; Watanabe et al., 2001; Weathers et al., 1988; Wieprecht et al., 2005; Wilkinson et al., 1999; Wobrock et al., 2001). All of these studies showed a high variability in the cloud chemical composition which is driven by both source proximity and local microphysics. Integration studies considering different cloud experiments can be difficult especially because cloud sampling methodologies are not standardized and not easily comparable (Laj et al., 2009). Some long term field measurements using automated cloud water collection systems were conducted in the past, mainly looking at the inorganic chemical composition of clouds (Acker et al., 1998; Baumgardner et al., 2003; Guo et al., 2012; Kim et al., 2006b).

For modeling purposes, statistical information on the variability of cloud chemical composition and its relationship with environmental factors, such as source regions, is

extremely useful. Long-term studies are required to derive statistically sound informa-
tion. Due to the transient nature of clouds, monitoring cloud chemical composition is not
trivial and is subject to difficulties such as sampling frequencies, samples conservation
and quality homogeneity on a long-term basis. Here, we present chemical data of the
condensed phase of a series of cloud events (73 cloud events representing 199 individ-
ual samples) sampled at the puy de Dôme (pdD) mountain (1465 m) that is classified
as a natural background site (Henne et al., 2010; Joly and Peuch, 2012; Putaud et al.,
2004). The observation of clouds and more largely of atmospheric variables at high
altitude remote sites brings additional valuable information on the extent of the anthro-
pogenic influence. Usually, these sites are rather influenced by long-range transport
than by local sources and hence provide information on the physico-chemical variabil-
ity of air masses on a regional scale. More precisely, due to the high altitude of the
station, the air mass composition is representative of the regional atmospheric back-
ground during the day and more representative of larger synoptic-scale air masses
during night-time (Asmi et al., 2011). The data set presented (pH, conductivity, redox
potential, total organic content, concentrations of the most abundant inorganic and or-
ganic chemical species, concentrations of oxidants: iron and hydrogen peroxide) could
be used as a cloud benchmark for natural free tropospheric conditions.

2   Material and methods

2.1   Cloud sampling

Sampling was performed at the pdD station (45°46′20″ N, 2°57′57″ E) which is part of
networks EMEP/GAW/ACTRIS. The observatory chalet is on top of a mountain rising
notably above the surrounding area with an altitude of 1465 m a.s.l.; the pdD mountain
is part of the Massif Central Mountains, a topography that is North–South oriented.
Clouds are frequently observed at the top of the site either during advection of frontal
systems or by the orographic rising of moist air. The urban area of Clermont-Ferrand

and its surrounding suburbs ($\approx$ 280 000 inhabitants) is situated 16 km east of the station at 396 m a.s.l.; its influence on the pdD measurements is fairly limited (especially during nighttime) and air masses producing clouds at the pdD summit from Eastern origin are extremely rare, as witnessed by primary anthropogenic tracers concentrations (NO,
[5] black carbon, etc.) and statistical studies on aerosol size distributions (Asmi et al., 2012; Henne et al., 2010). Most of the clouds are sampled during winter and spring and their corresponding air masses are representative of various geographically origins. A short summary of previous studies related to this site is given in the Supplement (SM) for information.
[10] Cloud sampling was performed between 2001 and 2011, with an average sampling time of 2 h (corresponding to an average sampling volume of 50 mL). However, between 2006 and 2009, the observatory at the pdD summit has been renovated, which greatly limited the cloud sampling operations (only 16 cloud events were collected during that period). Non-precipitating cloud droplets were sampled using a single-stage
[15] cloud collector similar to the one described by Kruisz (1993). Cloud droplets larger than 7 µm (cut-off diameter) (Brantner et al., 1994) were collected by impaction onto a rectangular aluminum plate. Droplets either froze upon impaction (super-cooled conditions) or were collected directly as a liquid. Possible changes in the cut-off diameter due to the building of ice onto the impaction plate are expected to be negligible given
[20] the limited volume of collected sample. Building of ice leads to more efficient sampling by collecting smaller drops.

2.2 Physico-chemical parameters and chemical analysis

Physico-chemical parameters were measured immediately after sampling: the pH, conductivity and redox potential were measured using a Consort[®] multi-parameter C830.
[25] Meteorological parameters were also monitored at the pdD station: wind speed and direction, temperature, pressure, and relative humidity. Measurements of Liquid Water Content (LWC) and effective radius of droplets were obtained from a Gerber PVM-100 probe.

After collection, cloud water samples were kept at 4 °C in the dark until the chemical and TOC analyses were conducted. Total organic carbon (TOC) was obtained with a Shimadzu TOC 5050A analyzer. The analytical method for ion chromatography analysis (material: Dionex DX320, column AS11 for anions, eluent KOH; Dionex ICS1500, column CS16 for cations, eluent hydroxymethanesulfonate) has been previously reported by Jaffrezo et al. (1998). Ion chromatography analysis of ten-fold diluted samples was made in triplicate or more and permitted to measure the concentrations of the major organic and inorganic ions (acetic, formic, succinic, malonic and oxalic acids, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+}). Total ion content (TIC) corresponds to the calculated sum of the concentrations of these species.

Measurements of H_2O_2 and iron concentrations by UV-Vis spectroscopy were done in triplicate or more; the derivatization of these reactive species in the samples allowed maintaining their concentrations until the analysis was performed in the laboratory; this was directly conducted after the end of the collection of cloud water. H_2O_2 concentration was measured by UV-Vis spectroscopy at 551 nm, following the method developed by Bader et al. (1988). This method is based on the oxidation of N,N-diethyl-p-phenylenediamine (DPD) by H_2O_2 in the presence of horseradish peroxidase, leading to the radical cation of DPD with an absorbance (at 551 nm) of $21\,000 \pm 500\,M^{-1}\,cm^{-1}$ at equimolar rate. Fe(II) concentration was measured by UV-Vis spectroscopy at 562 nm, using the method developed by Stookey (1970) based on the rapid complexation of iron with ferrozine. After reduction of Fe(II) by addition of hydroxylamine chlorhydrate, the total iron content Fe(tot) was detected. Fe(III) concentration was then calculated by deducing the concentration of Fe(II) from Fe(tot).

Measurements of carbonyl compounds were done by using a method which was specifically developed for the quantification of single aldehydes in environmental aqueous phases (Houdier et al., 2000). The method, which has been recently improved for the analysis of polyfunctional carbonyls (Houdier et al., 2011), is based on the derivatization of carbonyl compounds with an original oxyamino reagent i.e. dansylacetamidooxyamine (DNSAOA). Oximes which form in solution are subsequently sep-

arated and detected by using high performance liquid chromatography (HPLC) with fluorescence detection. The method exhibits limits of detection below 1 nM for the compounds targeted here i.e. formaldehyde (HCHO), acetaldehyde (CH_3CHO) and polyfunctional carbonyls glyoxal (CHOCHO), methylglyoxal (CH_3COCHO) and hydroxyacetaldehyde. ($HOCH_2CHO$) and the analyses of the carbonyl content of cloud samples were tripled for a quantitative approach. Samples were frozen until quantification of carbonyls, which was done once a year. Previous works highlighted the full recovery of carbonyls after samples were frozen and since they are analyzed right after their thawing (Domine et al., 2010; Houdier et al., 2011).

2.3 Statistical analyses

Principal component analysis (PCA) was performed using Simca-P + software (Umetrics). Air mass categories were determined with a hierarchical classification from PCA results. To highlight significant differences between data groups, the Kruskal–Wallis non parametric test was carried out with Past software (Hammer et al., 2001). Two air mass categories were declared different when the probability for the groups to have identical data distribution was lower than 5 % (p value < 0.05). This test was chosen due to the lack of normality of the data according to the Shapiro–Wilk normality test.

2.4 Back-trajectory plots

Seventy three-hour backward trajectories of the air masses collected at the puy de Dôme were calculated using the HYSPLIT model with the GDAS1 meteorological data archive and default settings (Draxler and Rolph, 2012).

3 Results

Seventy three cloud events have been sampled at the top of the pdD between 2001 and 2011, representing 199 individual samples. The cloud chemical composition as

well as the physico-chemical parameters measured at the pdD station can be found on a dedicated website (http://wwwobs.univ-bpclermont.fr/SO/beam/data.php). Table S1 indicates the physico-chemical analysis performed for each cloud event together with the origin of the air masses reaching the sampling site.

⁵   We decided in this study to classify our cloud samples according to a statistical analysis that considers physico-chemical parameters of the cloud samples. This approach is more robust than looking only at the back-trajectories of the air masses that reach the puy de Dôme station. Nevertheless, the back-trajectories are drawn for each cloud samples to confirm the statistical classification. Cloud events corresponding to 4 indi-

¹⁰ vidual samples (No. 19 and 27, Table S1) with air masses originating from the Sahara according to the corresponding back-trajectory plots were excluded due to their lack of representativeness in the dataset.

3.1   Origin of air masses – climatology

Individual samples were classified by principal component analysis (PCA). This tech-
¹⁵ nique was previously applied to inorganic ion concentrations in cloud water and to the air mass origin (Deininger and Saxena, 1997; Kim et al., 2006b). Here, this statistical approach is used to distinguish the parameters that are influencing the cloud sample characteristics.

At first, 13 variables measured at the pdD station were considered in the analysis:
²⁰ major ion concentration, total ion content, cloud water loading, liquid water content, pH, conductivity, redox potential, iron concentration and total organic carbon. Only six variables with the highest correlation with the two first principal components (PCs), i.e. the most discriminating variables between different groups, were kept to perform a second PCA: pH and Na^+, Cl^-, NO_3^-, NH_4^+ and SO_4^{2-} concentrations. Among all
²⁵ cloud events, only 138 samples corresponding to 56 events presented sufficient data for the analysis (one missing value at maximum). The two first PCs of this second analysis represented more than 80 % of the total variability of the samples (PC1: 50.41 %; PC2:

30.08 %) (Fig. 1a), i.e. 80 % of the disparity between groups is kept despite the fact that only two axes are used to represent six variables.

The hierarchical classification led to the constitution of 4 clusters. The first one exhibited high concentrations of Na^+ and Cl^- (means of 311 and 232 µM, respectively) and cloud samples from this cluster were thus classified as "highly marine". The second group exhibited low concentration of ions but elevated pH and corresponded to the "marine" category. Finally, the two remaining clusters were classified as "continental" and "polluted" with increasing concentrations of NH_4^+, NO_3^-, SO_4^{2-}. Despite the fact that the 4 categories are well separated, they partly overlap (Fig. 1a). Hence, air mass back-trajectories (not taken into account in the analysis presented on Fig. 1a) have also been considered for establishing this categorization. This also confirms that the tricky point for the selection is clearly the relevant criterion to distinguish marine and continental influence.

Based on this analysis, criteria intended to classify further cloud events have been defined; these are summarized in Table 1. Among the last 57 samples not considered in this statistical analysis, 12 were classified as highly marine, 25 as marine, 7 as continental and 13 as polluted.

In order to highlight the influence of the air mass origin on cloud droplet chemical composition, events were divided into four different sectors of origin according to the corresponding back-trajectory plots: West (W), Northwest/North (NW/N), Northeast (NE) and South/Southwest (S/SW) (Fig. 2). Cloud events from the West and the Northwest/North sectors were the most frequent, representing 72 % of the air masses sampled at the pdD station, among which the majority was categorized as "marine" or "highly marine". Air masses originating from West were mainly under Atlantic Ocean influence (80 % of the events from West) while the air masses originating from the Northwestern/Northern sector could also be subject to continental effects from United Kingdom (UK) (24 % of the events from NW/N were classified as continental). The Northeastern sector was characterized by air masses with high anthropogenic influence due to Eastern Europe emissions (55 % of the events were polluted). Air masses from the

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Southwest/South sector were dominated by a pronounced marine character (64 %) and a continental influence from Spain (36 %). During the past 10 yr, in total 13 % of the air masses sampled at the pdD station were under highly marine influence, 52 % under marine influence, 26 % under continental influence and 9 % under anthropogenic influence.

In the next part, we will focus on the variability of the chemical composition of cloud water as a function of air mass categories determined by our statistical analysis. Table S2 presents the physico-chemical parameters (pH, redox potential, conductivity, liquid water content) and concentrations of measured chemical compounds (average, minimum, maximum) as a function of air mass origins together with data from recent studies describing cloud chemical composition. Since the chemical makeup of clouds is sufficiently different from that of fog, primarily due to the environments in which they form (Collett et al., 2002; Straub et al., 2012; Weathers et al., 1988), data for fog have been excluded here. Although these studies featured a variety of cloud collection devices, different analytical techniques, and often a limited number of samples, some general comparisons can be made with our dataset.

3.2 Physico-chemical parameters

Table 2 summarizes the minimum, maximum, average and median values of TIC, pH, conductivity, redox potential, TOC and LWC for the whole data set; Table S2 shows the minimum, maximum and average values of the physico-chemical parameters for each category of air mass and Fig. 3 represents the distribution of these parameters as a function of air mass categories.

TIC values are relatively low and characteristic of European high-altitude sites, far from local pollution sources, such as Jungfraujoch (3450 m a.s.l., Switzerland, Baltensperger et al., 1998) or Sonnblick (3106 m a.s.l., Austria, Hitzenberger et al., 2000). Polluted air masses sampled at the pdD station are the most acidic (mean pH = 4.3 ± 1.1) and present significantly higher conductivity than the other types of air mass. TIC values are also higher for polluted and highly marine conditions due

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to the higher amount of nitrate, sulfate and ammonium for polluted air masses and sodium and chloride for highly marine clouds. These observations are confirmed by other studies (Cini et al., 2002; Collett et al., 2002; Kim et al., 2006a; Möller et al., 1996). For example, Collett et al. (2002) sampled cloud water on the West coast of the USA and at Mount Whiteface and Mount Mitchell. The average pH on the West coast was around 6.0, because of the marine influence of the Pacific Ocean, while the pH at Mount Whiteface and Mount Mitchell, two sites located close to urban areas, was very acidic (up to 2.4). Our cloud water samples present naturally well-correlated conductivity and TIC ($R = 0.92$); polluted air masses are more acidic, have the highest amount of ionic species and consequently they present a high conductivity and TIC (Kim et al., 2006a).

The redox potential of a water solution characterizes the average capacity of dissolved material to gain or lose electrons and reflects the reactivity. Many factors can limit the interpretation of the redox values measured in sampled cloud water such as temperature and pH. The redox potential also depends on the concentrations of reduced and oxidized forms of a large number of redox couples in solution, influencing their reactivity and equilibria in cloud water. However, if the direct interpretation of the redox potential data is not possible in natural environments, it is still possible to compare the oxidative capacities of cloud water from one event to the other. Figure 3 shows that the average redox potential E_h of cloud water in polluted air masses (122.3 mV) was significantly higher than in marine and highly marine air masses (22.0 and 4.3 mV, respectively) (p values: polluted/marine $= 4 \times 10^{-3}$; polluted/highly marine $= 7.1 \times 10^{-5}$). It is also interesting to note that in polluted air masses, E_h is always positive, demonstrating that polluted clouds are oxidant media in the atmosphere, while continental and marine cloud can be either oxidant or reducer. This observation could be the result of the higher abundance of transition metal ions (TMI) commonly measured in cloud water originating from polluted air mass. TMI, i.e. Fe, Mn, Cu, etc., present a higher standard redox potential than the species typically found in marine air such as Mg^{2+}, Na^+ and Ca^{2+} for example. In these cases, a subsequent continental or

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anthropogenic component of metals can be due to their dissolution from anthropogenic particles (such as ashes emitted from power plants, from combustion engine exhaust or from industrial operations). The concentrations of dissolved iron at the pdD station confirm this general statement (see Sect. 4.5). Some authors have even proposed the use of iron concentration as a parameter for determining the redox potential in hydrometeors, which would be feasible thanks to the limited range of pH and E_h in atmospheric aqueous samples (Sinner et al., 1994; Stumm and Morgan, 1996).

TOC is significantly higher in polluted air masses (with an average value of 12.4 mg C L^{-1}) than in continental, marine and highly marine ones (5.5, 3.3 and 4.8 mg C L^{-1}, respectively). In the case of polluted events, a further anthropogenic source of organic carbon can be superimposed to the background level. Few studies reported measurements of this parameter for cloud water (Table S3) and presented values within the same range than our data. A previous study at the pdD station from 2001 to 2002 reported a DOC (Dissolved Organic Carbon) ranging from 1.2 to 15.5 mg C L^{-1} (Marinoni et al., 2004). These values of DOC are quite close to the TOC values reported here for the same sampling site, suggesting a lower contribution of the water-insoluble organic carbon. Reyes-Rodriguez et al. measured the TOC and the DOC in cloud water from marine origin: the TOC ranged from 0.15 to 0.66 mg C L^{-1} and the DOC from 0.13 to 0.65 mg C L^{-1} (Reyes-Rodríguez et al., 2009) confirming that a significant fraction of TOC was composed of water-soluble organics (DOC/TOC = 0.79). Field measurements on fogs also reported that DOC constitutes about 80 % of the total organic carbon in the aqueous phase (Herckes et al., 2002; Raja et al., 2008; Straub et al., 2012). A supplementary organic contribution is also observed in highly marine clouds which presented significantly higher TOC values than marine clouds (p value = 4×10^{-4}).

As already mentioned, the liquid water content (LWC) measured at the pdD station exhibits rather limited variation with an average value of 0.28 ± 0.12 g m^{-3} (Fig. 3). Several studies discussed the relationship between LWC and solute inorganic concentrations (Elbert et al., 2000; Aleksic and Dukett, 2010) where non linear relationships were extracted and evaluated. These relationships reflect the fact that an increase in

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the LWC should lead to a dilution of the cloud solute content. In our study, we see no relationships between the LWC and the inorganic solute concentrations. Therefore, the variations observed in the solute concentrations are not due to variations in LWC ($R = -0.08$) and to dilution effect. For organic matter, we also observed no relationships between TOC and LWC (Fig. S1). The solute (both organic and inorganic) concentrations must be attributed to the various influences which cloud droplets are subjected: microphysics, meteorology, gas phase reactions, chemical reactions in the liquid phase and sedimentation (Herckes et al., 2013).

In the next sections, concentrations of inorganic, organic and oxidant species are presented and discussed as a function of our classification. To facilitate the comparison with other studies, we will present their concentrations expressed in µeq L^{-1} for ions.

3.3 Inorganic ions

The relative distribution of inorganic ions was calculated for each single event; the average values of the different air mass categories are presented in Fig. 4. Only cloud events where all the inorganic ions have been quantified are considered (6, 46, 66 and 16 cloud samples for polluted, continental, marine and highly marine categories, respectively). For a direct comparison of the 4 air mass categories, a radar chart plot presenting the relative contributions of each ion is also drawn on this figure. Table S2 shows the minimum, maximum and average concentration values of inorganic ions calculated for all cloud events.

The potential sources of nitrate, sulfate and ammonium in cloud water are multiple and include particles (ammonium sulfate and ammonium nitrate particles) and gases (from SO_2, HNO_3, NH_3) (Sellegri et al., 2003). The concentration of ammonium, nitrate and sulfate are significantly correlated within each category of air mass (R varies between 0.64 to 0.94, $n = 6$ to 70). This result can be related the higher contribution of their common particulate sources compared to their individual gaseous sources. In our study, nitrate, sulfate and ammonium ions are abundant as previously observed during studies at pdD (Leriche et al., 2007) and during other field campaigns (Aleksic et al.,

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2009; Löflund et al., 2002); these represent an average contribution to the TIC of 65 % (marine), 76 % (continental) and 85 % (polluted). For the highly marine clouds, their contribution to the TIC is much lower (25 %) due to the high concentrations of sodium and chloride; however, the absolute average concentrations of nitrate (59 µM), sulfate (79 µM) and ammonium (88 µM) ions are still rather elevated in this category of air mass. Observations made at the pdD station for marine and highly marine air masses are in agreement with those of Reyes-Rodriguezet al. and Gioda et al., who sampled air masses from Atlantic Ocean in Puerto Rico (Gioda et al., 2009; Reyes-Rodríguez et al., 2009) and showed similar pH and concentrations of inorganic ions. Blas et al. (Blas et al., 2008) sampled cloud water at the "Black Triangle", one of Europe's most industrialized regions: pH and inorganic ions concentrations in anthropogenic cloud water sampled at pdD were in the same range.

The contribution of nitrate to the TIC (from 6 % in highly marine cloud water to 48 % in polluted clouds) measured at the pdD site is higher than in field measurements at other locations. A possible explanation could be the remoteness of the pdD site from local sources and the efficient oxidation of NO_x compounds converted into nitric acid and then nitrate (Wang et al., 2011). The nitrate to sulfate equivalent ratio is shown on Fig. 5 for the 4 categories of clouds. This ratio is highest in polluted clouds (from 0.9 in highly marine air masses to 3.6 for polluted clouds) due to the high nitrate content in polluted air masses. Some studies showed that the NO_3^-/SO_4^{2-} ratio increases with the distance from the source of pollution, which makes this value an indicator of the remoteness of a site. At the pdD sampling site, since the origin of the air masses is variable with high nitrate fractions for polluted air masses, this conclusion cannot be applied. The ratio for all the categories of clouds sampled at the pdD is higher than most of the values reported elsewhere for cloud water samples, which are generally below 1 (Baltensperger et al., 1998; Bridges et al., 2002) for cloud water samples. This could be related to high NO_x emission and the predominance of nitrate over sulfate in the acidification of aerosols.

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Ammonium in cloud water results from the precursor aerosol particles or from the dissolution of gaseous ammonia. Its contribution to the TIC is relatively high in all air mass categories. Therefore, the pH of cloud water is influenced by ammonium related to emissions from agricultural activities. However, the sum of nitrate and sulfate con-
5 centrations is much higher than ammonium concentration for polluted cases, resulting in partial acid neutralization and acidic cloud water. The concentration of calcium is higher in polluted and continental air masses than in marine air masses, as a result of the higher contribution of its terrestrial source rather than its marine source. For highly marine clouds, the water is enriched in salts formed from the evaporation of sea
10 spray, such as $CaCO_3$ leading to a high Ca^{2+} concentration. Ca^{2+} also contributes to the neutralization of the acidity but to a smaller extend than ammonium. In marine air masses, the average ratio Cl^-/Na^+ is equal to 1.41 and reaches 1.06 for clouds defined as highly marine, a value that is below seawater (1.17) (Holland, 1978). This loss of chlorine may be caused by the deposition of HCl gas to the sea surface before its
15 absorption by cloud droplets (Watanabe et al., 2001). Another explanation could be due to the aerosol aging during its transport: in the aerosol phase, the reaction NaCl + HNO_3 gives $NaNO_3$ and HCl which volatilizes leading to a depletion of Cl^- (Bourcier et al., 2012; Sørensen et al., 2005). For polluted air masses, this ratio is 2.54, resulting from the enrichment of chloride over polluted areas. In fact, chloride ions have a marine
20 source from NaCl particles and also an anthropogenic source with the solubilization of gaseous HCl into the aqueous phase (McCulloch et al., 1999; Shapiro et al., 2007).

As the marine ratio for SO_4^{2-}/Na^+ is known (0.06 on a molar basis) (Holland, 1978), the contribution of SO_4^{2-} from anthropogenic sources, i.e. non sea-salt sulfate (nss-SO_4^{2-}) can be inferred. The contribution of nss-SO_4^{2-} ranges from 86 to 100 % of the
25 SO_4^{2-} dissolved in polluted clouds, whereas for marine clouds, this value is more disperse and ranges from 5 to 99 % with an average of 89 %. For highly marine clouds, the mean contribution of nss-SO_4^{2-} is much lower and reaches 47 %. This demonstrates that a significant natural source of sulfate exists in some clouds categorized as marine and highly marine. In fact, nss-SO_4^{2-} over the oceans derives principally from reduced

sulfur gases, primarily dimethylsulfide (DMS), which is produced by biological activity in the oceans and from sulfur compounds, primarily SO_2, derived from anthropogenic sources on the continents (Savoie et al., 2002). Sulfate can also be produced in cloud water by oxidation of SO_2 (Ghauri et al., 2001) that tends to acidify cloud droplets and to the production of new aerosol mass by nonvolatile sulfate.

In this study, 17 cloud samples (i.e., 7 events) are classified as polluted clouds in comparison with the 52, 101 and 25 samples for continental, marine and highly marine air masses respectively. From Fig. 4, we can conclude that the relative distribution of inorganic ions does not differ strongly for continental and marine air masses, even if the concentrations of the quantified species were different (see Table S2). This observation is well illustrated by the radar chart presented in Fig. 4, showing that the relative contribution of each inorganic ion is really close for marine and continental air masses. On the opposite, the two last categories exhibit contrasted behavior with respectively high level of nitrate for polluted air masses and high level of chloride and sodium for highly marine air masses.

3.4 Carboxylic acids – carbonyl compounds

Field investigations including recent observations aimed to characterize and quantify individual organic compounds in cloud water during specific field campaigns with a focus on small chain organic compounds such as mono- and di-carboxylic acids and some carbonyls and di-carbonyls (Herckes et al., 2013). Here, we present the concentrations of 5 carboxylic acids and 5 carbonyls as a function of the air mass origins.

Figure 6 shows the mean relative contribution of 5 carboxylic acids (formate, acetate, oxalate, malonate, succinate) for each air mass category. Only the cloud events where all these compounds have been measured are considered (2, 23, 31 and 14 samples for polluted, continental and marine and highly marine categories, respectively). Table S2 indicates the minimum, maximum and average values of carboxylic acid concentrations calculated for all events. Acetic and formic acids represent the most abundant of the five carboxylic acids, as previously observed (Khwaja, 1995;

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Löflund et al., 2002). Carboxylic acids, in the atmospheric aqueous phase, have different sources, such as anthropogenic and biogenic direct emissions in the gas and particulate phases or chemical transformations from organic precursors (Charbouillot et al., 2012; Chebbi and Carlier, 1996; Khare et al., 1999). Formic acid can result from the oxidation of methanol by radicals (mainly HO$^\bullet$ during daytime conditions). Acetic acid can be produced in the aqueous phase by the oxidation of various alcohols, like ethanol, ethylene glycol or 2-propanol (Tilgner and Herrmann, 2010). The transfer from the gas phase is also an important source of formic and acetic acids in the atmospheric aqueous phase, which Henry's law constant are equal to 5400 and 5300 M atm^{-1} respectively (Johnson et al., 1996). Moreover, the presence of acetic and formic acids can also be potentially the result of their production by microorganisms as they are common intermediates in different metabolic pathways (Husárová et al., 2011). Oxalic acid is the most abundant carboxylic acid after acetic and formic acids. Oxalic acid is produced through several steps of oxidation. In contrast to acetic and formic acids, oxalic acid in the aqueous phase does not originate from the gas phase, which can explain its lower concentration. Moreover, it efficiently creates metallic complexes with iron, which represents a sink through photolysis (Deguillaume et al., 2005). Finally, among the quantified acids, succinic and malonic acids are the less abundant in all air mass categories. Opposite to acetic and formic acids, succinic and malonic acids in the atmospheric aqueous phase are supposed to come exclusively from the particle phase. At present, to our point of view, only few studies highlighted the production of succinic and malonic acids from oxidation processes in the cloud aqueous phase (Perri et al., 2009; Charbouillot et al., 2012). This lack of potential sources by the aqueous phase reactivity of succinic and malonic acids could explain their lower concentrations in cloud water. They are also a lot less concentrated in the particulate phase than acetic, formic and oxalic acids (Legrand et al., 2007). Globally, concentrations of carboxylic acids that were monitored at the pdD station are similar to those measured at Mt Rax in Austria (Löflund et al., 2002) or at Mt Schmücke in Germany (van Pinxteren et al., 2005) (see Table S2), which are both away from local pollution. The concentra-

tion of these organic acids is higher for polluted clouds demonstrating the supplemental sources for air masses resulting from their travels over polluted area. For highly marine clouds, the amount of these acids is on the same order than the one for continental clouds showing a marine input of organic matter as confirmed by TOC measurements

5 (O'Dowd et al., 2004).

Only 2 cloud samples considered here are in the polluted category. Even if the amount of carboxylic acids was different for each category (see Table S2), the relative distributions for continental, marine and highly marine categories are similar and differ strongly from the polluted air masses, as illustrated by the radar chart presented

10 in Fig. 6.

By comparison with the TOC measurements, we can estimate the presence of other organic species in cloud water, like alcohols, carbonyl compounds, larger multifunctional structures that contain significant fraction of heteroatoms (S, N, O) (such as HUmic-LIke Substances (HULIS), fulvic material, organosulfur species) (Feng and

15 Möller, 2004; Graber and Rudich, 2006; LeClair et al., 2012) and also biologically-derived material (Bauer et al., 2002; Delort et al., 2010; Ekström et al., 2010). The proportion of undetermined organic matter in cloud water is around 90 % for the 4 categories showing the large unidentified portion of organic matter in cloud water (Fig. 6, see text above each pie-chart).

20 Carbonyl compounds have also been monitored at the pdD station: formaldehyde (F) was measured since 2000 and acetaldehyde (AC), glyoxal (GL), methylglyoxal (MGL) and hydroxyacetaldehyde (HA) were also quantified for 24 cloud samples between 2008 and 2011. Carbonyls in cloud water essentially result from their dissolution from the gas phase into the aqueous phase according to their Henry's law constants

25 (Matsumoto et al., 2005). In the aqueous phase, the oxidation of carbonyls produces carboxylic acids (Legrand et al., 2007) and also potentially leads to the formation of oligomers (Ervens and Volkamer, 2010) which can contribute, upon cloud droplets evaporation, to SOA. Particularly interesting with this scope in mind, is the key role of α-oxygenated carbonyls GL, MG and HA measured in this study. Oxidation by the HO$^\bullet$

radical of these highly water soluble compounds (Henry's law constant $H_{GL} = 3.6 \times 10^5$; $H_{MG} = 3.7 \times 10^3$, $H_{HA} = 4.14 \times 10^4$ M atm^{-1} at 25 °C) (Betterton and Hoffmann, 1988; Sander et al., 2006) was shown to yield formic and oxalic acids (Altieri et al., 2008; Carlton et al., 2007; Perri et al., 2009) but also, to a smaller extent, succinic and malonic acids (Perri et al., 2009). Concentration levels for F, GL and MGL have already been measured concomitantly in rain or cloud water (Igawa et al., 1989; Munger et al., 1995; van Pinxteren et al., 2005; Ervens et al., 2013), but only few studies have accounted for HA concentrations (see for instance, Matsumoto et al., 2005; Matsunaga and Kawamura, 2000). Figure 7 presents the relative contributions of these 5 carbonyls for the 4 air mass categories. The concentration (average, min, max) of the five carbonyl compounds for the whole data set is presented in Table 3.

The amount of carbonyls in cloud water is higher for polluted and continental clouds, reflecting the great variety of their possible primary (vehicle exhaust, biomass burning, industrial and plants emissions) and secondary (oxidation of hydrocarbons) sources (Altshuller, 1993; Hoekman, 1992; Possanzini et al., 2002). As expected, formaldehyde is the most abundant one in all cases with concentrations ranging from 5.0 μM for polluted clouds to 1.8 μM for marine ones. It is noteworthy that, except in marine samples, HA concentrations are higher than the ones of GL and subsequently MGL. Even if clouds form in rather different atmospheric environments, this result supports observations by Matsunaga and Kawamura (2000) that HA was the main α-oxygenated carbonyl in snow and rain samples. These authors attributed the relatively high abundance of HA in their samples to the fact that this carbonyl compound could form a cyclic hemiacetal dimer much less reactive toward oxidation than the free HA molecule. Despite relatively high gas phase concentrations expected for this compound (> 1 ppbv) (Matsumoto et al., 2005), concentrations of AC are lower compared to other carbonyls. This can be explained by its low Henry's law constant (11.4 M atm^{-1} while the other Henry's law constant ranged from 2.97×10^3 m atm^{-1} for F to more than 3×10^5 M atm^{-1} for GL) (Sander et al., 2006). These compounds are not well correlated demonstrating the

multiplicity of sources existing in the atmosphere and the different chemical transformations they can undergo once they are dissolved into cloud water.

Concentrations of carbonyls in cloud water represent only a small fraction of the organic matter in cloud water (from 0.8 to 1.8 % of the TOC depending on the air mass origins). However, quantifying their concentrations in other cloud samples at various sites would help for further investigations dedicated to the understanding of the in-cloud processes involved in the formation of SOA (Ervens et al., 2011, 2013; Tan et al., 2010). In particular, the importance of measuring HA when analyzing cloud water chemical composition should be underlined due to its relatively high concentration.

3.5 Oxidants: iron and hydrogen peroxide

Transition metal ions (TMI) are highly reactive in aqueous solutions and their reactivity is dependent on many factors such as pH, so that their oxidation state and their concentrations are still prone to large uncertainties (Deguillaume et al., 2005). These compounds, especially iron, are supposed to drive the oxidative capacity of the cloud water through the production of HO$^\bullet$ radicals (Long et al., 2013) but also accelerate the conversion of sulfite to sulfate (Harris et al., 2013). Measurements of iron concentrations in its different oxidation states were conducted on 129 samples (Table S1). The range of concentrations measured at the pdD exhibits much lower values than measurements in clouds or fogs collected near sources of heavy pollution such as big cities or industrial area (Kotronarou and Sigg, 1993); but they are in the same range as field measurements carried out at free tropospheric and marine sites such as South Germany (Sinner et al., 1994), Whiteface Mountain – US (Arakaki and Faust, 1998), Great Dun Fell – UK (Sedlak et al., 1997) or San Pedro Hill – US (Erel et al., 1993). However, the iron concentrations are significantly higher in polluted air masses where a significant anthropogenic component is added to the background level (Majestic et al., 2009).

Figure 8 shows the aqueous concentrations of soluble iron (Fe) in its two main oxidation states: Fe(II) and Fe(III). The ratio between the concentrations of Fe(II) and Fe(III) is a good indicator of the oxidizing capacity of hydrometeors. At the pdD station, Fe(II)

is the predominant oxidation state of iron in cloud water sampled: 83, 70, 54 and 77 % respectively for the polluted, continental, marine and highly marine categories. This confirms the previous results obtained at the pdD by Parazols et al. who found an average Fe(II)/Fe(tot) ratio of 0.76 ± 0.25 (Parazols et al., 2006). Siderophores produced by microorganisms or macromolecules such as HULIS or exopolymeric substances (EPS) could play a role in stabilizing iron in its reduced oxidation state and preventing its further re-oxidation. This is supported by the correlation existing between TOC and Fe(II) for continental and marine categories ($R = 0.70$ and 0.61, respectively). Interestingly, no relationship is observed for polluted and highly marine air masses.

H_2O_2 like iron is a strong oxidant of the cloud water; it originates from gas-to-liquid partitioning of H_2O_2 and $HO_2^\bullet$ radicals and from aqueous phase photo-production (Anastasio et al., 1994; Laj et al., 1997a). Measurements of the concentration of H_2O_2 were performed for 107 samples; it ranges from 0.1 to 57.7 µM (Table S2). Figure 8 shows the concentration of H_2O_2 for each air mass category. The concentrations of H_2O_2 are much more disperse in marine and highly marine air masses (standard deviation = 7.12 and 6.31 µM for highly marine and marine categories, respectively) compared to polluted clouds (standard deviation = 1.57 µM) characterized by the lowest average concentration of H_2O_2 (∼ 4.9 µM). Potential explanations are related to (1) efficient sinks of gaseous H_2O_2 by its reactions with NO_x and SO_2 present in large concentration and to (2) the efficient reduction of H_2O_2 in the aqueous phase by its reaction with sulfite leading to the sulfate production (Benedict et al., 2012; Shen et al., 2012). In addition, the study of Marinoni et al. presents diurnal trend with higher day-time concentration of aqueous H_2O_2 and concludes that the dominant source of hydrogen peroxide is the mass transfer from the gas to the liquid phase (Marinoni et al., 2011).

4   Conclusions and recommendations

Clouds incorporate the local pollution when droplets nucleate and then transform pollutants during its lifetime. In this context, the impact of regional and long-range transport

of chemical constituents at the puy de Dôme site is apparent and due to the remote (and elevated) geographical character. In this paper, a long-term database of the aqueous phase chemical composition of clouds sampled at the puy de Dôme station between 2001 and 2011 is presented. The abundance of inorganic and organic chemical

5 compounds as well as a series of physico-chemical parameters permitted the identification of various influences corresponding to distinct air-mass histories. A classification was performed by principal component analysis that allows to define discriminating factors (pH and concentrations of Na^+, Cl^-, NO_3^-, NH_4^+ and SO_4^{2-}) for 4 different categories: polluted, continental, marine and highly marine.

10 As shown in this study, chemical speciation is a powerful tool in analyzing air mass history. For example, the presence of inorganic compounds such as nitrate and sulfate followed in this study are due to anthropogenic emissions such as automobiles or power production. However, it is difficult to differentiate the various sources of these measured chemicals in cloud water due to the various potential processes (transfer

15 from the gas phase, dissolution of particles, aqueous chemical reactivity). In this frame, some chemical compounds that are molecular markers of emissions (such as levoglucosan, a marker of biomass burning) should be followed in the future to correlate cloud features with emissions.

Our results also underline that, although this database is rather complete, the char-

20 acterization of the organic matter is still incomplete since around 10 % of the dissolved organic matter is characterized. The measurements of carbonyls in the cloud water should be also continued in the future since they are precursors of oligomers that are observed in secondary organic aerosols (SOA). Polycyclic aromatic hydrocarbons (PAH) (Ehrenhauser et al., 2012), nitrosamines, phenols and nitrophenols (Hutchings

25 et al., 2010), BTEX (Hutchings et al., 2009) and pesticides (Millet et al., 1997) should be quantified for health reasons and their photosensitivity in clouds should be studied in natural and under controlled (i.e. in the laboratory) conditions. Important constituents of ambient atmospheric aerosols are also saccharides (Iinuma et al., 2009) such as sugar alcohols mono-, di- and tri-saccharides, anhydrosugars and polysaccharides; they are

released into the atmosphere by microorganisms, plants, and animals. For example, levoglucosan derives from cellulose; galactosans and mannosans from hemicelluloses during biomass burning (Medeiros et al., 2006; Schmidl et al., 2008). The intensity and the speciation of the sugar release into the atmosphere is dependent on the season (Fu et al., 2012), and vary with the diurnal cycle (Kundu et al., 2010). Until now, no quantitative measurements of sugar concentrations in cloud water have been performed. However, the presence of sugars in this aqueous compartment is likely to exist due to their high solubility in water; their amount in cloud water should be evaluated.

The oxidizing capacity of the cloud aqueous phase should be also quantified for various cloud events. This can be done by the quantification of the photo-production of hydroxyl radicals (HO$^{\bullet}$) as a function of cloud chemical composition, allowing the identification of the different sources and sinks of the most important oxidant of the atmosphere. Dissolved oxygen should also be followed in cloud water because recent study highlighted "its paradoxical role" in the aqueous formation of oligomers: O$_2$ seems to inhibit oligomerization reactions but on the other hand, it contributes to produce oligomerization initiator radicals (Renard et al., 2013).

Finally, even though they are theoretical, models permit to study – within the cloud system – the chemical pathways, the complex interactions between microphysics, chemistry and dynamics (i.e. transport) and the influence of environmental parameters on cloud chemistry. The present study aims at providing statistically robust cloud chemical characterizations and its relationship with environmental factors, such as source regions. These data can be used for modeling purpose as cloud benchmark for natural free tropospheric conditions.

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Table 1. Mean, minimum and maximum values for each discriminating parameters (pH, concentrations of Cl^-, Na^+, NO_3^-, SO_4^{2-}, NH_4^+) for the different categories of cloud events (Polluted, Continental, Marine and Highly marine) determined by the PCA analysis.

		pH	Cl^-	Na^+	NO_3^-	SO_4^{2-}	NH_4^+
			Concentrations ($\mu eq\,L^{-1}$)				
Polluted	Mean	4.0	142.0	115.5	451.1	158.7	357.1
	Min	3.8	28.7	86.3	368.4	147.6	331.8
	Max	4.2	203.3	171.9	516.5	171.0	376.3
Continental	Mean	4.9	30.9	31.5	104.9	94.4	141.8
	Min	3.9	4.8	5.6	31.9	26.4	72.7
	Max	7.0	87.3	99.0	297.9	218.4	339.6
Marine	Mean	5.7	29.9	32.5	24.6	28.0	42.6
	Min	4.7	0.5	0.4	0.8	2.6	4.2
	Max	7.6	231.5	315.7	93.2	78.1	96.2
Highly marine	Mean	6.2	231.9	311.0	72.2	73.1	95.6
	Min	4.7	110.5	138.0	23.7	33.2	47.9
	Max	6.9	394.0	678.6	231.8	144.4	190.0

Table 2. Minimum, maximum, mean and median values of physico-chemical parameters (pH, conductivity (C), total ion content (TIC), total organic content (TOC), redox potential (E_h), liquid water content (LWC)) for the whole data set.

	pH	C ($\mu S\,cm^{-1}$)	TIC ($\mu eq\,L^{-1}$)	TOC ($mg\,C\,L^{-1}$)	E_h (mV)	LWC ($g\,m^{-3}$)
Number of samples	143	90	140	106	93	105
Av	5.5	47.8	415.0	4.9	33.5	0.28
Min	3.1	2.0	19.5	0.3	−164.0	0.05
Max	7.6	348.0	1929.9	25.0	230.0	0.92
Med	5.6	25.0	334.7	3.2	35.0	0.27

Table 3. Minimum, maximum and mean values of concentrations (µM) of the 5 measured aldehydes measured for the different categories of cloud events. BDL: Below Detection Limit.

		Concentrations (µM)				
		Hydroxyacetaldehyde	Formaldehyde	Acetaldehyde	Glyoxal	Methylglyoxal
Polluted	Av	1.24	4.97	0.42	0.89	0.19
	Min	0.44	1.75	0.05	0.38	0.07
	Max	1.77	9.83	0.96	1.87	0.39
Continental	Av	0.79	5.06	0.31	0.73	0.22
	Min	0.05	0.73	0.02	0.17	0.01
	Max	2.34	9.80	0.64	2.29	1.10
Marine	Av	0.13	1.76	0.23	0.13	0.01
	Min	0.02	0.13	0.05	0.01	BDL
	Max	0.30	14.25	0.44	0.74	0.03
Highly marine	Av	0.64	2.01	0.52	0.23	0.02
	Min	0.28	0.70	BDL	0.01	BDL
	Max	1.24	4.20	1.00	0.36	0.06
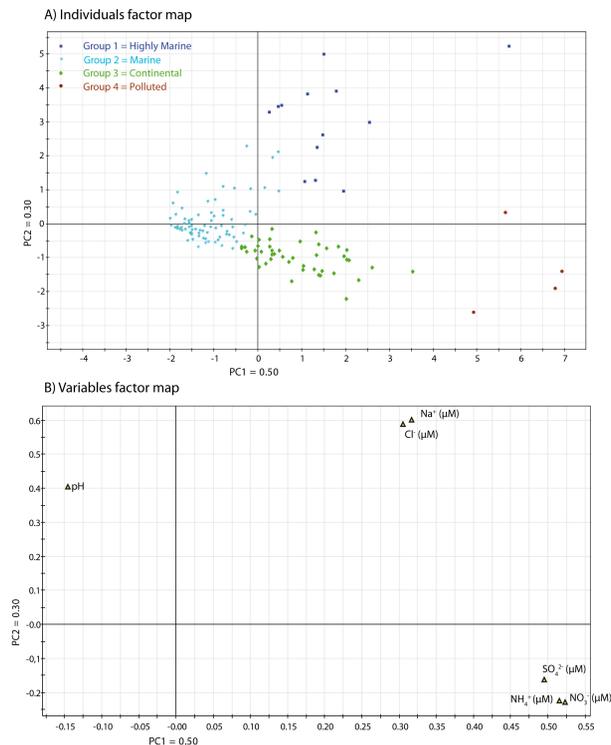
Fig. 1. (A) Individuals factor map: scores of the 138 cloud samples (i.e. 56 cloud events) on the plan PC1–PC2 obtained from the six selected variables. The different colors indicate the hierarchical classification using the Ward method. This led to the constitution of 4 clusters corresponding to polluted, continental, marine and highly marine categories. **(B)** Variables factor map: loadings of the 6 experimental variables (pH, $[Na^+]$, $[Cl^-]$, $[SO_4^{2-}]$, $[NO_3^-]$, $[NH_4^+]$).

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Cloud chemistry at the puy de Dôme mountain

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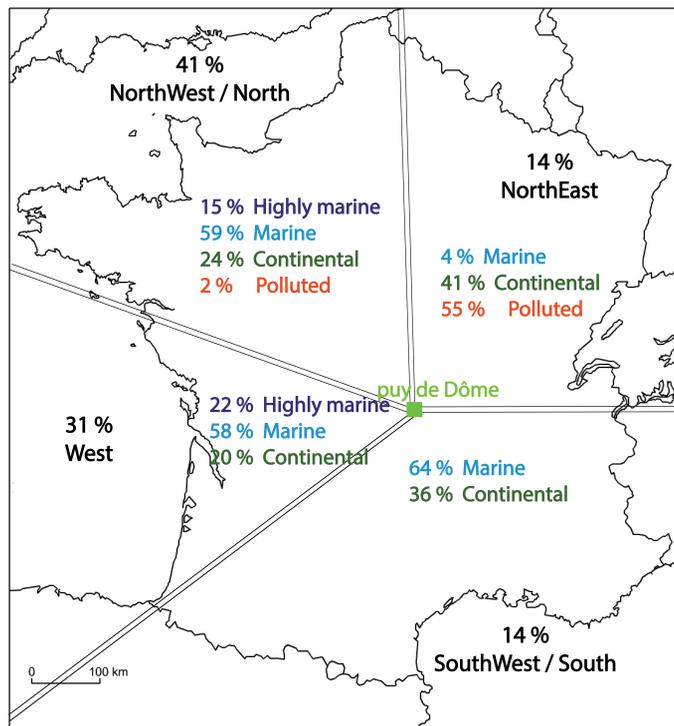
Fig. 2. Air masses reaching the puy de Dôme are divided into four distinct back-trajectory sectors: West (W), Northwest/North (NW/N), Northeast (NE) and South/Southwest (S/SW). Percentages in black represent the occurrence of cloud events in each sector. Percentages in dark blue, light blue, green and red represent the occurrence of cloud events in each sector with highly marine, marine, continental and polluted influences, respectively.
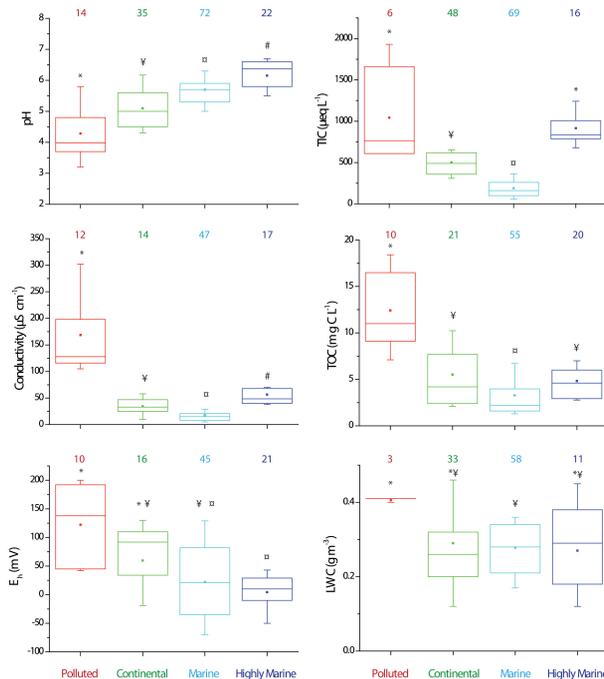
Fig. 3. Distribution of pH, total ion content (TIC), conductivity (*C*), redox potential (*E*$_h$), total organic carbon (TOC) and liquid water content (LWC) of the cloud water sampled at the pdD station for each air mass category. The number of samples analyzed is indicated above each box plot. The bottom and top lines correspond to 25th and 75th percentiles, respectively. The full line and the square symbol represent the median and mean values, respectively. The ends of whiskers are 10th and 90th percentiles. Statistically differences (Kruskal and Wallis test; *p* value < 0.05) between groups are indicated by symbols above box plots.
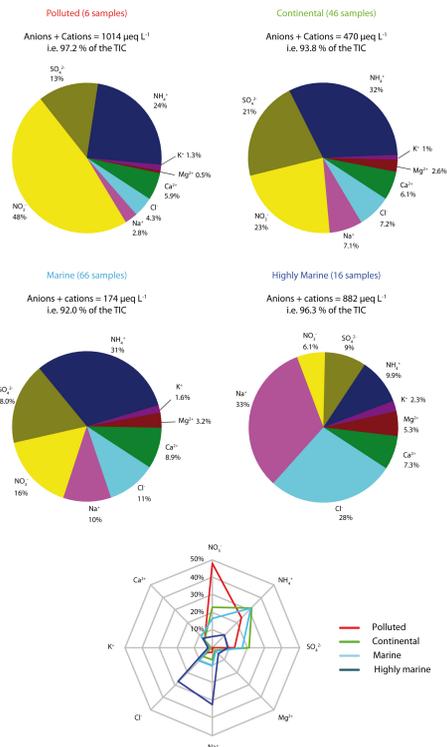
Fig. 4. Distribution of the major inorganic ions measured (Cl$^-$, NO$_3$$^-$, SO$_4$$^{2-}$, Na$^+$, K$^+$, NH$_4$$^+$, Mg^{2+} and Ca^{2+}) for each air mass category (% were calculated using the concentrations of ions in µeq L^{-1}). The sum of the concentrations of inorganic cations and anions in µeq L^{-1} is indicated as well as its contribution to the TIC. The radar chart shows the relative contribution of each inorganic ion as a function of the air mass categories.

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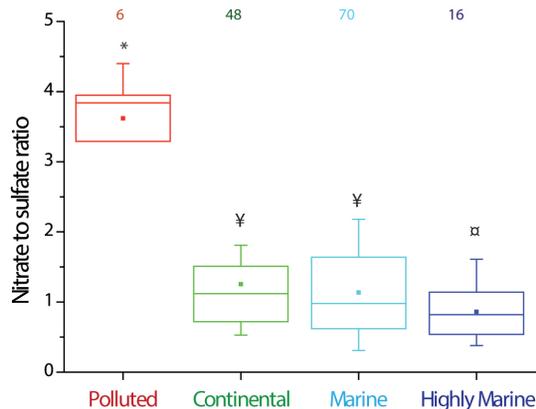
Fig. 5. Distribution of the ratio "nitrate to sulfate" concentrations (expressed in µeq L^{-1}) of the cloud water sampled at the pdD station as a function of air mass categories. Numbers above each box plots represent the number of samples analyzed. At least 3 data are required to represent a box plot. The bottom and top of box plots are 25th and 75th percentiles, respectively. The full line and the square symbol represent the median and mean values, respectively. The ends of whiskers are 10th and 90th percentiles. Statistically differences (Kruskal and Wallis test; p value < 0.05) between groups are indicated by symbols above box plots.

Fig. 6. Distribution of carboxylic acids (formic, acetic, oxalic, malonic and succinic acids) for each air mass category (% are calculated using concentration of individual ion in µeq L^{-1}). On the left part, the sum of the concentrations of these compounds in µg C L^{-1} is indicated as well as the percentage obtained by comparison with the TOC. The radar chart shows the relative contribution of each organic ion as a function of the air mass categories.
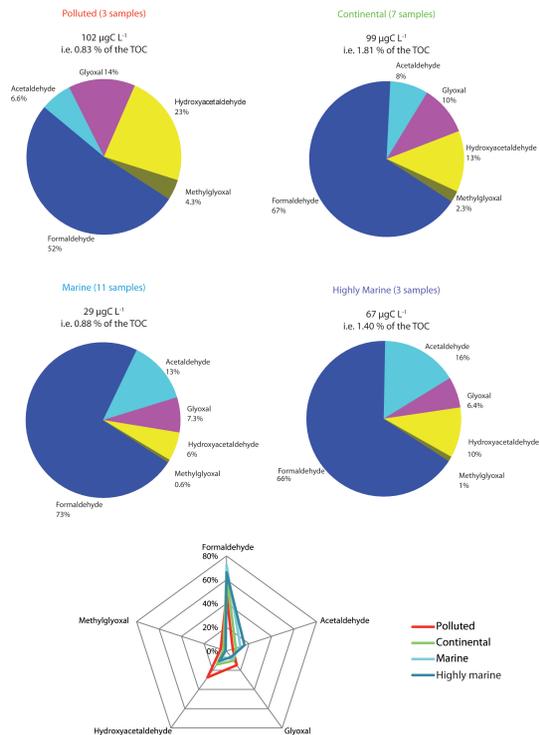
Fig. 7. Distribution of carbonyls (formaldehyde, acetaldehyde, glyoxal, methylglyoxal, hydrox-yacetaldehyde) as a function of air mass categories (% are calculated using concentration in µM). On the left part, the sum of the concentrations of these compounds in µg C L^{-1} is indicated as well as the percentage obtained by comparison with the TOC. The radar chart shows the relative contribution of each compound as a function of the air mass category.
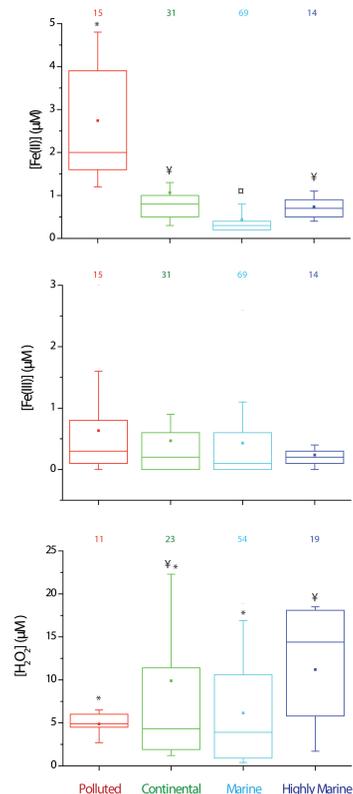
Fig. 8. Distribution of Fe(II), Fe(III) and H_2O_2 as a function of air mass categories. Numbers above each box plots represent the number of samples analyzed. At least 3 data are required to represent a box plot. The bottom and top of box plots are 25th and 75th percentiles, respectively. The full line and the square symbol represent the median and mean values, respectively. The ends of whiskers are 10th and 90th percentiles. Statistically differences (Kruskal and Wallis test; p value < 0.05) between groups are indicated by symbols above box plots.

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