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Classification of clouds sampled at the puy de Dôme (France) based on 10 yr of monitoring of their physicochemical 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. Physicochemical parameters, as well as the concentrations of the major organic and inorganic constituents, were measured and analyzed by multicomponent statistical analysis. Along with the corresponding back-trajectory plots, this allowed for distinguishing four different categories of air masses reaching the summit of the pdD: polluted, continental, marine and highly marine. The statistical analysis led to the determination of criteria (concentrations of inorganic compounds, pH) that differentiate each category 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”; these clusters had the second-highest and highest levels of NH₄⁺, NO₃⁻, and SO₂⁴⁻, respectively. This unique data set of cloud chemical composition is then discussed as a function of this classifica-

tion. Total organic carbon (TOC) is significantly higher in polluted air masses than in the other categories, which suggests additional anthropogenic sources. Concentrations of carboxylic acids and carbonyls represent around 10 % of the organic matter in all categories of air masses and are studied for their relative importance. Iron concentrations are significantly higher for polluted air masses and iron is mainly present in its oxidation state (+II) in all categories of air masses. Finally, H₂O₂ concentrations are much more varied in marine and highly marine clouds than in polluted clouds, which are characterized by the lowest average concentration of H₂O₂. This data set provides concentration ranges of main inorganic and organic compounds 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 interaction; here, the multiphase cloud system holds a particular interest. It contains 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; Selvegrì 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 cloud droplets, aqueous-phase reactions 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.

The role of clouds in the atmospheric cycle of inorganic substances has been discussed in many publications 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 (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, although the formation of SOA has been largely studied in the gas phase, 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 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 (El 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[•] and NO₃[•]) as well as oxidants such as ozone (O₃) and hydrogen peroxide (H₂O₂). 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 that biological processes are potentially involved in the transformation of soluble organic material in cloud droplets, even at low temperatures (Deguillaume et al., 2008; Husárová et al., 2011; Vaitilingom 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 in order to understand and quantify their mechanisms of transformation in the atmosphere. Several in situ investigations of cloud chemistry have already been reported, and most of them are based on specific single campaigns (Bower et al., 2000; Choulaton 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., 1997; 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; they mainly examined 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 information. 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 individual samples) sampled at the puy de Dôme (pdD) mountain, a high-altitude site (1465 m) that can generally be classified as "rural" (Henne et al., 2010; Joly and Peuch, 2012; Putaud et al., 2004). The observation of clouds and, more generally, of atmospheric variables at high-altitude, remote sites brings additional valuable information

on the extent of the anthropogenic influence. Usually, these sites are influenced by long-range transport rather than by local sources, and hence provide information on the physicochemical variability 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 background during the day and more representative of larger synoptic-scale air masses during nighttime (Asmi et al., 2011). The data set presented (pH, conductivity, redox potential, total organic content, concentrations of the most abundant inorganic and organic chemical species, concentrations of oxidants: iron and hydrogen peroxide) could be used as a reference for modeling work that simulates the chemical composition of tropospheric clouds in different scenarios.

2 Material and methods

2.1 Cloud sampling

Sampling was performed at the puy de Dôme (pdD) station (45°46'20" N, 2°57'57" E), which is part of the networks EMEP (the European Monitoring and Evaluation Programme), GAW (Global Atmosphere Watch), and ACTRIS (Aerosols, Clouds, and Trace gases Research Infrastructure). 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 because of 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 documented by primary anthropogenic tracers concentrations (NO, 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 geographical origins. A short summary of previous studies related to this site is given in the Supplement.

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 sampled during that period). Non-precipitating cloud droplets were sampled using a single-stage cloud collector similar to the one described by Krusiz (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 im-

paction (supercooled conditions) or were collected directly as a liquid. The water was transferred at room temperature, either directly or after a short melting period into glass vials. Possible changes in the cut-off diameter due to the formation of ice on the impaction plate are expected to be negligible given the limited volume of the collected sample. The accumulation of ice leads to more efficient sampling by collecting smaller drops.

2.2 Physicochemical parameters and chemical analysis

Physicochemical parameters were measured immediately after sampling; pH, conductivity and redox potential were measured using a Consort[®] multi-parameter C830. 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, which was regularly controlled and calibrated using a spinning optical disk.

After collection, cloud water samples were kept at 4 °C in the dark until the chemical and total organic carbon (TOC) analyses were conducted. TOC was obtained with a Shimadzu TOC 5050A analyzer. Potassium hydrogen phthalate and sodium carbonate aqueous solutions were used to calibrate the instrument for the total carbon content (TC) and the inorganic carbon content (IC). TOC quantification was then obtained by the difference between the measured TC and IC. 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 tenfold diluted samples was made in triplicate or more, and allowed for the measurement of 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–visible spectroscopy were done in triplicate or more; the derivatization of these reactive species in the samples allowed for 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–visible 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 $21\,000 \pm 500 \text{ M}^{-1} \text{ cm}^{-1}$ at equimolar rate. Fe(II) concentration was measured by UV–visible 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 the 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 that 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 that form in solution are subsequently separated 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 (CH₃CHO) and polyfunctional carbonyls glyoxal (CHOCHO), in addition to methylglyoxal (CH₃COCHO) and hydroxyacetaldehyde. HOCH₂CHO 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, since they are analyzed right after their thawing (Domine et al., 2010; Houdier et al., 2011). In cloud droplets, carbonyl compounds (in particular formaldehyde) form adducts with dissolved SO₂. For instance, significant amounts of hydroxymethanesulfonate (HMSA), the adduct of HCHO, have been measured in cloud or fog water where it constitutes a reservoir for both S(IV) species and HCHO (Ang et al., 1987; Munger et al., 1984). HMSA and more generally S(IV)-carbonyl adducts form rapidly and are stable towards dissociation in acidic media such as cloud droplets (Dasgupta et al., 1980; Munger et al., 1984). In this work, derivatization of carbonyls by DNSAOA was performed in an acidified (pH ~ 2) solution of the cloud sample. Dissociation of the carbonyl-S(IV) adducts in the course of the derivatization reaction is therefore unlikely, and carbonyl concentrations reported in this paper represent the free carbonyl concentrations ([carb]_{free}) and therefore lower estimates of the total carbonyl concentrations, with [carb]_{tot} = [carb]_{free} + [S(IV)-carb].

2.3 Statistical analyses

Principal component analysis (PCA) was performed using Simca-P + software (Umetrics). Air mass categories were determined with a “hierarchical clustering analysis” (HCA) from PCA results: cloud events or groups of cloud events were lumped together in pairs based on their similarities. In our analysis, only one missing value from the six variables (pH and Na⁺, Cl⁻, NO₃⁻, NH₄⁺ and SO₄²⁻ concentrations) used for the PCA was permitted to limit artifacts.

To highlight significant differences between data groups, the Kruskal–Wallis nonparametric 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 two-hour backward trajectories of the air masses collected at the puy de Dôme were calculated using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) 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 physicochemical parameters measured at the pdD station can be found on a website (<http://www.obs.univ-bpclermont.fr/SO/beam/data.php>). Table S1 indicates the physicochemical analysis performed for each cloud event together with the origin of the air masses reaching the sampling site.

For this study, we decided to classify our cloud samples according to a statistical analysis that considers physicochemical parameters of the cloud samples. This approach is more robust than considering only 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 individual 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 of the data set.

3.1 Origin of air masses – climatology

Individual samples were classified by principal component analysis (PCA). This technique 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 influence the cloud sample characteristics.

At first, 13 variables measured at the pdD station were considered in the analysis: major ion concentration (Na⁺, Cl⁻, NO₃⁻, NH₄⁺ and SO₄²⁻), total ion content, cloud water loading, liquid water content, pH, conductivity, redox potential, iron concentration and total organic carbon. Only the six variables that discriminated between the different groups most were kept to perform a second PCA: pH and Na⁺, Cl⁻, NO₃⁻, NH₄⁺ and SO₄²⁻ concentrations. Among all cloud events, only 138 samples, corresponding to 56 events, presented sufficient data for the analysis (one missing value at maximum). The two first PCs (principle components) of

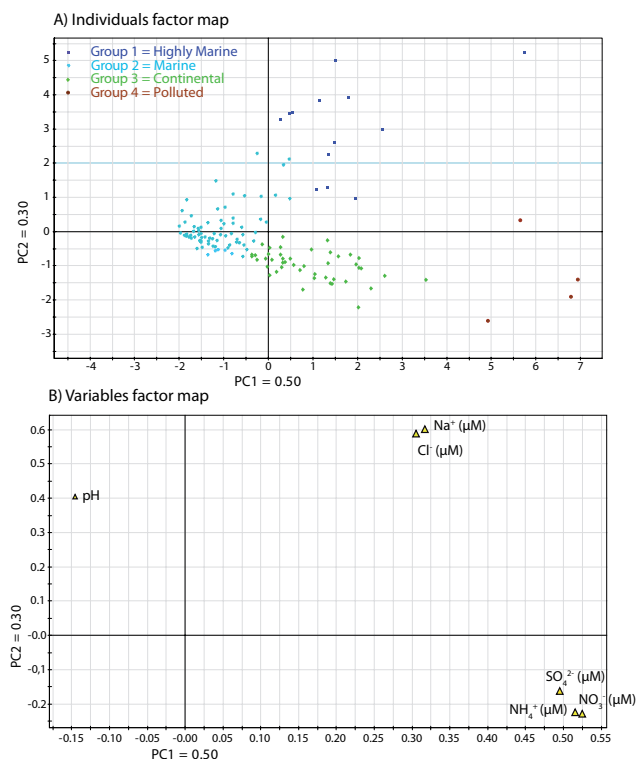


Fig. 1. (A) Individuals factor map: scores of the 138 cloud samples (i.e., 56 cloud events) on the plan PC1-PC2 obtained from the six selected variables. The different colors indicate the hierarchical classification using the Ward method. This led to the constitution of 4 four clusters corresponding to polluted, continental, marine and highly marine categories. (B) Variables factor map: loadings of the 6 experimental variables (pH, $[\text{Na}^+]$, $[\text{Cl}^-]$, $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$, $[\text{NH}_4^+]$).

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 clustering analysis led to the constitution of 4 four clusters. The first one, classified as “highly marine”, is characterized by high concentrations of Na^+ and Cl^- (with means of 311 and 232 μM , respectively) while for the second group, classified as “marine”, a low concentration of these ions is found. For both clusters (“marine” and “highly marine”), the pH range is elevated and similar. Finally, the two remaining clusters were classified as “continental” and “polluted”; these clusters had the second-highest and highest levels of NH_4^+ , NO_3^- , and SO_4^{2-} , respectively. Despite the fact that the four 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 deter-

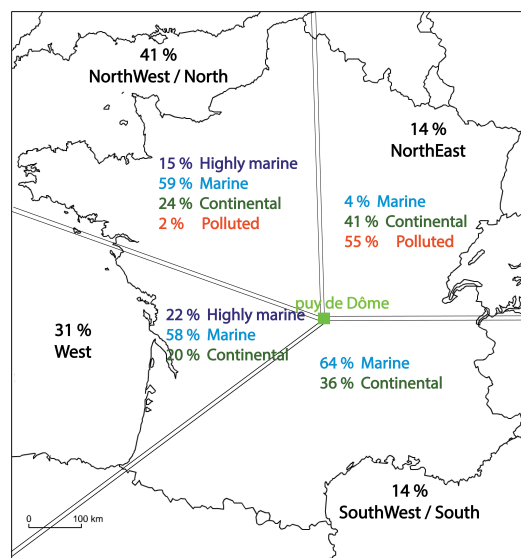


Fig. 2. Air masses reaching the puy de Dôme are divided into four distinct back-trajectory sectors: west (W), northwest/north (NW/N), northeast (NE) and south/southwest (S/SW). Percentages in black represent the occurrence of cloud events in each sector. Percentages in dark blue, light blue, green and red represent the occurrence of cloud events in each sector with highly marine, marine, continental and polluted influences, respectively.

mining the relevant criterion to distinguish marine and continental influence.

For each cluster, the mean, maximal and minimal values of the variables used for the statistical analysis were calculated; these values were used as criteria to classify cloud events that have not been considered in the PCA analysis. These criteria 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 ones, representing 72 % of the air masses sampled at the pdD station, the majority of which was categorized as “marine” or “highly marine”. Air masses originating from west were mainly under Atlantic Ocean influence (80 % of the events from the 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 southwest/south sector were dominated

Table 1. Mean, minimum and maximum values for each discriminating parameter (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.

		Concentrations ($\mu\text{eq L}^{-1}$)					
		pH	Cl^-	Na^+	NO_3^-	SO_4^{2-}	NH_4^+
Polluted	Mean	4.0	142	115	451	159	357
	Min	3.8	29	86	368	147	332
	Max	4.2	203	172	516	171	376
Continental	Mean	4.9	31	31	105	94	142
	Min	3.9	5	6	32	26	73
	Max	7.0	87	99	298	218	340
Marine	Mean	5.7	30	32	24	28	43
	Min	4.7	1	1	1	3	4
	Max	7.6	231	316	93	78	96
Highly marine	Mean	6.2	232	311	72	73	96
	Min	4.7	110	138	24	33	48
	Max	6.9	394	679	232	144	190

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 % were under marine influence, 26 % were under continental influence, and 9 % were under anthropogenic influence.

In the next part of this paper, 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 physicochemical 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 chemical composition of clouds. 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 data set.

3.2 Physicochemical 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 physicochemical 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 Jungfrauoch (3450 m a.s.l., Switzerland, Baltensperger et al., 1998) or Sonnblick (3106 m a.s.l., Austria, Hitzemberger et al., 2000). Polluted air masses sampled at the pdD station are the most acidic (mean $\text{pH} = 4.3 \pm 1.1$) and present significantly higher conductivity than the other types of air mass. TIC values are also higher for polluted and highly marine conditions due 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) (Collett et al., 2002). Regarding the work of Aleksic et al. (2009) at the Whiteface mountain during 12 yr from 1994 to 2006, no significant pH variation (close to 4) was reported over this period. Our cloud water samples present naturally well-correlated conductivity and TIC ($R = 0.92$); polluted air masses are more acidic and have the highest amount of ionic species; 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 a direct interpretation of the redox potential data is not possible in natural environments, it is still

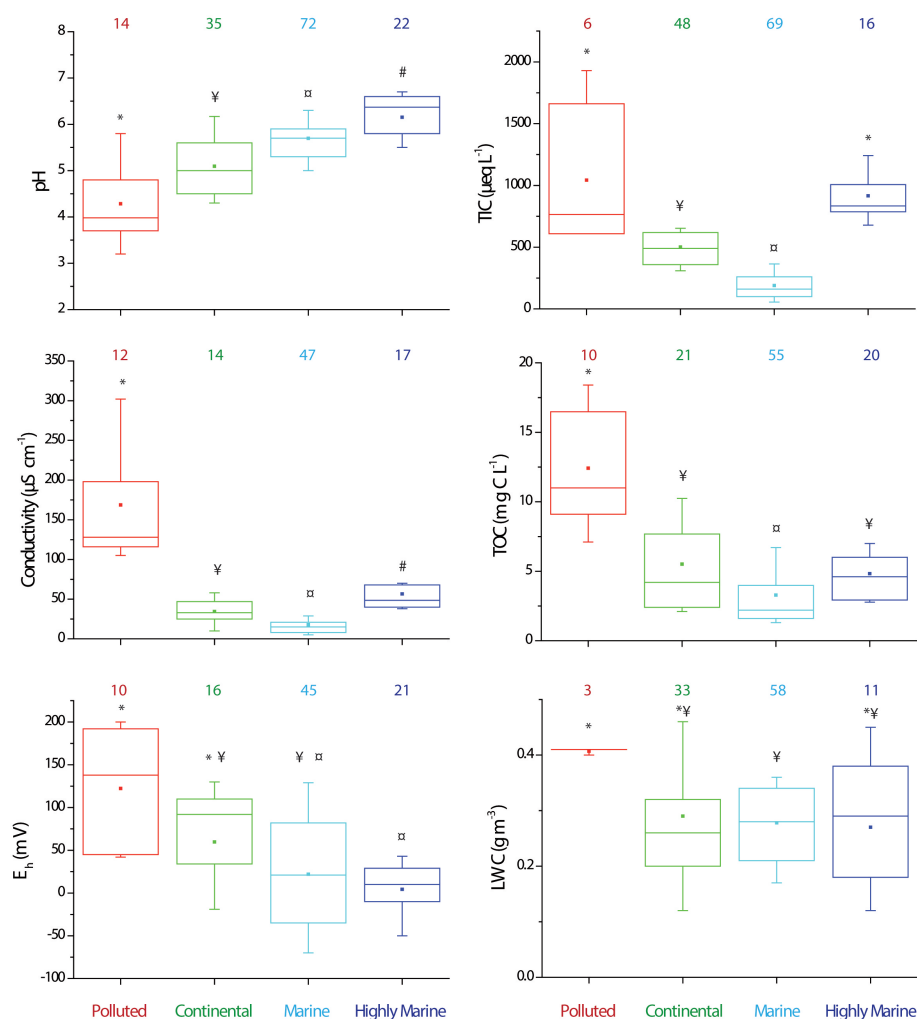


Fig. 3. Distribution of pH, total ion content (TIC), conductivity (C), redox potential (E_h), total organic carbon (TOC) and liquid water content (LWC) of the cloud water sampled at the pdD station for each air mass category. The number of samples analyzed is indicated above each box plot. The bottom 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. Statistical differences (Kruskal–Wallis test; p value < 0.05) between groups are indicated by symbols above box plots.

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 = 4×10^{-3} ; polluted/highly marine = 7.1×10^{-5}). It is also interesting to note that in polluted air masses, E_h is always positive, demonstrating that polluted clouds are oxidizing media in the atmosphere, while continental and marine cloud can be either an oxidizing or reducing medium. 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 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 the 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} ,

Table 2. Minimum, maximum, mean, and median values of physicochemical 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 ($\mu\text{S cm}^{-1}$)	TIC ($\mu\text{eq L}^{-1}$)	TOC (mgC L^{-1})	E_h (mV)	LWC (g m^{-3})
Number of samples	143	90	140	106	93	105
Av	5.5	48	415	5	33	0.28
Min	3.1	2	19	1	-164	0.05
Max	7.6	348	1930	25	230	0.92
Med	5.6	25	335	3	35	0.27

respectively). In the case of polluted events, a further anthropogenic source of organic carbon can be superimposed on the background level. A few studies reported measurements of this parameter for cloud water (Table S3) and presented values within the same range as our data. A previous study at the pdD station from 2001 to 2002 reported DOC (dissolved organic carbon) values ranging from 1.2 to 15.5 mgC 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-Rodríguez et al. (2009) measured the TOC and the DOC in cloud water from marine origin: the TOC ranged from 0.15 to 0.66 mgC L^{-1} and the DOC from 0.13 to 0.65 mgC L^{-1} (Reyes-Rodríguez et al., 2009) confirming that a significant fraction of TOC was composed of water-soluble organics ($\text{DOC/TOC} = 0.79$). Field measurements of fogs also reported that DOC constitutes about 80 % of the total organic carbon in the aqueous phase (Herckes et al., 2002a; 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 $0.28 \pm 0.12 \text{ g m}^{-3}$ (Fig. 3). Several studies discussed the relationship between LWC and solute inorganic concentrations (Aleksic and Dukett, 2010; Elbert et al., 2000) where nonlinear relationships were extracted and evaluated. These relationships reflect the fact that an increase in 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 might be attributed to the various influences to 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 func-

tions of our classification. To facilitate the comparison with other studies, we will present their concentrations expressed in $\mu\text{eq L}^{-1}$ for the 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 four air mass categories, a radar chart plot presenting the relative contributions of each ion is also drawn in 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 , N_2O_5) (Leaitch et al., 1988; Sellegri et al., 2003). The concentrations 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 attributed to the important contribution from nucleation scavenging of particles which prevails for nitrate, sulfate and ammonium to the overall cloud scavenging (Leriche et al., 2007). In our study, nitrate, sulfate and ammonium ions are abundant, as previously observed during studies at pdD (Sellegri et al., 2003) and during other field campaigns (Aleksic et al., 2009; Löflund et al., 2002); these represent an average contribution to the TIC of 65 % (marine), 76 % (continental) and 85 % (polluted). The highly marine clouds' 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 Gioda et al. (2009) and Reyes-Rodríguez et al. (2009) who sampled air masses from Atlantic Ocean in Puerto Rico and showed similar pH and concentrations of inorganic ions. Blas et al. (2008) sampled cloud water at the "Black Triangle",

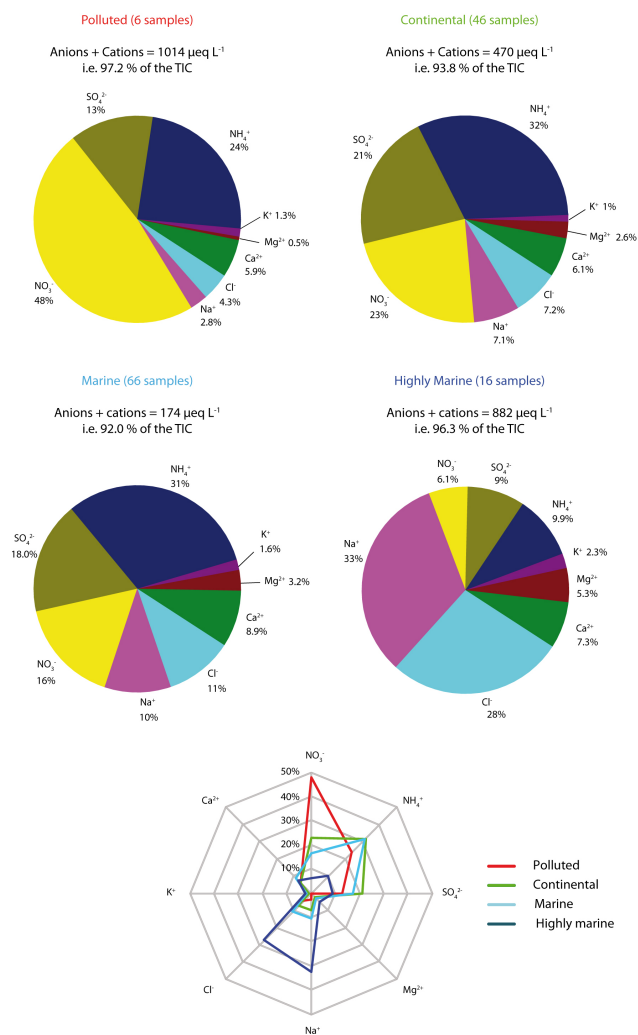


Fig. 4. Distribution of the major inorganic ions measured (Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , NH_4^+ , Mg^{2+} and Ca^{2+}) for each air mass category (percentages were calculated using the concentrations of ions in $\mu\text{eq L}^{-1}$). The sum of the concentrations of inorganic cations and anions in $\mu\text{eq L}^{-1}$ 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.

one of Europe's most industrialized regions; pH and inorganic ions concentrations in anthropogenic cloud water sampled at pdD were in the same range. In France, measurements of cloud chemical composition in the Vosges mountains show high sulfate and nitrate concentrations attributed to an anthropogenic additional source (Herckes et al., 2002b; Lammel and Metzigg, 1991). Such data are comparable to inorganic concentrations reported for polluted air masses at the puy de Dôme station.

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

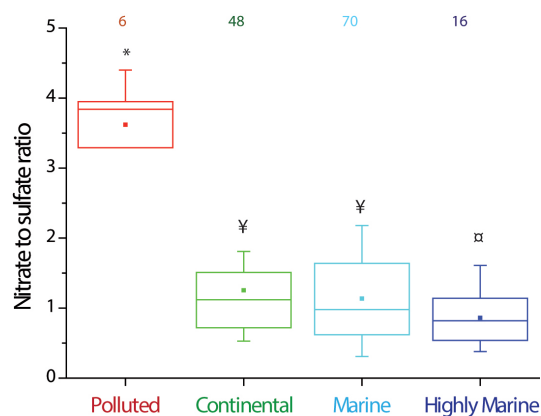


Fig. 5. Distribution of the ratio “nitrate to sulfate” concentrations (expressed in $\mu\text{eq L}^{-1}$) of the cloud water sampled at the pdD station as a function of air mass categories. Numbers above each box plot represent the number of samples analyzed. At least three data are required to represent 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. Statistical differences (Kruskal–Wallis test; p value < 0.05) between groups are indicated by symbols above box plots.

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 four 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 $\text{NO}_3^- / \text{SO}_4^{2-}$ ratio increases with the distance from the source of pollution, which makes this value an indicator of the remoteness of a site (Wang et al., 2011; Weathers et al., 1988). 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. Several values of this ratio reported elsewhere for cloud water samples were below 1 (Baltensperger et al., 1998; Bridges et al., 2002) but the observation of elevated NO_3^- relative to SO_4^{2-} in cloud water has been also reported in other studies (Brügemann et al., 2005; Hayden et al., 2008; Hill et al., 2007; Leitch et al., 1986; Lee et al., 2012). This could be related to high NO_x emission and the predominance of nitrate over sulfate in the acidification of aerosols.

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 concentrations is much higher than the 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 polluted air masses, it is possible that the Ca^{2+} and/or Mg^{2+} may have been present as nitrate salts (CaNO_3 , MgNO_3) ($R(\text{Ca}^{2+}/\text{NO}_3^-) = 0.47$; $R(\text{Mg}^{2+}/\text{NO}_3^-) = 0.78$) or sulfate salts (CaSO_4 , MgSO_4) ($R(\text{Ca}^{2+}/\text{SO}_4^{2-}) = 0.67$; $R(\text{Mg}^{2+}/\text{SO}_4^{2-}) = 0.54$) as suggested by Leaitch et al. (1986). For highly marine clouds, the water is enriched by salts formed from the evaporation of sea 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 extent 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 that of seawater (1.17; Holland, 1978). This loss of chlorine may be caused by the deposition of HCl gas to the sea surface before its absorption by cloud droplets (Watanabe et al., 2001). Another explanation could be that the aerosol ages during its transport: in the aerosol phase, the reaction $\text{NaCl} + \text{HNO}_3$ 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 source from NaCl particles and also an anthropogenic source with the dissolution of gaseous HCl into the aqueous phase (McCulloch et al., 1999; Shapiro et al., 2007).

As the marine ratio for $\text{SO}_4^{2-}/\text{Na}^+$ 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 SO_4^{2-} dissolved in polluted clouds, whereas for marine clouds, this value is more varied 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), which tends to acidify cloud droplets and lead 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 pre-

sented in Fig. 4, showing that the relative contribution of each inorganic ion is very similar for marine and continental air masses. By contrast, the polluted air masses exhibit much higher concentrations of nitrate in the cloud water, and the cloud water samples in highly marine air are characterized by relatively high levels of chloride and sodium.

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 dicarboxylic acids and some carbonyls and dicarbonyls (Herckes et al., 2013). Here, we present the concentrations of 5 carboxylic acids and 5 carbonyls as a function of the air mass categories.

Figure 6 shows the mean relative contribution of five carboxylic acids (formic, acetic, oxalic, malonic and succinic acids) 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; 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 Carrier, 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, whose Henry's law constants 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 (Sorooshian et al., 2006). 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 represent a sink through photolysis (Deguillaume et al., 2005). Finally, of the quantified acids, succinic and malonic acids are the least 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, only a few studies have highlighted the production of succinic and malonic acids from oxidation processes in the cloud aqueous phase (Charbouillot et al., 2012; Perri et al., 2009). This lack of aqueous-phase reactivity as a potential source of succinic and malonic acids could explain the lower concentrations of these acids in cloud water. They are also much 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 the Raxalpe mountains in Austria (Löflund et al., 2002) or at the Schmücke mountains in Germany (van Pinxteren et al., 2005) (see Table S2), which are both removed from local pollution. The concentration of these organic acids is higher for polluted clouds, demonstrating the supplemental sources for air masses resulting from their passage over polluted area. For highly marine clouds, the amount of these acids is on the same order as the one for continental clouds, showing a marine input of organic matter as confirmed by TOC measurements (O'Dowd et al., 2004).

Only two cloud samples considered here are in the polluted category. Even though 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 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 a significant fraction of heteroatoms (S, N, O) (such as humic-like substances (HULIS), fulvic material, organosulfur species) (Feng and 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 four categories showing the large unidentified portion of organic matter in cloud water (Fig. 6, see text above each pie chart).

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 (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, MGL and HA measured in this study. Oxidation by the HO \cdot radical of these highly water-soluble compounds (Henry's law constant $H_{GL} = 3.6 \times 10^5$;

$H_{MG} = 3.7 \times 10^3$, $H_{HA} = 4.1 \times 10^4$ M atm $^{-1}$ at 25 °C) (Berterton 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 lesser extent, succinic and malonic acids (Perri et al., 2009). Concentration levels for F, AC, GL and MGL have already been measured concomitantly in rain or cloud water (Igawa et al., 1989; Munger et al., 1995; Li et al., 2008; 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 five carbonyls for the four air mass categories. The concentration (average, min, max) of the five carbonyl compounds for the whole data set are 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 (Altshuler, 1993; Hoekman, 1992; Possanzini et al., 2002). As expected, formaldehyde is the most abundant one in all cases, with concentrations ranging from 5.0 μ M (for polluted clouds) to 1.8 μ M (for marine ones). It is noteworthy that, except in marine samples, HA concentrations are higher than those of GL and subsequently those of MGL. Even if clouds form in rather different atmospheric environments, this result supports the 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 the 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 highlighted due to HA's relatively high concentration.



Fig. 6. Distribution of carboxylic acids (formic, acetic, oxalic, malonic and succinic acids) for each air mass category (percentages are calculated using concentration of individual ion in $\mu\text{gC L}^{-1}$). On the left-hand side, the sum of the concentrations of these compounds in $\mu\text{gC L}^{-1}$ 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.

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

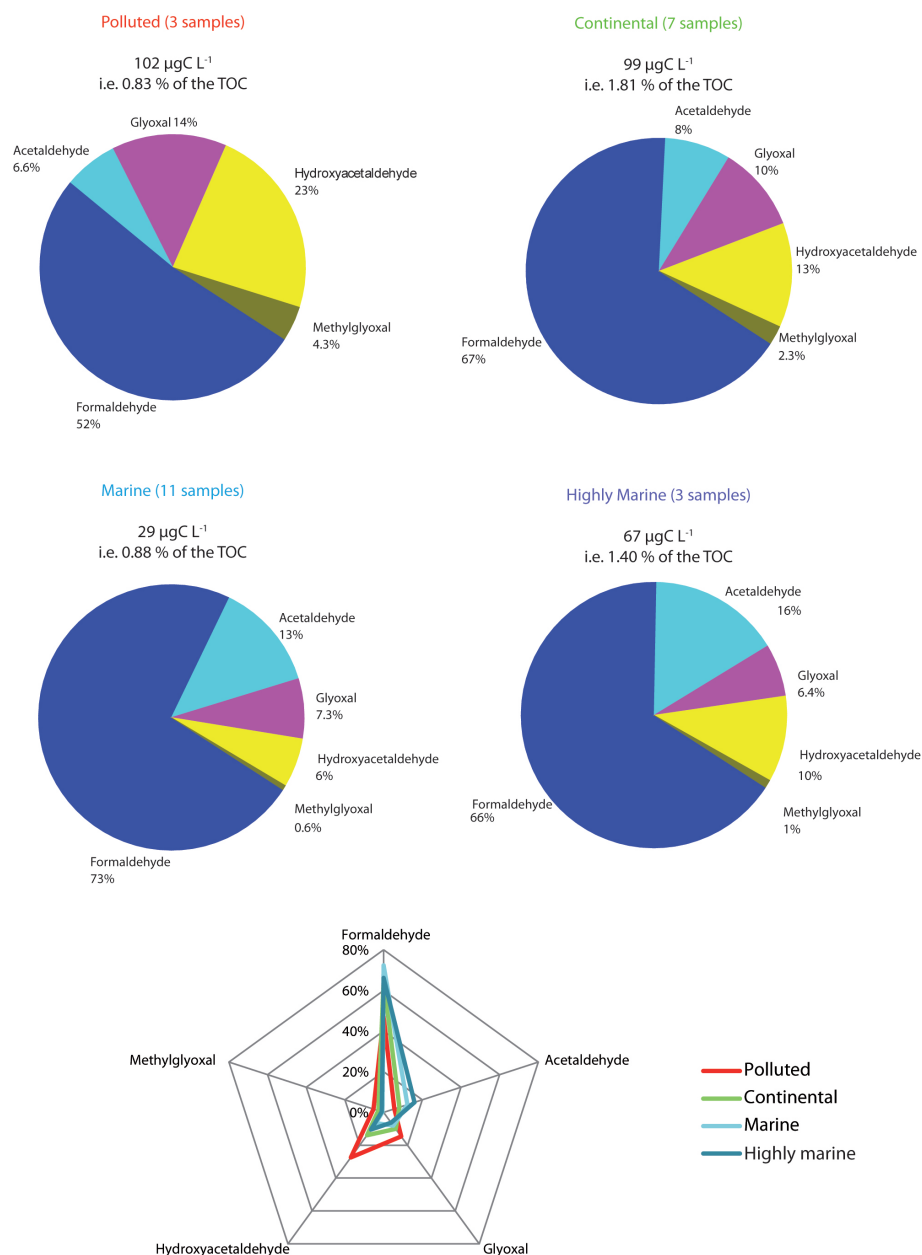


Fig. 7. Distribution of carbonyls (formaldehyde, acetaldehyde, glyoxal, methylglyoxal, hydroxyacetaldehyde) as a function of air mass categories (percentages are calculated using concentration in μM). On the left-hand side, the sum of the concentrations of these compounds in $\mu\text{gC L}^{-1}$ is 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.

near sources of heavy pollution, such as big cities or industrial areas (Kotronarou and Sigg, 1993); but they are in the same range as field measurements carried out at free tropospheric and marine sites such as southern Germany (Sinner et al., 1994), Whiteface Mountain in the US (Arakaki and Faust, 1998), Great Dun Fell in the UK (Sedlak et al., 1997) or San Pedro Hill in the USA (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 the cloud water sampled: 83, 70, 54, and 77 %, respectively, for the polluted, continental, marine, and highly

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 (the limit of detection (LOD) is 0.1 nM for hydroxyacetaldehyde, acetaldehyde, glyoxal, and methylglyoxal, and 0.8 nM for formaldehyde).

		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

marine categories. This confirms the previous results obtained at the pdD by Parazols et al. (2006) 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 ranged from 0.1 to $57.7 \mu\text{M}$ (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 varied in marine and highly marine air masses (standard deviation = 7.12 and $6.31 \mu\text{M}$ for highly marine and marine categories, respectively) compared to polluted clouds (standard deviation = $1.57 \mu\text{M}$) characterized by the lowest average concentration of H_2O_2 ($\sim 4.9 \mu\text{M}$). 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 (2) to 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. (2011) presents a 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 their 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 compounds as well as a series of physicochemical parameters permitted the identification of various influences corresponding to distinct air-mass histories. A classification was performed by principal component analysis that allows for defining the discriminating factors (pH and concentrations of Na^+ , Cl^- , NO_3^- , NH_4^+ and SO_4^{2-}) for four different categories: polluted, continental, marine and highly marine.

As can be expected, highly marine clouds exhibited high concentrations of Na^+ and Cl^- ; the marine category presented lower concentrations of ions but still elevated pH. Finally, the two remaining clusters were classified as “continental” and “polluted”; these clusters had the second-highest and highest levels of NH_4^+ , NO_3^- , and SO_4^{2-} , respectively. Furthermore, it was found that total organic carbon (TOC) is significantly higher in polluted air masses than in the other categories, due to additional anthropogenic sources. Concentrations of carboxylic acids and carbonyls represented around 10% of the organic matter in all categories of air masses. Acetic and formic acids were the most abundant of the five measured carboxylic acids, reflecting their multiple sources (gas phase, particle, aqueous reactivity) in the cloud aqueous phase. Oxalic acid, succinic and malonic acids were

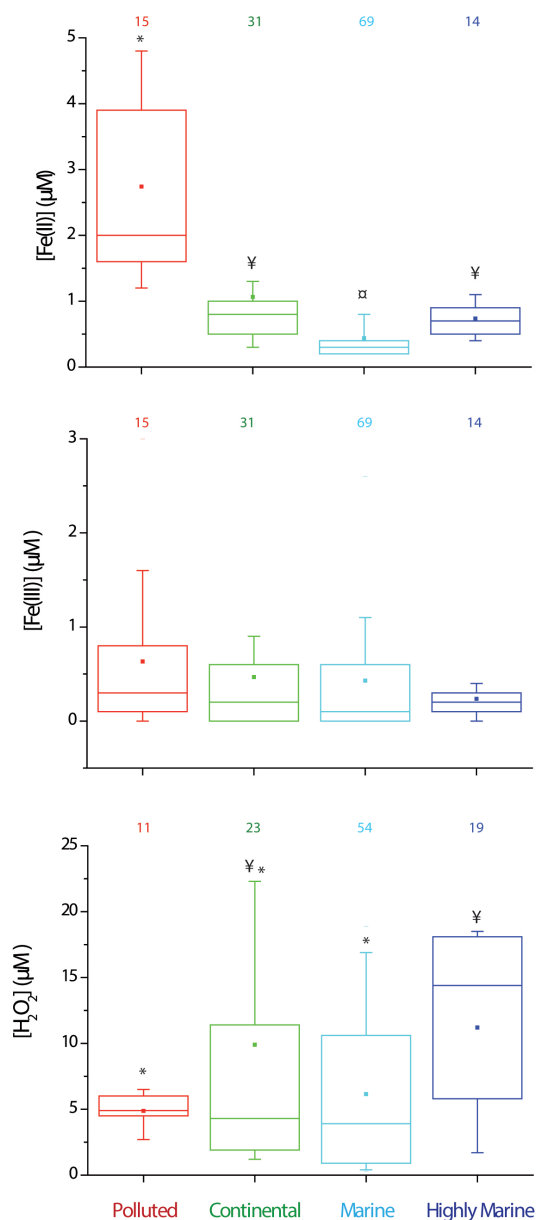


Fig. 8. Distribution of Fe(II), Fe(III) and H_2O_2 as a function of air mass categories. Numbers above each box plots represent the number of samples analyzed. At least 3 data are required to represent a box plot. The bottom and top of box plots are 25th and 75th percentiles, respectively. The full line and the square symbol represent the median and mean values, respectively. The ends of whiskers are 10th and 90th percentiles. Statistical differences (Kruskal–Wallis test; p value < 0.05) between groups are indicated by symbols above box plots.

less abundant in all categories of air masses. Carbonyl compounds were less abundant than carboxylic acids with a predominance of formaldehyde and unexpected high concentrations of hydroxyacetaldehyde. Iron concentrations were significantly higher for polluted air masses, and iron was mainly

present in its oxidation state (+II) in all categories of air masses. This potentially indicates that iron could be stabilized in its reduced oxidation state by the presence of strong complexing agents. Finally, H_2O_2 concentrations were much more varied in marine and highly marine clouds than in polluted clouds, which were characterized by the lowest average concentration of H_2O_2 .

As shown in this study, chemical speciation is a powerful tool for analyzing air mass history. For example, the presence of inorganic compounds such as nitrate and sulfate investigated in this study are due to anthropogenic emissions, such as those from 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 from the gas phase, dissolution of particles, aqueous chemical reactivity). In this context, some chemical compounds that are molecular markers of emissions (such as levoglucosan, a marker of biomass burning) should be followed in the future in order to correlate cloud features with emissions.

Our results also emphasize that, although this database is rather complete, the characterization 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 et al., 2010), volatile aromatic compounds such as BTEX (i.e., benzene, toluene, ethylbenzene, and xylene) (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 (Linuma et al., 2009) such as sugar alcohols mono-, di- and trisaccharides, anhydrosugars, and polysaccharides; they are released into the atmosphere by microorganisms, plants, and animals. For example, levoglucosan derives from cellulose; galactosans and mannosans derive 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 are 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 due to their high solubility in water; their amount in cloud water should be evaluated.

The oxidizing capacity of the cloud aqueous phase should also be 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 for 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 a recent study highlighted “its paradoxical role” in the aqueous formation of oligomers: O₂ 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 allow one to study the chemical pathways, the complex interactions between microphysics, chemistry and dynamics (i.e., transport) and the influence of environmental parameters on cloud chemistry within the cloud system. The present study aims to provide statistically robust cloud chemical characterizations and its relationship with environmental factors, such as source regions. These data can be used for modeling natural free tropospheric conditions.

Supplementary material related to this article is available online at <http://www.atmos-chem-phys.net/14/1485/2014/acp-14-1485-2014-supplement.pdf>.

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