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Anthropogenic and biogenic hydrophobic VOCs detected in clouds at the puy de Dôme station using Stir Bar Sorptive Extraction: Deviation from the Henry's law prediction

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ABSTRACT

Cloud droplets are able to trap many gaseous compounds and represent a very reactive media in the atmosphere. However, phase-partitioning of Volatile Organic Compounds (VOCs) between gaseous phase (interstitial air) and atmospheric liquid phase (cloud droplets) is still poorly characterized. In the present work, air samples and cloud water were collected simultaneously and hydrophobic organic compounds from anthropogenic and biogenic origins were quantified in order to evaluate their air/water partitioning. For this, cloud events were sampled at the puy de D ome station (PUY). A new analytical approach was optimized to explore dissolved VOCs in the aqueous phase by Stir Bar Sorptive Extraction (SBSE) and gaseous samples were collected using sorbent tubes. All samples were analyzed by Thermal Desorption (TD) Gas Chromatography (GC) coupled with Mass Spectrometry (MS). Extraction efficiencies by SBSE vary between 22% and 97% and the detection limit of VOCs in aqueous cloud samples lies between 1.0 and 8.7 ng L⁻¹. Experimental partitioning is evaluated towards the theoretical one described by the Henry's Law constants. Our results show that observed concentrations of hydrophobic VOCs are supersaturated by a factor of 10–10³ in comparison with Henry's law equilibrium. Calculations have been performed to evaluate the potential role of adsorption at the air/water interface and of sorption with non-dissolved organic carbon. However, the supersaturation in the cloud droplets requires more laboratory experiments to understand processes at the air/water interface and constrain cloud chemistry models.

1. Introduction

Volatile Organic Compounds (VOCs), including saturated, unsaturated, and other substituted hydrocarbons, play a major role in atmospheric chemistry (Atkinson, 2000). They are primarily emitted by anthropogenic and biogenic sources into the atmosphere and are also transformed *in situ* by chemical reactions, and more specifically, by photo-oxidation leading to the formation of ozone and Secondary Organic Aerosol (SOA) (Atkinson and Arey, 2003; Claeys, 2004; Kanakidou et al., 2005; Goldstein and Galbally, 2007; Carlton et al., 2009; Hallquist et al., 2009; Chen et al., 2018; Palm et al., 2018). By altering the organic fraction of aerosol particles, VOCs modify the Earth's radiative balance through a direct effect (absorption and scattering of solar radiation) or through indirect effect by altering cloud microphysical properties (Scott et al., 2014). They also have a direct effect on human health and on the environment (Zhu et al., 2018).

During their atmospheric transport, VOCs and their oxidation products, Oxygenated Volatile Organic Compounds (OVOCs), may partition between the gaseous and aqueous phases depending on their solubility. Clouds have a significant effect on tropospheric chemistry by redistributing trace constituents between phases and by providing liquid water in which aqueous phase chemistry can take place (Herrmann et al., 2015). Indeed, during the cloud lifetime, chemical compounds are efficiently transformed since clouds favor the development of "multiphase chemistry" that presents several particularities. First, photochemical processes inside the droplets are important in the transformation of chemical compounds (Barth, 2006; Vione et al., 2006). Second, aqueous chemical reactions are efficient and can be faster than the equivalent reactions in the gas phase. This can be related to the presence of strong oxidants such as hydrogen peroxide or Transition Metal Ions (TMI), which participate in the formation of radicals such as hydroxyl radicals (HO[•]) that favor oxidation processes

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(Deguillaume et al., 2005). Furthermore, the presence of viable microorganisms has been highlighted and shown to participate in the transformations of the chemical species (Delort et al., 2010; Vaitilingom et al., 2013; Bianco et al., 2019). Finally, these transformations in clouds are also strongly perturbed by microphysical processes that control formation, lifetime and dissipation of clouds. These processes will redistribute the chemical species between the different reservoirs (cloud water, rain, particle phase, gaseous phase, and solid ice phase) (Long et al., 2010; Marécal et al., 2010; Rose et al., 2018).

Measurements of chemical compounds in cloud aqueous phase have been conducted for decades and have been more recently focused on the characterization of the dissolved organic matter (Ervens et al., 2013; Cook et al., 2017; Zhao et al., 2013). Many secondary organic species such as carbonyls and carboxylic acids are formed during the gas phase oxidation of hydrocarbons; since they are highly soluble, they solubilize into the aqueous phase. They also result from aqueous phase processes (chemical and biological transformations). This explains why they are commonly measured in atmospheric waters (van Pinxteren et al., 2005; Matsumoto et al., 2005; Sorooshian et al., 2006). However, few studies have been conducted looking in parallel both compartments (gas and aqueous phases) in order to estimate how those compounds are partitioned. This can be partly explained by the inherent difficulty of sampling clouds.

In a first approach, the partitioning of organic compounds between gas and aqueous phases can be described by Henry's law constants that is to assume thermodynamic equilibrium for all species. However, cloud chemistry models (Lim et al., 2005; Barth, 2006; Ervens, 2015; Rose et al., 2018) and few observational studies (Facchini et al., 1992; Winiwarter et al., 1992; van Pinxteren et al., 2005; Li et al., 2008) have highlighted deviations from the Henry's law equilibrium. Many factors control the partitioning between these two phases such as the pH, the droplet size, and the reactivity in both phases. Kinetic transport limitations through the droplet surface have to be considered, as they can be perturbed by the presence of hydrophobic molecules at the air/water interface. In this frame, cloud chemistry models simulate the mass transfer between the two phases but those models have to be evaluated towards *in situ* estimates that are actually scarce (Winiwarter et al., 1994; van Pinxteren et al., 2005).

Therefore, the objective of this study is to quantify experimentally the air-water partitioning of VOCs in clouds. Previous work has highlighted the accumulation of hydrophobic compounds in the aqueous phase such as hydrocarbons (PAHs), total Polychlorinated biphenyl (PCBs) and total n-alkanes (Valsaraj, 1988a,b; Valsaraj et al., 1993). As a consequence, we decided to focus upon the analysis of VOCs of atmospheric interest from both anthropogenic and biogenic origin. They include benzene, toluene, ethylbenzene and xylenes (BTEX) as well as biogenic species like isoprene and other terpenes. These compounds are usually detected in the gas phase but are not expected to be present in the aqueous phase due to their low solubility. Beyond the health impact for some of them, like benzene (Cocheo et al., 2000), these compounds are also well-known to contribute to the formation of secondary pollutants like ozone and SOA (Hu et al., 2008; Fu et al., 2009).

To investigate partitioning, simultaneous cloud and air samples have been collected between 2012 and 2014 at the puy de Dôme station (PUY, France). Gaseous VOCs were sampled by off-line sorbent tubes and analyzed using a Gas Chromatograph–Mass Spectrometer system (GC–MS) connected to an automatic Thermal Desorption unit (Turbomatrix TD) (Keita et al., 2018). Cloud samples have been collected following the procedure described in (Deguillaume et al., 2014); those samples are systematically characterized chemically (ions, oxidants, etc.) (http://opgc.fr/vobs/so_forms.php?name=puycloud). For the first time at PUY, dissolved VOCs concentrations have been additionally measured. For dissolved gases in cloud samples, a new analytical technique based on Stir Bar Sorptive Extraction (SBSE) was used to pre-concentrate dissolved VOCs. Then analyses were performed using the same TD/GC–MS system. The analytical development is

described in the first part of the paper. In the second part, the concentrations of a series of VOCs in both phases, comparison with previous studies and the partitioning of the VOCs between both phases are discussed.

2. Methods/materials

2.1. Sampling site

The puy de Dôme (PUY) station (45.46 N, 2.57 E) is a regional background site located in the center of France with an altitude of 1465 m a.s.l. The observatory at the top of the mountain is part of the atmospheric survey networks of the European Monitoring and Evaluation Program (EMEP), Aerosols, Clouds, and Trace gases Research Infrastructure (ACTRIS) and Global Atmosphere Watch (GAW). In this frame, gases and aerosol particles are continuously characterized chemically and physically. Cloud water microphysical parameters, like liquid water content (LWC) and effective droplet radius, are measured continuously by a Particulate Volume Monitor (PVM Gerber 100 probe). Cloud water chemical composition is evaluated for each cloud event as described in Deguillaume et al. (2014) and briefly summarized below.

Physicochemical parameters such as pH, conductivity and redox potential were measured. Ion chromatography analysis allowed for the quantification of main organic and inorganic ions (acetic, formic, succinic, and oxalic acids, Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , NH_4^+ , Mg^{2+} and Ca^{2+}). Dissolved Organic Carbon (DOC) was also monitored as well as the concentrations of oxidants such as hydrogen peroxide (H_2O_2) and iron content and speciation.

2.2. Air and cloud sampling

Cloud samples were collected by using a dynamic one stage cloud collector similar to the one described by Kruijs (1993). Cloud droplets larger than 7 μm (cut-off diameter) (Brantner et al., 1994) were collected by impaction onto an aluminum plate, which has been already described in previous studies (Vaitilingom et al., 2013; Bianco et al., 2018). Samples are collected in clean bottles and cloud water is filtered using a 0.2 μm nylon filter within 10 min after sampling to eliminate microorganisms and larger particles. Cloud water samples were kept frozen until the analysis. For this study, nine cloud events were sampled between 2011 and 2014 during different seasons. Among one single cloud event, up to 3 different samples were collected, equaling a total of 16 samples. Sampling dates and durations for cloud sampling are indicated in Supplementary material (Table S1 and Fig. S1).

In parallel to the cloud sampling, gaseous VOCs sampling was conducted with Tenax® TA cartridges; Tenax® is chemical inert, highly hydrophobic and widely used for VOCs measurements of more than 4 carbon atoms (Rothweiler et al., 1991; Ho et al., 2018; Schieweck et al., 2018). Before sampling, Tenax® TA cartridges need a pre-conditioning step in order to prevent any contamination from the sorbent. Different conditioning temperatures (250 and 320 °C), conditioning durations (4, 5 and 6 h) and pure nitrogen flows (50–120 mL min^{-1}) were investigated. Finally, all tubes were conditioned for 5 h at 320 °C under a nitrogen flow of 100 mL min^{-1} . These conditions guarantee the presence of the target VOCs in the blank at levels lower than the detectable mass by the TD–GC–MS ensemble. Only benzene could be depicted but its peak intensity does not usually exceed 4% of the peak area corresponding to an ambient tube. The potential presence of benzene in the blank tubes has been taken into account in the quantification of its detection limits and the total uncertainty (Section 2.4). Therefore these conditions are optimal for achieving maximum sensitivity for all the compounds. The sampling was carried out by using a Smart Automatic Sampling System (TERA Environment) (SASS) with a controlled flow rate of 100 mL min^{-1} for duration of 180 min. The final sampling air volume of 18 L was lower than the breakthrough volume for all target

species except isoprene. Isoprene which is the most volatile VOC among target species was already shown to breakthrough at volume beyond 5.3 L per gram of Tenax TA at 24 °C (Simon et al., 1996). The partitioning of isoprene will therefore be discussed with caution as isoprene concentrations in air should be seen as a lower limit (Section 3.1). Figure S1 presents gas sampling that has been performed in parallel to cloud sampling. Among the 16 cloud samples, 5 gaseous samples were simultaneously collected.

2.3. VOCs analysis by GC-MS

The analysis of both VOCs in air and in cloud droplets is based on TD/GC-MS system. The thermal desorption TurboMatrix 650 TD system was composed by a multi-tubes auto-sampler equipped with an injected sample split flow automated re-collection system. The GC system was a Perkin Elmer Clarus 600 equipped with an Elite-5MS capillary column (60 m, 0.25 mm i.d. (inner diameter), film thickness: 0.25 μm , Restek Corporation, Bellefonte, USA). Cartridges are directly thermally desorbed and chromatographically separated with the following temperature program: from 35 to 250 °C with thermal ramps of 5 °C min^{-1} and hold about 2 min. The MS system was equipped with an electron ionization source (operated at an energy of 70 eV), used in the case of the injections of samples for structural identification and quantification. More details on analytical conditions can be found in Keita et al. (2018) and Dominutti et al. (2018). Cloud samples were first extracted by the SBSE technique before analysis via TD/GC-MS. The SBSE samples were then transferred into an empty cartridge following the same analytical procedure as described above. The SBSE optimization is discussed in the following section.

2.3.1. Extraction of VOCs from cloud waters: SBSE optimization

SBSE was used to investigate VOCs concentrations by extraction from the aqueous phase (Baltussen et al., 1999). VOCs have been already detected and analyzed by this method for different environmental media like river water, seawater, soil, food and flavor (Alves et al., 2005; Coelho et al., 2009; Tredoux et al., 2008), but not yet in cloud waters at low concentrations.

2.3.2. SBSE theory

SBSE is an application of stir bars coated with polydimethylsiloxane (PDMS), also called “Twisters”. This equilibrium technique leads to the extraction of solutes from the aqueous phase to the PDMS phase, which is controlled by the partitioning coefficient of the solutes between the PDMS phase and the aqueous phase. The partitioning coefficient is usually approximated to the octanol-water partitioning coefficient $K_{O/W}$. The extraction efficiency (E), which corresponds to the recovery of analytes from the samples, depends not only on the $K_{O/W}$ but also on the volume of water and the volume of PDMS (see more information on SBSE theory in SM S2). At a given $K_{O/W}$, a theoretical E can be determined from different volumes. As shown in Fig. 1A, the bigger the volume of PDMS is and the smaller the volume of the sample is, the higher the theoretical extraction efficiency is. In practice, other parameters are known to affect the solid-water equilibrium and the extraction efficiency as well (Ochiai et al., 2001; Kawaguchi et al., 2005; Portugal et al., 2008; Pang et al., 2011): extraction time, PDMS volume, sample volume and ionic strength. These factors have been optimized on modelled aqueous matrices in order to achieve optimal extraction of VOCs (Fig. 1B) as described in the following Section 2.3.3. Moreover the thermo-desorption step by the TD/GC-MS was optimized to guarantee the complete transfer of the studied compounds from the twister to the GC column. Thermo-desorption conditions are the same as for cartridges, which allows a total desorption for extracted compounds by Twisters. Furthermore, this step was verified and confirmed by performing a second thermo-desorption.

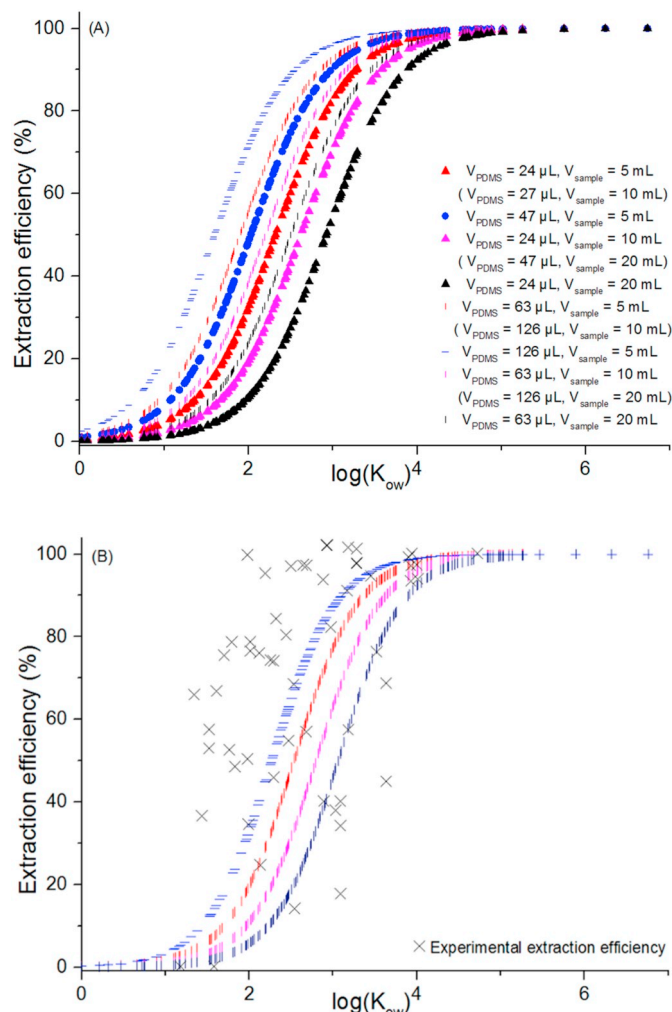


Fig. 1. Example of theoretical extraction efficiency for 5, 10 and 20 mL sample volumes and 24, 47, 63, 126 μL PDMS volumes (A) and comparison between experimental and theoretical extraction efficiency (B). Experimental conditions are based on 63 μL PDMS volume and 5 mL sample volume.

2.3.3. Optimization of extraction conditions

Tens of anthropogenic and biogenic compounds of atmospheric interest from pure commercial standards (Megamix standards and Terpenes standards, 200 $\mu\text{g}/\text{mL}$ for each compound in methanol, RESTEK, France) have been studied but not all of them are presented hereafter. The complete data set, however, is provided in SM (Table S2).

The design of the entire test protocol is based on several previous studies (Ochiai et al., 2001; Kawaguchi et al., 2005; David and Sandra, 2007). One polymer-coated stir bar was introduced into the diluted standard in Milli-Q water by immersion. The sample is stirred on a magnetic stirring plate for at least 2 h. After extraction the stir bar was removed from the sample solution, rinsed with distilled water in order to remove salts, sugars, proteins or other sample components and dipped on a clean paper tissue to remove water. This rinsing step is extremely important to avoid the formation of non-volatile material that can clog the desorption unit. Rinsing does not cause solute loss since the solutes are sorbed in the polymer phase (David and Sandra, 2007). A second polymer-coated stir bar was then placed into the sample after adding sodium chloride (NaCl) and stirred for at least 2 h. After extraction, the same protocol was applied. Several tests were performed to optimize the method for analysis cloud samples: the effect of PDMS volume (2.3.3.1), extraction time (2.3.3.2), sample volume (2.3.3.3) and ionic strength (2.3.3.4) were studied. Temperature

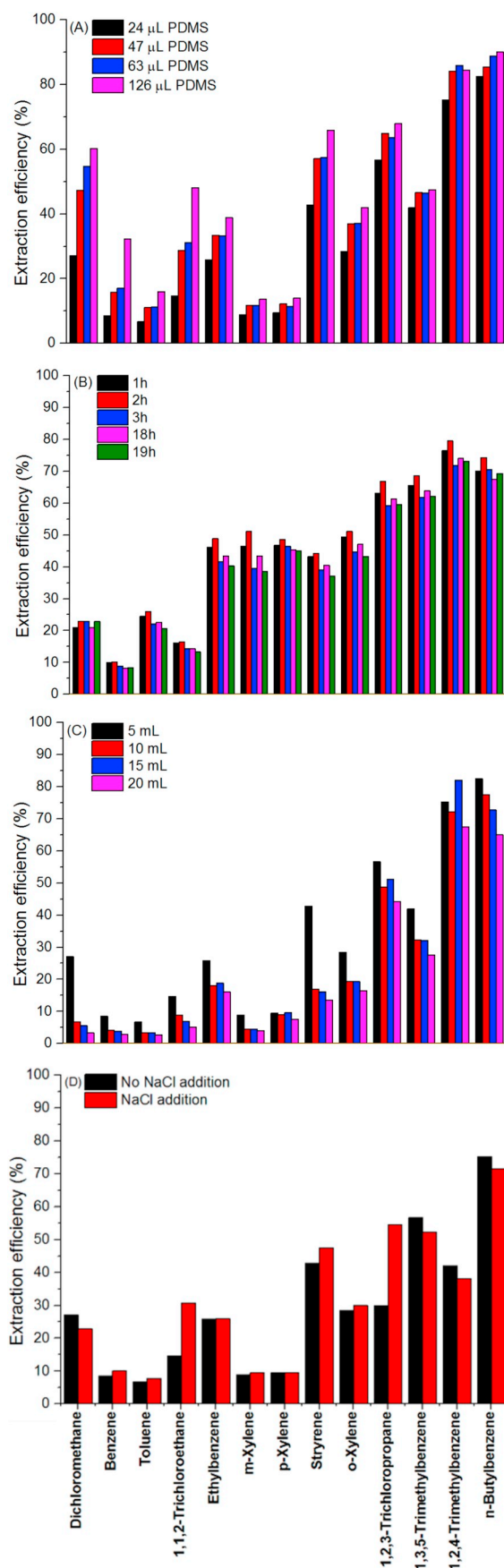


Fig. 2. Effects of PDMS volume (A), extraction time (B), sample volume (C) and NaCl effect (D) on the extraction efficiency E (%) for a selection of VOCs: dichloromethane, benzene, toluene, 1,1,2-trichloroethane, ethylbenzene, m-xylene, p-xylene, styrene, o-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trichlorobenzene and n-butylbenzene.

ranged between 20 and 22 $^{\circ}\text{C}$ during the experiment. pH of cloud samples varied from 4.9 to 6.8 and was not changed for the extraction tests. The range of cloud water concentrations of VOCs are expected to vary between 0 and 100 $\mu\text{g L}^{-1}$ (Aneja, 1993). All tests were performed for an intermediate aqueous concentration of VOCs of 20 $\mu\text{g L}^{-1}$ by introducing 0.5 μL of the standard mixture solution (Megamix) to 5 mL Milli-Q water.

2.3.3.1. PDMS volume. The effect of the PDMS volume of commercial Twisters (24, 63, 47 and 126 μL) on the extraction efficiency was investigated. Extraction experiments were carried out during 2 h on 5 mL Milli-Q water with 20 $\mu\text{g L}^{-1}$ standards. The extraction efficiency as a function of the PDMS volume is reported in Fig. 2A for selected VOCs. As expected, compounds with a $\log K_{O/W}$ lower than 2.5 show the lowest extraction efficiency (e.g. benzene, toluene, dichloromethane, 1,1,2-trichloroethane) with values below 45%. On the opposite, compounds with a $\log K_{O/W}$ higher than 3.5 show greatest extraction efficiencies (e.g. xylenes, 1,3,5-trimethylbenzene, 1,2,3-trichlorobenzene) with values higher than 70%. For all compounds, the stir bar with the highest PDMS volume (126 μL) provided the best extraction efficiency and was chosen for cloud water extraction (Fig. 2A). Benzene ($\log K_{O/W} = 1.99$) and 1,1,2-trichloroethane ($\log K_{O/W} = 2.4$) are the most sensitive to PDMS volume change with an increase of their extraction efficiency by +200% with PDMS volume. Indeed, the SBSE partitioning theory predicts the most significant changes of extraction efficiency for $\log K_{O/W}$ values between 2.0 and 3.5 (Fig. 1A).

2.3.3.2. Extraction time. Five extractions were carried out at extraction times varying between 1 and 19 h with the 24 μL PDMS twister on 5 mL Milli-Q water with 20 $\mu\text{g L}^{-1}$ standards. Generally, extraction during two hours was the most efficient for these compounds with extraction efficiency around 10 to 80% as shown in Fig. 2B. However, the variation of extraction efficiency between 1 and 19 h lies from 3 to 12%. This fluctuation is within the measurement uncertainty range. Since 2 h is convenient for laboratory conditions, this extraction time was chosen.

2.3.3.3. Sample volume. A decrease of extraction efficiencies with increasing sample volume is observed for all compounds (Fig. 2C). It is in agreement with the SBSE partitioning theory which predicts a decrease in extraction efficiency at a constant stir bar PDMS volume (Fig. 1A). As a consequence, a 5 mL sample volume is appropriate and increases the extraction efficiency for most of the studied compounds. This small volume is also convenient since sampled cloud water volumes are usually rather low.

2.3.3.4. Ionic strength. NaCl is often added to a sample matrix to enhance the extraction efficiency (León et al., 2003; Ochiai et al., 2006) as it contributes to the salting-out effect in SBSE which increases the recoveries of polar compounds (i.e., for the compounds with $\log K_{O/W} < 3$ or $\log K_{O/W} \approx 3$).

The effect of ionic strength on the extraction efficiency was first investigated (Fig. 2D and SM Fig. S2) with 2 g of NaCl added to the 5 mL volume. The extraction efficiency increased almost for all polar compounds ($\log K_{O/W} < 3.18$). Meanwhile, the extraction efficiency decreased for non-polar compounds ($\log K_{O/W} > 3.18$). The extraction efficiency of SBSE for all target VOCs increased with the increase of NaCl concentration from 30 to 40% and then remained stable or

decreased with further increase of NaCl concentration up to 60%. This phenomenon can be explained by two processes that occur during the extraction process. Initially, the extraction efficiency for VOCs compounds increases with the enhancement of NaCl concentration due to the salting out effect, which drives more VOCs into the PMDS layer. The further addition of NaCl increases the solution viscosity, which may potentially decrease the extraction efficiency (Quintana et al., 2007; Pang et al., 2011). Consequently, 40% of NaCl in the sample solution is chosen as the optimal ionic strength. In the presence of 40% NaCl, the extraction efficiency of benzene, toluene, o-xylene, styrene and 1,1,2-trichloroethane is enhanced up to 20% with intermediate $\log K_{O/W}$ between 1.99 and 3.09.

All results described above confirm the judicious choice to carry out a “sequential SBSE” (Ochiai et al., 2006) which takes place in two stages: a first extraction without salt which will extract the non-polar compounds followed by a second extraction after salt addition, which allows extracting the polar compounds remaining in solution.

2.3.4. Final protocol for VOCs extraction from cloud waters

The following protocol has been chosen for the extraction of VOCs from cloud water samples: 5 mL of cloud water is introduced in a glass bottle (10 mL size); then, a first 126 μL stir bar is placed into the bottle under magnetic stirring at 80 rpm. The extraction takes 2 h at ambient temperature (between 20 and 22 °C) with the objective to get the maximum extraction of non-polar compounds. This stir bar is rinsed with Milli-Q water and dried with an absorbent paper. A second extraction is additionally performed using a second 126 μL stir bar after 2 g NaCl salt addition. This allows extracting remaining polar compounds from the sample. This second bar is also rinsed with Milli-Q water and dried with an absorbent paper. Finally, stir bars are placed in a desorption tube (empty cartridge) and analyzed by TD/GC–MS. Extraction efficiencies of VOCs vary between 22.4% for isoprene and 96.8% for m + p-xylenes (see SM Table S3–2). A comparison of the experimental extraction efficiencies for styrene ($\log K_{O/W} = 2.89$), ethylbenzene ($\log K_{O/W} = 3.03$), m + p-xylenes ($\log K_{O/W} = 3.09$) and naphthalene ($\log K_{O/W} = 3.17$) showed a good consistency with the theoretical extraction efficiencies (88.6–96.7%). For other compounds with $\log K_{O/W} < 3$, the experimental extraction efficiency is lower than the theory. Detection limits were estimated (see SM Table S3–1) demonstrating the ability of the SBSE technique to quantify low concentrations (1.0–8.7 ng L^{-1}).

2.4. Uncertainty calculations of VOCs measurements

The concentration of VOCs in gaseous and aqueous phases depends on the mass of the compound trapped on the Tenax® TA cartridge (gas sampling) or on PDMS phase of Twister (cloud sampling) divided by the sampling volume. As a result, the associated uncertainty will depend on uncertainties related to these two factors. The uncertainty associated to each concentration is determined using the method developed within ACTRIS network (Hoerger et al., 2015).

The VOCs concentration uncertainty $u(C_i)$ is expressed with the equation:

$$\frac{u^2(C_i)}{C_i^2} = \frac{u^2(m_{i,mes})}{m_{i,mes}^2} + \frac{u^2(V)}{V^2} \quad (1)$$

where $u(V)$ is the variance associated with the sampling volume V and $u(m_{i,mes})$ is the variance associated with the mass trapped on Tenax® TA or twister of compound $m_{i,mes}$. This equation allows calculating the relative standard uncertainty of VOCs concentrations in both gas and aqueous phases. More information about calculations of VOCs measurement uncertainties is given in SM S3.

The relative uncertainties on concentrations range from 17.0 to 25.2% depending on the compounds shown in Table 1. The uncertainty on $m_{i,mes}$ contributes the most to the total uncertainty and the standard

Table 1
Extended (28) calculated uncertainties of VOC concentrations in air and cloud waters.

Compound	Uncertainty (%) for air samples	Uncertainty (%) for cloud water samples
Benzene	19.6	11.8
Toluene	17.4	10.2
Ethylbenzene	17.4	16.0
m + p-xylene	18.2	17.8
o-Xylene	17.0	16.2
Styrene	17.0	16.6
Cumene (isopropylbenzene)	20.2	11.0
n-Propylbenzene	25.2	25.2
1,3,5-Trimethylbenzene	23.0	23.0
1,2,4-Trimethylbenzene	20.4	20.6
Naphtalene	20.4	18.8
Isoprene	22.2	20.4
α -Pinene	19.4	19.4
β -Pinene	20.8	20.8
Limonene	17.8	18.8
Nopinone	17.2	19.6

term and linearity term are identified as the most important sources of uncertainty on $m_{i,mes}$ as detailed in SM S3. For gas sampling by Tenax® cartridges, the standard term accounts for 44.2 to 97.8%. For cloud sampling by Twisters, the linearity term accounts for 3.4 to 95.6% depending on the compounds.

2.5. Partitioning coefficient “q”

To describe the deviation from thermodynamic equilibrium, the partitioning of chemical compounds between the gas and aqueous phases can be represented by a partitioning coefficient q , defined by Audiffren et al. (1998) and used in other studies such as in van Pinxteren et al. (2005) and Rose et al. (2018) which is defined as:

$$q = \frac{C_{aq}}{LWC \times H_{eff} \times R \times T \times C_{gas}} \quad (2)$$

where C_{aq} and C_{gas} are, respectively, the aqueous and gaseous concentrations of compound of interest in molec cm^{-3} , the LWC liquid water content of the cloud event in vol / vol . H_{eff} is the effective Henry's law constant in M atm^{-1} and $R = 0.08206 \text{ atm M}^{-1} \text{ K}^{-1}$.

This factor q indicates whether X is at the Henry's law equilibrium ($q = 1$), undersaturated in the aqueous phase ($q < 1$) or supersaturated in the aqueous phase ($q > 1$).

3. Results & discussion

3.1. VOCs in gaseous and cloud aqueous phases

16 cloud samples corresponding to 9 cloud events sampled between 2011 and 2014 at different seasons were classified by the same approach described in Deguillaume et al. (2014) using principal component analysis (PCA) with hierarchical clustering analysis (HCA) (see more details in SM S4). Chemical cloud water concentrations of main inorganic ions (SO_4^{2-} , NO_3^- , NH_4^+ , Na^+ , and Cl^-) and pH values are variables used to constrain this statistical analysis. The back-trajectories of the air masses that reach the PUY station for each cloud event were also calculated with HYSPLIT trajectory model to confirm the classification (see SM S4). Among all cloud events, the majority were classified as “marine” clouds, except for one cloud event sampled on March 26th, 2014 classified as “continental”. This is explained by higher concentrations of NH_4^+ and NO_3^- that are typical of continental emissions. Cloud events classified as marine show air mass back-trajectories coming from different sectors: west, northwest/north, and south/southwest. The “continental” cloud event is characterized by a back-trajectory coming from the west/northwest sector.

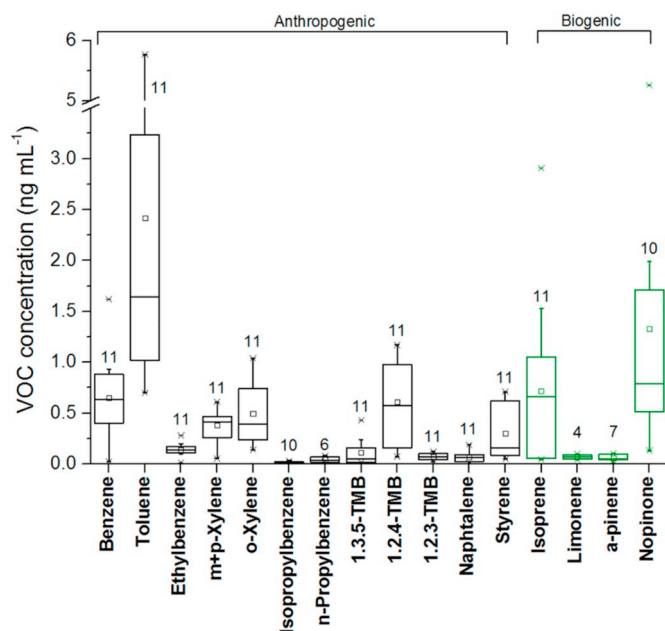


Fig. 3. Distribution of VOC concentrations (ng mL^{-1}) in cloud waters sampled at PUY station for VOC from anthropogenic sources (black boxplots) and from biogenic origin (green boxplots). The number of samples analyzed is indicated above each box plot. The bottom and top of box plots are the 25th and 75th percentiles, respectively. The full line and the open square symbol represent the median and mean values, respectively. The ends of whiskers are 10th and 90th percentiles. The asterisks are maximum and minimum values. Note that 1,3,5-TMB, 1,2,4-TMB, 1,2,3-TMB stand for 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The concentrations of compounds detected in cloud waters are summarized in SM (Table S5) (in ng mL^{-1}). The distributions of concentration values are reported in Fig. 3. The median concentrations are rather low and lie between 0.01 and 2.4 ng mL^{-1} . In average, the total concentration of these chemical compounds represent $\sim 0.5 \text{ ng mL}^{-1}$, corresponding to $< 0.1 \mu\text{mol L}^{-1}$. These compounds represent in mass a small fraction of the organic carbon in cloud water ($< 0.1\%$ of the measured DOC). As a comparison, carboxylic acids measured systematically at the PUY station represent $\sim 10\%$ of the measured DOC for cloud classified as marine (Deguillaume et al., 2014). Toluene was the most abundant anthropogenic compound in all the samples; cloud event C9 presents the higher concentration observed in this work, reaching 5.77 ng mL^{-1} (by a factor 3 in average).

Few studies have already reported the presence of hydrophobic VOCs from anthropogenic origin in cloud water or fog droplets (Table 2). Measurements performed at the remote Gibbs peak (Mt. Mitchell State Park, 2006 m a.s.l., USA) have shown average concentrations of ethylbenzene, o-xylene, toluene and trimethyl-benzenes ~ 0.17 , 0.45 , 0.60 and 0.34 ng mL^{-1} (Aneja, 1993) by GC-MS and GC coupled with Flame Ionization Detector (FID) Electron Capture Detector (ECD). Other organic compounds like alkanes and polycyclic aromatic hydrocarbons (PAH) were also detected in urban fogwater in Dubendorf (Switzerland) (Leuenberger et al., 1988; Capel et al., 1990; Li et al., 2011). At Dubendorf, ethylbenzene, xylenes, trimethylbenzenes were also detected in rain and snow with concentration ranges of 0.015 – 0.44 , 0.02 – 0.30 and 0.020 – 0.21 ng mL^{-1} , respectively (Czuczwa et al., 1988). The values at PUY are in the same order of magnitude than the ones reported in those studies. Among the selected compounds,

nopinone has been already detected in cloud waters sampled at the PUY station (Lebedev et al., 2018) by GC \times GC-TOF-MS. In that study, phenols (i.e., phenol, benzyl alcohol, p-cresole, 4-ethylphenol, 3,4-dimethylphenol, 4-nitrophenol) have been quantified in cloud water and present mass concentrations in the same range (0.03 to 0.74 ng mL^{-1}) than compounds detected in this work. Non-targeted analysis by FT-ICR MS in clouds sampled at the same site in previous studies showed the presence of oxidation products of nopinone (Bianco et al., 2018). Additionally, this product was also observed in clouds sampled at the Storm Peak laboratory (Colorado, USA) (Zhao et al., 2013).

Detected VOCs were mostly primary aromatics (benzene, toluene, ethylbenzene, xylenes) and terpenoids (isoprene, limonene, α -pinene and nopinone). These compounds are known to be present in the gas phase as revealed by the five sampling during cloud events (Fig. S1). These families of compounds are released into the atmosphere by either anthropogenic or biogenic sources. Aromatics are usually related to fossil fuel combustion and evaporation emissions as well as solvent use related activities (Borbon et al., 2018). Terpenoids are released by terrestrial vegetation. On the one hand isoprene is emitted by deciduous trees and is light and temperature dependent. Terpenes are emitted by conifers (Fuentes et al., 2000). Nopinone is a secondary product of biogenic compounds oxidation (Cahill et al., 2006).

The range of concentrations of VOCs detected both in cloud and air samples are presented in Fig. 4. Toluene, benzene, isoprene and nopinone which are the most abundant in the gas phase also show the highest concentrations in cloud droplets. One should note that isoprene levels in air are probably underestimated due to its breakthrough for 18-L sampled air. Samples were collected during spring 2014 when biogenic emissions begin to increase, which may explain the large presence of biogenic compounds in the multiphase samples. Nopinone is a secondary products resulting from the oxidation of for example β -pinene by the hydroxyl radicals (HO^\bullet) (Aschmann et al., 1998; Fry et al., 2009); this last compound is surely consumed, possibly explaining its absence in the collected samples.

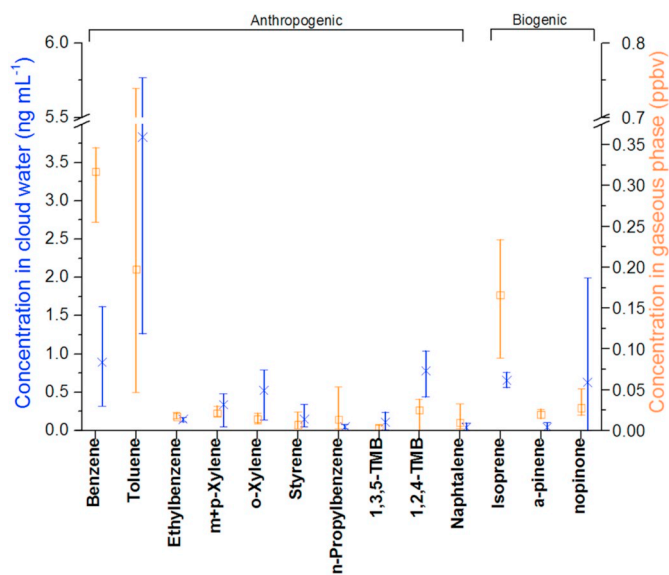


Fig. 4. Concentration variability of VOCs in gas phase in ppbv (in orange) and in cloud water samples in ng mL^{-1} (in blue) during parallel sampling periods of 2014 at PUY station (clouds number C5 S1, C8 S2, C9 S1, C9 S2 and C9 S3). The top and bottom of line are maximum and minimum values. The square and asterisk symbols represent the mean values of VOCs in gas phase and in cloud water samples, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

Comparison of VOC concentrations (min-max, mean value) in gaseous and cloud aqueous phases measured at PUY with similar measurements performed at other sampling sites.

Conc. Range (ng mL ⁻¹)	Sampling site		
	PUY station	Gibbs Peak	EAWAG
	Mt. puy de Dôme	Mt. Mitchell State	Dübendorf
	1465 m a.s.l.	Park 2006 m a.s.l.	400 m a.s.l.
	France	United States	Switzerland
	Remote site	Remote site	Urban area
	Cloud	Cloud	Rain
Ethyl-benzene	0.01–0.28 (0.12)	(0.17)	0.02–0.05 (0.04)
o-Xylene	0.14–1.04 (0.50)	(0.45)	0.02–0.13 (0.03)
Toluene	0.70–5.77 (2.42)	(0.60)	/
Trimethyl-benzenes	/	(0.34)	/
1,3,5-TMB	0.02–0.43 (0.11)	/	/
1,2,4-TMB	0.07–1.17 (0.61)	/	0.02–0.04 (0.03)
1,2,3-TMB	0.02–0.12 (0.07)	/	/
Naphtalene	0.02–0.19 (0.07)	/	0.02–0.04 (0.03)

Conc. Range (ppb)	Sampling site		
	PUY station	Observatorium Hohenpeißenberg	Po Valley Observatory
	Mt. puy de Dôme	Hohenpeißenberg	Mt Cimone
	1465 m a.s.l.	977 m a.s.l.	2165 m a.s.l.
	France	Germany	Italy
	Remote site	Remote site	Urban area
	Air	Air	Air
Benzene	0.26–0.35 (0.32)	0.06–0.30 (0.13)	0.13–0.19 (0.16)
Toluene	0.05–0.74 (0.20)	0.02–0.33 (0.81)	0.02–0.08 (0.05)
Ethylbenzene	0.02–0.03 (0.02)	0.01–0.04 (0.02)	0.00–0.01 (0.01)
(m + p)-Xylene	0.02–0.03 (0.02)	0.01–0.12 (0.03)	0.00–0.02 (0.01)
o-Xylene	0.01–0.02 (0.01)	/	0.00–0.01 (0.01)
Isoprene	0.09–0.23 (0.17)	0.01–0.08 (0.01)	/

/: below detection limit.

Gaseous VOCs measurements were also conducted in other Global Atmosphere Watch (GAW) program sites such as: (1) Mt. Cimone (2165 m a.s.l.) (CMN), the highest peak of the Northern Apennines influenced by two distinct climatic regions (continental Europe and Mediterranean Basin) and (2) Hohenpeißenberg station (HPB) (980 m a.s.l.), located at pre-Alpine hill and sticking out 300 m above the surrounding forest/grassland and representative of rural central European environment (see Table 2). VOCs concentrations at these two sites by GC-FID online measurements have been extracted from the EBAS database (<http://ebas.nilu.no/Default.aspx>) averaged over the period of March and April 2014 where the cloud samples have been collected. Mount Cimone during this period can be considered as representative of free tropospheric conditions and often under the influence of the Mediterranean basin/south Europe air masses (Bonasoni et al., 2000; Henne et al., 2010). BTEX concentrations for HPB and CMN range, respectively, from 0.01 to 0.33 ppb and from 0 to 0.19 ppb in comparison to PUY values varying between 0.01 and 0.74 ppb. VOCs concentrations monitored at CMN are therefore in the same range as what is observed at the PUY station for the cloud samples from marine origin. Concentrations monitored at the HPB station are also similar to

the ones from the PUY station; this is explained by the remoteness of the HPB.

3.2. Phase-partitioning of VOCs in cloud

The q factors for the selected VOCs characterized in this study are estimated using gaseous and aqueous measurements of these compounds, considering the temperature during the sampling and the mean liquid water content. H_{eff} are also used in this study and are extracted from the database presented in Sander (2015); calculations are presented in SM (Table S6).

The partitioning between the gas and aqueous phases cannot be described by a thermodynamic equilibrium assumption (Ervens, 2015). The factor q can evolve with time, since cloud microphysical properties, mass transfer and chemical reactivity modify the partitioning of the species in the gas and aqueous phases. Fig. 5A shows that hydrophobic VOCs measured in this study are all largely supersaturated by a factor of 1–3000 compared to Henry's law equilibrium ($q = 1$). For isoprene, factor q (around 100 on average) is probably overestimated due to isoprene's breakthrough during its atmospheric gaseous sampling (see Section 2.2) but is expected to stay in a range higher than 1.

Previous studies investigated the partitioning of small carboxylic acids and carbonyls that have been commonly measured in cloud aqueous phase, such as formic, acetic, oxalic acids and formaldehyde (Winiwarter et al., 1988; Voisin et al., 2000). In these works, the calculated partitioning coefficient is in agreement with the one that is expected considering Henry's law equilibrium. Some deviations have been observed for formic and acetic that are found undersaturated in certain case (Facchini et al., 1992). For cloud waters with $\text{pH} < 3$, these compounds are inversely found slightly supersaturated (Winiwarter et al., 1994). Solubility of carboxylic acids and carbonyls is a function of temperature and pH (for the acids) and observed deviations commonly increases with increasing pH. Several explanations have been in the past proposed to explain the observed deviations (Facchini et al., 1992; Winiwarter et al., 1994; Voisin et al., 2000).

Sampling artefacts can lead to bias in measured aqueous concentrations. In the air, cloud droplets are in equilibrium with the interstitial air. By grouping all of them in a bulk sample, this equilibrium is perturbed with respect to the original conditions (Perdue and Beck, 1988; Pandis and Seinfeld, 1991; Keene et al., 1992). The pH values of bulk water is also different from individual droplets and may modify the Henry's law values of acids (Ervens et al., 2003). Outgassing of organic molecules could also occur from the sample and effects resulting from temperature differences from the field to the lab have to be considered and may change the partitioning.

Deviations can be due to kinetic transport limitations through the air/water surface; gas phase diffusion and transfer of molecules at the gas/liquid interface (phase/phase transition and diffusion from the surface) are critical steps to consider. Notably, parameters such as droplet lifetime and accommodation coefficient α are difficult to estimate and the experimental measurements are scarce (Noone et al., 1992; Davidovits et al., 2006). This mass transfer is also perturbed by the presence and potential accumulation of hydrophobic compounds on the droplet surfaces (Capel et al., 1990; Gill et al., 1983).

In the present study, we investigate the partitioning of more hydrophobic molecules from both biogenic and anthropogenic origins. In van Pinxteren et al. (2005), carbonyl compounds have been measured both in the gaseous and aqueous phases and they have shown that larger and less soluble compounds (valeraldehyde, methyl ethylketone, methyl vinyl ketone, heptanal, octanal, and benzaldehyde) are supersaturated by a factor of 100 to 1000 in clouds sampled during the FEBUKO campaign at Mount Schmücke in Germany. Those results have been compared to measured values of the present study (Fig. 5B). q factor is plotted for both studies as a function of the effective Henry's law constant. In both studies, we observe that the q factor is higher when the Henry's law constant is small. Similar observations are

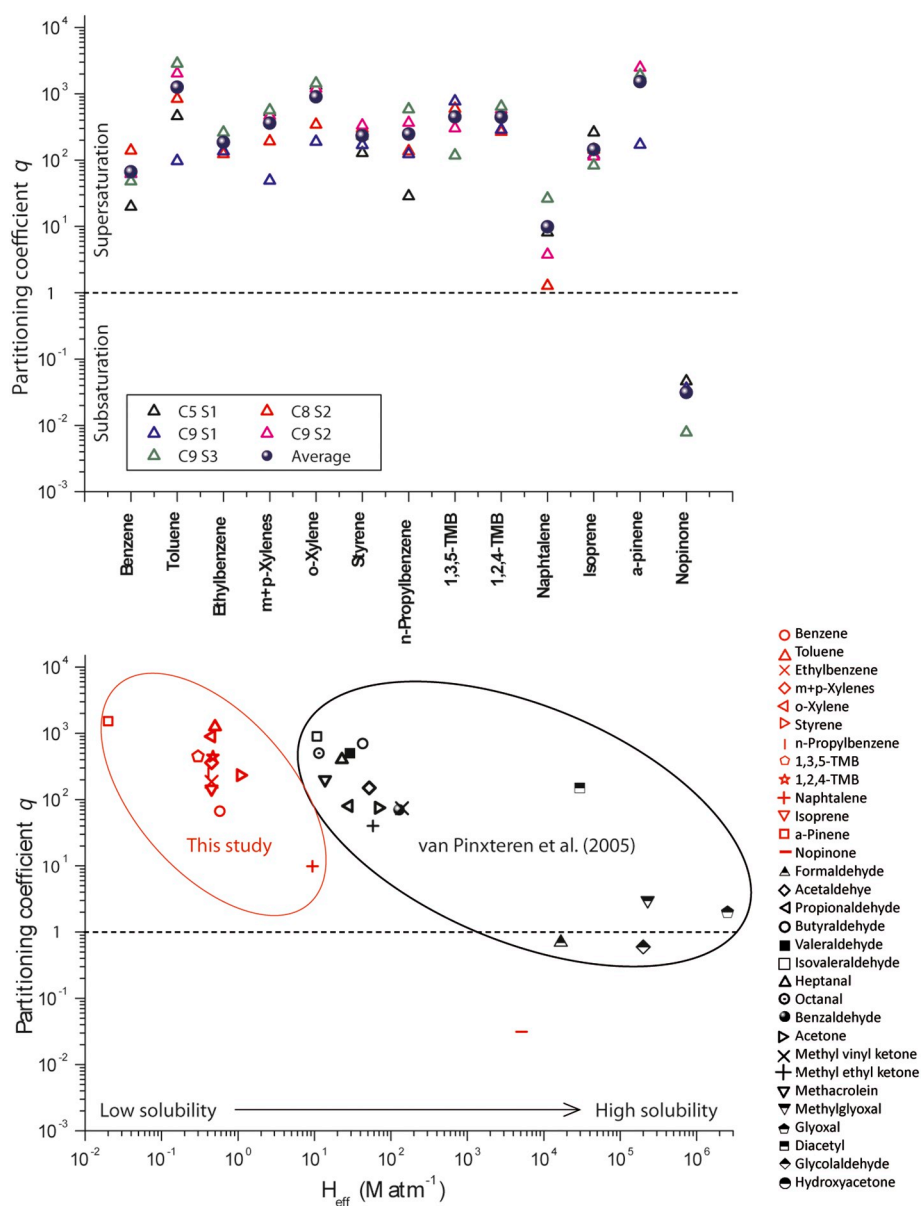


Fig. 5. (A) q factor calculated for each cloud sample and for each chemical compound (blue circles correspond to mean values); (B) mean q factors calculated in this study are compared with the study from van Pinxteren et al. (2005); chemical compounds are classified as a function of their effective Henry's law constants. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reported for different hydrophobic compounds such as certain pesticides, PAHs, polychlorinated biphenyls (PCBs), and alkanes in fog water (Glotfelty et al., 1987; Valsaraj et al., 1993). A possible explanation for this could be that hydrophobic compounds are associated with dissolved or colloidal organic matter. This tendency of colloids to bind hydrophobic compounds has been already observed in both soil-water and sediment-water media (Kile and Chiou, 1989; Capel et al., 1990; Schomburg et al., 1991). Another reason could be the effect of air/water interface presenting very high specific area available for adsorption of hydrophobic compounds (Djikaev, 2003). The hydrophobicity of those compounds are correlated with the $K_{O/W}$. Therefore, phase partitioning could not be predicted by Henry's law values but using $K_{O/W}$. Thus, to investigate that point, a new figure has been drawn linking the $K_{O/W}$ coefficient with an "enrichment factor" E (Fig. 6) that considers the effect of both adsorption of hydrophobic compounds at the air/water interface and their association to the colloids in cloud water media. This parameter has been initially proposed by Valsaraj et al. (1993) and is calculated as following:

$$E = 1 + \frac{3}{r}K_a + \rho_s^*K_{oc} \quad (3)$$

with r : cloud droplet radius; K_a : is the partition constant for hydrophobic organic carbon between the air-water interface and water. The term of $\frac{3}{r}K_a$ is relative to the air-water interfacial adsorption. The term $\rho_s^*K_{oc}$ results from the adsorption on filterable solids and the sorption on non-filterable dissolved organic carbon in cloud water as described in previous works (Valsaraj, 1988a, 1988b; Thoma et al., 1991; Morel and Gschwend, 1987) and calculated as following:

$$\rho_s^* = \rho_s f_{oc} + \rho_{col} \quad (4)$$

$$K_{oc} \approx K_{col} \quad (5)$$

- ρ_s^* : concentration of all non-dissolved organic carbon in cloud droplets (mgC L^{-1});
- ρ_s : concentration of all non-dissolved organic carbon that has been filtered (mgC L^{-1});
- f_{oc} : fraction of all non-dissolved organic carbon that has been

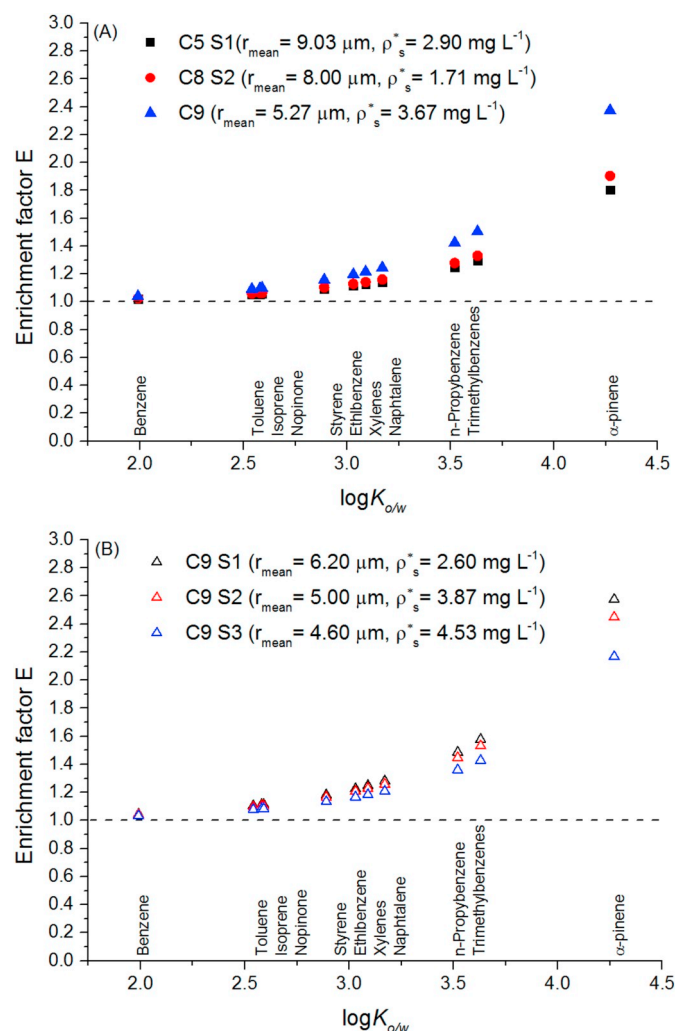


Fig. 6. (A) Enrichment factors E for each chemical compound and for each cloud sample presenting different mean droplet radius r_{mean} and concentrations of non-dissolved organic carbon (ρ_s^*). For C9 cloud event, is presented the E coefficient averaged for the 3 samples (mean radius and mean non-dissolved organic carbon); (B) Enrichment factors E for each chemical compound of samples from cloud event C9 with mean droplet radius r_{mean} for samples and different concentrations of non-soluble organic compounds.

filtered;

- ρ_{col} : concentration of all non-dissolved organic carbon under the form of colloids (non-filtered) (mgC L^{-1}).

K_{oc} is the partition constant ($\text{cm}^3 \text{g}^{-1}$) for hydrophobic organic carbon between the organic carbon fraction in filterable solids and cloud water; K_{col} is the partition constant ($\text{cm}^3 \text{g}^{-1}$) between the colloidal dissolved organic carbon and cloud water. We assume that K_{oc} and K_{col} are equal as proposed by Thoma et al. (1991) and Morel and Gschwend (1987).

Based on previous work from in Schomburg et al. (1991) and Hartkopf and Karger (1973), Valsaraj (1988a,b) proposed the following empirical relationships to express K_{oc} and K_a as a function of $K_{o/w}$:

$$K_{oc} = 5.6 \times K_{o/w}^{0.82} \quad (6)$$

$$K_a = 3 \times 10^{-7} \times K_{o/w}^{0.68} \quad (7)$$

The enrichment factor E can be finally given as:

$$E = 1 + 3 \times 10^{-7} \times \frac{3}{r} \times K_{o/w}^{0.68} + 5.6 \times \rho_s^* \times K_{o/w}^{0.82} \quad (8)$$

The E factors for the selected VOCs characterized in this study are estimated using gaseous and aqueous measurements of these compounds, considering average cloud droplet effective radius during the sampling and 10% of total organic compound as non-soluble organic carbon. More details about calculations are presented in SM Table S7.

The predictions from the above equation are shown in Fig. 6. The calculation predicts a small enrichment for compounds in cloud samples, except for α -pinene which has a high $K_{o/w}$ value. Enrichment factors E of each cloud sample increase when cloud droplet radius decrease. When the cloud droplet radius is constant, enrichment factors E do not vary significantly as a function of ρ_s^* non-soluble organic carbon. It is clear that the contribution to the enrichment factor from surface adsorption is much more important than that from dissolved or colloidal organic matter. This is explained by the fact that the concentration of colloids and non-soluble organic carbon in cloud water samples at PUY are much less important (around a factor of 100 less concentrated) than what is observed for fog event in the study from Valsaraj et al. (1993). The contribution of adsorption calculated for the cloud samples is also less important in the present study since the mean cloud droplet radius ($\sim 6\text{--}10 \mu\text{m}$) is more important than the one measured for fog droplets ($\sim 1 \mu\text{m}$). It is clear from these calculations that evaluated adsorption processes seem to contribute in a minor way to the cloud water enrichments observed at PUY for these cloud samples.

4. Conclusions

These results emphasize the fact that the partitioning of hydrophobic compounds in clouds are poorly understood and that further laboratory and field investigations are needed to understand the interfacial processes and to better constrain cloud chemistry models. These numerical tools commonly consider the mass transfer as a kinetic process. For example, Schwartz (1986) proposed a parametrization of the mass transfer considering a transfer coefficient that depends on gaseous diffusion and interfacial transport constrained by the accommodation coefficient (α) (Davidovits et al., 2006, 2011) and the droplet radius. Cloud chemistry models also consider the solubility of chemical compounds based on the Henry's law constants (Mouchel-Vallon et al., 2017). Finally, those models are able to simulate the partitioning of organic and inorganic compounds that are perturbed by microphysical processes, mass transfer and gaseous and aqueous chemical reactivity (Mouchel-Vallon et al., 2013; Ervens, 2015; Rose et al., 2018; Hoffmann et al., 2018). Those models predict small deviations from the Henry's law equilibrium that can be explained by the LWC, droplet radius and pH variations. It seems clear that for hydrophobic compounds those models will not be able to simulate the strong observed supersaturation of those species in the aqueous phase. For those compounds, additional processes (mainly at the air/water interface) should be considered in cloud chemistry models since phase partitioning cannot be predicted considering only the solubility of organic compounds.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosres.2020.104844>.

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