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Detection of semi-volatile compounds in cloud waters by GC×GC-TOF-MS. Evidence of phenols and phthalates as priority pollutants[☆]

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ABSTRACT

Although organic species are transported and efficiently transformed in clouds, more than 60% of this organic matter remains unspeciated. Using GCxGC-HRMS technique we were able to detect and identify over 100 semi-volatile compounds in 3 cloud samples collected at the PUY station (puy de Dôme mountain, France) while they were present at low concentrations in a very small sample volume (<25 mL of cloud water). The vast majority (~90%) of the detected compounds was oxygenated, while the absence of halogenated organic compounds should be specially mentioned. This could reflect both the oxidation processes in the atmosphere (gas and water phase) but also the need of the compounds to be soluble enough to be transferred and dissolved in the cloud droplets. Furans, esters, ketones, amides and pyridines represent the major classes of compounds demonstrating a large variety of potential pollutants. Beside these compounds, priority pollutants from the US EPA list were identified and quantified. We found phenols (phenol, benzyl alcohol, p-cresole, 4-ethylphenol, 3,4-dimethylphenol, 4-nitrophenol) and dialkylphthalates (dimethylphthalate, diethylphthalate, di-n-butylphthalate, bis-(2-ethylhexyl)-phthalate, butylbenzylphthalate, di-n-octyl phthalate). In general, the concentrations of phthalates (from 0.09 to 52 $\mu g\,L^{-1}$) were much higher than those of phenols (from 0.03 to 0.74 $\mu g\,L^{-1}$). To our knowledge phthalates in clouds are described here for the first time. We investigated the variability of phenols and phthalates concentrations with cloud air mass origins (marine *vs* continental) and seasons (winter *vs* summer). Although both factors seem to have an influence, it is difficult to deduce general trends; further work should be conducted on large series of cloud samples collected in different geographic areas and at different seasons.

1. Introduction

Organic compounds enter the atmosphere as gases (VOC: Volatile Organic Compounds) or aerosols (POA: Primary Organic Aerosols) from natural and anthropogenic sources. During their atmospheric lifetime, those compounds are transported and efficiently transformed. The origin, transformations, and fate of organic species in the air have been widely studied as they play a central role in human health, biogeochemical cycles, atmospheric chemistry and climate (Kanakidou et al., 2005; Fowler et al., 2009).

The analysis of the organic fraction of the aerosol and of the organic gases reveals that the atmospheric organic matter is composed of a complex mixture of both primary and secondary chemical products (Goldstein and Galbally, 2007). Thousands of individual compounds chemically evolve over their atmospheric lifetimes, mainly by oxidation processes that lead to subsequent gas-to-particle partitioning and to formation of the SOA (Secondary Organic Aerosols) (Hallquist et al., 2009). In this context, clouds and fogs affect organic gases and aerosols through efficient chemical and physical processes. The soluble fraction of condensation nuclei dissolves in the water phase and water soluble organic compounds (WSOC) are taken up by cloud droplets, where their chemical

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transformation may take place (Herrmann et al., 2015). Oxidation processes in the aqueous phase are notably responsible for the formation of aqueous SOA ("aqSOA") (Ervens et al., 2011).

Since 1990s cloud studies have had the objectives to characterize the dissolved organic matter and to determine the sources and the aqueous processes. Bulk characterization is commonly performed by analyzing the dissolved organic content (DOC) although many works have been done to identify and quantify individual organic species (Herckes et al., 2013). Small chain carboxylic acids (formic, acetic, oxalic, succinic) and carbonyl compounds (formaldehyde, glyoxal, methylglyoxal, acetone) have been commonly targeted (Benedict et al., 2012; Deguillaume et al., 2014; Ervens et al., 2013; Guo et al., 2012; Li et al., 2017; Wang et al., 2011; van Pinxteren et al., 2005) and analyzed by Ion Chromatography (IC). Those species have been studied because they are produced in the aqueous phase being potentially involved in the formation of high molecular-weight compounds. Besides these highly polar species, several studies investigated the presence of anthropogenic molecules such as BTEX (Hutchings et al., 2009), polycyclic aromatic hydrocarbons (PAH) (Ehrenhauser et al., 2012; Li et al., 2010), nitrosamines (Hutchings et al., 2010), phenols and nitrophenols (Lüttke and Levsen, 1997; Lüttke et al., 1999; Hofmann et al., 2008). Finally, due to the occurrence of organic nitrogen species in the atmosphere, biologically produced molecules such as amino acids and amines were also investigated (Zhang and Anastasio, 2001, 2003; Bianco et al., 2015, 2016).

However, even when several analytical tools are used to characterize the organic matter in the clouds, more than 60% of it remains unspecified. In this context, mass spectrometry is the most efficient tool for the non-targeted analysis, allowing working with the most complex mixtures of organic compounds at trace levels (Lebedev, 2013). It has been already used for other environmental matrices such as rain and snow which are more easily sampled than clouds (Czuczwa et al., 1988; Leuenberger et al., 1988, Sempére and Kawamura, 1994; Wania et al., 1998, Lebedev et al., 2003, Herbert et al., 2006, Krawczyk and Skret, 2005, Polyakova et al., 2012, Lebedev et al., 2013, Mazur et al., 2016, Švancárová et al., 2016, Mazur et al., 2017, Lebedev et al., 2018). Recent studies using high resolution mass spectrometry from Zhao et al. (2013), and Cook et al. (2017) demonstrate the complexity of the cloud samples with thousands of molecular features detected. Several detected sulfur- and nitrogen-containing compounds are presumed to be coming from biogenic and anthropogenic volatile organic precursors.

Here we focus on the detection in the cloud water of the semi-volatile anthropogenic compounds which are partitioned among the gas and the particulate phases in the atmosphere. Those compounds can therefore be dissolved in the cloud water droplets. Comprehensive two-dimensional gas chromatography (GC × GC) coupled to high resolution time-of-flight mass spectrometry is used for the non-targeted identification of these semi-volatile compounds in the cloud water samples collected at the top of puy de Dôme (PUY), Clermont-Ferrand (France) during the period of 2013–2016. Our attention was mostly focused on phenolic compounds that have been detected in the past studies along with phthalates. Phenolic compounds reactivity in the cloud water is also suspected to contribute to the aqSOA formation (Yu et al., 2014; Sun et al., 2010) and they are also part of the visible light-absorbing organic matter of atmospheric aerosols referring as "brown carbon" (Desyaterik et al., 2013). Phthalates have been detected in the aerosols (Fu et al., 2010), rain (Teil et al., 2006), snow (Polyakova et al., 2012; Lebedev et al., 2018), and other environmental samples but never in the cloud water, to our knowledge.

2. Materials and methods

2.1. Cloud sampling

Samples of the cloud water were collected using cloud impactor installed on the roof of the atmospheric observatory at the top of the puy de Dôme Mountain (PUY, 1465 m above the sea level, 45°46′ North, 2°57′ East, France). The PUY station is part of the atmospheric survey networks ACTRIS (Aerosols, Clouds, and Trace gases Research Infrastructure), EMEP (the European Monitoring and Evaluation Program), and GAW (Global Atmosphere Watch). The method of sampling is described in details in Deguillaume et al. (2014). To eliminate microorganisms and particles, samples were filtered using a 0.20-μm nylon filter within 10 min after sampling and then stored at −25 °C in sterile Falcon® tubes until extraction. To assess potential contamination of the cloud samples during filtration and storage processes, the blanks were also prepared from ultrapure water (3 × 30 mL) using the same procedure.

The dates, number and volume of samples for the 3 cloud events are summarized in Table 1. pH was measured immediately after sampling; the concentrations of the main anions and cations were determined by IC analysis (see Table S1 in SI). Clouds 1 and 3 have been collected during winter whereas Cloud 2 has been sampled in summer but during the night. During these periods, the top of the mountain is mostly found to be in the free troposphere (Venzac et al., 2009). Thus, we can argue that the site is not influenced by local emissions.

Following the method described in Deguillaume et al. (2014), samples were classified by considering their physico-chemical properties (pH and the concentrations of the inorganic ions) as variables. A PCA/HCA statistical analysis allows classifying Cloud 1 as "Marine" and Clouds 2 and 3 as "Continental". The back-trajectory plots are used to evaluate this statistical classification. They are calculated using the NOAA HYSPLIT trajectory model at an interception height of 1465 m a.s.l., corresponding to the PUY summit. The models show that air masses were coming from the West for Cloud 1 and Cloud 2 and from the North-East for Cloud 3. Cloud 1 contains notably low concentration of NH_4^+ explaining its classification as "marine". Cloud 2 and 3 are characterized by high concentration of NH_4^+ and sulfate SO_4^{2-} justifying their origin as "continental". We can also notice that Cloud 3 shows relatively high concentration of nitrate NO_3^- (>200 μM) comparing to Cloud 2. More technical details about this classification of clouds are given in the SI section.

2.2. Sample preparation

Sample preparation of 3 cloud samples and the blanks (see section 2.1.) was carried out according to US EPA 8270 Method. Triplicate extraction with dichloromethane (10 mL) was followed by drying over sodium sulfate and concentrating. Concentrated (0.5 mL) basic (pH 11) and acidic (pH 2) dichloromethane extracts were merged, dried over sodium sulfate and concentrated (0.5 mL) before the injection. Perdeuterated PAHs (SV Internal Standards, Restek, USA) were used as the internal standards.

To take into account all possible sources of contamination

Table 1
Cloud samples analyzed in the present study.

Cloud event	Date	Classification	Volume
Cloud 1	05.11.2013	Marine	25 mL
Cloud 2	27.06.2014	Continental	25 mL
Cloud 3	16.02.2016	Continental	18 mL

during the sample preparation, reference samples of ultrapure water (5 × 30 mL) and pure dichloromethane (5 × 50 mL) were also prepared for the analysis. More details are given in SI.

2.3. GC/MS analysis

All experiments were performed using time-of-flight (TOF) high resolution mass-spectrometer Pegasus GC-HRT (LECO Corporation, Saint Joseph, MI, USA) with Folded Flight Path (FFP™) multiple reflecting geometry mass analyzer coupled with an Agilent 7890A Gas Chromatograph (Agilent, Palo Alto, CA, USA). The system was controlled by the ChromaTOF-HRT® software version 1.91 (LECO Corporation), which was also used for spectra collection and data processing. The multi-point mass calibration on FC-43 (PFTBA) mass spectra was performed before running the samples as a part of the automated tuning routine. The mass spectrometer's hardware and acquisition software allows minimizing mass drift during data collection.

Concentrated basic and acidic dichloromethane extracts were merged before the injection. Compounds detected in blanks and/or reference samples, even at lower levels than in cloud samples, were not considered. Phthalates represent an exception as it is almost impossible to avoid their presence at least in the trace levels. Some phthalates were detected in the blanks, however their levels were over 100-fold lower than in the cloud water samples.

GC–TOFMS: Column: Rxi-5SilMS 30 m × 0.25 mm (id) x 0.25 mm (df) (Restek Corporation, Bellefonte, PA) was used with constant helium flow rate 1 mL/min. Injected volumes - 1 μL, splitless. The injector and the transfer line were kept at 270 °C and 320 °C, respectively. The GC oven temperature program: 5 min isothermal at 35 °C, then 10 °C min-1 ramping to 330 °C and 2 min isothermal hold at 330 °C. EI Source temperature 250 °C, electron energy 70 eV, mass range *m/z* 15–520, spectra acquisition rate 12 spectra/second, resolving power – 25,000 at *m/z* 219 (FWHM), mass accuracy <1 ppm.

GC × GC–TOFMS: Column 1: Rxi-5MS 30 m × 0.25 mm (id) x 0.25 mm (df) (Restek Corp, Bellefonte, PA) and column 2: Rxi-17silMS 2 m × 0.25 mm (id) x 0.25 mm (df) (Restek Corp, Bellefonte, PA) were used at constant helium flow rate 1 mL/min. Injected volumes - 1 μL, splitless. The injector and the transfer line were at 270 °C and 320 °C, respectively. The GC oven temperature program: 5 min isothermal at 35 °C, then 10 °C min-1 ramping to 330 °C and 2 min isothermal hold at 330 °C. Secondary oven temperature offset 5 °C with modulator temperature offset 15 °C. Second dimension time 5 s with hot pulse time 1.9 s. EI source temperature 250 °C, electron energy 70 eV, mass range *m/z* 15–520, spectra acquisition rate 200 spectra/second with resolving power – 25,000 at *m/z* 219 (FWHM) with mass accuracy <1 ppm.

3. Results

3.1. Overview of the semi-volatile compounds identified in cloud samples by GC × GC-TOFMS

Looking for semi-volatile compounds in the cloud water samples was very challenging considering the limited amount of sample available (from 18 to 25 mL), very low concentration of the compounds and the complexity of the mixtures. In this context, GC × GC-TOFMS, with very high sensitivity and resolution as well as ability to conduct accurate mass measurements was considered as the most appropriate method. Earlier we have successfully implemented that approach to the analysis of snow in Moscow and in Arctic (Lebedev et al., 2013; Mazur et al., 2017; Lebedev et al., 2018). A typical 2-D chromatogram of a cloud water sample (Cloud 3) is presented in Fig. 1.

Thanks to this powerful method, over one hundred compounds were identified in the samples with various levels of reliability. Twelve compounds (Table 2) were identified and quantified using their standards (Megamix mixture, Restek Corp, Bellefonte, PA). We have assigned Level 1 identification reliability to those analytes. Sixty seven compounds were identified at the reliability Level 2 based on their retention time matches, high similarity scores after searching against the NIST14 mass spectral library, the accurate masses matches of all fragment ions, and correspondence of the presumed fragment ions to the general rules of fragmentation of organic compounds under electron ionization conditions (Tureček and McLafferty, 1994) (Table S2). Forty two analytes were assigned as partially identified as their elemental composition matches accurate mass data and some molecular structures can be explained from certain characteristic fragment ions (Table S3).

3.2. Priority pollutants: phenols and phthalates

Table 2 summarizes the levels of the priority pollutants (US EPA list) measured in the cloud samples. These compounds are phenols and phthalates, both groups represent oxygen-containing species. In general, the concentrations of the phthalates (from 0.09 to 52 $\mu g\,L^{-1}$) were much higher than those of phenols (from 0.03 to 0.74 $\mu g\,L^{-1}$).

3.2.1. Phthalates

Because phthalates are present in most environments and particularly in laboratories, it is easy to contaminate the sample during its preparation. Due to this fact we were very cautious with sample contamination, analyzing all possible blanks. However the mentioned phthalates (Table 2) were absent in all the blank samples or their levels were 2 orders of magnitude lower.

We have detected dimethylphthalate (DMP), diethylphthalate (DEP), di-n-butylphthalate (DnBP), butylbenzyl phthalate (BBP), bis–(2-ethylhexyl)-phthalate (DHEP) and di-n-octyl-phthalate (DNOP) in all samples. These phthalates may be considered as exclusively anthropogenic constituents as their formation due to cloud chemistry looks hardly possible. These phthalates are found in many industrial products and are produced in high volume, over 470 million pounds per year (EPA, 2006). They are used as plasticizers in plastics (mainly in poly(vinyl chloride) products) but also in personal care products, fragrances and detergents. Phthalates are of special environmental concern being the endocrine disrupting chemicals (EDGCs) (Salapasidou et al., 2011). Recent studies report the presence of alkyl phthalates in aerosols. In particular DHEP, DBP, DINP (di-isononyl phthalates) and DEP were present on $PM_{2.5}$ in the Moravian-Silesian region of the Czech Republic (Růžičková et al., 2016) while DHEP and DBP were the major phthalates detected in $PM_{2.5}$ and PM_{10} in Mexico city (Quintana-Belmares et al., 2018). DEHP, DBP and DEP were also detected in the air in such remote areas as the Enewetak Atoll (Xie et al., 2005) and the Arctic (Xie et al., 2007) as well as in such urban regions as Paris (Teil et al., 2006) or Thessaloniki (Salapasidou et al., 2011). Dimethylphthalate was detected in the Arctic snow (Lebedev et al., 2018). It is difficult to compare the concentrations measured in these various studies due to the fact that they were measured in solid aerosols, air samples, precipitates, and in the aqueous phase of the clouds. Indeed the resulting concentrations depend on the various properties of volatilization, solubilization and partition of phthalates between these different atmospheric phases. An easier comparison can be made between cloud water and rain samples. Teil et al. (2006) have measured the following phthalate concentrations in rainwater: DMP, 0.116 $\mu g\,L^{-1}$, DEP, 0.333 $\mu g\,L^{-1}$, DBP 0.592 $\mu g\,L^{-1}$; BBP 0.081 $\mu g\,L^{-1}$, DEHP 0.423 $\mu g\,L^{-1}$; DnOP 0.010 $\mu g\,L^{-1}$. Thuren and Larsson (1990) found similar range of concentrations for DBP

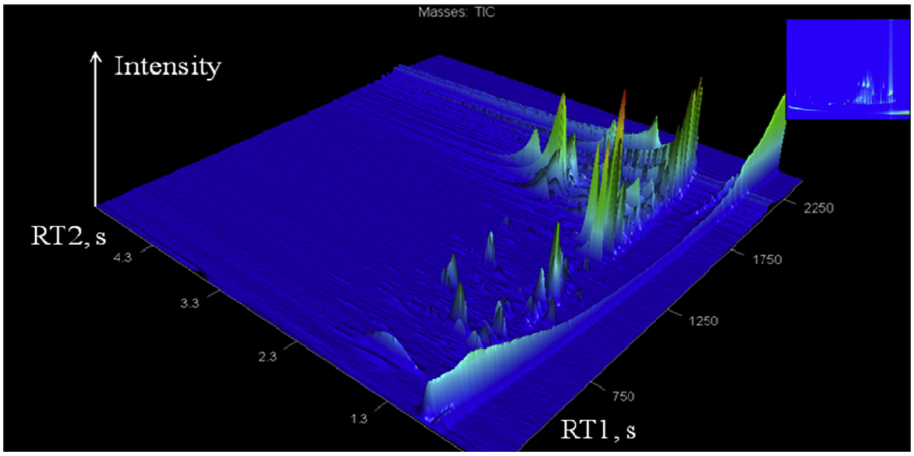

Fig. 1. 2D chromatogram (total ion current) of Cloud 1.

Table 2
Compounds identified at level 1 and belonging to the EPA priority list with their LOQ and LOD. Concentrations are expressed in μg L^{-1}.

№	Name	R.T. (s)	Cloud 1 05.11.13	Cloud 2 27.06.14	Cloud 3 16.02.16	LOQ	LOD
1	Phenol	683.524	0.52	0.74	0.74	0.02	0.005
2	Benzyl alcohol	749.275	0.03	0.05	0.03	0.03	0.01
3	p-Cresol	798.100	0.11	0.22	0.27	0.02	0.005
4	4-Ethylphenol	865.384	0.66	0.33	0.50	0.02	0.005
5	3,4-Dimethylphenol	901.774	0.33	<[LOQ]	<[LOQ]	0.03	0.01
6	4-Nitrophenol	1241.83	<[LOQ]	0.03	0.07	0.03	0.01
7	**Total phenols**		**1.65**	**1.37**	**1.61**		
8	Dimethylphthalate (DMP)	1180.30	0.65	30.00	0.09	0.01	0.002
9	Diethylphthalate (DEP)	1297.06	5.00	52.00	4.70	0.01	0.002
10	Di-n-butylphthalate (DnBP)	1500.51	2.70	1.80	6.30	0.01	0.002
11	Butylbenzylphthalate (BBP)	1858.26	15.00	31.00	28.00	0.01	0.002
12	Bis-(2-Ethylhexyl)-phthalate (DHEP)	1910.28	11.00	5.20	20.00	0.01	0.002
13	Di-n-octyl phthalate (DnOP)	1930.2	<[LOQ]	1.70	8.00	0.03	0.01
14	**Total phthalates**		**34.35**	**121.7**	**67.09**		

(0.003–0.496 μg L^{-1}) and DEHP (0.008–0.429 μg L^{-1}). We would like to notice that except for the case of DMP in Cloud 2 and 3 samples (0.09 and 0.65 μg.L^{-1}), the phthalate concentrations measured in all three cloud samples (from 1.8 to 52 μg L^{-1}, Table 2) are much higher (up to 100 times) compared to those measured in rain waters.

Besides these dialkylphthalates from the EPA priority pollutants list, dimethyl terephthalate which is widely used in the production of polyesters was also detected (see Fig. S1 for its identification by GC × GC-TOFMS). Although terephthalates are notably less widespread in the environment in comparison with isomeric ortho-phthalates, dimethyl terephthalate more and more often appears in the environmental samples being a high tonnage chemical (Tullo, 2015).

3.2.2. Phenols

Phenols including p-cresol, 4-ethylphenol, 3.4-dimethylphenol, and 4-nitrophenol as well as related benzyl alcohol, have been detected in the cloud samples (Table 2). The concentrations of phenol are below 1 μg.L^{-1} (0.52–0.74 μg L^{-1}), being within the same range but globally lower than those reported earlier in the cloud samples (3.0–5.4 μg L^{-1}) (Harrison et al., 2005). We measured 4-nitrophenol in the levels from 0.03 to 0.07 μg L^{-1} in the cloud samples collected at the PUY station while Harrison et al. (2005) reported much higher concentrations in other cloud samples (2.2–21 μg L^{-1}). 4-Ethylphenol (0.33–0.66 μg L^{-1}) and 3,4-dimethylphenol concentrations (0.33 μg L^{-1}) measured in our study were 10 times higher than 4-nitrophenol in the same samples. p-Cresol concentrations were within the same range of magnitude (0.11–0.27 μg L^{-1}) while those of benzyl alcohol were ten times lower (0.03–0.05 μg L^{-1}).

3.2.3. Variability of phenol and phthalate concentrations with clouds air mass origins and seasons

Cloud waters sampled at the PUY station reflect long distance travel of air masses and are not impacted by the local area emissions. Cloud 1 is classified as marine, Clouds 2 and 3 are classified as continental. Clouds were sampled at two different seasons: summer (Cloud 2) and winter (Clouds 1 and 3). Fig. 2 and Table 2 show the concentrations of phenols and phthalates in the different clouds.

3.2.3.1. Phenols. Concerning phenols (Fig. 2a) no major impact of the air mass origin, the physico-chemical composition of cloud water neither of the season is really noticeable. A slight difference could be observed when the general profile of the Cloud 1 sample which is a marine cloud, was compared to those samples of the Cloud 2 and 3 which are the continental ones (Fig. 2a). In the continental clouds the levels of phenol, p-cresol and 4-nitrophenol were higher. On the contrary 4-ethylphenol and 3,4-dimethylphenol were more concentrated in the marine cloud. Few papers report the presence of phenol and 4-nitrophenol in

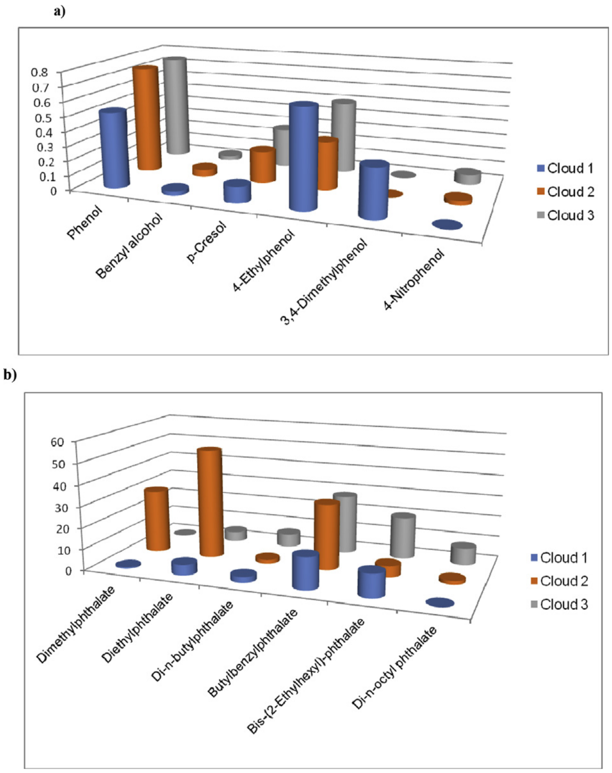

Fig. 2. Concentrations (in $\mu g\,L^{-1}$) of phthalates (a) and phenols (b) in Clouds 1, 2 and 3.

clouds collected in various places with increasing degrees of anthropization: Harrison et al. (2005) reported 3.5 $\mu g\,L^{-1}$ of phenol and 5.5 $\mu g\,L^{-1}$ of 4-nitrophenol in rural clouds, 5.4 $\mu g\,L^{-1}$ of phenol and 2.2 $\mu g\,L^{-1}$ of 4-nitrophenol in continental clouds and finally 3.0 $\mu g\,L^{-1}$ of phenol and 21 $\mu g\,L^{-1}$ of 4-nitrophenol in polluted clouds. At the PUY station phenol concentration varies from 0.52 $\mu g\,L^{-1}$ in the marine cloud (Cloud 1) to 0.74 $\mu g\,L^{-1}$ in the two continental clouds (Clouds 2 and 3) (Table 2). 4-Nitrophenol concentration could not be detected in Cloud 1 while it could be measured in Cloud 2 (0.03 $\mu g\,L^{-1}$) and Cloud 3 (0.07 $\mu g\,L^{-1}$). Although the anthropization of the air masses seems to increase the levels of phenol and 4-nitrophenol in the clouds (our work and the literature), it is not completely clear for the other compounds; the opposite can be even observed. More cloud events should be analyzed in the future to perform statistics; also the transformation of these compounds occurring in the cloud systems should be investigated.

3.2.3.2. Phthalates. In the case of phthalates the range of concentration is wider; therefore some differences appear depending on the cloud event. Clearly Cloud 2 has a phthalate profile completely different compared to Clouds 1 and 3 (Fig. 2b). The concentrations of light phthalates as DMP (30 $\mu g\,L^{-1}$) and DEP (52 $\mu g\,L^{-1}$) are much higher in Cloud 2 compared to Cloud 1 (0.65 and 5 $\mu g\,L^{-1}$ respectively) and Cloud 3 (0.09 and 4.7 $\mu g\,L^{-1}$, respectively) (Table 2). On the contrary heavier phthalates are less concentrated in Cloud 2 (1.8 $\mu g\,L^{-1}$, DHEP 5.2 $\mu g\,L^{-1}$, DNOP 1.4 $\mu g\,L^{-1}$) than in Clouds 1 and 3 (DBP 2.7–6.3 $\mu g\,L^{-1}$, DHEP 11–20 $\mu g\,L^{-1}$, DNOP 8 $\mu g\,L^{-1}$). BBP remains approximately the same for all three samples (15–31 $\mu g\,L^{-1}$).

The main characteristic of Cloud 2 sample differentiating it from others is the fact that it was sampled in summer instead of winter. The literature shows that the concentration of phthalates in atmospheric samples varies with the seasons or the temperature. Růžičková et al. (2016) reported an increase from 5 to 10 fold of the concentrations of DEHP, DBP, DINP and DEP in $PM_{2.5}$ collected during winter compared to those collected during summer. They argued that combustion of plastics during the heating time as well as a lower level of phthalate photodegradation in winter could explain this increase. However opposite result was obtained for $PM_{2.5}$ by Quintana-Belmares et al. (2018) who found higher concentrations of DBP and DEHP in summer. Teil et al. (2006) also reported a higher concentration (x4) of DEP, DNP and DHEP in rain waters sampled in winter compared to those sampled in summer. In our cloud samples DNOP, DHEP and DBP concentrations were higher in winter (Clouds 1 and 3) compared to summer (Cloud 2) but we observed the reverse situation of light phthalates DMP and DEP which concentrations were much higher in Cloud 2 sample collected in summer (up to 10 fold higher).

Several papers report the influence of geography on the concentration of phthalates in the air, as DEHP, DBP and DEHP concentrations can vary at least 10 fold between different sites including isolated (Xie et al., 2005; Xie et al., 2007) and urban ones (Teil et al., 2006; Salapasidou et al., 2011). However this variation does not seem to be related to the degree of anthropization of the site but rather to transport-loading processes. In our case we did not see the influence of the air mass origin (marine or continental) on the final concentrations of phthalates.

It is difficult to deduce general trends on the impact of the air mass origins and the seasons on the concentration of phenols and phthalates in the clouds, and both factors seem to have an influence but the number of samples studied so far is too low, more work should be performed.

3.3. Organic compounds identified at the level 2

In addition to the compounds from the EPA list of semi volatile priority pollutants (US EPA list), over 90% of all detected compounds belong to the oxygen-containing chemicals while the absence of halogenated organic compounds should be specially mentioned. Furans, acids, aldehydes, ethers, esters, ketones, alkylpyridines represent the largest group of the identified compounds.

Several examples of the identified compounds' mass spectra are shown in SI. These examples are selected: i) to demonstrate the developed GC × GC-HRMS method of the non-targeted screening and ii) to present cases for compounds relevant from the environmental point of view and also representing certain groups of chemicals, including both biogenic and anthropogenic compounds.

3.3.1. Biogenic compounds

Fig. S2 represents the mass spectrum of 6,6-dimethylbicyclo [3.1.1] heptan-2-one, a primary oxidation product of β-pinene which is a well-known biogenic compound emitted from the vegetation and responsible for SOA production in the atmosphere (Mutzel et al., 2016). Very high library similarity score (903) and matching accurate masses for all the fragment ions prove the accuracy of the assignment. Coumarin (Fig. S3) is another natural compound found in various plants. Coumarin is often present in water, air or precipitates, e.g. recently it was reported in Moscow snow samples (Mazur et al., 2017). High score (895) and matching accurate masses of the fragment ions confirm the reliability of the assignment.

3.3.2. Anthropogenic compounds

Fig. S4 shows the EI mass spectrum of 2-methylmercaptobenzothiazole. Accurate masses prove the elemental composition of all the ions, while fragmentation pattern fully corresponds to the fragmentation rules for these compounds under EI conditions. 2-Methylmercaptobenzothiazole belongs to the large family of the benzothiazole derivatives widely used as pharmaceuticals, rubber vulcanizers, pesticides. These industrial pollutants have been detected in many environmental samples (Richardson, 2012; Reemtsma, 2000). It is one of a few examples of sulfur-containing compounds in the analyzed cloud samples. Besides 2-methylmercaptobenzothiazole, some other related compounds have been detected in Cloud 2, namely N-ethyl-2-benzothiazolamine and 2(3H)-benzothiazolone (Table S2).

N,N-Dimethylformamide (Fig. S5) was detected in Cloud 3 sample. It is a representative of nitrogen-containing compounds, being an industrial anthropogenic pollutant detected in the cloud samples with high similarity score (906). Dibutylformamide was also detected in three cloud samples (Table S2). Dialkylformamides are often present in precipitations (Polyakova et al., 2012). Four other N,N-dimethylamino derivatives were also detected in the analyzed samples, however their full structures were not elucidated (Table S3), as their molecular ions are not stable enough in EI conditions.

Among other nitrogen-containing compounds two methylpyridines, dimethylpyridine and methoxypyridine were identified (Table S2). These compounds quite often appear in precipitates. Thus, alkylpyridines were detected in snow in highly polluted urban area (Moscow) (Polyakova et al., 2012) and in rather clean Arctic (Lebedev et al., 2018). A representative array of alkylpyridines in rather high concentrations was detected in rain in Moscow (Russia) and Baku (Azerbaidjan) (in preparation).

Triethylphosphate was the only phosphor-containing compound detected in the samples. Actually trialkylphosphates are more and more actively used as plasticizers and flame retardants worldwide. As a result they constantly present in precipitations. A number of organophosphates including chlorinated ones were reported in Moscow snow (Polyakova et al., 2012) in 2012 and it is worth mentioning that these compounds represent the only class of compounds which concentrations are increasing in Moscow snow from 2013 to 2018 (in preparation).

3.4. The benefits of accurate mass measurements and GC × GC separation

Accurate mass measurements were very important for the reliable identification of the analytes since NIST14 library contains only low resolution mass spectra. Quite often an isobaric compound was assigned by the library as the best hit with the highest matching score after searching against the NIST data base, but the HR-TOFMS high mass accuracy data allow making correct selection among the entries of the hit list (Lebedev et al., 2013).

The high peak capacity of chromatographic separation provided by the GC × GC technique was also very helpful for our studies as illustrated by the following example. Fig. 3a illustrates a mass spectrum at the top of a small chromatographic peak at RT 646.46 s (sample Cloud 2). Either ion of *m/z* 100.0521 ($C_5H_8O_2$) or of *m/z* 112.0521 ($C_6H_8O_2$) theoretically may be considered as molecular ion of the analyte. However the lighter one cannot be molecular ion as there was a heavier one present. Besides its elemental composition cannot be explained as the fragment of the heavier ion as the difference in mass between them is 12.0000, i.e. one carbon atom. The loss of just one carbon atom cannot take place during fragmentation of radical-cations formed in EI conditions (Tureček and McLafferty, 1994). Therefore, here we are dealing with two perfectly coeluting analytes, as it is demonstrated by the corresponding mass chromatograms in Fig. 3b. Hence, the library search of the resulted mass spectrum did not provide any adequate results. Nevertheless the problem was easily resolved in GC × GC mode. Fig. 3c presents 3D chromatogram plot of the corresponding region. Two peaks are nicely separated along the secondary (polar) column dimension. Separated peaks were reliably assigned after the library search as dihydro-5-methyl-2(3H)-furanone (*m/z* 100) and dimethyl-2(5H)-furanone (*m/z* 112).

4. Discussion and conclusions

Clouds take part in the cycle of chemical compounds in the atmosphere (Fig. 4). Gases can enter cloud droplets through absorption of soluble gases depending on their Henry's law constants. Aerosol particles can penetrate cloud droplets and can also be scavenged by impaction into the aqueous phase. The soluble fraction of the aerosol then dissolves into the aqueous phase, where the chemical compounds undergo efficient chemical and or biological transformations.

Since a large fraction of clouds do not precipitate, processed chemical compounds are released back to the atmosphere as gases or particles physically and chemically modified. For example, several earlier studies demonstrated that particle matter is produced via aqueous phase oxidation such as particulate sulfate or secondary organic aerosol. These transformations consequently influence the air quality. Another aspect of the cloud processing is that chemical compounds during the cloud lifetime are also transported and redistributed spatially in the atmosphere through, for example, the updraft and downdraft often linked to convective clouds and through precipitation which brings the chemical species to the ground. Consequently cloud can represent an effective atmospheric sink for gases and aerosol particles but impact consequently the recipient ecosystems on the ground.

The vast majority (~90%) of the over 100 semi-volatile compounds detected in the cloud water was oxygenated. This fact suggests that highly oxidative conditions take place in the clouds (Fig. 4). It is also worth special mentioning that there was not a single representative of halogenated substances among the detected analytes in all confidence groups. Since many chlorinated and brominated compounds are rather widespread environmental pollutants this result was quite unexpected. A first explanation is related to the low Henry's law constant of those compounds that are consequently not efficiently transferred into cloud droplets (Sander, 2015). Another putative reason could be the oxidative conditions encountered in clouds that could lead to a dehalogenation of those compounds, when halogen atoms can eventually leave the molecule as radical species, anions or hydrogen halide molecules.

Priority pollutants from the US EPA list (phenols and dialkylphthalates) identified with the highest reliability level are also worth discussion. To our knowledge phthalates in clouds are described here for the first time. They can be emitted directly from materials present in the soil to the gas phase and then transferred to the water phase of the clouds (Fig. 4). They can also be absorbed by aerosol particles ($PM_{2.5}$, PM_{10}) and then dissolved in the cloud droplets. Another potential source of phthalates in the clouds could be the leakage from microplastics or nanoplastics present in the cloud waters. Indeed microplastics and nanoplastics could serve as CCN (Cloud Condensation Nuclei) and thus be present in cloud droplets. They can be easily collected in cloud water samples using cloud impactors. A recent review reports the presence of airborne microplastics (Prata, 2018) which have been mainly detected in the Great Paris region. These microplastics can be called “secondary microplastics” resulting from the fragmentation of plastic materials (plastic bags, clothes, house furniture, building material) or “primary microplastics” directly released as plastic particles (cosmetics, fertilizers). When the size of these particles becomes as small as 1–100 nm they are named nanoplastics (Gigault et al., 2018). In addition to phthalates which are plastic additives, these microplastics could carry hazardous hydrophobic organic chemicals (HOC) absorbed at their surface (Koelmans et al., 2016) that

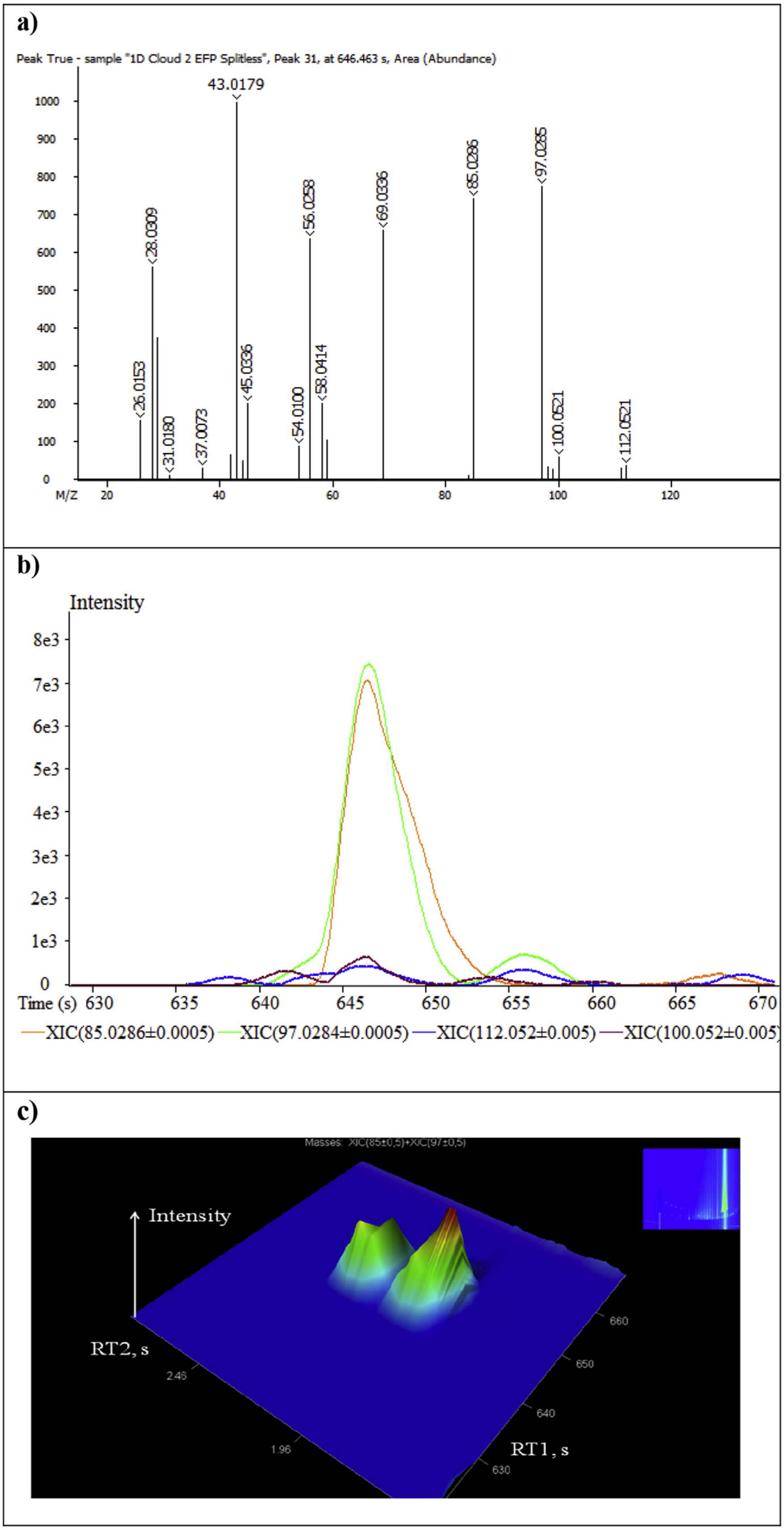

Fig. 3. a) Mass spectrum at the top of a chromatographic peak at 646.46 s (Cloud 2); b) Mass chromatograms based on the current of ions of m/z 100.0521 and 112.0521; c) Separation of the co-eluting compounds on the second column.

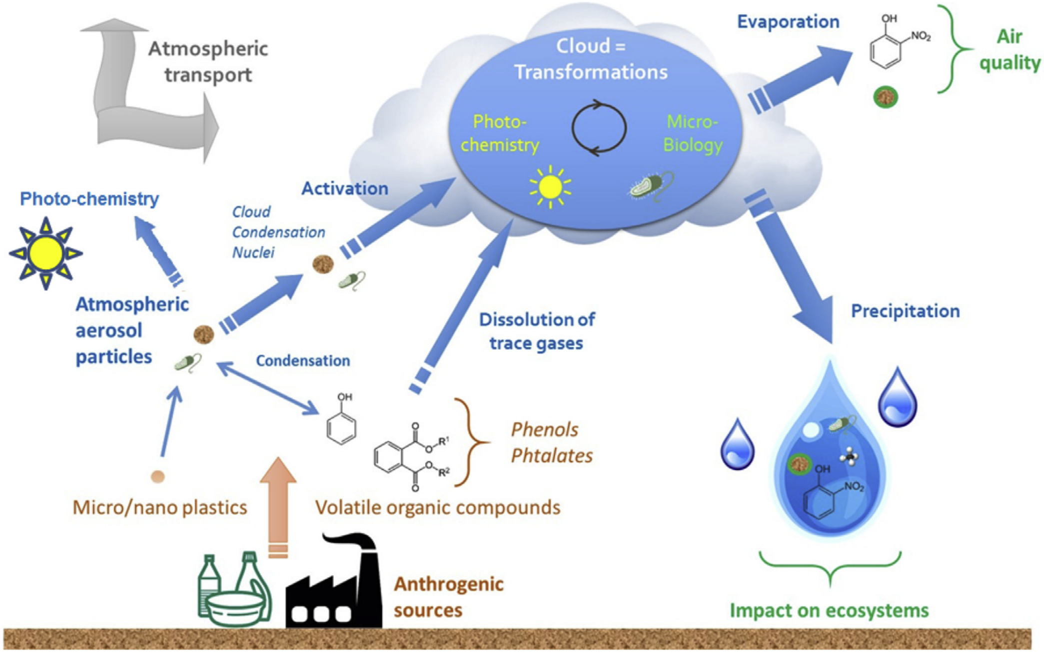

Fig. 4. Pollutant fate in the atmosphere: the specific role of clouds.

can dissolve in the droplets or be deposited later on soil by precipitation. We do not have any solid arguments concerning airborne plastic as the most probable source of phthalates in the clouds so far. However with increasing plastic use and due to its persistency, plastic particles in the atmosphere are likely to increase (if current use and disposal is maintained) and to eventually contaminate altitudes where clouds are present.

Contrarily to phthalates which are only of anthropogenic origin, phenol and its derivatives can result from a primary emission from industrial or biogenic sources, or can be considered as secondary products of transformations in the gas phase or in the cloud medium. For instance the world production of phenol was estimated at 1.7 Tg/year in 2016 (merchant and Consulting ltd), it can also result from biomass combustion or be the product of photo transformation of benzene in the gas phase (Volkamer et al., 2002). Since phenol is rather polar, 10% of it can be transferred from the gaseous to the water phase of the clouds (Feigenbrugel et al., 2004). Radical chemistry can also take place in the liquid phase: p-cresol can result from the photo transformation of alkylbenzene (Herrmann et al., 2015; Rayne et al., 2009) and 4-nitrophenol from nitration of phenol (Harrison et al., 2005). Recent studies demonstrate that direct photolysis of phenols can lead to the production of SOA (Sun et al., 2010; Yu et al., 2014).

Measured phthalates represent the most important fraction of the TOC (1.1–2.2%) and phenols are less concentrated and represent only 0.03–0.12% of the TOC dealing with the detected species (Table S4). Even though the selected compounds represent a minor fraction of the TOC, they are enough toxic to have an impact on the air quality. Moreover we can expect that all the other detected anthropogenic compounds could contribute to a significant fraction of the TOC. In addition if the liquid water content of the clouds is considered, the atmospheric concentrations (in ng/m^3 of air) of such toxic compounds transported in the atmosphere are significant and of importance both for the environment and the human health (Fig. 4). Clouds are the obvious source of precipitations, therefore the pollutants present in cloud waters will be transferred to the recipient ecosystems, it is thus important for the environment. Besides, pollutants in the cloud droplets can be thus transferred back to the air when cloud evaporates and thus modify the air quality and be of importance for human health.

In conclusion, this paper represents a very first description of pollutants in the clouds; further work should be conducted on larger sets of cloud samples collected in the various geographic areas and seasons. It could be combined with other complementary non-targeted techniques like FT-ICR-MS for instance (Cook et al., 2017; Mazur et al., 2016).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.05.089.

References

Benedict, K.B., Lee, T., Collett, J.L., 2012. Cloud water composition over the southeastern Pacific Ocean during the VOCALS regional experiment. Atmos. Environ. 46, 104–114.

Bianco, A., Passananti, M., Perroux, H., Voyard, G., Mouchel-Vallon, C., Chaumerliac, N., Mailhot, G., Deguillaume, L., Brigante, M., 2015. A better understanding of hydroxyl radical photochemical sources in cloud waters collected at the puy de Dôme station – experimental versus modelled formation rates. Atmos. Chem. Phys. 15, 9191–9202.

Bianco, A., Voyard, G., Deguillaume, L., Mailhot, G., Brigante, M., 2016. Improving the characterization of dissolved organic carbon in cloud water: amino acids and their impact on the oxidant capacity. Sci. Rep. 6, 37420.

Cook, R.D., Lin, Y.H., Peng, Z., Boone, E., Chu, R.K., Dukett, J.E., Gunsch, M.J., Zhang, W., Tolic, N., Laskin, A., Pratt, K.A., 2017. Biogenic, urban, and wildfire influences on the molecular composition of dissolved organic compounds in cloud water. Atmos. Chem. Phys. 17, 15167–15180.

Czuczwa, J., Leuenberger, Ch., Giger, W., 1988. Seasonal and temporal changes of organic compounds in rain and snow. Atmos. Environ. 22, 907–916.

Deguillaume, L., Charbouillot, T., Joly, M., Vaïtilingom, M., Parazols, M., Marinoni, A., Amato, P., Delort, A.M., Vinatier, V., Flossmann, A., Chaumerliac, N., Pichon, J.M., Houdier, S., Laj, P., Sellegri, K., Colomb, A., Brigante, M., Mailhot, G., 2014. Classification of clouds sampled at the puy de Dôme (France) based on 10 yr of monitoring of their physicochemical properties. Atmos. Chem. Phys. 14, 1485–1506.

Desyaterik, Y., Sun, Y., Shen, X., Lee, T., Wang, X., Wang, T., Collett, J.L., 2013. Speciation of “brown” carbon in cloud water impacted by agricultural biomass burning in eastern China. J. Geophys. Res. Atmos. 118, 7389–7399.

Ehrenhauser, F.S., Khadapkar, K., Wang, Y., Hutchings, J.W., Delhomme, O., Kommalapati, R.R., Herckes, P., Wornat, M.J., Valsaraj, K.T., 2012. Processing of atmospheric polycyclic aromatic hydrocarbons by fog in an urban environment.

J. Environ. Monit. 14, 2566–2579.

EPA, 2006. According to the Version of 20.04.2018. https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/phthalates.

Ervens, B., Turpin, B.J., Weber, R.J., 2011. Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies. Atmos. Chem. Phys. 11, 11069–11102.

Ervens, B., Wang, Y., Eagar, J., Leaitch, W.R., Macdonald, A.M., Valsaraj, K.T., Herckes, P., 2013. Dissolved organic carbon (DOC) and select aldehydes in cloud and fog water: the role of the aqueous phase in impacting trace gas budgets. Atmos. Chem. Phys. 13, 5117–5135.

Feigenbrugel, V., Le Calvé, S., Mirabel, P., Louis, F., 2004. Henry's law constant measurements for phenol, o-, m-, and p-cresol as a function of temperature. Atmos. Environ. 38, 5577–5588.

Fowler, D., Pilegaard, K., Sutton, M.A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi, S., Schjoerring, J.K., Granier, C., Neftel, A., Isaksen, I.S.A., Laj, P., Maione, M., Monks, P.S., Burkhardt, J., Daemmgen, U., Neirynck, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen, J.P., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T.N., Ro-Poulsen, H., Cellier, P., Cape, J.N., Horváth, L., Loreto, F., Niinemets, A., Palmer, P.I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M.W., Vesala, T., Skiba, U., Braggemann, N., Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M.C., de Leeuw, G., Flossman, A., Chaumerliac, N., Erisman, J.W., 2009. Atmospheric composition change: ecosystems - Atmosphere interactions. Atmos. Environ. 43, 5193–5267.

Fu, P.Q., Kawamura, K., Pavuluri, C.M., Swaminathan, T., Chen, J., 2010. Molecular characterization of urban organic aerosol in tropical India: contributions of primary emissions and secondary photooxidation. Atmos. Chem. Phys. 10, 2663–2689.

Gigault, J., Halle, A.t., Baudrimont, M., Pascal, P.-Y., Gauffre, F., Phi, T.-L., El Hadri, H., Grassl, B., Reynaud, S., 2018. Current opinion: what is a nanoplastic? Environ. Poll. 235, 1030–1034.

Goldstein, A.H., Galbally, I.E., 2007. Known and unexplored organic constituents in the Earth's atmosphere. Environ. Sci. Technol. 41, 1514–1521.

Guo, J., Wang, Y., Shen, X., Wang, Z., Lee, T., Wang, X., Li, P., Sun, M., Collett Jr., J.L., Wang, W., Wang, T., 2012. Characterization of cloud water chemistry at Mount Tai, China: seasonal variation, anthropogenic impact, and cloud processing. Atmos. Environ. 60, 467–476.

Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, J.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T.F., Monod, A., Prévôt, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R., Wildt, J., 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. Atmos. Chem. Phys. 9, 5155–5236.

Harrison, M.A.J., Barra, S., Borghesi, D., Vione, D., Arsene, C., Iulian Olariu, R., 2005. Nitrated phenols in the atmosphere: a review. Atmos. Environ. 39, 231–248.

Herbert, B.M.J., Villa, S., Halsall, C.J., 2006. Chemical interactions with snow: understanding the behavior and fate of semi-volatile organic compounds in snow. Ecotoxicol. Environ. Saf. 63, 3–16.

Herckes, P., Valsaraj, K.T., Collett Jr., J.L., 2013. A review of observations of organic matter in fogs and clouds: origin, processing and fate. Atmos. Res. 132–133, 434–449.

Herrmann, H., Schaefer, T., Tilgner, A., Styler, S.A., Weller, C., Teich, M., Otto, T., 2015. Tropospheric aqueous-phase chemistry: kinetics, mechanisms, and its coupling to a changing gas phase. Chem. Rev. 115, 4259–4334.

Hofmann, D., Hartmann, F., Herrmann, H., 2008. Analysis of nitrophenols in cloud water with a miniaturized light-phase rotary perforator and HPLC-MS. Anal. Bioanal. Chem. 391, 161–169.

Hutchings, J., Robinson, M., McIlwraith, H., Triplett Kingston, J., Herckes, P., 2009. The chemistry of intercepted clouds in Northern Arizona during the North American monsoon season. Water Air Soil Pollut. 199, 191–202.

Hutchings, J.W., Ervens, B., Straub, D., Herckes, P., 2010. N-Nitrosodimethylamine occurrence, formation and cycling in clouds and fogs. Environ. Sci. Technol. 44, 8128–8133.

Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., Wilson, J., 2005. Organic aerosol and global climate modelling: a review. Atmos. Chem. Phys. 5, 1053–1123.

Koelmans, A.A., Bakir, A., Burton, G.A., Janssen, C.R., 2016. Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies. Environ. Sci. Technol. 50, 3315–3326.

Krawczyk, E., Skret, U., 2005. Organic compounds in rainfall at Hornsund, SW Spitsbergen: qualitative results. Pol. Polar Res. 26, 65–76.

Lebedev, A.T., Sinikova, N.A., Nikolaeva, S.N., Poliakova, O.V., Khrushcheva, M.L., Pozdnyakov, S., 2003. Metals and organic pollutants in snow surrounding an iron factory. Environ. Chem. Lett. 1, 107–112.

Lebedev, A.T., 2013. Environmental mass spectrometry. Annu. Rev. Anal. Chem. 6, 163–189.

Lebedev, A.T., Polyakova, O.V., Mazur, D.M., Artaev, V.B., 2013. The benefits of high resolution mass spectrometry in environmental analysis. Analyst 138, 6946–6953.

Lebedev, A.T., Mazur, D.M., Polyakova, O.V., Kosyakov, D.S., Kozhevnikov, A.Yu., Latkin, T.B., Andreeva, Yu.I., Artaev, V.B., 2018. Semi volatile organic compounds in the snow of Russian Arctic Islands: Archipelago Novaya Zemlya. Environ. Pollut. 239, 416–427.

Leuenberger, Ch., Czucwa, J., Heyerdahl, E., Giger, W., 1988. Aliphatic and polycyclic aromatic hydrocarbons in urban rain, snow and fog. Atmos. Environ. 22, 695–705.

Li, J., Wang, X., Chen, J., Zhu, C., Li, W., Li, C., Liu, L., Xu, C., Wen, L., Xue, L., Wang, W., Ding, A., Herrmann, H., 2017. Chemical composition and droplet size distribution of cloud at the summit of Mount Tai, China. Atmos. Chem. Phys. 17, 9885–9896.

Li, P.-h., Wang, Y., Li, Y.-h., Wang, Z.-f., Zhang, H.-y., Xu, P.-j., Wang, W.-x., 2010. Characterization of polycyclic aromatic hydrocarbons deposition in PM2.5 and cloud/fog water at Mount Taishan (China). Atmos. Environ. 44, 1996–2003.

Lüttke, J., Levsen, K., 1997. Phase partitioning of phenol and nitrophenols in clouds. Atmos. Environ. 31, 2649–2655.

Lüttke, J., Levsen, K., Acker, K., Wieprecht, W., Möller, D., 1999. Phenols and nitrated phenols in clouds at Mount Brocken. Int. J. Environ. Anal. Chem. 74, 69–89.

Mazur, D.M., Harir, M., Schmitt-Kopplin, Ph, Polyakova, O.V., Lebedev, A.T., 2016. High field FT-ICR mass spectrometry for molecular characterization of snow board from Moscow regions. Sci. Total Environ. 557, 12–19.

Mazur, D.M., Polyakova, O.V., Artaev, V.B., Lebedev, A.T., 2017. Novel pollutants in the Moscow atmosphere in winter period: gas chromatography-high resolution time-of-flight mass spectrometry study. Environ. Pollut. 222, 242–250.

Mutzel, A., Rodigast, M., Iinuma, Y., Böge, O., Herrmann, H., 2016. Monoterpene SOA – contribution of first-generation oxidation products to formation and chemical composition. Atmos. Environ. 130, 136–144.

Polyakova, O.V., Mazur, D.M., Seregina, I.F., Bolshov, M.A., Lebedev, A.T., 2012. Estimation of contamination of atmosphere of Moscow in winter. J. Anal. Chem. 67, 1039–1049 (Original Russian version in Mass-spektrometria (Rus). 2012, 9, 5 – 15.

Prata, J.C., 2018. Airborne microplastics: consequences to human health? Environ. Pollut. 234, 115–126.

Quintana-Belmares, R.O., Krais, A.M., Esfahani, B.K., Rosas-Pérez, I., Mucs, D., López-Marure, R., Bergman, Å., Alfaro-Moreno, E., 2018. Phthalate esters on urban airborne particles: levels in PM10 and PM2.5 from Mexico City and theoretical assessment of lung exposure. Environ. Res. 161, 439–445.

Rayne, S., Forest, K., Friesen, K.J., 2009. Mechanistic aspects regarding the direct aqueous environmental photochemistry of phenol and its simple halogenated derivatives. A review. Environ. Int. 35, 425–437.

Reemtsma, T., 2000. Determination of 2-substituted benzothiazoles of industrial use from water by liquid chromatography/electrospray ionization tandem mass spectrometry. Rapid Commun. Mass Spectrom. 14, 1612–1618.

Richardson, S.D., 2012. Environmental mass spectrometry: emerging contaminants and current issues. Anal. Chem. 84, 747–778.

Růžičková, J., Raclavská, H., Raclavský, K., Juchelková, D., 2016. Phthalates in PM2.5 airborne particles in the Moravian-Silesian Region, Czech Republic. Perspectives in Science 7, 178–183.

Salapasidou, M., Samara, C., Voutsa, D., 2011. Endocrine disrupting compounds in the atmosphere of the urban area of Thessaloniki, Greece. Atmos. Environ. 45, 3720–3729.

Sander, R., 2015. Compilation of Henry's law constants (version 4.0) for water as solvent. Atmos. Chem. Phys. 15, 4399–4981.

Sempére, R., Kawamura, K., 1994. Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere. Atmos. Environ. 28, 449–459.

Sun, Y.L., Zhang, Q., Anastasio, C., Sun, J., 2010. Insights into secondary organic aerosol formed via aqueous-phase reactions of phenolic compounds based on high resolution mass spectrometry. Atmos. Chem. Phys. 10, 4809–4822.

Švancárová, R., Kosová, I., Janiga, M., Poganyová, A., 2016. Organic components in the different types of precipitation - Ružomberok experimental area. Oecol. Montana 25, 15–26.

Teil, M.J., Blanchard, M., Chevreuil, M., 2006. Atmospheric fate of phthalate esters in an urban area (Paris-France). Sci. Total Environ. 354, 212–223.

Thuren, A., Larsson, P., 1990. Phthalate esters in the Swedish atmosphere. Environ. Sci. Technol. 24, 554–559.

Tullo, A.H., 2015. Plasticizer makers want a piece of the phthalates pie. Chem. Eng. News 16–18.

Tureček, F., McLafferty, F.W., 1994. Interpretation of mass spectra, 4th ed. J. Chem. Educ. 71, 290.

van Pinxteren, D., Plewka, A., Hofmann, D., Müller, K., Kramberger, H., Svrcina, B., Bächmann, K., Jaeschke, W., Mertes, S., Collett Jr., J.L., Herrmann, H., 2005. Schmücke hill cap cloud and valley stations aerosol characterisation during FEBUKO (II): organic compounds. Atmos. Environ. 39, 4305–4320.

Venzac, H., Sellegri, K., Villani, P., Picard, D., Laj, P., 2009. Seasonal variation of aerosol size distributions in the free troposphere and residual layer at the puy de Dôme station, France. Atmos. Chem. Phys. 9, 1465–1478.

Volkamer, R., Klotz, B., Barnes, I., Imamura, T., Wirtz, K., Washida, N., Becker, K.H., Platt, U., 2002. OH-initiated oxidation of benzene Part I. Phenol formation under atmospheric conditions. Phys. Chem. Chem. Phys. 4, 1598–1610.

Wang, Y., Guo, J., Wang, T., Ding, A., Gao, J., Zhou, Y., Collett Jr., J.L., Wang, W., 2011. Influence of regional pollution and sandstorms on the chemical composition of cloud/fog at the summit of Mt. Taishan in northern China. Atmos. Res. 99, 434–442.

Wania, F., Hoff, J.T., Jia, C.Q., Mackay, D., 1998. The effects of snow and ice on the environmental behavior of hydrophobic organic compounds. Environ. Pollut. 102, 25–41.

Xie, Z., Ebinghaus, R., Temme, C., Caba, A., Ruck, W., 2005. Atmospheric concentrations and air–sea exchanges of phthalates in the North Sea (German Bight). Atmos. Environ. 39, 3209–3219.

Xie, Z., Ebinghaus, R., Temme, C., Lohmann, R., Caba, A., Ruck, W., 2007. Occurrence and air–sea exchange of phthalates in the Arctic. Environ. Sci. Technol. 41, 4555–4560.

Yu, L., Smith, J., Laskin, A., Anastasio, C., Laskin, J., Zhang, Q., 2014. Chemical characterization of SOA formed from aqueous-phase reactions of phenols with the triplet excited state of carbonyl and hydroxyl radical. Atmos. Chem. Phys. 14, 13801–13816.

Zhang, Q., Anastasio, C., 2001. Chemistry of fog waters in California's Central Valley-Part 3: concentrations and speciation of organic and inorganic nitrogen. Atmos. Environ. 35, 5629–5643.

Zhang, Q., Anastasio, C., 2003. Free and combined amino compounds in atmospheric fine particles (PM2.5) and fog waters from Northern California. Atmos. Environ. 37, 2247–2258.

Zhao, Y., Hallar, A.G., Mazzoleni, L.R., 2013. Atmospheric organic matter in clouds: exact masses and molecular formula identification using ultrahigh-resolution FT-ICR mass spectrometry. Atmos. Chem. Phys. 13, 12343–12362.