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A new method for assessing the aerosol to rain chemical composition relationships

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ABSTRACT

Measurements were conducted at three sampling sites located at different altitudes in the centre of France during two years, both in the rain and aerosol phases. The rain was sampled at a boundary layer site while the aerosol particles were collected at two different altitudes, which allow a better characterization of the vertical atmospheric column being washed out. Various chemical analyses were performed to characterize reactive (NO_3^- , SO_4^{2-} , NH_4^+ and K^+) and inert (^7Be , ^{210}Pb and ^{137}Cs) species transfer from the aerosol to the rain phase. This set-up was ideal to calculate the washout ratio (W_R) using different concentrations of the aerosol phase. Using the classical W_R calculated with the aerosol concentration sampled at the same altitude than the rain collectors, we observed a seasonality of W_R , with higher value in winter and lower value in summer for radionuclides. At the higher altitude site, local contaminations do not influence the aerosol concentration, which then should be representative of the whole atmospheric column. The annual variability is high at this site maybe because aerosol concentrations can be less concentrated than the whole atmospheric column when this later one is not well mixed. In order to increase the reliability of the W_R , we propose a new method for calculating washout ratio from measurements at the rain collector level. This new calculation takes into account the height of the boundary layer, we observed that it decreased the variability of the washout ratio (for ^7Be , ^{210}Pb and NO_3^-), with less dependence to the season.

1. Introduction

Pollutants emitted into the atmosphere or formed there by chemical reactions or radioactive decay may be deposited to the ground by wet and dry removal mechanisms. Wet removal is the most efficient process of the two. The rainwater composition may have different compositions reflecting the atmospheric pollution level, which may result in various environmental consequences such as acid rains.

The rainwater composition results from two series of mechanisms operating consecutively (Junge, 1963; Codina and Lorente, 1993). The first process, termed 'rainout', corresponds to mechanisms that occur within the cloud (i.e. condensation of water vapour on aerosol particles, incorporation of gases and

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aerosol particles in cloud droplet). The second process refers to the 'washout' mechanism that occurs in the below-cloud atmosphere during precipitation events when the raindrops carry and incorporate particles and gases along their fall (Seinfeld and Pandis, 2006).

Washout is the second most important mechanism for the wet removal of atmospheric particulate pollutants from the atmosphere after rainout. Murakami et al. (1983) calculated from field studies that below cloud scavenging contributes to about 30% of the total aerosol mass in rain water. Similar results are found using modelling tools by Schumann et al. (1988) and Flossmann (1994). For highly soluble tracers, Barth et al. (2001) found that the below-cloud scavenging was three orders of magnitude smaller than the in-cloud scavenging. Previous experimental studies have shown that the washout process is predominant at the beginning of the rain event; while the rainout is more important from the middle to the end of the rain (Makhon'ko, 1967; Magono et al., 1974; Murakami et al., 1981, 1983; Ishikawa et al., 1995).

In order to characterize the below cloud scavenging of pollutants, former studies on particles scavenging by precipitation have focused on the dependence of the scavenging processes on the particles size (Frank and Tschiersch, 1992; Volken and Schumann, 1993; Sparmacher et al., 1993; Andronache, 2003). Other investigations have pointed out the influence of the raindrop size on the chemical content in precipitation (Baechmann et al., 1993, 1995). Relationships between ion concentration and rainfall rate have been reported (Gatz and Dingle, 1971) and relationships between rain concentrations and meteorological conditions have been studied (André et al., 2007).

The processes controlling the composition of rain are complex and difficult to study experimentally in the natural atmosphere. Thus, attempts to directly relate aerosols concentrations to the rain composition has been performed in the past by defining the scavenging coefficient (Λ) (Mircea et al., 2000; Laakso et al., 2003; which is $dc/dt = -\Lambda c$) and the washout ratio W_R (Jaffrezo and Colin, 1988; McNeary and Baskaran, 2003). The washout ratio is commonly defined as the ratio of the concentration in precipitation collected at ground level to concentration of the same chemical compound in air at some convenient altitude. Thus, it includes both the rainout and washout processes. The most appropriate atmospheric concentration data would refer to air at the level where scavenging occurs (i.e. the whole air column below cloud), but for practical considerations, concentrations in air near the surface are usually used.

Since radionuclides such as ^7Be and ^{210}Pb have been widely used as useful non-reactive tracers for the study of global atmospheric processes (Dueñas et al., 2009), we present an experimental study of the washout ratio of both inorganic compounds and radionuclides sampled in the vicinity of Clermont-Ferrand, France, with a new set-up that involves three different measurement sites.

2. Measurements

2.1. Sampling sites

Measurements were conducted at three sampling sites: Cézeaux, Opme and the puy de Dôme (pdD). These three

sampling sites are separated by a maximum of 12 km horizontally and 800 m vertically.

Cézeaux (394 m a.s.l.) lies within the planetary boundary layer (PBL) and is classified as a near city background site following Putaud et al. (2004). It is located at the south-east of Clermont-Ferrand. The temperature varies between -8 and 15 °C during winter and between 8 and 35 °C during summer. Sampling was performed from the roof of a building (ca. 12 m a.g.l.).

Opme is a measurement site with rural features according to the site classification of Putaud et al. (2004). It is located at 660 m a.s.l., and 7 km from Clermont-Ferrand. Considering its low altitude, it also usually lies within the PBL. The temperature varies between -10 and 15 °C during the winter and between 5 and 30 °C during the summer. The samplers were located in a restricted area, only accessible to scientists who visited the site once a day.

The pdD (1 465 m a.s.l.) is a middle altitude site, located 16 km west of Clermont-Ferrand. Previous studies have shown that it lies within the PBL during daytime and in the free troposphere/residual layer during night-time, with PBL periods being longer during summer compared to winter (Venzac et al., 2009). The temperature varies between -10 and 10 °C during winter and between 5 and 20 °C during summer. The station is a restricted area during winter. During summer, only buses are allowed to access to the summit and car access is permitted only from March to June and from September to November. Sampling devices are located within a military area, not accessible to the public.

2.2. Sampling methods

2.2.1. Aerosol phase

Aerosol particles were sampled on a 3–4 d basis with total Teflon filters for further analysis of their water soluble inorganic composition.

At Cézeaux, sampling was performed from March 2007 to March 2008; with a flow rate of 8 lpm and no cut-off concerning the diameter of sampled aerosol particles. Aerosol sampling inlet was located on the roof of the institute (i.e. 1 m above the institute's roof, i.e. >13 m a.g.l.).

At pdD, the aerosol particles sampling period is from November 2005 to October 2007 with a flow rate of 30 lpm. Aerosol sampling inlet (1 m above the station roof, i.e. >2.5 m a.g.l.) was designed to sample during clear sky conditions as well as during cloudy conditions using a whole air inlet (WAI) which ensures efficient sampling of both cloud droplets residues and interstitial aerosol in the presence of clouds. Wind speed is decreased in the vicinity of the WAI by a series of metallic fences ensuring efficient sampling even at elevated wind speed. Based upon theoretical considerations, the WAI is capable of efficiently (50% efficiency) sampling droplets <35 μm for wind-speed <10 m s^{-1} . During cloudy conditions, interstitial aerosols and cloud droplets residues were sampled simultaneously at a relative humidity close to 50% by mean of heating coil. After collection by the WAI, an additional PM_{10} cut-off limits the filter aerosol sampling to sub-micron particles.

The radionuclides were sampled in the frame of OPERA network (Permanent Observatory of the Radioactivity, IRSN) with very high volume samplers (300 m^3 h^{-1} at Opme and 700 m^3 h^{-1} at pdD) for further determination of the activity

levels of ^7Be , ^{210}Pb and ^{137}Cs . Aerosol sampling inlets are about 1.5 m a.g.l. Sampling was performed from November 2004 to July 2008 within the PBL station and from October 2005 to December 2007 in the altitude station.

2.2.2. Rainwater collection

The rainwater was collected on a monthly basis (only for radionuclides), in the frame of OPERA network, from November 2004 to December 2007 with a 3 m² rain collector. It was also collected on a daily basis (for inorganic ions) at Opme from November 2005 to September 2007 with an automatic precipitation collector (Eigenbrodt NSA 181/KHS), details provided in [Bertrand et al. \(2008\)](#). In the present study, we calculated a monthly volume-weighted mean from the inorganic daily concentrations (from 4 to 18 samples per month) to facilitate the comparison with the radionuclides monthly concentrations. Data quality was first checked from the electroneutrality (e.g. [Appelo and Postma, 1994](#); [Bertrand et al., 2008](#)), which is respected in most water samples ([Fig. 1](#)) but with a more pronounced deviation in the more concentrated samples. This deviation lies with the fact that these samples usually correspond to high bicarbonate content and that this element was analyzed on the field through the Gran method, less precise than ionic chromatography and because of possible CO₂ degassing between rain event and sampling.

The rainfall rate and the volumic diameter of rain droplets were measured by mean of an impact disdrometer installed at Opme from April 2006 to January 2007.

Sampling periods of aerosol and rain overlapped from November 2005 to September 2007 for water soluble inorganic ion analysis at pdD, from March 2007 to September 2007 for water soluble inorganic ions in PBL and from October 2005 to December 2007 for radionuclides analysis (both sites).

2.3. Analysis

Teflon filters and rainwater were analyzed with ionic chromatography (IC), to determine the concentrations of nitrate (NO₃⁻), sulphate (SO₄²⁻), ammonium (NH₄⁺) and potassium (K⁺). The method used was adapted from one of [Ricard et al. \(2002\)](#). The filter sample were extracted with methanol and pure water and then, analyzed with the IC. The rain samples were diluted 10 times before being analyzed with IC and the same analytical protocol. When concentration is lower than the detection limit, the level was set at the

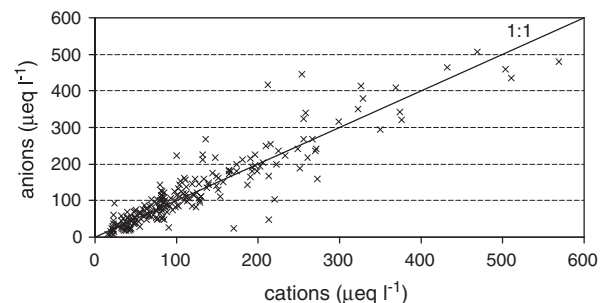


Fig. 1. Anions versus cations (in $\mu\text{eq l}^{-1}$) relationships in the rain samples collected at Opme. The 1:1 relationship represents the relation in case of electroneutrality (complete analyses).

detection limit for the calculation, which is therefore upper limit. More details can be found in [Bourcier et al. \(2012\)](#).

Radionuclide analysis was performed by γ spectrometry at the LMRE (Laboratory of Measurement of Radioactivity in the Environment, IRSN) at Orsay, France. The aerosol samples preparation is described in [Bourcier et al. \(2011\)](#) and samples were analyzed according to the method described by [Kerlau et al. \(1999\)](#). The liquid samples were evaporated and analyzed following the method of [Gurriaran et al. \(2004\)](#).

3. Washout ratio calculation

The washout ratio is classically calculated with the formula ([Jaffrezo and Colin, 1988](#); [McNeary and Baskaran, 2003](#)):

$$W_R = \frac{\rho \cdot C_{rain}}{C_{air}} \quad (1)$$

where the air density (ρ) is constant at 1.2 kg m⁻³ (T= 20 °C); C_{rain} is the concentration ($\mu\text{Bq kg}^{-1}$ or $\mu\text{g kg}^{-1}$) of compounds in the rainwater and C_{air} is the concentration ($\mu\text{Bq m}^{-3}$ or $\mu\text{g m}^{-3}$) of compounds in the aerosol particle phase.

Since the measured concentrations in the rain result from both rainout and washout processes, W_R describes implicitly and without distinction the rainout and the washout processes.

4. Results

4.1. Radionuclides

The mean atmospheric levels of ^7Be and ^{210}Pb were respectively $6900 \pm 1800 \mu\text{Bq m}^{-3}$ and $750 \pm 220 \mu\text{Bq m}^{-3}$ at pdD and $4500 \pm 1300 \mu\text{Bq m}^{-3}$ and $640 \pm 130 \mu\text{Bq m}^{-3}$ at Opme. We observed a seasonal behaviour with a summer maximum and a winter minimum at both sites ([Fig. 2](#)). More details are given in [Bourcier et al. \(2011\)](#). In the rainwater, the activity levels of ^7Be and ^{210}Pb are $1400 \pm 330 \text{mBq l}^{-1}$ and $180 \pm 70 \text{mBq l}^{-1}$ respectively. As for the aerosol, the ^7Be presents a seasonal behaviour with a summer maximum whereas the ^{210}Pb does not present seasonal pattern.

The W_R values presented in [Fig. 2](#) were obtained from [Eq. \(1\)](#). In order to study the influence of the aerosol sampling site, we calculated W_R (for radionuclides) on a monthly basis with aerosol particle concentrations either sampled at the rain collector level (Opme) and at the cloud level (pdD). The mean values of W_R are given in [Table 1](#) for both sites.

When calculated with the rain collector level aerosol concentrations, the W_R of ^7Be and ^{210}Pb are (380 ± 200 and 300 ± 150 respectively), which is of the same order than those of [Ishikawa et al. \(1995\)](#) and [Dueñas et al. \(2005\)](#) and references therein. The W_R of ^{137}Cs calculated from aerosol sampled at rain collector level are higher than the ones reported in [Facchinelli et al. \(2002\)](#) ($W_R = 610$; value issued from a deposition model during the Chernobyl period) and [Cambay et al. \(1987\)](#) (W_R comprised between 230 and more than 23000; the month after the Chernobyl accident).

The value of $W_R(^7\text{Be})$ and $W_R(^{137}\text{Cs})$ are higher when calculated from the aerosol concentrations calculated at rain collector level than when calculated from the high altitude concentrations, in agreement with the fact that ^7Be and ^{137}Cs

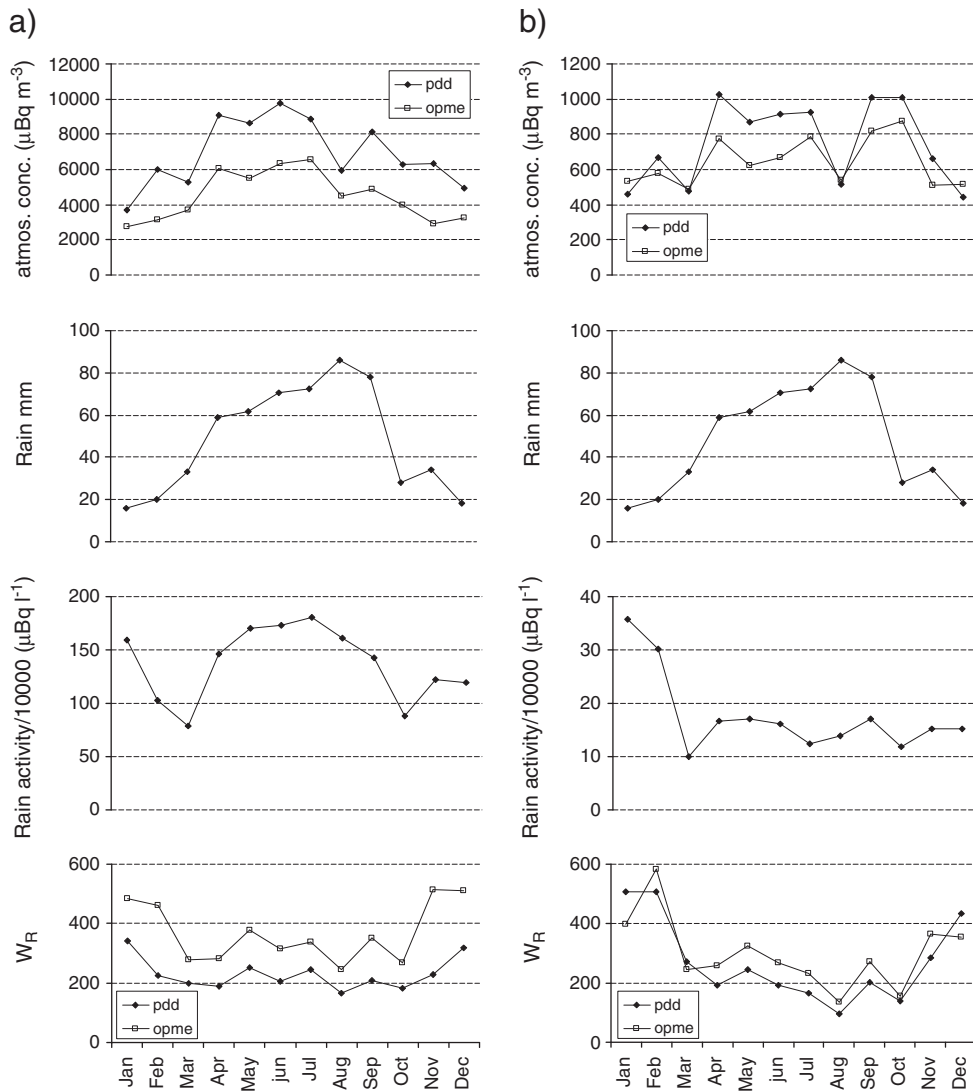


Fig. 2. Monthly mean for a 2 y period of the washout ratio for ^{7}Be (a) and ^{210}Pb (b), the rain activity, the rain quantity and the atmospheric concentrations from November 2005 to December 2007. The particle concentration has been sampled at rain collector level (Opme) and at cloud level (pdD).

aerosol concentrations are higher at pdD than at Opme (Bourcier et al., 2011). For ^{210}Pb , as expected due to equivalent activity levels at both sampling sites, the W_R is equivalent at both sites.

Table 1

Mean and standard deviation (variability) W_R calculated with the aerosol sampled at cloud level (pdD) and at rain collector level (PBL) for radionuclides and inorganic compounds on a monthly basis.

	pdD	PBL
^{7}Be	230 ± 110 (48%)	380 ± 200 (54%)
^{210}Pb	270 ± 170 (62%)	300 ± 150 (51%)
^{137}Cs	750 ± 450 (61%)	1800 ± 2000 (113%)
NO_3^-	13000 ± 12000 (90%)	2900 ± 1900 (63%)
SO_4^{2-}	2200 ± 2200 (104%)	780 ± 310 (40%)
NH_4^+	2700 ± 2800 (105%)	240 ± 70 (28%)
K^+	84000 ± 63000 (75%)	18000 ± 6400 (36%)

N.B.: the W_R for ions in the PBL has been calculated only on a 7 month period.

We observe that the variability of the washout ratio of ^{137}Cs is lower when the aerosol activity levels are issued from the altitude site sampling. This can be explained by the fact that the ^{137}Cs activity levels are highly influenced by long-range transport occurring mainly at high altitudes (such as Saharan dust events), and they are occasionally higher at the pdD station than at the rain collector level site (Bourcier et al., 2010). On those occasions, the activity levels of ^{137}Cs found in the rain are mainly influenced by the high activity levels measured at high altitude than of the low activity level present in the rain collector level. The same is found for ^{7}Be , which is also mostly influenced by high altitude sources. On the contrary, the variability of the washout ratio of ^{210}Pb is higher when calculated from the pdD measurements than when calculated from the rain collector site. Although ^{210}Pb is well mixed in the atmosphere, its sources are located within the PBL and the rain composition is more reliably linked to the PBL aerosol activity levels than to the pdD aerosol activity levels.

Because ^{137}Cs measurements require large sampling volumes and hence are not always possible, we investigated if there were any similar behaviour between the W_R of ^{137}Cs and the W_R of some inorganic ions. Surprisingly, it has been observed that the ^{137}Cs had a behaviour similar to the one of K^+ in aerosol phase and in the rainwater (Bourcier et al., 2010) but not in the way it is transferred from the aerosol to the rain since their W_R are different. This is possibly because of the different vertical gradient that the two species have.

Besides being well mixed in the atmosphere, ^{210}Pb has other advantages that make it a valuable tracer for atmospheric processes from aerosols to rain water. It is not present in the gas phase and thus it is mainly integrated in the liquid phase from the particulate phase, and once it is present in the liquid phase it does not react with other compounds. As a consequence, we can use the washout ratio of ^{210}Pb as a reference for assessing other processes involved in the apparent washout ratio of other compounds.

Figs. 2 show that W_R is not constant throughout the year, indicating that it does not reflect a combination of constant transfer functions (particle to cloud droplet, cloud droplet to rain drop, rain drop from cloud level to ground level). W_R has a seasonal behaviour with lower values during summer. This behaviour can be due to: (1) the seasonal variation of the atmospheric radionuclide activity levels and (2) the seasonal variation of the rainwater activity levels or (3) a combination of both with different amplitudes.

We will hereafter investigate these possibilities.

- (1) Be^{-7} and the ^{210}Pb exhibit a seasonal behaviour in the aerosol phase, with a summer maximum at both sites, which can partly explain that W_R is minimum during this season.
- (2) In the rainwater, ^7Be activity levels are higher in summer and the ^{210}Pb activity levels do not present any seasonal behaviour. Hence, for ^7Be , the activity levels in the cloud water also contribute to the seasonal variation of W_R while for ^{210}Pb only the activity levels in the aerosol phase is the main driving parameter of W_R variability. The concentrations in the rainwater are themselves influenced by the concentration in the aerosol phase, but also by other parameters, such as the typology of rain. We investigated the influence of the rain typology, rain droplet diameter, rainfall rate and integrated amount of rain water. No significant relationship of the rain water concentration with rain droplet diameter, neither with the rainfall rate was observed. However, we can notice that during winter, there is less than 35 mm of rain whereas in summer, we observe up to 90 mm of rain. When plotted against the integrated amount of rain monthly collected, W_R shows a decreasing tendency indicating that the integrated amount of rainwater is influencing the value of W_R .

The W_R is higher with low amount of rain, which is consistent with the fact that the concentrations are usually higher at the beginning of the rain event (Seymour and Stout, 1983; Ali et al., 2011). For higher rain quantities, the W_R is 3 to 4 times smaller compared to low amounts of rain. Because no correlation with the rain drops diameter were found,

dilution does not seem to be the cause of lower W_R for high rain quantities.

4.2. Inorganic ions

The mean atmospheric concentrations at pdD of NO_3^- , SO_4^{2-} , NH_4^+ and K^+ are $0.6 \mu\text{g m}^{-3}$, $1.0 \mu\text{g m}^{-3}$, $0.2 \mu\text{g m}^{-3}$ and $0.02 \mu\text{g m}^{-3}$ respectively. At the Cézeaux (from March to September 2007), the mean atmospheric concentrations of NO_3^- , SO_4^{2-} , NH_4^+ and K^+ are $1.5 \mu\text{g m}^{-3}$, $2.4 \mu\text{g m}^{-3}$, $1.0 \mu\text{g m}^{-3}$ and $0.1 \mu\text{g m}^{-3}$ respectively. The particulate concentration of NO_3^- does not present any clear seasonal pattern at pdD for the period of study (November 2005–September 2007). The sampling at the Cézeaux continued till March 2008. Even if not adapted to our rain data set, it permitted us to observe that NO_3^- has a seasonal behaviour at rain collector level with higher concentrations in winter, possibly due to stronger sources and/or pollution trapping within a thinner PBL during winter. On the contrary, SO_4^{2-} , NH_4^+ and K^+ show a late spring–summer maximum (Fig. 3) at pdD and no clear seasonal behaviour at rain collector level. At the Cézeaux, in the rainwater, NO_3^- , SO_4^{2-} and K^+ show a summer maximum (Fig. 4) while NH_4^+ is showing a summer minimum. We can note a secondary maximum NO_3^- during winter. The seasonal variations of the concentrations of inorganic species in the rain water are different from the ones of the aerosol concentrations at rain collector level. This clearly indicates that the rain composition is influenced by other factors than solely the aerosol concentration at rain collector level.

The values of $W_R(\text{NO}_3^-)$, $W_R(\text{SO}_4^{2-})$ and $W_R(\text{NH}_4^+)$ calculated from the aerosol sampled at rain collector level are comparable to those observed by Casado et al. (1996) in Spain (and references therein), which is not the case for K^+ (they observed lower W_R due to much higher atmospheric concentration) (Table 1). Nevertheless, we can note that $W_R(\text{NO}_3^-)$ and $W_R(\text{K}^+)$ are significantly higher than $W_R(\text{SO}_4^{2-})$ and $W_R(\text{NH}_4^+)$, which has also been observed by Casado et al. (1996). Andronache (2003) showed that the below cloud scavenging was less efficient for accumulation mode particles compared to the rainout and was very important for very small particles (diameter < 0.01 μm) and for coarse particles (diameter > 2 μm). SO_4^{2-} and NH_4^+ are mostly submicronic particles while NO_3^- can be present in the accumulation and the coarse mode. In the coarse mode, the nitrate is usually linked to alkaline sea salt and mineral dust particles (Harrison and Kitto, 1990; Pakkanen et al., 1996; Zhang et al., 2003; Hanke et al., 2003; Krueger et al., 2004; Ro et al., 2005;

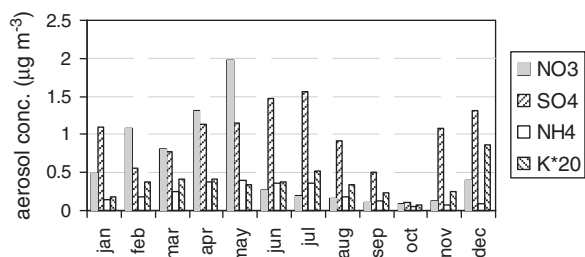


Fig. 3. Monthly mean for a 2 y period of the atmospheric concentrations of NO_3^- , SO_4^{2-} , NH_4^+ and K^+ at pdD.

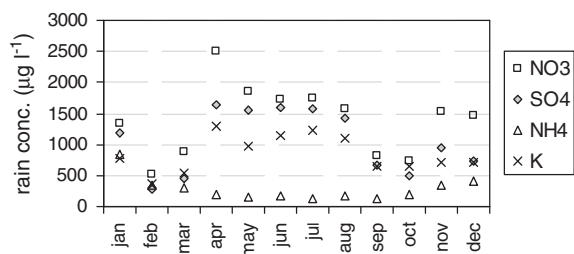


Fig. 4. Monthly mean for a 2 y period of the rainwater concentrations of NO_3^- , SO_4^{2-} , NH_4^+ and K^+ at Opme.

Sullivan et al., 2007). In particular, KNO_3 particles are present in aged smoke (Li et al., 2003).

The W_R of inorganic ions is higher at pD, opposite feature of radionuclides, due to lower aerosol concentrations at the higher altitude (data not shown here).

Concerning the temporal evolution of W_R calculated from aerosol concentration sampled at pD, $W_R(\text{K}^+)$ does not present any clear seasonal pattern while $W_R(\text{NO}_3^-)$ is higher in summer-autumn, $W_R(\text{SO}_4^{2-})$ shows a slight seasonal pattern with a minimum in spring-summer and $W_R(\text{NH}_4^+)$ a marked spring-summer minimum (Fig. 5). No conclusion can be made on the seasonal behaviour of W_R calculated from aerosol concentrations sampled at rain collector level since we have only six months overlap.

As already mentioned, the particulate concentration of K^+ presents a slight seasonal pattern at pD for the concerned period (November 2005–September 2007) and in the rainwater. Moreover, the K^+ does not have gaseous contribution. Thus, it seems consistent not to observe clear seasonal evolution of $W_R(\text{K}^+)$. For the NO_3^- , the W_R is higher in late spring-summer, as in the rain while the aerosol concentration of NO_3^- at pD does not have clear seasonal pattern. This, together with the fact that $W_R(\text{NO}_3^-)$ is higher than $W_R(\text{K}^+)$, might indicate that the gaseous contribution of NO_3^- to the

rainwater is significant. For the SO_4^{2-} and NH_4^+ , in the aerosol phase at pD, the aerosol concentrations showed a spring-summer maximum (Legrand and Puxbaum, 2007; Bourcier et al., 2012). In the rain, the NH_4^+ concentrations are slightly higher during winter while for SO_4^{2-} , the concentration follows the same seasonal evolution as the one of aerosol phase. Interestingly, for the four inorganic compounds we studied, we observed that above a certain concentration in the aerosol phase ($0.5 \mu\text{g m}^{-3}$ for NO_3^- and SO_4^{2-} ; $0.1 \mu\text{g m}^{-3}$ for NH_4^+ and $0.02 \mu\text{g m}^{-3}$ for K^+), W_R is low and constant, indicating that the atmosphere cannot be efficiently scavenged when the PM concentrations are higher than those limits.

Again from the analysis of the W_R of inorganic species, it is clear that neither the aerosol concentrations of aerosols at the rain collector level nor the aerosol at the cloud level are completely determining the W_R and that other parameters should be taken into account. To investigate the influence of the rain typology (rain droplet diameter and rainfall rate), we related W_R with the data provided by the impact disdrometer installed at Opme and did not observe any relationship. As observed for radionuclides, when W_R is plotted against the integrated amount of rain monthly collected, W_R shows a decreasing tendency.

The variability of the washout ratio of inorganic compounds varies according to the altitude of the aerosol sampling. It is lower at rain collector level, which implies that the aerosol particle composition at rain collector level is better adapted for accurately predict the rain composition if an average W_R has to be employed. This is most likely due to the natural gradient of aerosol concentration in PBL (large aerosol concentration close to ground level and low concentration at higher altitudes), involving that the concentration of inorganic species in the rain are more influenced by the lower altitude aerosol concentrations.

It is possible to evaluate the gradient between the rain collector level concentrations and the pD concentrations for different inorganic compounds. When looking at the gradient

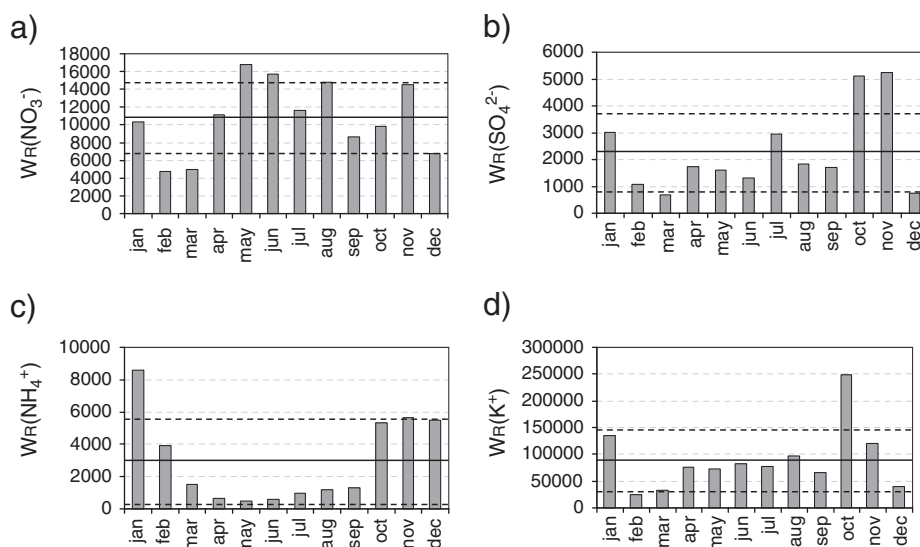


Fig. 5. Yearly mean of W_R for a) NO_3^- , b) SO_4^{2-} , c) NH_4^+ and d) K^+ . The W_R is calculated with the aerosol composition at pD from November 2005 to October 2007. The straight plain line is the average value of W_R and the dashed lines are the mean $\pm \sigma$.

of aerosol concentrations between rain collector level and pDD, we observed that the ratio slightly differ from one inorganic specie to the other (79% for NO_3^- , 22% for SO_4^{2-} , 32% for NH_4^+ and 27% for K^+). This indicates that different average vertical gradients for different chemicals partly contribute to different average W_R values between species.

The vertical gradient is however very different from one season to the other, due to the seasonal variation of the PBL height (Bourcier et al., 2012). For the NO_3^- and the SO_4^{2-} , the two compounds with the highest temporal variability, this vertical gradient might explain 63% and 39% respectively of the temporal variability of their W_R .

Overall, we hypothesize that a major parameter determining the composition of rainwater is the aerosol concentration integrated over the whole PBL column. Hence, in order to lower the variability on the W_R , the aerosol concentrations at the rain collector level should be integrated over the height of the PBL.

5. A new method for assessing the relationship between aerosol and rain composition

It should be pointed out that the Eq. (1) is not dimensionless, but is expressed as kg (air)/kg (rain water), which cannot be considered as mixing ratio by modellers and make the utilization more difficult. Moreover, the height of the scavenged atmospheric column is not taken into account.

In order to homogenise the unities of the washout ratio and to take into account the height of the scavenged atmosphere, we define another formula to estimate the removal of particles:

$$W_B = \frac{V_{\text{rain}}}{h_{\text{bl}}} \times \frac{C_{\text{rain}}}{C_{\text{air}}} \quad (2)$$

where C_{rain} is still the concentration ($\mu\text{Bq L}^{-1}$ or $\mu\text{g L}^{-1}$) of compounds in the rain water and C_{air} is the concentration ($\mu\text{Bq m}^{-3}$ or $\mu\text{g m}^{-3}$) of compounds in the aerosol particle phase at rain collector level. The air density is replaced by a term which can be compared to the liquid water content in the cloud phase. It represents the quantity of rainwater by air volume in the PBL, assumed to correspond to the total column under the cloud. It is calculated with V_{rain} , the amount of rain water (L m^{-2}) and h_{bl} , the height of the boundary layer (m) provided from modelling tools. In the following, the h_{bl} value used is the monthly average.

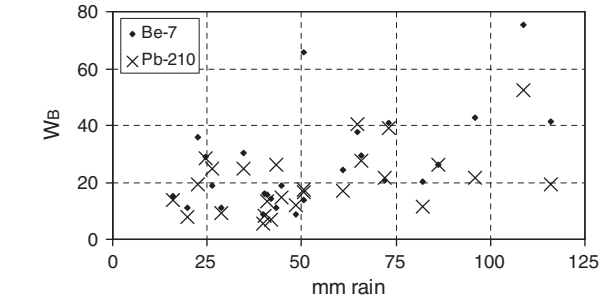
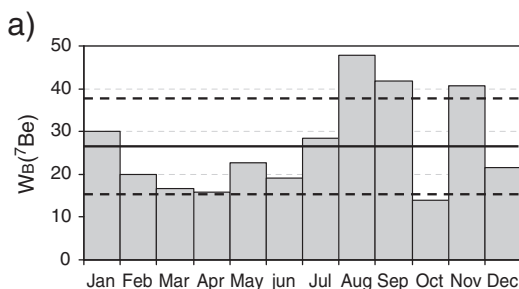


Fig. 7. W_B of ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ in function of the rain quantity on a monthly basis.

The evolution of $W_B({}^7\text{Be})$ and $W_B({}^{210}\text{Pb})$ do not present any clear seasonal pattern (Fig. 6), differently to what we observed for W_R . Thus, the addition of the PBL height would make easier the use of such washout ratio.

Contrarily to the previous section which showed a decrease of W_R while the rain quantity is increasing, W_B is positively correlated with the amount of rain (Fig. 7).

For the inorganic compounds, the sampling periods did not allow us to have 1 y overlap between aerosol data from the Cézeaux and rain data from Opme. Thus, we cannot conclude on any eventual seasonal behaviour.

The mean value of the W_B is reported in Table 2.

As observed for W_R , ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ have the same W_B , lower than $W_B({}^{137}\text{Cs})$. Moreover, the variability of $W_B({}^7\text{Be})$ and $W_B({}^{210}\text{Pb})$ decreases by 14 and 18% respectively compared to W_R at rain collector level (Table 2), this calculation would be more accurate to determine the rain activity levels.

For the inorganic ions, $W_B(\text{NO}_3^-)$ and $W_B(\text{K}^+)$ are again significantly higher than $W_B(\text{SO}_4^{2-})$ and $W_B(\text{NH}_4^+)$ (Table 2). The variability is lower for NO_3^- but there is no improvement for the other ions.

The W_B of submicron radionuclides is in the same order of magnitude as W_B of submicron inorganic compounds, in agreement with the fact that below-cloud scavenging is mainly governed by physical parameters such as droplet size distribution and aerosol size distribution and not the chemical properties of compounds. Theoretically, $W_B(\text{SO}_4^{2-})$ and $W_B(\text{NH}_4^+)$ could be influenced by the gas phase (incorporation of SO_2 then oxidized and NH_3 acidified in the droplets). The similar W_B with those of radionuclides could mean that the influence of gas incorporation during the precipitation event is negligible, which has already been observed by Casado et al. (1996).

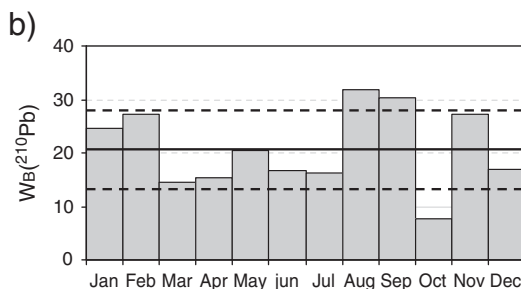


Fig. 6. Monthly W_B of ${}^7\text{Be}$ (a) and ${}^{210}\text{Pb}$ (b) in function of the time from November 2005 to December 2007.

Table 2

Monthly mean and standard deviation of the washout ratio calculated with the new formula – W_B – for inorganic compounds and radionuclides.

Compound	W_B	Compound	W_B
NO_3^-	140 ± 70	^7Be	27 ± 11
SO_4^{2-}	43 ± 22	^{210}Pb	21 ± 7
NH_4^+	14 ± 8	^{137}Cs	96 ± 77
K^+	950 ± 380		

6. Conclusion

Measurements of radionuclides and inorganic ions concentrations were conducted at three sampling sites located at different altitudes in the centre of France during two years, both in the rain and aerosol phases. This set-up was ideal to calculate the washout ratio (W_R) using concentrations of the aerosol phase at two different altitudes. Samples were collected with a high temporal resolution, providing the opportunity to use of a monthly value for the calculation of W_R instead of an annual mean value, less accurate.

We observe a seasonality of the washout ratio of radionuclides with minimum values in summer. The W_R of NO_3^- , SO_4^{2-} and K^+ did not present clear seasonal pattern while $W_R(\text{NH}_4^+)$ had the same seasonal behaviour as radionuclides. The W_R showed a decreasing tendency with the integrated amount of rainwater (for both radionuclides and ions). $W_R(^7\text{Be})$ and $W_R(^{137}\text{Cs})$ are higher at rain collector level and $W_R(\text{ions})$ is higher in altitude. However, $W_R(^{210}\text{Pb})$ is equivalent at both locations. These observations indicate that the washout ratio, which is usually used as a constant value, depends on many factors. Additionally to the compound chemical nature, W_R depends on the altitude of sampling and on the season. Because W_R should be a process-based parameter that should be as stable as possible, we propose to tend to lower the variability of the transfer function between aerosol and rain phases.

We observed that taking into account the height of the boundary layer decreased the variability of the washout ratio (for ^7Be , ^{210}Pb and NO_3^-), with less dependence to the season, compared to the classical calculation. It showed that the atmospheric structure is an important parameter to take into account to estimate the washout of pollutants that take place in the whole atmospheric column. Contrarily to W_R , W_B showed a positive relationship with the rainwater amount.

References

- Ali, N., Khan, E.U., Akhter, P., Rana, M.A., Rajput, M.U., Khattak, N.U., Malik, F., Hussain, S., 2011. Wet deposition fluxes of ^{210}Pb - and ^7Be -bearing aerosols at two different altitude cities of North Pakistan. *Atmos. Environ.*, <http://dx.doi.org/10.1016/j.atmosenv.2011.07.032>.
- André, F., Jonard, M., Ponette, Q., 2007. Influence of meteorological factors and polluting environment on rain chemistry and wet deposition in a rural area near Chimay, Belgium. *Atmos. Environ.* 41, 1426–1439.
- Andronache, C., 2003. Estimated variability of below-cloud aerosol removal by rainfall for observed aerosol size distributions. *Atmos. Chem. Phys.* 3, 131–143.
- Appelo, C.A.J., Postma, D., 1994. *Geochemistry, Groundwater and Pollution*. A.A.Balkema ed., Rotterdam. (536 pp.).
- Baechmann, K., Haag, I., Roeder, A., 1993. A field study to determine the chemical content of individual raindrops as a function of their size. *Atmos. Environ.* 27, 1951–1958.
- Baechmann, K., Haag, I., Steigerwald, K., 1995. Determination of transition metals in size-classified rain samples by atomic absorption spectrometry. *Atmos. Environ.* 29, 175–177.
- Barth, M.C., Stuart, A.L., Skamarock, W.C., 2001. Numerical simulations of the July 10 stratospheric-tropospheric experiment: radiation, aerosols, and ozone/deep convection storm: redistribution of soluble tracers. *J. Geophys. Res.* 106, 12381–12400.
- Bertrand, G., Celle-jeanton, H., Laj, P., Rangognio, J., Chazot, G., 2008. Rainfall chemistry: long range transport versus below cloud scavenging. A two-year study at an inland station (Opme, France). *J. Atmos. Chem.* 60, 253–271.
- Bourcier, L., Sellegri, K., Laj, P., Masson, O., Zangrando, R., Barbante, C., Gambaro, A., Pichon, J.-M., Chausse, P., Paulat, P., 2010. Experimental evidence of biomass burning as a source of atmospheric ^{137}Cs , puy de Dôme (1465 m a.s.l.), France. *Atmos. Environ.* 44, 2280–2286.
- Bourcier, L., Masson, O., Laj, P., Pichon, J.M., Paulat, P., Freney, E., Sellegri, K., 2011. Comparative trends and seasonal variation of ^7Be , ^{210}Pb and ^{137}Cs at two altitude sites in the central part of France. *J. Environ. Radioact.*, <http://dx.doi.org/10.1016/j.jenvrad.2010.12.005>.
- Bourcier, L., Sellegri, K., Chausse, P., Pichon, J.M., Laj, P., 2012. Seasonal variation of aerosol size-segregated chemistry at the puy de Dôme station (1465 m a.s.l.), France. *J. Atmos. Chem.*, <http://dx.doi.org/10.1007/s10874-012-9229-2>.
- Cambray, R.S., Cawse, P.A., Garland, J.A., Gibson, J.A.B., Johnson, P., Lewis, G.N.J., Newton, D., Salmon, L., Wade, B.O., 1987. Observations on radioactivity from the Chernobyl accident. *Nucl. Energy* 26, 77–101.
- Casado, H., Encinas, D., Lacaux, J.P., 1996. Relationship between the atmospheric particulate fraction and the ionic content of precipitation in an area under influence of a waste incinerator located in the Basque country (Spain). *Atmos. Environ.* 30, 1537–1542.
- Codina, B., Lorente, J., 1993. Rain acidity during a storm: results from a simple acid-monitoring device. *Weather* 48, 181–185.
- Dueñas, C., Fernández, M.C., Carretero, J., Lige, E., Cañete, S., 2005. Deposition velocities and washout ratios on a coastal site (southern Spain) calculated from ^7Be and ^{210}Pb measurements. *Atmos. Environ.* 39, 6897–6908.
- Dueñas, C., Fernández, M.C., Cañete, S., Pérez, M., 2009. ^7Be to ^{210}Pb concentration ratio in ground level air in Málaga (36.7°N, 4.5°W). *Atmos. Res.* 92, 49–57.
- Facchinelli, A., Magnoni, M., Gallini, L., Bonifacio, E., 2002. ^{137}Cs contamination from Chernobyl of soils in Piemonte (North-West Italy): spatial distribution and deposition model. *Water Air Soil Poll.* 134, 341–352.
- Flossmann, A.L., 1994. A 2-D spectral model simulation of the scavenging of gaseous and particulate sulphate by a warm marine cloud. *Atmos. Res.* 32, 233–248.
- Frank, G., Tschiersch, J., 1992. Parametrisation of below-cloud scavenging at low precipitation intensities by using a fluorescent tracer method. *J. Aerosol Sci.* 23 (Suppl. 1), S885–S888.
- Gatz, D.F., Dingle, A.N., 1971. Trace substances in rain water: concentration variations during convective rains and their interpretation. *Tellus* 23, 14–27.
- Gurriaran, R., Barker, E., Bouisset, P., Cagnat, X. And, Ferguson, C., 2004. Calibration of a very large ultra-low background well-type Ge detector for environmental sample measurements in an underground laboratory. *Nucl. Instrum. Meth. A* 524, 264–272.
- Hanke, M., Umann, B., Uecker, J., Arnold, F., Bunz, H., 2003. Atmospheric measurements of gas-phase NH_3 and SO_2 using chemical ionization mass spectrometry during the MINATROC field campaign 2000 on Monte Cimone. *Atmos. Chem. Phys.* 3, 417–436.
- Harrison, R.M., Kitto, A.-M.N., 1990. Field intercomparison of filter pack and denuder sampling methods for reactive gaseous and particulate pollutants. *Atmos. Environ.* 24A, 2633–2640.
- Ishikawa, Y., Murakami, H., Skine, T., Yoshihara, K., 1995. Precipitation scavenging studies of radionuclides in air using cosmogenic ^7Be . *J. Environ. Radioact.* 26, 19–35.
- Jaffrezzo, J.L., Colin, J.L., 1988. Rain-aerosol coupling in urban area: scavenging ratios measurements and identification of some transfer processes. *Atmos. Environ.* 22, 929–935.
- Junge, C.E., 1963. *Air Chemistry and Radioactivity*. Academic Press.
- Kerlau, G., Cagnat, X., Bouisset, P., Barker, E., Calmet, D., 1999. Amélioration des mouvements propres des chaînes de spectrométrie gamma pour la mesure d'échantillons de l'environnement. *Journées Techniques CETAMA* – 14 et 15 Septembre 1999, pp. 397–403.
- Krueger, B.J., Grassian, V.H., Cowin, J.P., Laskin, A., 2004. Heterogeneous chemistry of individual mineral dust particles from different dust source regions: the importance of particle mineralogy. *Atmos. Environ.* 38, 6253–6261.
- Laakso, L., Grönholm, T., Rannik, Ü., Kosmala, M., Fiedler, V., Vehkamäki, H., Kulmala, M., 2003. Ultrafine particle scavenging coefficients calculated from 6 years field measurements. *Atmos. Environ.* 37, 3605–3613.
- Legrand, M., Puxbaum, H., 2007. Introduction of the CARBOSOL project: present and retrospective state of organic versus inorganic aerosol over Europe. *J. Geophys. Res.*, <http://dx.doi.org/10.1029/2006JD008271>.
- Li, J., Pósfai, M., Hobbs, P.V., Buseck, P.R., 2003. Individual aerosol particles from biomass burning in southern Africa: 2, compositions and aging of

- inorganic particles. *J. Geophys. Res.* 108 (D13), 8484, <http://dx.doi.org/10.1029/2002JD002310>.
- Magono, C., Endoh, T., Harimaya, T., Kubota, S., 1974. A measurement of scavenging effect of falling snow crystals on the aerosol concentration. *J. Meteorol. Soc. Japan* 52, 407–416.
- Makhon'ko, K., 1967. Simplified theoretical notion of contaminant removal by precipitation from the atmosphere. *Tellus* XIX, 467–476.
- McNeary, D., Baskaran, M., 2003. Depositional characteristics of ^{7}Be and ^{210}Pb in southeastern Michigan. *J. Geophys. Res.* 108 (D7), 4210.
- Mircea, M., Stefan, S., Fuzzi, S., 2000. Precipitation scavenging coefficient: influence of measured aerosol and raindrop size distributions. *Atmos. Environ.* 34, 5169–5174.
- Murakami, M., Hiramatsu, C., Magano, C., 1981. Observation of aerosol scavenging by falling snow crystals at two sites of different heights. *J. Meteorol. Soc. Japan* 59, 763–771.
- Murakami, M., Kimura, T., Magono, C., Kikuchi, K., 1983. Observations of precipitation scavenging for water-soluble particles. *J. Meteorol. Soc. Japan* 61, 346–358.
- Pakkanen, T.A., Kerminen, V.-M., Hillamo, R.E., Mäkinen, M., Mäkelä, T., Virkulla, A., 1996. Distribution of nitrate over sea-salt and soil derived particles: implications from a field study. *J. Atmos. Chem.* 24, 189–205.
- Putaud, J.-P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M.-C., Decesari, S., Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., Ten Brink, H., Tørseth, K., Wiedensohler, A., 2004. A European aerosol phenomenology-2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. *Atmos. Environ.* 38, 2579–2595.
- Ricard, V., Jaffrezo, J.-L., Kerminen, V.M., Hillamo, R.E., Sillanpää, S., Ruellan, S., Lioussé, C., Cachier, H., 2002. Two years of continuous aerosol measurements in northern Finland. *J. Geophys. Res.* 107 (D11), 10 (1029.ACH 10).
- Ro, C.J., Hwang, H., Kim, H.K., Chun, Y., Van Grieken, R., 2005. Single-particle characterization of four "Asian dust" samples collected in Korea, using low-Z particle electron probe X-ray microanalysis. *Environ. Sci. Technol.* 39 (6), 1409–1419.
- Schumann, T., Zinder, B., Waldvogel, A., 1988. Aerosol and hydrometeor concentrations and their chemical composition during winter precipitation along a mountain slope—I. Temporal evolution of the aerosol, microphysical and meteorological conditions. *Atmos. Environ.* 22, 1443–1459.
- Seinfeld, J.H., Pandis, S.N., 2006. *Atmospheric Chemistry and Physics*. A Wiley Inter science Publication, John Wiley & Sons, Inc., New York.
- Seymour, M.D., Stout, T., 1983. Observations on the chemical composition of rain using short sampling times during a single event. *Atmos. Environ.* 17, 1483–1487.
- Sparmacher, H., Fuelber, K., Bonka, H., 1993. Below-cloud scavenging of aerosol particles: particle-bound radionuclides-experimental. *Atmos. Environ.* 27, 605–618.
- Sullivan, R.C., Guazzotti, S.A., Sodeman, D.A., Prather, K.A., 2007. Direct observations of the atmospheric processing of Asian mineral dust. *Atmos. Chem. Phys.* 7, 1213–1236.
- 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 (4), 1465–1478.
- Volken, M., Schumann, T., 1993. A critical review of below-cloud aerosol scavenging, results on Mt. Rigi. *Water. Air Soil Pollut.* 68, 15–28.
- Zhang, D., Iwasaka, Y., Shi, G., Zang, J., Matsuki, A., Trochikine, D., 2003. Mixture state and size of Asian dust particles collected at southwestern Japan in spring 2000. *J. Geophys. Res.* 108 (D24), 4760, <http://dx.doi.org/10.1029/2003JD003869>.