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Michel Legrand, Valérie Gros, Susanne Preunkert, Roland Sarda-Estève, Anne-Mathilde Thierry, et al.. A reassessment of the budget of formic and acetic acids in the boundary layer at Dumont d'Urville (coastal Antarctica): The role of penguin emissions on the budget of several oxygenated volatile organic compounds. *Journal of Geophysical Research: Atmospheres*, 2012, 117 (D6), pp.n/a-n/a. 10.1029/2011JD017102 . hal-03117271

**HAL Id: hal-03117271**

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Submitted on 21 Jan 2021

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# A reassessment of the budget of formic and acetic acids in the boundary layer at Dumont d'Urville (coastal Antarctica): The role of penguin emissions on the budget of several oxygenated volatile organic compounds

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Received 10 November 2011; revised 1 February 2012; accepted 3 February 2012; published 27 March 2012.

[1] Initiated in 1997, the year-round study of formic and acetic acids was maintained until 2011 at the coastal Antarctic site of Dumont d'Urville. The records show that formic and acetic acids are rather abundant in summer with typical mixing ratios of 200 pptv and 700 pptv, respectively. With the aim to constrain their budget, investigations of their potential marine precursors like short-chain alkenes and acetaldehyde were initiated in 2011. Acetic acid levels in December 2010 were four times higher than those observed over summers back to 1997. These unusually high levels were accompanied by unusually high levels of ammonia, and by an enrichment of oxalate in aerosols. These observations suggest that the guano decomposition in the large penguin colonies present at the site was particularly strong under weather conditions encountered in spring 2010 (important snow storms followed by sunny days with mild temperatures). Although being dependent on environmental conditions, this process greatly impacts the local atmospheric budget of acetic acid, acetaldehyde, and acetone during the entire summer season. Present at levels as high as 500 pptv, acetaldehyde may represent the major precursor of acetic acid, alkene-ozone reactions remaining insignificant sources. Far less influenced by penguin emissions, the budget of formic acid remains not fully understood even if alkene-ozone reactions contribute significantly.

**Citation:** Legrand, M., V. Gros, S. Preunkert, R. Sarda-Estève, A.-M. Thierry, G. Pépy, and B. Jourdain (2012), A reassessment of the budget of formic and acetic acids in the boundary layer at Dumont d'Urville (coastal Antarctica): The role of penguin emissions on the budget of several oxygenated volatile organic compounds, *J. Geophys. Res.*, *117*, D06308, doi:10.1029/2011JD017102.

## 1. Introduction

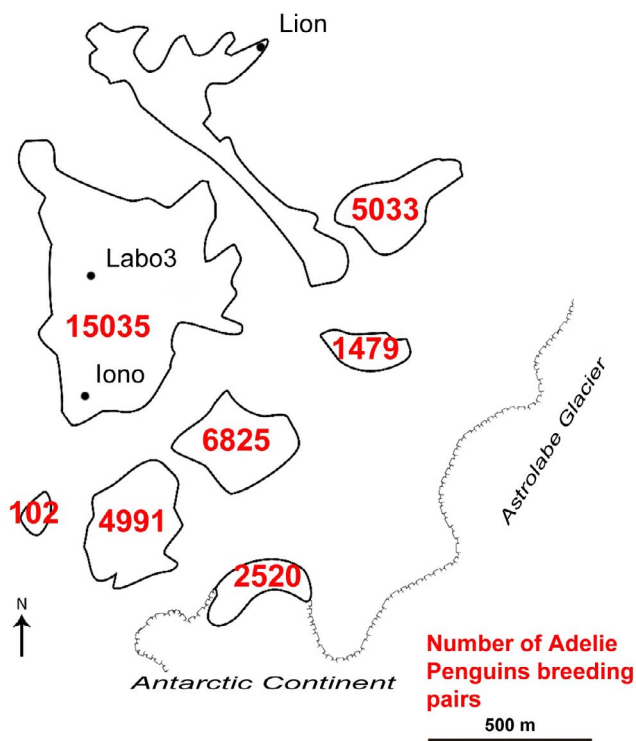
[2] In addition to inorganic acids ( $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{SO}_3\text{H}$ ,  $\text{HNO}_3$ , and  $\text{HCl}$ ), light monocarboxylic acids can also contribute to the acidity of the atmosphere in many regions of the World. Both natural and anthropogenic sources of monocarboxylic acids exist but, until very recently, their relative contributions were not quantified. The sources include various primary emissions as well as secondary productions from organic precursors in the gas or aqueous phase (see *Chebbi and Carlier* [1996] for a review). Over continents, primary emissions include biomass burning [*Talbot et al.*, 1990],

vehicular exhausts [*Kawamura and Kaplan*, 1987], and emissions from vegetation [*Kesselmeier and Staudt*, 1999]. The oxidation of isoprene emitted by vegetation also represents a possible significant source of formic acid over continents [*Jacob and Wofsy*, 1988]. The reaction of numerous alkenes emitted by the continental and marine biosphere with ozone produces formic and acetic acids [*Calvert and Stockwell*, 1983]. Finally in-cloud oxidation of formaldehyde can produce formic acid [*Jacob*, 1986] and the gas phase reaction of peroxy acetyl radical with  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$  may produce acetic acid in low  $\text{NO}_x$  environments [*Madronich and Calvert*, 1990]. The study of the trends of formate and acetate along a deep ice core extracted from a high-elevation Alpine site showed that, except at the end of the 1970s when the anthropogenic input was as high as the natural one, natural sources appear to dominate the budget of the two mono-carboxylates in the European mid-troposphere [*Legrand et al.*, 2003]. The first detailed budget of formic and acetic acids was recently established by *Paulot et al.* [2011] pointing out indeed the importance of secondary productions from biogenic volatile organic compounds (VOCs).

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**Figure 1.** Map of “Pointe Géologie” archipelago showing the main island where “labo 3” and “iono” sampling lines are located and smaller islands located around. Numbers refer to the breeding pairs of Adélie penguins living in summer on these islands [Micol and Jouventin, 2001].

[3] Predominantly present in the gas phase, the mixing ratio of formic and acetic acids generally lies in the range of a few ppbv in urban regions [Lawrence and Koutrakis, 1994] but remains close to 1 ppbv in remote continental regions [Khwaja, 1995]. With respect to these levels observed at continental sites, slightly lower values in the range of a few hundreds of pptv were observed in the remote marine boundary layer [Arlander *et al.*, 1990; Baboukas *et al.*, 2000]. Data gained in remote marine regions remain however limited in time, essentially restricted to low and mid latitudes. A study of formic and acetic acid levels conducted in the very remote boundary layer of the coastal Antarctic site of Dumont d’Urville (DDU) indicated summer levels ranging between 120 and 310 pptv for formic acid and from 300 to 700 pptv for acetic acid [Legrand *et al.*, 2004]. Discussions on the origins of acetic acid in summer pointed out the possible oxidation of propene emitted from the ocean into acetaldehyde and its subsequent efficient oxidation into acetic acid in a low  $\text{NO}_x$  environment. The origin of formic acid in summer remained basically unexplained even considering the ozone reaction with C2-C5 alkenes emitted by the ocean.

[4] With the aim to further investigate the budget of these two carboxylic acids in Antarctica, the year-round study of these species was extended to the 2005–2011 years at DDU. In addition, their potential marine precursors, particularly short-chain alkenes and acetaldehyde, were investigated during summer 2010/2011. Finally, backup information were gained by conducting a year-round study (2009–2010) of carboxylic acids at the inland site of Concordia ( $75^\circ\text{S}$ ,  $123^\circ\text{E}$ ,

3220 m above sea level). These new data are used to highlight the budget of carboxylic acids at DDU and to address the impact of local emissions related to the presence of large penguin colonies at the site in summer.

## 2. Sampling and Methods

[5] Samplings were carried out at Dumont d’Urville ( $66^\circ40\text{S}$ ,  $140^\circ10\text{E}$ ), a site located on a small island (43 m above sea level) located 1 km offshore from the coastline. The different locations where samplings were carried (labo 3, iono, and lion) are reported in Figure 1. Measurements included gas phase formic and acetic acids, ammonia, non methane hydrocarbons (NMHCs), acetaldehyde, and acetone. Backup information on the chemical composition of aerosol was also obtained.

### 2.1. Formic and Acetic Acids, and Ammonia

[6] As done from 1997 to 2002 by Legrand *et al.* [2004], gas phase samplings of formic and acetic acids were continued at “labo 3” until December 2010 by using two mist chambers placed in series downstream a Teflon Millipore FALP (37 mm diameter) filter with an airflow rate of  $0.36 \text{ m}^3 \text{ h}^{-1}$ . Blanks were done at least once per week showing values lower than  $10 \text{ ng m}^{-3}$  (i.e., 5 pptv) for formic acid and  $15 \text{ ng m}^{-3}$  (i.e., 6 pptv) for acetic acid. These values remain insignificant with respect to atmospheric levels, even in winter. 1500 runs of mist chambers were done from late 2005 to the end of 2010. From May 2007 to December 2008 unusually low levels of carboxylic acids were observed whereas the levels of other acidic species like  $\text{HNO}_3$  or  $\text{SO}_2$  remained similar to those observed over the preceding years. A development of bacterial activity inside the chambers was suspected to cause the problem and the chambers were cleaned with  $\text{H}_2\text{O}_2$  and extensively rinsed with ultrapure water. Following this treatment the level of carboxylic acids recovered and the 371 samples collected from May 2007 to mid December 2008 were discarded from the data set.

[7] A gas sampling line of 3 annular denuder tubes placed in series and coated with  $\text{Na}_2\text{CO}_3$  [Jourdain and Legrand, 2002] was also run with a flow rate of  $0.6 \text{ m}^3 \text{ h}^{-1}$  from December 2005 to December 2010 (270 runs). The coating was made with a solution of  $\text{Na}_2\text{CO}_3$  at  $10^{-2} \text{ M}$  (50% ultrapure water, 50% HPLC methanol) and tubes were then dried by flowing clean air inside. Since carboxylic acids are commonly present at levels as high as several ppbv in ambient air of laboratories, a special line was designed in which air is sucked through a 1M NaOH solution and a tube filled with silica gel and active coal. At each denuder tube series, one tube was used as a blank to control the quality of the preparation procedure and the effect of storage of tubes before their use (a day or a few days later). With sampling interval of 4 to 12 h in summer the blank values correspond to atmospheric level of  $60 \text{ ng m}^{-3}$  for  $\text{HCOOH}$  and  $150 \text{ ng m}^{-3}$  for  $\text{CH}_3\text{COOH}$ . In winter the longer sampling interval (12 to 24 h) leads to lower values ( $\sim 20 \text{ ng m}^{-3}$ ). Being significant with respect to atmospheric levels, in particular in winter, these blank values were subtracted to concentrations. As discussed by Preunkert *et al.* [2007], another difficulty in using denuder tubes is the limited capacity of their coating that could lead to a poor trapping efficiency. The use of 3 denuder tubes placed in series allows checking the collection

efficiency of the sampling line. Tests were done in the field showing that the coating of tubes with a solution of  $\text{Na}_2\text{CO}_3$  at  $10^{-2}$  M (50% ultrapure water, 50% HPLC methanol) is adequate in winter even for a sampling time as high as 24 h. In summer (from November to February) the concentration of the coating solution was doubled and sampling time restricted to 12 h.

[8] Ammonia was sampled using mist chambers from February 1995 to January 2000 (220 runs). Most of samplings were done during daytime, except 54 samples continuously collected (i.e., 4 samples per day) from January 23 to February 5 1999. At that time, less stringent conditions were applied compared to those applied since 2005 for carboxylic acids, and  $\text{NH}_3$  blank values were as high as  $1000 \text{ ng m}^{-3}$ . Being significant with respect to atmospheric levels these values were subtracted. Quantification limits, taken as three times the standard deviation of the blanks, ranged between 100 and  $200 \text{ ng m}^{-3}$ . A good agreement (not shown) was found with ammonia data obtained by sampling air with three denuder tubes coated with phosphoric acid.

[9] During the end of December 2010, ammonia, formic and acetic acids were continuously monitored over a few days at “labo3” and then over 5 weeks (from January 2 to February 6) at the main OPALE sampling site (“iono,” Figure 1) by deploying a URG-9000D Ambient Ion Monitor (AIM). Air is sucked in the device at a flow of  $3 \text{ L min}^{-1}$  through a Liquid Diffusion Denuder [Takeuchi *et al.*, 2004] where  $\text{NH}_3$  and acidic gases are removed. Next, the air stream enters an aerosol super-saturation chamber where atmospheric aerosol grows and is subsequently trapped in a liquid water solution [Khlystov *et al.*, 1995]. Gas and aerosol samples are collected over one hour and four liquid samples of 5 mL are used for anions and cations determinations in gas and aerosol. Samples are analyzed by two Dionex ICS 2000 ion chromatographs (anions and cations) equipped with pre-concentrator columns (UTAC-XLP1 and TCC-XLP1) during collection of the next air sample. Ion separation is achieved with 2 mm analytical columns (AG and AS18 for anions and CG and CS12 for cations). The blank of the AIM sampling was regularly checked by flowing air provided by a zero air generator (Geophysics PAG 003) over several hours. The typical AIM sampler atmospheric quantification limits (taken as three times the standard deviation of the blanks) remain in the range of a few  $\text{ng m}^{-3}$  or lower (i.e., around 1 pptv).

[10] In addition to these gas phase samplings, some background information on the chemical composition of aerosol collected at “labo 3” and “iono” were obtained. A year-round sampling of aerosol collected at “labo 3” is done since 1991 in the framework of the French environmental observation service CESOA (Etude du cycle atmosphérique du Soufre en relation avec le climat aux moyennes et hautes latitudes Sud, <http://cesoa.ore.fr>) dedicated to the study of the sulfur cycle at middle and high southern latitudes. The 1991–2001 data set already discussed by Jourdain and Legrand [2002] was extended to January 2009. In addition to aerosol data gained at “iono” with the IAM (see above), daily aerosol filters collected in December 2010 at “labo 3” were retrograded and analyzed at LGGE back from the fields with the aim to get background information for the OPALE sampling period.

[11] Finally, samplings of carboxylic acids with denuder tubes were regularly done from January 2009 to January

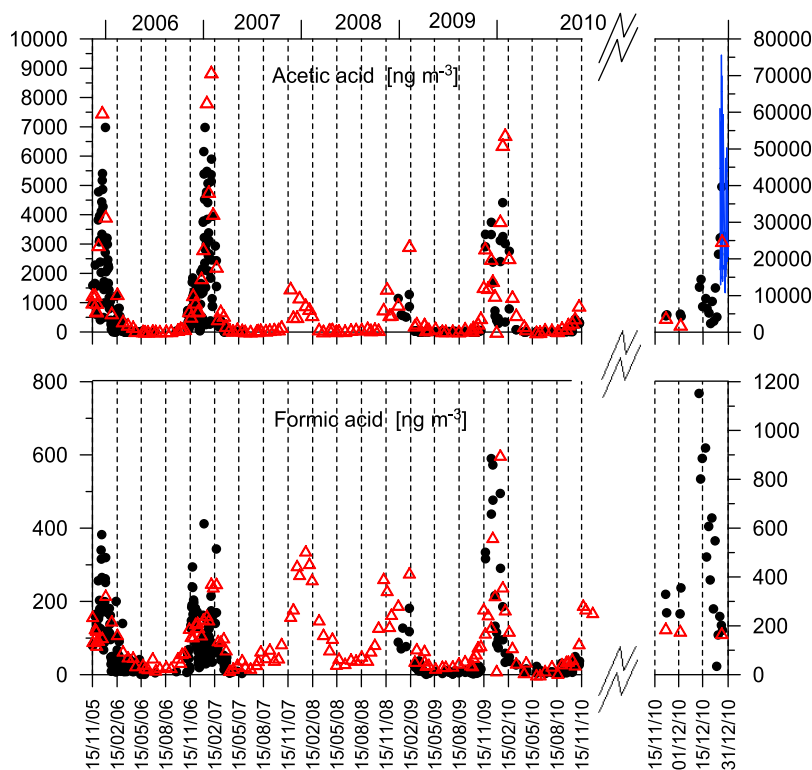
2011 (90 runs) at the inland Antarctic site of Concordia. With a typical sampling interval of 2 days in summer and 6 days in winter, blank values correspond to  $1\text{--}2 \text{ ng m}^{-3}$  for formic acid and close to  $5 \text{ ng m}^{-3}$  for acetic acid.

## 2.2. Measurements of Acetone, Acetaldehyde, and Light NMHCs

[12] Acetone and acetaldehyde were measured at “iono” from 30 December 2010 to 24 January 2011 with a high-sensitivity PTR-MS (Proton Transfer Mass Spectrometry, IONICON, Austria). This technique is already extensively described in the literature (see Blake *et al.* [2009] for a review). We here report results for acetaldehyde ( $m/z = 45$ ) and acetone ( $m/z = 59$ ). Working conditions during the campaign were as following: pressure in the reaction chamber was maintained at 2.2 mbar, number of primary ions  $\text{H}_3\text{O}^+$  ( $m/z = 21$ ) was on average 11 millions and all data were normalized against  $m/z$  of 21. Air was sucked in a 12 m Teflon line (1/8" inner diameter) protected from sunlight at a flow of  $0.4 \text{ L min}^{-1}$ . Time resolution of measurements was 10 min, with an integration time of 30 s for each mass (about 30 masses were monitored, but only two were selected for the present study). The instrumental background level was determined by switching incoming air over a catalytic converter Platinum coated wool heated at  $250^\circ\text{C}$  and values were subtracted from atmospheric signals. Calibration was achieved in the fields by injecting different amounts (between 0 and 5 ppbv, with 4 levels below 1 ppbv) of a multicomponent standard gas containing acetone and acetaldehyde, using the calibration unit facility (GCU, Ionimed, Austria). The calibration was done at 53% humidity, close to the mean value of 60% encountered during the campaign. Calibrations previously performed in the laboratory at different humidity have shown less than 10% over the range 30–90%.

[13] Light NMHCs (C2–C6) were measured with a portable gas chromatograph equipped with Flame Ionization Detector (GC-FID, Chromatotec, France). The device is described in details by Gros *et al.* [2011]. Air was drawn through a 1/8" diameter 12 m long stainless-steel tube and then a Nafion Dryer to reduce water content. The Peltier element was not working correctly and thus reliable data only concern C3–C6 species. A contamination of the field lab through the Nafion dryer was identified and obliged us to remove it. Consequently a shift of retention times of species rendered difficult identification of C4–C5 compounds. As first measurements revealed no detectable levels, we increased the air sample volume (0.65 instead of 0.18 L). Measurements took place 17 to 19 January 2011 with this final configuration, afterwards it was no more possible to avoid a too rapid saturation of the water trap in the absence of Nafion. January 17, a certified calibration gas (National Physics Laboratory) containing a mixture of hydrocarbons in the 4 ppb range was used for species identification and quantification. With these working conditions, the quantification limit was 30 pptv for propane, propene, *i*- and *n*-butane. The correct identification of butenes was difficult due to the above mentioned shift in the retention times.

[14] In addition, 0.8 L stainless steel canisters were used to sample air at DDU and were analyzed four months later in the laboratory by GC-FID (with the same system as described by



**Figure 2.** Time series of formic and acetic acid concentrations at “labo 3” from November 2005 to December 2010. Solid black circles refer to 24 h averaged values derived from mist chamber samplings, open red triangles to 24 h averaged values derived from denuder tube samplings. The thin blue line reported at the right of the acetate record corresponds to continuous measurements (1 h time resolution) made between December 25 and December 30 2010 with the Ambient Ion Monitor (see section 2.1). Note the change of y-scales for the two acids at the end of the record (November and December 2010).

*Touaty and Bonsang* [2000]). Two canisters sampled at “iono” were used here to determine the level of ethane, the NMHC compound with the longest lifetime.

### 3. Data Presentation

[15] As already pointed out by *Legrand et al.* [2004], a well-marked diurnal cycle of the level of formic and acetic acid is observed in summer at DDU. The applied day/night sampling frequency was variable over the years (depending of the operator). Therefore to avoid any bias related to a variable portion of day versus night sampling on the inter-annual variability we only consider data for which day and night sampling were done and all data are presented as 24 h averaged values (Figure 2). In this way from 1150 mist chamber runs, 420 values were calculated as 24 h averaged. Similarly, from the 270 denuder tube runs, 132 values were derived as 24 h averaged. As seen in Figure 2 there is an overall good agreement between the two data sets over the years when the two sampling were successfully conducted. Note also that the continuous determination of acetic acid done end of December (see the blue line reported in Figure 2) is in excellent agreement with the corresponding denuder tube and mist chamber samplings.

[16] Since a local source of acetic acid related to the presence of penguins was identified at the beginning of the 2010/2011 campaign (see section 4.2), end of December 2010 the sampling of carboxylic acids was moved from “labo 3” to

“iono,” a site far less influenced by penguin emissions than “labo 3” (see Figure 1) where precursors of carboxylic acids (OCOVs, and NMHCs) were measured.

### 4. The Budget of Formic and Acetic Acids at DDU

#### 4.1. The 2005–2010 Year-Round Record

[17] The 2005–2010 year-round records of formic and acetic acids exhibit well-marked November–February maxima (Figure 2). The mean mid-winter (May to August) levels remain as low as  $36 \pm 9 \text{ ng m}^{-3}$  for acetic and  $21 \pm 5 \text{ ng m}^{-3}$  for formic acid. The corresponding winter mixing ratios ( $\sim 5$  pptv; see Table 1) are one order of magnitude lower than those previously reported by *Legrand et al.* [2004] (i.e., 25 pptv for formic acid, and an upper limit of 70 pptv for acetic). Such a difference is clearly related to the improvement of blank values ( $\sim 5$  pptv, see section 2.1) since the study from *Legrand et al.* [2004] (blank values of 28 pptv and 46 pptv for formic and acetic acids, respectively). From November to February mean mixing ratios ( $630 \pm 100$  pptv of formic acid, and  $92 \pm 15$  pptv of acetic acid, Table 1) are consistent within a factor of 2 with those reported by *Legrand et al.* [2004] (from 400 to 700 pptv for acetic acid, around 200 pptv for formic acid). Given the existing inter-annual variability in summer (Figure 2) and the fact that our record is restricted to 24 h averaged data (not in the work of *Legrand et al.* [2004]) the two data sets can be considered as consistent for the summer season. Figure 2 indicates a significant inter-



**Table 1.** Monthly Means for Levels of Acetic Acid, Formic Acid, and Ammonia at DDU<sup>a</sup>

Months	Acetic Acid (ng m <sup>-3</sup> ) (Mixing Ratio (pptv))	Formic Acid (ng m <sup>-3</sup> ) (Mixing Ratio (pptv))	Ammonia (ng m <sup>-3</sup> ) (Mixing Ratio (pptv))
January	1733 ± 1109 (717 ± 459)	172 ± 103 (93 ± 56)	8460 ± 7612 (11,470 ± 10,318)
February	1644 ± 1132 (688 ± 468)	149 ± 95 (81 ± 52)	16,600 ± 13,000 (22,502 ± 17,615)
March	163 ± 189 (68 ± 78)	53 ± 44 (29 ± 24)	3730 ± 2700 (5056 ± 3660)
April	55 ± 36 (23 ± 15)	30 ± 31 (16 ± 17)	1020 ± 605 (1383 ± 820)
May	37 ± 27 (15 ± 11)	19 ± 11 (10 ± 6)	400 ± 180 (542 ± 244)
June	24 ± 15 (10 ± 6)	17 ± 9 (9 ± 5)	340 ± 160 (542 ± 244)
July	40 ± 31 (16 ± 13)	20 ± 15 (11 ± 8)	170 ± 120 (230 ± 163)
August	45 ± 39 (18 ± 16)	30 ± 23 (16 ± 12)	170 ± 150 (230 ± 203)
September	68 ± 31 (28 ± 13)	32 ± 20 (18 ± 11)	450 ± 300 (610 ± 407)
October	96 ± 52 (40 ± 21)	59 ± 38 (32 ± 21)	1270 ± 1595 (1721 ± 2162)
November	1202 ± 351 (497 ± 145)	151 ± 37 (82 ± 20)	20,640 ± 20,032 (27,978 ± 27,143)
December	1490 ± 977 (616 ± 404)	202 ± 102 (109 ± 55)	20,630 ± 14,470 (27,963 ± 19,614)

<sup>a</sup>Standard deviations represent the year-to-year variability between November 2005 and October 2010 for carboxylic acids, the daily variability between February 1995 and January 2000 for ammonia. Values in parentheses are mixing ratios.

annual variability of summer levels, in particular for acetic acid with mean November–February values twice lower during summer 2007/2008 and 2008/2009 (995 ng m<sup>-3</sup>) than during summer 2005/2006, 2006/2007, and 2009/2010 (1870 ng m<sup>-3</sup>). The interannual variability of summer levels is less marked for formic acid which does not follow the change of acetic acid. For instance, the mean summer level of formic acid was higher in 2007/2008 and 2008/2009 than during other summers (210 ng m<sup>-3</sup> instead of 140 ng m<sup>-3</sup>).

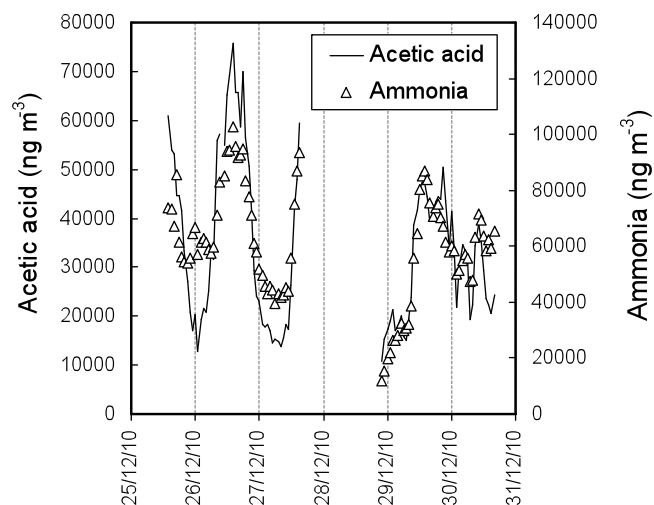
#### 4.2. The Unusually High Levels of December 2010

[18] As seen in Figure 2 the concentrations of acetic acid were out of range at the beginning of summer 2010/2011. For instance, the averaged acetic concentration in December 2010 was at least four times higher than those observed over all other summer months back to 2005. Note that acetic acid samplings carried out in December 2010 include sixteen 24 h averaged mist chamber runs and one denuder tube run that, as previously emphasized in section 3, were found to be in good agreement.

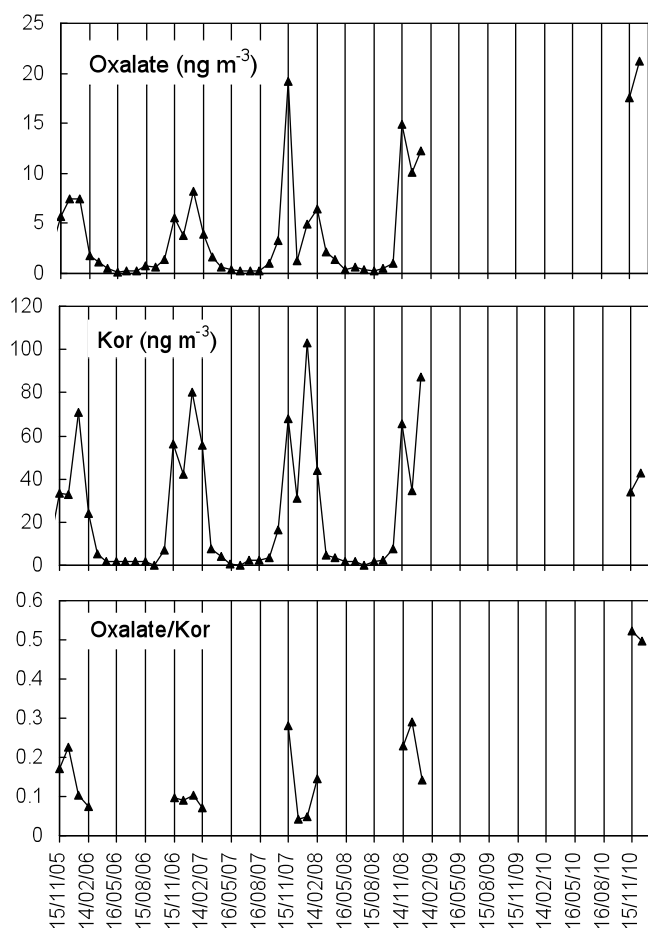
[19] These high acetic acid values were recorded at the time we set up the AIM device in view to start continuous measurements of SO<sub>2</sub> in the framework of the CESOA program (see section 2.2). As seen in Figure 3 the AIM continuous gas sampling made over the last days of December 2010 indicates that not only acetic acid but also ammonia exhibits unusually high concentrations. Indeed ammonia levels recorded at “labo 3” end of December 2010 (60,000 ± 20,000 ng m<sup>-3</sup>) are also far higher than those previously observed over summer 1995–2000 (around 20,000 ng m<sup>-3</sup>, Table 1). As previously discussed by *Legrand et al.* [1998], NH<sub>3</sub> present in the summer atmosphere at DDU is released by ornithogenic soils related to the large Adélie penguin colonies present at that site during the breeding season. The term “ornithogenic soils” [*Ugolini, 1972*] is used for soils consisting of a well-defined layer of guano resting sharply on mineral soil. Such a correlation between atmospheric concentrations of acetic acid and ammonia was not detected in the preceding study of *Legrand et al.* [2004] but, as discussed later in section 4.3, the ratio between ammonia and acetic acid concentrations appears to be highly variable.

[20] Another indication that emissions related to the presence of penguins were very high in December 2010 merges from examination of the chemical composition of aerosol collected at “labo 3.” As discussed by *Legrand et al.* [1998],

aerosol related to ornithogenic soil emissions contains among others oxalate, produced together with ammonium following the bacterial decomposition of uric acid, the alkaline nature of occupied ornithogenic soils permitting the subsequent loss of ammonia to the atmosphere. Relation between released gaseous nitrogen (or carbon) derived species and emitted oxalate aerosol following bacterial decomposition of guano is likely complex. For instance the moisture of ornithogenic soils favors the guano decomposition [*Speir and Cowling, 1984*] but limits emission of soil particles containing oxalate towards the atmosphere. An attempt was therefore made to examine the ratio of oxalate to another compound present in ornithogenic soils but not linked to the uric acid degradation, such as potassium. Following *Jourdain and Legrand* [2002] the amount of potassium related to ornithogenic soil emissions (K<sub>or</sub>) can be separated from the sea-salt contribution and estimated from total sodium (Na<sup>+</sup>) and potassium (K<sup>+</sup>) ([K<sub>or</sub>] = ([K<sup>+</sup>] - 0.037 \* [Na<sup>+</sup>])/0.933). Monthly



**Figure 3.** Hourly mean concentrations of ammonia (open triangles, right scale) and acetic acid (solid line, left scale) observed at “labo 3” end of December 2010 by deploying the Ambient Ion Monitor (see section 2.1). Note that the large amount of acetic acid present at that period rendered difficult under ion chromatographic working conditions to accurately quantify formic acid levels.



**Figure 4.** Monthly mean concentrations of (top) oxalate and (middle) potassium related to ornithogenic soil emissions (denoted Kor, see section 4.2) between November 2005 and January 2009 and in November/December 2010. (bottom) Monthly summer means of the mass ratio of oxalate to potassium related to ornithogenic soil emissions.

atmospheric mean levels of oxalate, potassium related to ornithogenic soils, and of the ratio between the two species are reported in Figure 4. Clearly the mass ratio of oxalate to potassium corresponding to ornithogenic soil emissions was in November/December 2010 (0.5) the highest value since 2005. These observations of unusually high levels of ammonia, and of an enrichment of oxalate in ornithogenic soil particles suggests that the guano decomposition was particularly strong under conditions encountered in spring 2010 and that this process seems also to partly control the local atmospheric budget of acetic acid and possibly formic acid.

[21] To assess this rather unexpected origin of acetic acid, samplings were simultaneously conducted at three different selected sites of the Archipelago between 11:00 and 14:00 December 27. The first site is “labo 3” where both mist chambers and AIM analyzer show high acetic acid level ( $28,000 \pm 2000 \text{ ng m}^{-3}$ ) at that time. The two other sites where mist chamber samplings were done are “iono” and “lion,” two sites where penguins are far less present (see Figure 1). Both samplings indicated far lower values ( $1000 \pm$

$300 \text{ ng m}^{-3}$ ), clearly confirming the importance of a local source of acetic acid related to the presence of large penguin colonies at the site. Interestingly, the level of formic acid remained in the same range at the three sites ( $\sim 300 \text{ ng m}^{-3}$ ). This observation and the preceding differences seen in the interannual summer variability of the two acids suggest that the contribution of penguin emissions to the level of formic acid is far less important than it is for acetic acid.

[22] Such a weak emission of formic acid from penguin deposits is clearly confirmed by the comparison of carboxylic acid levels at DDU and Concordia, an inland Antarctic site totally free of penguin colonies. Indeed, as seen in Table 2, whereas summer levels of acetic acid are far lower at DC compared to DDU ( $150 \text{ ng m}^{-3}$  instead of  $1500 \text{ ng m}^{-3}$ ), the ones of formic acid remain very similar ( $170 \text{ ng m}^{-3}$  at DDU against  $180 \text{ ng m}^{-3}$  at DC). We can therefore conclude that, whereas penguin emissions strongly influence the acetic acid level at DDU, its impact on the budget of formic acid remains insignificant.

### 4.3. Factors Controlling the Temporal Variability of Penguin Emissions

[23] In this section we investigate possible causes which can explain temporal variability of ammonia and acetic acid concentrations pointed out in section 4 including the case of the very particular spring/summer 2010.

#### 4.3.1. Temporal Variability of Ammonia Levels

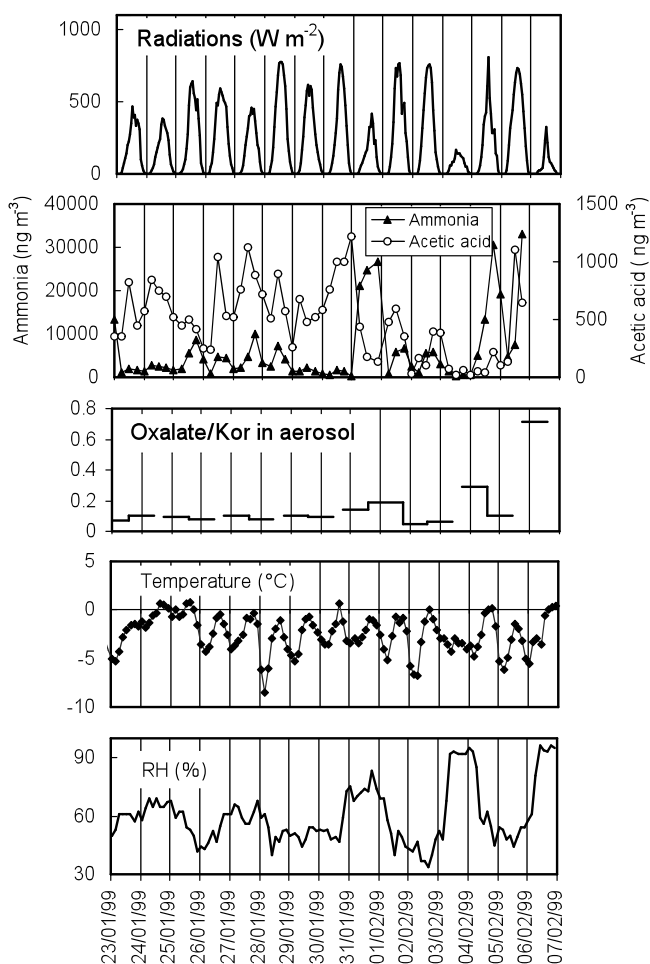
[24] In a first step we try to identify meteorological parameters that may strengthen emissions from ornithogenic soils by checking the atmospheric record of ammonia since its origin (bacterial decomposition of uric acid into ammonium and the subsequent release toward the atmosphere of ammonia from alkaline soils) is better understood than carboxylic acid emissions (see further discussions).

[25] In addition to the 3–4 days of AIM measurements made at the end of December 2010 (Figure 3) the unique continuous record of ammonia available at “labo 3” was obtained with mist chamber runs from January 23 to February 5 1999 (see section 2.1). As seen in Figure 5, two ammonia events took place over that period with concentrations as high as  $25,000 \text{ ng m}^{-3}$  January 31 and February 4 and 5. These events coincide with two snowfalls that occurred during that period as seen by the increase of relative

**Table 2.** Monthly Means for Levels of Acetic and Formic Acids at Concordia<sup>a</sup>

Months	Acetic Acid ( $\text{ng m}^{-3}$ ) (Mixing Ratio (pptv))	Formic Acid ( $\text{ng m}^{-3}$ ) (Mixing Ratio (pptv))
January	$160 \pm 85$ ( $66 \pm 35$ )	$144 \pm 72$ ( $78 \pm 39$ )
February	$149 \pm 100$ ( $62 \pm 41$ )	$133 \pm 79$ ( $72 \pm 43$ )
March	$26 \pm 13$ ( $11 \pm 5$ )	$36 \pm 22$ ( $20 \pm 12$ )
April	$6 \pm 5$ ( $3 \pm 2$ )	$8 \pm 3$ ( $4 \pm 2$ )
May	$9 \pm 7$ ( $4 \pm 3$ )	$5 \pm 5$ ( $3 \pm 3$ )
June	$7 \pm 4$ ( $3 \pm 2$ )	$7 \pm 7$ ( $4 \pm 4$ )
July	$8 \pm 4$ ( $3 \pm 2$ )	$5 \pm 4$ ( $3 \pm 2$ )
August	$13 \pm 4$ ( $5 \pm 2$ )	$8 \pm 4$ ( $4 \pm 2$ )
September	$24 \pm 12$ ( $10 \pm 5$ )	$22 \pm 8$ ( $12 \pm 4$ )
October	$63 \pm 53$ ( $26 \pm 22$ )	$89 \pm 53$ ( $48 \pm 29$ )
November	$154 \pm 72$ ( $64 \pm 30$ )	$224 \pm 113$ ( $121 \pm 61$ )
December	$170 \pm 95$ ( $70 \pm 39$ )	$264 \pm 170$ ( $143 \pm 92$ )

<sup>a</sup>Standard deviations represent the daily variability between January 2009 and January 2011. Values in parentheses are mixing ratios.

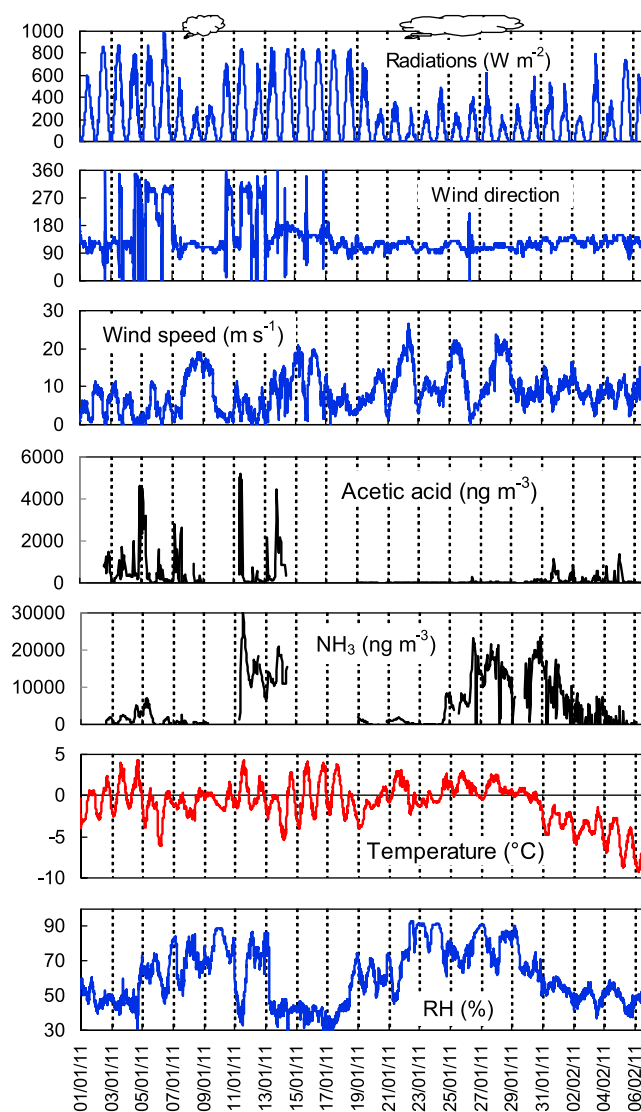


**Figure 5.** Continuous record of atmospheric ammonia and acetic acid derived from mist chamber samplings and of the ratio of oxalate to potassium in aerosols emitted from ornithogenic soils (see section 4.2.) between January 23 and February 6 1999 at “labo 3” along with encountered weather conditions.

humidity and low solar radiation on January 31 and February 3. Note also that the two events were consistently accompanied by an increase of oxalate in aerosols emitted by ornithogenic soils (Figure 5). The enhanced soil moisture following snow melting after a precipitation event is very likely the cause of these ammonia events. Indeed the biological uric acid breakdown is mainly controlled by temperature, moisture and enzyme activity. Under summer conditions, since bacterial biomass is very high in occupied ornithogenic soils, moisture would be the dominant limiting factor of the process [Speir and Ross, 1984].

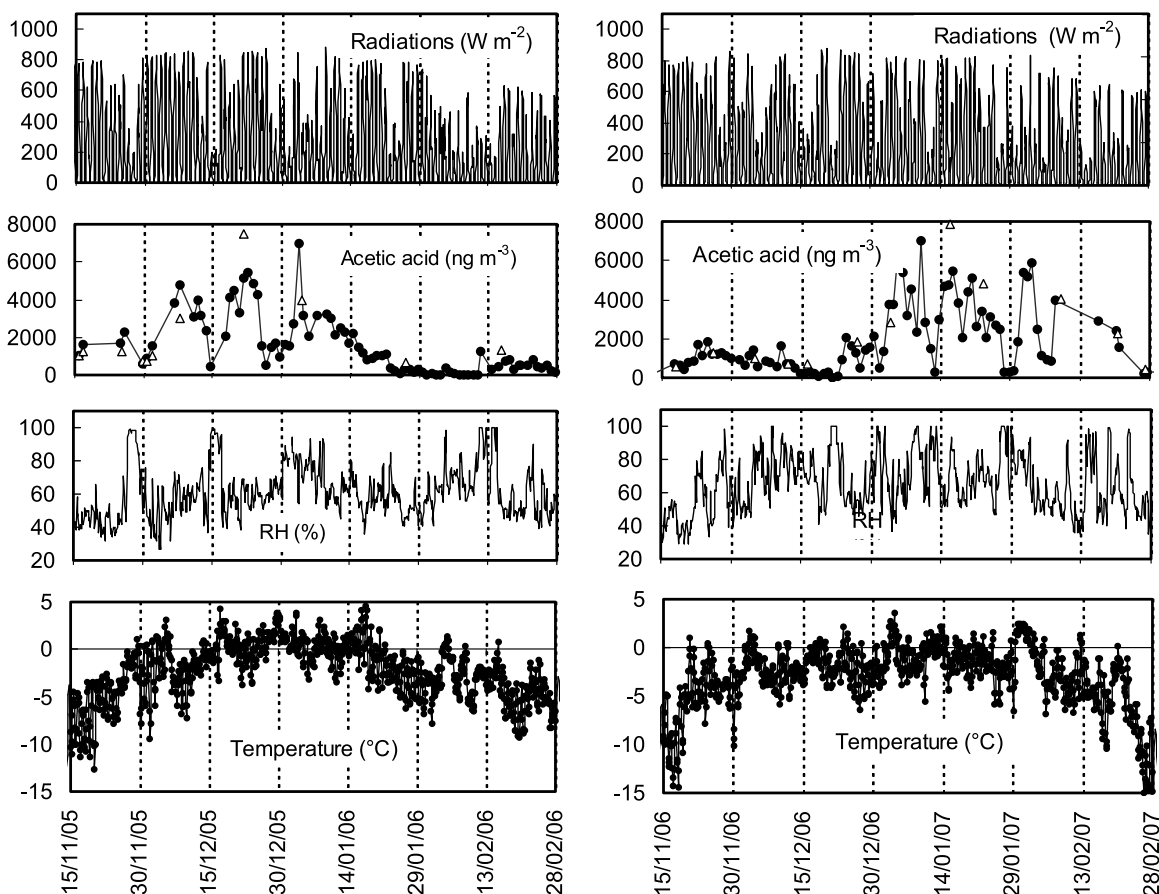
[26] Less straightforward is information extracted from the ammonia record obtained at “iono.” Indeed, whereas the ammonia record at “labo 3,” a site surrounded by penguin colonies, is not very sensitive to the wind direction, the influence of penguin emissions at “iono” is highly dependent on this parameter (Figure 1). During the two first weeks of January 2011, wind direction often changed jumping from  $270^{\circ}E$ , an oceanic sector free of penguins, to the  $0-60^{\circ}E$  a sector occupied by the largest penguin colonies of the Archipelago, as seen in Figure 6. The effect of changes in

wind direction is detected in the record with a drop of ammonia levels when wind direction shifted from the  $0-60^{\circ}E$  sector to  $270^{\circ}E$ , for instance January 5 (Figure 6). In spite of this strong influence of wind conditions, the ammonia record at “iono” clearly shows a recovery of high ammonia concentrations following the strong snowstorm that occurred January 8 to January 10 in the morning. The effect of weather conditions on ammonia levels becomes easier to examine from mid January to the first week of February, a period during which wind permanently blew from southeast where small islands occupied by penguins are located. This period started with a few days of fine conditions followed by 5 days with snow and mild temperatures (from January 23 to January 28). These humid weather conditions have likely strengthened bacterial decomposition of uric acid as suggested by the strong increase of ammonia concentrations



**Figure 6.** Quasi-continuous record of ammonia and acetic acid obtained with the AIM device between January 2 and February 6 2011 at “iono” along with encountered weather conditions. Periods of snowfalls are denoted with a symbol depicting cloudy conditions on top of radiation and relative humidity (RH) plots.





**Figure 7.** Acetic acid concentrations during summer (left) 2005/2006 and (right) 2006/2007 along with encountered weather conditions.

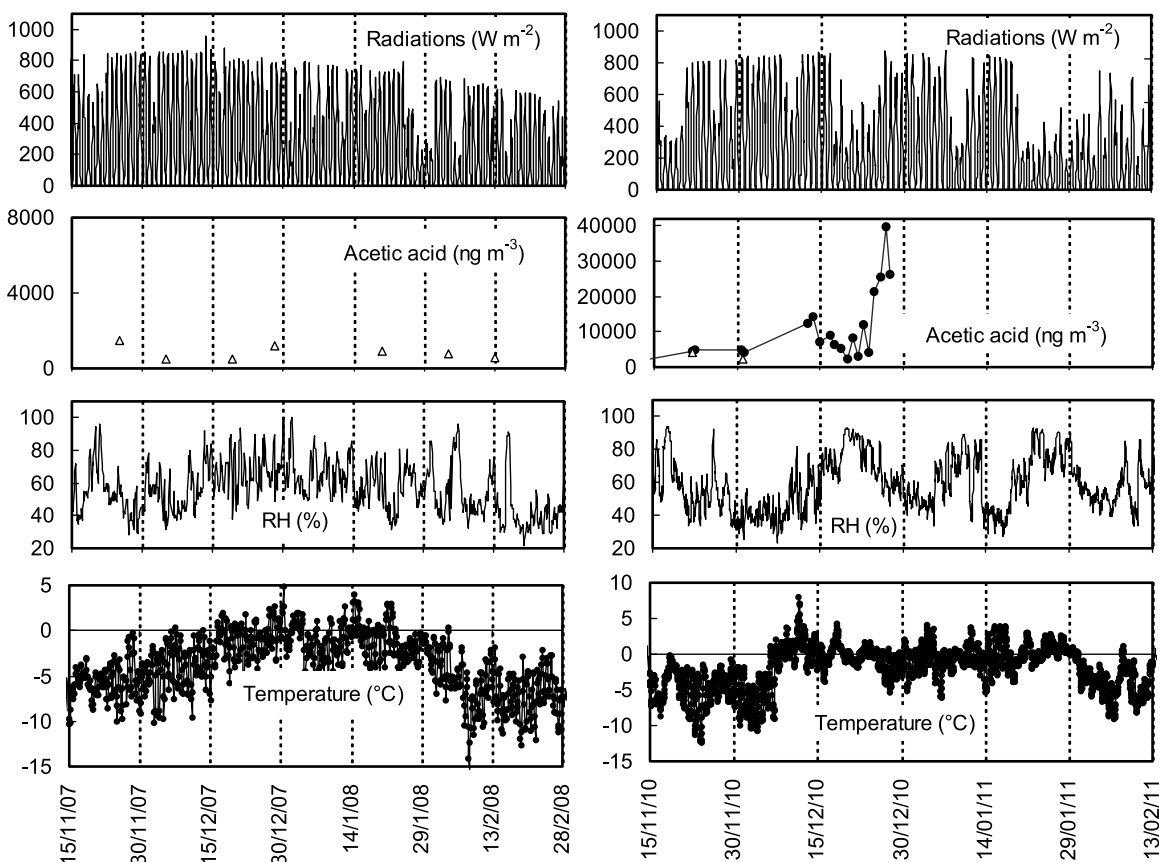
seen January 24 in the afternoon. In addition to humidity, the ammonia record at “iono” also highlights the effect of temperature on the strength of ammonia emissions. The regular drop of temperatures over the first week of February coincided with decreasing ammonia concentrations as expected. In addition to moisture, favorable temperature conditions are indeed required for a rapid breakdown of penguin guano [Orchard and Corderoy, 1983], optimal conditions for bacterial activity ranging from 3 to 11°C [Zdanowski *et al.*, 2005]. Furthermore Zhu *et al.* [2009] reported enhanced emission rates of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> from ornithogenic soils following thawing. The absence of “freezing-thawing” cycles during the first week of February (Figure 6) may have contributed together with the overall decrease of temperatures to the lowering of atmospheric ammonia concentrations.

[27] Figures 5 and 6 show that the day-to-day variability of acetic acid and ammonia levels in summer is different. For instance, Figure 5 tends to suggest that the diurnal cycle of ammonia is partly because of diurnal change of temperatures as suggested by the absence of ammonia diurnal increase January 23, 24, and February 3, when temperature weakly increased during the course of days. Diurnal cycle of acetic acid concentrations tends to vanish under cloudy conditions as seen January 31 and February 3, two days characterized by low solar radiation (Figure 5). Note also that the recovery of high ammonia concentrations during snowfall period at

the end of January 2011 (Figure 6) was not immediately accompanied by the one of acetic acid, this latter only appearing when high solar radiations recovered during the first week of February.

#### 4.3.2. Temporal Variability of Acetic Acid Levels

[28] We here examine the variability of summer levels of acetic acid with respect to weather conditions encountered at the site. In addition to the unusually high value in December 2010, the summer levels of acetic acid exhibit lower concentrations in 2007/2008 and 2008/2009 compared to those in 2005/2006 and 2006/2007 (Figure 2). Acetic acid levels reached similar high levels between 4000 and 6000 ng m<sup>-3</sup> during summers 2005/06 and 2006/07 but they took place during the first summer half in 2005 and the second half in 2007 (Figure 7). Over the two summers, weather conditions were characterized by several periods of significant snowfall followed by sunny days. In 2005/06 four main snowfall events took place during the end of November, mid December, the first week of January and mid February. After the first two snow events, weather improved during several days with positive temperatures and the levels of acetic acid showed a large increase above 4000 ng m<sup>-3</sup>. After the snowy period at the beginning of January 2006 weather remained rather cloudy and the recovery of acetic acid concentrations was limited around 3000 ng m<sup>-3</sup>. Finally a response of acetic acid to the last snow event can be observed but remained weak possibly due to temperatures remaining well below



**Figure 8.** Same as Figure 7 for summer 2007/2008 and 2010/2011. Note the change of y-scales in 2010 for acetic acid concentrations as well as for the temperatures.

zero and/or decreasing solar radiations at the end of summer. Summer 2006/07 was rather similar to 2005/06 one, but high levels (4000 to 6000  $\text{ng m}^{-3}$ ) of acetic acid occurred later (in January and during the first half of February) when the most important snowfalls followed by sunny periods with positive temperatures took place (Figure 7). With respect to these two summers, summer 2007/08 was a bit colder and far more sunny and drier with very few snow events except in February when temperatures already became already negative. Drier conditions are likely responsible for the rather low concentrations of acetic acid that never exceeded 2000  $\text{ng m}^{-3}$ . Similar sunny conditions also occurred during summer 2008/09, at least until mid January (not shown).

[29] Spring 2010 was characterized by a set of several severe snowstorms accompanying the arrival of low-pressure systems (938 hPa September 5, 939 hPa October 24, and 949 hPa November 17). The persistence of negative temperatures until December 6 (Figure 8) led to an exceptional accumulation of snow at the ground. Then temperatures suddenly rose to reach the exceptional value of  $+8^{\circ}\text{C}$  on December 11. The second part of December was marked by cloudy conditions, with frequent little snowfalls accompanied by mild temperatures. These conditions led to maintain high humidity in ornithogenic soils. Finally the recovery of sunny conditions during the last days of December accompanied the unprecedented high level of acetic acid (Figure 8). These unusual weather conditions also affected birds breeding success, with lower hatching success in 2010 compared to

previous years. There were on average  $1.25 \pm 0.18$  chicks per nest at hatching in 2010/11 instead of  $1.46 \pm 0.12$  and  $1.60 \pm 0.19$  in 2009/10 and 2008/09, respectively. Indeed, Adélie penguins facing severe weather conditions (blizzard followed by warm temperatures) showed decreased incubation temperatures, which might affect embryonic development and chicks' condition at hatching.

[30] In conclusion, the presence of large penguin colonies at DDU from November to February is responsible for local emissions of ammonia as well acetic acid. The efficiency of the bacterial decomposition of guano seems to highly depend on the occurrence of favorable weather conditions (snowfalls followed or accompanied by positive temperatures) providing enough moisture in ornithogenic soils. An additional condition leading to high atmospheric concentrations of acetic acid appears to be high solar radiations. This last point will be discussed in the two next sections.

## 5. On the Origins of Volatile Organic Compounds Released From Ornithogenic Soils

[31] The ratio of ammonia to acetic acid concentrations appears to be very variable. Ammonia and acetic acid trapped in mist chamber samples collected at "labo 3" between February 1995 and January 2000 (see ammonia values reported in Table 1), indicate a typical median ratio of 8 (4 and 20 for 25th and 75th quartiles, respectively) in summer (from November to February) with values ranging between

2 and 295. A similar range is observed for the continuous record (January/February 1999 at “labo 3”) reported in Figure 5 with values of the ratio ranging between 1 and 300 (median value of 7 with 3.2 and 23 for 25th and 75th quartiles, respectively). At the end of December 2010 at “labo 3” the ratio of ammonia to acetic acid concentrations was close to 3–4 during night and 1.5 at noon (Figure 3). At “iono” (Figure 6), discarding the period over which the wind was blowing from the marine sector as January 5 in the afternoon (see section 4.3), the first week of January was characterized by ratios remaining in the lower range (median value of 2.6 with 1.3 and 7 for 25th and 75th quartiles, respectively) as it was observed at “labo 3” a few days before (end of December 2010). Two days after the January 8–10 snowstorm values of the ammonia to acetic acid ratio ranged between 10 and 60 for 25th and 75th quartiles, respectively. During the second main snow event (January 23–28), ammonia to acetic acid ratio reached very high values (median value of 750 with 600 and 880 for 25th and 75th quartiles, respectively). Then they gradually dropped to a median value of 78 (with 27 and 180 for 25th and 75th quartiles, respectively) from January 31 to February 1 and to 50 (with 8 and 100 for 25th and 75th quartiles, respectively) during the first days of February (Figure 6). The overall tendency that merges from the respective changes of ammonia and acetic acid is that a high ratio of ammonia to acetic acid is generally observed during and just after a snow event and that the ratio rapidly drops a few days later with recovery of sunny conditions.

[32] As detailed in Appendix A (though more detailed documentation on the respective content of ammonium and acetate and their changes over days are urgently needed), it seems that the high ratio of ammonia to acetic acid seen in the atmosphere corresponds to the early stage of bacterial decomposition induced by a moisture input in soil. This is consistent with the soil composition and the Henry law equilibriums with such alkaline wet material. In the following we discuss parameters and processes that may cause the observed decrease of the ratio of ammonia to acetic acid in the atmosphere after the occurrence of a snowfall. First, it is well known that bacterial decomposition concerns nitrogen at the early stage and carbon later on [Paul, 2007]. Such a difference can be seen in the changes of carbon and nitrogen content in the course of penguin guano decomposition [Zdanowski *et al.*, 2005]. The authors reported a rapid decrease of the nitrogen content from 11% to 5.7–6.4% within the first 6 days as a result of uric acid degradation and the subsequent ammonia volatilization from the alkaline material whereas the carbon content decreased less rapidly. Potential precursors of acetic acid and others oxygenated volatile organic compounds (OVOCs, see below) are to be looked for in penguin guano. After deposition, guano is transformed into material that becomes ornithogenic soil in the end, through complex biological and physical processes [Tatur and Myrcha, 1984]. In particular, bacteria play an important role in penguin guano decomposition [Zdanowski *et al.*, 2005] with changes resulting from decomposition of fats, proteins, chitin, nitrogen and carbon, as well as mineral recycling. The role of recovering solar radiation on the decreasing ratio between ammonia and acetic acid may have several causes. First, solar radiation cleaves dissolved organic matter in the top layer of the soil, producing low-

molecular-weight compounds [Kieber *et al.*, 1990; Mopper *et al.*, 1991], while also affecting living organisms through more frequent DNA mutations. Bacteria can rapidly recover from UV stress once they are mixed into deeper layers of the soil or the water column, where they efficiently use the photolytically cleaved dissolved organic material [Kaiser and Herndl, 1997]. Second, as discussed in section 6 (see also Appendix A), acetaldehyde is also released from ornithogenic soils and once in the atmosphere it is oxidized by OH radicals into acetic acid.

## 6. The Role of NMHCs and OVOCs for the Carboxylic Acid Budget

[33] In this section we first discuss the levels of NMHCs and of some OVOCs (other than formic and acetic acids) that were measured in January 2011 at DDU. Then we examine in what extent some of them can act as significant precursors of carboxylic acids.

### 6.1. The NMHC Levels

[34] NMHCs were investigated at “iono” from January 17 to January 19. Over these 3 days, propane, propene, *i* and *n*-butane were most of time below 30 pptv. As discussed in section 2.2, the correct identification of the butenes was difficult but all species detected in the chromatogram in the region of C4-C5 compounds had levels between 0 and 50 pptv. The mixing ratio of ethane measured in the 2 canisters sampled at “iono” was 203 pptv.

[35] Beyersdorf *et al.* [2010] have recently reported levels of light NMHCs (C2-C4) below 10 pptv (except 100 pptv for ethane) at the South Pole in summer. We note that this value of ethane (100 pptv) is in the lowest range of the values measured in the summer marine boundary layer of the southern hemisphere (126–300 pptv [Read *et al.*, 2007]). Our alkanes data (ethane close to 200 pptv, propane and butane lower than 50 pptv) are consistent within a factor of two with measurements obtained in summer by Gros *et al.* [1998] on a Tasmania to the Ross sea transect, by Clarkson *et al.* [1997] at Scott Base (77°51' S, coastal Antarctica) and Read *et al.* [2007] at Halley (75°35' S, coastal Antarctica).

[36] Concerning C3-C4 alkenes, mixing ratios detected at DDU are consistent with the low values reported by Read *et al.* [2007] at Halley in summer (propene mixing ratios ranging from 5 to 40 pptv). On the other hand, Rudolph *et al.* [1989] reported a value of 150 pptv of propene in the coastal Antarctic troposphere in January (monthly averaged over of four years of measurements). The differences between data are not necessarily related to analytical problems since a high variability of mixing ratio of this short live species (lifetime of 1 to 2 days) in relation with a high variability of the marine source is possible. Indeed, a high variability of the marine source of alkenes was recently observed in the Southern Indian Ocean (49°S) by Bonsang *et al.* [2008]. These authors reported alkene mixing ratios in the range of few tens of pptv (with values up to 100–200 pptv), attributing these relatively high values to a marine source. However, they conclude that alkene marine emissions observed at that site may not be representative of a larger scale due to the particular situation of the sampling site characterized by high chlorophyll and high biological activity as suggested by levels of DMS up to

**Table 3.** Estimated Mixing Ratios of Formic and Acetic Acids After 7 Days due to Ozone Alkene Reactions and Production of Acetic Acid From OH Oxidation of acetaldehyde Under Different Mixing Ratios of Ozone, NO and OH<sup>a</sup>

CH <sub>3</sub> CHO (pptv)	O <sub>3</sub> (ppbv)	NO (pptv)	OH (molecules cm <sup>-3</sup> )	HCOOH (pptv)	CH <sub>3</sub> COOH (pptv)
0	15			39 (23)	4 (2)
	30			79 (46)	8 (5)
70	15	1.5	2.5 10 <sup>5</sup>	39 (23)	62 (36)
	30	15	2.1 10 <sup>6</sup>	79 (46)	220 (128)
	30	30	2.1 10 <sup>6</sup>	79 (46)	126 (73)
500	15	1.5	2.5 10 <sup>5</sup>	39 (23)	376 (218)
	30	15	2.1 10 <sup>6</sup>	79 (46)	1518 (882)
	30	30	2.1 10 <sup>6</sup>	79 (46)	849 (494)

<sup>a</sup>Using 24 h averaged values; see section 6. Calculations were made assuming 100 pptv of ethene, 30 pptv of propene, and 50 pptv for butene and pentene (see section 6). Numbers in parentheses are obtained when a dry deposition process of formic and acetic is assumed.

700 pptv measured at the same time. In January 2011 the DMS levels at DDU ranged between 13 and 290 pptv (70 ± 70 pptv) (not shown). The few NMHCs data available at DDU in January correspond to a period during which DMS levels remained rather moderated (60–80 pptv). However, no hydrocarbon measurements were performed during the period with high DMS levels, as on January 5 (290 pptv of DMS) in relation with a marine air mass advected at the site (see S. Preunkert et al., Oxidant Production over Antarctic Land and its Export (OPALE) project: An overview of the 2010–2011 summer campaign, submitted to *Journal of Geophysical Research*, 2012). Therefore we cannot exclude that higher levels of alkenes can occasionally be observed.

## 6.2. The OVOC Levels

[37] As discussed in section 5, levels of both acetaldehyde and acetone as well as those of ammonia may be influenced by the presence of penguin colonies at DDU. The two periods over which ammonia levels were very low (January 7 to January 9, and January 19 to January 23, Figure 6) are also characterized by the lowest mixing ratios of acetone and acetaldehyde. For instance, the period between 00:00 and 12:00 January 22 can be considered as representative of background conditions since wind continuously blowing from the continent (120°–140°E) at a very high speed (20 m s<sup>-1</sup>) would have strongly minimized the effect of local emissions (Figure 6). The hereby determined background values are 80 ± 12 pptv and 128 ± 9 pptv for acetaldehyde and acetone, respectively. Over the rest of the time, penguin emissions significantly impacted the site and higher values were observed for the two species. For instance, between January 11 and January 14 when, as suggested by high levels of ammonia (Figure 6), the site was significantly impacted by penguin emissions, higher mixing ratios (not shown) were observed (270 ± 70 pptv of acetaldehyde and 230 ± 70 pptv of acetone).

[38] The background value of acetone is consistent with several other measurements made in the high southern latitude marine boundary layer. Deploying a PTR-MS at Cape Grim (Tasmania, 40.68°S), *Galbally et al.* [2007] reported acetone values of 118 ± 5 pptv for late summer 2006. The values at Cape Grim and DDU are among the lowest measured in the troposphere and are also in good agreement

with those (121 ± 34 pptv) observed by *Williams et al.* [2010] on a cruise in the southern Atlantic Ocean. Note also that the minimum of acetone mixing ratio reported by *Colomb et al.* [2009] along a southern Indian Ocean transect (from 24° to 49°S) in December 2004 was much higher (420 ± 90 pptv) than values we observed at DDU. However, given the acetone lifetime of several weeks, the values reported by *Colomb et al.* [2009] may have still be influenced by continental emissions as suggested by the latitudinal decrease observed by the authors (from more than 1 ppbv at 24°S to less than 400 pptv at 40°S).

[39] Our background level of acetaldehyde at DDU lies in the lower range of those observed in the Indian Southern Ocean at 40°S (120 ± 40 pptv [*Colomb et al.*, 2009]). Measurements of acetaldehyde at Cape Grim [*Galbally et al.*, 2007] showed a much lower value, below 4 pptv during 15 days of measurements in February–March 2006. Recently, *Millet et al.* [2010] establishing the first global atmospheric budget of acetaldehyde demonstrated that oceans represent the second largest source at the global scale. The authors simulated annual mean mixing ratios in the lower troposphere at high southern latitudes and the annual average ranging between 5 and 50 pptv. Such a high variability of the oceanic source has to be considered when comparing the levels at Cape Grim and at DDU.

## 6.3. The Production of Formic and Acetic Acids From Oxidation of NMHCs and OCOVs

[40] In Table 3 we estimated the productions of formic and acetic acids from alkene-ozone reactions and of acetic acid from the OH oxidation of acetaldehyde in summer at DDU. We here have neglected the production of acetic acid from the OH reaction of acetone that is two orders of magnitude slower than the acetaldehyde one (1.5 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> instead of 1.7 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, see Table 4). Calculations were made at a temperature of 273 K using kinetic rates summarized in Table 4 and yields from *Carter* [1990]. A dry deposition velocity of 0.2 cm s<sup>-1</sup> was assumed for carboxylic acids leading to a lifetime of 6 days for a marine boundary layer of 1000 m height. Referring to above discussions, calculations were made assuming 100 pptv of ethene, 30 pptv of propene, and

**Table 4.** Temperature-Dependent Kinetic Rates (k in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) Used in Discussion<sup>a</sup>

Reactions	Kinetic and Thermodynamic Data
Ethene + O <sub>3</sub> → CH <sub>2</sub> OO + CH <sub>2</sub> O	2.0 10 <sup>-12</sup> exp [438/T] Formic yield (0.37)
Propene + O <sub>3</sub> → CH <sub>2</sub> OO + CH <sub>3</sub> CHO	5.5 10 <sup>-15</sup> exp [-1878/T] Formic yield (0.185), Acetic yield (0.10)
Butene + O <sub>3</sub> → CH <sub>2</sub> OO + C <sub>2</sub> H <sub>5</sub> CHO	3.4 10 <sup>-15</sup> exp [-1744/T] Formic yield (0.185)
Pentene + O <sub>3</sub> → CH <sub>2</sub> OO + C <sub>4</sub> H <sub>9</sub> CHO	3.4 10 <sup>-15</sup> exp [-1744/T] Formic yield (0.185)
CH <sub>3</sub> CHO + OH → CH <sub>3</sub> CO	5.6 10 <sup>-12</sup> exp [310/T]
CH <sub>3</sub> CO <sub>3</sub> + HO <sub>2</sub> → CH <sub>3</sub> COOH + O <sub>3</sub>	4.3 × 10 <sup>-13</sup> exp [1040/T] γ <sub>1</sub> = 8.5 10 <sup>-3</sup> exp [1020/T]
CH <sub>3</sub> CO <sub>3</sub> + CH <sub>3</sub> O <sub>2</sub> → CH <sub>3</sub> COOH + HCHO + O <sub>2</sub>	5.1 10 <sup>-12</sup> exp [272/T] γ <sub>2</sub> = 6.1 10 <sup>-6</sup> exp [2990/T]
CH <sub>3</sub> CO <sub>3</sub> + NO → CH <sub>3</sub> COO + NO <sub>2</sub>	7.5 10 <sup>-12</sup> exp [290/T]

<sup>a</sup>Gas phase reaction kinetics are from *Atkinson* [1997] and *Atkinson et al.* [1997] and references therein.

50 pptv for butene and pentene. For acetaldehyde calculations were made using different acetaldehyde mixing ratios (Table 3) since as previously discussed the level of this species is strongly influenced by penguin emissions. Sensitivity tests were made with respect to oxidative capacity of the lower atmosphere at DDU. That includes “a low oxidant case” with typical oxidants and NO levels for remote marine boundary layer at 66°S simulated by the 3-D transport and chemistry IMAGE model [Müller and Brasseur, 1995]. Levels of ozone [Legrand *et al.*, 2009; Preunkert *et al.*, submitted manuscript, 2012] and OH (A. Kukui *et al.*, Measurements of OH and RO<sub>2</sub> radicals at the coastal Antarctic site of Dumont d’Urville (East Antarctica) in summer, submitted to *Journal of Geophysical Research*, 2012) observed at DDU largely exceed model simulations. Thus a “high oxidant case” related to the export of very oxidizing inland Antarctic air masses reaching the coast, that would represent a more realistic assumption for DDU, was also considered. As discussed by Kukui *et al.* (submitted manuscript, 2012) the observed 24 h averaged OH concentrations of 2.1 10<sup>6</sup> molecules cm<sup>-3</sup> requires NO ranging between 6 and 30 pptv. Table 3 shows that the production of formic acid from alkene-ozone reactions can account for significant levels (from 20 to 50 pptv after 7 days). They remain however below the observed summer mixing ratio of 100 pptv (Table 1).

[41] Whereas alkene-ozone reactions produce even less acetic acid than formic acid in summer at DDU (Table 3), the oxidation of CH<sub>3</sub>CHO may represent a significant secondary source of acetic acid. Note that the efficiency of this production is enhanced at high OH concentrations but, due to the destruction of CH<sub>3</sub>CO<sub>3</sub> by NO, the increase is partly counteracted by the concomitant increase of NO. Considering a moderated NO level of 15 pptv, acetic acid mixing ratio would reach 900 pptv after 7 days if a high mixing ratio of acetaldehyde (500 pptv) is assumed as it was the case at “iono” during periods of significant impact of penguin emissions. Note this value would be even higher at “labo 3” due to quasi-permanent emissions from penguin colonies. This significant secondary production of acetic acid from OH acetaldehyde reaction would partly explain the absence of high levels of acetic acid when solar radiations remained low, as emphasized in section 4.3. Note that when an acetaldehyde mixing ratio representative of free penguin conditions is assumed (70 pptv), between 40 and 130 pptv of acetic acid can accumulate over 7 days (Table 3). These ranges are consistent with values observed at DC (60 pptv, section 4.2) but are 10 times lower than observations made at DDU.

[42] For winter, calculations were made assuming ethene and propene winter mixing ratios reported for Halley by Read *et al.* [2007] (13 and 5 pptv, respectively) and an ozone mixing ratio of 35 ppbv [Legrand *et al.*, 2009]. With that ozone alkene reactions may account for the few pptv of formic and acetic acids detected in winter at DDU (Table 1).

## 7. Conclusions

[43] This second study of formic and acetic acid present in the lower atmosphere at the coastal Antarctic site of DDU confirms their abundance in this very remote marine boundary layer in summer with mixing ratio reaching 100 pptv for formic acid and 700 pptv for acetic acid. However,

investigated levels of their potential marine alkene precursors were well below 100 pptv and failed to explain such high summer acetic acid values. In addition, the even larger acetic acid levels observed beginning of summer 2010/2011 (mean value of 5 ppbv) claimed to reassess the budget of light carboxylic acids at this site. These unusually high levels of acetic acid were accompanied by unusually high levels of ammonia (up to 80 ppbv end of December), and by an enrichment of oxalate in aerosols with respect to preceding summers. These observations suggest that guano decomposition from the large penguin colonies present at the site in summer was particularly strong under weather conditions encountered in spring 2010 (snowstorms followed by mild temperatures providing moisture in ornithogenic soils). It appears that at DDU these ornithogenic emissions represent the main source of acetic acid in summer. This local source also significantly impacts the local atmospheric budget of other OVOCs like acetaldehyde and acetone, and in a lesser extent of formaldehyde. These large emissions of ammonia and OVOCs have some consequences in local sources and sinks of OH and RO<sub>2</sub> radicals as discussed in the companion paper from Kukui *et al.* (2012).

[44] Finally, formic acid mixing ratios close to 100 pptv observed at both DDU and DC in summer, may correspond to background atmospheric Antarctic conditions. As already concluded in several previous studies (see Baboukas *et al.* [2000] for marine remote conditions at southern latitudes), the chemistry of alkenes is not sufficient alone to explain such formic acid levels. In contrast, the chemistry of acetaldehyde can account for 40–130 pptv of acetic acid, a value close to those observed inland Antarctica and thought to be representative of background atmosphere Antarctic conditions (free of penguin emissions).

## Appendix A: The Release of Gases From Ornithogenic Soils

[45] The chemistry of ornithogenic soils was documented by Speir and Cowling [1984], including pH values, often found to be close to 8. The authors reported nitrogen composition of soils occupied by Adélie penguin showing that, aside from uric acid which represents more than a half of nitrogen mass, ammonium is the dominant ion (53 mg per g<sup>-1</sup> soil instead of 300 μg g<sup>-1</sup> soil and 15 μg g<sup>-1</sup> soil for nitrate and nitrite, respectively). To our knowledge, only one study investigated acetate in occupied ornithogenic soils showing rather scattered values, 700 ± 500 mg per g<sup>-1</sup> soil as a mean (±1 standard deviation) of three replicates [Roser *et al.*, 1994]. The ratio of ammonia to acetic acid concentrations (C<sub>NH<sub>3</sub></sub>/C<sub>CH<sub>3</sub>COOH</sub>) in an atmosphere in equilibrium with an ornithogenic soil is proportional to the ratio of ammonium to acetate content of the soil (M<sub>NH<sub>4</sub><sup>+</sup></sub>/M<sub>CH<sub>3</sub>COO<sup>-</sup></sub>) and inversely proportional to the ratio of ammonia to acetic acid effective Henry’s laws coefficients as follows:

$$\frac{C_{\text{NH}_3}}{C_{\text{CH}_3\text{COOH}}} = \left( \frac{M_{\text{NH}_4^+}}{M_{\text{CH}_3\text{COO}^-}} \right)_{\text{soil}} \frac{H_{\text{CH}_3\text{COOH}}}{(1 + K_a/[H^+]) / H_{\text{NH}_3} (1 + K_b/[OH^-])} \quad (\text{A1})$$

Calculations were made at a temperature of 273 K using Henry Law’s equilibrium (H) and acidity constants (K<sub>a</sub> or K<sub>b</sub>) reported in Table A1. Assuming that 700 mg of acetate [Roser *et al.*, 1994] and 53 mg of ammonium [Speir and



Cowling, 1984] are present in one gram of soil, equation 1 suggests that around 6000 more ammonia than acetic acid would be present in the gas phase in equilibrium with a soil at a pH of 8. Less ammonia and more acetic acid leading to a factor of 60 are expected at a pH of 7.

[46] Preceding calculations, based on very limited chemical documentation of the ornithogenic soils, have to be considered carefully since, as discussed later, the ratio of ammonium to acetate in soils likely varies over time. We therefore conducted an experiment in the field on water sampled January 25 in a pool of water formed on the occupied ornithogenic soils in the vicinity of “labo 3” during melting of snow accumulated at the ground January 22 and 23 (see Figure 6 for weather conditions) The 1 L water sample was purged by pumping air through a fritted glass at a flow rate of 3.5 L per min. The escaping gases were trapped in two mist chambers in series for determinations of anions and cations including ammonium and carboxylates. A blank of the experiment was done by purging 1 L ultrapure water with air and was found to be insignificant. Data reported in Table A2 indicate that ammonia was some 300 times more abundant than acetic acid. A similar experiment was replicated in the LGGE lab (by mixing ornithogenic soil also sampled nearby “labo 3” in ultrapure water) giving a similar ratio of ammonia to acetic acid (600). Interestingly these values of the ratio between ammonia and acetic acid are consistent with the median ratio of 745 observed in the atmosphere at DDU from January 23 to January 28 (see section 5).

[47] The gases escaping were also sucked into the PTR-MS device for OVOCs investigations as well as in an Aerolaser (AL 4021) to analyze HCHO (see details provided by Preunkert et al. (submitted manuscript, 2012)). As seen in Table A2, in addition to acetic acid other OVOCs were also released in particular acetaldehyde and acetone. Consistently with a higher effective Henry law constant (see Table A1) and a lower amount in ornithogenic soils [Roser et al., 1994], less formic acid than acetic acid was released (Table A2). Finally a small amount of HCHO was found to escape from the water collected on ornithogenic soils (Table A2). Such a

**Table A1.** Henry’s Law Coefficients (H in M atm<sup>-1</sup>) Used in Discussion<sup>a</sup>

Gases	Henry’s Law Equilibrium (H) and Acidity Constant (K)
HCHO	3200 exp [6800 (1/T – 1/298)]
CH <sub>3</sub> CHO	14 exp [5600 (1/T – 1/298)]
CH <sub>3</sub> COCH <sub>3</sub>	30 exp [4600 (1/T – 1/298)]
HCOOH	H <sub>HCOOH</sub> = 5400 exp [5700 (1/T – 1/298)] K <sub>a</sub> = 1.8 10 <sup>-4</sup> exp [151 (1/T – 1/298)]
CH <sub>3</sub> COOH	H <sub>CH<sub>3</sub>COOH</sub> = 5500 exp [6300 (1/T – 1/298)] K <sub>a</sub> = 1.7 10 <sup>-5</sup> exp [50 (1/T – 1/298)]
HONO	H <sub>HONO</sub> = 50 exp [4900 (1/T – 1/298)] K <sub>a</sub> = 5.1 10 <sup>-4</sup> exp [–1260 (1/T – 1/298)]
HNO <sub>3</sub>	H <sub>HNO<sub>3</sub></sub> = 2.1 10 <sup>5</sup> exp [8700 (1/T – 1/298)] K <sub>a</sub> = 15.4 exp [8700 (1/T – 1/298)]
NH <sub>3</sub>	H <sub>NH<sub>3</sub></sub> = 27 exp [2100 (1/T – 1/298)] K <sub>b</sub> = 1.75 10 <sup>-5</sup> exp [–450 (1/T – 1/298)]

<sup>a</sup>Henry’s law coefficients of HCHO, CH<sub>3</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub>, HCOOH, and CH<sub>3</sub>COOH are from Staudinger and Roberts [1996], HONO from Becker et al. [1996], HNO<sub>3</sub> from Lelieveld and Crutzen [1991], and NH<sub>3</sub> from Dean [1992]. Acid equilibrium constants (K<sub>a</sub> in M) are from Chao and Zwolinski [1978] for HCOOH and CH<sub>3</sub>COOH, from Schwartz and White [1981] for HONO and HNO<sub>3</sub>, and Smith and Martell [1976] for NH<sub>3</sub>.

**Table A2.** Mixing Ratios and Concentrations of Species Detected in Air Escaping From a Liquid Ornithogenic Soil Sample Collected at DDU in January 2011<sup>a</sup>

Compounds	Concentrations (ng m <sup>-3</sup> )	Mixing Ratios (ppbv)
HCHO	1150	1.0
HCOOH	2950	1.6
CH <sub>3</sub> CHO	28,850	16
CH <sub>3</sub> COOH	36,900	15
CH <sub>3</sub> COCH <sub>3</sub>	57,050	24
NH <sub>3</sub>	11434,000	15,500

<sup>a</sup>See section 5. Note that, apart from ammonia, no significant amount of other nitrogen species like HONO or HNO<sub>3</sub> were detected.

small release of HCHO from ornithogenic soils is in agreement with the estimated rather weak contribution of this source to the mean level observed at “labo 3” by Pépy [2011] (on average 80 pptv compared to a mean observed HCHO level of 260 pptv in January). Finally, aside from ammonium, no other nitrogen species (neither nitrite nor nitrate) were detected in the mist chambers. The absence of HONO and HNO<sub>3</sub> in the escaping gases is expected given their very high solubility in water at pH 8 with respect to the ammonia one and their weaker abundance in soils reported by Speir and Cowling [1984]. For instance, HONO is 8000 times more soluble than NH<sub>3</sub> in water at pH 8 (see Table A1) and 3000 times less abundant in soils (15 μg g<sup>-1</sup> soil) than ammonium. According to equation (A1) its presence in soils would therefore not significantly impact atmospheric levels of HONO which is present at DDU at mixing ratio of a few pptv (M. Kerbrat et al., Nitrous acid at Concordia on the East Antarctic Plateau and its transport to the coastal site of Dumont d’Urville, submitted to *Journal of Geophysical Research*, 2012). Whereas the significance of ornithogenic soil emissions on the lower atmosphere at a local scale were already pointed out for ammonia [Legrand et al., 1998] and greenhouse gases like CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O [Zhu et al., 2009], to our knowledge the present study first reports on the significance of emissions of several OVOCs from the decomposition of organic compounds present in guano.

[48] **Acknowledgments.** We thank the over-wintering crews at Dumont d’Urville and Concordia for careful sample collection as well as performing the measurements at Dumont d’Urville. We thank Mireille RACCURT from laboratoire de Physiologie Intégrative, Cellulaire et Moléculaire - PICM (CNRS, Université Lyon 1) for fruitful discussions during the summer campaign. We thank Météo France, who provides us meteorological data. National financial support and field logistic supplies for winter and summer campaigns were provided by Institut Polaire Français-Paul Emile Victor (IPEV) within program 414. This work was also partly funded by the Centre National de la Recherche Scientifique (INSU), CEA and the region Ile de France, and the OPALÉ project supported by the ANR (Agence National de Recherche, contract ANR-09-BLAN-0226).

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