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Marine and land-based influences on atmospheric ammonia and ammonium over Tenerife

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ABSTRACT

Concentrations of gaseous ammonia ($[NH_3]$) and aerosol ammonium ($[NH_4^+]$) were measured across Tenerife as part of the ACE-2 "HILLCLOUD" experiment to assess the effect of cloud processing on the marine budget of reduced nitrogen (NH_x). Several methods for measuring NH_3 were applied: continuous rotating annular denuder, diffusion scrubber and multi-stage filter packs, with the latter also measuring NH_4^+. The measurement sites were located both upwind and downwind of the hill-cloud. Terrestrial NH_3 sources provide a major constraint in addressing marine NH_x from land-based studies, and the measurements showed local NH_3 emissions from both decomposing potato fields and livestock. $[NH_3]$ was correlated between upwind and downwind sites; at high $[NH_3]$ ($>0.5\ \mu g\ m^{-3}$) values were larger downwind than upwind, indicating the importance of island sources. In contrast, at high $[NH_4^+]$ ($>0.5\ \mu g\ m^{-3}$), $[NH_4^+]$ was significantly smaller downwind than upwind, while at low $[NH_4^+]$ ($0.2\ \mu g\ m^{-3}$), the opposite was observed. The decrease in $[NH_4^+]$ suggests that cloud processing in high $[NH_4^+]$ conditions may enhance the evaporation of NH_3 from NH_4^+ in cloud, while NH_4^+ aerosol formation could occur at low $[NH_4^+]$. Analysis of the average diurnal variability in $[NH_3]$ and $[NH_4^+]$ at the different sites suggests that both NH_3 emissions and post-cloud evaporation of NH_4^+ to NH_3 are largest during the day, coupled with increased temperatures and reduced relative humidities. Although the marine NH_4^+ aerosol is mostly present as non-volatile ammonium sulphate, evaporation of NH_4^+ at high $[NH_4^+]$ may be explained by in-cloud mixing with nitrate and chloride leading to the production of NH_4NO_3 and NH_4Cl which are subsequently volatilized on leaving the cloud.

1. Introduction

Atmospheric ammonia (NH_3) is well known to be the dominant gaseous base for reaction with atmospheric acids in both terrestrial and marine atmospheres. As such it plays a central role in regulating the partitioning between gaseous and particulate phases. The reaction of NH_3 with acidic sulphate aerosol is generally seen as irreversible, because the vapour pressure of ammonium sulphate is small (Seinfeld and Pandis, 1998). However, reaction with both nitric acid and hydrochloric acid is reversible, due to the significant vapour pressures of ammonium nitrate and ammonium chloride (Pio and Harrison, 1987; Mozurkewich, 1993). Since atmospheric residence times of the aerosol and gaseous phases are

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different, NH_3 plays an important role in regulating the transport distances of atmospheric acids. In addition, through direct light scattering effects and indirect effect of aerosol as cloud condensation nuclei (CCN), aerosols provide the largest negative radiation forcing potential of trace atmospheric constituents on global climate (IPCC, 1996). Hence, while concentrations of NH_3 are far too small to have any direct warming effect, NH_3 can have a significant negative effect on radiative forcing through the production of ammonium (NH_4^+) containing aerosols. Although these effects have been known for a number of years, there remain large uncertainties in the estimates of the radiative forcing of aerosols, with the greatest uncertainty being in the estimates of the indirect effect linked to cloud processing.

The North Atlantic Regional Aerosol Characterisation Experiment (ACE-2) was established to help characterise these effects, thereby reducing uncertainty of the estimates and providing data for global climate models (Raes et al., 2000). ACE-2 consisted of 5 major experiments, of which HILLCLOUD was established to utilise a hill cap cloud on the north east Anaga ridge of Tenerife to investigate cloud processes from land-based measurements (Bower et al., 2000). As part of HILLCLOUD, gaseous NH_3 and aerosol NH_4^+ measurements were made upwind and downwind of the Tenerife ridge, together with ground-based measurements of cloud NH_4^+, made during times when the ridge was immersed in cloud.

In the present paper we examine whether it is possible to detect unaffected marine $[NH_3]$ and $[NH_4^+]$ from land-based measurements. Other key questions are whether effects of cloud processing can be detected from measurements up and downwind of a cap cloud and what other influences, apart from cloud, might affect the budget of NH_3 and NH_4^+, as they are advected over a mountain ridge. In order to answer these questions we consider vertical concentration profiles of $[NH_3]$, compare $[NH_3]$ and $[NH_4^+]$ at the different sampling sites and examine the diurnal variability of these concentrations. Anticipated influences which are considered include emission of NH_3 from terrestrial and marine sources, deposition of NH_3 and NH_4^+, gas-aerosol reactions and cloud processing. A fuller investigation of the role of NH_3 and NH_4^+ in cloud processing will be conducted at a later stage together with the application of cloud chemistry models (Bower et al. 1995).

2. Sites and measurement methods

2.1. Measurement sites

Atmospheric ammonia (NH_3) and ammonium (NH_4^+) were measured at 3 locations in the ACE-2 campaign to provide inputs for the cloud processing project HILLCLOUD. Two of these sites were upwind of cloud; the first was located in the village of Taganana at 220 m above sea level (asl), 1 km inland, and the other was located at a lighthouse at Punta del Hidalgo (lighthouse top, 55 m asl), approximately 10 km west of Taganana. The downwind site was at Paiba (500 m asl), approximately 1 km SE of the Anaga ridge which runs WSW–ENE at the E end of Tenerife. The measurements at Paiba were made in a small agricultural clearing in the low cloud-forest characterized by *Erica arborea* L. (tree heath), typically 2–4 m tall. In addition to these main sites, shorter duration measurements of NH_3 were made at the ridge top site, El Bailadero (660 m asl), for a period when the site was not immersed in cloud. Sampling at this site was immediately above the forest. For a map and full description of the location and nature of these sites see Bower et al. (2000).

2.2. Measurement methods

Three different measurement techniques were applied during the ACE-2 campaign, summarised in Table 1. The first technique involves an instrument referred to as AMANDA (Ammonia Measurement by ANnular Denuder sampling with online Analysis). This technique captures gaseous ammonia in a continuous flow annular denuder using a stripping solution of 3.6 mM sodium hydrogen sulphate ($NaHSO_4$) and determines the concentration online by analysing the conductivity. A full description of this method is given in Wyers et al. (1993) and Sutton et al. (1997). The instrument was operated with a 2-min time resolution and therefore allows a detailed investigation of the underlying processes determining NH_3 concentrations. Calibrations were conducted weekly with aqueous standards of NH_4^+. The detection limit is approximately 0.02 $\mu g\, m^{-3}$ NH_3 in air.

The instrument can operate with 3 denuders which when placed at 3 heights allow vertical gradient measurements to be made. Alternatively, 2 of the denuders can be utilised to measure concentration differences between inlet and outlet of a cuvette, a method regularly used to investigate gas exchange with vegetation (Husted and Schjoerring, 1995). An estimate of the precision can be obtained from duplicate sampling at Punta del Hidalgo (Fig. 5), the standard deviation of the difference in concentration estimates was 0.03 $\mu g\,m^{-3}$ at a mean concentration of 0.23 $\mu g\,m^{-3}$ ($n = 677$, 10-min values).

The other automatic technique used to measure NH_3 was a semi-continuous diffusion scrubber flow-injection analyser (Genfa et al., 1989; Dasgupta, 1993). The system was designed to operate continuously. However, failure of a switching valve at the start of the experiment required the instrument to be redeployed using a 30-min time resolution. This system was also calibrated in the field with aqueous standards. Sampling during a period of near constant $[NH_3]$ gives an upper estimate of the system precision; at a concentration of 0.38 $\mu g\,m^{-3}$ the standard deviation of concentration estimates was 0.03 $\mu g\,m^{-3}$ ($n = 10$, half-hourly values).

In addition to these measurements, gaseous NH_3 and aerosol NH_4^+ were measured throughout most of the campaign by multi-stage filter packs, with a 3-h time resolution. Aerosol was collected in 2 size fractions, coarse (aerodynamic diameter >2.5 μm) and fine (aerodynamic diameter <2.5 μm) on 12 μm pore size Nucleopore polycarbonate filters and 1 μm pore size PTFE prefilters, respectively. A range of other gases (HCl, HNO_3, SO_2, CH_3COOH and HCOOH) were captured on alkali impregnated Whatman 41 cellulose filters whilst NH_3 was captured on a subsequent acidified cellulose filter (Whatman 41). For further details on the implementation and analytical procedures for the filter packs see Allen et al. (1997). Detection limits were determined as 3 standard deviations of field blanks ($n = 6$) and were 5.9, 0.6 and 0.6 $ng\,m^{-3}$ for NH_3, $NH_4^+ < 2.5$ μm and $NH_4^+ > 2.5$ μm, respectively (given a sample volume of 5.4 m^3). Measurements of size segregated chemical composition of the aerosol were also made at Punta del Hidalgo (Bower et al., 2000).

A wide range of meteorological measurements were made to support the interpretation of the chemical measurements, including wind direction and speed, boundary layer depth, height of cloud base, temperature and humidity (Bower et al., 2000). For the present paper, interpretation is restricted to interactions with air temperature, relative humidity and windspeed.

2.3. Measurement strategy

The HILLCLOUD measurement campaign lasted 6 weeks with NH_x sampling covering the period 18/6 to 25/7/1997. During most of this

Table 1. *Summary of NH_3 and NH_4^+ measurement techniques operated during the ACE-2 HILLCLOUD experiment*

Method technique	Measurements	Sites (site code)	Period	Operating institute
AMANDA continuous annular denuder	NH_3	Paiba (TG3)	18–25/6/97	ITE, UK
		El Bailadero (TG2)	25–26/6/97	
		Taganana (TG1)	26/6–15/7/97	
		Punta del Hidalgo (PDH)	15–23/7/97	
Filter packs	NH_3, NH_4^+ (fine and coarse aerosol)	Paiba (TG3)	28/6–23/7/97	University of Birmingham, UK
		Taganana (TG1)	28/6–23/7/97	
		Punta del Hidalgo (PDH)	29/6–25/7/97	Lancaster University, UK
Diffusion scrubber FIA	NH_3	Paiba (TG3)	18/6–23/7/97	ITML, Sweden

period the filter packs and diffusion scrubber operated continuously whilst the AMANDA was deployed at 4 different locations (Table 1). Initially, the AMANDA was located at Paiba (TG3) to conduct an intercomparison with the diffusion scrubber. The intercomparison was essential in order to allow between-site differences in concentrations to be interpreted with confidence during the main period of the campaign. The availability of the 3 denuders of AMANDA permitted vertical profiles of $[NH_3]$ to be determined at Paiba (0.2–5.5 m above ground). As will be shown in Section 3, the vertical profiles indicated the existence of local sources of NH_3 at Paiba. Since the AMANDA provides on-line analysis, this was recognized directly in the field. The AMANDA system was therefore then used to identify the potential sources. This was done at Paiba by measuring emissions from plant material placed in a clear 3-litre PET cuvette (dynamic chamber). Two of the denuders were used to measure inlet and outlet concentrations (χ) and hence the NH_3 emissions. An estimate of the vegetation flux (F_l) per fresh weight of leaves (in $\mu g\ s^{-1}\ kg^{-1}$ fresh weight), was calculated as:

$$F_l = \frac{\chi_{in} - \chi_{out})}{(f_{air} M_l)}, \quad (1)$$

where χ_{in} and χ_{out} are $[NH_3]$ at the cuvette inlet and outlet, respectively, f_{air} is the air sampling rate through the cuvette ($27\ l\ min^{-1}$), and M_l is the mass of leaves in the cuvette.

After the initial intercomparison period at Paiba, the AMANDA was briefly deployed at El Bailadero (TG2) in order to establish the existence or absence of local sources of NH_3 (sampling height 2–4 m above the top of the cloud-forest). On 26/7/97 the AMANDA was set up at Taganana (TG1) and operated there for the majority of the campaign, providing $[NH_3]$ prior to cloud processing as air passed over the Anaga ridge. Again, the multi-denuder system of the AMANDA was used to quantify vertical profiles of $[NH_3]$ (1–12 m above ground) and identify local sources at Taganana.

As at Paiba, the AMANDA $[NH_3]$ profiles suggested the existence of local NH_3 sources at Taganana. In order to determine the marine background $[NH_3]$ without interference from terrestrial sources the AMANDA was moved during the latter part of the campaign to the lighthouse at Punta del Hidalgo (PDH). Measurements were made on the uppermost terrace of the lighthouse at an elevation of 55 m asl.

3. Intercomparison of NH_3 measurement techniques and assessment of local sources

The following sections detail the intercomparison of NH_3 measurement techniques and the assessment of vertical concentration profiles according to the chronological sequence of sampling at Paiba, El Bailadero, Taganana and Punta del Hidalgo.

3.1. Paiba

The intercomparison period between the AMANDA and the diffusion scrubber highlighted an initial poor temporal agreement between the 2 systems. This was due to the failure of the switching valve on the diffusion scrubber with adsorption/desorption occurring on an inlet line. The inlet was modified, improving agreement between the diffusion scrubber and AMANDA. It should be noted that for NH_3, experiments with teflon and polythene inlets show short-term adsorption/desorption but do not lead to net losses of NH_3 (Mennen et al., 1996; M. A. Sutton, unpublished data). The reason for the problem with the initial inlet of the diffusion scrubber was that the system only flushed the inlet for 10% of the time and at a small flow rate ($3\ l\ min^{-1}$). Fig. 1 shows the level of agreement achieved after the modification, for 30-min sampling periods, which is typically $\pm 35\%$ at an average concentration of $0.25\ \mu g\ m^{-3}$. While the scatter is substantial, the overall agreement is reasonable given the small $[NH_3]$.

A major feature of the AMANDA sampling at Paiba was the observation of significant vertical gradients in $[NH_3]$. Fig. 2 shows example profiles with $[NH_3]$ of approximately $0.3\ \mu g\ m^{-3}$ at 5.5 m above the ground increasing to around $0.7\ \mu g\ m^{-3}$ at 0.2 m. These profiles clearly indicate the existence of local ground-based emissions of NH_3 at Paiba. The most likely source was anticipated to be small potato fields at approximately 10 to 40 m upwind, west and north of the sampling location, particularly the field to the west which had recently been harvested and contained decomposing potato

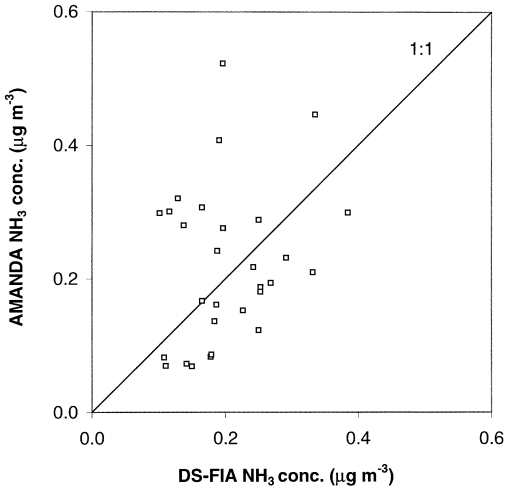

Fig. 1. Comparison of NH_3 concentrations estimated using the AMANDA continuous-flow denuder and the diffusion scrubber with flow injection analysis (DS-FIA) at Paiba (TG3).

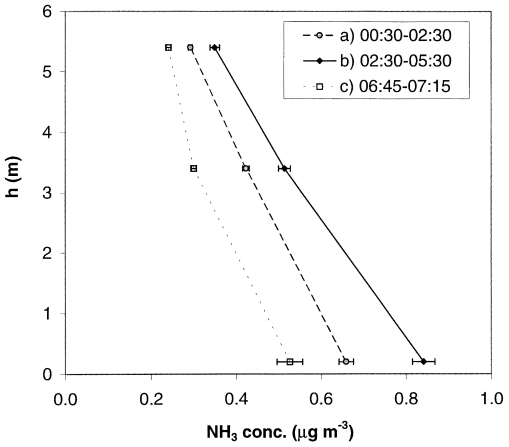

Fig. 2. Example vertical profiles of ammonia concentration measured at Paiba (TG3) on 23 June 1997 using the 3-denuder AMANDA system. Values presented are means of the period $\pm$standard errors (SE), $n = 24$, 36, 6 for the periods (a), (b), and (c), respectively. The uncertainty in the mean estimate includes variability due to changing air concentrations during the sampling period.

leaves. The AMANDA system was used with the cuvette to assess the potential for NH_3 emissions from samples of both live and decaying potato leaves. While no emission flux could be detected from the live leaves, substantial NH_3 was released from the decaying leaves. For example, a sample of approximately 200 g fresh weight provided an NH_3 concentration in the outflow of the cuvette (χ_{out}) of 400 $\mu g\ m^{-3}$, equivalent to an emission of 0.93 $\mu g\ s^{-1}\ kg^{-1}$ fresh weight. Scaling up, for an estimate of fresh weight per hectare, indicated an NH_3 emission flux of the order of 1.4 $kg\ ha^{-1}\ day^{-1}$, or for the field area of approximately 225 m^2, a total emission of 30 g $NH_3\ day^{-1}$. At the sampling height of 5.5 m the effects of localised ground-level sources become indistinguishable from background concentrations, although the measured concentrations may nevertheless include NH_3 from other sources on the island.

3.2. *El Bailadero*

After the initial intercomparison period, the AMANDA was briefly deployed at El Bailadero, which was a site directly above the forest and therefore not expected to be affected by local NH_3 sources. $[NH_3]$ at El Bailadero showed little short term (< 1 h) temporal variability, indicating the presence of well mixed air masses and an absence of local sources. Values of $[NH_3]$ were $< 0.1\ \mu g\ m^{-3}$, with the site not immersed in cloud during this period.

3.3. *Taganana*

With the sampling at Taganana taking place on the edge of a village, it was again considered important to investigate the possibility of local sources of NH_3. A much larger height range was possible with sampling made between 5 m and 10 m above ground on the 3-storey house. It should be noted that the house was located on a ridge, so the aerodynamic height above ground of the upper levels for NW winds was probably much larger (e.g., > 20 m). Measurements of NH_3 were made simultaneously using the AMANDA and filter pack systems located at the same height on a scaffold (10 m) permitting a comparison of the sampling methods (Fig. 3). The existence of local sources was clearly established by the presence of strong gradients of NH_3 with concentration increasing towards the ground. At Taganana the height of the layer affected by local sources was also clearly much larger than at Paiba, with evidence of $[NH_3]$ enhancement even at 8 m. Agricultural land and animals are widely distrib-

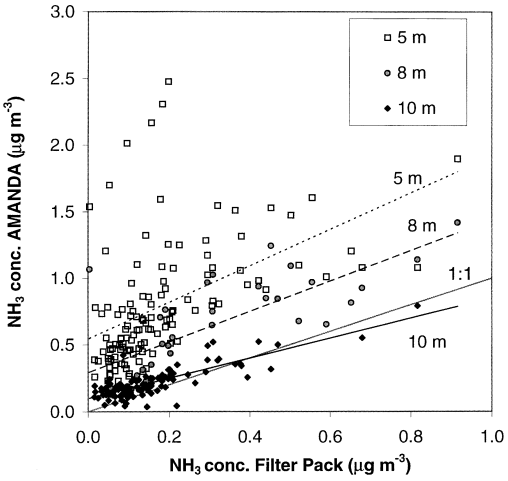

Fig. 3. Comparison of ammonia concentrations sampled at 3 heights by the AMANDA against filter packs (mounted at 10 m), Taganana (TG1).

uted in the vicinity of Taganana, whereas Paiba consists of only a small clearing in the forest. The increased concentration at ground level was probably a result of many small sources including crops, goats and donkeys. For example, sampling within the stable of a single donkey at the immediate base of the house (1 m above ground) gave $[NH_3]$ of 9 $\mu g\,m^{-3}$ during the day, which could have contributed to the elevated $[NH_3]$ at 5 m. This concentration is, in fact, rather small compared with large intensive animal houses where concentrations can exceed 1000 $\mu g\,m^{-3}$.

The comparison between the AMANDA and the filter packs was encouraging, and generally within $\pm 30\%$ at 0.25 $\mu g\,m^{-3}$. Nevertheless, the AMANDA appeared to sample slightly more NH_3 in very clean conditions than the filter packs, with an offset of approximately 0.1 $\mu g\,m^{-3}$ (Fig. 3). The reason for this is not clear, but may be partly due to scatter in the filter pack blanks. Concentration estimates were, of course, corrected for blank values, although it should be noted that the blanks were consistently small. Uncertainties in the AMANDA calibration are also possible, but less likely since calibration was made in situ in the field. A similar pattern was seen for indirect comparisons at Paiba (data not shown).

Having established the existence of more widespread local sources near Taganana, a key question is whether the measurements at the usual top sampling height of 10 m were affected by these sources. To address this, a comparison was made of $[NH_3]$ measured at the different heights against windspeed, since at smaller windspeeds an increase in $[NH_3]$ would be expected from local sources. An example period is shown in Fig. 4, which also compares the results of the AMANDA and filter pack sampling at 10 m. At 5 m above the ground a clear anti-correlation between windspeed and $[NH_3]$ is seen. The increase in $[NH_3]$ is most clear for the night of 1 July 1997, when windspeeds drop to near calm conditions (0.2 $m\,s^{-1}$). In contrast, there appears to be no relationship for $[NH_3]$ at 10 m. This suggests that these measurements were made above the height affected by local sources, although it is possible that the concentrations were still affected by more distant terrestrial NH_3 emissions.

3.4. *Punta del Hidalgo*

Given the uncertainties indicated from the profile measurements at Taganana, the AMANDA measurements at Punta del Hidalgo were made in order to establish $[NH_3]$ for marine air masses unaffected by passage over land. Since the AMANDA provides fast response sampling, the analysis of NH_3 concentrations in relation to wind sectors could be used to establish marine $[NH_3]$. From the measurements at Taganana, concentrations of <0.3 $\mu g\,m^{-3}$ were expected, while significant vertical gradients were not expected since the measurements were made at 55 m. To maximise sensitivity in this situation, NH_3 was sampled in duplicate through 2 denuders, while the third denuder continuously sampled unexposed stripping solution, to provide a continuous estimate of the instrument zero, allowing for any baseline drift during sampling. The temporal structure of the measured NH_3 is shown in Fig. 5, alongside wind direction. Concentrations at this site were in the range 0.07–0.93 $\mu g\,m^{-3}$, with a mean of 0.23 $\mu g\,m^{-3}$ and peak concentrations occurring when the air mass had passed over land (80–240°). Possible terrestrial sources include nearby banana plantations, as well as livestock and a small town more than 0.5 km from the lighthouse.

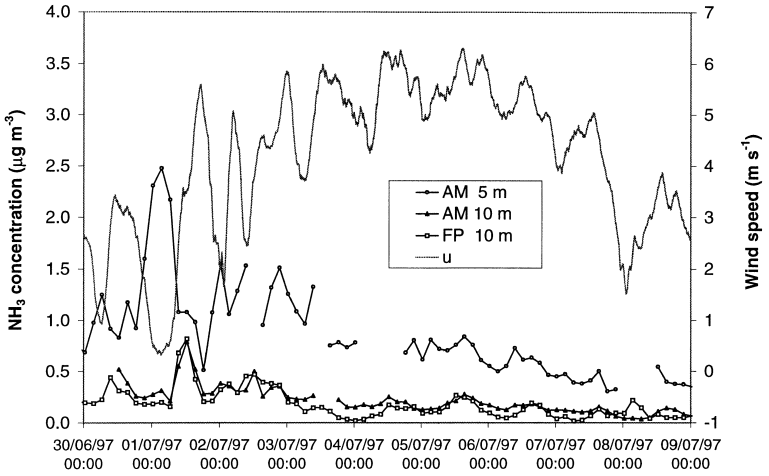

Fig. 4. Comparison of measured ammonia concentrations for different sampling heights at Taganana (TG1) with measured windspeed for a period of 10 days. Sampling at 10 m shows estimates by both the AMANDA (AM) and filter packs (FP).

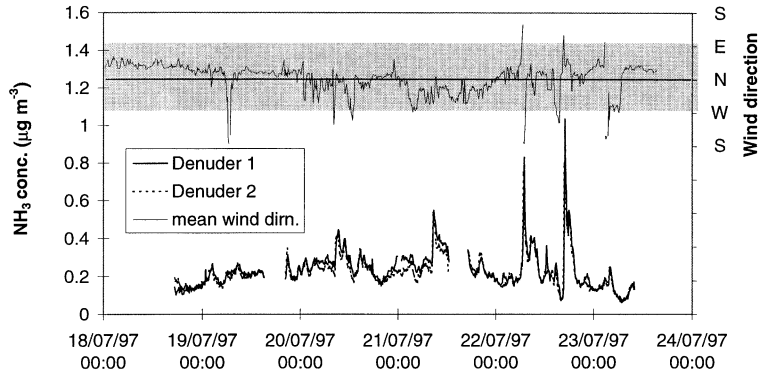

Fig. 5. Ammonia concentrations measured at 55 m elevation on the lighthouse at Punta del Hidalgo (PDH) compared with wind direction. The 2 denuders indicate duplicate sampling. The sector 80–240° (ENE–SW) represents land.

4. Comparison of NH_3 and NH_4^+ across the Anaga ridge

4.1. Differences in concentrations between measurement sites

A summary of the statistics of $[NH_3]$ and $[NH_4^+]$ at the different sampling sites is shown in Tables 2, 3. For NH_3 it is notable that the concentration at Taganana (10 m) is almost identical to that at Punta del Hidalgo, which provides further indication that this sampling height was little affected by local sources. In contrast, $[NH_3]$ at Taganana (5 m) is 4× larger, illustrating the substantial local contribution at this height. Although sampling was only conducted for a short period at El Bailadero, this site provides the smallest mean and minimum concentrations. This is most likely due to both the forest and cloud above the summit acting as a sink for NH_3 emitted both by the sea surface and terrestrial sources. The largest $[NH_3]$ was recorded at Paiba, with a mean concentration of 0.28 μg m^{-3}. The elevated concentrations at this site (for the highest measurement point) are almost certainly a result of terrestrial sources of NH_3, although it is not possible to say how much this was influenced by sources in the immediate vicinity of the sampling.

Table 2. *Summary of the ammonia concentrations measured at the different sampling sites using the AMANDA continuous denuder*

Location (height)	TG3 Paiba (5.5 m)	TG2 El Bailadero (2–4 m)	TG1 Taganana (5 m)	TG1 Taganana (10 m)	PDH Punta del Hidalgo (55 m)
measurement period	22/6–25/6/97	25/6–26/6/97	26/6–15/7/97	26/6–15/7/97	18/7–25/7/97
mean	0.28	0.10	0.87	0.22	0.23
median	0.27	0.09	0.72	0.19	0.21
min	0.09	0.06	0.18	0.01	0.07
max	0.65	0.19	4.53	0.89	0.93

Values show the averages and range of 10-min estimates ($\mu g\ m^{-3}$). Sampling heights are stated in relation to ground level at each site.

Table 3. *Summary of gaseous ammonia and ammonium aerosol concentrations measured by filter packs at the different sampling sites*

Location	Paiba (5.5 m) NH_3/NH_4^+	Taganana (10 m) NH_3/NH_4^+	Punta del Hidalgo (55 m) NH_3/NH_4^+
measurement period	28/6–23/7/97	28/6–23/7/97	29/6–25/7/97
mean	0.31/0.493	0.18/0.514	0.28/0.517
median	0.17/0.369	0.14/0.377	0.22/0.390
min	0.00/0.053	0.00/0.072	0.00/0.003
max	1.52/1.684	0.92/1.665	1.39/2.714

Aerosol values include both fine ($<2.5\ \mu m$) and coarse ($>2.5\ \mu m$) aerosol. Punta del Hidalgo values are reported for winds arising from the marine sector only (sample pumps were turned off for terrestrial wind directions and low windspeeds).

The filter pack $[NH_3]$ estimates (Table 3) also show the largest values at Paiba and the smallest values at Taganana. It may be noted that the filter pack estimates of $[NH_3]$ are larger at Punta del Hidalgo than at Taganana, which was not expected. In this case, the comparison with parallel AMANDA data indicated relative overestimates by the filter packs at Punta del Hidalgo. This could have arisen from well-known artefacts sometimes associated with filter packs (Harrison and Kitto, 1990), but is more likely to have been caused by a bias in the sampling blanks as the NH_3 and NH_4^+ filters from the Punta del Hidalgo filter packs were analysed in the laboratory much later than the samples from other sites. Despite this small uncertainty in the absolute values, the relative changes temporally at Punta del Hidalgo are considered to be reliable. Overall, Table 3 shows little apparent change in $[NH_4^+]$ between Punta del Hidalgo, Taganana and Paiba.

A more detailed comparison of the $[NH_3]$ and $[NH_4^+]$ measured at Taganana and Paiba using the filter packs may be made since the sampling was performed concurrently. A paired comparison of the simultaneous estimates at the 2 sites is shown in Fig. 6. Concentrations of both NH_3 and NH_4^+ are significantly correlated between the 2 sites (NH_3: $P<0.01$, $n=200$, NH_4^+: $P<0.001$, $n=200$), with the relationship being closest for NH_4^+. The reduced correlation for NH_3 is expected, given the importance of local sources on the island, although that the correlation is still significant indicates common influences on the $[NH_3]$ at both sites. Temperature, humidity and the presence or absence of cloud between Taganana and Paiba followed similar patterns in the coupled air flow (Bower et al., 2000) and are expected to be key factors, with larger concentrations expected in warm, dry conditions which favour partitioning to the gas phase as compared with cool, wet conditions.

The strong correlation ($P<0.001$) between $[NH_4^+]$ at Taganana and Paiba (Fig. 6b) almost certainly indicates coupling of the air masses at

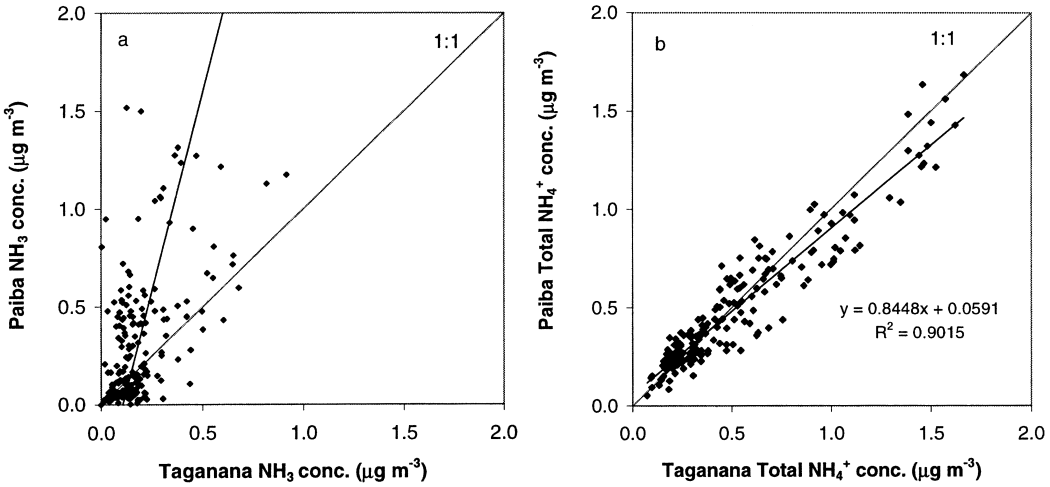

Fig. 6. Comparison of NH_x concentrations between Taganana (TG1) and Paiba (TG3) for simultaneous 3-h sampling with filter packs during period 28/6–23/7/97. (a) gaseous $[NH_3]$, (b) aerosol $[NH_4^+]$. The correlation of 6a is significant at $P = 0.01$ according to both product–moment correlation and Spearman rank correlation at $R^2 = 0.30$ and $S^2 = 0.23$, respectively ($n = 200$). The correlation of 6b is significant at $P = 0.001$ ($R^2 = 0.90$).

the 2 sites, with NH_4^+ present throughout the boundary layer and undergoing long range transport. Fig. 9 shows that most of the aerosol NH_4^+ mass is contained in the size range < 2.5 μm, with the exact figure being 96%. The regression of Fig. 6b is therefore dominated by the behaviour of fine aerosol, which is mostly present as ammonium sulphate. Although coarse aerosol $[NH_4^+]$ is present in only small quantities, this fraction increases at Paiba (Fig. 9), and is not positively correlated between the 2 sites (data not shown). In addition to the effects of common environmental influences, correlation between Taganana and Paiba for $[NH_3]$ is also likely to be partly due to coupling of the air masses between the 2 sites, although clearly the $[NH_3]$ is substantially modified during passage across the island.

A notable feature shown in Fig. 6b is that in polluted conditions with high $[NH_4^+]$ there is less NH_4^+ at Paiba than Taganana, while with low $[NH_4^+]$ there is more $[NH_4^+]$ at Paiba than Taganana. Although only a modest % effect, this is statistically significant with the regression of Fig. 6b being $\chi_{\text{Paiba}} = 0.84[0.81–0.88]\chi_{\text{Taganana}} + 0.06[0.03–0.08]$ (μg m^{-3}) where the values in parentheses are lower and upper 95% confidence limits. In contrast, with high $[NH_3]$ at Taganana, $[NH_3]$ at Paiba is even larger, while in clean conditions $[NH_3]$ at Paiba is less than at Taganana. The following discussion examines these changes between Paiba and Taganana for the contrasting conditions of clean vs polluted air masses.

4.2. *Periods with high $[NH_4^+]$: less NH_4^+ at Paiba than at Taganana*

The small, but statistically significant, decrease in $[NH_4^+]$ at Paiba compared with Taganana, observed in polluted (high $[NH_4^+]$) conditions, could be the result of a number of different processes:

(a) sampling artefacts;
(b) evaporation of existing NH_4^+ aerosol (without cloud interactions);
(c) entrainment of air with lower $[NH_4^+]$ during passage of the air mass over the ridge;
(d) dry deposition of NH_4^+ occurring during passage of the air mass over the ridge;
(e) recombination of NH_4^+ (originating from marine aerosol $(NH_4)_2SO_4$) in cloud with either Cl^- or NO_3^-, to give volatile salts which would liberate gaseous NH_3 as cloud drops evaporate. This process has been shown to occur in hill cap clouds in England (Wells et al., 1998).

If a sampling artefact is hypothesized as the cause of the differences, then this would be

expected to apply differently at the 2 sites, depending on mean temperatures and humidity. In this case, possible evaporation of NH_4^+ collected on prefilters would be expected to be largest at Taganana (due to larger temperatures and smaller relative humidity), so that $[NH_4^+]$ would be smaller at Taganana. This is contrary to observations, suggesting that sampling artefacts are not responsible for the decrease in $[NH_4^+]$. It should also be noted that the filter packs were operated with 3-h sampling periods. Pio (1992) found that problems of apparent filter pack overestimation of NH_3 and underestimation of NH_4^+ only occurred upon extension of sampling periods to over 24 h, linked to higher aerosol loadings on the filter packs than experienced here.

The same arguments can be used to show that NH_4^+ aerosol would be unlikely to undergo net evaporation between Taganana and Paiba, particularly since $[NH_3]$ was larger at Paiba. Similarly, it is noted that the NH_4^+ in the marine air mass was largely present as non-volatile ammonium sulphates in fine mode aerosol as indicted by both the filter pack measurements (data not shown) and results from a Micro-Oriface Uniform Deposit Impactor, MOUDI (Bower et al., this issue).

The question of entrainment is discussed in detail by Flynn et al. (2000). The authors conclude that the effects of entrainment were negligible during cloud events and certainly not sufficient to explain the decrease in $[NH_4^+]$.

Dry deposition of NH_4^+ during passage of the air from the west (Taganana) to east (Paiba) could also explain some depletion of $[NH_4^+]$. The scale of this effect can be estimated on the basis of the transport time (τ_{trans}) between the 2 sites, boundary layer depth (H_{bl}) and the deposition velocity (V_d) of NH_4^+ (Möller and Schieferdecker, 1985). Given an average windspeed (u) of 5 m s^{-1} and a distance (x) between Taganana and Paiba of 4 km results in a transport time (t_{trans}) of 13 min:

$$t_{trans} = \frac{x}{u}. \quad (2)$$

Using a typical value of H_{bl} of 1000 m and an upper limit of aerosol V_d to shrubland of 5 mm s^{-1} (Duyzer, 1994), a residence time for dry deposition (τ_{V_d}) of 3300 min (eq. (3)) may be estimated from:

$$\tau_{V_d} = \frac{H_{bl}}{V_d}. \quad (3)$$

Dividing t_{trans} by τ_{V_d} indicates that at most 0.4% of $[NH_4^+]$ could be removed by this process. Clearly, this is much smaller than the observed differences between Taganana and Paiba, so that this explanation can be discounted.

In contrast to effects (a) to (d), effect (e) could easily explain the loss of $[NH_4^+]$ from Taganana to Paiba in polluted conditions. Additional evidence is to be found in the changes in molar ratios of $[NH_4^+]:[SO_4^{2-}]$ observed for fine (<2.5 μm diameter) aerosol between Taganana and Paiba (data not shown). Since ammonium sulphate is non-volatile, such a change in ratio would necessitate changes to be mediated via cloud processing. The change in average ratio, from 1.4 at Taganana to 1.2 at Paiba, suggests that up to 14% of NH_4^+ originally present as fine marine aerosol could have been released as NH_3 during cloud droplet evaporation. This figure is close to the reduction of 16% shown for high $[NH_4^+]$ in Fig. 6b.

4.3. *Periods with low $[NH_4^+]$: more $[NH_4^+]$ at Paiba than at Taganana*

By contrast to situations with high $[NH_4^+]$, periods of low $[NH_4^+]$ showed an increase in $[NH_4^+]$ at Paiba compared with Taganana. This observation might be explained by:

(a) sampling artefacts;
(b) reaction of NH_3 to form NH_4^+, without cloud processing;
(c) reaction of NH_3 to form NH_4^+, through the action of cloud processing.

Separating these possible effects is somewhat harder, since they are closely inter-related, each involving reaction (either in the atmosphere or on pre-filter surfaces) of NH_3 to form NH_4^+. However, since sampling periods were short and filter pack loadings for these clean runs were very small, the sampling artefacts are expected to have been minimal (Harrison and Kitto, 1990; Pio, 1992).

Direct gas-aerosol reactions may have occurred between NH_3 and acid sulphate, nitric acid or hydrochloric acid to form ammonium sulphate,

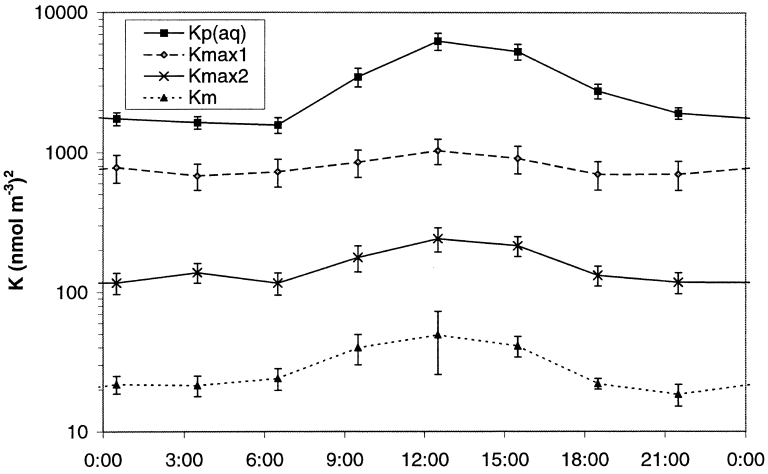

Fig. 7. Diurnal course of measured and theoretical equilibrium $[NH_3][HNO_3]$ at Paiba. K_m, measured concentration product of gaseous NH_3 and HNO_3; $K_{p(aq)}$, theoretical equilibrium concentration product given measured air temperature and relative humidity (according to Mozurkewich 1993); K_{max}, maximum possible measured concentration product if all NH_x and NO_3^- were in the gas phase: K_{max1}, including both fine and coarse aerosol; K_{max2}, including just fine aerosol (<2.5 μm). K_m and K_{max} from filter pack measurements. Standard errors are shown where $n \approx 25$.

nitrate or chloride, respectively:

$$(2)NH_{3(g)} + H_2SO_{4(g)} \rightarrow NH_4HSO_{4(aq,s)}, (NH_4)_2SO_4 \quad (4)$$

$$NH_{3(g)} + HNO_{3(g)} \leftrightarrow NH_4NO_{3(aq,s)} \quad (5)$$

$$NH_{3(g)} + HCl_{(g)} \leftrightarrow NH_4HCl_{(aq,s)}. \quad (6)$$

Alternatively, the same reactions may have been mediated through processing as the air mass passes through cloud above the Anaga ridge. Of these possibilities, direct gas-aerosol reactions to form NH_4NO_3 or NH_4Cl are unlikely to explain the changes given the clean air masses, with measured gas phase concentration products, $K_m(NH_4NO_3) = [NH_3][HNO_3]$ and $K_m(NH_4Cl) = [NH_3][HCl]$, at these sites being much less than the theoretical value required for aerosol formation ($K_{p(aq)}$). This is demonstrated in Fig. 7, which compares K_m with $K_{p(aq)}$ for NH_4NO_3 given measured mean $[NH_3]$, $[HNO_3]$, air temperature and air relative humidity over a diurnal cycle. Here $K_{p(aq)}$ is calculated for aqueous aerosol above the deliquescence point according to the formulation of Mozurkewich (1993). Since $K_m \ll K_{p(aq)}$ it is clear that direct formation of NH_4NO_3 is unlikely. In contrast, any NH_4NO_3 (or similarly NH_4Cl, not shown) that was formed, for example through cloud processing, would be expected to decompose to the precursor gases.

In addition to K_m, the maximum possible values of K_m are shown in Fig. 7 which would apply if all NH_x and NO_3^- were in the gas phase accounting for all aerosol (K_{max1}) or just the fine mode aerosol (K_{max2}). The reason for the separation between K_{max1} and K_{max2} is that NO_3^- is largely confined to the coarse aerosol and NH_4^+ to the fine aerosol. This size segregation shows that there is little possibility for formation of ammonium nitrate aerosol in either case. As an explanation of the increased $[NH_4^+]$ at Paiba, direct aerosol reactions of NH_3 with HCl and HNO_3 are therefore unlikely.

The most likely explanation of the increase of $[NH_4^+]$ observed at Paiba compared with Taganana in low $[NH_4^+]$ conditions is therefore reaction of NH_3 with acidic sulphate aerosol either directly or via cloud processing. This would correspond to the observed decrease in $[NH_3]$ between Taganana and Paiba in clean conditions.

It is important to consider why NH_4^+ production would occur in conditions of low $[NH_4^+]$, while evaporation of NH_4^+ would occur in conditions with high $[NH_4^+]$. In the former, NH_4^+ is more likely to occur in the presence of excess

SO_4^{2-}. This would favour formation of ammonium sulphates both via gas-aerosol reactions and cloud processing. In contrast, with higher $[NH_4^+]$, in-cloud mixing would allow an increased fraction to associate with nitrate and chloride forming NH_4NO_3 and NH_4Cl, which would then tend to evaporate following cloud processing.

5. Diurnal variability of NH_3 and NH_4^+ at the different sampling sites

Further insight into the different processes affecting $[NH_3]$ and $[NH_4^+]$ can be gained by considering the mean diurnal variability of the components at the different measurement sites. This is plotted for Paiba, Taganana and Punta del Hidalgo in Fig. 8.

5.1. *Diurnal variability in NH_3 concentrations*

Measured $[NH_3]$ was largest during the day for all 3 sites, with the largest diurnal variation at Paiba. These increased concentrations during the day may reflect both (a) the larger potential for emissions (marine or terrestrial) and (b) the larger potential for evaporation of volatile aerosol during warmer, drier daytime conditions. There is much less variation in aerosol NH_4^+, with total $[NH_x]$ increasing during the day, and this indicates that much of the change in NH_3 is due to increased emissions rather than partitioning with aerosol. A further factor, which might have affected the diurnal variability in $[NH_3]$, is variations in mixing depth of the boundary layer. Contrary to typical terrestrial meteorology, the mixing depth of the marine boundary layer (MBL) over Tenerife during the experiment was often smaller during the day than at night (Nielsen, 1998; McFadyen, 1999, unpublished data). This observation is consistent with models of the stratocumulus capped marine boundary layer (Turton and Nicholls, 1987). The variation in mixing depth of the MBL could account for some of the increase in NH_3 concentrations during the day. However, the observation of $[NH_3]$ decreasing with height (both locally and comparing El Bailadero with the other sites) indicates that the main factor controlling diurnal variability in $[NH_3]$ is likely to be the magnitude of NH_3 emissions from either marine or terrestrial sources.

Ammonia exchange with both living terrestrial vegetation and sea water is controlled to a large degree by the NH_3 compensation point, which is the air concentration at equilibrium with dissolved NH_3 in either the sea surface or water surface inside plant stomata (Sutton et al., 1994, 1995; Barrett, 1998). The temperature dependence of the combined solubility and dissociation equilibria is well established (Bates and Pinching, 1950; Dasgupta and Dong, 1986). Using an empirical fit to these estimates $[NH_3]$ may be given as:

$$[NH_3]_{gas} = f(T)\frac{[NH_4^+]_{aq}}{[H^+]_{aq}}, \quad (7)$$

where T is in Kelvin and all concentrations are mol l^{-1}. If it is hypothesized that emissions and air concentrations are controlled by a compensation point, then the equilibrium $[NH_3]_{gas}$ may be calculated for a given (constant) ratio of $[NH_4^+]$ to $[H^+]$ in solution, as a function of temperature. The ratio $[NH_4^+]/[H^+]$ is referred to here as Γ. The value of $[NH_3]$ calculated according to this temperature function is shown on Fig. 8 for each of the sites, scaled using the measured air temperatures and Γ selected to fit the mean measured $[NH_3]$. This provides estimates of Γ for Paiba, Taganana and Punta del Hidalgo of 115, 52 and 63, respectively. These values are typical for semi-natural vegetation (Sutton et al., 1995) but rather large compared with previously measured values for non-coastal surface sea water (Quinn et al., 1990; Barrett, 1998).

This analysis gives a broad indication of the possible magnitude of the influence of temperature on NH_3 emissions using the concept of compensation points. However, it may be noted that the actual diurnal variation in $[NH_3]$ is much larger than modelled $[NH_3]$ obtained using the above formulation (Fig. 8). For terrestrial sources this would be expected, since surface wetness (linked to relative humidity) plays a major role in reducing net NH_3 emissions in humid conditions. As a result the $[NH_3]$ may vary more than indicated by the temperature function. It is difficult to gauge this effect directly (since it is a function of many competing processes at the surface), but an indirect scaling may be made by reference to the combined temperature and humidity effects on $K_{p(aq)}$ for NH_4NO_3. Counting only the temperature effects, the parametrization of Mozurkewich (1993) reduces to an almost identical temperature

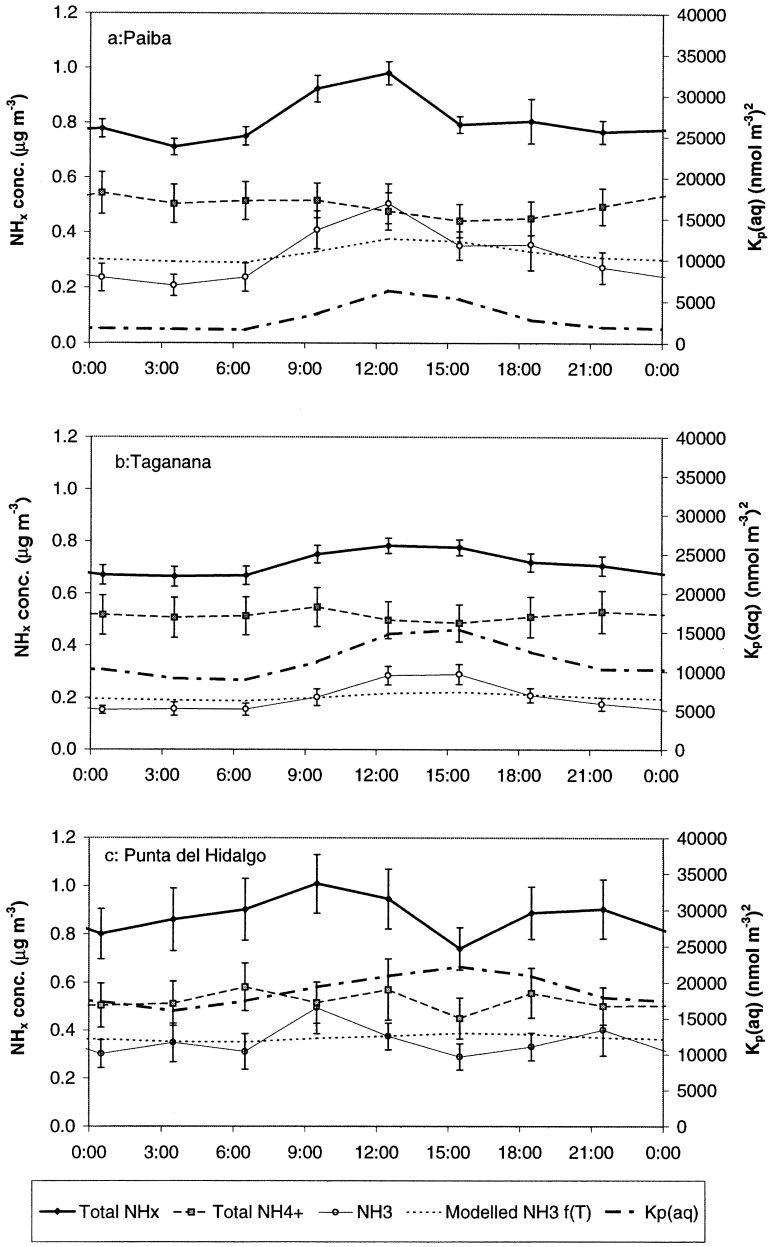

Fig. 8. Mean diurnal variability of gaseous NH_3 and total aerosol NH_4^+ concentrations at (a) Paiba (TG3), (b) Taganana (TG1) and (c) Punta del Hidalgo (PDH). Also shown are the diurnal variability in NH_3 as a function of air temperature according to solubility equilibria, modelled NH_3 $f(T)$ (according to Sutton et al., 1994) and the diurnal variability in $K_{p(aq)}$ for NH_4NO_3 as a function of temperature and relative humidity (according to Mozurkewich, 1993). Values for Punta del Hidalgo are for on-shore winds only. Standard errors are shown, where $n \approx 25$.

response as eq. (7). In contrast, including the effects of relative humidity for aerosol above the deliquescence point, the Mozurkewich (1993) parametrization can be applied as a model of the potential for NH_3 emissions including humidity effects. Fig. 8 shows that the $[NH_3]$ at each site match much more closely with $K_{p(aq)}$, suggesting that changes in relative humidity may explain part of the additional variability of $[NH_3]$, especially for Paiba and Taganana.

It is instructive to contrast the diurnal patterns of the inland sites (Taganana and Paiba) with the coastal site of Punta del Hidalgo. At this site, the maximum value of $K_{p(aq)}$ occurred during mid-afternoon at around 15:00 hours. The value of $[NH_3]$ was at minimum at this time, while the maximum occurred at 09:00. This suggests that other factors are important in controlling marine $[NH_3]$. Emissions would not be expected to be a function of humidity (since the surface is wet), and the diurnal course would have been expected to follow modelled $[NH_3]$ as a function of temperature. It is not clear why peak $[NH_3]$ at Punta del Hidalgo should occur during mid-morning and this issue deserves further investigation. Nevertheless, in the case of Punta del Hidalgo the error bars are larger (as only data for on-shore winds are shown), the analytical uncertainty is larger and the morning peak is only seen for the 09:00 period. These points indicate the need for some caution in the interpretation of this observation.

5.2. *Diurnal variability in NH_4^+ concentrations*

Fig. 8 provides further information to assess the occurrence of NH_4^+ aerosol formation and evaporation. At Punta del Hidalgo $[NH_4^+]$ is similar during day and night. In contrast, at Taganana and particularly at Paiba, $[NH_4^+]$ is slightly lower during the daytime than at night, suggesting that $[NH_4^+]$ evaporation may be occurring, especially at Paiba downwind of the Anaga ridge. Any decrease occurring during the day, when the value of $K_{p(aq)}$ is greatest, is consistent with evaporation of volatile NH_4^+ containing aerosol, since a reduction in the marine boundary layer depth during day would tend to increase daytime $[NH_4^+]$. As the effect is largest at Paiba, these observations in conjunction with the conclusions drawn in Section 4, indicate that cloud processing may have promoted the evaporation of $NH_4^+]$.

A closer comparison of the $[NH_4^+]$ at Paiba and Taganana is shown in Fig. 9, which also distinguishes the fine and coarse aerosol fractions. As noted earlier, most of the $[NH_4^+]$ is present in the fine mode, with sulphate as the major anion. Fig. 9 shows that the $[NH_4^+]$ in the fine fraction is on average lower at Paiba than Taganana throughout the day, suggesting that the cloud processing effect operates both during day and night, although the effect may be slightly more during the day. The concentrations of $[NH_4^+]$ in the coarse mode are very small, nevertheless there is a clear difference in the diurnal pattern between Paiba and Taganana. During the night coarse aerosol $[NH_4^+]$ increases slightly at Paiba compared with Taganana, while concentrations in the middle of the day are similar at the 2 sites. This suggests that coarse aerosol NH_4^+ produced during night-time (either by direct reactions with acid sulphates or via in-cloud reactions) becomes partly associated with the nitrate and chloride that dominate the coarse aerosol anions, and is therefore able to volatilize during daytime conditions when $K_{p(aq)}$ is largest.

6. Influence of cloud processing on marine aerosol ammonium

Both the paired comparison of $[NH_4^+]$ at Taganana and Paiba, and the diurnal profiles of partitioning between NH_3 and NH_4^+ indicate that formation and destruction of NH_4^+ occurs. In particular, the comparison between Taganana and Paiba is instructive since with mostly NW surface winds and frequently low cloud, the air at Paiba would frequently have been modified through cloud processing. These analyses suggest that cloud processing over the Anaga ridge may have resulted in:

(a) Evaporation of NH_4NO_3 and NH_4Cl formed in cloud when NH_4^+, originally associated with SO_4^{2-} in the fine aerosol, is mixed with NO_3^- and Cl^- from coarse aerosol in cloud droplets. This is particularly associated with conditions of high $[NH_4^+]$.

(b) Mixing between coarse and fine mode aerosol providing an increase $[NH_4^+]$ in the coarse fraction (associated with chloride and nitrate). The

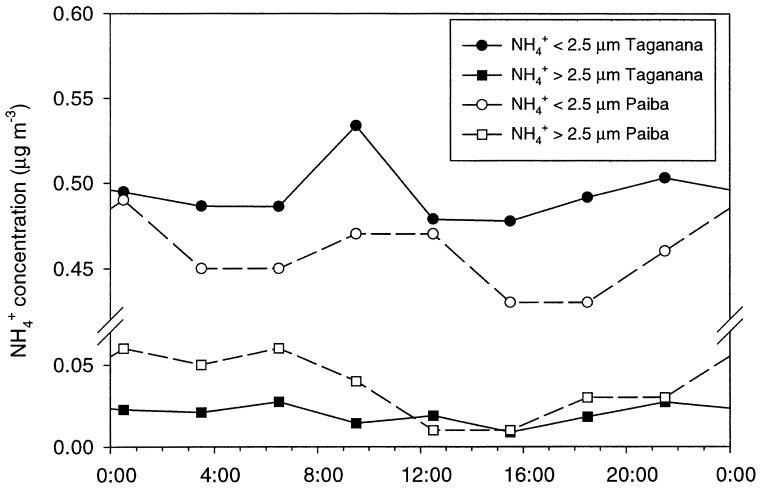

Fig. 9. Mean diurnal variability of fine mode (< 2.5 µm) and coarse mode (> 2.5 µm) aerosol ammonium for Taganana (TG1) and Paiba (TG3). Coefficient of variation of the mean estimates is 14% for fine and 26% for coarse aerosol; $n \approx 25$ for each 3-h diurnal sector.

effect is observed at night, but evaporation appears to release the additional NH_4^+ during the day.

(c) Formation of NH_4^+ aerosol during low $[NH_4^+]$ conditions. This may be related to reaction of more acidic aerosol with NH_3 emitted from both marine and terrestrial sources.

In the case of (a) cloud processing appears to provide the only mechanism to permit this effect. In contrast, for (b) and (c), while cloud processing is expected to have been important, direct gas-aerosol reactions producing NH_4^+ may also have played a role.

These combined processes provide a feedback mechanism that would be expected to regulate ammonium sulphate aerosol in the marine environment, with formation at low $[NH_4^+]$ and evaporation (through cloud processing) following exchange to form NH_4Cl and NH_4NO_3 at high $[NH_4^+]$. As noted in Subection 4.2, formation at low $[NH_4^+]$ would result from a relative excess of SO_4^{2-} allowing formation of non-volatile ammonium sulphates; in contrast, mixing in cloud in the presence of higher $[NH_4^+]:[SO_4^{2-}]$ ratios would allow a greater fraction NH_4^+ to associate with NO_3^- or Cl^- and thereby volatilize. This effect has been previously shown for air masses in a cool temperate terrestrial environment (Wells et al., 1997). Such reactions will affect the radiative properties of marine aerosol, as well as atmospheric transport residence times of the component species, and are therefore highly relevant. By providing a buffer on $[NH_4^+]$, these reactions regulate the contribution of NH_4^+ aerosol to light scattering. On the one hand, the presence of NH_4^+ increases the aerosol burden, with a direct contribution to light scattering, since NH_4^+ is mostly associated with the fine aerosol fraction that acts as cloud condensation nuclei. By contrast, the neutralization of acid SO_4^{2-} by NH_4^+ increases the deliquescence point and may therefore partly offset the negative radiative forcing effect that would result from unneutralized SO_4^{2-}.

Further work to elucidate and quantify the processes discussed in this paper will focus on particular case studies which typify the different reaction conditions. These measurements will then be used as inputs for developing and validating cloud chemistry models.

7. Conclusions

The spatial and temporal dynamics of gaseous NH_3 and aerosol NH_4^+ have been studied using ground based measurements on Tenerife as part of the ACE-2 experiment "HILLCLOUD". Intercomparison of measurement techniques provided a robust basis for assessing NH_3 concentrations, especially since these were often affected by

local sources (decomposing vegetation, animals, crops). From measurements of vertical $[NH_3]$ profiles and meteorological conditions it was possible to consider the extent to which measured $[NH_3]$ was affected by local sources and identify representative background concentrations.

Concentrations of NH_3 showed a diurnal pattern which was much larger than predicted by the temperature effect of the Henry and aqueous dissociation equilibria. For $[NH_3]$ measured at inland sites (Taganana, Paiba), it is likely that this was also influenced by air relative humidity and ground surface wetness, as indicated by diurnal patterns in the calculated value of $K_{p(aq)}$ (the temperature and relative humidity dependent equilibrium concentration product for formation of NH_4NO_3). This behaviour did not hold for a coastal site (Punta del Hidalgo) for on-shore winds, where the largest $[NH_3]$ was recorded for mid-morning.

While local sources account for an increase in $[NH_3]$ over the island, processes such as entrainment and dry deposition are unable to explain the changes in $[NH_4^+]$. Comparisons of $[NH_4^+]$ at sites upwind and downwind of the island ridge showed evidence of cloud processing and gas-aerosol interconversion affecting the partitioning between NH_3 and NH_4^+. The measurements indicate that, at low $[NH_4^+]$, there is a net production of aerosol NH_4^+, either by direct reactions or via cloud processing. In contrast, with higher $[NH_4^+]$ ($>0.5\ \mu g\ m^{-3}$), cloud processing results in partial destruction of ammonium sulphate aerosol. This appears to be mediated through in-cloud reactions with nitrate or chloride from the coarse aerosol fraction. Evaporation to form NH_3, HCl, HNO_3 occurs following exit from the cloud, since the measured concentration products $[NH_3][HNO_3]$ and $[NH_3][HCl]$ are much smaller than $K_{p(aq)}$. During night, some increase in coarse mode $[NH_4^+]$ associated with Cl^- and NO_3^- occurs, although this appears to be subsequently volatilized during the day. Such reactions have been observed previously in terrestrial atmospheres in N. Europe, and play a significant role in regulating both aerosol light scattering and atmospheric transport distances.

8. Acknowledgements

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