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New insights in the global cycle of acetonitrile: release from the ocean and dry deposition in the tropical savanna of Venezuela

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Using the proton transfer reaction mass spectrometry (PTR-MS) technique, acetonitrile was measured during the wet season in a Venezuelan woodland savanna. The site was located downwind of the Caribbean Sea and no biomass burning events were observed in the region. High boundary layer concentrations of 211 ± 36 pmol/mol (median, ± standard deviation) were observed during daytime in the well mixed boundary layer, which is about 60 pmol/mol above background concentrations recently measured over the Mediterranean Sea and the Pacific Ocean. Most likely acetonitrile is released from the warm waters of the Caribbean Sea thereby enhancing mixing ratios over Venezuela. Acetonitrile concentrations will probably still be much higher in biomass burning plumes, however, the general suitability of acetonitrile as a biomass burning marker should be treated with care.

During nights, acetonitrile dropped to levels typically around 120 pmol/mol, which is consistent with a dry deposition velocity of ∼0.14 cm/s when a nocturnal boundary layer height of 100 m is assumed.

1. Introduction

Acetonitrile (methyl cyanide, CH$_3$CN) is an ubiquitous trace gas in the atmosphere. Chemically relatively stable it reaches the stratosphere and is one of the ligands of positive stratospheric cluster ions (e.g. Arnold et al., 1978). Biomass burning has been identified to be by far the dominant source of acetonitrile and has therefore been proposed as a tracer for biomass burning emissions (Lobert et al., 1990; Holzinger et al., 1999). However, the atmospheric budget of acetonitrile is poorly understood. The estimated lifetime ranges from 0.45 (Hamm and Warneck, 1990) to 1.5 years (Hamm et al., 1984); wet deposition and reaction with HO radicals lead to the longer lifetime, whereas accounting for a potentially strong oceanic sink produces short lifetimes of 5.4 (Hamm and Warneck, 1990) and 6.8 months (Singh et al., 2003). Recently, some papers re-
ported oceanic uptake of acetonitrile (Karl et al., 2003; Warneke and de Gouw, 2001; Singh et al., 2003; Jost et al., 2003) thereby emphasizing a shorter atmospheric lifetime of acetonitrile. The oceanic sink is estimated to be larger than or of the same order as chemical degradation via reaction with the HO radical. With current knowledge it is hard to balance acetonitrile’s global budget – even if the highest estimates of biomass burning emission are considered, the assumed sinks are larger. Consequently, there has been much speculation about additional major sources. However, there is little evidence for such additional sources. In this paper we present a dataset of PTR-MS measurements revealing new insights into the global cycle of acetonitrile. Daytime mixing ratios at a Venezuelan savanna site downwind the Caribbean Sea were clearly above background levels thereby giving evidence of CH$_3$CN being released from the ocean. In addition dry deposition of acetonitrile into the local savanna ecosystem was observed.

2. Field site characteristics

Figure 1 shows the location of the measurement site (Calabozo). In most part of Venezuela the climate is driven by seasonal movements of the equatorial trough (Intertropical Convergence Zone). The changing position of the trough influences seasonal rainfall. During winter when the trough is in the Southern Hemisphere, a five-month dry season occurs (December to April), while a seven-month wet season occurs when the trough is over Venezuela (May to November). The distinction between dry and rainy season becomes progressively less marked toward the equator (i.e. latitudes lower than 6° N) where frequent rains also occur during the dry season, whereas in the northern part of the region very marked dry and rainy seasons are observed. A region of trade winds lies between the equatorial trough and the sub-tropical highs. These wind systems are steadiest at the surface and are weaker in the wet season than in the dry season. Northeast to east-northeast trades are the prevailing winds for the area north of 5° N, indicating that a large amount of surface air reaching the savanna region
comes from the ocean, spending less than one day over land.

Continuous measurements were made in the Biological Station of the Plains (Estación Biológica de los Llanos) located nearby Calabozo (8°53’ N; 67°19’ W), during the wet season 24 September 17 October 1999. The site is located in the central part of Venezuela and is little influenced by urban or industrial pollution sources. No biomass burning was observed during the wet season campaign. The surrounding woodland savanna is covered with graminea grasses (e.g. Trachypogon sp, Axonopus canescens, Hiparrhenia rufa) interrupted by trees and scrubs (e.g. Curatella american, Boudichia virgilioides, Byrsonima crassifolia). The rainfall at the site shows a 22-year average of 1315 mm. Around 98% of the rainfall occurs between April and November. The annual mean temperature is 27.6°C.

3. Measurement techniques

Acetonitrile was measured on line by Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) which has been described elsewhere in detail (Lindinger et al., 1998).

The air to be analyzed was led through a 15 m Teflon tube (PFA, ID 1.6 mm), the inlet of which was positioned 5 m above ground. The response time of the gas inlet system was kept below 20 s by applying an appropriate gas flow through the tube. The instrumental background levels were measured by directing the sample flow through a catalytic converter. The converter consisted of a stainless steel tube filled with Platinum-coated quartz wool (Shimadzu) heated to 350°C, which efficiently removed the volatile organic compounds (VOCs) from the sample. The catalytic converter did not remove water vapor from the sample, which is important because the background impurities may depend on the humidity of the sampled air. The PTR-MS instrument consists of three parts: ion source, reaction chamber, and a quadrupole mass spectrometer. The primary H$_3$O$^+$ ions enter the reaction chamber which is flushed with the air to be analyzed. On the way to the mass spectrometer each H$_3$O$^+$ ion collides a 1000 times with neutral molecules – mostly with non-reactive N$_2$, O$_2$, Ar, and CO$_2$ molecules. However,
a proton will be transferred on almost every collision between a H$_3$O$^+$ ion and a VOC with a proton affinity higher than water. Thus most of the VOC species are detected at their protonated mass which is the molecular mass +1. The collision energy of the ions with neutral compounds is maintained at a sufficiently high value by the applied electric field (electric field to number density: E/N ≈ 130 Td; 1 Td = 1 Townsend = 10$^{-17}$ V cm$^2$) so that clustering of the hydronium ions with water molecules to form higher hydrates is strongly suppressed. The electric field also controls the transient time (t) for the H$_3$O$^+$ ions traversing the reaction chamber thus allowing to calculate the neutral trace gas density from the relation \[ [\text{VOC} \cdot \text{H}^+] \approx [\text{H}_3\text{O}^+] [\text{VOC}] k_{\text{VOC}} t, \] where $k_{\text{VOC}}$ is the reaction rate constant for the proton transfer from H$_3$O$^+$ to compound VOC.

Acetonitrile is detected at protonated mass 42. Potential interference at this mass might come from compounds which produce ion signals at mass 41 (C$_3$H$_5^+$, e.g. protonated propyne or fragmented isoprene). About 3% of this non-acetonitrile signal will be detected at mass 42 due to the natural $^{12}$C/$^{13}$C-isotope distribution. The reaction of O$_2^+$ (an impurity coming from the ion source) with some alkenes might also produce a signal at mass 42 (C$_3$H$_6^+$). However, we continuously monitored reasonable low levels at masses 32 and 41; thereby excluding considerable interferences of this kind. Studies done with a coupled GC-PTR-MS system demonstrated that the ions associated with acetonitrile are free from significant interference (De Gouw et al., 2003; Warneke et al., 2003).

The accuracy of the data is about ±15%. Gravimetrically mixed standards with acetonitrile levels of 400–1500 nmol/mol have been measured to confirm correct computation of mixing ratios. The data presented here are highly averaged; that is to say every number presented here is based on good counting statistics for both primary H$_3$O$^+$ ions and protonated acetonitrile. Therefore errors due to precision are considered to be minor (~5–10%).

Carbon monoxide concentrations were measured using a reduction-gas-detector (Trace Analytical) in combination with a molecular sieve 5A column for CO separation. Every 15 min gas samples were automatically supplied to the injection valve by
a Metal Bellow pump (model MB-21). High-pressure mixtures of CO in synthetic air (258 ppbv) were used for calibration in the field.

4. Results and discussion

Figure 2 depicts a diurnal cycle of CH$_3$CN and CO into which all data have been included that were obtained during the three weeks of measurement. For both acetonitrile and CO a significant diurnal variation was observed. Acetonitrile levels continuously decreased during night when vertical mixing was suppressed by the nocturnal inversion layer. The breaking of the nocturnal inversion each morning coincided with a rapid increase of acetonitrile concentrations due to mixing with the residual layer. Daytime mixing ratios between 11:00 and 16:00 local time (LT, UTC less 5 h) are considered representative for boundary layer concentrations. Decreasing levels of acetonitrile during night can only be explained by dry deposition; poor reactivity and low variability exclude chemistry and advection from being a reasonable explanation of the observed nighttime losses of acetonitrile. In contrast, CO is not deposited but measured at highest levels late in the evening. During night the steady Northeasterly wind flow collapsed occasionally and local traffic emissions were advected from nearby Calabozo. CO was very well correlated to other traffic tracers such as benzene and toluene (Holzinger et al., 2001). The lack of correlation between acetonitrile and CO is indicative of the absence of a common source (i.e. biomass burning emissions).

Reported mixing ratios of acetonitrile and CO are compared in Table 1 with boundary layer levels (11:00–16:00 LT) measured in this study. Surprisingly, concentrations of acetonitrile were clearly above levels measured in other regions with little biomass burning contamination. We figured out following three possible explanations for the high concentrations: i) a regional land-surface source; ii) long-range transport of biomass burning emissions; and iii) a marine source. A land-surface related source must be homogeneously distributed all the way upwind of the site. Otherwise the variability of acetonitrile would have been much larger and plumes would have been
detected. Potentially emissions from the vegetation or from the soil could be such a source. However, emissions from both vegetation and soil would be triggered by temperature and/or light variations. For this reason both would result in a different diurnal cycle than observed. Like for isoprene, increasing mixing ratios during daytime are expected for light-triggered sources (Holzinger et al., 2002); temperature-triggered sources would produce high concentrations in the evenings, when emissions are still strong but vertical mixing is suppressed by the developing nocturnal boundary layer. Biomass burning emissions of CH$_3$CN coincide with substantial emissions of CO and a correlation between the two gases can be expected. However, no correlation between daytime levels of CO and acetonitrile (11:00–16:00 LT) was observed ($r^2 < 0.05$) if two short periods with significant correlation (7 August, 13:30–14:30; 8 August, 13:30–14:30) were disregarded. In addition, if the high concentrations were due to biomass burning emissions we would rather expect more variability in the acetonitrile dataset. It seems very unlikely that constant biomass burning influence prevailed over the whole period of three weeks. An oceanic source is not triggered by air temperature or solar radiation. The transport of dissolved acetonitrile to the atmosphere is primarily driven by Henry’s Law and by the mixing efficiency of both, the upmost layer of the ocean and the lowest layer of the atmosphere. Since the meteorological conditions were stable during the time of measurements, such a source explains much better the constant elevated mixing ratios during daytime hours when no nocturnal inversion layer is decoupling the ground from the boundary layer (~09:00–18:00 in Fig. 2). We consider acetonitrile emission from the ocean to be the only reasonable assumption to explain both the high mixing ratios and the diurnal cycle of acetonitrile. This does not necessarily mean that the ocean is an additional source of acetonitrile. Perhaps more likely, the ocean acts as reservoir for acetonitrile: gas-phase acetonitrile is dissolved into seawater in regions were the ocean is cold. Dissolved acetonitrile might be released back into the atmosphere when the ocean warms up in tropical regions. The oceanic sink is probably much smaller than previously assumed if this speculation proves to be true and dissolved acetonitrile is not hydrolyzed or efficiently removed by microorganisms.
However, a new non-biomass-burning source has to be assumed if acetonitrile is not stable enough to be transported over long distance in seawater. The general suitability of CH$_3$CN as a biomass burning marker should be treated with care; even if there is no hydrolysis or other loss of dissolved acetonitrile.

Dry deposition over terrestrial ecosystems is a sink of acetonitrile that has not been accounted in global budgets so far. To our knowledge this is the first report of acetonitrile deposition over land. Unfortunately we do not have sufficient meteorological parameter to reliably calculate the deposition velocity. Assuming a completely isolated well mixed nocturnal inversion layer of 100m (Octavio et al., 1987) a very rough estimate yields a deposition velocity ($v_d$) of $\sim$0.14 cm s$^{-1}$ according to

$$v_d = (d_{42} \times h)/(av_{42} \times t),$$

with $h$ being the boundary layer height (100 m), $t$ the duration of the night, $d_{42}$ the average drop (90 pmol/mol), and $av_{42}$ the mean concentration of acetonitrile during nights (165 pmol/mol, see Fig. 2). During the 7 month long wet season over 2.7 mgN/m$^2$ would be deposited, and if the value generally holds for tropical savannas (6.68 $\cdot$ 10$^6$ km$^2$, Guenther et al., 1995) 0.053 Tg acetonitrile would be deposited into savannas in this time period. Compared with the total estimated source of CH$_3$CN of $\sim$0.4 Tg N/yr (Singh et al., 2003), the loss in savannas would be significant, but not major. However, if similar deposition velocities prevail also over other ecosystems, dry deposition over land might be a dominant sink for acetonitrile. Further measurements are needed to confirm or disprove this speculation.

5. Conclusions

High levels of acetonitrile were measured at the studied savanna region, in the absence of biomass burning emissions. The analysis of the data strongly suggests that acetonitrile is released from the Caribbean Sea. Recently, oceanic uptake of acetonitrile has been repeatedly reported. This study presents the first evidence that the ocean also

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acts as a source of acetonitrile. However, we speculate that rather than being produced acetonitrile is sequestered and transported in the ocean.

Also for the first time dry deposition of acetonitrile over a terrestrial ecosystem is reported in this article. If this happens in other ecosystems too, the roughly estimated deposition velocity implies the potential of dry deposition being a major sink of acetonitrile. This study provides new insights in the global cycle of acetonitrile. Acetonitrile is important as tracer for biomass burning; one of the largest global pollution sources. Further research is urgently needed. Improved understanding of the mechanisms controlling the atmospheric abundance of this gas would aid the quantification of global biomass burning emissions and help to improve the performance of global atmospheric chemistry models.

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Table 1. Atmospheric mixing ratios of CH$_3$CN (pmol/mol) at various locations

| Reference                        | Average | SD  | Median | Range     |
|----------------------------------|---------|-----|--------|-----------|
| This work (Karl et al., 2003)    | 212     | ±36 | 211    | 159–272   |
| (Warneke and de Gouw, 2001)      | 142     | ±20 |        | 70–200    |
| (Sprung et al., 2001)            |         |     |        | 70–200    |
| (Pöschl et al., 2001)            |         |     |        | 90–270    |
| (Singh et al., 2003)             | 149     | ±56 | 138    | 93–205    |
| (Holzinger et al., 2003)         | 156     |     | 150    | 123–200   |
| (Sahhuez et al., 2001)           | 150     | ±70 | 140    |           |

a Mauna Loa Baseline Station, Hawaii.
b Northwest Indian Ocean, boundary layer.
c Tropical Indian Ocean boundary layer and free troposphere.
d Tropical rainforest in Surinam, 0–12 km.
e Pacific Troposphere, 0–12 km.
f Mediterranean Troposphere, 0–13 km.
g La Gran Sabana region, Venezuela.
Fig. 1. Map indicating the monitoring site.
Fig. 2. Diurnal variation of acetonitrile and CO mixing ratios at the Calabozo savanna site. All data collected between 24 September and 17 October 1999 have been superimposed and smoothed by the formation of a running mean out of 15 neighboring points.