

setup using a calibration gas unit provided by the Laboratoire des Sciences du Climat et de l'Environnement (LSCE, Climat and Environment Sciences Laboratory), which contains ethanol, showed a very low calibration coefficient for ethanol. Additionally, large ion signals recorded during periods when the observatory was under the influence of biomass burning events located in southern Africa and Madagascar (Verreyken et al., 2020) suggested that these signals were mainly due to HCOOH. Potential interference at m/z 61 may originate from ambient concentrations of glycolaldehyde, ethyl acetate, and peroxyacetic acid (Baasandorj et al., 2015). However, the strong co-variation between CH_3COOH and HCOOH, which have similar sources and sinks in the atmosphere, suggests that the signal at m/z 61 could correspond mostly to CH_3COOH . Air was sampled 2.86 m above the roof of the observatory (8.20 m above ground) and pumped towards the instrument through a 10.35 m long 3/8 in. (outer diameter) perfluoroalkoxy (PFA) Teflon sampling tube (Dyneon 6502T, Fluortechnik-Deutschland, Germany) at a flow rate of 8 L min^{-1} . The sampling line was heated ($5\text{--}10^\circ$ above ambient temperature) and thermally insulated to prevent condensation. The sampled air was filtered for particles 2.48 m downstream of the sampling point by a polytetrafluoroethylene (PTFE) membrane filter (Zefluor, Pall Laboratory, MI, USA) with a pore size of $2\text{ }\mu\text{m}$. Part of the sampled air was sent through a catalytic converter (type HPZA-3500, Parker Hannifin Corp., OH, USA) for zero-VOC measurements, which took place every 4 h and lasted 30 min, of which only the last minutes were taken into account. The transport time of ambient air between the sampling point and the drift tube reaction of the hs-PTR-MS instrument is about 3.2 s (2.5 s in the main sampling line and 650 ms in the hs-PTR-MS sampling line). Calibration of the hs-PTR-MS for the target VOCs was performed every 3–4 d by dynamically diluting a VOC/ N_2 calibration mixture (Apel-Riemer Environmental Inc., FL, USA; stated accuracy of 5% (2σ) on the VOC mixing ratios) in zero air. In April 2018 and March 2019, the instrument was also calibrated with a commercial gas calibration unit (GCU, Ionicon Analytik GmbH, Austria) from LSCE (Laboratoire des Sciences du Climat et de l'Environnement). Calibration factors for the (O)VOCs of interest obtained with the two calibration systems were found to be in excellent agreement. Calibration factors for compounds that were not present in the calibration mixture – i.e., HCOOH and CH_3COOH – were determined indirectly, as mentioned in Verreyken et al. (2020). Specifically, for CH_3COOH , the calibration factor was inferred from that of CH_3COCH_3 by considering the calculated collision rate constants of H_3O^+ with CH_3COOH and CH_3COCH_3 (Su, 1994; Zhao and Zhang, 2004), by considering the contribution of the protonated molecules to the respective product ion distributions (Schwarz et al., 2009; Inomata and Tanimoto, 2010), and by assuming the same hs-PTR-MS transmission efficiency for ions with a mass difference of 2 Da. The same principle was applied to calculate the calibration factor of

HCOOH from that of CH_3CHO . The humidity dependence of the calibration factors was determined approximately every 2 months by controlling the humidity of the zero air with a dew point generator (LI-COR LI-610, NE, USA). The ion signal at m/z 37 was used as a proxy for air humidity. Of all compounds present in the calibration mixture, only the calibration factors for formaldehyde, isoprene, Iox, and MEK showed a non-negligible humidity dependence. The humidity dependence of calibration factors for carboxylic acids – not present in the calibration mixture – was retrieved from Baasandorj et al. (2015) for HCOOH and from the experimentally determined humidity-dependent fractional contribution of protonated CH_3COOH to the $\text{H}_3\text{O}^+ / \text{CH}_3\text{COOH}$ product ions.

2.2.2 Additional measurements

The Maïdo observatory was recently officially registered as an ICOS (Integrated Carbon Observation System, <https://www.icos-cp.eu/>, last access: 7 January 2021) atmospheric measurement site and a GAW (Global Atmospheric Watch, <https://public.wmo.int/en/programmes/global-atmosphere-watch-programme>, last access: 7 January 2021) station. In this capacity, the observatory continuously houses a suite of both in situ and remote sensing instruments. A list of all regular measurements can be found online (<https://osur.univ-reunion.fr/observations/osu-r-stations/opar/>, last access: 11 December 2020). In this study we will focus on carbon monoxide (CO) mixing ratios taken by a Picarro G2401 instrument (Picarro Inc., CA, USA). We will use the CO data to better characterize the presence of biomass burning (BB) plumes at Maïdo. Auxiliary data (wind direction, ambient temperature, and solar radiation) were recorded by a meteorological station. The measurements of radiation have been made using a SPN1 Sunshine pyranometer (Delta-T Devices Ltd., UK), with a stated accuracy of 5% for both direct and diffuse radiation. Mixing ratios of NO_x have been recorded using a chemiluminescence photometer (T200UP, Enviconrol, France).

2.3 Source attribution tools

2.3.1 Positive matrix factorization

Air composition was studied using the positive matrix factorization (PMF) multivariate receptor model software released by the United States Environmental Protection Agency (EPA), EPA PMF 5.0 (Norris et al., 2014). PMF is a popular tool in atmospheric source attribution studies (e.g., Rocco et al., 2020; Pernov et al., 2021). The mathematical principle behind the PMF algorithm is based on the decomposition of measurements (x_{ij}) in a linear combination of factor profiles (f_{kj}) and factor contributions (g_{ik}) and a residual (ϵ_{ij}):

$$x_{ij} = \sum_{k=1}^p g_{ik} \times f_{kj} + \epsilon_{ij}. \quad (1)$$