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EDITED BY Akinori Ito, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Japan

REVIEWED BY
Sohiko Kameyama,
Hokkaido University, Japan
Lokesh Sahu,
Physical Research Laboratory, India

*CORRESPONDENCE
Manon Rocco,

■ manon.rocco@univ-amu.fr
Olivier Magand,

■ Olivier.magand@univ-reunion.fr

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Monitoring and volatile organic compounds characterization (isoprene, monoterpene and BTEX) in a tropical-oceanic environment in Reunion island (Indian ocean, south hemisphere)

Olivier Magand^{1*}, Patricia Boulanger², Pierre Staménoff¹, Magali David¹, Patrick Hernandez¹, Eric Golubic¹, Yann Hello¹, Claudine Ah-Peng^{1,3}, Valentin Duflot^{4,5}, Olivier Ktata⁶ and Manon Rocco^{4,6,7}*

¹Observatoire des sciences de l'univers de La Réunion (OSU-Réunion), UAR3365, UR, CNRS, Météo-France, IRD, Saint Denis, La Réunion, France, ²Laboratoire Départemental d'Analyses de la Réunion, Saint-Denis, La Réunion, France, ³UMR PVBMT, Université de La Réunion, Saint-Pierre, France, ⁴LACy, Laboratoire de l'Atmosphère et des Cyclones UMR 8105 CNRS, Université de La Réunion, Météo-France, Saint-Denis, France, ⁵Department for Atmospheric and Climate Research, NILU, Kjeller, Norway, ⁶Now at Aix Marseille University, CNRS, LCE, Marseille, France, ⁷Now at CNRS, Aix Marseille University, IRD, Avignon University, IMBE, Marseille, France

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1 Introduction

Volatile Organic Compounds (VOCs) are key components in the atmospheric oxidative capacity. They play a key role in aerosol formation (secondary organic aerosol, SOA), atmospheric chemistry by the ozone formation, and cloud formation implying high sanitary and climatic impacts (Seinfeld and Pandis, 2016; Tripathi et al., 2022).

Despite being considered to be a dominant source of biogenic VOCs (BVOCs) such as isoprene and monoterpenes, their measurement-based studies are very limited (Guenther et al., 2012; Paton-Walsh et al., 2022). Minimizing uncertainties in estimates of BVOC emissions necessitates further observations (Guenther, 2013). Conducting experiences to evaluate BVOCs fluxes such as leaf-level enclosure, tower and aircraft-based above the canopy is essential to enhance our understanding of the processes influencing BVOC diversity. Furthermore, the recent use of satellite data aims to provide tendencies and variability of VOC emissions in the atmosphere (Bauwens et al., 2022) and can be useful for flux measurements.

Réunion Island (21° S, 55° E), located 700 km east of Madagascar and characterized by a complex orography due to its volcanic origin (Gillot and Nativel, 1989), is often considered as a natural laboratory of the exchanges between the atmosphere with the biosphere (ocean and tropical forests). The island presents a tropical climate, specific atmospheric dynamics due to steep slopes covered by forests, boundary layer variations and sea breeze phenomenon, facilitating the transport of VOCs to the mountain summit and enhancing the cloud formation (Garratt, 1994; Monti et al., 2002; Davis et al., 2020).

In the aim to fill the uncertainties related to VOCs in tropical areas, numerous field campaigns have been organized at Réunion island with the aim to understand ambient

VOC concentrations, emissions and behavior (Callewaert et al., 2022; Dominutti et al., 2022; Duflot et al., 2017; Duflot et al., 2019, Duflot et al., 2022; Rocco et al., 2020; Rocco et al., 2022, Rocco et al., 2024; Amelynck et al., 2021; Verreyken et al., 2019; Verreyken et al., 2021; Leriche et al., 2023) considering the context of dynamical local circulations (Lesouëf et al., 2011; 2013; Foucart et al., 2018; Verreyken et al., 2021). However, to highlight tendencies of VOC diversity and concentrations, long-term measurements are required.

Located at an altitude of 2,160 m, OPAR-Maïdo Observatory (MO, 21.079° S, 55.383° E) is an ideal place to perform coupled dynamical and chemical atmospheric studies in a tropical mountain island context and is essential for our comprehension of emissions in background sites, comprising VOC. OZC-R Mare-Longue forest research field station (MALO, 21.350° S, 55.743°E), located on the south-eastern coast at Saint-Philippe, is dedicated to the observation and research of native forest ecosystems on Réunion island. This second site is an ideal place for studying variability and long-term trends in VOC emissions in lowland forests and VOCs of marine aerosols contribution to atmospheric chemistry in the forest environment.

This study presents unique VOC datasets (Isoprene, monoterpene–represented by α -pinene, β -pinene, limonene–and BTEX–as Benzene, Toluene, Ethylbenzene and Xylenes -) obtained from measurements at the multi-instrumented MO and MALO observations and research stations, for more than 3 years and 1 year, respectively. The sustainability of these data and more particularly VOC concentrations, are crucial to monitor seasonal and annual variability and long trends of VOC concentrations in the southern hemisphere.

2 Materials and methods

2.1 Sampling site description

MO site lies at an altitude of 2,160 m above sea level (asl) on the western flank of the Island (Supplementary Figure S1). This GAW global (WMO region I, Africa) and numerous international observation networks (IR-ACTRIS, IR-ICOS notably) labelled atmospheric research station is directly under the influence of marine and biogenic air masses coming from the west-north-west downhill slope, partially covered by a dense montane forest dominated by the endemic Acacia heterophylla Willd tree (see Supplementary Figure S2 for some examples of plant species on site). The part of the mountain slope characterized by dense forest dominates the coastal sector where the closest urban areas (Saint Paul and Le port, 13 and 15 km from the observatory, respectively) are located (Rose et al., 2019). Over the dense forest and surrounded by subalpine shrublands, the station can also collect air masses coming from lush tropical vegetation found further to the north-east, in the Cirque de Mafate (a densely vegetated volcanic caldera). Being inside the marine boundary layer during daytime and near the free troposphere during nighttime, the site is dedicated to atmosphere studies (Baray et al. (2013); Zhou et al. (2018); Simu et al. (2021); Koenig et al. (2023); Gantois et al. (2024); Vimeux et al. (2024); Sicard et al. (2025) and references therein). VOC collection is made on the instrumented roof of the station (6 m above ground level).

MALO site is a monitored lowland tropical rainforest, characterized by a diverse vegetation, composed of 40% of Mascarene endemic trees and 20% of Réunion endemic trees. This is the last remnant lowland forest for the Mascarene's archipelago and the geographical isolation associated with its insularity makes it a recognized biodiversity hotspot (Myers et al., 2000). The site (Nature reserve) is located in the south-east of the island, on the slopes of the active volcano Piton de La Fournaise (2,632 m asl), between 100 and 700 m asl. Classified as a biological reserve in 1958, the 23 ha Mare Longue reserve was enlarged to 68 ha in 1981, and has been part of the Réunion National Park since 2008. Main part of the primary forest is surrounded by secondary vegetation and sugar cane fields. The site is characterized by an upper canopy (up to 25 m) of mixed vegetation growing on a near 360-year-old basaltic flow (Albert et al., 2020), the main plant species and families being listed in Kirman et al. (2007) (see Supplementary Figure S3). VOC are sampled in an area of the forest close to 300 m asl, as close as possible to research experiments conducted in the area (Machacova et al., 2021; Hoang et al., 2023) in the framework of OZC-R Mare-Longue research field station works.

2.2 Sampling procedure

Active gaseous VOC sampling was conducted with Tenax®TA sorbent cartridges (Tenax®TA 60–80 mesh, 250 mg) using Gilian® Gilair Plus pump with a controlled and constant flow rate of 100 mL min⁻¹ for duration being 40 or 60 min, depending on the site. The axial Tenax®TA sorbent tubes contain porous polymer chemically inert, highly hydrophobic and widely used for VOCs measurements of more than 4 C-atoms (Rothweiler et al., 1991; Ho et al., 2018; Schieweck et al., 2018). VOCs are weekly collected at MO site, over a day, with one daytime sample (1 p.m.–5 p.m.) and one at nighttime (10 p.m. - 00 a.m.), for better representation of the specific environmental conditions occurring on site. Sampling in MALO is carried out once or twice a month, depending on environmental conditions and access capacity to the site.

2.3 Chemicals and material

VOC standards, with a purity better than 98%, (except the β -pinene compound with a purity of 95%) are purchased from Sigma-Aldrich, CPA Chem and A2S. The Internal standard Toluene D8 is obtained from A2S, with a purity of no less than 99%. Methanol for gas chromatography system with a purity better than 99% is issued from Carlo Erba Reagents SAS (Val de Reuil, France). Helium with a high purity of 99.9999% is used as the carrier gas. Tenax®TA (60/80 mesh) adsorbent cartridges (90 mm/3.5 inches length and 6.35 mm/¼ inch OD and 5 mm ID stainless steel inert coated, pre-packed) are purchased from Supelco (Bellefonte, PA, United States). The instrumental platform used in this study for VOC analysis is composed of an Automated Thermal Desorption unit (ATD, PerkinElmer®, TurboMatrix 650) connected to a gas chromatograph (GC, PerkinElmer®, Clarus 680) and coupled to a mass spectrometer (MS, PerkinElmer®, 600T).

TABLE 1 Analytical conditions.

| ATD system | GC system | MS system |
|---|---|-----------------------------------|
| Carrier gas: Helium (99.9999%) | Carrier gas: Helium | Run time: 3,400 min |
| Primary desorption: 270 °C, 25 min | Column temperature program | Mode: MS scan Mass: 50–300 amu |
| Total primary desorption flow rate: 40 mL min ⁻¹ | Initial temperature: 35 °C for 5 min | |
| Outlet split flow-rate: 40 mL min ⁻¹ | Ramp1: 5.0 deg min ⁻¹ –160 °C, hold for 25 min | |
| Secondary desorption flow rate: 0.5 mL min ⁻¹ | Ramp2: 45.0 deg min ⁻¹ –250 °C, hold for 2 min | |
| Valve temperature: 250 °C | | |
| Secondary desorption: 300 °C, 15 min | | |
| Transfer line temperature: 250 °C | | |

TABLE 2 List of the studied compounds with related limits of detection for Tenax (R)TA cartridge (LOD in ppt).

| Compound | Class | CAS number | Molecular formula | LOD (ppt) |
|----------------|--------------------------|-------------|-------------------------------|-----------|
| Isoprene | Hemiterpene | 78-79-5 | C_5H_8 | 26 |
| Benzene | Aromatic HC ^a | 71-43-2 | C ₆ H ₆ | 121 |
| Toluene | Aromatic HC ^a | 108-88-3 | C_7H_8 | 112 |
| Ethylbenzène | Aromatic HC ^a | 100-41-4 | C_8H_{10} | 20 |
| (m + p)-xylène | Aromatic HC ^a | 106-42-3 | C_8H_{10} | 40 |
| (o)-Xylène | Aromatic HC ^a | 95-47-6 | C_8H_{10} | 58 |
| α-pinene | Monoterpene | 7785-70-8 | $C_{10}H_{16}$ | 11 |
| β-pinene | Monoterpene | 19,902-08-0 | $C_{10}H_{16}$ | 8 |
| Limonene | Monoterpene | 5989-54-8 | $C_{10}H_{16}$ | 40 |

^aHC means hydrocarbon

2.4 Sample extraction and instrumental setup for VOC analysis

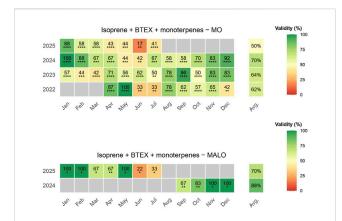
The global analytical methodology for VOC determination using Tenax®TA (60/80 mesh) adsorbent cartridges is well known and available in the literature from nearly several decades (Pankow et al., 1982; Hellén et al., 2024). We will consequently limit ourselves here to summarize analytical conditions applied in the framework of this work in Table 1.

2.5 Quality control and quality assurance

The use of Tenax®TA cartridges is subject to precautions to be considered in order to ensure the reliability and data quality. Among these precautions, it is obviously fundamental that the recycled tubes, reused for new collections, no longer contain any of the VOC species that we wish to sample and measure, but also that successive cartridges recycling does not degrade the loading capacity of the resins. In line with previous studies (De Bortoli et al., 1992; Arnts, 2010), no Tenax®TA cartridge was used or recycled more than 10 times during the entire collection period, even though some studies have shown no change in adsorbent capacity with old

cartridges or cartridges recycled up to 20 times. This precaution coupled to purchase of new fresh Tenax®TA batches allow us to ensure that there is no aging or recycling effect occurring during this study. Random analysis of the regenerated cartridges shows a total absence (up to 50% of all analyses) or restricted presence of the VOC compounds sought in our sites at concentrations below the estimated limits of detection (LOD) (Table 2) related to our analytical setup.

Percentages of usable VOC concentration data, i.e., analytical results of samples for which we have (i) detected a compound and (ii) validated a concentration value above the detection limit, are expressed in Figure 1. Variability observed in the percentage of valid and usable VOC data versus the number of TENAX cartridges collected and compounds searched for is dependent on several factors related (i) to the compounds under consideration (compounds with a low or high presence that are emitted into the studied environment), (ii) to environmental conditions and time period (season) related to field sampling (weather conditions including cyclone events, biomass growth period), and also to the analytical capacity employed in laboratory. Considering all VOC compounds and all classes combined since collection started at each site, the monthly percentage of usable concentration data is not below 17%. Some months showed 100% of valid data, i.e. 100% data



Annual average and monthly percentage of usable (qualified) VOC concentrations data (Isoprene, monoterpene–represented by α -pinene, β -pinene, limonene -) and BTEX–as Benzene, Toluene, Ethylbenzene and Xylenes) observed since April 2022 and August 2024 in OPAR–Maïdo observatory (MO - upper panel) and at the MareLongue tropical forest natural reserve related to OZC–R Mare–Longue research station (MALO - lower panel), respectively. Stars represent the monthly number of collected TENAX cartridges in each sampling site: $1 \le * <= 3; \ 4 \le * * 6; \ 7 = < * * * < 9; * * * * * * 10. Grey squares represent no sampling.$

on VOC concentrations above detection limits for all the compounds investigated. On an annual basis and even if we have to consider the lower collection frequency in MALO site compared to MO one, more than 50% of data are at least valid in MO versus more than 70% in MALO.

Usable data related to each VOC classes (isoprene alone as hemiterpene, BTEX and monoterpenes) are also shown in supplementary material (Supplementary Figure S4,S5). Isoprene measurements in MO show a validity rate up to 80% both in 2023 and 2024 for complete years of collection (Supplementary Figure S4) while the lowest annual validity rates are observed for the BTEX class for this same site. For monoterpenes measurements, the findings are more mixed with alternatively high rate in valid and usable data in 2022 (82%) and 2024 (85%) compared to 2023 (50%) and 2025 (37%) although the years 2022 and 2025 should be treated with caution due to the incomplete time series. In MALO and always on an annual basis, 100% of the isoprene and BTEX data are valid and usable, compared with around 60% for compounds in the monoterpene class.

3 VOC distribution from both sites

Concentrations of qualified data (Figure 1) for all time period collection are presented for each VOC in Figure 2 and briefly described. Only results issued from each group of VOCs in MO are shown, as there are currently too few VOC data from MALO to be well represented graphically. However, the VOCs concentrations currently recorded at the MALO site are discussed below in comparison with those observed at MO. Qualified data (Rocco et al., 2025a; Rocco et al., 2025b) from both sites can be freely downloaded (open data access) via the GEOSUR website managed by OSU-Réunion and as referenced in the data availability statement.

High concentrations of isoprene are reported at both sites. Average concentrations are 439 \pm 325 pptv and 1100 \pm 597 pptv for isoprene in MO (number of data n = 210) and MALO (n = 15), respectively. Our measurements are in range with previous measurements reported at MO site which showed concentrations from few pptv to ~250 pptv on average (Duflot et al., 2019; Rocco et al., 2020; Rocco et al., 2022; Verreyken et al., 2021) and highest concentrations up to 550 pptv. In other background site measurement in South Africa (Welgegund, Jaars et al., 2018), values are lower than our measurements. Indeed, averaged VOC concentrations VOC were 28 and 23 pptv for isoprene in Jaars et al. (2018) for two different field campaigns. Endemic tropical forests are known to be high emitters of VOC compounds, MALO concentrations are normally higher in area where isoprene is the dominated emitted compound (Rocco et al., 2024). In comparison, another Réunion's site, a tropical montane cloud forest (Bélouve forest, 1200 m asl) average concentration is 400 ± 160 pptv and showed concentrations up to 750 pptv. In comparison, other southern hemisphere tropical forests of several ppb (Tripathi et al., 2021; Paton-Walsh et al., 2022 and references therein) and site such as Amazon forest showed concentrations 2 to 10 times over our concentration (2 x 10³ to 10 x 10³ pptv, Wei et al., 2018). More recently, a study reported BVOC emissions from tropical forest in Thailand with averaged annual concentrations of 4253 \pm 1354 pptv (Pripdeevech et al., 2025).

BTEX show high concentrations in MO (total n = 268) with average concentration of 160 \pm 75 pptv for ethylbenzene, 674 \pm 499 pptv for toluene, 314 \pm 113 pptv for (m, p) xylenes, 364 \pm 143 pptv for (o) xylenes and 706 ± 513 pptv for benzene. These measurements are one order of magnitude higher than measured in previous studies realized during 2018-2019 in the same site (benzene, 12-25 pptv/80 pptv; xylenes, <40 pptv in Rocco et al., 2020; Verreyken et al., 2021). This is probably due to the difference of measurement techniques used. Indeed, in these other studies, different instrumentation was used for BTEX measurements. Furthermore, TENAX tubes are known to have residual concentration of benzene for which we have paid particular attention to the treatment and regeneration of TENAX cartridges (Wong and Webster, 2021). Also, high concentrations have been reported in Welgegund background site up to 290 pptv for benzene, 8590 pptv for toluene, 2040 pptv for ethylbenzene, 5800 pptv for (m + p)-xylenes and 1820 pptv for o-xylene (Jaars et al., 2018). Over all the year, the concentration of BTEX at MALO (n = 31) reached on average 557 ± 859 pptv (versus 342 ± 335 pptv for MO from April 2022 to July 2025) with highest values for benzene concentration (from 440 to 4899 pptv). It is now known that a part of measured BTEX can be produces by leaves as a stress indicator (Heiden et al., 1999; Misztal et al., 2015). Other studies showed fewer or similar BTEX concentration in tropical forests (<150 pptv, Kesselmeier et al., 2000; ~96 pptv, 1286 pptv, 30-150 pptv for benzene, toluene and xylenes in Paralovo et al., 2016 and 324 \pm 168 pptv, 181 \pm 110 pptv and 97 \pm 33 pptv in Pripdeevech et al., 2025).

At MO, α -pinene, β -pinene and limonene concentrations have been recorded of 145 ± 87 pptv, 175 ± 121 pptv and 249 ± 75 pptv, respectively. Previous studies showed concentrations at the same order of magnitude (<200 pptv in Rocco et al., 2020). At Welgegund background station, α -pinene, β -pinene and limonene concentrations were lower than our measurements with

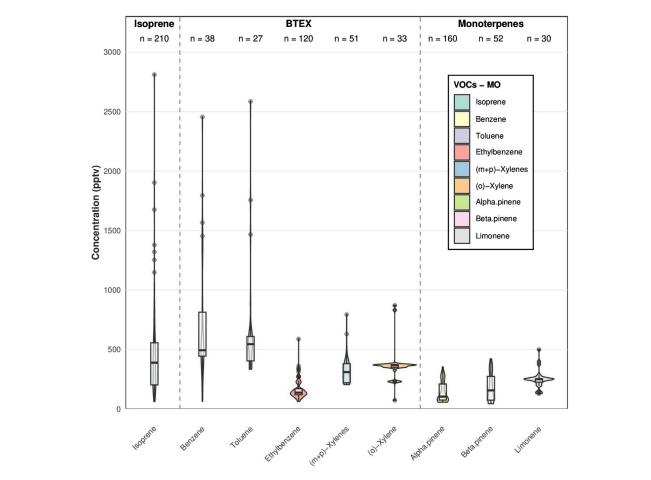


FIGURE 2 VOCs concentrations (expressed in pptv - STP conditions) at the OPAR-Maïdo observatory (MO) (statistics from April 2022 to July 2025) for isoprene, α -pinene, β -pinene and limonene (monoterpenes), benzene, toluene, ethylbenzene, (m + p + o)-xylenes (BTEX),. The violin plots and boxplots represent the data distribution. The horizontal line within each box indicates the median. The lower and upper edges of the box correspond to the first (Q1) and third (Q3) quartiles, respectively, defining the interquartile range (IQR). The whiskers extend to 1.5 times the IQR above Q3 and below Q1. Data points outside this range are considered outliers and are plotted individually. The width of the "violin" reflects the data density at different values.

concentrations of 71 pptv, 19 pptv and 30 pptv, respectively (Jaars et al., 2018). In MALO, only concentrations of α -pinene and limonene have been reported (314 pptv and 367 pptv in average, respectively). Previous study showed that endemic species from MALO are mostly isoprene emitters (~50 pptv at emission in Rocco et al., 2024; Supplementary Material S1). In comparison with other studies, concentrations at MO were <50 pptv (Rocco et al., 2020; Verreyken et al., 2021) and close to 200 pptv in another tropical forest in Reunion Island (Bélouve). In Thailand and Amazon forests (Pripdeevech et al., 2025; Kesselmeier et al., 2000), concentrations of 145 \pm 72 pptv of limonene and ~200 pptv of total monoterpenes have been reported. In background site, average total concentration of monoterpenes was up to 215 pptv, in line with our measurements.

4 Conclusion

Isoprene, monoterpene (α -pinene, ß-pinene, limonene) and BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) are investigated in the OPAR-Maïdo observatory (MO) and in the Mare-Longue lowland forest related to OZC-R Mare-Longue

forest research station (MALO) from 2022 to 2024, respectively. Monitoring of such VOC, based on discrete sampling with adsorbent tubes (Tenax®TA) followed by GC-MS analysis, provides a unique dataset in the Southern Hemisphere, in an area (Indian Ocean) where few VOC data are available. Combined with ancillary variables (meteorology, chemistry species out of VOC as O3, NOx in particular), data collected in this study should contribute to a better knowledge of VOC (BVOC in particular) concentrations, their behavior and related evolutionary trends in primary tropical forests and specific tropical insular mountain environments, in the context of global climate change and associated impacts on the natural environment. These measurements are notably essential for a better understanding of secondary organic aerosol (SOA) formation, atmospheric chemistry - particularly ozone formation - and cloud formation, all of which have significant implications for human health and climate. These two datasets, currently in progress, should lead to modelling improvements in such coupled tropical-oceanic environment. They should also lead to better mapping of VOC spatial distribution with the integration into last version dedicated models, from the synoptic scale to the turbulent scales, as in the

Meso-NH mesoscale meteorological research model (Lac et al., 2018) including the MEGAN (Model of Emissions of Gases and Aerosols from Nature) tool focused on fluxes of biogenic compounds (Guenther et al., 2006; 2012). Lastly, these data are also invaluable for identifying the links between BVOC emissions and local vegetation (atmosphere-biosphere relationship in the study of the critical zone), and for assessing biotic responses to climate stress and global change (Méndez et al., 2023).

Data availability statement

The datasets presented in this study can be found in online repositories (Geosur data catalog in https://www.osureunion.fr/en/home/). The names of the repository/repositories and accession number(s) can be found in the article via the following two references: (Rocco et al., 2025a; Rocco et al., 2025b). Requests for better understanding of data and their use should be addressed to the correspondence authors.

Author contributions

OM: Conceptualization, Data curation, Funding acquisition, Project administration, Resources, Supervision, Validation, Visualization, Writing - original draft, Writing - review and editing. PB: Conceptualization, Data curation, Formal Analysis, Methodology, Software, Writing - review and editing. PS: Conceptualization, Data curation, Resources, Writing - review and editing. MD: Data curation, Resources, Writing - review and editing. PH: Data curation, Resources, Writing - review and editing. EG: Data curation, Resources, Writing - review and editing. YH: Data curation, Resources, Writing - review and editing. CA-P: Data curation, Funding acquisition, Project administration, Resources, Writing - review and editing. VD: Funding acquisition, Resources, Writing - review and editing. OK: Data curation, Investigation, Visualization, Writing – review and editing. MR: Conceptualization, Data curation, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing - original draft, Writing - review and editing.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2025.1704158/full#supplementary-material

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