Isotopic biomonitoring of anthropic carbon emissions in a megalopolis

Edison Armando Díaz-Álvarez 1, Erick de la Barrera Corresp. 2

1 Instituto de Investigaciones Forestales, Universidad Veracruzana, Xalapa, Veracruz, Mexico
2 Instituto de Investigaciones en Ecosistemas y Sustentabilidad, Universidad Nacional Autónoma de México, Morelia, Michoacán, Mexico

Corresponding Author: Erick de la Barrera
Email address: delabarrera@unam.mx

Atmospheric pollution has become a serious threat for human health and the environment. However, the deployment, operation, and maintenance of monitoring networks can represent a high cost for local governments. In certain locations, the use of naturally occurring plants for monitoring pollution can be a useful supplement of existing monitoring networks, and even provide information when other types of monitoring are lacking. In this work, we i) determined the tissue carbon content and the δ¹³C values for the epiphytic CAM bromeliad Tillandsia recurvata and the relationship of both parameters with the existing CO concentrations in the Valley of Mexico basin, and ii) mapped the spatial distribution of such elemental and isotopic composition for this plant within the basin, in order to assess its potential as an atmospheric biomonitor of carbon monoxide, a pollutant with important repercussions on public health. The CO concentrations in the basin ranged from 0.41 ppm at rural locations to 0.81 ppm at urban sites. The carbon content of T. recurvata which averaged 42.9 ± 0.34% (dry weight), was not influenced by the surrounding CO concentration. In contrast, the δ¹³C depended on the sites where the plants were collected. For example, the values were –13.21‰ in rural areas and as low as –17.47‰ in an urban site. Indeed, the isotopic values had a positive linear relationship with the atmospheric CO concentrations. Given the close relationship observed between the isotopic composition of T. recurvata with the CO concentrations in the Valley of Mexico, the δ¹³C values can be useful for the detection of atmospheric carbonaceous emissions.
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Edison A. Díaz-Álvarez¹, Erick de la Barrera²

¹ Instituto de Investigaciones Forestales, Universidad Veracruzana, Xalapa, Veracruz 91070, Mexico
² Instituto de Investigaciones en Ecosistemas y Sustentabilidad, Universidad Nacional Autónoma de México, Morelia, Michoacán 58190, Mexico

Corresponding Author:
Erick de la Barrera²
Antigua Carretera a Pátzcuaro 8701, Morelia, Michoacán 58190, Mexico
Email address: delabarrera@unam.mx

Abstract
Atmospheric pollution has become a serious threat for human health and the environment. However, the deployment, operation, and maintenance of monitoring networks can represent a high cost for local governments. In certain locations, the use of naturally occurring plants for monitoring pollution can be a useful supplement of existing monitoring networks, and even provide information when other types of monitoring are lacking. In this work, we i) determined the tissue carbon content and the δ¹³C values for the epiphytic CAM bromeliad Tillandsia recurvata and the relationship of both parameters with the existing CO concentrations in the Valley of Mexico basin, and ii) mapped the spatial distribution of such elemental and isotopic composition for this plant within the basin, in order to assess its potential as an atmospheric biomonitor of carbon monoxide, a pollutant with important repercussions on public health.

The CO concentrations in the basin ranged from 0.41 ppm at rural locations to 0.81 ppm at urban sites. The carbon content of T. recurvata which averaged 42.9 ± 0.34% (dry weight), was not influenced by the surrounding CO concentration. In contrast, the δ¹³C depended on the sites where the plants were collected. For example, the values were −13.21‰ in rural areas and as low as −17.47‰ in an urban site. Indeed, the isotopic values had a positive linear relationship with the atmospheric CO concentrations.

Given the close relationship observed between the isotopic composition of T. recurvata with the CO concentrations in the Valley of Mexico, the δ¹³C values can be useful for the detection of atmospheric carbonaceous emissions.
Introduction
Atmospheric pollution has become a serious threat for human health and the environment. This is especially worrying for populous cities, which is a frequent case throughout Latin America (Kampa & Castanas, 2008; Rioja-Rodríguez et al., 2016). For example, Mexico City, with vigorous industrial and household activities, as well as numerous motor vehicles of all classes, has seen an increase of emissions of different pollutants to the atmosphere. This has resulted in a higher incidence of respiratory and cardiovascular diseases, which already cause at least 9,600 premature deaths annually just in this megalopolis and 20,000 in the whole country (Stevens et al., 2008; INEGI, 2011). In addition, atmospheric pollution is one of the leading causes of biodiversity loss and ecosystem change both, from nitrogen deposition and the release of greenhouse gas emissions (Sala et al., 2000; Rockström et al., 2009; Hooper et al., 2012).

Carbon monoxide (CO) is among the main atmospheric pollutants with public health repercussions. Not only can acute exposure to high concentrations of CO lead to death, but the chronic exposure to low concentrations of this gas has been associated with cardiovascular and neurological damage (WHO, 1999; Townsend & Maynard, 2002; Prockop, 2005; Chen et al., 2007). CO results from the combustion of carbonaceous fuels, which also produces carbon dioxide. The proportion in which they are emitted depends on the quality of the combustion. For example, if a motor works in optimal conditions, i.e., when the mixture of air, fuel, and temperature inside an automobile engine is ideal, a complete combustion of the fuel is achieved, resulting in a complete oxidation of carbon and the subsequent emission of CO₂, predominantly. For example, 3.8 liters of gasoline, whose weight is 2.7 kilograms, can emit 9 kilograms of CO₂ and ideally very low or insignificant amounts of CO (Salameh, 2014). Nevertheless, when the engine conditions are not optimal, an incomplete combustion/oxidation generates higher emissions of CO; this generally occurs in the engines of old cars and during heavy traffic congestions, which are frequent in the Valley of Mexico, where the vehicular fleet commonly exceeds 20 years of operation (Williams, 1990; Turnbull et al., 2011a; Silva et al., 2013; Salameh, 2014; SEDEMA, 2016a).
A characterization of air quality, by means of monitoring the concentration and distribution of atmospheric pollution, is thus imperative, including the monitoring of carbon emissions. However, the deployment, operation and maintenance of monitoring networks can represent high costs that in some cases exceed the budget and priorities of the local governments (Díaz-Álvarez et al., 2019). For example, only 77 cities from 17 countries in Latin America and the Caribbean have public information about atmospheric pollution, while 16 countries in the region do not release data at all (Rioja-Rodriguez et al., 2016). In Mexico, federal environmental and health regulations mandate the deployment of air quality monitoring networks for cities whose population exceeds half a million and for settlements with emissions surpassing 20,000 tons of regulated pollutants per year (SEMARNAT, 2012). However, as it occurs all over Latin America and the Caribbean, the monitoring of air quality is not evaluated in many localities as required (Rioja-Rodriguez et al., 2016; Instituto Nacional de Ecología y Cambio Climático, 2017).

The use of naturally occurring plants as biomonitors can supplement existing air quality monitoring systems and in some cases, when a monitoring system is lacking, be utilized for the early detection of increasing atmospheric pollution, considering that the elemental and isotopic composition of plant tissues can respond to the concentration of some pollutants (Díaz-Álvarez et al. 2018, 2020). Once the origin and concentration of the pollution is determined, reduction and mitigation actions can be implemented. A particularly suitable group of plants for biomonitoring are those that depend exclusively from atmospheric sources for their mineral nutrition, commonly named “atmospheric plants” (Markert et al. 2003; Vianna et al. 2011; Pellegrini et al. 2014; Díaz-Álvarez & de la Barrera 2018; Díaz-Álvarez et al. 2018). One of such species is Tillandsia recurvata (L.) L (Schmitt et al., 1989). This CAM bromeliad is distributed from the southern United States to Argentina and Chile, and it is commonly found growing on different built structures in cities (Schrimpff, 1984; Díaz-Álvarez & de la Barrera 2018). Additionally, the plant can remain physiologically active year-round and, thanks to its absorptive trichomes, carry out bioaccumulation of
different atmospheric pollutants including heavy metals, polycyclic aromatic hydrocarbons, nitrogen, sulfur, and carbon (Schrimpff, 1984; Zambrano et al., 2009; Castañeda et al., 2016; Díaz-Álvarez & de la Barrera 2018; Piazzetta et al. 2018). Although, the carbon isotopic composition of this plant has been reported for polluted and non-polluted sites, this is the first time that a specific relationship between carbon emissions and the plant’s responses is determined.

By means of an extensive sampling throughout the Valley of Mexico, we i) determined the carbon content and the $\delta^{13}C$ values for the epiphytic CAM bromeliad *Tillandsia recurvata* and their relationship with the prevailing CO concentrations, and ii) mapped the spatial distribution of such elemental and isotopic composition of this plant in the basin, in order to assess the potential that this plant has as an atmospheric biomonitor of carbon monoxide.

**Materials & Methods**

**Study region**

The study was conducted in the Valley of Mexico basin which covers an area of 7500 km$^2$, with a mean elevation of 2240 m, and a mean annual precipitation of 600 mm that can reach up to 1300 mm in the surrounding mountains at 5400 m (Fig. 1; Calderon and Rzedowski, 2001; SMN, 2016). The basin includes portions of the states of Hidalgo, Mexico, and Mexico City. Pachuca, the capital of Hidalgo, at the north has a population of 3 million. At the southern portion of the Valley sits Mexico City, whose population reaches 20 million. Additionally, various small towns and settlements with industrial or agricultural activities contribute to the 30 million inhabitants of the basin (INEGI, 2011; Díaz-Álvarez & de la Barrera 2018).

**Atmospheric CO concentration and biomonitoring**

The Mexico City environmental authority has deployed an Automatic Atmospheric Monitoring Network (http://www.aire.cdmx.gob.mx/default.php) comprised of 33 stations, which monitor different parameters,
including wet N deposition, O$_3$, NOx, NO$_2$, NO, PM$_{10}$ PM$_{2.5}$ and CO (Fig. 1). We calculated the mean concentration of CO (ppm) between January and November 2014 for each one of the 21 stations that recorded this parameter during 2014.

We determined the relationship between CO concentrations in the Valley of Mexico and the carbon content and the $^{813}$C values was determined for the epiphytic CAM bromeliad Tillandsia recurvata, which has an ample distribution in the Americas. This plant has been utilized as a biomonitor of atmospheric pollution and can be easily found in the Valley of Mexico (Zambrano et al., 2009; Díaz-Álvarez et al., 2018; Diaz-Álvarez & de la Barrera, 2018; Piazzetta et al., 2018). Sampling sites were determined in two steps. First, potential sites for the occurrence of *T. recurvata* were identified utilizing Google Earth’s satellite scenes, followed by a corroboration by means of the StreetView function where available. In particular, we identified the presence of natural protected areas, vegetation stands in rural/agricultural areas, or parks and other vegetated features in urban areas, where trees and shrubs that could act as phorophytes for *T. recurvata* were be present. A total of 73 sites were identified within the basin. Second, a stratified sampling (within the identified vegetated sites; Wang et al. 2012) was conducted on 3–15 November 2014, which occurred towards the end of the rainy season, late in the growing period for *T. recurvata*. After discarding those sites where *T. recurvata* was not found and those where access was not possible, plant samples were collected for elemental and isotopic analyses from 22 sites (Fig. 1), including urban parks (7 sites), built urban structures (4 sites), agricultural sites (6 sites), and natural protected areas (5 sites).

At each site, newly formed, fully developed leaves, which can be visually differentiated from those that grew in previous years, were collected (Permit SGPA/DGGFS/712/2767/14, Secretaría de Medio Ambiente y Recursos Naturales, Mexico) from 5 mature individuals growing at least 5 m apart (Harmens et al., 2008; Díaz-Álvarez et al., 2019). The samples were dried at 60°C in a gravity convection oven until reaching constant weight. Sample preparation for stable isotope analyses was conducted following Díaz-Álvarez and de la Barrera (2018). The carbon isotope ratios, reported in parts per
thousand were calculated relative to Vienna–Pee Dee Belemnite (VPDB). The analytical precision for the
$\delta^{13}$C was 0.2 ± 0.07‰ (SD). The natural abundances of $^{13}$C were calculated as:

$$\delta^{13}C \text{ (‰ versus V-PDB)} = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

where, R is the ratio of $^{13}$C/$^{12}$C for carbon isotope abundance for a given sample (Ehlenringer and
Osmond, 1989; Evans, 2001).

Statistical and spatial analyses

Data were analyzed following Díaz-Álvarez & de la Barrera (2018). In particular, linear regressions were
calculated to determine the relationship between CO concentrations and carbon content (% dry weight),
as well as the isotopic composition ($\delta^{13}$C values) for Tillandsia recurvata in the Valley of Mexico. The
differences between sites for the carbon content and the $\delta^{13}$C values were determined by means of the
Kruskal-Wallis one-way analysis of variance by ranks, followed by a Nemenyi’s post-hoc tests for
pairwise multiple comparisons ($p \leq 0.05$). The analyses were conducted using the Pairwise multiple
comparison of mean ranks package (PMCMR) in R (version 3.5.3, R Core Team, R foundation for
Statistical Computing, Vienna, Austria; Pohlert, 2014).

Data interpolation for CO concentration within Mexico City and for T. recurvata tissue carbon
content and $\delta^{13}$C values throughout the Valley of Mexico were conducted with the Ordinary Kriging
model contained in ArcGIS 10.5 (ESRI, Redlands, CA, USA), which was also utilized to create the maps.
This interpolation method is based on the assumption that data are spatially autocorrelated (Cressie, 1988;
Wang et al., 2002; Wong et al., 2004), which generally is the case for atmospheric pollutants, as their
concentration is higher with proximity to the source, thus influencing the ensuing plant responses
(Stevens et al., 2004; Díaz-Álvarez et al., 2018). This allows the estimation of parameters of interest in
relatively large geographical regions (Liao et al., 2017), where only a sparse sampling is available (Oliver
& Webster, 2014). While interpolation protocols have been developed that improve on Ordinary Kriging,
this model is among the most utilized methods in environmental studies, including those considering
Results

Spatial distribution of CO concentrations

The CO concentration, averaged 0.67 ± 0.03 ppm in Mexico City, where the monitoring network is deployed (Fig. 2). The central and northern portions had the highest concentrations of CO, reaching a maximum of 0.81 ppm, and the lowest concentration was found at the northeast end of the distribution of the monitoring network, where it reached a mean value of 0.41 ppm (Fig. 2).

Carbon content and isotopic composition for Tillandsia recurvata

On average, the tissue carbon content was 42.91 ± 0.34% (dry weight) ranging from 38.43% for plants collected in the urban area of a small town at the north-west portion of the Valley, to 44.92% at the southern part of the Valley, in the middle of the Mexico City (Fig. 3A). However, the carbon content was not affected by the CO concentration recorded during 2014 by the Mexico City monitoring network ($R^2 = 0.015$; Fig. 4A).

Contrasting with what occurred for the carbon content, the $\delta^{13}C$ values responded positively to the atmospheric CO concentration, being lower in sites with higher concentrations than in those with lower CO concentrations (Fig. 4B; $R^2 = 0.675$). For example, the $\delta^{13}C$ values reached −16.16‰ in Pachuca, a populous city at the north of the Valley, which is lower than in some rural sites further south (Fig. 3B). The $\delta^{13}C$ values were as negative as −17.47‰ for plants collected in an urban site where the mean CO concentration averaged 0.70 ppm during 2014 (Fig. 3B). In contrast, the highest $\delta^{13}C$ values of −13.21‰ were found for plants growing at the archeological site of Teotihuacan, whose CO concentration was the lowest recorded inside the monitored area ($p < 0.05$; Fig. 3B).
Discussion

The atmospheric concentration of CO in the area covered by the monitoring network tended to be higher in the vicinity of the numerous important and busy motorways that have been built in this region and are utilized by the 5.2 million vehicles registered in Mexico City and its metropolitan area, in addition to various thousands of visiting vehicles from other cities and states (SEDEMA 2016a). Indeed, motor vehicles are the main source of CO for the region, contributing with 96% of the total emissions, which amount to nearly 700 million tons just in Mexico City; the remaining 4% originated from industrial and domestic sources (SEDEMA, 2016b). However, it is worth mentioning that the CO concentrations of 3.8 ppm measured in Mexico City and its metropolitan area during this study did not exceed the Mexican standard (exposure to 11 ppm for 8 hours) nor the World Health Organization's (9 ppm) and the United States Environmental Protection Agency's criteria for this pollutant (9 ppm; WHO, 1999; SEMARNAT, 2012; SEDEMA, 2016a).

While the carbon content of *T. recurvata* was insensitive to the CO concentration, the $\delta^{13}$C of newly formed leaves adequately biomonitored the prevailing atmospheric pollution, with values that were substantially more negative in polluted sites than in "clean" sites, a pattern that has been previously documented with atmospheric biomonitors (Martin, 1994; Lichtfouse et al., 2003; Zambrano et al., 2009; Cobley & Pataki, 2019). When interpreting the isotopic signature of carbon biomonitors it is important to consider that while CO is but a small fraction of the urban carbonaceous emissions, it is produced from combustion simultaneously with CO$_2$, a gas that is usually not included in urban air quality monitoring protocols (SEMARNAT 2012; SEDEMA 2016b). Thus, the plants are in fact mostly recording the isotopic signal of CO$_2$ assimilated by photosynthesis. However, the relationship between atmospheric CO and CO$_2$ concentrations is usually linear, so that the "calibration" conducted in the present study utilizing CO (the only carbon gas that is monitored) as an integrative proxy for urban carbon emissions could be utilized in other unmonitored cities (Turnbull et al. 2011b; Silva et al. 2013; Gromov et al. 2017).

The carbon content in plant tissues is commonly ca. 50% on a dry mass basis, although it varies
depending on different factors, such as the developmental stage, organ, species, latitude, water availability, nutrient availability, and the CO$_2$ concentration prevalent during organ development (Díaz-Álvarez et al., 2015; Ma et al., 2018). High CO$_2$ concentrations, such as those found in urban environments, like Mexico City, are among the factors leading to higher photosynthetic rates in CAM plants (Drennan and Nobel, 2000; Andrade et al., 2007; Smith et al., 2009; Zotz et al., 2010; SEDEMA, 2016a). However, when plants are exposed to different concentrations of hazardous gases such as NOx, SO$_2$ and CO, the net photosynthetic rate and the photosynthetic pigment content can decrease, because the resulting oxidative stress alters the carboxylation process, leading to a net reduction of the carbon content (Bytnerowicz et al., 2001; Mittler, 2002; Muneer et al., 2014). Such gases are monitored and have actually been detected in areas of Mexico City and Pachuca, although it appears that their concentration is not high enough to cause a tissue carbon reduction for *Tillandsia recurvata* (Díaz-Álvarez and de la Barrera 2018; SEDEMA, 2016a). In this respect, this species displays a physiological resistance to O$_3$ and SO$_2$, which may contribute to the results observed (Benzig et al., 1992).

Three factors can help explain the general carbon isotopic pattern observed for *T. recurvata* throughout the study. The first factor is a large difference in the isotopic signature for CO$_2$ from different sources. In particular, the δ$^{13}$C values of the air from natural environments can reach –8‰ (Pichlmayer et al., 1998; Widory & Javoy, 2003). In contrast, the carbon in the air is depleted of $^{13}$C in sites where motor vehicles and the industrial activities are common. In this regard, the δ$^{13}$C values for coal burning, gasoline, diesel, and natural gas range from –25 to –42‰ (Pichlmayer et al., 1998; Röckman et al., 2002; Pataki et al., 2003; Widory & Javoy, 2003; Semmens et al., 2004; Naus et al., 2018).

A second factor is an increasing isotopic discrimination against $^{13}$C that occurs for CAM plants exposed to high CO$_2$ concentrations (Zhu et al., 1999). In this case, given that increasing concentrations of CO$_2$ can inhibit the activity of phosphoenolpyruvate carboxylase (PEPc), which is already near saturation at natural concentrations of CO$_2$ (Ting, 1994). PEPc has an isotopic discrimination that ranges between 2 and 10‰, which explains the common δ$^{13}$C values for CAM plants. However, if PEPc is inhibited, the ribulose bisphosphate carboxylase/oxygenase, an enzyme with a higher discrimination of
22–27‰, will conduct most of the carboxylation, resulting in the observed $\delta^{13}\text{C}$ values, which were more negative in polluted sites (Ehleringer & Osmo, 1989; Farquhar et al., 1989; Ting 1994; McNevin et al., 2007; Smith et al., 2009; Cernusak et al., 2013).

A third potential factor influencing the observed pattern is air temperature in cities. Warmer than natural nocturnal air temperatures, such as those resulting from the urban heat island in Mexico city, drive changes in the carbon fixation cycle of CAM plants, which in turn leads to an increased isotopic discrimination against $^{13}\text{C}$ (Troughton & Card, 1975; Farquhar et al., 1989; Jauregui, 1997; Zhu et al., 1999; Cui & de Foy, 2012; Cernusak et al., 2013).

**Conclusions**

Owing to the close relationship observed between the isotopic composition of *Tillandsia recurvata* and the atmospheric CO concentration in the Valley of Mexico, the $\delta^{13}\text{C}$ values can be useful for characterizing carbonaceous pollution. In addition, given that the emissions of CO and CO$_2$ are accompanied by the emission of other pollutants, such as NOx, SO$_2$, and heavy metals, which results in the formation of secondary pollutants such as O$_3$ and particulate matter, this plant can be deemed as an ideal candidate for implementing broader monitoring studies in regions where automatic monitoring networks are not available and the bromeliad is abundant.

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References

Andrade JL, de la Barrera E, Reyes-García C, Ricalde MF, Vargas-Soto G, Cervera JC (2007) El Metabolismo ácido de las crasuláceas diversidad, fisiología ambiental y productividad. Boll. Soc Bot México 81:37–51.

Benzing, D. H., Arditti, J., Nyman, L. P., Temple, P. J., & Bennett, J. P. (1992). Effects of ozone and sulfur dioxide on four epiphytic bromeliads. Environmental and Experimental Botany, 32(1), 25–32. doi:10.1016/0098-8472(92)90026-x

Bytnerowicz, A., Padgett, P.E., Parry, S.D., Fenn, M.E., Arbaugh, M.J., 2001. Concentrations, deposition, and effects of nitrogenous pollutants in selected California ecosystems. Sci. World J. 1, 304e311. Doi: 10.1100/tsw.2001.395.

Calderón, R. G., Rzedowski, J. Flora fanerógamica del Valle de México. pp.1406. (Instituto de Ecología y CONABIO, Xalapa, Veracruz, México 2001).

Castañeda Miranda, A. G., Chaparro, M. A. E., Chaparro, M. A. E., & Böhnel, H. N. (2016). Magnetic properties of Tillandsia recurvata L. and its use for biomonitoring a Mexican metropolitan area. Ecological Indicators, 60, 125–136. doi:10.1016/j.ecolind.2015.06.025

Cernusak, L. A., Ubierna, N., Winter, K., Holtum, J. A. M., Marshall, J. D., & Farquhar, G. D. (2013). Environmental and physiological determinants of carbon isotope discrimination in terrestrial plants. New Phytologist, 200(4), 950–965. doi:10.1111/nph.12423

Chen TM, Kushner WG, Gokhale J, Shofer S. 2007. Outdoor air pollution: nitrogen dioxide, sulfur dioxide, and carbon monoxide health effects. Am. J. Med. Sci. 333, 249–256.

Cobley, L.A.E., & Pataki, D. E. (2019). Vehicle emissions and fertilizer impact the leaf chemistry of urban trees in Salt Lake Valley, UT. Environmental Pollution, 254, 112984. doi:10.1016/j.envpol.2019.112984

Cressie, N. 1988. Spatial prediction and ordinary Kriging. Math. Geol 20, 405–421.
Cui, Y. Y., & de Foy, B. (2012). Seasonal Variations of the Urban Heat Island at the Surface and the Near-Surface and Reductions due to Urban Vegetation in Mexico City. Journal of Applied Meteorology and Climatology, 51(5), 855–868. Doi: 10.1175/jamc-d-11-0104.1

Díaz-Álvarez E.A., de la Barrera E. 2018. Characterization of nitrogen deposition in a megalopolis by means of atmospheric biomonitors. Scientific Reports, 8:13569. Doi: 10.1038/s41598-018-32000-5

Díaz-Álvarez E.A. Lindig-Cisneros R, de la Barrera E. 2015. Responses to simulated nitrogen deposition by the neotropical epiphytic orchid *Laelia speciosa*. PeerJ 3: e1021.

Díaz-Álvarez, E. A., Lindig-Cisneros, R. de la Barrera, E. 2018. Biomonitors of atmospheric nitrogen deposition: potential uses and limitations. Conserv. Physiol. Conserv 6, coy011. Doi: 10.1093/conphys/coy011

Díaz-Álvarez E. A., de la Barrera, E., Arciga-Pedraza A. Arróniz-Crespo M. 2019. Bryophyte enzymatic responses to atmospheric nitrogen deposition: A field validation for potential biomonitors. The Bryologist. 122: 396–403. Doi: 10.1639/0007-2745-122.3.396.

Díaz-Álvarez EA, de la Barrera E, Barrios-Hernández EY, Arróniz-Crespo M. 2020. Morphophysiological screening of potential organisms for biomonitoring nitrogen deposition. Ecological Indicators 108: 105729. DOI: 10.1016/j.ecolind.2019.105729

Drennan P.M. Nobel P.S. 2000. Responses of CAM species to increasing atmospheric CO2 concentrations. Plant Cell and Environment. 23: 767–781.

Ehleringer, J. R., Osmond, B. O. 1989. Stable isotopes. *Plant physiological ecology*. (ed. Pearcy, R. W., Ehleringer, J. R., Mooney, H. A., Rundel, P. W.) 281-300 (Chapman & Hall, 1989).

Evans R. 2001. Physiological mechanisms influencing plant nitrogen isotope composition. *Trends Plant Sci* 6:121–126.

Farquhar, G. D., Ehleringer, J. R., & Hubick, K. T. (1989). Carbon Isotope Discrimination and Photosynthesis. Annual Review of Plant Physiology and Plant Molecular Biology, 40(1), 503–537. Doi:10.1146/annurev.pp.40.060189.0024
Gómez-Losada A, Santos FM, Gibert K, Pires JCM. 2019. A data science approach for spatio
temporal modelling of low and resident air pollution in Madrid (Spain): Implications for
epidemiological studies. Computers, Environment and Urban sysems 75: 1-11. DOI:
10.1016/j.compenvurbsys.2018.s12.005

Gromov S, Nreninkmeije CAM, Jöckel P. 2017. Proxies and uncertainties for 13C/12C ratios of
atmospheric reactive gases emissions. Atmospheric Chemistry and Physics Discussions 17:
doi:10.5194/acp-2016-1138

Gupta S, Pebesma E, Mateu J, Degbelo A. 2018. Air quality monitoring network design
optimisation for robust land use regression models. Sustainability 10: 1442. DOI:
10.3390/su10051442

Harmens D, Norris D, Cooper D, Hall J. 2008. Spatial trends in nitrogen concentrations in
mosses across Europe in 2005/2006. Report on Nitrogen in European Mosses Work
Package 4. The UNECE International Cooperative Program on Vegetation,
https://icpvegetation.ceh.ac.uk/

Hooper, D. U., Adair, E. C., Cardinale, B. J., Byrnes, J. E. K., Hungate, B. A., Matulich, K. L.,
O’Connor, M. I. (2012). A global synthesis reveals biodiversity loss as a major driver of
ecosystem change. Nature, 486(7401), 105–108. doi:10.1038/nature11118

Huang S, Xiang H, Yang W, Zhu Z, Tian L, Deng S, Zhang T, Lu Y, Liu F, Li X, Liu S. 2020.
Short-term effect of air pollution on tuberculosis based on Kriged data: a time-series
analysis. International Journal of Environmental Research and Public Health 17: 1522.
DOI: 10.3390/ijerph17051522

Instituto Nacional de Ecología y Cambio Climático (INECC). 2017. Informe Nacional de
Calidad del Aire 2016, México.
Jauregui, E. (1997). Heat island development in Mexico City. Atmospheric Environment, 31(22), 3821–3831. Doi: 10.1016/s1352-2310(97)00136-2

Kampa, M., & Castanas, E. (2008). Human health effects of air pollution. Environmental Pollution, 151(2), 362–367. doi:10.1016/j.envpol.2007.06.012

Liao Y, Li D, Zhang N. 2017. Comparison of interpolation models for estimating heavy metals in soils under various spatial characteristics and sampling methods. Transactions in GIS 22: 409–434. DOI: 10.1111/tgis.12319

Lichtfouse E, Lichtfouse M, Jaffrèzic A. 2003. $\delta^{13}$C values of grasses as a novel indicator of pollution by fossil-fuel-derived greenhouse gas CO$_2$ in urban areas. Environmental Science and Technology 37: 87–89.

Ma, S., He, F., Tian, D., Zou, D., Yan, Z., Yang, Y., Zhou T., Huang K., Shen H., Fang, J. (2018). Variations and determinants of carbon content in plants: a global synthesis. Biogeosciences, 15: 693–702. Doi: 10.5194/bg-15-693-2018

Markert, B.A., Breure, A.M., Zechmeister, H.G. 2003. Definitions, strategies and principles for bioindication/biomonitoring of the environment. In: Markert, B.A., Breure, A.M., Zechmeister, H.G. (eds.) Bioindicators and Biomonitors: Principles, Concepts and Applications. Elsevier, Oxfourt. Pp. 3–40.

Martin, C. E. 1994. Physiological ecology of the Bromeliaceae, Bot. Rev., 60(1), 1–82.

McNevin, D. B., Badger, M. R., Whitney, S. M., von Caemmerer, S., Tcherkez, G. G. B., & Farquhar, G. D. (2007). Differences in Carbon Isotope Discrimination of Three Variants of D-Ribulose-1,5-bisphosphate Carboxylase/Oxygenase Reflect Differences in Their Catalytic Mechanisms. Journal of Biological Chemistry, 282(49), 36068–36076. doi:10.1074/jbc.m706274200
Mittler R (2002). Oxidative stress, antioxidants and stress tolerance. Trends Plant Sci. 7: 405–410.

Muneer, S., Kim, T. H., Choi, B. C., Lee, B. S., Lee, J. H. (2014). Effect of CO, NOx and SO2 on ROS production, photosynthesis and ascorbate–glutathione pathway to induce Fragaria × annása as a hyperaccumulator. Redox Biology. 2: 91-98. DOI: 10.1016/j.redox.2013.12.006

Naus, S., Röckmann, T., Popa, M. E. (2018). The isotopic composition of CO in vehicle exhaust. Atmospheric Environment, 177, 132–142. doi:10.1016/j.atmosenv.2018.01.015

Oliver MA, Webster R. 2014. A tutorial guide to geostatistics: Computing and modelling variograms and kriging. Catena 113: 56–69. DOI: 10.1016/j.catena.2013.09.006

Pataki DE, Bowling DR, Ehleringer JR. 2003. Seasonal cycle of carbon dioxide and its isotopic composition in an urban atmosphere: Anthropogenic and biogenic effects. Journal of geophysical research. 108. D23, 4735. Doi: 10.1029/2003JD003865.

Pellegrini E, Lorenzini G, Loppi S, Nali C. 2014. Evaluation of the suitability of Tillandsia usneoides (L.) L. as biomonitor of airborne elements in an urban area of Italy, Mediterranean basin. Atmospheric Pollution Research 5: 226–235.

Piazzetta, K.D., Ramsdorf, W. A. & Maranho, L.T. (2018) Use of airplant Tillandsia recurvata L., Bromeliaceae, as biomonitor of urban air pollution. Aerobiologia, 35: 125. Doi: 10.1007/s10453-018-9545-3

Pichlmayer, F., Schoner, W., Seibert, P., Stichler, W., Wagen-bach, D. 1998: Stable isotope analysis for characterization of pollutants at high elevation alpine sites, Atmos. Environ., 32(23), 4075–4085, 1998

Pohlert T. (2014). The Pairwise Multiple Comparison of Mean Ranks Package (PMCMR). R package. http://CRAN.R-project.org/package=PMCMR.

Prockop LD. 2005. Carbon monoxide brain toxicity: clinical, magnetic resonance imaging, magnetic resonance spectroscopy, and neuropsychological effects in 9 people. J. Neuroimaging 15, 144–149.
Rioja-Rodríguez H., Soares da Silva A., Texcala-Sangrador JL., Moreno-Banda GL. 2016 Air pollution management and control in Latin America and the Caribbean: implications for climate change. Rev Panam Salud Publica. 2016;40(3):150–59.

Röckmann T, Jöckel P, Gros V, Bräunlich M, Possne G. Brenninkmeijer CAM. 2002. Using $^{14}$C, $^{13}$C, $^{18}$O and $^{17}$O isotopic variations to provide insights into the high northern latitude surface CO inventory. Atmospheric Chemistry and Physics, 2(2):147–159, 2002.

Rockström, J., W. Steffen, K. Noone, Å. Persson, F. S. Chapin, III, E. Lambin, T. M. Lenton, M. Scheffer, C. Folke, H. Schellnhuber, B. Nykvist, C. A. De Wit, T. Hughes, S. van der Leeuw, H. Rodhe, S. Sörlin, P. K. Snyder, R. Costanza, U. Svedin, M. Falkenmark, L. Karlberg, R. W. Corell, V. J. Fabry, J. Hansen, B. Walker, D. Liverman, K. Richardson, P. Crutzen, and J. Foley. 2009. Planetary boundaries: exploring the safe operating space for humanity. Ecology and Society 14(2): 32.

Sala OE, Chapin III SF, Armesto JJ, Berlow E, Bloomfield J, Dirzo R, Huber-Sanwald E, Huenneke LF, Jackson RB, Kinzig A, Leemans R, Lodge DM, Mooney HA, Oesterheld M, Poff NL, Sykes MT, Walker BH, Walker M, Wal DH (2000) Global biodiversity scenarios for the year 2100. Science 287:1770–1774. doi: 10.1126/science.287.5459.1770.

Salameh, Z. (2014). Factors Promoting Renewable Energy Applications. Renewable Energy System Design, 1–32. doi:10.1016/b978-0-12-374991-8.00001-5

Schmitt, A. K., Martin, C. E., and Lutgge, U. E.: Gas exchange and water vapor uptake in the atmospheric bromeliad *Tillandsia recurvata* L., Bot. Acta, 102, 80–84, 1989.

Schrimpff, E. (1984). Air pollution patterns in two cities of Colombia, S. A. According to trace substances content of an epiphyte (*Tillandsia recurvata* L.). Water, Air, and Soil Pollution, 21(1-4), 279–315. doi:10.1007/bf00163631

SEDEMA, Secretaría del Medio Ambiente de la Ciudad de México. 2016a. Inventario de emisiones de la CDMX, contaminantes criterio, tóxicos y de efecto invernadero 2014. Dirección General de Gestión de la Calidad del Aire, Dirección de Monitoreo Atmosférico. México, D. F.
SEDEMA, Secretaría del Medio Ambiente de la Ciudad de México. 2016b. Calidad del aire en la Ciudad de México, informe 2015. Dirección General de Gestión de la Calidad del Aire, Dirección de Monitoreo Atmosférico. México, D. F.

SEMARNAT 2012. Norma Oficial Mexicana NOM-156-SEMARNAT-2012, Establecimiento y operación de sistemas de monitoreo de la calidad del aire. México D.F.

Semmens C, Ketler R, Schwendenmann L, Nesic Z, Christen A. 2014. Isotopic composition of CO2 in gasoline, diesel and natural gas combustion exhaust in Vancouver, BC, Canada. A technical report of the University of British Columbia. pp. 1-12. Doi: 10.14288/1.0103591.

Servicio Meteorológico Nacional (SMN). Normales climatológicas por estado 1981-2010.

http://smn.cna.gob.mx/es/informacion-climatologica-ver-estado?estado=df
http://smn.cna.gob.mx/es/informacion-climatologica-ver-estado?estado=gto
http://smn.cna.gob.mx/es/informacion-climatologica-ver-estado?estado=mex (2016).

Silva, S. J., Arellano, A. F., & Worden, H. M. (2013). Toward anthropogenic combustion emission constraints from space-based analysis of urban CO2 / CO sensitivity. Geophysical Research Letters, 40(18), 4971–4976. doi:10.1002/grl.50954

Smith SD, Tissue DT, Huxman TE, Loik ME. 2009. Ecophysiological responses of desert plants to elevated CO2: environmental determinants and case studies. In: de la Barrera E, Smith WK (eds.) Perspectives in Biophysical Plant Ecophysiology: A Tribute to Park S. Nobel. UNAM, Mexico City. Pp. 363-390.

Stevens CJ, Dise NB, Mountford JO, Gowing DJ. 2004. Impact of nitrogen deposition on the species richness of grasslands. Science 303: 1876–1879. DOI: 10.1126/science.1094678.

Stevens G, Dias RH, Thomas KJA, Rivera JA, Carvalho N, Barquera S. Hill K. Ezzati M. 2008. Characterizing the Epidemiological Transition in Mexico: National and Subnational Burden of Diseases, Injuries, and Risk Factors. PLOS Medicine 5(7): e163. Doi:

10.1371/journal.pmed.0050163
Ting I.P. (1994) CO2 and Crassulacean acid metabolism plants: a review. In Regulation of Atmospheric CO2 and O2 by Photosynthetic Carbon Metabolism (eds N.E. Tolbert & J. Preiss), pp. 176–183, Oxford University Press, Oxford.

Townsend CL, Maynard RL. 2002. Effects on health of prolonged exposure to low concentrations of carbon monoxide. Occup. Environ. Med. 59, 708–711.

Troughton, J. H., & Card, K. A. (1975). Temperature effects on the carbon-isotope ratio of C3, C4 and crassulacean-acid-metabolism (CAM) plants. Planta, 123(2), 185–190. doi:10.1007/bf00383867

Turnbull JC, Karion A, Fischer ML, Faloona I, Guilderson T, Lehman SJ, Miller BR, Miller JB, Montzka S, Sherwood T, Saripalli S, Sweeney C, Tans PP. 2011a. Assessment of fossil fuel carbon dioxide and other anthropogenic gas emissions from airborne measurements over Sacramento, California in spring 2009. Atmospheric Chemistry and Physics 11: 705–721.

Turnbull, J. C., Tans, P. P., Lehman, S. J., Baker, D., Conway, T. J., Chung, Y. S., … Zhou, L.-X. 2011b. Atmospheric observations of carbon monoxide and fossil fuel CO2 emissions from East Asia. Journal of Geophysical Research: Atmospheres, 116(D24), n/a–n/a. doi:10.1029/2011jd016691

Vianna NA, Gonçalves D, Brandao F, de Barros RP, Amado Filho GM, Meire RO, Torres JP, Malm O, D'Oliveira Júnior A, Andrade LR. 2011. Assessment of heavy metals in the particulate matter of two Brazilian metropolitan areas by using Tillandsia usneoides as atmospheric biomonitor. Environmental Science and Pollution Research International 18: 416–427. DOI: 10.1007/s11356-010-0387-y

Wang J, Liu J, Zhuan D, Li L, Ge Y. 2002. Spatial sampling design for monitoring the area of cultivated land. International Journal of Remote Sensing 23: 263–284. DOI: 10.1080/01431160010025998

Wang W, Pataki DE 2010. Spatial patterns of plant isotope tracers in the Los Angeles urban region. Landsc Ecol 25:35–52.

Widory D., Javoy M. (2003). The carbon isotope composition of atmospheric CO2 in Paris. Earth and Planetary Science Letters, 215(1-2), 289–298. doi:10.1016/s0012-821x(03)00397-2
Williams, A. (1990). Pollutant formation and control. Combustion of Liquid Fuel Sprays, 127–160. doi:10.1016/b978-0-408-04113-3.50009-9

Wong DW, Yuan L, Perlin SA. 2004. Comparison of spatial interpolation methods for the estimation of air quality data. Journal of Exposure Analysis and Environmental Epidemiology 14: 404-415. DOI: 10.1038/sj.jea.7500338

World Health Organization WHO 1999. Environmental Health Criteria 213, Carbon monoxide (second edition). Geneva, Pp. 464

Zambrano A, Medina C, Rojas A, López D, Chang L, Sosa G (2009) Distribution and sources of bioaccumulative air pollutants at Mezquital Valley, Mexico, as reflected by the atmospheric plant Tillandsia recurvata L. Atmos Chem Phys 9:6479–6494.

Zhu J., Goldstein G. & Bartholomew D.P. (1999) Gas exchange and carbon isotope composition of Ananas comosus in response to elevated CO2 and temperature. Plant, Cell and Environment 22, 999–1007.

Zotz G, Wiebke B, Hietz P, Nadine K (2010) Growth of epiphytic bromeliads in a changing world: The effects of CO2, water and nutrient supply. Acta Oecol 36:659–665. Doi: 10.1016/j.actao.2010.10.003
Figure 1

Region in central Mexico where the study was conducted.

Location of the Valley of Mexico (blue polygon) in Mexico (A). Spatial distribution of the collecting sites throughout the Valley represented by the red squares. The stations belonging to the automatic monitoring network are indicated by yellow dots (B). This network is located between Mexico City and the State of Mexico in the most populated zone of the region.
Figure 2

Carbon monoxide concentrations in Mexico City

Ordinary kriging for the carbon monoxide concentrations, in parts per million, inside the area covered by the air quality network in the Valley. The data consisted of mean concentration of CO during the period that comprises January to November 2014. The data utilized for this analysis are available at http://www.aire.cdmx.gob.mx.
Figure 3

Biomonitor carbon status in the Mexico valley

Ordinary kriging for the carbon content (A) and $\delta^{13}$C values (B) for *Tillandsia recurvata* in the Valley of Mexico.
Figure 4

Biomonitor responses to carbon monoxide

Linear regression for the relationship between CO concentration in ppm during 2014 and the carbon content (A), and the δ¹³C values (B) for Tillandsia recurvata at the Valley of Mexico (n = 5).
A

Carbon content (% dry weight)

R^2 = 0.015

B

δ^{13}C (%)

R^2 = 0.675

CO (ppm)