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Sources and transport of $\Delta^{14}C$ on CO_2 within the Mexico City Basin and vicinity

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Abstract

Radiocarbon samples taken over Mexico City and the surrounding region during the MILAGRO field campaign in March 2006 exhibited an unexpected distribution: (1) relatively few samples (23%) were below the North American free tropospheric background value (57‰) despite the fossil fuel emissions from one of the world's most highly polluted environments; and (2) frequent enrichment well above the background value was observed. Correlate source tracer species and air transport characteristics were examined to elucidate influences on the radiocarbon distribution. Our analysis suggests that a combination of radiocarbon sources biased the "regional radiocarbon background" above the North American value thereby decreasing the apparent fossil fuel signature. These sources included the release of bomb or "hot" radiocarbon sequestered in plant carbon pools via the ubiquitous biomass burning in the region as well as the direct release of radiocarbon as CO_2. Plausible large local perturbations include the burning of hazardous waste in cement kilns; medical waste incineration; and emissions from the Laguna Verde Nuclear Power Plant. These observations provide insight into the use of $\Delta^{14}CO_2$ to constrain fossil fuel emissions in the megacity environment, indicating that underestimation of the fossil fuel contribution to the CO_2 flux is likely wherever biomass burning coexists with urban emissions. Our findings increase the complexity required to quantify fossil fuel-derived CO_2 in source-rich environments characteristic of megacities, and have implications for the use of $\Delta^{14}CO_2$ observations in evaluating bottoms-up emission inventories and their reliability as a tool for validating national emission claims of CO_2 within the framework of the Kyoto Protocol.

1 Introduction

With over 10 million inhabitants, megacities are a major source of air pollution given their high traffic densities, energy consumption rates, industrial processes, and elevated levels of biomass combustion from land clearing, trash burning and both domes-

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tic and industrial use of wood fuels (Gaffney et al., 2008). As their number increases worldwide, there is a growing recognition that airborne emissions from these large urban and industrial centers change the chemical content of the downwind troposphere, influencing both air quality and climate change on multiple scales (Molina et al., IGACtivities, 2008).

The Mexico City metropolitan area (MCMA) is the second largest megacity worldwide, the most populous city in North America, and was the initial case study for MILAGRO (**M**egacity **I**nitiative: **L**ocal **A**nd **G**lobal **R**esearch **O**bservations); an international collaborative project to examine the behavior and export of atmospheric pollutants generated in megacities. The interaction of physical and cultural factors in the Valley of Mexico and surrounding region creates a spectrum of air pollutants extremely diverse in chemical characteristics (deBauer and Krupa, 1990; Collins and Scott, 1993). The NASA DC-8 was one of seven instrumented research aircraft participating in MILAGRO, providing in situ and remote observations of trace gases and aerosols from a regional-scale perspective. Instrumentation for measurement of carbon dioxide and the collection of whole air samples for radiocarbon analyses was integrated on the DC-8 to investigate the various local and regional sources contributing to the measured total atmospheric CO_2 signal.

The direct effect of fossil fuel emissions is arguably the most significant influence of urbanization on the carbon cycle (Pataki et al., 2006). $\Delta^{14}C$ is a particularly sensitive tracer of fossil fuel emissions (Hsueh et al., 2007) because fossil fuel-derived CO_2 is the only source of atmospheric CO_2 that is devoid of ^{14}C (Suess, 1955; Levin et al., 1980; Turnbull et al., 2009). Seasonal and regional variability in atmospheric $\Delta^{14}C$ is clearly visible in many contemporary observations and has the potential to provide additional information about the source, age, and magnitude of regional fluxes (Randerson et al., 2002). When combined with atmospheric CO_2 concentration measurements, observations of $\Delta^{14}C$ can potentially be used to constrain fossil fuel emissions at local and regional scales.

The purpose of this paper is to present the processes regulating the distribution of atmospheric $\Delta^{14}C$ in the MCMA environment in March 2006, and to discuss the implications of those measurements as they pertain to alterations to the carbon cycle and the quantification of anthropogenic carbon sources.

2 Methods

2.1 Field deployments

In 2006, NASA's Tropospheric Chemistry Program (TCP) sponsored the INTEX-B (Intercontinental Chemical Transport Experiment-B) mission which consisted of two separate field deployments. The initial phase investigated the extent and persistence of outflow of pollution from Mexico during MILAGRO (1–30 March 2006) with flights based out of Houston, Texas (4–19 March 2006). The DC-8 then transited to Moffett Field, California, and after a three-week break, began making measurements over the North Pacific to quantify the impact of the long-range transport of accelerating Asian emissions on the changing chemical composition of the troposphere. The DC-8 conducted three local flights out of Honolulu, Hawaii followed by four local sorties out of Anchorage, Alaska. This study focuses on data obtained from the Houston-based flights and invokes the transit flight data over the North Pacific. Data from the local flights out of Hawaii and Alaska are the topic of a forthcoming manuscript.

2.2 Airborne measurements

A modified LI-COR model 6252 non-dispersive infrared gas analyzer was used to determine CO_2 mixing ratios. This dual-cell instrument achieves high precision by measuring the differential absorption between sample air and a calibrated reference gas that is traceable to the World Meteorological Organization primary CO_2 standards maintained by NOAA ESRL. The LI-COR-based CO_2 sampling system was operated at constant

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pressure (250 torr) and had a precision of ±0.1 ppm (1 σ) and accuracy of ±0.25 ppm. Experimental procedures are described in detail by Anderson et al. (1996) and Vay et al. (1999, 2003). The MILAGRO/INTEX-B in situ CO_2 data are archived at 1 s resolution and are publically available via http://www-air.larc.nasa.gov.

The ^{14}C content of CO_2 was determined from air remaining in a select subset of whole air canister samples collected onboard the DC-8 for measurements of hydrocarbons and halocarbons (Blake and Rowland, 1995). Post-mission, measurements of the radiocarbon content on CO_2 were made at the W. M. Keck Carbon Isotope Accelerator Mass Spectrometer Facility at the University of CA-Irvine and are described below.

Complementary data used here from numerous instruments has a long history of inclusion in the NASA DC-8 TCP payload, and the techniques were essentially identical to those previously described by Jacob et al. (2003). Our multi-tracer analysis utilized data for CO, CH_4, C_2H_6, C_2Cl_4, CH_3CN, HCN, isoprene and isopentane. An overview of the mission is given by Singh et al. (2009) and Molina et al. (2008).

2.3 Analytical procedures

Preparation of the samples for isotopic analysis was done on a combustion vacuum line that separates CH_4, CO, and CO_2 trace gases from whole air (and from each other) while further converting CH_4 to CO_2 and H_2O and converting CO to CO_2 as the air stream moves toward the pump. Most of the details regarding the vacuum line design and procedure as well as improvements made over time have been reported previously (e.g., Tyler et al., 1999 and references therein). In this study, only the CO_2 fraction from the total air sample was recovered. In brief, for a given sample, a series of cryo traps condensed trace gases such as CO_2 and H_2O vapor at liquid N_2 temperature (−196°C), leaving less-readily condensable gases such as CO and CH_4 in the air stream. The CO_2 was then separated from H_2O using a dry ice/ethanol slush bath (−80°C) and saved for isotopic analysis.

Measurements of ^{14}C content in samples of CO_2 from selected air samples were made following previously described methods (Southon et al., 2003). In brief, CO_2 gas

is graphitized to pure carbon in the presence of H_2 and hot zinc metal. Next, graphite targets are formed and then mounted into a sample target wheel where they are subsequently measured in the accelerator mass spectrometer. Overall $\Delta^{14}C$ measurement precision is ±2‰, where $\Delta^{14}C$ is defined by Stuiver and Polach (1977).

3 Large-scale distribution

The large-scale distribution of $\Delta^{14}C$ during MILAGRO and the INTEX-B Pacific transit flights is presented in Fig. 1. These data are shown as a function of pressure altitude since the MCMA lies in an elevated basin 2240 m above sea level. Any anthropogenic emissions emitted from this megacity are therefore introduced into the atmosphere at altitudes considered to be in the free troposphere. The INTEX-B transit flight data from Moffett Field, California to Honolulu, Hawaii (17 April 2006) and from Honolulu to Anchorage, Alaska (30 April 2006) are invoked to obtain a representative background radiocarbon value (57.0‰) for this study. This value is in good agreement with a mean March 2006 $\Delta^{14}C$ value of 56.6‰ determined from observations at Niwot Ridge, Colorado (40 N, 105 W, 3526 m a.s.l.), a proxy for North American free tropospheric air (Turnbull et al., 2007). An interesting feature of the MILAGRO data is that 76% (N=16) of the radiocarbon values were above the assigned 57‰ background, with surprisingly few samples (N=5) indicating a fossil-fuel influence (<57‰). An anomalously high ^{14}C content (>112‰) was found in three of the collected samples and these results are examined in more detail in Sect. 3.3.

Canister sample collection locations and their associated radiocarbon values are illustrated in Fig. 2. This figure depicts the degree of spatial coverage within the region and provides a detailed look at the $\Delta^{14}C$ distribution. The flights on the 9 and 16 March had different science objectives, sampling emissions over the Gulf of Mexico and Mexico City, respectively. We use these two flights to explore sources contributing to the total measured CO_2 signal in Sects. 3.1 and 3.2.

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3.1 Mexico City mega-plex

An objective of the 16 March (Thursday) science flight was the sampling of fresh Mexico City (MC) pollution during weekday conditions. The flight track, altitude, and data for a portion of this flight are presented in Fig. 3. The DC-8 approached MC from the south, flew a south-north transect over the city along the same line of longitude, and then conducted a terrain-following path just north of the city. Collection sites for the isotope samples are indicated along the DC-8 flight track (blue diamonds). Inset above, in situ CO_2 and CO measurements are plotted with the $\Delta^{14}C$ observations. The radiocarbon values fell within the range of 20.1‰ to 120.4‰ with the lowest values observed directly over MC where the highest in situ CO_2 and CO mixing ratios were measured. Using a $\Delta^{14}C$ depletion of 2.8‰ per ppm of fossil fuel CO_2 added to the current atmosphere (Turnbull et al., 2006), and assuming a plausible value for a $\Delta^{14}C$ enriched source(s), which must also be present based on the $\Delta^{14}C$-weighted mass balance for source(s) and background combined, we estimate the minimum fossil fuel contribution to the total measured CO_2 signal to range between 4 to 15 ppm in the three samples lowest in $\Delta^{14}C$ value.

Collection of the isotope samples in clusters permitted partitioning of the flight segment into distinct regions labeled as A, B, C (Fig. 3). Regional correlations between CO_2 and CO are illustrated in Fig. 4. Following the method outlined in Yokelson et al. (1999) emission ratios (ERs) were obtained from the slope of the least-squares line, with the intercept forced to zero, in a plot of one set of excess mixing ratios versus another. Background values of 382.61 ppm and 112 ppb were used for CO_2 and CO, respectively based on the determined median. For comparison, median CO_2 and CO for Mauna Loa (19 N, 155 W, 3397 m a.s.l.) over the MILAGRO sampling window were 382.87 ppm and 105 ppb, respectively. Each cluster shows a distinct relationship, indicating a mixture of different sources that is also evident in the radiocarbon data.

Sampling over MC occurred during the January-June dry season. The level of fire activity in March 2006 was above normal and more typical of that seen in April. The

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Mexico City basin was influenced by emissions from forest fires in the pine-savannas that dominate the mountains surrounding the city (Yokelson et al., 2007). Both ground-based (E. Alvarado, personal communication) and airborne observers (DC-8 pilots, instrumentalists) reported reduced visibility from smoke generated by widespread wildfires and agricultural burning in south-central Mexico that, at times, obscured the ground. The radiocarbon samples from south of Mexico City [Region A] were collected over the study area [19–20 N; 98–100 W] of Yokelson et al. (2007) who used a Twin Otter research aircraft to make various measurements of fire emissions during MILAGRO. We find that our molar emission ratio derived for Region A (0.024) compares well with Yokelson's (0.028) which was determined from measurements conducted the following day over a prescribed burn.

In Fig. 5, the radiocarbon data are plotted along with other chemical tracers to better evaluate the source influence for each sample. The source tracer species invoked are ACN or acetonitrile (biomass burning); C_2Cl_4 (industrial emissions); isopentane (vehicular emissions); and isoprene (biogenic emissions). ACN is above background throughout; only over MC [Region B] are C_2Cl_4 and isopentane elevated; north of the city [Region C] isoprene emissions are notable. Observations from the NSF C-130 during MILAGRO of highly elevated concentrations of cyanides further substantiates biomass burning emissions significantly impacting regional air quality (Crounse et al., 2009). Aerosol samples collected at the MILAGRO ground-based super sites T-0 (19.488 N, 99.147 W, 2240 m a.s.l.) and T-1 (19.703 N, 98.982 W, 2273 m a.s.l.) (Fig. 2) and later analyzed for carbon isotopes (Marley et al., 2009; Gaffney et al., 2008) revealed that significant contributions (45–78%) to the organic and elemental fractions of the carbonaceous aerosols arose from biomass burning sources in MC and the surrounding region. Both stable and radiocarbon data indicate that the peripheral site T-1 was more impacted than the urban T-0 site by grassfires occurring in the region (Gaffney et al., 2008; Marley et al., 2009). Stone et al. (2008) found that the aerosol generated by biomass burning on the perimeter of the city (T-1) was highly correlated with vegetative detritus and chemically different from the point-source wood-burning

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events that pollute the downtown area (T-0). These cumulative results suggest that a likely contributor to the mass excess in our $\Delta^{14}C$ observations was the release of sequestered old bomb-carbon back to the atmosphere by the consumption of biomass in wildfires and local/regional burning activities. Using the variability in these observations to partition a two-point source mixing curve, we surmised that the age of carbon released to account for the excess mass would need to be from vegetation and soil organic matter that had fixed atmospheric CO_2 during the past several decades for a plausible fit.

3.2 Gulf of Mexico

On 9 March, the meteorological conditions were favorable for the sampling of outflow from Mexico City to the Gulf of Mexico. At takeoff the DC-8 climbed to 8.25 km, and then began descending while heading south over the Gulf in preparation for a boundary layer (BL) run. At this lowest level (~200 m a.s.l.) the air masses had an unusual composition, containing high amounts of CH_4 (2.1 ppm) and CO_2 (400 ppm). The radiocarbon content of the whole air samples collected during this southbound BL leg (N=4) show a decreasing trend as the DC-8 progressed further south (Fig. 2). CO_2, CO, and CH_4 observations, averaged to the sampling time of the whole air samples, are presented in Fig. 6. As the CO_2, CH_4, and CO mixing ratios increase, the $\Delta^{14}C$ values become more depleted. We were able to fit the data corresponding to these four $\Delta^{14}C$ samples with linear correlations that produced 0.285 ppmv/ppbv CO+349.63, R^2=0.98; and 0.068 ppmv/ppbv CH_4+262.15, R^2=0.98. These tight correlations likely reflect co-located sources. Examination of other source tracer species revealed $\Delta^{14}C$ correlated with ACN, HCN, and isoprene however, exhibiting the opposite relationship with isopentane, and C_2H_6 (i.e. following CO_2, CO, and CH_4).

The largest natural gas and principal oil fields in Mexico are located around the Gulf of Mexico states of Veracruz, Tabasco, and Campeche. We use the Lagrangian particle dispersion model FLEXPART (Stohl et al., 1998) to explore the transport characteristics

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associated with meteorological transport processes in the region. Details of the model simulations are given by Stohl et al. (2002). Briefly, backward simulations are done from along the flight track and include full turbulence and convection parameterizations. Every simulation consists of 40 000 particles released in the volume of air sampled whenever the DC-8 covered a distance of 0.18° or changed its altitude by 8 hPa. As emissions originate at the surface, we focus on the residence times (ns/kg) in the FLEXPART regional footprint product, which shows the emission sensitivity averaged over the lowest 100 m adjacent to the ground. We also examined the Retroplume summary product to establish the fraction of particles in the BL as a function of time.

The air mass sampled in the BL during the southbound leg originated over Northern Mexico, then flowed in a clockwise direction over the southern United States, the Gulf of Mexico, portions of Central America, and southern Mexico prior to interception over the Gulf (not shown). Inspection of Fig. 7 shows an initially narrow (Fig. 7a) influence footprint that broadens (Fig. 7b) with increasing proximity to the southern Mexico oil and gas center. A day prior to sampling, FLEXPART estimates an air mass fraction ≥60% traveling within the atmospheric boundary layer over the petroleum industry center as well as over fires in Guatemala and the Mexican states of Chiapas and Oaxaca. The corresponding decreasing trend of ACN, HCN, isoprene and $\Delta^{14}C$ while approaching the Mexican coastline with a commensurate increase in CO_2, CO, CH_4, C_2H_6, and isopentane suggests a biomass burning influence initially dominating the radiocarbon signal that became increasingly obscured by the influence of anthropogenic emissions associated with the petroleum industry. These results are supported by the FLEXPART emission sensitivity products (Fig. 7).

There are some notable differences in the composition of the two remaining BL (~200 m a.s.l) samples collected in the western Gulf later that same day. Where $\Delta^{14}C$=53.3‰ or corresponding to a minimum of 7.5 ppm of added fossil fuel CO_2, Fig. 7c shows a high emission sensitivity from both MC and a producing field in northern Veracruz coupled with a widespread biomass burning influence. HCN (582 pptv), ACN (182 pptv), C_2Cl_4 (7.4 pptv), and C_2H_6 (5371 pptv) mixing ratios are higher than

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the other 9 March samples, reflecting the proximity to and different relative contributions from the varied emission sources of the two regions. Though exhibiting similar CH_4 mixing ratios, respective CO and CO_2 relationships differ (Fig. 6), reflecting interception of an air mass that passed over the petroleum center in SE Mexico then Veracruz (not shown).

The gas released when crude oil is brought to the surface is known as associated gas. Drilling companies routinely flare or vent this material for safety reasons or where no infrastructure exists to bring it to market. Flaring is where the gas is burned and emitted as CO_2, and venting, where the gas is simply released to the atmosphere as CH_4 (Christen, EST, 2004). After CH_4, ethane is the second most abundant constituent of natural gas and both chemical tracers have some common sources: fossil fuel production, biofuel combustion, and biomass burning (Xiao et al., 2008). We examined the CH_4:C_2H_6 molar ratios for these atmospheric observations conducted downwind of these major source regions for source attribution and found CH_4:C_2H_6 ratios (34–114) typical of those for "dry" natural gas fields (i.e. absence of condensate or liquid hydrocarbons) (Xiao et al., 2008). These findings point to the sampling of a complex mixture of emissions attributable to both the venting and flaring of associated gas, fugitive emissions associated with the oil and gas industry, biomass burning, and fossil fuel combustion (based on the isopentane signal) as influences on the radiocarbon content of the atmospheric $\Delta^{14}C$ observations.

3.3 "hot sources"

Anomalously enriched $\Delta^{14}C$ values (>112‰) were measured in three of the whole air samples, nearly double the radiocarbon in the background atmosphere. The excess levels of ^{14}C cannot be attributed to the release of old bomb carbon from biomass burning as a plausible result using a two-point mixing curve for determination of the relative age of carbon was not realized. The associated CO, CH_4, and CO_2 mixing ratios also do not support a stratospheric influence. The 120.4‰ value was measured in a sample collected south of MC (Fig. 2) at 2.6 km (i.e. near the altitude of MC or 0.75 km radar

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altitude) in an atmospheric layer rich in combustion and urban related trace gases. The other two highly enriched samples (112.6‰ and 132.0‰) were augmented with the biomass burning tracers ACN and HCN yet devoid of an elevated industrial and vehicular emission signature (i.e. C_2Cl_4 or i-pentane), likely a result of sampling on a Sunday (20060319) within a long weekend. These observations were made during a low pass over Monterrey in Nuevo León, and while on approach to MC over the state of Hidalgo, respectively (Fig. 2).

The possible causes of these perturbations in $\Delta^{14}C$ were investigated and a number of potential sources of the emitted radiocarbon identified: production of $^{14}CO_2$ from the boiling water reactors (BWRs) of the Laguna Verde nuclear power plant located in Veracruz; and/or medical and hazardous waste incineration. Mexico has two hazardous waste landfills, 13 fuel blending plants, 11 private hazardous waste incinerators, and 22 medical waste incinerators (Reed et al., 2000). Most of the medical waste incinerators are located in the Mexico City metropolitan area, although one has been permitted in Monterrey, Nuevo León (Reed et al. 2000). Moreover, Mexico's cement industry has embraced the incineration of hazardous wastes in their cement kilns as an energy recycling strategy. This incineration has been led by the two largest cement producers in Mexico, which have joint ventures with U.S. transnational companies to blend hazardous waste into fuels before burning the waste in their kilns (Reed and Gonzalez, 1997). Twenty one of 30 cement plants throughout Mexico have received either test-burn permits or annual authorizations to burn a variety of hazardous wastes with twelve of these plants located in central Mexico (Reed and Gonzalez, 1997). The locations of some of these potential "hot" sources are shown in Fig. 2.

The nuclear-waste problem involves not just what existing nuclear power plants produce, but also the low-level radioactive material found in hospitals, universities and in other industries. Most of the ^{14}C released into the environment by BWRs and incinerators is in the form of gaseous emissions (Magnusson et al., 2004) mainly via the stack gas, with CO_2 as the main carrier of ^{14}C. This radiocarbon or "hot source" released into the atmosphere is then available to enter plant carbon pools through photosyn-

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thesis or leads to an increase of the local ^{14}C concentration. High radiocarbon concentrations (97–184 pMC) in vegetation were noted in areas more than 100 km distant from a nuclear power plant (Mikhajlov et al., 2004); Trumbore et al. (EOS, 2002) measured $\Delta^{14}CO_2$ values 190–6000‰ over background in oak leaves sampled near two hazardous waste incinerators; TROICA-8 observations of $\Delta^{14}CO_2$ were influenced by nuclear reactor emissions along the route (Turnbull et al., 2009); and Levin et al. (2003) reported a small contribution to the Heidelberg $^{14}CO_2$ data from a nuclear power plant situated about 25 km southwest of their sampling site.

We examined 5-day kinematic backward trajectories and several FLEXPART data products calculated along the DC-8 flight tracks for each sampling location and time (not shown) which reveal local influences from the northern and southern sectors of the MCMA for the highest $\Delta^{14}C$ observations, 132.0‰ and 120.4‰ respectively. The substantial $^{14}CO_2$ enrichment (112.6‰) observed near Monterrey also appears to have a local influence south-southwest of the city. From Fig. 2, a close correspondence between these elevated radiocarbon values and local cement kilns is indicated. The transport history of the radiocarbon enriched air parcels consistently reflects an air mass fraction >40% in the ABL 24 h prior to sampling. Given the widespread and varied "hot" emission sources within the region identification is complicated as the observational influence could be from a direct smokestack emission or ^{14}C, emitted from any of the above-mentioned hot sources, incorporated into plant tissue prior to MILAGRO and subsequently released by the pervasive biomass burning occurring during March 2006. The possibility of either scenario exists in our MILAGRO data set and offers a plausible explanation for the three anomalously high $\Delta^{14}C$ values observed.

4 Conclusions

Only 23% of the radiocarbon measurements from MILAGRO indicate a distinct fossil fuel influence, an unexpected result for the MCMA sampling environment. Inspection of correlate source tracer species and air mass transport histories suggests that the fos-

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sil fuel detection capability of the radiocarbon method was obfuscated by contributions from other local and regional CO_2 sources emitting higher $\Delta^{14}C$ than the background atmosphere. By 2025, the number of megacities is predicted to reach twenty seven, with the majority located in the developing world, each with their own unique emission signatures, all likely major sources of atmospheric CO_2. Observations during MILAGRO have shown the complexity of radiocarbon cycling in the megacity environment and indicate adding detailed simultaneous measurements of other chemical tracers to the isotopic marker ^{14}C are highly desirable for better evaluation of the various sources contributing to the total measured CO_2 signal.

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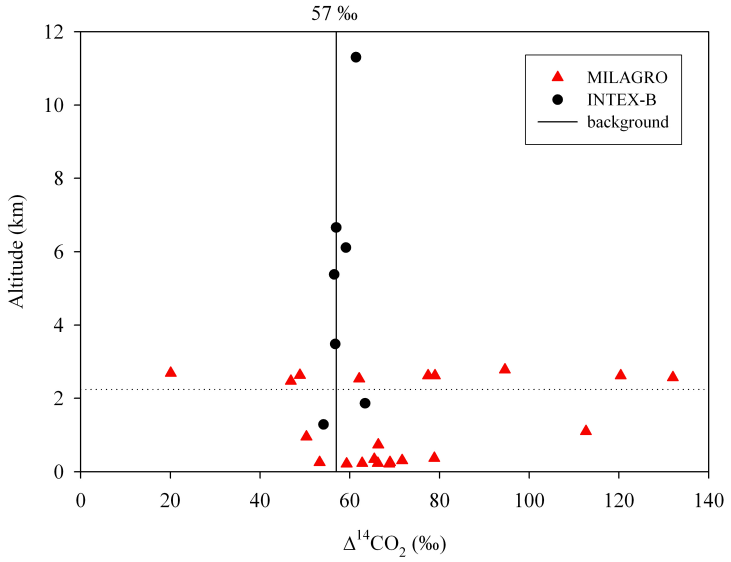

Fig. 1. Radiocarbon observations as a function of pressure altitude for the MILAGRO and INTEX-B Pacific transit flights. Median radiocarbon measured over the eastern North Pacific was 57‰. Horizontal dotted line depicts the height of Mexico City (2240 m a.s.l.).

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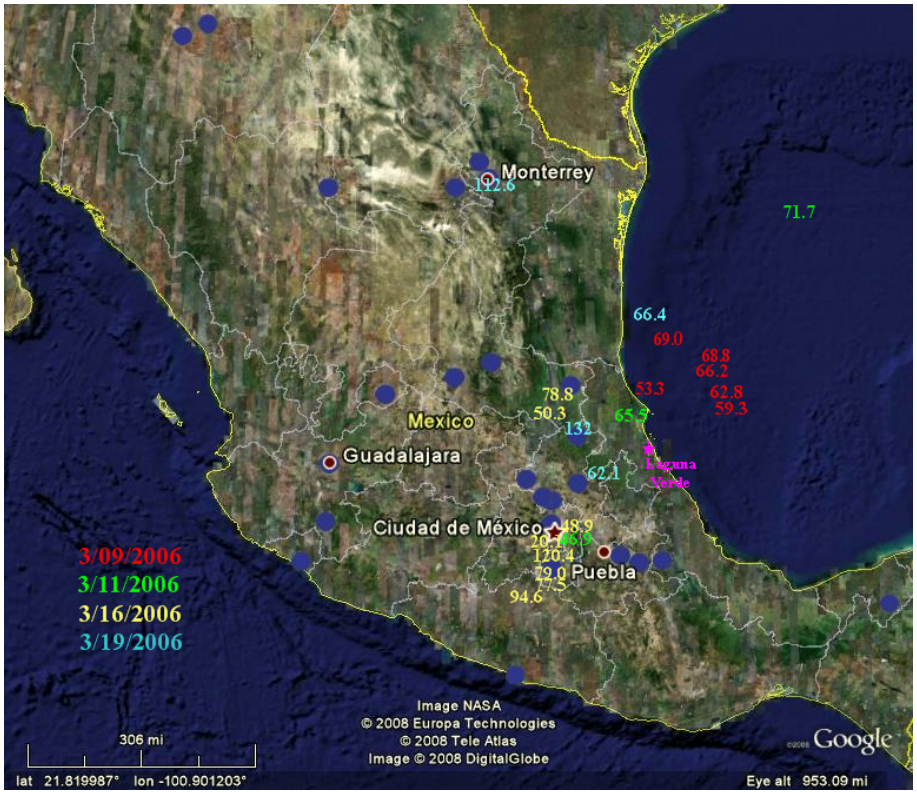

Fig. 2. Whole air sample collection locations and associated radiocarbon values color-coded by DC-8 flight date. Blue circular symbols represent locations of cement kilns.

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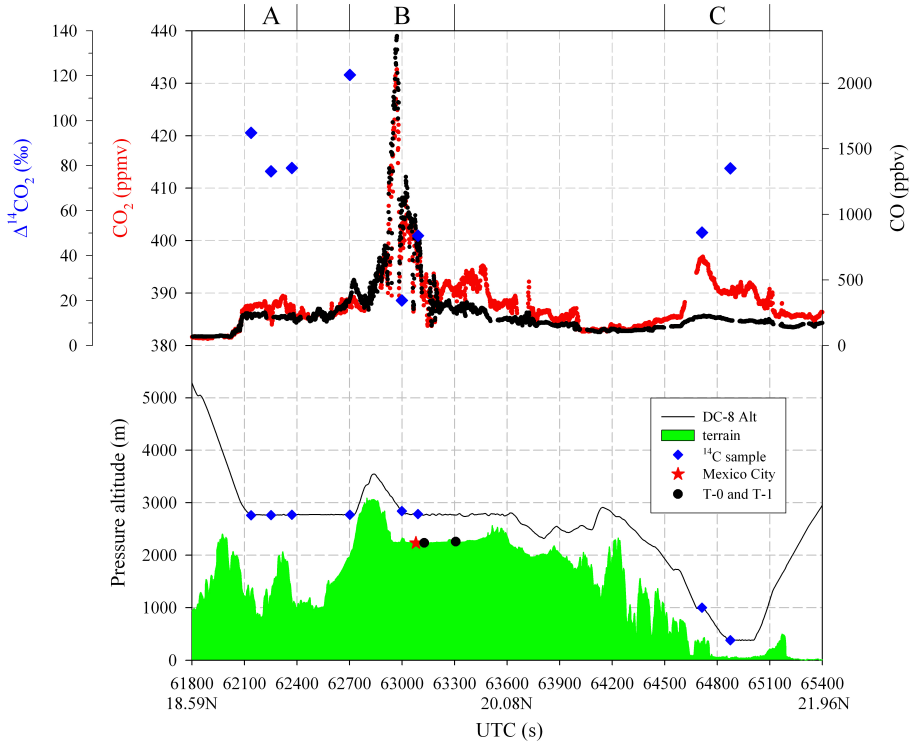

Fig. 3. Radiocarbon collection locations (blue diamonds) shown during a terrain-following flight track over Mexico City and vicinity on 16 March 2006 along with T-0 and T-1 ground-based MILAGRO super-sites (bottom panel). In situ CO_2 and CO data recorded during the flight with corresponding $\Delta^{14}CO_2$ values (top panel).

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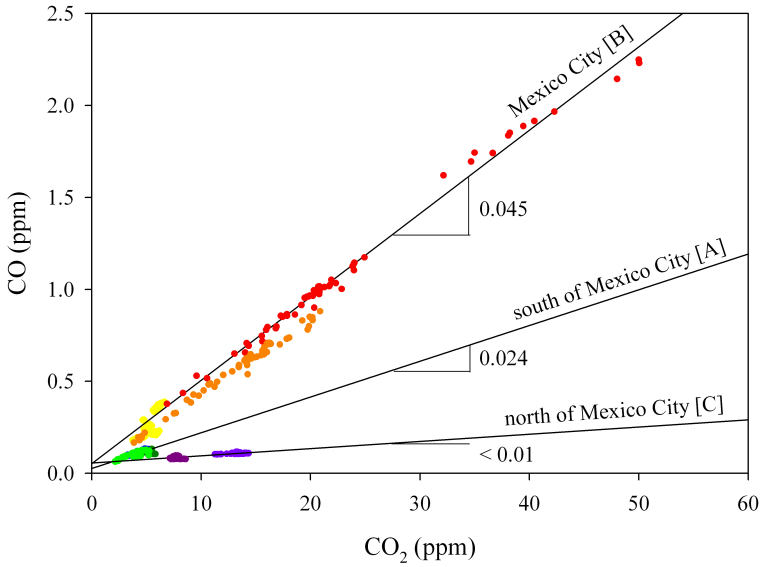

Fig. 4. Regional correlations between CO_2 and CO for radiocarbon sample collection intervals.

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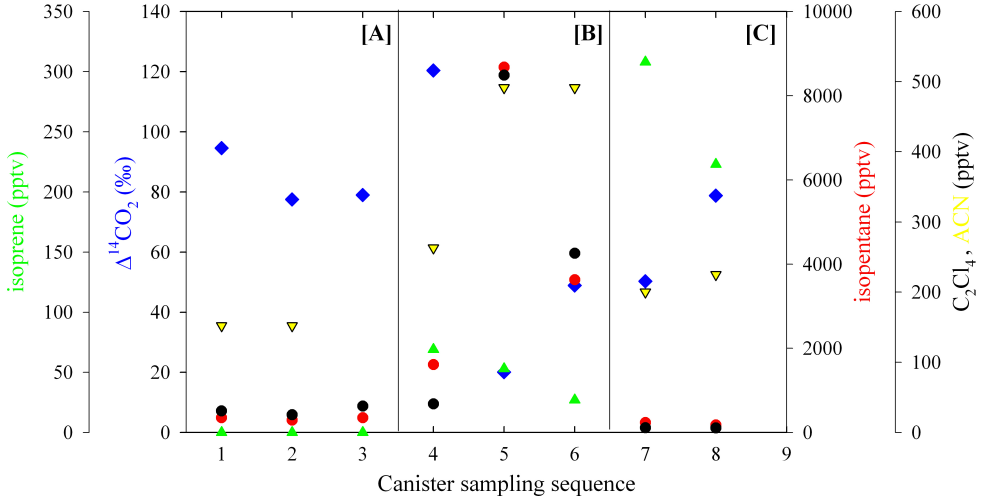

Fig. 5. Source tracer species concentrations for each radiocarbon sample collected on 16 March 2006.

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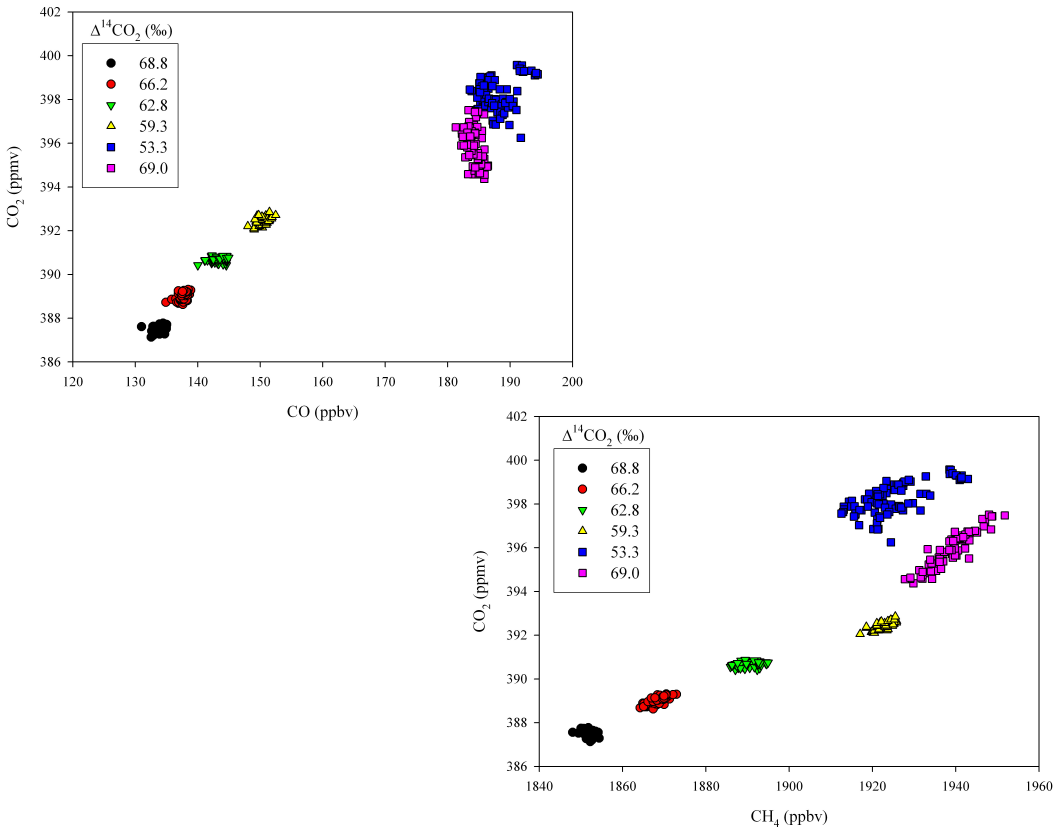

Fig. 6. Relationship of CO and CH_4 to CO_2 for the radiocarbon samples collected over the western Gulf of Mexico on 9 March 2006.

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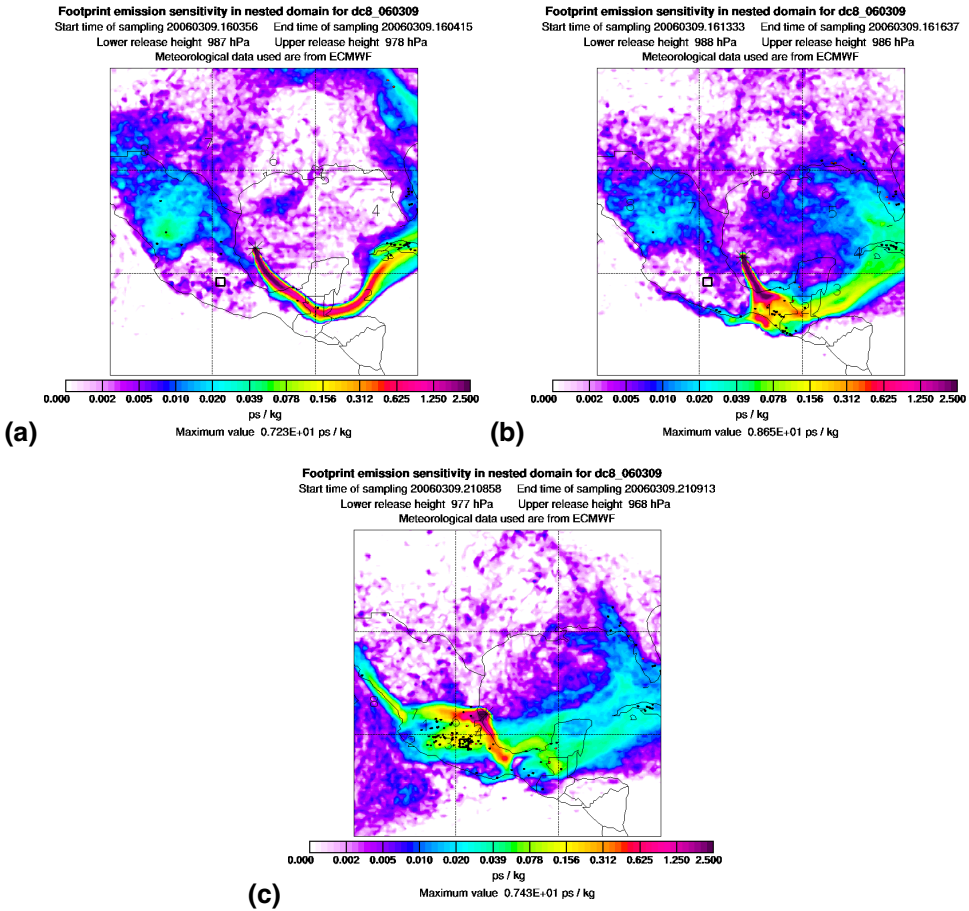

Fig. 7. FLEXPART footprint emission sensitivity product, averaged over the lowest 100 m, indicating where emissions were likely taken up. Fire hot spots from the MODIS sensor are marked as black dots; red dots if on forested land. Corresponding radiocarbon values are **(a)** 68.8‰, **(b)** 59.3‰, and **(c)** 53.3‰ respectively.

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