

Determination of carbonyls and their sources in three sites of the metropolitan area of Costa Rica, Central America

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Abstract Ambient levels of carbonyl compounds and their possible sources were studied at three places in the metropolitan area of Costa Rica, including a residential, an industrial, and a commercial downtown area with high vehicular flow, during the periods of April–May and September–December 2009. Fifteen carbonyl compounds were identified in the ambient air, of which acetone was the most abundant carbonyl, followed by formaldehyde and acetaldehyde. Concentrations were highest in rainy season at all sites and lower in dry season. These decreases in concentration are explained by the influences of both photochemical reactions and local meteorological conditions. The strong correlation between C1–C2 and C3 indicated a common origin for these carbonyls. The C1/C2 ratios varied between 0.49 to 1.05, values which can be considered typical of an urban area.

Keywords Carbonyl compounds · Air pollution · Costa Rica

Introduction

Carbonyl compounds (aldehydes and ketones) are of critical importance in the complex set of chemical reactions that occur in the troposphere. Carbonyls may be emitted directly into the atmosphere by mobile and stationary sources and produced in situ by the photo-oxidation of gas-phase hydrocarbons. Natural sources also contribute to atmospheric concentrations of several carbonyls through biogenic emissions of some plants (Ciccioli et al. 1993; Kesselmeier et al. 1997; Müller et al. 2002; Wildt et al. 2003; Villanueva et al. 2004) and photochemical oxidation of naturally emitted hydrocarbon precursors, e.g., isoprene (Grosjean et al. 1993).

Carbonyls are major contributors to urban photochemical smog, being significant sources of free radicals in the atmosphere and acting as precursors to the formation of organic aerosols. Carbonyls are in turn direct precursors of peroxyacylnitrates and ozone through peroxyradicals (HO_2 , RO_2 , and RC(O)O_2) generated by photolysis or OH radical attack (Possanzini et al. 1996).

Monitoring carbonyl compounds in the ambient air is fundamental to the understanding of the oxidation paths of volatile organic compounds in

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the atmosphere, and in assessing their role in the formation of tropospheric ozone (Carlier et al. 1986; Grosjean 1996; Possanzini et al. 2002).

The lifetimes of formaldehyde and acetaldehyde in the troposphere have been estimated to be in the order of few hours due to photolysis and OH photo-oxidation reactions (Macdonald et al. 2001; Seinfeld and Pandis 1998). At night, dry and/or wet deposition is a major sink of formaldehyde (Finlayson-Pitts and Pitts 2000), while acetaldehyde is removed mostly through a reaction with NO₃ radicals (Finlayson-Pitts and Pitts 2000; Slemr and Junkermann 1996). However, the alkene ozonolysis reaction plays an important role in increasing nocturnal acetaldehyde concentrations (Bakeas et al. 2003; Christensen et al. 2000; Possanzini et al. 1996). These compounds are also associated with adverse health impacts, because they have been reported to exhibit carcinogenic and mutagenic properties (Seinfeld and Pandis 1998) and are precursors of toxic radical intermediates in the atmosphere (Possanzini et al. 2002). Measurements of ambient aldehydes have been performed in cities of industrialized countries such as Los Angeles, Denver, Paris, Budapest, and Atlanta (Grosjean and Fung 1984; Salas and Singh 1986; Kalabokas et al. 1988; Haszpra et al. 1991; Grosjean et al. 1993). Also, these measurements have been done in cities of developing countries like Rio de Janeiro, Sao Paulo, and Mexico, among others (Tanner et al. 1988; Grosjean et al. 1990; Báez et al. 2000). No measurements of carbonyl compounds have been conducted in Costa Rica.

The metropolitan area of Costa Rica has an average altitude of 1,100 m, accounting for 75% of the vehicle fleet (approximately 734,200 units), 65% of the domestic industry, and 60% of the country's population (2,490,000), according to data from the last population census conducted in 2000 (INEC 2000). The metropolitan area is the highest-ranking center in the urban system in Costa Rica as a result of productive activity and economic and public service that are concentrated in this area. Four cities form the metropolitan area (Alajuela, Heredia, Cartago, and San Jose) and many smaller population centers that, a few years ago, were islands in the middle of crop areas, but now, due to the region growth pattern,

have been consolidated into a single urban center together with the main cities. Lack of urban planning has implicated a considerable deterioration of air quality, as a result of growth experienced by the cities of the GAM during the past 20 years.

This paper reports levels of the major carbonyls in tree sites of the metropolitan area of Costa Rica.

Experimental

Sampling

For sampling of carbonyls, three monitoring sites were selected (Table 1). The sites were representative of commercial, industrial, and residential areas, all located in the municipalities of San Jose, Heredia, and Belen belonged to Costa Rica metropolitan area. The sampling was carried out in two periods: 25 April to 20 May and 23 September to 11 December 2009. Totally 81 samples were collected.

The carbonyl compounds were collected by pumping sample air through commercially available cartridges (SKC catalog number: 226-119) filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated silica. The downstream end of the cartridge was connected to a calibrated flow meter. Air was passed through the cartridge at a flow rate of 1 l min⁻¹ at 12–20-h intervals. An ozone scrubber was connected to the upstream end of the cartridge to avoid degradation of hydrazone derivatives. Each cartridge was immediately sealed with Teflon caps, then wrapped in aluminum foil and refrigerated.

The collection efficiency of DNPH cartridges was evaluated by spiking the cartridge with standard solutions of the carbonyls. The collection efficiencies for all the studied compounds was found to be $98.8 \pm 0.7\%$.

Chemical analysis

The analytical methodology for the determination of carbonyls was based on the TO-11 USEPA Method (1999). Cartridges were extracted with 3 ml acetonitrile (HPLC grade, Fisher) and the eluate was analyzed by HPLC (DIONEX model

Table 1 Description of sampling sites for the collection of carbonyls in the metropolitan area of Costa Rica

	Site identification	Province	Canton	Address	Site description
1	CAT-SJ	San Jose	Central	Facilities of the Metropolitan Cathedral in the city of San José	Commercial area with high traffic flow 6.75 m of the street and 3 m above the ground
2	REC-HE	Heredia	Central	Rectory building of the Nacional University	Commercial area with high traffic flow 5.5 m of the highway and 6 m above the ground level
3	CCLR-BE	Heredia	Belén	Flat roof of La Ribera Commercial Center	Industrial area, wind exit of the study area 6 m of the highway and 5 m above the ground

ICS-3000). The analytical conditions are indicated in Table 2.

Calibration was done by direct injection of standard mixtures with known amounts of solid hydrazones dissolved in acetonitrile. These standard mixtures gave linear responses of 0.02 to 15 mg l⁻¹ corresponding hydrazones. The calibration curve was made using a certified stock solution containing a mixture of 15 hydrazones from 15 mg l⁻¹ (Supelco catalog number 4M7285-U). The certified stock solution includes the hydrazones derivated of the following compounds: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, butyraldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde, 2,5-dimetilbenzaldehyde, and hexaldehyde. Table 3

shows some important performance parameters of the analytical method.

The detection limits were calculated according to Meier and Zünd (2001). This method is based on calculating the minimum signal noise statistically distinguishable from the baseline. For this we looked for a signal to noise ratio equal to 3 for a confidence level of 99%. In the case of the limit of quantification was searched for a signal to noise ratio equal to 10 for a confidence level of 99%.

To set the precision of the method, five replica of an intermediate pattern were analyzed, during three consecutive days according to ISO 5725-2: 1999.

The amount of the individual carbonyl compounds on unexposed cartridges was less than 0.04 µg.

Table 2 Instrumental conditions for carbonyl analysis by HPLC

Mobile phase	1 ml/min		
	Time (min)	% Acetonitrile	% Deionized water
Gradient mobile phase with linear ramp	0	60	40
	21.4	75	25
	32.0	100	0
	33.0	60	40
	38	60	40
Column temperature gradient	Time (min)	Temperature (°C)	
	0	30.00	
	11.7	20.00	
Autosampling temperature	31.0	30.00	
Injection volume	20.00°C		
Detector UV/VIS	25 µl		
	360 nm		

Table 3 Performance parameters for the analytical method determined in their validation process

Compound	Repeatability variation coefficient $CV_R(\%)$	Reproducibility variation coefficient $CV_R(\%)$	Detection limit (mg l^{-1})	Quantification limit (mg l^{-1})	Recovery percentage at low concentration
Formaldehyde	0.2	1.2	0.04	0.08	97.5
Acetaldehyde	0.2	1.1	0.04	0.10	98.3
Acrolein	1.0	1.7	0.06	0.13	98.1
Acetone	1.1	1.2	0.06	0.13	96.5
Propionaldehyde	0.2	1.1	0.04	0.10	98.8
Crotonaldehyde	0.2	1.1	0.06	0.13	98.4
Butiraldehyde	0.3	1.1	0.04	0.10	99.2
Benzaldehyde	0.3	1.3	0.04	0.10	97.9
Isovaleraldehyde	0.8	1.5	0.06	0.13	98.2
Valeraldehyde	0.7	1.5	0.04	0.10	98.8
<i>o</i> -tolualdehyde	0.3	1.1	0.04	0.08	99.1
<i>m</i> -tolualdehyde	0.9	1.5	0.04	0.08	98.4
<i>p</i> -tolualdehyde	0.7	1.3	0.06	0.13	98.7
Hexaldehyde	1.2	1.2	0.04	0.10	98.9
2,5-dimetilbenzaldehyde	1.2	1.3	0.06	0.13	99.2

Results

Arithmetic mean concentrations of carbonyl compounds were listed in Table 4. Crotonaldehyde was not detected in all the ambient air samples, *p*-tolualdehyde only presented in four samples and isovaleraldehyde was detected in eight samples. To analyze the type of distribution that follow the carbonyls concentrations obtained, we used “Kolmogorov–Smirnov” test. For all sam-

pling sites, the critical value of z was found to be very small (less than 0.05) as the distribution of samples is not normal for all parameters.

Of the 15 carbonyls listed in Table 4, acetone was the most abundant carbonyl in many samples and accounted for 24–39% of the total ambient carbonyl concentrations. High levels of acetone may be caused by a mixture of direct emissions plus the oxidation of hydrocarbons that occurs mainly during daytime hours. Chatfield et al. (1987)

Table 4 Concentrations of carbonyl compounds in the sampling sites ($\mu\text{g m}^{-3}$)

Compounds	CAT-SJ (arithmetic mean \pm SD)	REC-HE (arithmetic mean \pm SD)	CCLR-BE (arithmetic mean \pm SD)
Formaldehyde	2.5 ± 0.9	3.1 ± 1.5	2.0 ± 0.7
Acetaldehyde	2.4 ± 1.3	3.8 ± 2.3	4.1 ± 3.2
Acrolein	0.14 ± 0.01	0.15 ± 0.04	0.14 ± 0.03
Acetone	1.8 ± 1.4	5.0 ± 2.6	4.6 ± 3.9
Propionaldehyde	0.13 ± 0.03	0.12 ± 0.02	0.14 ± 0.04
Crotonaldehyde	nd	nd	nd
Butiraldehyde	0.13 ± 0.03	0.09 ± 0.02	0.12 ± 0.02
Benzaldehyde	0.21 ± 0.06	0.33 ± 0.18	0.17 ± 0.13
Isovaleraldehyde	nd	nd	0.20 ± 0.02
Valeraldehyde	0.13 ± 0.02	0.10 ± 0.01	0.12 ± 0.02
<i>o</i> -tolualdehyde	0.22 ± 0.12	0.17 ± 0.02	0.22 ± 0.10
<i>m</i> -tolualdehyde	0.11 ± 0.04	0.16 ± 0.06	0.10 ± 0.02
<i>p</i> -tolualdehyde	0.13 ± 0.01	nd	nd
Hexaldehyde	0.12 ± 0.02	0.12 ± 0.02	0.13 ± 0.03
2,5-dimetilbenzaldehyde	0.15 ± 0.03	0.17 ± 0.04	0.16 ± 0.02

reported that the formation of acetone in the troposphere occurs through OH radical attack on some alkanes and alkenes. Della et al. (2001) have previously reported that carbonyls with increasing number of C atoms are less abundant in the ambient air.

Another reason for the high acetone concentrations in the ambient air was that the lifetimes of acetone for removal by photolysis and OH reaction were approximately 40 and 20 days in the atmosphere, respectively. In contrast, the lifetimes of formaldehyde and acetaldehyde for reaction with OH were roughly 1.5 h to 1 day (Shepson et al. 1991; Atkinson 2000). It thus seemed reasonable to expect that acetone concentrations should be higher (Shepson et al. 1991).

To determine the degree of similarity or difference for carbonyls concentrations between the different sampling sites, divergence ratio was measured, and it is defined as follows (Park and Kim 2004):

$$CD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2}, \quad (1)$$

where x_{ij} represents the average concentration of each carbonyl i in a given sampling site. Meanwhile, $j, j,$ and k represent two sampling sites and p the number of carbonyl compounds. If the value of CD is close to zero, data from both sites are considered similar. On the contrary, if the value tends to one, both are seen as different values. Table 5 presents obtained CD values for the sampling sites. Based on the results, it can be noticed that differences between coefficients are very small, so it can be inferred that there are no significant differences between them.

Figure 1 illustrated the seasonal variations in concentration observed during the measurement period at two sampling sites. In the case of acetaldehyde, acetone and propionaldehyde higher

concentrations occur in the rainy season. This could be explained by the fact that during the rainy season, trade winds decrease in intensity, and the Pacific breezes are allowed entry into the metropolitan area (responsible for the generation of rain), causing a drop in wind speed close to 42% compared to that during dry season, hindering transport of pollutants to other regions.

It is well known that vehicle emissions are major sources of carbonyls. The formaldehyde and acetaldehyde are produced generally from vehicle emissions and photochemical oxidation of hydrocarbons. Secondary sources and sinks are also factors that influence the ambient concentrations of carbonyl. Della et al. (2001) reports that the occurrence of environmental temperature and higher solar radiation during a time of year not only enriches the photochemical reactions of carbonyl generation but also accelerates the photolysis of secondary carbonyls to form hydroxyl radicals, which are very important sink of carbonyls.

The principal reactions of formaldehyde and acetaldehyde with OH radicals are:



$$(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 1.1 \times 10^{-11} \quad (2)$$



$$(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 1.6 \times 10^{-11} \quad (4)$$



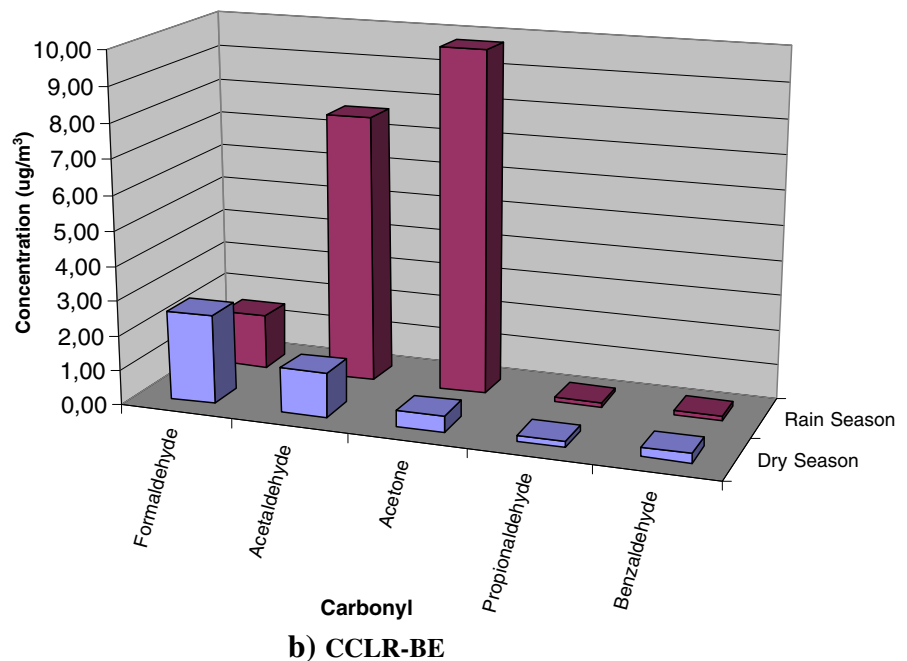
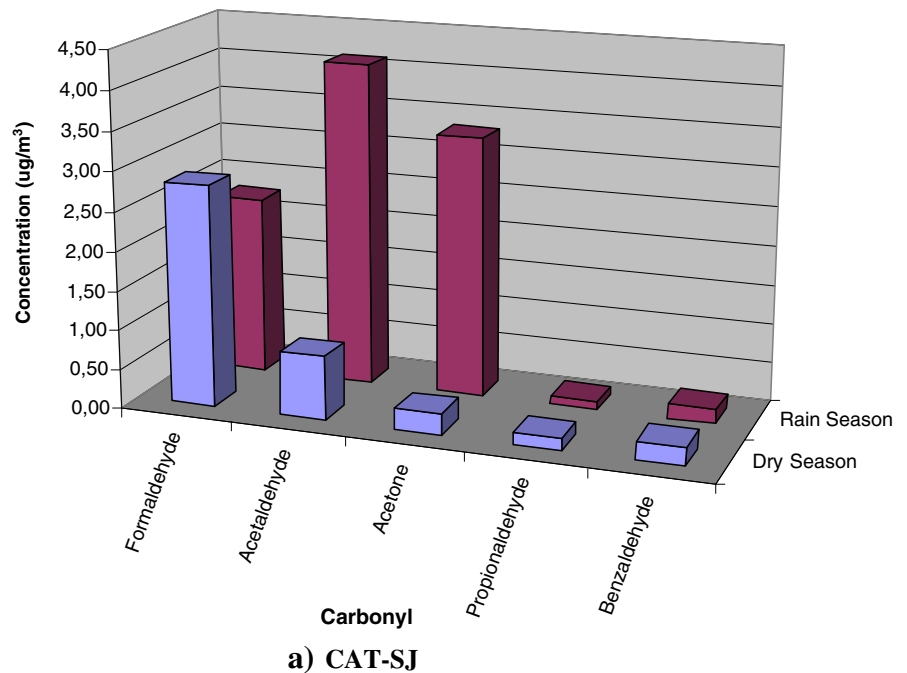
Because the photolysis of acetaldehyde is much lower than formaldehyde and acetaldehyde's, reaction with hydroxyl radical is slightly faster; reactions with hydroxyl radical is more significant as a sink that photolysis acetaldehyde (Anderson et al. 1996).

Shepson et al. (1991) and Possanzini et al. (1996) found that the ratios between formaldehyde and acetaldehyde are usually larger (>7) for rural than for urban areas (0.7 to 3) and stated that these ratios may indicate a biogenic source of formaldehyde. Grosjean (1992) reported that

Table 5 Values of the divergence coefficient obtained for the sampling sites

	CCLR-BE	CAT-SJ	REC-HE
CCLR-BE	–	–	–
SJ-CAT	0.152	–	–
REC-HE	0.147	0.189	–

Fig. 1 a, b Seasonal variation of some carbonyl concentrations in two sites of sampling



the ratios often show large variations. In this study, the value obtained in the samples analyzed for CAT-SJ (1.03), REC-HE (0.82), and CCLR-BE (0.49) suggesting that anthropogenic hydrocarbons local participation is important in the generation of aldehydes in the sampling site. The ratios in this study and other studies were listed in

Table 6. The ratio acetaldehyde/propionaldehyde has been proposed as another indicator of anthropogenic origin of the aldehydes found in ambient air samples, as the propionaldehyde is uniquely associated with anthropogenic sources (Anderson et al. 1996). The value of this ratio for the city of San José corresponds to 24.5. This value agrees

Table 6 Comparison of C₁/C₂ and C₂/C₃ concentration ratios in the metropolitan area of Costa Rica and in other areas

Location	C ₁ /C ₂	C ₂ /C ₃	Reference
CAT-SJ	1.04	18.4	This study
REC-HE	0.82	31.6	This study
CCLR-BE	0.49	29.3	This study
Rome, Italy (urban)	2.1	5.2	Possanzini et al. (1996)
Mexico City (urban)	2.91		Báez et al. (2000)
Hong Kong, China (urban)	2.1	8.38	Ho and Yu (2002)
New Jersey, USA (semiurban)	5.8	2.30	Zhang et al. (1994)
Los Angeles, USA (urban)	0.91	3.84	Grosjean (1996)

with those reported for cities with low levels of contamination.

The correlations between carbonyls detected in all samples in the ambient air were shown in Table 7. It can be observed that high positive correlations were obtained between formaldehyde and acetaldehyde at CAT-SJ, REC-HE, and CCLR-BE and good correlation between acetone and acetaldehyde. The strong correlation between formaldehyde and acetaldehyde throughout the study period suggests that these aldehydes are coming from common sources.

The high correlation found between acetone, formaldehyde, and acetaldehyde seems to indicate a common anthropogenic source. It has been reported that secondary reactions could explain the acetone amounts in the ambient air. Acetone

is formed by ozone reactions with some alkenes, and it is the main end product of OH radical oxidation of propanone, isobutene, isopentene, and higher isoalkanes (Báez et al. 2000). It has been suggested that oxidation of propane is the main source of acetone. Propane is the main constituent of liquefied petroleum gas, which is the fuel most commonly used in hotels, houses, and many small industries. It could thus be an important source of acetone in the metropolitan area of Costa Rica. Formaldehyde had bad correlations with other carbonyls, indicating that photochemical reactions might be another important source at noon in dry season other than primary emissions from vehicular exhaust.

To assess the relationships between concentrations of the carbonyls studied, factor analysis

Table 7 Spearman rank correlations for carbonyl concentrations in the metropolitan area of Costa Rica

	Formaldehyde	Acetaldehyde	Acetone	Propionaldehyde	Benzaldehyde
CAT-SJ (N = 28)					
Formaldehyde	1,000				
Acetaldehyde	0.838	1,000			
Acetone	-0.341	0.818	1,000		
Propionaldehyde	0.785	-0.488	-0.474	1,000	
Benzaldehyde	0.835	-0.197	-0.165	0.653	1,000
REC-HE (N = 26)					
Formaldehyde	1,000				
Acetaldehyde	0.814	1,000			
Acetone	0.224	0.838	1,000		
Propionaldehyde	0.502	0.275	0.141	1,000	
Benzaldehyde	0.797	0.224	0.224	0.511	1,000
CCLR-BE (N = 27)					
Formaldehyde	1,000				
Acetaldehyde	0.859	1,000			
Acetone	-0.449	0.905	1,000		
Propionaldehyde	0.814	-0.118	-0.172	1,000	
Benzaldehyde	0.572	-0.089	-0.147	0.556	1,000

Bold numbers are significant at $p \leq 0.05$

Table 8 Factor statistical 6.4 analysis for all data and all variables

	Factor 1	Factor 2	Factor 3
Formaldehyde SJ	-0.192	0.322	-0.744
Formaldehyde HE	0.091	0.308	0.830
Formaldehyde BE	-0.526	0.359	-0.049
Acetaldehyde SJ	0.883	0.004	0.090
Acetaldehyde HE	0.902	-0.034	0.190
Acetaldehyde BEL	0.206	-0.959	-0.032
Acetone SJ	0.871	-0.139	-0.038
Acetone HE	0.846	0.008	0.257
Acetone BEL	-0.047	-0.961	0.001
% Total variance	38.2	24.3	15.1

Factor loading normal varimax extraction. Principal components (bold numbers are significant at >0.5)

(principal component analysis) was applied. Table 8 shows the factor loading normalized with varimax rotation. Varimax rotation aims to maximize the variance of square normalized factor loading across variables for each factor and makes interpretation easier. Three factors from the principal component analysis were sufficient to explain 77.6% of the total variance. Factor 1 explained 38.2% of the total variance, with high loading on formaldehyde, acetaldehyde, and acetone in CCLR-BE and CAT-SJ. The high loadings on formaldehyde, acetaldehyde, and acetone suggest that these carbonyls come from anthropogenic sources (vehicle emissions), although as noted above, acetone also comes from photochemical reactions. Factor 2 indicates a high loading on acetone and acetaldehyde in CCLR-BE, explaining 24% of the total variance. These results also indicate a contribution from anthropogenic sources.

Conclusions

Atmospheric levels of carbonyl compounds and their possible sources in metropolitan area of Costa Rica were measured in this study. Acetone was the most abundant carbonyl in the ambient air, accounting for 24–40% of the total carbonyls. Acetone, formaldehyde, and acetaldehyde were the dominated carbonyls and accounted for 55–74% of the total carbonyls. The long lifetime of acetone resulted in higher concentrations in the atmosphere.

The strong correlations between C1–C2 and C3 indicated that motor vehicle exhaust is the

main source of these carbonyls. The lower concentrations observed in dry season indicated that photochemical reactions and local meteorological conditions can account for the decrease in this season. Currently, a more intensive effort to measure carbonyls is underway, in which carbon monoxide measurements are included in order to determine the anthropogenic origin of the principal carbonyls more precisely, independently of photochemical reactions.

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