

# Concentrations and Source Characteristics of Airborne Carbonyl Compounds Measured Outside Urban Residences

**Weili Liu**

*Joint Graduate Program in Exposure Assessment, Rutgers University and University of Medicine and Dentistry of New Jersey, Piscataway, NJ*

**Junfeng (Jim) Zhang**

*School of Public Health, University of Medicine and Dentistry of New Jersey, Piscataway, NJ; and Environmental and Occupational Health Sciences Institute, Piscataway, NJ*

**Jaymin Kwon, Clifford Weisel, and Barbara Turpin**

*Environmental and Occupational Health Sciences Institute, Piscataway, NJ*

**Lin Zhang**

*School of Public Health, University of Medicine and Dentistry of New Jersey, Piscataway, NJ*

**Leo Korn**

*New Jersey Department of Environmental Protection, Trenton, NJ*

**Maria Morandi and Tom Stock**

*University of Texas-Houston, Houston, TX*

**Steve Colome**

*Integrated Environmental Sciences, Irvine, CA*

## ABSTRACT

This paper presents the analysis of ambient air concentrations of 10 carbonyl compounds (aldehydes and ketones) measured in the yards of 87 residences in the city of Elizabeth, NJ, throughout 1999–2001. Most of these residences were measured twice in different seasons; the sampling duration was 48 hr each time. The authors observed higher concentrations for most of the measured carbonyl compounds on warmer days, reflecting larger contributions of photochemical reactions on warmer days. The estimated contributions of photochemical production varied substantially across the measured carbonyl

compounds and could be as high as 60%. Photochemical activity, however, resulted in a net loss for formaldehyde. The authors used stepwise multiple linear regression models to evaluate the impact of traffic sources and meteorological conditions on carbonyl concentrations using the data collected on colder days (with lower photochemical activities). They found that the concentrations of formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, benzaldehyde, glyoxal, and methylglyoxal significantly decreased with increasing distance between a measured residence and one or more major roadways. They also found significant negative associations between concentrations for most of the measured carbonyl compounds and each of the following meteorological parameters: mixing height, wind speed, and precipitation.

## IMPLICATIONS

Carbonyls (aldehydes and ketones), several of which are on the U.S. Environmental Protection Agency list of hazardous air pollutants, are present at elevated levels in polluted urban atmospheres. Understanding concentrations and source characteristics of urban carbonyls is an important step toward effective strategies for managing health risks associated with carbonyl exposures. In this paper, concentrations of 10 common carbonyls measured in the yards of residences within an urban community are reported, providing insights on impacts of local traffic emissions, atmospheric photochemical reactions, and stationary source emissions in different seasons.

## INTRODUCTION

Carbonyl compounds are characterized by a polarized reactive carbonyl functional group (C = O bond). This class of compounds is found ubiquitously in ambient air. Some carbonyl compounds (e.g., formaldehyde, acetaldehyde, and acrolein) are classified as hazardous air pollutants (also known as air toxics) by U.S. Environmental Protection Agency (EPA) because of their adverse health effects, including cancer and irritation of the eyes and respiratory tract.<sup>1–5</sup> Carbonyl compounds in the atmosphere are produced from primary and secondary sources.

Primary sources include natural emissions from vegetation, which contribute to the background levels of carbonyl compounds, and anthropogenic sources, such as emissions from motor vehicles and industrial facilities.<sup>6-10</sup> Carbonyl compounds are also formed via atmospheric oxidation of hydrocarbons, especially during photochemical smog episodes.<sup>11-13</sup> Understanding the contributions of both primary emissions and secondary formations to ambient carbonyl levels is important for developing control strategies. However, because of the complexity of the behaviors of carbonyl compounds in the atmosphere, it is challenging to quantify their sources. Furthermore, although a number of studies have examined ambient concentrations of carbonyl compounds, none has done so with a spatial scale at individual residence level within a community.<sup>14-19</sup>

In the current analysis, the authors used part of the data collected in the Relationship of Indoor, Outdoor, and Personal Air (RIOPA) study to examine the relationships between outdoor residential concentrations and potential ambient sources for 10 carbonyl compounds measured in the yards of the RIOPA homes in the city of Elizabeth, NJ.<sup>20,21</sup> As shown in Figure 1,<sup>22</sup> Elizabeth is surrounded by congested local streets and major highways, including the New Jersey Turnpike on the east and the Garden State Parkway on the west, the two major north-south toll roads in New Jersey. In addition, Route 1&9, the major north-south non-toll road, bisects Elizabeth and carries a large amount of both passenger and truck traffic, including traffic emanating from Newark Liberty International Airport. Most of these RIOPA homes were located close to one or more interstate or intrastate

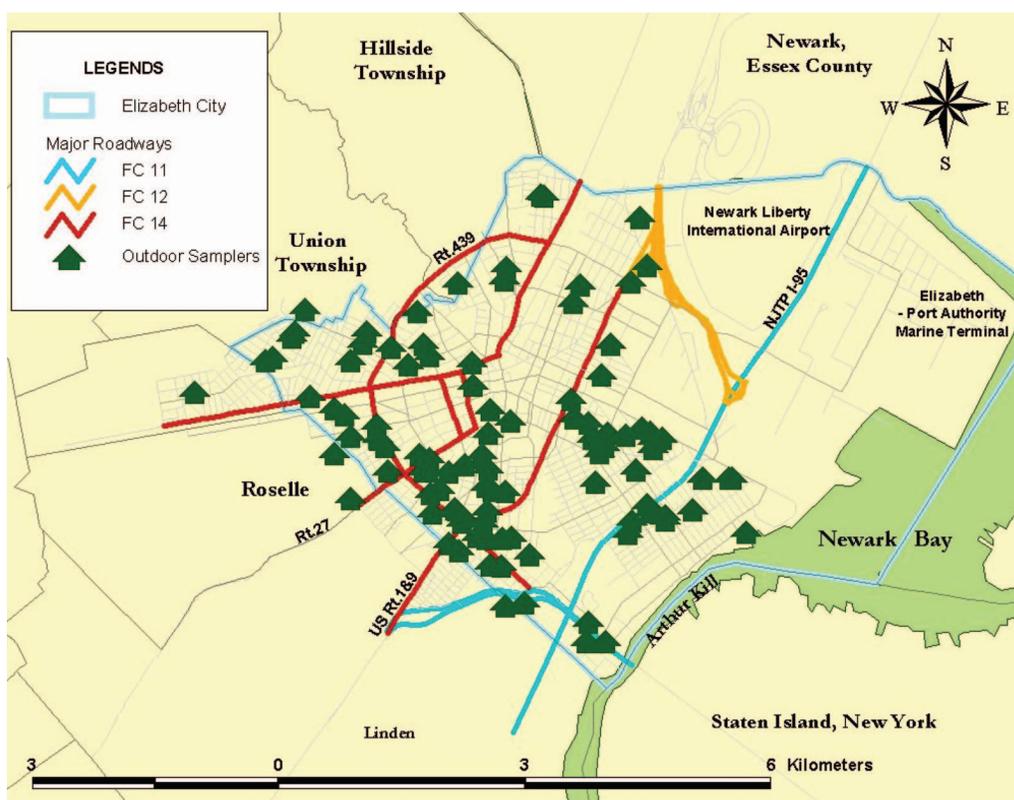
highways. Therefore, vehicular traffic source may be an important contributor to the measured carbonyl compounds in the city, and its impact on residential outdoor carbonyl concentrations is one of the focal points of the current analysis.

Photochemical reactions in the atmosphere can either increase or decrease the ambient carbonyl concentrations, because carbonyl compounds are oxidation products of hydrocarbons, and, on the other hand, certain carbonyl compounds (e.g., formaldehyde) readily undergo photolysis in the atmosphere. The contribution of the secondary formation or loss may overwhelm the primary emissions of carbonyl compounds under favored atmospheric conditions.<sup>11,14,23</sup> Through an analysis of carbonyl concentrations in relation to ozone ( $[O_3]$  an indicator of photochemical activity) and to CO (an indicator of primary emissions related to incomplete combustions, mainly vehicular emissions in Elizabeth), the authors attempt to gain insights about relative contributions of primary emissions and photochemical formations/losses for the measured carbonyl compounds.

## EXPERIMENTAL WORK

### Data Description

The concentration data used in this analysis include 48-hr averaged concentrations of 10 carbonyl compounds collected in the yards of 87 homes of nonsmoking residents living in Elizabeth. The concentrations were measured from the summer of 1999 to the spring of 2001. Fifty-one of these homes were monitored twice with a time interval >3 months between the two sampling events. The carbonyl samples were collected using the Passive Aldehydes



**Figure 1.** The location of RIOPA homes and nearby major roads in Elizabeth, NJ.<sup>22</sup>

and Ketones Sampler and analyzed using an high-performance liquid chromatography fluorescence method.<sup>24</sup>

To identify the contributions from primary emissions and secondary formations/losses to ambient carbonyl levels, local CO and O<sub>3</sub> data were used as indicators for primary combustion sources and photochemical activities, respectively. The RIOPA study did not conduct side-by-side measurements of O<sub>3</sub> and CO along with the carbonyl compounds. Hence, hourly concentrations were extracted for O<sub>3</sub> and CO during the corresponding 48-hr sampling period from the EPA Air-Data database, which were collected at the Elizabeth air monitoring station authorized by EPA.<sup>25</sup> Average and maximum hourly concentrations for each 48-hr sampling period were calculated for O<sub>3</sub> and CO.

To analyze traffic impact on the residential outdoor carbonyl concentrations, the distance (proximity) between each RIOPA home and major roads (highways and freeways) was used as a traffic source indicator. These proximity data were obtained by extracting a Geographical Information System (GIS) database constructed for the RIOPA-Elizabeth.<sup>22</sup> The annual emission inventory data were obtained for four carbonyl compounds, formaldehyde, acetaldehyde, acrolein, and propionaldehyde, from the National Emission Inventory database<sup>26</sup> to estimate annual total carbonyl emissions for the entire Union County within which Elizabeth is located. The meteorological data in Elizabeth, including ambient temperature, wind speed, atmospheric mixing height, and precipitation, were obtained from the National Climatic Data Center (NCDC)/National Oceanic and Atmospheric Administration (NOAA). The data were collected at the central meteorological observation station in Newark International Airport. The temperature and wind speed data were averaged to match the ~48-hr sampling period for each residence. Mixing height data obtained from NCDC/NOAA were reported as a.m. (morning) and p.m. (afternoon) mixing heights and were averaged for individual homes to correspond with the sampling time period. Precipitation (in.) was the sum of the hourly precipitation for the 48-hr sampling period for the Elizabeth area.

### Data Analysis

*Estimating Carbonyl Contributions from Primary Emissions and Secondary Productions/Losses.* CO has been used as a tracer for combustion-related emissions because it is relatively stable compared with other pollutants emitted to the urban atmosphere. This is true especially in cities with pollution mainly from automobile emissions. It has been estimated that motor vehicle emissions accounted for as much as 95% of the total CO emissions in metropolitan areas.<sup>27</sup> To estimate the contributions from primary emissions and secondary formations/losses to the ambient carbonyl levels, the authors first assume that the ratio between primary-emitted carbonyls to the CO emissions does not change after dispersion to ambient level during the periods when photochemical activities are negligible. Therefore, the expected primarily produced carbonyl compounds are estimated by applying a regression analysis to a subset of data collected at the time when the photochemical activities were negligible. The secondarily generated or decomposed carbonyl compounds can then

be estimated by subtracting the expected primary carbonyls from the total observed ambient carbonyl concentrations:

$$C_{\text{pri}} = \beta_0 + \left( \frac{E_{\text{carbonyl}}}{E_{\text{CO}}} \right)_{\text{pri}} \times C_{\text{CO}} \quad (1)$$

$$C_{\text{sec}} = C_{\text{Tot}} - C_{\text{pri}} \quad (2)$$

In this model,  $C_{\text{pri}}$  represents the carbonyl concentrations contributed from primary emissions;  $C_{\text{co}}$  is the average hourly CO concentrations during the 48-hr sampling period for each home;  $E_{\text{carbonyl}}/E_{\text{CO}}$  is the ratio of carbonyl emission rate to CO emission rate from primary sources, which is estimated by the slope of the regression line;  $C_{\text{sec}}$  is the carbonyl concentrations contributed from photochemical formations/losses;  $C_{\text{Tot}}$  is the measured outdoor carbonyl concentrations for each home; and  $\beta_0$  represents the background level (noncombustion sources) of carbonyl compounds in the air and is estimated by the intercept of the regression line. In the analysis, the 25th percentile of 48-hr maximum hourly O<sub>3</sub> concentration for RIOPA NJ data ( $\leq 36$  ppb) was set as the cutoff point for low photochemical activity days.  $\beta_0$  and  $(E_{\text{carbonyl}}/E_{\text{CO}})$  were obtained by fitting the regression model using the carbonyl and CO concentration data collected on the days when the 48-hr maximum hourly O<sub>3</sub> concentration was  $< 36$  ppb (eq 1). Robust regression was used to fit the data to minimize the influence of outliers in both the independent variable and the response variable. The basic ideas of this method are from the previous work on estimating the formation of secondary aerosols.<sup>28,29</sup>

*Examining the Impact of Traffic Sources.* The Bureau of Transportation and Development in Department of Transportation of New Jersey classifies the roads located in Elizabeth according to traffic density and function as follows: interstate highway (F<sub>11</sub>), other freeway and expressway (F<sub>12</sub>), other principal arterial (F<sub>14</sub>), urban minor arterial (F<sub>16</sub>), collector (F<sub>17</sub>), and local road (F<sub>19</sub>; shown in Figure 1).<sup>30</sup> In this analysis, only roads with significant emissions of carbonyl compounds were considered as indicated by the emission inventory data. More than 90% of the on-road emissions of carbonyl compounds came from interstate highways (F<sub>11</sub>), freeways and expressways (F<sub>12</sub>), and principal arterials (F<sub>14</sub>), with approximately equal contribution from each type, whereas other type of local roads (F<sub>16</sub>, F<sub>17</sub>, and F<sub>19</sub>) together represented  $< 10\%$  of the total on-road emissions. Therefore, only the first three types of roads, F<sub>11</sub>, F<sub>12</sub>, and F<sub>14</sub>, were considered in the model construction. There are two subtypes of roads (e.g., F<sub>11-1</sub> and F<sub>11-2</sub>) for each road type.

A multiple linear regression model was constructed to examine the impact of on-road traffic emissions on measured residential outdoor carbonyl concentrations. Stepwise selection with criteria of  $P \leq 0.05$  was used to identify significant contributors to outdoor carbonyl concentrations. In this model, outdoor concentration was treated as the dependent variable, and the following parameters were treated as independent variables: proximities (the actual distances between a home and its surrounding major roads), atmospheric mixing height, wind

speed, and precipitation. The concentration data were natural-logarithm transformed to reduce the skewness associated with the original data distributions. The model is described as follows:

$$\ln(C) = \beta_0 + \beta_1 F_{11,1} + \beta_2 F_{11,2} + \beta_3 F_{12,1} + \beta_4 F_{14,1} + \beta_5 F_{14,2} + \beta_6 F_{14,2} + \beta_7 S + \beta_8 U + \beta_9 P + \varepsilon \quad (3)$$

where the dependent variable,  $\ln(C)$ , is the natural-log-transformed value of the carbonyl concentration;  $\beta_0$  is the intercept of this model;  $\beta_1$  to  $\beta_6$  represent the coefficients of the proximity variables (the distances of six major roads to the each house,  $F_{11,1}$  to  $F_{14,2}$ , km);  $\beta_7$ ,  $\beta_8$ , and  $\beta_9$ , are the coefficients for meteorological variables, atmospheric mixing height (S, km), wind speed (U, m/sec), and precipitation (P, in.), respectively.  $\varepsilon$  is the error term of the regression model. To avoid the interference of photochemical activities on the carbonyl compounds, only the data collected on low  $O_3$  days were used (peak  $O_3 \leq 36$  ppb). Furthermore, carbonyl samples below the method detection limits (MDLs) or not detected were removed before the analysis.

## RESULTS AND DISCUSSION

### Concentrations by Season

Residential outdoor carbonyl concentrations measured at the 87 RIOPA-Elizabeth homes are summarized by season in Table 1. Seasons were simply defined as follows: spring being from March to May, summer from June to August, fall from September to November, and winter from December to February. A total of 138 valid carbonyl measurements were obtained in Elizabeth. Except for acrolein, crotonaldehyde, and acetone, the concentrations for all of the other compounds had >90% of the samples above their MDLs. Acetone was above MDL in 85.5% of the samples. For the two unsaturated carbonyl compounds, acrolein and crotonaldehyde, 59.4% and 55.1% of the samples had concentrations above the MDLs, respectively. Concentrations below the respective MDL were substituted with one half of the MDL before the comparison. As expected, formaldehyde and acetaldehyde had

the highest concentrations among all of the measured carbonyl compounds and together accounted for 60%, on a mass concentration basis, of the sum of the 10 carbonyl compounds reported in Table 1. All of the measured compounds show significant seasonal differences ( $P < 0.05$ , Kruskal Wallis test). The concentrations of propionaldehyde, acrolein, benzaldehyde, glyoxal, methylglyoxal, and hexaldehyde were generally higher in the spring and summer than in the fall and winter. The medians of the average ambient temperature during the 48-hr sampling period in the spring, summer, fall, and winter were 17.0, 24.0, 13.7, and 1.1 °C, respectively. Thus, higher concentrations, measured in the spring and summer, were associated with higher average ambient temperatures. This observation is consistent with the fact that photochemical activities are generally stronger on days with more hours of sunlight, which are frequently warmer days, leading to higher production of secondary carbonyl compounds in the atmosphere.<sup>31–33</sup> Recent studies conducted in urban areas of Rome, Italy, and at a semirural site in Denmark showed similar seasonal variations in ambient carbonyl concentrations for most of the carbonyl compounds measured in this study, with highest concentrations observed during summer times.<sup>27,34</sup> The exception was formaldehyde in the current study.

Formaldehyde had markedly lower concentrations in the summer than in the other three seasons in the RIOPA-Elizabeth homes. One explanation is that local primary sources of formaldehyde might be stronger in the other three seasons of the study area. Another more plausible explanation is that the photolysis of formaldehyde might have overridden the photochemical generation of formaldehyde during the summer in Elizabeth, as reported similarly for other urban areas.<sup>15</sup>

### Simple Source Indicators

The concentration ratios of formaldehyde to acetaldehyde (C1/C2) and acetaldehyde to propionaldehyde (C2/C3) have been suggested to reflect different emission sources of ambient carbonyl compounds. Scatter plots of C1 versus C2 and C2 versus C3 for the RIOPA Elizabeth

**Table 1.** Outdoor air concentrations ( $\mu\text{g}/\text{m}^3$ ) of 10 carbonyl compounds measured in 87 residences in Elizabeth, shown by season.

Variable	D%	Spring				Summer				Fall				Winter				P Value <sup>a</sup>
		N	Mean	SD	Median	N	Mean	SD	Median	N	Mean	SD	Median	N	Mean	SD	Median	
Formaldehyde	99.3	22	7.08	2.49	8.20	43	5.17	3.07	4.68	41	6.26	2.63	6.90	32	7.59	2.30	8.18	<0.01
Acetaldehyde	98.6	22	9.33	5.50	9.69	43	9.07	6.53	8.65	41	11.6	7.68	0.6	32	4.77	2.35	3.94	<0.01
Acetone	85.5	22	3.90	2.95	3.44	43	2.29	2.09	1.96	41	4.87	4.02	4.37	32	4.01	2.75	3.38	0.05
Acrolein	59.4	22	1.87	2.27	0.54	43	1.03	1.25	0.59	41	0.40	0.47	0.14	32	0.69	0.73	0.50	0.03
Propionaldehyde	90.6	22	2.00	0.91	1.75	43	1.51	0.92	1.37	41	0.75	0.64	0.61	32	0.89	0.93	0.62	<0.01
Crotonaldehyde	55.1	22	0.20	0.30	0.07	43	0.51	1.18	0.17	41	0.32	0.35	0.19	32	0.44	0.47	0.36	0.06
Benzaldehyde	91.3	22	1.88	1.09	1.78	43	2.36	1.26	2.14	41	1.35	0.74	1.40	32	0.87	1.23	0.54	<0.01
Glyoxal	100	22	1.86	0.69	2.03	43	1.83	1.07	1.70	41	1.32	0.77	1.31	32	1.16	0.59	1.08	<0.01
Methylglyoxal	94.2	22	2.08	0.82	2.09	43	2.18	0.98	2.24	41	1.21	0.94	1.03	32	1.60	0.96	1.51	<0.01
Hexaldehyde	98.6	22	2.05	0.83	2.18	43	2.06	0.73	2.04	41	1.01	0.93	0.68	32	0.82	0.85	0.68	<0.01

Notes: D% = percent of samples with concentrations higher than MDL; concentrations below the respective MDLs were substituted with one half of the MDL before the comparison.; <sup>a</sup>P values based on Kruskal-Wallis test for interseason differences in carbonyl concentrations assuming that the dependence between samples is weak;  $P < 0.05$  indicates that the difference is significant at  $\alpha = 0.05$ .

data were shown in Figure 2. High ratios of C1/C2 indicate biogenic emissions because some biogenic hydrocarbons, when oxidized, can yield proportionally more formaldehyde than acetaldehyde.<sup>33</sup> C1/C2 ratios usually vary from 1–2 in urban areas to ~10 in forest areas.<sup>27</sup> As indicated in Figure 2, more data points were close to the axis of acetaldehyde, with 64% of the samples having C1/C2 ratios <1, and the median of the ratios is 0.78, lower than C1/C2 ratios observed in other urban areas.<sup>14,27,35,36</sup> Because carbonyl concentrations were affected by seasonality, as shown above, the ratio calculations were stratified by average ambient temperature during the 48-hr sampling period, that is, the colder-season group (average temperature  $\leq 10$  °C) versus the warmer-season group (average temperature  $\geq 20$  °C). For the colder-season group, the median C1/C2 ratio was 1.70, very close to the ratios reported in other studies. However, for the warmer-season group, the median of C1/C2 ratios was only 0.54, further supporting our formaldehyde photolysis explanation of lower formaldehyde concentration in the summer, because the reported photolysis rate of formaldehyde is 10 times higher than that of acetaldehyde.<sup>15,37</sup> It needs to be noted that some previous studies did not identify significant seasonal effects for formaldehyde or observed higher formaldehyde concentrations in summer, probably because of the differences in study designs (e.g., different sampling durations, sampling times, and sampling locations).<sup>14,27,36</sup>

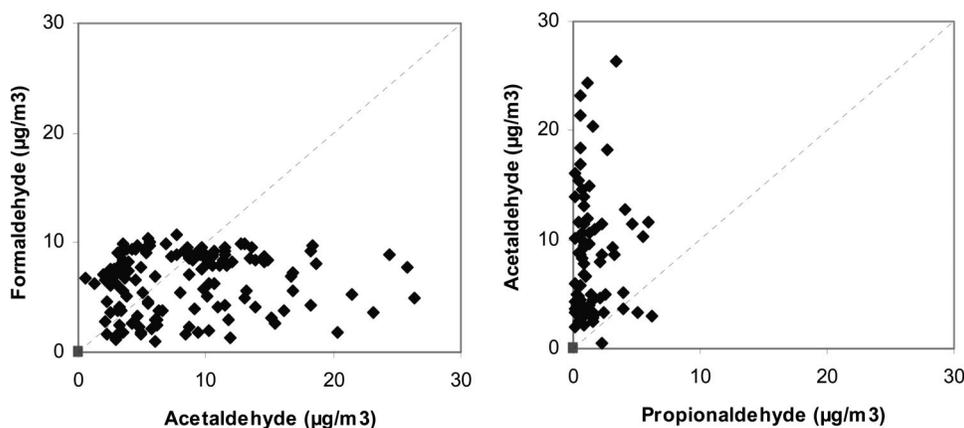
Because propionaldehyde (C3) does not have known natural (biogenic) sources, C2/C3 ratios may reflect relative contributions of anthropogenic sources and biogenic production of carbonyl compounds.<sup>27,33</sup> Typically the C2/C3 ratio is high in rural atmospheres and low in polluted urban air. The median C2/C3 ratio in this study was 8.05 (Figure 2), which was within the range of the ratios observed in other urban areas, such as Hong Kong (C2/C3, ~8.38), Rome (C2/C3, ~5.2), and Athens (C2/C3, ~7.35), indicating that the carbonyl compounds measured in the RIOPA-Elizabeth homes were derived mainly from anthropogenic sources.<sup>14,27,36</sup>

### Primary and Secondary Contributions

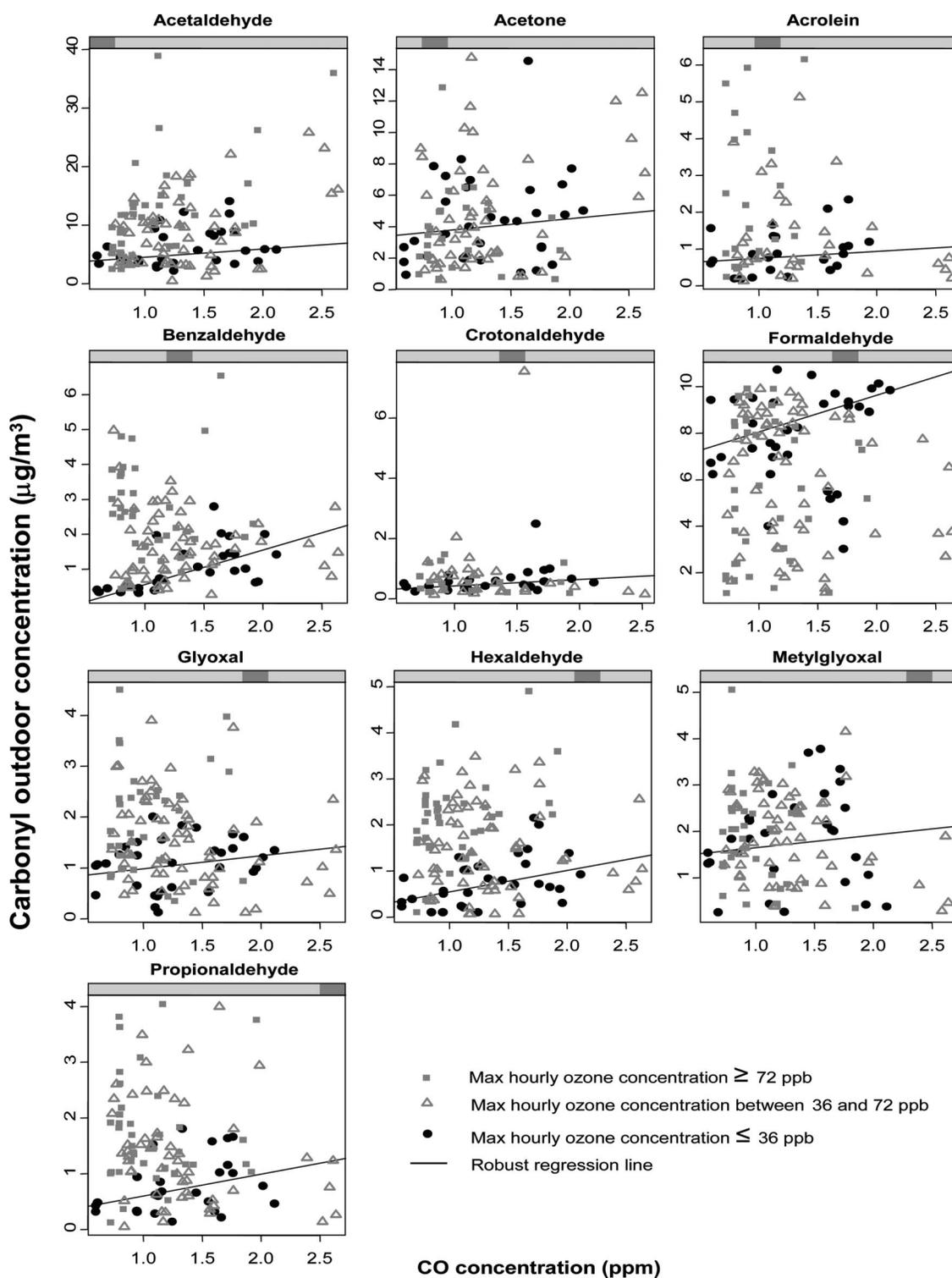
The concentration scatter plots of carbonyl compounds versus CO are shown in Figure 3. Concentrations below

the MDL or nondetected samples were not included in the analysis. The concentrations of acetaldehyde, acrolein, benzaldehyde, hexaldehyde, glyoxal, and propionaldehyde collected on lower-O<sub>3</sub> days (Figure 3, solid circles,  $\leq 36$  ppb) are apparently lower compared with those collected on higher-O<sub>3</sub> days (Figure 3, solid squares and triangles). For these compounds, >80% of data with the maximum hourly O<sub>3</sub> concentration  $\geq 72$  ppb (Figure 3, solid squares) were above the regression line. In contrast, the photochemical impact on acetone, crotonaldehyde, and methylglyoxal was not apparent based on the scatter plots, because the concentrations on lower-O<sub>3</sub> dates and higher-O<sub>3</sub> dates were randomly distributed on the scatter plots for these three compounds. Formaldehyde had a reversed pattern, with a large fraction of data points below the regression line, indicating its net loss because of photolysis on higher-O<sub>3</sub> days. This supports the observed “reversed” seasonal effects for formaldehyde and the low C1/C2 ratio in the summer, as discussed above.

Table 2 shows the results of the robust regression analysis of the concentration data collected on the lower-O<sub>3</sub> days. The regression results for acetone, methylglyoxal, and crotonaldehyde were not presented, because no apparent secondary productions/losses were observed. The intercepts of formaldehyde and acetaldehyde were 1 order of magnitude higher than those of other compounds, suggesting substantially higher levels of the noncombustion-related background (mainly biogenic emissions) for these two compounds than for the other measured carbonyl compounds. The slopes represent mixing ratios of carbonyl compounds to CO emission rates, which varied largely from 0.26 for glyoxal to 1.58 for formaldehyde. Large variation in the estimated slope for each compound was observed. The variation may result from different emission ratios for different vehicles, different primary combustion sources. Diurnal variation and seasonal fluctuations may also contribute to the variations in the ratio. It has been noted that the variations in mixing ratios of primary emissions (the regression slope) are a weakness of this approach.<sup>38</sup> However, the data did not provide sufficient information for identifying these variations.



**Figure 2.** Scattered plots of outdoor concentrations of formaldehyde vs. acetaldehyde (C1 vs. C2) and acetaldehyde vs. propionaldehyde (C2 vs. C3).



**Figure 3.** Scatter plots of measured carbonyl concentrations vs. CO concentration.

Another source of variations results from the CO concentrations used in the current analysis. The CO concentrations were measured at a central monitoring station at Elizabeth, which only reflected the regional primary emissions. These variations are also reflected with the low  $R^2$  values of the robust regressions. Despite the limitation, this method is still a reasonable approximation of primary emissions of carbonyl compounds based on the data currently available.

The relative contributions from secondary productions for acetaldehyde, acrolein, propionaldehyde, benzaldehyde, glyoxal, and hexaldehyde are presented in Table 3. The photochemical loss of formaldehyde is also seen in this table. Given expected seasonal impact on the relative importance of primary emissions versus secondary productions/losses of carbonyl compounds, the results were stratified by season. Most data points in the winter had  $O_3$  concentrations  $<36$  ppb (Figure 4), which

**Table 2.** Results from a robust regression of carbonyl concentrations vs CO concentrations on low ozone days (maximum hourly ozone concentrations for 48-hr sampling period  $\leq 36$  ppb).

Variable	Intercept $\pm$ SE	Slope $\pm$ SE	R <sup>2</sup>
Formaldehyde	6.46 $\pm$ 1.77	1.58 $\pm$ 1.27	0.14
Acetaldehyde	2.94 $\pm$ 2.48	1.46 $\pm$ 1.23	0.06
Acrolein	0.58 $\pm$ 0.65	0.15 $\pm$ 0.36	0.01
Propionaldehyde	0.18 $\pm$ 2.85	0.40 $\pm$ 0.31	0.11
Benzaldehyde	-0.43 $\pm$ 0.61	0.99 $\pm$ 0.43	0.32
Glyoxal	0.73 $\pm$ 0.38	0.26 $\pm$ 0.17	0.06
Hexaldehyde	0.13 $\pm$ 0.28	0.41 $\pm$ 0.21	0.12

were used in the robust regression model to estimate the primary emissions. Therefore, the sample size of the winter data is smaller than that of the data from other seasons. The seasonal effects on secondary productions/losses are statistically significant ( $\alpha = 0.05$ ) for most of the carbonyl compounds in Table 3 except formaldehyde and acetaldehyde. However, the secondary losses for formaldehyde tend to be higher during summer and fall, whereas the secondary productions for acetaldehyde are apparently lower during winter than during the other seasons. For all of the other compounds, the secondary productions were generally higher during spring/summer. The secondary productions of acrolein, propionaldehyde, benzaldehyde, and hexaldehyde contributed  $\leq 50$ – $60\%$  of their concentrations in spring/summer. For acetaldehyde and glyoxal, the secondary productions represented  $\sim 40\%$  of the concentrations, on average, during spring and summer.

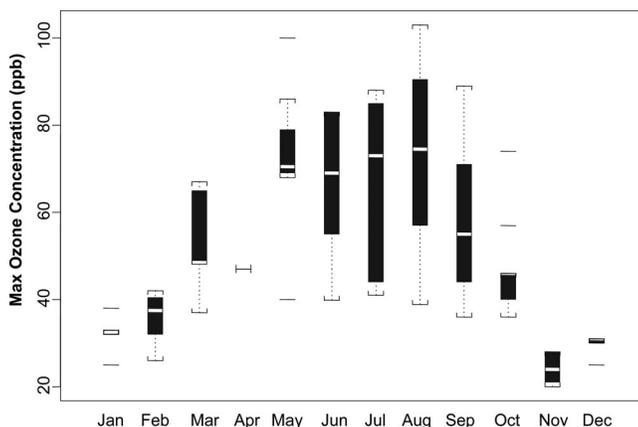
Previous studies have shown that photochemical reactions during summer may contribute to as high as 80–90% of the total carbonyl concentrations in polluted air.<sup>11,14,27</sup> The estimated mean contributions were lower than these literature-reported values. One explanation is the difference in study designs. The previous studies usually only collected samples during warmest hours (with strong solar radiations) of the day, whereas the 48-hr integrated concentrations may average out peak episodes of secondary productions. Furthermore, most of the RIOPA data were collected at homes close to traffic sources (Figure 1). Therefore, primary emissions may have greater

**Table 3.** Estimated percent contributions of secondary productions/losses to measured carbonyl compounds in the RIOPA-Elizabeth study.

Compounds	Spring		Summer		Fall		Winter		P Value <sup>c</sup>
	%	N	%	N	%	N	%	N	
Formaldehyde <sup>a</sup>	-20.4 $\pm$ 26.1	20	-39.6 $\pm$ 34.8	39	-35.2 $\pm$ 27.9	29	-23.2 $\pm$ 32.5	10	0.517
Acetaldehyde <sup>b</sup>	40.4 $\pm$ 28.7	20	37.0 $\pm$ 28.0	40	44.6 $\pm$ 24.0	30	7.20 $\pm$ 11.6	9	0.703
Acrolein <sup>b</sup>	67.6 $\pm$ 28.7	10	35.3 $\pm$ 34.6	23	12.2 $\pm$ 20.2	15	34.1 $\pm$ 29.1	6	0.005
Propionaldehyde <sup>b</sup>	61.5 $\pm$ 19.1	20	51.4 $\pm$ 29.2	38	26.6 $\pm$ 27.2	25	36.8 $\pm$ 33.3	10	0.001
Benzaldehyde <sup>b</sup>	51.6 $\pm$ 29.7	20	65.3 $\pm$ 29.1	37	37.0 $\pm$ 25.8	27	31.0 $\pm$ 26.6	10	0.002
Glyoxal <sup>b</sup>	39.8 $\pm$ 22.5	20	36.7 $\pm$ 28.3	41	23.7 $\pm$ 24.6	29	17.6 $\pm$ 19.1	11	0.024
Hexaldehyde <sup>b</sup>	64.9 $\pm$ 20.2	20	67.8 $\pm$ 18.6	40	29.9 $\pm$ 32.8	29	33.1 $\pm$ 28.8	10	<0.001

Notes: <sup>a</sup>The secondary loss for formaldehyde is calculated as the difference between measured concentration and estimated concentration from primary emissions divided by estimated primary concentration; <sup>b</sup>The secondary productions are calculated as the difference between measured concentrations and estimated concentrations from primary emissions divided by measured concentrations; <sup>c</sup>P values based on Kruskal-Wallis test for interseason differences in medians assuming that the dependence between samples is weak;  $P \leq 0.05$  indicates the difference is significant at  $\alpha = 0.05$ .

impacts on the residential outdoor carbonyl concentra-

**Figure 4.** Boxplots of maximum hourly ozone concentrations during the sampling periods of RIOPA study by month.

tions. This might be particularly true for formaldehyde, for which primary emissions dominated the residential outdoor concentrations. The photochemical reactions only led to a net loss for this compound.

### The Impact of Traffic Sources

Table 4 presents the parameter estimates obtained from the multiple linear regression models for measured carbonyl compounds. Through stepwise selection at an  $\alpha$  of 0.05, only the variables having significant contributions to the model response variable "outdoor concentration" were included in the final models. The results for acetone were not presented in the table, because neither the proximity variables nor the meteorological variables were selected by the model. Overall, the model explained  $>50\%$  of the variations in outdoor concentrations of acrolein, propionaldehyde, benzaldehyde, glyoxal, and methylglyoxal, whereas 20–40% of the variations were explained for the other carbonyl compounds. Significant negative associations between one or more proximity variables ( $F_{11-1}$ ,  $F_{12-1}$ ,  $F_{12-2}$ ,  $F_{14-1}$ , and  $F_{14-2}$ ) with the carbonyl outdoor concentrations for formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, benzaldehyde, glyoxal, and methylglyoxal, indicating that traffic

**Table 4.** Results from a multiple linear regression for identifying the impact of local traffic.

Compounds	N	Intercept	F <sub>11,1</sub>	F <sub>12,1</sub>	F <sub>12,2</sub>	F <sub>14,1</sub>	F <sub>14,2</sub>	Mixing Height (S)	Wind Speed (U)	Precipitation (P)	R <sup>2</sup>
Formaldehyde	32	2.12	-0.33					-0.36			0.32
Acetaldehyde	33	3.16	-0.20						-0.30	-0.07	0.39
Acrolein	32	1.75			-0.27				-0.46	-0.13	0.55
Propionaldehyde	24	1.57			-0.25			-2.78		-0.36	0.60
Crotonaldehyde	26	0.82		-0.29					-0.27		0.33
Benzaldehyde	23	1.64	-0.15						-0.49		0.60
Glyoxal	28	4.22	-0.48	-0.44			-1.36	-1.67		-0.11	0.50
Methylglyoxal	33	1.48	-0.34			-0.61				-0.28	0.67
Hexaldehyde	29	0.96							-0.42		0.25

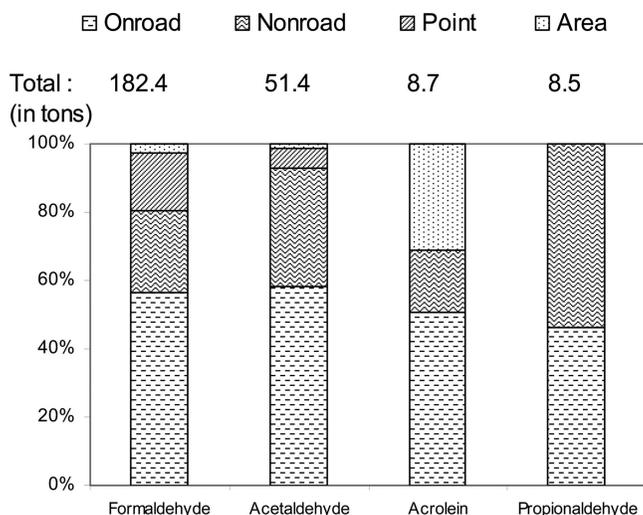
sources, contribute significantly to ambient carbonyl levels measured at residences, and proximities to major roadways can be potential predictors for residential outdoor concentrations of these carbonyl compounds when primary sources are dominant. F<sub>11,1</sub> was more frequently selected in the models for five of the nine carbonyl compounds. F<sub>11,1</sub> represents NJ Turnpike, a major north-south toll road in New Jersey, and had heavy traffic volume, presumably strong emissions from automobiles. Meteorological variables (mixing height, wind speed, and precipitation) were also selected by the model for some carbonyl compounds. An increase in either mixing height or wind speed (improved atmospheric dispersion condition) was significantly associated with a decrease in concentrations for all of the listed carbonyl compounds except methylglyoxal. Washout or rainout effect (precipitation scavenging) was identified for acetaldehyde, acrolein, propionaldehyde, glyoxal, and methylglyoxal.

The unexplained variations by the regression models might result from emissions of some stationary sources in Elizabeth and its surrounding areas, such as industrial and commercial sources. These stationary sources were classified into three categories: nonroad emissions (from operating construction and mining equipment, lawn and gardening equipment, etc.), point sources (industrial

sources), and area sources (from residential heating, open burning, industrial boilers, etc.). The annual emission inventories of four of the measured carbonyl compounds are available for Union County in 1999.<sup>26</sup> As shown in Figure 5, the on-road sources contributed 56, 58, 51, and 46% of annual emissions of formaldehyde, acetaldehyde, acrolein, and propionaldehyde, respectively; the nonroad sources contributed 24, 35, 18, and 54% of the annual emissions of formaldehyde, acetaldehyde, acrolein, and propionaldehyde, respectively; and the point sources contributed 17 and 6% of the emissions of formaldehyde and acetaldehyde, respectively. No point sources were reported for acrolein and propionaldehyde. Although the area sources only contributed 1 and 3%, respectively, of the total formaldehyde and acetaldehyde emissions and had no contributions to propionaldehyde emissions, 31% of the total emissions of acrolein were from area sources. The emissions inventory data suggest that local sources other than traffic emissions may be important contributors for some of the carbonyl compounds measured outside the RIOPA-Elizabeth homes. It is possible that certain localized sources might have overwhelmed the traffic sources in contributing to carbonyl levels measured outside of the homes that were very close to the local sources.

## CONCLUSIONS

Carbonyl compounds measured in the yards of the 87 RIOPA homes located in the city of Elizabeth showed significant seasonal variations. The estimated secondary productions for acrolein, propionaldehyde, benzaldehyde, and hexaldehyde can reach 50–60% and 40% for acetaldehyde and glyoxal on warmer sampling days. In contrast, a net loss of formaldehyde, because of strong photolysis, was observed on warmer days. Primary emissions of carbonyl compounds were mainly from anthropogenic sources including traffic emissions, the largest contributor for formaldehyde and several other compounds. The impact of the local traffic was significant on colder days when photochemical activities were lower, because concentrations of most of the measured carbonyl compounds significantly decreased with an increase in the proximity of the home to major traffic roads. Meteorological conditions, such as mixing height, wind speed, and precipitation, were also found to affect measured carbonyl concentrations that generally decreased with an improved atmospheric dispersion condition and with an increased atmospheric precipitation.



**Figure 5.** Carbonyl annual emission inventories in Union County, where Elizabeth is located, in 1999. (Adapted from National Emission Inventory<sup>26</sup>).

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## About the Authors

Weili Liu is a Ph.D. candidate in the joint graduate program in exposure assessment between Rutgers University, New Brunswick, NJ, and University of Medicine and Dentistry of New Jersey (UMDNJ), Piscataway, NJ. Junfeng (Jim) Zhang is an associate professor at UMDNJ School of Public Health and a member of Environmental and Occupational Health Sciences Institute (EOHSI), NJ. Jaymin Kwon is a postdoctoral fellow in EOHSI. Clifford Weisel is a professor at UMDNJ-Robert Wood Johnson Medical School and a member of EOHSI. Lin Zhang is a research associate at UMDNJ-School of Public Health. Leo Korn is a researcher in New Jersey Department of Environmental Protection in Trenton, NJ. Barbara Turpin is a professor at Rutgers University and a member of EOHSI. Maria Morandi is an assistant professor and Tom Stock is an associate professor at University of Texas-Houston, Houston, TX. Steve Colome is a principal scientist with Integrated Environmental Sciences in Irvine, CA. Address correspondence to: Junfeng (Jim) Zhang, UMDNJ-School of Public Health, 683 Hoes Lane West, Piscataway, NJ 08854; phone: +1-732-445-0158; fax: +1-445-0116; e-mail: jizhang@ehsi.rutgers.edu.