Frontier Analysis in Air Pollution

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ABSTRACT

Carbon containing aerosol is the most abundant particulate air pollutant species. It causes poor visibility and can be toxic. Tracing its origins is an important step in environmental management and control. This study analyzes the carbon concentrations at Duarte, CA (a suburban site near Los Angeles) and in Lennox, CA (a site next to a Los Angeles freeway). Concentrations inside a tunnel are also available and used to derive a motor vehicle emission profile. A new approach is proposed for calculating the motor vehicle contribution to organic carbon and the amount of background carbon found at the two sites. Regression analysis provides insight in the formation of organic carbon and frontier analysis is used to calculate the motor vehicle contribution to organic carbon and the amount of background carbon in the atmosphere. The information obtained from this analysis can be used in the regulation of motor vehicle emissions and in air pollution control.

Keywords: Environmental studies, Regression, Linear Programming

INTRODUCTION

Suspended particles in the atmosphere can be grouped into two categories: organic or carbonaceous, and inorganic. Carbonaceous particles constitute the largest fraction of particulate air pollutants in urban areas, cause poor visibility and can be toxic. Tracing the origins of these particles is an important step in environmental analysis and control. Unlike inorganic particles, carbonaceous compounds do not retain their molecular identity as they are transported from a pollution source to a receptor site. Only about 5% of these compounds can be identified on a molecular basis[1]. As a result, carbonaceous particles are empirically characterized by their solubility in various solvents, their volatility as a function of temperature, and their functional groups as determined by infrared or mass spectroscopy[2]. Using thermal analysis, the fraction of carbonaceous particle that is volatile between temperatures of 0^oC - 450^oC is called organic carbon, while the remaining fraction that is volatile at temperatures greater than 450^oC is called black carbon.

Source contribution of particles is defined as primary when compounds retain their molecular identity, and secondary when the molecular identity is lost from the source to the receptor. Black carbon is attributed to primary emissions (primarily combustion sources) as it is formed by high temperature processes. Organic carbon, however, results from primary emissions, secondary contributions that come from gas-to-particle conversion of gases and vapors in the atmosphere, and background or biogenic contributions. The latter two contributions are quite hard to quantitatively estimate because of the lack of tracers and the variability of atmospheric conditions. Motor vehicles are a primary emission source for black and organic carbon. They are also a secondary source for organic carbon as they emit gases and vapors that undergo chemical reactions in the atmosphere and result in particulate organic compounds.

For the analysis presented in this paper, carbon concentrations collected at different sites and a pollution source (motor vehicles in this case), in the same year, were necessary. Samples of atmospheric particles were randomly collected in 1983 at Duarte, CA, a suburban residential site located about 35 km inland to the east of downtown Los Angeles, and in Lennox, a sampling site near the Pacific Coast located next to a major freeway near the Los Angeles International Airport. One set of 35 samples collected at Duarte and one set of 20 samples collected at Lennox were selected for analysis. All particulate data at Duarte and Lennox were collected by Global Geochemistry Corp. (GGC) following standard quality control / quality assurance procedures[3]. Organic and inorganic particles and carbon monoxide (CO) concentrations were also collected at the Caldecott Tunnel, Berkeley, CA, in 1983 and used to develop motor vehicle emission profiles[4].

Regression analysis is used on the samples collected at the Caldecott Tunnel to relate Black and Organic Carbon emitted by motor vehicles. Different regression models are tried on the tunnel data and tested on the samples collected at Duarte and Lennox. Frontier analysis is then applied at the two sites in order to estimate the amount of background organic carbon and the primary contribution of motor vehicles to organic carbon at the two sites.

RELATIONSHIP BETWEEN ORGANIC CARBON AND BLACK CARBON

The Caldecott Freeway Tunnel is located east of Berkeley, California on highway 24. The freeway serves as a major commuter route linking the San Joaquim Valley to the business district of San Francisco Bay Area. Thirteen samples were taken inside the tunnel and three samples were collected outside the tunnel. Since motor vehicles is the only source emitting particles in the tunnel, the measurements inside the tunnel can be used to develop a relationship between the amount of organic and black carbon emitted by motor vehicles. The measurements taken outside the tunnel represent the background carbon found in the area.

Regression analysis was used to analyze the data in the tunnel and relate Organic Carbon (OC) to Black Carbon (BC). The OC concentration was set as the dependent variable while the BC concentration was the independent variable, since it can be attributed to primary sources only. Traditionally, it was believed that the Organic to Black carbon ratio (OC/BC) is constant at the source, thus a linear regression model would represent this relationship. From the thirteen points in the Tunnel, the following regression model was obtained,

$$[OC] = 13.17 + 0.56\,[BC] \qquad (1)$$

As shown in Figure 1, the model explains the data very well and the resulting R^2 is 94.55%. Due to the relatively small sample size, the adjusted (shrunken) R-squared, R_{adj}^2 was also calculated and it is equal to 94.06%. The expression in (1) suggests that the background OC in the tunnel is 13.2 $\mu g/m^3$. This is an over-prediction since ambient data suggest an ambient concentration at about 3 $\mu g/m^3$.

Another model was tested assuming that gas-to-particle conversion on the black carbon surface contributes to the concentration of particulate organics in the atmosphere[5]. The derivation of the model is found in Appendix A. In terms of a regression model, this relationship is expressed as,

$$[OC] = \beta_0 + \beta_1\,[BC]^{2/3} \qquad (2)$$

The first term corresponds to background or biogenic organic carbon. Applying this regression equation to the tunnel data of OC and BC, gives

$$[OC] = 3.14\,[BC]^{2/3} \qquad (3)$$

Equation (3) suggests that no OC exists in the tunnel without the presence of BC. Figure 1 gives the regression model having an R^2 of 95% and an R_{adj}^2 equal to 94.56% which is also a good match. Figure 1, also shows background data of OC and BC taken outside the tunnel. This model nicely explains these data too.

Both regression models fit the tunnel data well, though the surface reaction model can predict the background measurements taken outside the tunnel. The latter model suggests that BC catalyzes the formation of OC. A key question is whether there are direct particulate emissions of OC (as would be represented by a linear term) as well as emission of gases that convert into OC particles by condensation on BC particles (i.e. 2/3 term). When both terms were included in the regression model, most of the data variance was explained by the fraction of OC attributed to 2/3 dependence on BC mass, and the linear term was not statistically significant.

Carbon concentrations in the tunnel are very high (up to 100 $\mu g/m^3$) while ambient concentrations are in the order of 10 $\mu g/m^3$. The two models are visibly different at these low concentrations. Both models were tested on the Lennox data. Since this site is next to a major highway, almost all of its carbon is emitted from motor vehicles and the measurements can be considered as source emissions. Figure 2 shows the two regression models with the Lennox and Tunnel data and a logarithmic scale for BC. It is clear from this figure that the surface reaction model predicts the ambient data much better than the linear model. When a regression model was run through the combined data (Tunnel and Lennox), the following model was obtained

$$[OC] = 3.11\,[BC]^{2/3} \qquad (4)$$

with an R^2 of 97.8% and R_{adj}^2 equal to 97.67%. The coefficient in (4) is very close to the one in (3), indicating that the surface reaction model represents the data quite well.

A similar analysis was performed for the Duarte data. Duarte is a residential area and the motor vehicle contribution to the organic carbon at the site is expected to be low. The linear model had most of the sample points below the line and suggested that motor vehicles contribute a high percentage of the OC found at the site, which is contrary to what is expected. The surface reaction model, on the other hand, suggested a modest motor vehicle contribution to OC and had most of the sample points above the regression model. This indicates that other sources contribute to the OC concentration at the site, and further supports the use of the 2/3 model to explain the data.

SEPARATING PRIMARY AND OTHER SOURCE CONTRIBUTIONS

Henry[6] proposed plots of the organic versus black carbon concentrations for estimation of primary and other source contributions. He originally proposed drawing a straight line representing the OC/BC ratio from the source (motor vehicles) and obtaining the amount of other contributors to OC. Other contributors can include secondary emissions, biogenic sources and anthropogenic sources without a BC component. The regression analysis, however, showed that the BC and OC relationship is better explained by a 2/3 model. Furthermore, using the appropriate relationship to construct a lower envelope of the data, would give a better indication of motor vehicle and other contributions to OC at a site.

Since the development of data envelopment analysis, the efficient frontier analysis has been applied to several business problems[7]. Schmidt[8] describes the four basic groups that cover the methods for estimating frontier functions: deterministic parametric and nonparametric, and stochastic parametric and nonparametric. Parametric and nonparametric refer to whether a relationship is prescribed or not. A deterministic approach makes no assumptions about the stochastic properties of the data, whereas a stochastic approach depends on such assumptions. A deterministic parametric approach was applied in this study, and a model approach similar to Camm and Grogan[9] was used. Using a two-thirds relationship, a mathematical programming model was used to minimize the sum of the one-sided deviations:

$$\text{Minimize} \quad \sum_{i \in I} U_i$$

Subject to $\quad f(i) + U_i = OC_i \quad i \in I$

$$U_i \geq 0 \qquad i \in I$$

where I is the index set containing the measurements of black and the organic carbon, U_i is restricted to be nonnegative and gives the deviation of the measurement from the frontier, OC_i is the ith organic carbon measurement, and f(i) is the equation of the frontier, which is equivalent to equation (2). The frontier is linear in its parameters, β_0, β_1 and the parameters were unrestricted in sign.

Figure 3 gives a plot for the black and organic carbon concentrations at Lennox. The lower frontier gives the primary contribution to organic carbon in terms of black carbon concentration. The equation of the frontier is,

$$[OC] = 1.43\,[BC]^{2/3} \qquad (5)$$

The above expression suggests that no background OC exists at this testing site, which makes sense since the site is dominated by the motor vehicle source. Furthermore, the frontier attributes 55.45% of the OC to primary emissions resulting from motor vehicles.

A similar analysis was done for Duarte. Figure 4 gives the lower frontier and the measurements at this site. The new frontier,

$$OC = 2.1 + 1.46\,(BC)^{2/3} \qquad (6)$$

indicates that the amount of background OC at Duarte is 2.1 $\mu g/m^3$. As expected, the amount of background OC is higher at the residential area (Duarte) than the amount of background OC next to the freeway (Lennox). Since Duarte is an inland residential site, it receives a higher carbon concentration because of transport from the coastal area and products of photochemical secondary aerosols[3, 10]. Background and primary emissions explain 64.1% of the OC at this site. When the background amount was subtracted, 37.2% of OC was attributed to primary emissions while background was responsible for 26.9%.

In order to compare the results from the frontier analysis, similar contributions were calculated using carbon monoxide (CO) as a tracer for motor vehicles. Using the data collected at the Caldecott Tunnel[4], the concentrations of BC and CO were compared. The correlation coefficient between BC and CO is 0.80 indicating that CO can be used as a tracer of motor vehicle emissions. Furthermore the correlation coefficient between the two variables at Duarte is 0.75, which is very close to the Caldecott ratio, further suggesting the use of CO as a tracer for motor vehicles.

Using the tunnel OC/CO ratio, the motor vehicle contribution to organic carbon at Lennox in 1983, was 45% $\pm$ 21% (Table 1). This estimate is lower than the frontier estimate of 55.5% $\pm$ 18.7% but not statistically different from it. For comparison the Los Angeles basin average for 1982[10] is shown in the Table. Both estimates (tracer ratio and frontier analysis) are higher than the emission inventory estimate of 35% since this site is dominated by primary emissions, while the basin average is over a 50 x 50 mile grid in the South Coast Air Basin.

At Duarte, using the tunnel OC/CO ratio, the mean motor vehicle contribution to OC was 20% $\pm$ 7%. This estimate is lower than that of frontier analysis (37.2% $\pm$ 13%) and the basin average. The frontier estimate, on the other hand, is very close to the basin average.

CONCLUSIONS

In this study, carbonaceous concentrations taken at the Caldecott Tunnel were used to develop a relationship that can attribute organic carbon to motor vehicles. This relationship was applied at two different sites and the motor vehicle contribution to organic carbon was calculated. Regression analysis provided insight on the mechanics of gas-to-particle conversion that contributes to the concentration of particulate organics in the atmosphere. The findings suggest that motor vehicles emit Black Carbon and Organic Carbon vapors that react on the Black Carbon surface and result in Organic Carbon particulate matter. Frontier analysis was used to calculate the motor vehicle contribution to organic carbon at Lennox and Duarte, CA. The results obtained from this analysis were compared to contributions obtained from tracer ratio analysis and emission inventories and found to be similar. This suggests that frontier analysis can be used as a method for estimating organic carbon contribution of different pollution sources. Frontier analysis was also used to calculate background or biogenic organic carbon at the two sites. The estimation of the biogenic carbon and the contribution of pollution sources to the ambient carbon concentrations is an important step in environmental management and air pollution control, as carbon containing aerosol is the most abundant particulate air pollutant species.

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Appendix A

Derivation of model assuming that gas-to-particle conversion on the black carbon surface contributes to the concentration of particulate organics in the atmosphere

The mass of organic carbon, OC, increases by surface reaction on the black carbon surface as follows[5],

$$d\,OC / dt = a_{BC} \left(\sum_i R_{si} \right) \quad \text{(A1)}$$

where a_{BC} is the surface area (cm^2) of a black carbon particle, and R_{si} is the surface reaction of species i ($g/cm^2.s$) on the surface of a black carbon particle, which is nearly constant at atmospheric conditions. The surface is given by,

$$a_{BC} = \pi d_p^2 \quad \text{(A2)}$$

where d_p is the particle diameter. The black carbon mass is given by,

$$BC = \rho_{BC} \pi d_p^3 / 6 \quad \text{(A3)}$$

where ρ_{BC} is the black carbon density. By substituting (A3) in (A2) and (A1) and integrating keeping in mind that no new BC can be generated in the atmosphere by chemical reactions, the mass of OC is related to the mass of BC by,

$$OC = (OC)_{Background} + (36\pi / \rho_{BC}^2)^{1/3} \left(\sum_i R_{si} \right) t\, BC^{2/3} \quad \text{(A4)}$$

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