Characterization of urban PM_{10} pollution by the investigation of the real mass transport of the pollutants

Balint Alfoldy
European Commission, Joint Research Centre
I-21027 Ispra (VA), Italy

As a new approach the urban air pollution was characterized based on the columnar mass (CM) of the pollutants. The columnar mass was estimated as the product of the pollutant's concentration and the mixing height. Concentration data were taken from the metropolitan air quality monitoring network of Budapest, while mixing height was calculated by the meteorological AERMET model code. New features of the emissions as well as post-emission modifications of the pollutants are manifested in this study, which are mostly masked in the concentration time series by the variation of the mixing height.

1. Introduction

Air pollution directly affects the quality of life, human and other beings health, climate, and indirectly has an effect on water and soil pollution. Because of its general environmental and health impact, air pollution is continuously monitored worldwide in the bigger cities.

The atmospheric level of air pollutants is determined by the emissions of local sources, the transportation, the post emission modification of the pollutants such us chemical conversion, and the deposition. In addition, the evolved concentrations depend on the dimension of the volume within the pollution is mixed. This volume is characterized by its vertical expanse, what is the thickness of the boundary layer (or mixing height, MH).

Generally, the air pollution is characterized by concentration, since the majority of the receptors (e.g. human population) are affected by the concentration. However, the variation of the concentration does not reflect the real mass transport of the pollutants, since it is affected by the variation of the mixing height.

In contrary the concentration, the time variation of columnar mass (CM) reflects the real mass transport of the pollution (emission, transportation, chemical modification, deposition, advection). Consequently, analysis of CM's time derivative (mass flux) provides direct information on the diurnal history of the air pollution.

In this work time variation of columnar mass was studied as derived from pollution concentration multiplied by the mixing height. Time profile of combustion sources was characterized by the CO mass flux. Diurnal time variation of particle mass under 10 μm particle diameter (PM_{10}, d_p<10 μm) and 2.5 μm ($PM_{2.5}$) were described by mass fluxes.

Ozone mass flux was demonstrated as well, as an example of pollution entrainment from the residual layer.

2. Methodology

2.1 Data sources

In this work, time variation of columnar mass of the air pollution was studied as derived from the concentration multiplied by the mixing height. Concentration data originated from one month long measurements by the metropolitan air quality monitoring system of Budapest (capital of Hungary, 2 million inhabitants) during June, 2007. From the monitored species carbon monoxide (CO), particle mass (PM) and ozone (O_3) are considered here.

The thickness of the boundary layer, the so-called mixing height (MH), is the parameter connecting the columnar mass to the concentration. MH was calculated by AERMET, which is the meteorological preprocessor of the AERMOD dispersion model.

In the interest of better interpretation of the results, averaged diurnal cycles were calculated. The averaging over the days reduced the uncertainties and effect of noise in the measured as well as the modeled time series, and provided smoother concentration, MH, as well as CM time profiles.

2.2 Calculation CM and its time variation

Assuming that the pollution is well mixed in the boundary layer the product of the concentration and the mixing height provides the columnar mass of the pollutant. However, under stable air conditions – during early morning hours – pollution emitted at the surface slowly blends in the mixing layer forming significant vertical gradients of the concentration. Considering that sampling is taken at a few meters height, the product of concentration and mixing height may overestimate the CM during this period. Since the time derivative of CM was taken and interpreted in the following, from which the constant additive is eliminated, the possible overestimation of CM is not manifested in the results.

The time derivative of CM can be expressed as follows:

$$\frac{d}{dt}CM = f(t) + c(t) \cdot \frac{d}{dt}MH \,, \tag{1}$$

where $f(t)$ is the so-called mass flux in $\mu g \cdot m^{-2} \cdot h^{-1}$, and $c(t)$ is the pollution concentration in the 1) residual layer, if $dMH/dt>0$; 2) mixing layer, if $dMH/dt<0$. The $f(t)$ mass flux describes the real pollution mass transport as the resultant of emission, transportation, chemical production (positive flux), and deposition, advection and chemical loss (negative flux).

3. Results

3.1 Carbon monoxide

Figure 1 shows the diurnal profile of the CO concentration averaged over the monitoring stations (right panel), and the corresponding mass flux (left panel). Diurnal

profile of the mixing height is also presented (right panel). The time evaluation of the CO concentration follows the same pattern at each station; a traffic related emission peak at 8:00 is followed by concentration decrease due to the dilution of the pollution caused by the building up of the daily boundary layer. In the late afternoon the concentration increases again according to the higher emission rate of the evening rush hours. The CO mass flux was calculated based on Eq.1. In the calculation 100 μg m^{-3} CO concentration was considered in the residual layer (Balzani-Lööv, 2008).

Two mass flux peaks are shown in the figure in accordance the morning and evening rush ours. In between, the mass flux is low as a consequence of the lower emission, and higher intensity of removal processes. The mass flux is positive over the day, except 13:00 when it is slightly negative, which indicates that the outflux exceeds the influx. The outflux can be ascribed to air mass exchange between a less polluted rural area and the city (advection). Other CO removal processes such as chemical degradation cannot be considered since CO is one of the most stable air pollutants with several months atmospheric residence time. This property makes CO appropriate tracer for characterization of combustion sources.

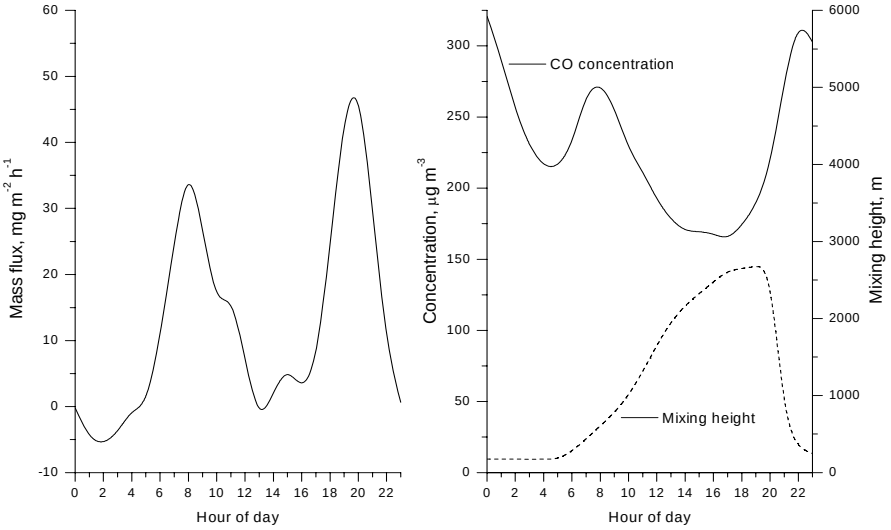

Figure 1. Averaged diurnal cycle of the CO concentration and the mixing height (right panel) and the CO mass flux (left panel).

3.2 Particle mass

Averaged diurnal cycle of PM_{10} mass flux is presented in Fig. 2. It becomes positive around 5:00 coincided by CO mass flux, according to the beginning of traffic emission. The mass flux increases until 8:00, than it forms a local maximum. After 9:00 a new peak is forming with roughly 2 times higher maximum at 12:00. From 15:00 a third PM_{10} mass flux peak forms.

In the figure the diurnal profile of $PM_{2.5}$ mass flux is presented as well. Mass fraction of the 2.5 μm $<d_p<$ 10 μm particle size interval is also presented in the figure, defined as a

difference of the PM_{10} and $PM_{2.5}$ mass fluxes. This mass fraction is referred as coarse particle mass in the following (PM_C), whereas the $PM_{2.5}$ fraction as fine particle mass (PM_F). It is seen in the figure that the mass fluxes of PM_C and PM_F become positive at 5:00 in accordance with the starting time of traffic activity. These mass fluxes can be attributed to the direct emission of traffic. The source of PM_F may be the fuel combustion of the vehicles, whereas PM_C can be related with the resuspension of road dust induced by vehicle movements. After 9:00, PM_F mass flux increases due to secondary aerosol formation. It is seen that PM_F has determinative contribution to the PM_{10} mass flux at noon that indicates mainly secondary formation origin of the appearing PM_{10} mass. After 12:00 the PM_{10} mass flux decreases that seems to be driven by the decrease of PM_F mass flux. After 13:00 the PM_F mass flux becomes negative, what means that the mass loss exceeds the production. This intensive $PM_{2.5}$ loss may be attributed to deposition as well as the intensive advection due to air mass movement having maximal velocity around noon. Evaporation of semi-volatile particles must be also considered, since the PM_F mass loss coincides with the diurnal temperature maximum. At the same time PM_C mass flux increases during this period (10:00-14:00) that may be attributed to resuspension of road dust caused by air movement, which has maximal velocity around noon (Escudero et al., 2007).

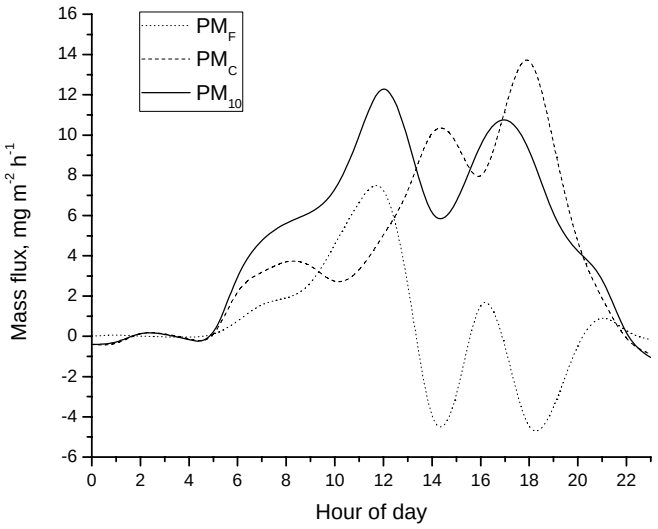

Figure 2. Averaged diurnal cycle of the PM_{10} mass flux and its fine (d_p<2.5 μm) and coarse (2.5 μm <d_p<10 μm) components.

At 16:00 the PM_F mass flux becomes positive again, probably due to the afternoon traffic activity (see Fig. 1). After that the PM_F mass flux suddenly decreases, with a simultaneous increase of PM_C mass flux. Their sum, the PM_{10} mass flux also increases during this period. In contrast with the situation at noon, the PM_C has determinative contribution to the PM_{10} mass flux during this period. The simultaneous decrease of PM_F mass flux and increase of PM_C mass flux indicates that these two processes may be

dependent during this period. This dependence can be explained by the conversion of PM_F aerosol mass to PM_C via particle growth. Condensation of volatile, semi-volatile compounds to the surface of pre-existing fine aerosol, as well as their hygroscopic growth increase the particle diameter, and may convert them to the coarse mass fraction. The atmospheric conditions favor for these processes, namely the temperature decreases and the relative humidity increases during this period. Considering that the vehicle emission likely occurs in the fine fraction, rapid exchange must be assumed between the fine and coarse fractions.

3.3 Ozone

Figure 3 presents the two components of ozone flux related to entrainment and non-entrainment processes. The non-entrainment processes include chemistry, advection, deposition, etc. Since chemical reactions dominate the non-entrained ozone fluxes, it will be referred as "chemistry" in the following. The resultant ozone flux is presented in the figure as well. For the calculation of the entrainment 100 μg m^{-3} ozone mixing ratio was assumed in the residual layer, a value taken from aircraft based measurement performed in the morning residual layer over Budapest during summer 2008 (Alföldy et al., 2009).

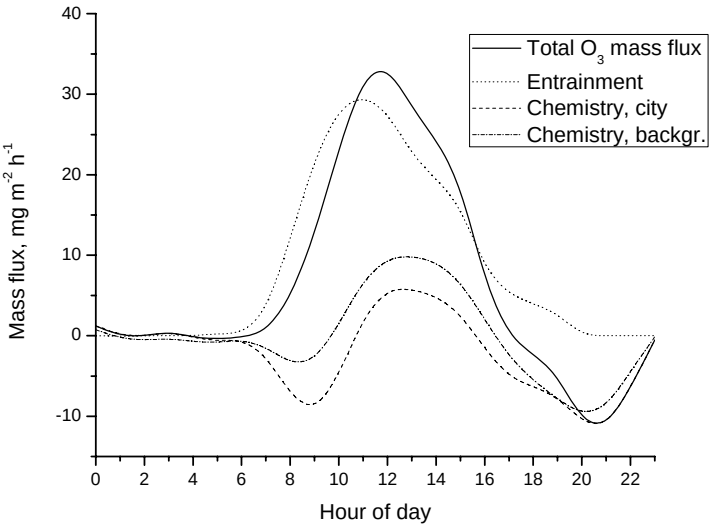

Figure 3. Averaged diurnal cycles of the O_3 mass flux and its entrained and chemically produced (lost) components. Chemical flux regarding a background environment is presented as well.

Between 5:00 and 10:00 significant negative chemical flux can be observed in the figure as a consequence of titration by the freshly emitted NO from traffic sources. After 10:00 the chemical flux becomes positive, and with the contribution of the entrained ozone results a maximum of the resultant ozone flux at 12:00. In the afternoon the chemical flux changes sign again at 17:00, and one hour later exceeds the entrainment resulting negative total flux.

Despite of the chemical flux peak at 12:00, the chemical balance is negative over the entire day. It means that chemistry (including production and degradation, as well as deposition) is a net ozone consumer in a polluted air.
Same analysis was made on background ozone concentration measured at K-puszta, a meteorological background station at the Hungarian Great Plane. Assuming same residual layer ozone level than over Budapest, same values were obtained for the entrainment. The chemical flux is significantly higher as the dash-dot curve indicates in Fig. 3. The higher net chemical influx results higher maximal ozone concentration. Our results support the supposition that entrainment dominates the surface ozone level in polluted air (Kim et al., 2007).

4. Conclusions

In this work Budapest's air pollution was analyzed based on the time variation of columnar mass that was calculated as the product of the concentrations and the mixing height. Pollution concentrations were measured by the metropolitan air quality monitoring network, while mixing height was calculated by the meteorological AERMET model code. Since the time variation of CM describes the real mass transport of the pollution, variation the pollution level can be directly studied.
The main conclusions are the following:
1) The diurnal urban CO cycle is determined by two main flux peaks according to the morning end evening traffic rush hours. Between them, the emission is lower, and the advection results lower flux.
2) The diurnal urban PM_{10} cycle is determined by three emission events. The first event is the direct emission of the traffic that respects the fine and coarse aerosol fractions. The second event is an intensive fine aerosol production around noon by secondary aerosol formation. The third event is the direct traffic emission during the evening rush hour. Rapid conversion of the fine aerosol emitted by vehicles to the coarse fraction must be assumed during this period.
3) The balance of photochemical production, chemical degradation and deposition of ozone obtained negative over the entire day, what means that the polluted urban atmosphere is a net ozone consumer. Consequently, entrainment has the dominant contribution to the formation of the diurnal ozone level in the city. Higher contribution of photochemical production was obtained at rural background area, due to lower level of ozone consuming air pollutants.

References

Alföldy B., Groma V., Börcsök E., Nagy A., Czitrovszky A., Török Sz., 2009. European Aerosol Conf., 2009, Karlsruhe, Abstract T200A03.

Balzani-Lööv J.M., Henne S., Legreid G., Staehelin J., Reimann S., Prevot ASH., Steinbacher M., Vollmer MK., 2008. J. Geophys. Res. 113, D22305, doi: 10.1029/2007JD009751.

Escudero M., Querol X., Avila A., Cuevas E., 2007. Atm. Env. 41, 730-744.

Kim SW., Yoon SC., Won JG., Choi SC., 2007. Atm. Env. 41, 7069-7081.