# Analysis of Ozone Data by Photochemical Pollution Indicators in Colorado

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*Abstract.* In order to assess the situation with air pollution by ozone in Colorado region during sunny part of the year (April to September), recently introduced photochemical pollution (PP) indicators have been applied on acquired ozone data, *i.e.* hourly ozone volume averages. PP indicators show very low values at the majority of stations except for the two located in Denver and Arvada which are located in the centre of the highly populated area covered by this assessment. Some other stations (*e.g.* National Renewable Energy Labs) have somewhat high number of excess times during the growth period; total daily turnover of ozone is, however, rather low indicating absence of other photochemical pollutants (*e.g.* NO$_x$) which, therefore, justify low values of PP indicators. Generally, our assessment method shows very low PP in the assessed area which is central, most populated part of the state of Colorado. (doi: 10.5562/cca2357)

*Keywords:* photochemical pollution, pollution indicators, ozone, ozone precursors, growth season

## INTRODUCTION

Various photochemical oxidants in the lower troposphere, which are considered to be part of photochemical smog, are widely recognised as dangerous to both plants and animals (including humans).[1,2] That is especially true for the most polluted areas in the world such as, for example, Pearl River Delta in China.[3,4] As one of the most dangerous oxidants in atmosphere, ozone is one of the major tropospheric pollutants and an important component of the photochemical smog. It should not, however, be omitted its important role as a protector of the life on Earth as part of the stratospheric ozone layer. Major sources of the elevated ozone concentration in the troposphere are of anthropogenic origin. Whether as a result of a natural background generation of precursors (*e.g.* terpenes), direct generation by wildfires or lightnings or as a result of human activities which produce higher quantities of ozone precursors, production of ozone is connected with several cycles. In those cycles, major ozone precursors, such as NO$_x$ (NO, NO$_2$), CO and various VOCs (volatile organic compounds), participate. Since overall pollution is essentially not reduced enough, it can be concluded that the level of ozone in the boundary layer of the atmosphere is going to rise.[5,6] Ozone monitoring is therefore imperative at least in the foreseeable future and, since it can be easily measured, various ozone–concentration–based indicators are already proposed.[7] Photochemical pollution indicators based on the ratio of maximum and minimum daily value of hourly ozone volume fractions have already shown its potential to become good measure for the photochemical pollution.[8,9] Those proposed indicators, that have shown good predictive power in the case of central European, Mediterranean (Italy, Slovenia, Croatia) and at the UK sets of stations, will be questioned and discussed here. For good comparison, it was decided that the same year range will be used as in the case of California.[10] California is well known as one of the most problematic regions in the USA concerning ozone pollution. However, it has been shown that, following the rapid urbanisation and increased carbon fuel consumption, ozone is becoming major problem in the eastern parts of Rocky Mountains area as well,[11] although exceedance in ozone levels is still considered highly related to natural causes, *e.g.* wildfires.[12] According to the most recent analyses, oil and natural gas operations in Colorado represent high new source of volatile organic compounds which, in the end, causes elevated ozone values in the area.[13]

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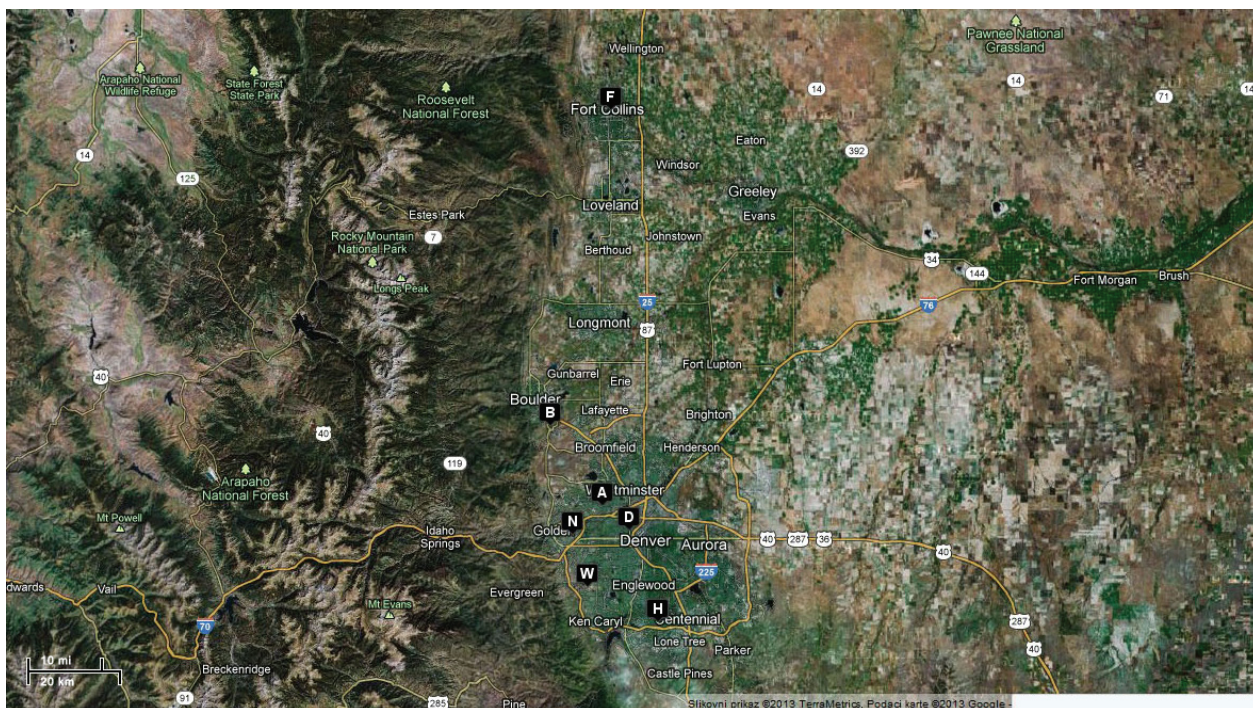
**Figure 1.** Map of Colorado showing the locations of the monitoring sites. The names of the stations, abbreviations and their geographical coordinates are given in Table 1.

## METHODS

All of the used data were obtained from the US Environmental Protection Agency (http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm). In Table 1 are given the locations of monitoring sites used in this paper. Locations are, also, shown on Figure 1. US EPA gives volume fractions in ppm, which are, for the sake of this analysis, all converted to ppb.

The calculation used in this article for the data analysis has been already described.[8–10] It was, originally developed by analysing ten years of ozone data from European EMEP stations, but has proven applicable for other stations, too. Indicators that we used can be defined as:

$$P_1 = RM/A \tag{1}$$

$$P_2 = R(1+168 t_{exc}/N) \tag{2}$$

$$P_3 = \sqrt{P_1 \cdot P_2} \tag{3}$$

where $R$ is the average of daily maximum-to-minimum ratios, $M$ is the seasonal average of daily maximum values, $A$ is the average of all seasonal data, $t_{exc}$ is the duration in hours the limit of 80 ppb was exceeded ("excess time") and $N$ is the total number of hourly averages of ozone volume fractions measured over some period of time. The 168 factor in $P_2$ arises from

**Table 1.** Geographical coordinates of monitoring sites

| Monitoring station | Station abbrev. | N Latitude | W Longitude | Altitude/ m |
|---|---|---|---|---|
| Denver | D | 39.751761° | 105.030681° | 1621 |
| Boulder | B | 39.957212° | 105.238458° | 1669 |
| Highland Reservoir | H | 39.567887° | 104.957193° | 1747 |
| Arvada | A | 39.800333° | 105.099973° | 1640 |
| Welch | W | 39.638781° | 105.139480° | 1742 |
| Natl. Renew. Energy Labs | N | 39.743724° | 105.177989° | 1832 |
| Fort Collins CSU | F | 40.577470° | 105.078920° | 1524 |

the arbitrary 1 hour/week average excess time that, if present, would double the $R$ value.

All indicators are based on daily maximum-to-minimum ratios. The minimum value is set to 0.8 if recorded as zero in accordance with the detection limit of the instruments in order to avoid division with zero which would be mathematically impossible. It is very important to see that indicators and $R$ tend to have very high values in cases of near-zero values of minimum, therefore PPI (photochemical pollution indicators) have to be applied with care. It is, however, correct for indi-

cators to show high values in cases where all ozone has been spent since that occur in the presence of various pollutant species in the atmosphere (*e.g.* $NO_x$). Connection between high PPI values with low minima can be seen from frequency distribution which is also shown in this article.

Although these indicators have been developed in order to adjust simple maximum-to-minimum ratio of daily hourly volume fractions of ozone as a measure for a photochemical pollution, they are still very dependent on the *R*-value. *R*-value indirectly reflects the daily ozone turnover. Our indicators may also be a good measure for different effects which may occur on either organisms or materials.

**RESULTS AND DISCUSSION**

The results for all stations are shown in Table 2. Data in the table include (in the order of the columns) location, name of the station followed by corresponding average values of the ozone volume fraction ($A$/ppb), average of daily maximum-to-minimum ratios ($R$), average of daily maxima ($M$/ppb), average excess time during which the 80 ppb limit was exceeded ($t_{exc}$/h) and averages of indicators $P_1$, $P_2$ and $P_3$. The last column gives the total number of recorded and validated hourly average ozone volume fractions. Calculations were made for the period from April to September. For every station 6-year periods from 2000 to 2005 has been covered.

In the case of Colorado stations, it cannot be concluded whether basic indicators $P_1$ or $P_2$ contribute to the combined indicator of $P_3$ differently, as in the case of California where the influence of $P_2$ is higher,[10] or the same as in the moderate climate region.[8] In this case with mountain climate, for the majority of stations this difference is negligible, while in the case of two stations – Highland Reservoir and National Renewable Energy Labs – contribution of $P_2$ to the $P_3$ is much higher. However, those two stations also have the highest number of exceedances over the 80 ppb threshold which is the main contributor to the $P_2$ indicator.

As can be seen from the data for the $P_3$ indicator, the majority of these stations are much less photochemically polluted than the stations in California. For the 5 stations value of $P_3$ is lower than 40. In fact many stations have the $P_3$ indicator value less than 20. Only centrally positioned (in the middle of the most densely populated area of the state of Colorado) stations of Denver and Arvada have high $P_3$ values of slightly over 100. Those two stations may be certainly proclaimed as polluted and one may also conclude that ranges established for the moderate climate region are more appropriate here than those applied in California. Stations in California, which is also known as the very photochemically polluted area, have much higher $P_3$ values comparable to those in the Pearl River Delta (maximum $P_3$ value there was 277), while these stations show in almost every case very low pollution. For further comparison, $P_3$ values for three Louisiana stations (8-year averages) were from 57 to 71.[4]

Somewhat higher average number of exceedances can be attributed to the situation in the year 2003 when all stations have many exceedances. Other results show low number of excess times at all stations even if we compare this number with those for Louisiana stations not to mention California. It is, however, still noticeable that two stations with the highest value of $t_{exc}$ still have low value of $P_3$ (17.6 at Higland Reservoir and 12.3 at National Renewable Energy Labs). Those two stations have small difference between daily maximum and minimum fraction. Possible reason for that is a transfer of ozone from the nearby heavily polluted areas (Denver, Arvada) and lack of destruction of ozone in this area.

Generally, it should be noted that all exceedances at all sites in the covered period are observed during summer season (*i.e.* April–to–September). Monthly averages and averages of daily maxima of ozone concentrations for all stations are all significantly higher (up to double) for April–to–September period than for the October–to–March. This is consistent also with the already observed[10] significant shift in the period of year with high yield of ozone; after 100 % here, April–to–September period covers over 95 % of high ozone

**Table 2.** Seasonal (April-to-September) values of various parameters and PP-indicators for 7 monitoring sites in Colorado

| Station | $A$ / ppb | $R$ | $M$ / ppb | $t_{exc}$ / h | $P_1$ | $P_2$ | $P_3$ | $N$ |
|---|---|---|---|---|---|---|---|---|
| Denver | 27.9 | 48.0 | 58 | 31 | 100.4 | 109.1 | 102.7 | 25242 |
| Boulder | 37.6 | 4.5 | 58 | 31 | 6.9 | 10.0 | 8.1 | 25792 |
| Highland Reservoir | 40.5 | 8.6 | 62 | 47 | 13.2 | 24.1 | 17.6 | 25311 |
| Arvada | 28.4 | 45.5 | 58 | 37 | 92.7 | 111.7 | 100.3 | 25883 |
| Welch | 32.2 | 10.0 | 51 | 11 | 15.9 | 14.1 | 14.8 | 25738 |
| Natl. Renewable Energy Labs | 42.4 | 5.2 | 63 | 75 | 7.6 | 20.3 | 12.3 | 25810 |
| Fort Collins CSU | 30.9 | 21.0 | 55 | 19 | 38.3 | 36.3 | 37.0 | 24602 |
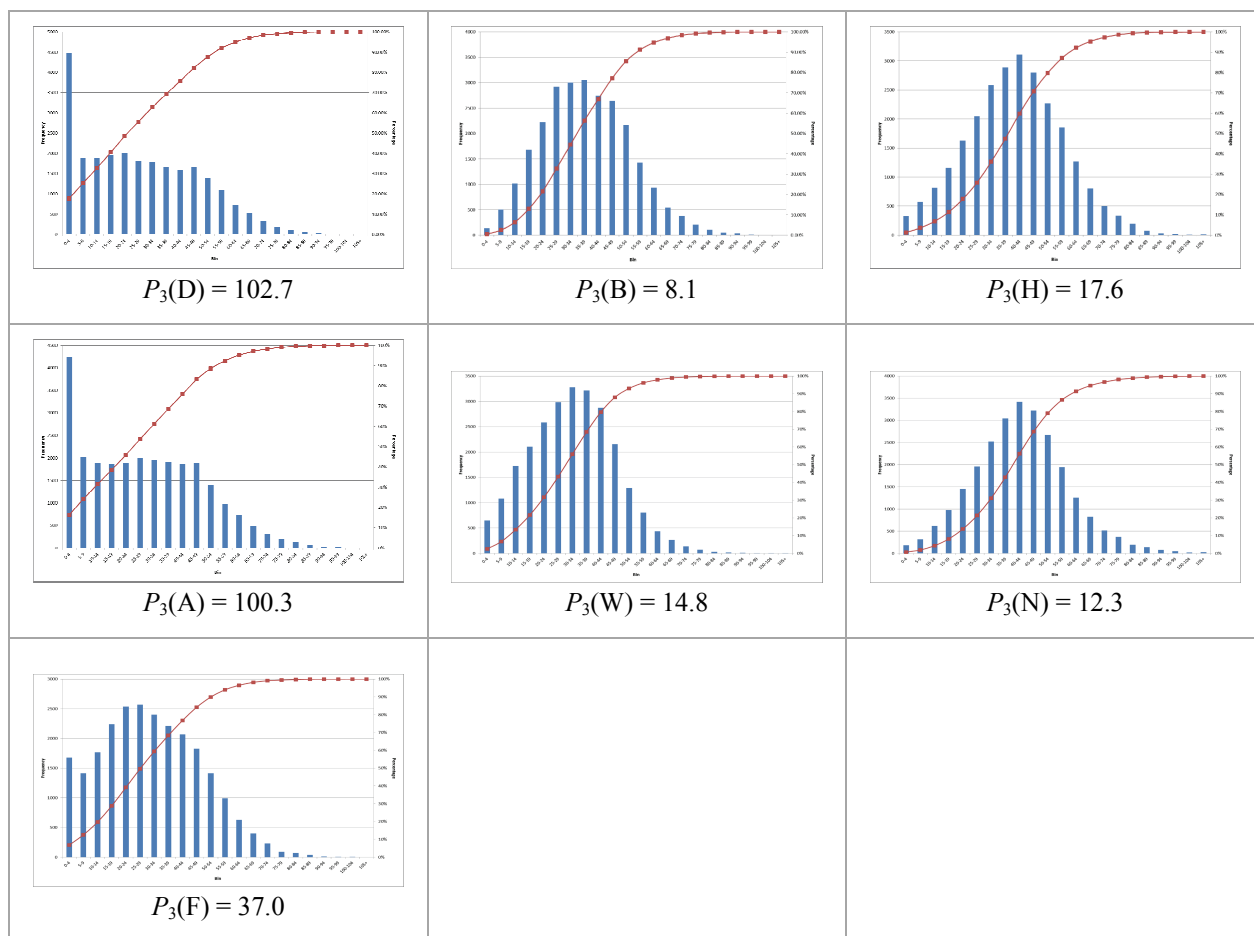
**Figure 2.** Histogram representations of frequency distributions of ambient ozone fractions (in 5 ppb intervals). Station abbreviations are shown in Table 1.

events in Europe, 91 % in Louisiana and in the most abundant June-November period only 84 % of the events in Pearl River Delta.[4] Since low values of average ozone hourly data critically affect the $R$-value and finally PP assessment, comparison of the shape of the ozone data frequency distribution with the $P_3$ for Colorado stations was also taken into account.

As it can be seen form the Figure 2., sites with low values of a $P_3$ indicator have quasi-normal distribution of hourly ozone volume fractions averages, while those with higher values of $P_3$, especially Denver and Arvada, have higher frequency of the very low ozone volume fractions which, logically, highly influences their $P_3$ values. On the example of the Fort Collins station transformation from one to another distribution can easily be observed. If cumulative probability distribution is compared with $P_3$ values, it can be seen that its shape transfers from sigmoidal to non-sigmoidal with the growth of $P_3$. It can, therefore, be concluded that there is a strong correlation between the value of $P_3$ and the shape of ozone data distribution.

Finally, a global applicability of the PPI can be discussed as they were already used for the assessment

of ozone values at different sites in the world.[4,8–10] Although applied on the very diverse sets of data (*e.g.* sets of data from the areas with different climate, from subtropic highly polluted areas of China, over Mediterranean area and lowlands of Great Britain to the mountains and high plateaus of Colorado), simple PPIs such as $P_1$, $P_2$ and, the most importantly, $P_3$ prove to be a good measurement for the assessment of a photochemical pollution. Low values are connected to the low PP, while high values have a direct connection with higher PP. Profiles of the distribution of the hourly ozone volume averages are also directly connected with the PPIs. The major problem about PPIs may be a nonlinear relation between their high and low values. Much higher values (for example, for a ten or a hundred times) do not mean that the pollution is higher for the same level. That is making difficult, at least for now, to give a correct range of PPIs for a polluted or non-polluted sites at the global scale (please compare references 8 and 10). It is, however, something that can be expected since the indicators are based on the average of daily maximum-to-minimum ratios of ozone hourly concentrations (volume fractions) which

probably has no physical meaning. Another potentially important relation of PPIs with the slope of ozone turnovers will be investigated in the future for all sites.

## CONCLUSION

The assessment of photochemical pollution on the stations in the state of Colorado during the growth season from April–to–September using photochemical pollution indicators based on hourly ozone volume fraction averages during the years 2000 to 2005 shows that those sites are generally far less polluted than any other previously assessed using this method. Except for two stations positioned in the densely populated areas, all other stations can be pronounced fairly clean. During another half of the year there are absolutely no photochemical pollution problems in this area which also can be seen from the fact that not a single exceedance of the 80 ppb threshold was observed during that part of the year. In all the other assessed areas which we covered in our previous papers[9,10] at least few percent of the exceedance occurred during non-growth period. It was shown that the indicators reflect the distribution of hourly average ozone volume fractions very well. High indicator values are associated with a significantly higher frequency of low hourly ozone volume data values.

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