PM$_{2.5}$ AND OZONE CO-CONTROL

DEVELOPED BY PROF. HAJIME AKIMOTO
APCAP SCIENCE PANEL VICE CHAIR
NATIONAL INSTITUTE FOR ENVIRONMENTAL STUDIES, JAPAN
This policy brief aims to justify the need for co-control of PM$_{2.5}$ (fine particles with a diameter of less than 2.5 um) and photochemical oxidant represented by ozone (O$_3$). In recent years, scientists have determined that PM$_{2.5}$ and O$_3$ have the largest impact on human health in urban and suburban areas in most parts of Asia and that those pollutants should be the main targets for controlling air pollution in most countries on the continent. Issues related to PM$_{2.5}$ and O$_3$ traditionally have been treated as separate air pollution problems. However, considering the relationship between them, it would be practical to co-control them by, for example, applying a multi-pollutant, multi-effect approach.

Ozone pollution is highest in the spring and summer when ultraviolet (UV) radiation is the strongest and the temperature is the highest in the mid-latitude, but it can be lowest in the sub-tropics because the summer monsoon brings rain and clean oceanic air. Meanwhile, the highest PM concentration tends to be in the winter months because of greater consumption of fossil fuels for heating and the adverse meteorological conditions.

However, as emission control for primary fine particles and sulfur dioxide (SO$_2$) from fossil fuel combustion takes effect, seasonal concentration of PM$_{2.5}$ tends to shift from winter to spring to summer, similar to O$_3$, and the major component of PM$_{2.5}$ shifts to secondary aerosols, which are produced during photochemical reactions of precursors. O$_3$, meanwhile, itself acts as an active species to become PM$_{2.5}$ by reacting with anthropogenic and biogenic hydrocarbons.

The first step in the effort to co-control PM$_{2.5}$ and ozone should be to reduce SO$_2$ and nitrogen oxides (NO$_x$) emissions from fossil fuel combustion simultaneously. This can decrease PM$_{2.5}$ by decreasing the formation of sulfate (SO$_{4}^{2-}$) and nitrate (NO$_3$) and also reduce O$_3$, and NO$_x$ is a precursor of O$_3$. Next, NO$_x$ and VOC (volatile organic compounds) should be reduced simultaneously, which can further reduce O$_3$ and PM$_{2.5}$.

To pave the way forward towards setting a co-control policy of PM$_{2.5}$ and O$_3$, the scientific community needs to develop proper chemistry-transport models. Some recommended steps for doing this are the following:

(a) Model simulation for effective NO$_x$ and VOC control for O$_3$ reduction;
(b) Control of primary PM$_{2.5}$ emissions;
(c) Control of SO$_2$ and NH$_3$ emissions for the reduction of secondary PM$_{2.5}$; and
(d) Control of NO$_x$ and VOC for reduction of secondary PM$_{2.5}$. 


INTRODUCTION

Historically, sulfur dioxide (SO$_2$), carbon monoxide (CO), coal ash and mechanical dust have been viewed as “primary air pollutants, especially during the industrialization age. Those species are released directly from anthropogenic sources and can severely affect human health and the environment, prompting national and local governments to control them.

After the pollution caused by those species was controlled to some extent, many countries then began to observe haze pollution typified by PM$_{2.5}$ (fine particles with a diameter of less than 2.5 um) and photochemical oxidant represented by ozone (O$_3$). In recent years, scientists have determined that PM$_{2.5}$ and O$_3$ have the largest impact on human health in urban and suburban areas in most parts of Asia.

A recent review on the status of PM$_{2.5}$ and O$_3$ pollution in East Asia (Acid Deposition Monitoring Network in East Asia (EANET), Scientific Advisory Committee (SAC) and Acid Deposition Monitoring Network in East Asia (EANET) 2015) reveals that their concentrations far exceeds the World Health Organization (WHO) air quality guidelines of 100 mg/m$^3$ 8-hr mean for O$_3$, and 10mg/m$^3$ annual mean and 25 mg/m 8-hr mean for PM$_{2.5}$ (World Health Organization (WHO) 2005), while Silva et al (2013) indicate a global annual premature human mortality of 0.47 (95 percent confidence interval, 0.14-0.90) million and 2.1 (1.3-3.0) million can be caused by anthropogenic O$_3$ and PM$_{2.5}$, respectively (Figure 1).

Other studies have indicated a similar range of results (Anenberg et al. 2010; Fann et al. 2012; Weichenthal et al. 2013; WHO 2014). Based on this information, PM$_{2.5}$ and ozone should be the main target for air pollution control in most countries in Asia.

Some PM$_{2.5}$ is directly emitted, but most of it and all O$_3$ are formed in the atmosphere through complex chemical reactions, referred to as “secondary air pollutants.” Control of secondary air pollutants is much more difficult compared to primary air pollutants because they are formed when other pollutants (primary air pollutants and other precursors) react in the atmosphere. For example, the relative contribution of nitrogen oxides (NO$_x$) and volatile organic compounds (VOCs) to O$_3$ formation varies under different concentration ranges and specific meteorological and topographical conditions (Finlayson-Pits and Pitts 2000, pp.882-886; Akimoto 2016, pp.319-325). The contribution to PM$_{2.5}$ formation by SO$_2$, NO$_x$ and VOC are also dependent on their relative emission ratio.

Meanwhile, the level of primary air pollutants in the atmosphere is generally proportional to the emission strength, assuming similar meteorological conditions. This implies that pollution control policy can be more targeted, as reducing emission sources of primary pollutants is expected to result directly in improved ambient concentration.
Figure 1: Current premature mortality caused by anthropogenic air pollution, in deaths per year - 1000km

As $O_3$ is formed from chemical reactions between oxides of nitrogen ($NO_x$) and VOC under sunlight, the highest ozone pollution occurs in spring and summer when UV radiation is the strongest and the temperature is the highest in the mid-latitude. However, $O_3$ during the summer months can be low in the sub-tropics in Asia because the summer monsoon brings rain and clean oceanic air. Meanwhile, the highest $PM_{2.5}$ concentrations are often observed in the winter months because of greater consumption of fossil fuels for heating and adverse meteorological conditions.

However, as emission control measures for primary fine particles and $SO_2$ from fossil fuel combustion take effect, seasonal concentration of $PM_{2.5}$ tends to shift from winter to spring to summer similar to $O_3$, as observed in many developed countries. At this stage, the major component of $PM_{2.5}$ shifts to secondary aerosols, which are produced during photochemical reactions of precursors, such as $SO_2$, VOCs, and $NO_x$. Chemical processes that produce secondary $PM_{2.5}$ are similar to photochemical air pollution.
Meanwhile, ozone itself acts as an active species to form PM$_{2.5}$ by reacting with anthropogenic and biogenic hydrocarbons (a schematic diagram showing the simultaneous formation of secondary PM$_{2.5}$ and O$_3$ is illustrated in Figure 2).

Considering this relationship, it makes sense to apply a co-control approach for PM$_{2.5}$ and ozone, similar to the successful multi-pollutant control policy applied in the European Union (Box 1).

**Figure 2**: Schematic diagram of formation of O$_3$ and secondary PM$_{2.5}$ from NO$_x$, VOCs and SO$_2$ emitted from various sources

**Box 1**: Multi-pollutant, multi-effect approach

In the European Union, a so-called **multi-pollutants, multi-effect control policy**, which was set in the 1990s (European Environment Agency (EEA) 1997), has become a well-established approach for co-controlling pollutants. The air pollution in Europe over the last few decades originated from acid deposition and then came from photochemical ozone and PM$_{2.5}$. To mitigate air pollution, the European Environmental Agency (EEA) opted to focus comprehensively on the pollutants instead of individuals, as the pollutants had many common precursors, as seen above. The multi-pollutant, multi-effect control policy in now being applied to combat climate change and for CO$_2$ control together with other traditional air pollutants (Amann 2010).
To effectively co-control PM$_{2.5}$ and O$_3$, the first step should be to reduce SO$_2$ and NOx emissions from the fossil fuel combustion, simultaneously, followed by the reduction of NOx and VOC simultaneously.

The first step of the SO$_2$ and NOx co-control can reduce PM$_{2.5}$ by decreasing the formation of sulfate (SO$_4^{2-}$) and nitrate (NO$_3^-$). It can also reduce O$_3$, as NOx is a precursor of O$_3$. The application of simultaneous emission control of SO$_2$ and NOx in the United States provides a good example, as mentioned in Box 2.

The second step entails the simultaneous reduction of NOx and VOC, which, in turn, can further reduce O$_3$ and PM$_{2.5}$.

Specifically, because it is well established that NOx and VOCs are precursors of O$_3$, the co-control of them is known to decrease the production of O$_3$ in the atmosphere (Finlayson-Pits and Pitts 2000, pp.882-886; Akimoto 2016, pp. 319-325).

While for PM$_{2.5}$, there is a substantial amount of secondary organic aerosols (SOA) formed from VOC (Jimenez et al 2009). Accordingly, the co-control of NOx and VOC can reduce PM$_{2.5}$ by decreasing the formation of NOx and SOA.

However, the reaction scheme for the O$_3$ and SOA formation from NOx and VOC is rather complex as illustrated in Figure 3, and numerical model simulation is generally required to control NOx and VOC most effectively.

**Box 2: Simultaneous emission control of SO$_2$ and NOx in the United States**

According to the US Acid Rain Program (Title IV of the 1990 Clean Air Act Amendment), emissions of SO$_2$ and NOx from power plants in the United States have fallen. Estimates indicate that from 1990 to 2010, annual emissions of SO$_2$ and NOx from power generation declined 40 and 25 percent, respectively, resulting in a substantial reduction of PM$_{2.5}$ and O$_3$ concentrations throughout the country. This, in turn, has resulted in significant benefits in terms of human health, as can be seen by a reduction in PM$_{2.5}$ and O$_3$ mortality and morbidity (Chestnut and Mills 2005).
Future milestones of co-control policy of PM$_{2.5}$ and O$_3$

As the discussion of simultaneous reduction of PM$_{2.5}$ and O$_3$ is relatively new, there is still limited understanding of the effects of NO$_x$ and VOC control on the formation of SOA. To pave the way towards a co-control policy of PM$_{2.5}$ and O$_3$, the scientific community needs to develop proper chemistry-transport models to help inform policy development. Recommended steps for the co-control of PM$_{2.5}$ and O$_3$ and model development are presented below:

1. Model simulation for effective NO$_x$ and VOC control for O$_3$ reduction

Even though the chemistry-transport models consisting mainly of gas-phase homogeneous reactions to predict O$_3$ formation are well developed, some essential points still need to be clarified before a reliable recommendation for future control policy of NOx and VOC can be given. Most state-of-the-art models have been validated for observed O$_3$ by demonstrating agreement of model simulation results with observed levels within certain acceptable uncertainty. However, calculated concentrations of NOx and VOC have rarely been verified with observed data. Lack of observed data is a crucial limitation of model simulation studies when they are applied to effects of projected emissions. This is because reliability of them cannot be assured when the present concentrations of NOx and VOC by baseline emissions are not reproduced well. In that context, continuous monitoring data of individual species of VOC is required. Consequently, policymakers should consider supporting that type of monitoring programme.
2. Control of primary PM$_{2.5}$ emissions

It is important to quantify the proportion of primary versus secondary aerosols in a certain area in order to establish an efficient control policy of PM$_{2.5}$. Controlling primary aerosols (emitted directly from a source) are easier than controlling secondary aerosols and can guarantee an improvement in air quality to a certain extent (depending on its contribution to total PM$_{2.5}$).

3. Control of SO$_2$ and NH$_3$ emissions for the reduction of secondary PM$_{2.5}$

Sulfate (SO$_4^{2-}$) and ammonium (NH$_4^+$) ions are major species of secondary PM$_{2.5}$. Accordingly, emission control of their precursors (SO$_2$ and NH$_3$) is essential, and should be prioritized for SOA control. However, it should be noted that the ratio of SO$_4^{2-}$ to SO$_2$ in the atmosphere changes depending on the concentrations of NO$_x$ and VOC. In contrast to SO$_2$, which is emitted from fossil fuel combustion, the major emission source of NH$_3$ is from agriculture, fertilizer, livestock and waste treatment. Although the control of emissions from agricultural sources may be more difficult than those from industrial sources, control of NH$_3$ is very important to reduce the mass concentration of secondary aerosols in PM$_{2.5}$.

4. Control of NO$_x$ and VOC for reduction of secondary PM$_{2.5}$

The control of NO$_x$ and VOC for O$_3$ reduction has been discussed extensively, as compared with only limited discussion on their role in the reduction of PM$_{2.5}$ in haze. It is clear that the reductions of NO$_x$ and VOC contribute to the mitigation of PM$_{2.5}$ pollution by reducing NO$_x$ and SOA, respectively. Although it is also clear that the reduction of O$_3$ by controlling the emissions of NO$_x$ and VOC reduces SOA and PM$_{2.5}$, the quantitative relationships between them are rather complex, and further model simulation is required. In that case, models to simulate PM$_{2.5}$ need be validated with observed data not only by the total mass concentration of PM$_{2.5}$, but also by several individual SOA components. In order to develop reliable models for PM$_{2.5}$ for policy development, scientific research on laboratory experiments, modelling and field observational studies of those aspects need to be mobilized in the next decade.

Table 1: Relevance of precursors to PM$_{2.5}$ and ozone formation in the atmosphere

<table>
<thead>
<tr>
<th>Targeted species</th>
<th>Precursor species</th>
<th>NO$_x$</th>
<th>VOCs</th>
<th>SO$_2$</th>
<th>NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>Yes</td>
<td>Low-volatility product forming VOCs</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Ozone</td>
<td>Yes</td>
<td>OH - reactive VOCs</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
</tbody>
</table>

Shows relevance of NO$_x$, VOCs, SO$_2$ and NH$_3$ as precursors for the formation of O$_3$ and PM$_{2.5}$. NO$_x$ and VOC are common precursors of O$_3$ and PM$_{2.5}$, and SO$_2$ and NH$_3$ are precursors of PM$_{2.5}$ only. It also shows that components of VOCs, to form O$_3$ and PM$_{2.5}$, are not necessarily the same type.
As a practical approach to co-control PM$_{2.5}$ and O$_3$, the simultaneous reduction of SO$_2$ and NO$_X$ emissions from fossil fuel combustions should be the first step, then followed by the reduction of NH$_3$ emissions. The reduction of NO$_X$ and VOC emissions with the objective to reduce O$_3$ can be incorporated in efforts to mitigate PM$_{2.5}$ mitigation with the aid of state-of–art model simulations.

04 REFERENCES