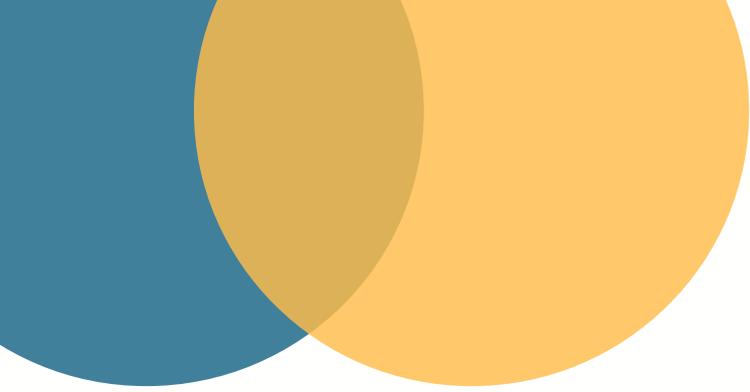




PM_{2.5} AND OZONE CO-CONTROL

DEVELOPED BY PROF. HAJIME AKIMOTO
APCAP SCIENCE PANEL VICE CHAIR
NATIONAL INSTITUTE FOR ENVIRONMENTAL
STUDIES, JAPAN



SUMMARY

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 μm) 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 $PM_{2.5}$.

01 INTRODUCTION

Historically, sulfur dioxide (SO₂), 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 µm) and photochemical oxidant represented by ozone (O₃). In recent years, scientists have determined that PM_{2.5} and O₃ have the largest impact on human health in urban and suburban areas in most parts of Asia.

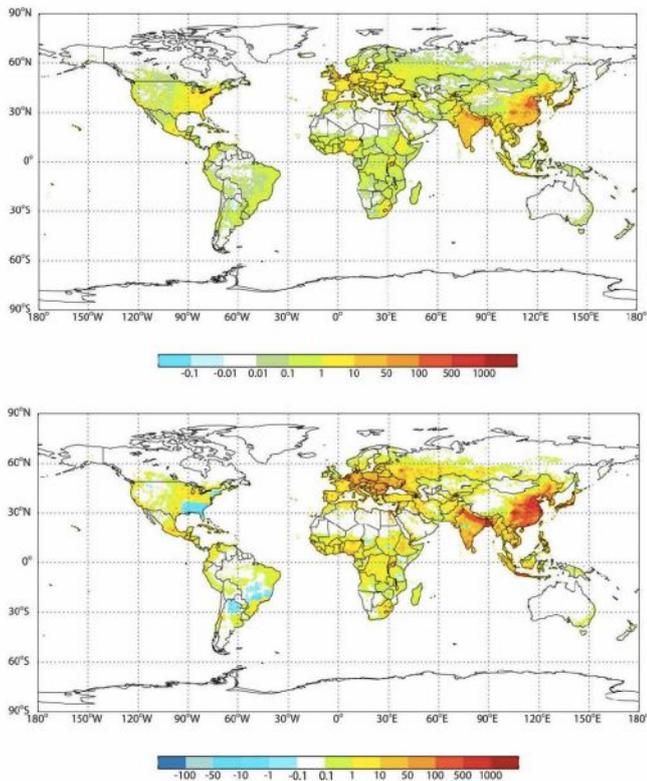
A recent review on the status of PM_{2.5} and O₃ pollution in East Asia (Acid Deposition Monitoring Network in East Asia (EANET), Scientific Advisory Committee (SAC) and Acid Deposition Monitoring Network in East Asia (EANET) 2015) reveals that their concentrations far exceeds the World Health Organization (WHO) air quality guidelines of 100 mg/m³ 8-hr mean for O₃, and 10mg/m³ annual mean and 25 mg/m³ 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 O₃ 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 O₃ 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 O₃ formation varies under different concentration ranges and specific meteorological and topographical conditions (Finlayson-Pitts and Pitts 2000, pp.882-886; Akimoto 2016, pp.319-325). The contribution to PM_{2.5} formation by SO₂, 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



Note: Multi-model mean for ozone (top) and PM_{2.5} (bottom)
Source: Silva et al. (2013).

In contrast, **to control secondary air pollutants effectively, a more careful and detailed analysis of precursor emissions is required based on sophisticated air quality models composed of chemistry and transport.** Such an approach is often referred to as “control strategy”.

Rationale for PM_{2.5} and O₃ co-control

Ozone and PM_{2.5} related-issues have traditionally been treated as separate air pollution problems. This is mainly based on the historical context: O₃ in

photochemical air pollution has, since 1950's been associated with “Los Angeles smog” (Finlayson-Pitts and Pitts 2000, pp.4-8), while in the 1990s, PM_{2.5} was seen to cause severe haze. Also, it should be noted that the concentrations of O₃ and PM_{2.5} do not necessarily correlate well temporally on a daily or seasonal basis.

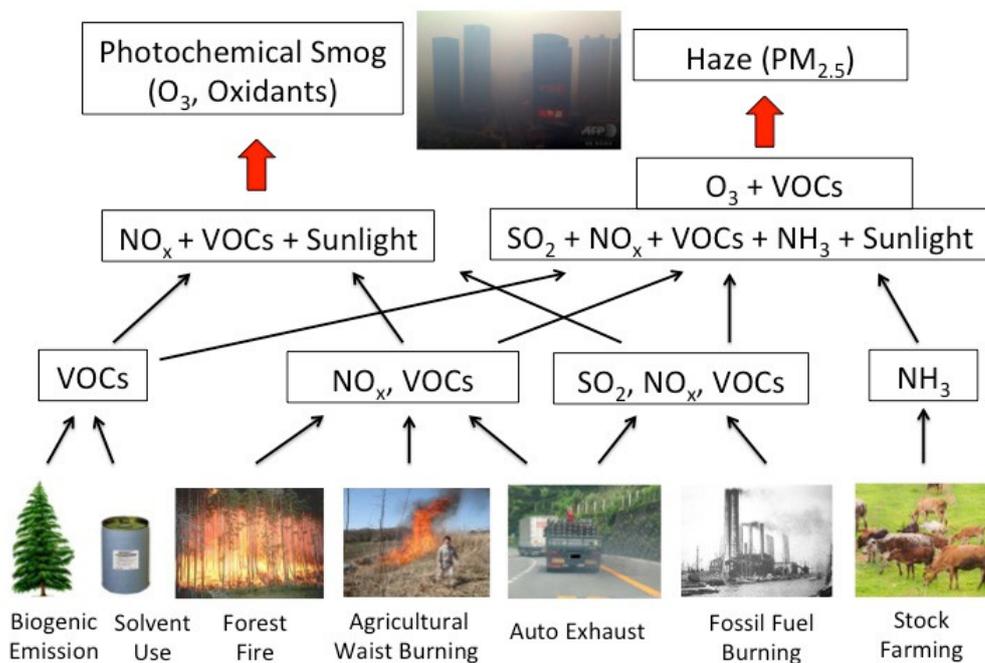
As O₃ is formed from chemical reactions between oxides of nitrogen (NO_x) and VOC under sunlight, the highest ozone pollution occurs in spring and summer when UV radiation is the strongest and the temperature is the highest in the mid-latitude. However, O₃ during the summer months can be low in the sub-tropics 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 SO₂ from fossil fuel combustion take effect, seasonal concentration of PM_{2.5} tends to shift from winter to spring to summer similar to O₃, 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 SO₂, 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 is now being applied to combat climate change and for CO_2 control together with other traditional air pollutants (Amann 2010).

02 GUIDING PRINCIPLES FOR CO-CONTROL OF PM_{2.5} AND O₃

To effectively co-control PM_{2.5} and O₃, the first step should be to reduce SO₂ and NO_x emissions from the fossil fuel combustion, simultaneously, followed by the reduction of NO_x and VOC simultaneously.

The first step of the SO₂ and NO co-control can reduce PM_{2.5} by decreasing the formation of sulfate (SO₄²⁻) and nitrate (NO₃⁻). It can also reduce O₃, as NO_x is a precursor of O₃. The application of simultaneous emission control of SO₂ and NO_x in the United States provides a good example, as mentioned in Box 2.

The second step entails the simultaneous reduction of NO_x and VOC, which, in turn, can further reduce O₃ and PM_{2.5}.

Specifically, because it is well established that NO_x and VOCs are precursors of O₃, the co-control of them is known to decrease the production of O₃ in the atmosphere (Finlayson-Pitts and Pitts 2000, pp.882-886; Akimoto 2016, pp. 319-325).

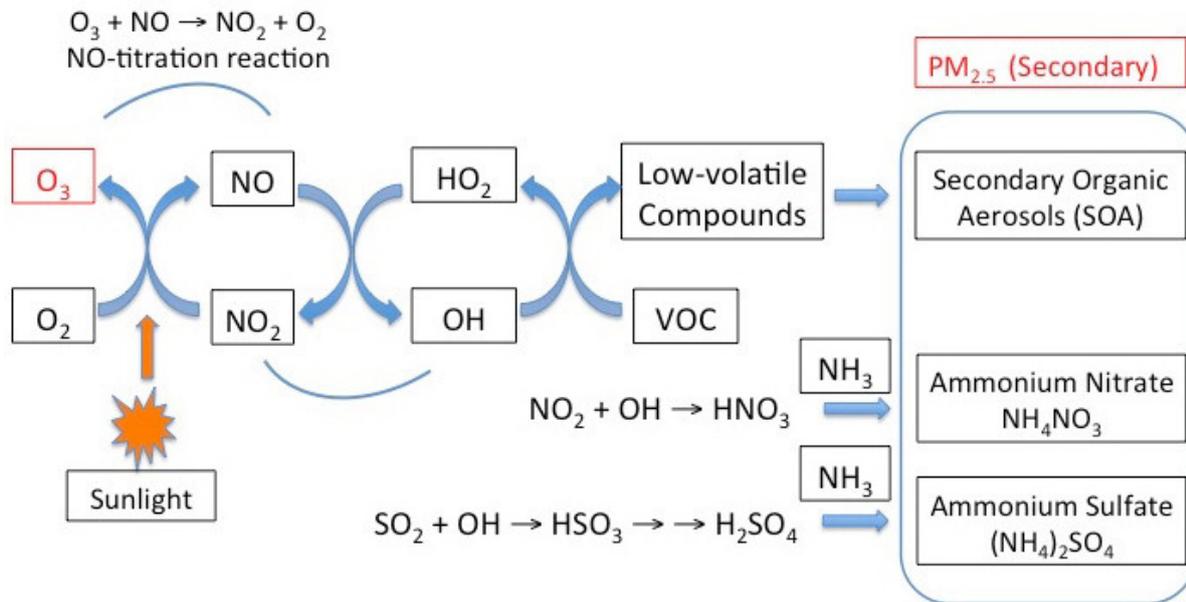
While for PM_{2.5}, there is a substantial amount of secondary organic aerosols (SOA) formed from VOC (Jimenez et al 2009). Accordingly, the co-control of NO_x and VOC can reduce PM_{2.5} by decreasing the formation of NO_x and SOA.

However, the reaction scheme for the O₃ and SOA formation from NO_x and VOC is rather complex as illustrated in Figure 3, and numerical model simulation is generally required to control NO_x and VOC most effectively.

Box 2: Simultaneous emission control of SO₂ and NO_x in the United States

According to the US Acid Rain Program (Title IV of the 1990 Clean Air Act Amendment), emissions of SO₂ and NO_x from power plants in the United States have fallen. Estimates indicate that from 1990 to 2010, annual emissions of SO₂ and NO_x from power generation declined 40 and 25 percent, respectively, resulting in a substantial reduction of PM_{2.5} and O₃ 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 O₃ mortality and morbidity (Chestnut and Mills 2005).

Figure 3: Schematic reaction system linking O₃ and secondary PM_{2.5} formation from NO_x, VOC, SO₂ and NH₃



Future milestones of co-control policy of PM_{2.5} and O₃

As the discussion of simultaneous reduction of PM_{2.5} and O₃ 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 O₃, 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 O₃ and model development are presented below:

1. Model simulation for effective NO_x and VOC control for O₃ reduction

Even though the chemistry-transport models consisting mainly of gas-phase homogeneous reactions to predict O₃ formation are well developed, some

essential points still need to be clarified before a reliable recommendation for future control policy of NO_x and VOC can be given. Most state-of-the-art models have been validated for observed O₃ by demonstrating agreement of model simulation results with observed levels within certain acceptable uncertainty. However, calculated concentrations of NO_x 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 NO_x 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 SO₂ and NH₃ emissions for the reduction of secondary PM_{2.5}

Sulfate (SO₄²⁻) and ammonium (NH₄⁺) ions are major species of secondary PM_{2.5}. Accordingly, emission control of their precursors (SO₂ and NH₃) is essential, and should be prioritized for SOA control. However, it should be noted that the ratio of SO₄²⁻ to SO₂ in the atmosphere changes depending on the concentrations of NO_x and VOC. In contrast to SO₂, which is emitted from fossil fuel combustion, the major emission source of NH₃ 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 NH₃ 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 O₃ 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 O₃ 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

Targeted species	Precursor species			
	NO _x	VOCs	SO ₂	NH ₃
PM _{2.5}	Yes	Low-volatility product forming VOCs	Yes	Yes
Ozone	Yes	OH - reactive VOCs	No	No

Shows relevance of NO_x, VOCs, SO₂ and NH₃ as precursors for the formation of O₃ and PM_{2.5}. NO_x and VOC are common precursors of O₃ and PM_{2.5}, and SO₂ and NH₃ are precursors of PM_{2.5} only. It also shows that components of VOCs, to form O₃ and PM_{2.5}, are not necessarily the same type.

03 CONCLUSION

As a practical approach to co-control PM_{2.5} and O₃, the simultaneous reduction of SO₂ and NO_x emissions from fossil fuel combustions should be the first step, then followed by the reduction of NH₃ emissions. The reduction of NO_x and VOC emissions with the objective to reduce O₃ can be incorporated in efforts to mitigate PM_{2.5} mitigation with the aid of state-of-art model simulations.



04 REFERENCES

- Akimoto, H. (2004). Atmospheric Reaction Chemistry. Tokyo: Springer Japan.
- Akimoto, H., Kurokawa, J., Sudo, K., Nagashima, T., Takemura, T., Klimont, Z., et al. (2015). SLCP co-control approach in East Asia: tropospheric ozone reduction strategy by simultaneous reduction of NO_x/NMVOC and methane. *Atmospheric Environment* 122, 588-595.
- Amann, M. (ed.). (2010), Greenhouse gases and air pollutants in the European Union, baseline projections up to 2030., EC4MAACS Interim Assessment.
- Anenberg, S.C.L., Horowitz, L.W., Tone, D.Q. Tong and West J.J. (2010). An estimate of the global burden of anthropogenic ozone and fine particulate matter on premature human mortality using atmospheric modeling. *Environmental Health Perspectives* 118(9), 1189-1195.
- Chestnut, L., and Mills, D.M. (2005). A fresh look at the benefits and costs of the US Acid Rain Program. *Journal of Environmental Management* 77, 252-266.
- EANET, SAD and TFRC (2015). Review on the state of air pollution in East Asia. February.
- EEA (1997). Air Pollution in Europe 1997. Executive summary. Copenhagen, EEA.
- Fann, N., Lamson, A.D., Anenberg, S.C., Wesson, K., Risley, D. and Hubbell, B. J. (2012) Estimating national public health burden associated with exposure to ambient PM_{2.5} and O₃. *Risk Analysis* 32(1): 81-95.
- Finlayson-Pitts, B.J. and Pitts, Jr., J.N. (2000). Chemistry of the Upper and Lower Atmosphere. Cambridge, MA: Academic Press.
- Jimenez, J.L., Canagaratna, M.R., Donahue, N.M., Prevot, A.S.H., Zhang, Q., Kroll, J.H. et al. (2009). Evolution of organic aerosols in the atmosphere. *Science* 326(5959): 1525-1529,
- Silva, R.A., West, J.J., Zhang, Y., Anenberg, S.C., Lamarque, J-F., Shindell, D.T. et al.(2013). Global premature mortality due to anthropogenic outdoor air pollution and the contribution of past climate change. *Environmental Research Letters* 8(3).
- Weichenthal, S.A., Pollitt, K.G., And Villeneuve, P.J. (2013). PM_{2.5}, oxidant defense and cardiorespiratory health: a review. *Environmental Health* 12(40).
- WHO (2005). WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide. Global updates. Summary of risk assessment. Geneva: WHO Press, Geneva.
- WHO (2014). 7 million premature deaths annually linked to air pollution. 25 March. <http://www.who.int/mediacentre/news/releases/2014/air-pollution/en/>, 2014.