Atmospheric pollutants in a changing environment: key issues in reactivity and monitoring, global warming, and health

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Atmospheric pollutants change our environment in a variety of ways. Specifically, airborne pollution is known to harm forests, crops, wildlife, aquatic ecosystems, and freshwater. In addition to damaging the natural environment, air pollution also affects buildings and the cultural material heritage such as outdoor sculptures and carvings.

Direct effects of atmospheric pollutants on local and regional air quality and therefore on human health are a major concern. The European Environment Agency (EEA 2013) reported that despite the significant decrease of emissions over the past decades, the levels of air pollutants still frequently exceed the thresholds set by the European Union Air Quality Directives. In many parts of Europe, the levels of sulfur dioxide (SO₂), nitrogen oxides (NO_x), ammonia (NH₃), and non-methane volatile organic compounds (NMVOCs) are becoming a public health risk issue. The same applies to particulate matter (PM) levels. The World Health Organization has recently reported that black carbon (BC) may not be a major toxic component of fine PM, but it may operate as a universal carrier of a wide variety of toxic chemicals to

different parts of the body (Janssen et al. 2012). High levels of pollutants, especially tropospheric ozone (O₃), adversely affect human health by causing respiratory problems and vegetation and ecosystem damage (EPA). Ozone is formed from the atmospheric degradation of NMVOCs, such as alkanes, alkenes, and oxygenated compounds (aldehydes and esters), in the presence of NO_x and sunlight. Ground-level ozone is also a potent greenhouse gas (GHG) that modifies the atmospheric radiative forcing and, thus, global temperatures. GHGs such as carbon dioxide (CO₂) and methane (CH₄) and, in a lesser extent, nitrous oxide (N₂O) and fluorinated compounds are behind pressing global environmental problems such as the warming of Earth's atmosphere. Another climate forcer of combustion-related air pollution is BC aerosols (commonly referred to as “soot”), which directly absorb both the incoming and reflected sunlight and the infrared radiation, increasing the surface air temperature.

This Special Issue (SI) of *Environmental Science and Pollution Research* addresses some of those problems, with special emphasis on tropospheric reactivity, gas monitoring, and the potential impacts of air pollution on climate and people and biota. Drawing from selected contributions to the 2013 *Energy and Environment Knowledge Week* (E2KW International Congress, Toledo, Spain), the SI gathers novel and timely research on how atmospheric pollutants modify our environment, also highlighting the many links between energy Research Development and Demonstration (RD&D) policies and GHG emissions.

Air quality: gaseous pollutants and nanoparticles

Unraveling the complex photochemical processes in the atmosphere is one of the key topics likely to bring new insight into the role of pollutants in the environment. For that reason, the knowledge of the atmospheric chemistry of emitted

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pollutants and the potential to form ground-level O_3 are of great importance in the evaluation of their effects on air quality and climate change. Pollutants homogeneously react with the main tropospheric oxidants, especially with highly reactive radical species such as OH and Cl. Therefore, it is not surprising that detailed analysis of free radical-molecule reaction kinetics and mechanisms of NMVOCs has been a subject of continuous interest in environmental studies. It is deemed that the chemical kinetic and mechanistic studies on potential high GWP HFC substitutes, like $CF_3CH=CH_2$ (HFO-1243zf) (González et al. 2015), on hydrocarbons emissions from vehicle exhaust, like cycloalkanes (Ballesteros et al. 2015), and on primary and secondary pollutants, like alkyl esters (Ifang et al. 2015), can help to understand the key interplay between human/natural activity and air pollution phenomena induced by photochemical processes and therefore drive further advance in the field. While reaction initiated by OH radicals is the main degradation pathway (González et al. 2015; Ballesteros et al. 2015), chlorine chemistry can be a competitive process at dawn in the marine/coastal boundary layer (Ballesteros et al. 2015; Ifang et al. 2015). The comprehensive degradation mechanisms proposed by Ballesteros et al. (2015) and Ifang et al. (2015) can be included in chemical transport models. The subtle details involved in the description of these photochemical processes illustrate the complex relationships emerging from the joint considerations of just a few species and a single process. Thus, the atmospheric fate of NMVOCs depends on their atmospheric lifetimes and the reaction degradation products, mainly oxygenates and ultimately ozone in high NO_x environments. Further degradation of secondary pollutants—ketones and aldehydes—initiated by sunlight can be an important removal pathway in the atmosphere (Ballesteros et al. 2015; Ifang et al. 2015). However, this route represents a negligible contribution to the elimination process for their atmospheric precursors, HFO-1243zf (González et al. 2015), for methylcyclohexanes (Ballesteros et al. 2015) and alkyl esters (Ifang et al. 2015). González et al. (2015) confirm that the potential of HFO-1243zf to form ground-level ozone is low enough to rule it out as a substantial contributor to photochemical smog.

A major challenge in tropospheric chemistry is to accurately model the important and complex chemistry in solid (heterogeneous chemistry) or liquid particles (multi-phase chemistry) (Ravishankara 1997). Fossil fuel and biomass combustion are the main sources of atmospheric aerosols. Particularly, BC nanoparticles formed in the incomplete combustion of hydrocarbons in diesel engines are of great interest nowadays because they present a wide range of geophysical and environmental problems, ranging from local issues (e.g., pollution toxicity) to the global scale (e.g., climate change). In some cases, its environmental impact is even greater than gaseous pollutants. Indeed, as the effects of black carbon have become better understood in recent years, it is increasingly

seen as an important target of environmental control. Therefore, laboratory kinetic measurements of uptake coefficients in such aerosols, as those presented in this SI for a diesel soot by Tapia et al. (2015), are extremely important.

Special attention is also drawn in this SI to the monitoring and dispersion modeling of atmospheric pollutants (Esbrí et al. 2015). This is a key issue for increasing our knowledge on the role of these gases on local and regional air quality. The dispersion model developed by Esbrí et al. (2015) is a very useful tool for assessing the risk of the mercury exposure to the local population close to a mercury cell chlor-alkali plant. The atmospheric Hg dispersion model demonstrates that the most Hg-polluted atmosphere in Spain is located around a mercury cell chlor-alkali plant close to the Ebro River basin. Currently, the Hg levels are above international thresholds for residential areas (Esbrí et al. 2015).

Another relevant aspect of air pollution is indoor air quality since indoor air is eventually mixed with outdoor air before passing through ventilation ducts (Da et al. 2015). Especially in food industries, experimental protocols for a better control of aerosol particle transport and deposition in the ventilation ducts are of great help (Da et al. 2015).

Global warming and GHG emissions

In addition to combustion of fossil fuels, biomass burning including forest fires and agricultural waste burning is one of the major sources of GHG CO_2 and thus deserve a special focus in terms of policymaking. The role of forest in carbon cycle and H_2O budget is well known. For that reason, wildfires greatly modify CO_2 and H_2O fluxes. In this special issue, Dadi et al. (2015) evaluate the effect of wildfires in the CO_2 and H_2O flux exchange between a Mediterranean ecosystem (Spanish coniferous forest) and the atmosphere 2 years after the event. Dadi et al. (2015) concluded that post-wildfires are a carbon source while the water flux was less dramatically affected.

Precise measurements and modeling are also critical to provide further advance in reducing GHG emissions and to inform environmental policies. Notwithstanding that the reduction in GHG emission observed in Europe over the last two decades is a result of the economic restructuring that occurred in the Eastern Europe Area (EEA) in the 1990s (Balsalobre et al. 2015), the EU is making sustained progress towards achieving its emission reduction targets: Between 1990 and 2008, EEA countries collectively reduced greenhouse gas emissions by 7.5 % and per capita emissions from 10.9 to 9.3 metric tonnes CO_2 equivalent. The EU-27 has recently set an independent target to reduce greenhouse gas emissions by 2020 by at least 20 % compared to the 1990 levels. On this direction, the characterization of the radiative properties of emerging solutions for industrial problems is a

must. This is the case of the substitution of HFC-134a (CF_3CFH_2) by HFO-1243zf in air-conditioning units. González et al. (2015) report that the contribution of HFO-1243zf to global warming is expected to be negligible compared with that of the potent greenhouse gas HFC-134a. Here and given the major role of fossil fuels on carbon emissions, careful characterization of soot from diesel engines (Tapia et al. 2015) is critical for a better understanding of the global radiative effects of these atmospheric aerosols and thus on the overall role of pollutants in the environment.

Impacts on health

Health is another key topic that merits specific attention. Thus, for instance, heavy metal emissions exert a direct effect on biota, having been widely recognized as a public health concern. Considerable progress has been made in Europe to reduce emissions and traditional careless exposure to heavy metals. As shown by Esbrí et al. (2015), even in developed areas, the levels of atmospheric Hg have been for too long consistently exceeding the thresholds set by the World Health Organization, as featured in series from 1900 to as far as 2000 in the Almadén Hg mining district (Tejero et al. 2015). Even though clinical studies have not been performed on the general population of this mining area, studies on exposed workers (García-Gómez et al. 2007) describe high Hg levels in blood and urine and detrimental effects on the central nervous and urinary systems. Here, case studies illustrate the importance of policy action: Improved controls on Hg cells used in industrial processes (e.g., in the chlor-alkali process) resulted in emissions reduced by 66 % between 1990 and 2011 (EEA 2013). This example also highlights the importance of measurement protocols and cycle analyses, as significant differences between diurnal and nocturnal Hg concentrations are observed.

As already stated, particle organic compounds present on the BC nanoparticle surface may trigger oxidative or harmful degradation mechanisms. Characterization of the interfacial functional groups of the BC nanoparticles from diesel exhaust (Tapia et al. 2015) reveals the exceptional reducing properties of the investigated soot which may have potential toxicological effects. However, to better examine the effect of these aerosols on the human health, the use of a biological marker is required.

The papers presented in this SI show cutting edge research on how atmospheric pollutants change our environment focusing on air quality, global warming, and the impacts on health. Authors and reviewers are greatly acknowledged for their contributions as well as Dr. Philippe Garrigues, ESPR Editor-in-Chief, and Emmanuelle Pignard-Péguet and Laure Beugnot, Editorial Assistants, for their help and support during the preparation of this special issue. For additional information about the E2KW 2013 conference speakers and titles,

please visit <http://congresse2kw.uclm.es/e2kw-2013>. This conference is organized by the Energy and Environment Science and Technology Campus of International Excellence—CYTEMA of the University of Castilla-La Mancha (Spain).

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