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Air pollution: new insight from direct measurements of ozone production

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Since the early 1950s, after Arie Jan Haagen-Smit discovered that the main element of the photochemical smog in the cities is ozone, scientists' efforts in monitoring ozone and its precursors, have been constantly growing[1]. Enormous progresses have been made, in the last sixty years, in the understanding of the way in which ozone builds up in the lower atmosphere. Networks of observation sites around the world and a number of intensive campaigns have been made to study in detail the mechanisms that control surface ozone. Although the advancements achieved so far[2], several evidences suggest that we are not completely understanding all the mechanisms involved in the production of ozone. Inconsistent results in control strategies, like strong changes in the ozone precursors concentrations not followed by changes in the ozone levels, suggest the need for other approaches in ozone studies [2,3,4,5,6]. Observations carried out with a recently developed instrument, which directly measures the ozone production rate, seems to be promising to improve our

knowledge of ozone chemistry. This new system can be potentially integrated in the existing network of observation sites and contribute to increase the value of the control strategies of ozone precursors [3].

Unlike many other air pollutants, ozone is not directly emitted in the atmosphere neither by natural processes nor by human activities: it is a secondary pollutant formed from photochemical reactions of nitrogen oxides (NO_x), which can be directly emitted in the atmosphere or produced in the oxidation chains of carbon monoxide, methane and volatile organic compounds (VOC). The ambient ozone level in a site is the result of the local photochemical production, the surface deposition, and vertical and horizontal exchanges[4]. The photochemistry is driven by the nitrogen oxides level with a strong non-linear dependence of the ozone production rate on nitrogen oxides concentrations, whereas transport and deposition are triggered by meteorological conditions.

Because ozone is not directly emitted in the atmosphere, the control strategies have been based on the reduction of the emissions of NO_x and VOC, which are the ozone main precursors. These reductions have resulted in a strong drop of ozone precursors: more than a third of NO_x emissions between 1990 and 2005 in Europe [4]., and about 52% between 1980 and 2010 in the USA [6]. This decline has not regarded countries with a growing economy like Asia and China where, between 2001 and 2006, it has been reported an increase of NO_x emissions of 44% and 55%, respectively[7]. Controversial effects on the ozone concentrations have been observed around the world: there are sites where the precursors control has resulted in a contraction of the ozone levels, but also several sites where, unexpectedly, ozone has not changed or even increased[2,4,8]. This occasionally ineffective control of the ozone precursors is one of the evidence that concomitant processes contribute to the production of ozone, and this is why it is challenging connecting ozone concentrations with those of its precursors. Ozone concentrations measurements are not indicative of its sources because it could be locally produced and/or imported from other areas. For this reason a system for the measurement of the ozone production rate ($P(O_3)$) could help to understand the

local ambient ozone formation and its evolution, and could help to split-up the contribution due to the local photochemical production from the transported one[3].

A technique able to measure the ozone production rate was proposed in the early 70s by Harvey Jeffries (University of North Carolina, USA) but it has never been used in atmospheric observations and remained unnoticed for decades. Independently from Jeffries's works, a sensor for the ozone production rate, called MOPS (Measurement of Ozone Production Sensor), has recently revived thanks to Prof. Brune's group at the Pennsylvania State University. It uses two identical chambers where ambient air is pulled: one where all the chemical processes of the atmosphere are permitted (including ozone formation) and another one where ozone formation is forbidden thanks to a UV-blocking film that cuts short wavelengths of the Sun radiation, those needed to produce ozone photochemically. The O_3 production rate is the difference between the O_3 + NO_2 signals detected at the end of each chamber[3,9]. Observations during recent field campaigns show a good agreement among the measured ozone production rate and what calculated using the measured nitric oxide, hydroperoxyl and hydroxyl radical. On the other hand, the comparison between measured and modelled $P(O_3)$ using a detailed chemical model, shows that the model underpredicts observed $P(O_3)$ by more than 50%[3,8]. This discrepancy has implications on our understanding of the atmospheric chemistry, but it has even more repercussions on control policies of ozone precursors that use models to estimate the ozone budget and to find a link between precursors emissions and the ozone observed concentrations.

Air quality models, even those very detailed and complex, suffer from emission inventories and transport uncertainties and, sometimes, parts of their chemical schemes need revision and upgrades[10,11]. The system, recently developed to measure the ozone production rate (a key parameter not observed yet), is promising in giving a new chance to make progresses in our knowledge of the atmospheric pollution buildup. In fact, $P(O_3)$ measurements can be used to tell apart local production from transport by comparing the rate-of-change in ambient ozone against $P(O_3)$. Moreover, measured $P(O_3)$ can be used to determine if the ozone production is NO_x-limited

or VOC-limited and this information can be used to reduce model uncertainties in simulating ozone concentrations. Observations in other sites and more instrument characterizations are needed to confirm the results reported so far. From these new measurements we expect possible improvements in the study of surface ozone chemistry and its control strategies, that may have implication on the quality of our life, on ecosystems and economy.

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