AIR POLLUTION

The South Asian monsoon—pollution pump and purifier

J. Lelieveld[1,2]*, E. Bourtsoukidis[1], C. Brühl[1], H. Fischer[1], H. Fuchs[3], H. Harder[1], A. Hofzumahaus[3], F. Holland[3], D. Marno[1], M. Neumaier[4], A. Pozzer[1], H. Schlager[5], J. Williams[1,2], A. Zahn[4], H. Ziereis[5]

Air pollution is growing fastest in monsoon-affected South Asia. During the dry winter monsoon, the fumes disperse toward the Indian Ocean, creating a vast pollution haze, but their fate during the wet summer monsoon has been unclear. We performed atmospheric chemistry measurements by aircraft in the Oxidation Mechanism Observations campaign, sampling the summer monsoon outflow in the upper troposphere between the Mediterranean and the Indian Ocean. The measurements, supported by model calculations, show that the monsoon sustains a remarkably efficient cleansing mechanism by which contaminants are rapidly oxidized and deposited to Earth's surface. However, some pollutants are lofted above the monsoon clouds and chemically processed in a reactive reservoir before being redistributed globally, including to the stratosphere.

Nearly two decades ago, the Indian Ocean Experiment uncovered a large pollution haze downwind of South Asia during the dry monsoon, from December to March (*1*, *2*). The composition of the haze, termed "atmospheric brown cloud," indicated major contributions from biofuel use, agricultural burning, and fossil fuel combustion, affecting air quality, climate, and the hydrologic cycle (*3*–*9*). Although incomplete biomass combustion predominated at first, associated with relatively low NO_x (NO and NO_2) concentrations, more recently the NO_x emissions and consequent ozone (O_3) formation have increased significantly (*10*, *11*). Whereas in East Asia sulfur dioxide (SO_2) and NO_x emissions have decreased since about 2010, following the negative trends in Europe and North America, they are rapidly increasing in South Asia by about 10 and 5% per year, respectively, for example, from coal-fired power plants and smelters (*12*). Between 2005 and 2015, carbon dioxide (CO_2) emissions from fuel combustion decreased in North America and Europe, whereas they strongly increased in Asia (*13*). In South Asia, CO_2 emissions from coal consumption have more than doubled during this period (*13*). The Oxidation Mechanism Observations (OMO) aircraft campaign aimed to identify atmospheric impacts of associated air pollution emissions at regional and global scales during the South Asian summer monsoon.

Deep cloud convection in the monsoon establishes an enormous, quasi-stationary anticyclone in the upper troposphere and lower stratosphere, where the air flows in a clockwise rotation. It is a globally predominant meteorological phenomenon, extending from the Mediterranean to the Pacific between tropical and temperate latitudes (from 10°N to 40°N). Satellite observations have shown coincident enhancements of water vapor and air pollution within the anticyclone, attributed to convective transport, which provide a pathway from the troposphere into the stratosphere (*14*–*18*). Moist convection is deepest over Tibet and the Himalayas, as it is triggered at high elevation, transporting air from the surface to

[1]Max Planck Institute for Chemistry, 55128 Mainz, Germany. [2]The Cyprus Institute, 1645 Nicosia, Cyprus. [3]Institute for Energy and Climate Research, Research Center Jülich, 52425 Jülich, Germany. [4]Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany. [5]Institute of Atmospheric Physics, Germany Aerospace Center, 82234 Oberpfaffenhofen, Germany.
*Corresponding author. Email: jos.lelieveld@mpic.de

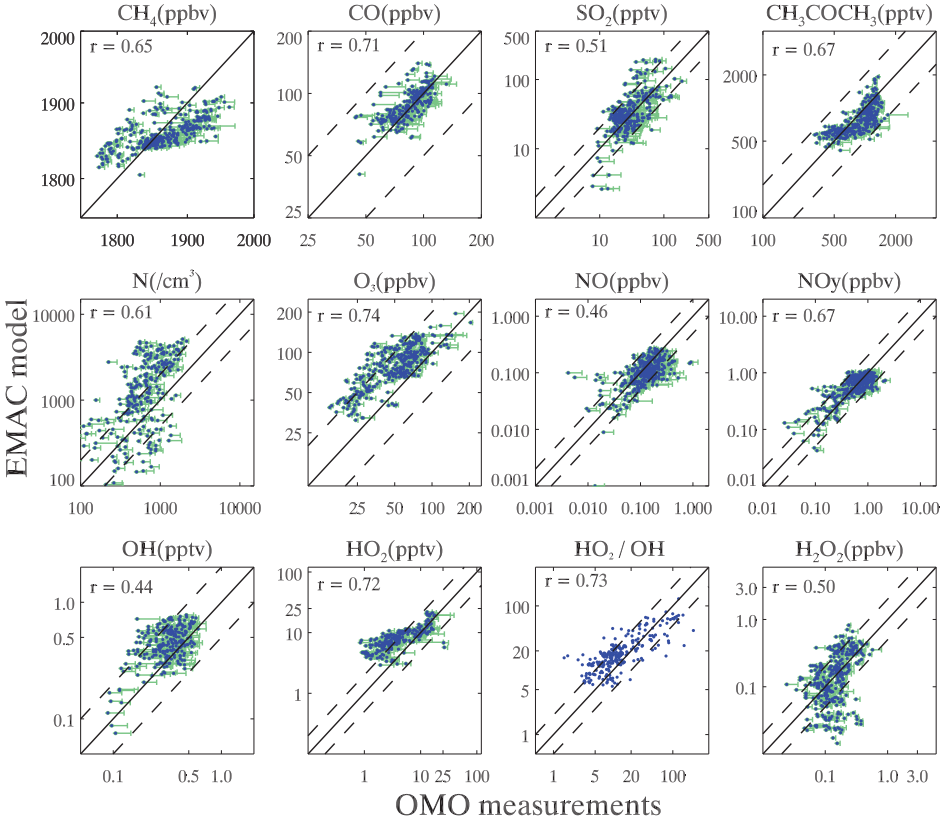

Fig. 1. Model results versus measurement data. Trace species measured in the OMO aircraft campaign at 300 to 120 hPa (9 to 15 km altitude), with error bars in green, compared with EMAC model results (correlation coefficients *r*). The solid lines indicate ideal agreement, and the dashed lines indicate agreement within a factor of two. Model results realistically represent the measurements, although O_3 is high biased, probably through overestimated transport from the stratosphere, but with negligible impact on OH calculations. Modeled particle number concentrations (N) seem high biased, though the relative enhancement in the anticyclone is well captured. Note that particle size distributions were not measured, which limits rigorous evaluation. Modeled H_2O_2 agrees well at altitudes where pressure is below 250 hPa but is low biased in the lower part of the anticyclone, possibly owing to rainout in the monsoon. Modeled OH and HO_2 radical concentrations, and their ratios, generally agree with the measurements.

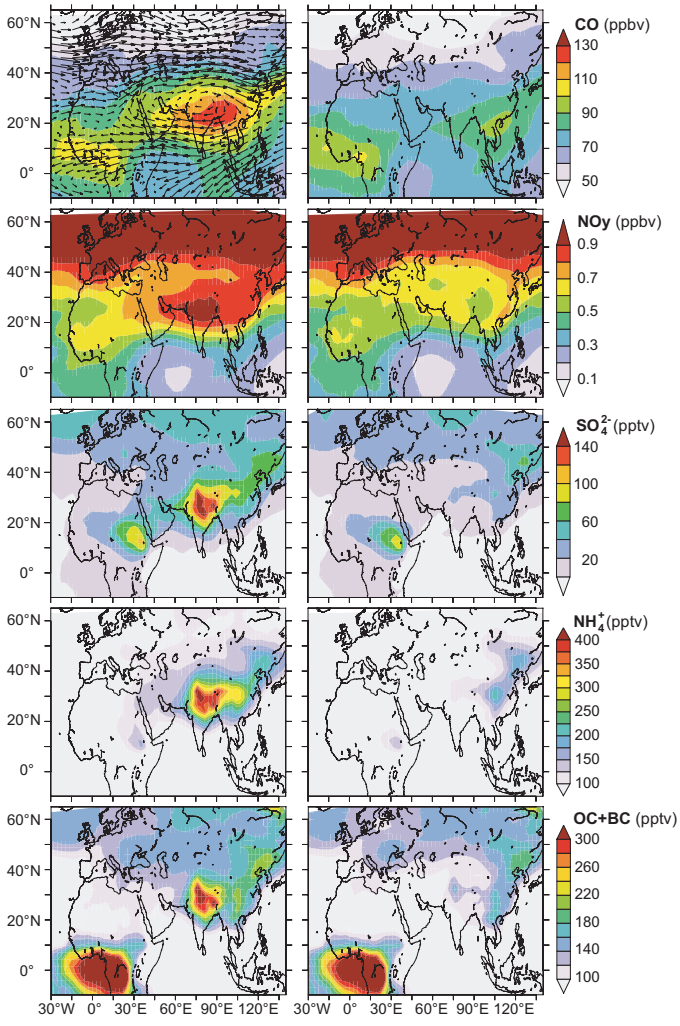

Fig. 2. Influence of South Asian emissions. Model-calculated mean CO, plus wind field, NO_y (NO_x and all other oxidized nitrogen species except N_2O), sulfate, ammonium, and carbonaceous (OC and BC) aerosol at 200 hPa (~12 km altitude) during summer. Results with all emissions (left) and without South Asian anthropogenic emissions (right) are shown. For additional results, also at 100 hPa (~16 km altitude), see figs. S6 to S12.

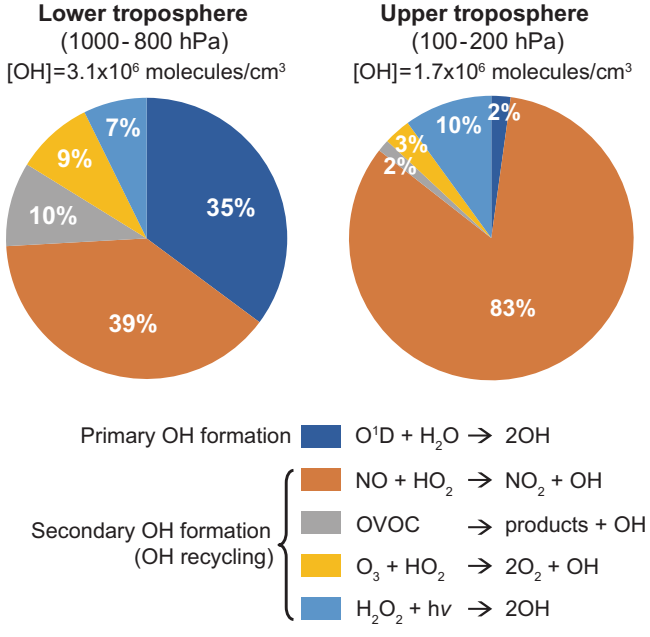

Fig. 3. Modeled OH concentrations and formation pathways. Model-calculated diel mean OH concentrations and formation pathways in the lower and upper troposphere in the geographic area of the monsoon anticyclone during summer. OVOC are oxidation intermediates of VOC. Model results and measurements indicate that OH concentrations are 30 to 40% higher within the anticyclone than outside, despite higher pollution concentrations. The concomitant loss pathways are shown in fig. S13. *hν* indicates light, where *h* is Planck's constant and ν is the photon frequency.

about 10 to 12 km altitude within hours, which may dominate the chemical composition and water budget of the monsoon anticyclone (*15*, *19*). However, trend analysis of satellite observed peroxyacetyl nitrate (PAN) in the anticyclone indicates increasing NO_x and volatile organic compound (VOC) emissions (*20*), which are more likely related to pollution from South Asia than from Tibet, as the former has a population 500 times that of the latter.

Our hypothesis is that the monsoon anticyclone is infused by South Asian convection that carries air pollution emissions upward from this region, with possible additional contributions from East Asia and Africa (*17*, *21*). In the OMO campaign, we performed measurements with the High Altitude and Long Range Research Aircraft (HALO) between 9 and 15 km altitude in July and August 2015 (fig. S1). HALO flew from the eastern Mediterranean (Cyprus) to the Indian Ocean (Maldives), traversing the western part of the anticyclone, where an integral signature of pollution sources can be expected after about 1 to 2 weeks of chemical processing of emissions from South Asia (figs. S2 to S4). We measured oxidants, including hydroxyl (OH) and hydrogen peroxyl (HO_2) radicals, peroxides, actinic radiation, VOCs and their oxidation products, oxides of sulfur and nitrogen, aerosols, and tracers to identify pollution sources. Campaign details, including the instrument configuration, can be found at www.halo.dlr.de/science/missions/omo/omo.html. Furthermore, we used the global ECHAM/MESSy Atmospheric Chemistry (EMAC) general circulation model, covering the lower and middle atmosphere, to support the data analysis. We refer to www.messy-interface.org, where the model and output data can be accessed, and to fig. S5 for references.

Figure 1 presents a comparison of model results and measurement data from 9 km altitude upward (<300 hPa). We obtain overall good agreement, although O_3 in the model is somewhat high biased. Because the O_3 precursor concentrations are calculated accurately, we attribute this to overestimated transport, for example, from the stratosphere, related to the limited horizontal grid resolution of the model (~2.8° latitude and longitude). However, the impact of this bias on OH radical concentrations, that is, the main oxidant in the troposphere, is small. Additional OH sources are the photodissociation of hydrogen peroxide (H_2O_2), organic peroxides (e.g., peroxyacetic acid), and acetone (CH_3COCH_3). Our model results indicate that OH concentrations most strongly depend on NO_x concentrations, as NO recycles OH by reacting with peroxy radicals (e.g., $NO + HO_2 \rightarrow NO_2 + OH$). A key NO_x source, in turn, is lightning associated with monsoon convection, which provides a near-continuous supply of fresh NO during upward transport. In the upper troposphere, the reaction of NO with HO_2 is faster than the loss reaction $NO_2 + OH (+M) \rightarrow HNO_3 (+M)$, as the latter is pressure dependent (M is an air molecule). When we exclude lightning NO_x from our model, the mean OH mixing ratios within

the monsoon anticyclone drop by a factor of two to three, that is, they become comparable to the much lower values over the central Indian Ocean (fig. S5).

We diagnosed air from within the anticyclone in our measurement data through the mixing ratio of methane (CH_4), which is remarkably enhanced, mostly owing to emissions from rice fields during the monsoon. The isolated character of the upper tropospheric anticyclone, with relatively strong winds acting as a transport barrier, is manifest in many of the measured tracers, and it is most unambiguously defined by a CH_4 threshold of 1879.8 parts per billion by volume (ppbv) (mean plus 2σ standard deviation). We find that, within the anticyclone, carbon monoxide (CO), chloromethane, chloroform, acetone, and benzene are higher by up to a factor of two (fig. S3), whereas dichloromethane, carbon tetrachloride, and carbon disulfide are similar inside and outside the anticyclone, indicating that South Asia is an important source of the former, but not of the latter, gases. Even though many pollutants react with OH, depressing its concentration, OH is significantly enhanced within the anticyclone (fig. S3). We find that OH is effectively recycled through reaction with NO, with lightning being the main regulating source. This implies that the monsoon convection not only transports pollutants upward but also simultaneously provides a cleansing mechanism, with a key role for lightning NO_x in sustaining relatively high OH concentrations. Then, OH oxidizes the pollutant gases into products that are typically less volatile and more soluble, which can be removed by precipitation.

Figure 2 presents model results of the impact of South Asian pollution emissions on the upper troposphere in July to August of 2015 (see fig. S4 for regional boundaries and figs. S5 to S12 for additional results). Clearly, South Asian emissions dominate the anticyclone composition, even though East Asian sources are generally stronger (122 versus 156 Tg CO/year, 6.6 versus 17.6 Tg NO_x/year, 23.4 versus 25.5 Tg SO_2/year, respectively). We find that OH mixing ratios are reduced by the South Asian pollution (25 to 50%); however, the effect would be greatly enhanced without the compensating effect by OH recycling from lighting NO_x (fig. S5). Our model calculations suggest that nitrogen oxides (NO_y) in the anticyclone are predominantly PAN (~50%) and, to a lesser extent, NO_x, HNO_3, and nitrate (15 ± 5% each). At 200 hPa (~12 km altitude), sulfate is about 50% in excess of SO_2, which increases to 100% at 100 hPa (~16 km altitude), as the oxidation of SO_2 continues during ascent, considering that OH increases from about 0.25 to 0.5 parts per trillion by volume (pptv) between 200 and 100 hPa (figs. S7 and S8).

Figure 3 illustrates the high efficiency of OH recycling in the monsoon anticyclone in the upper troposphere, as the primary source from the photolysis of O_3 (yielding O^1D) only forms 2% of the OH, whereas the reaction of NO with HO_2 contributes 83%. In the lower troposphere, these fractions are 35 and 39%, respectively. Although the OH concentration near the tropopause is about 45% lower compared to that near Earth's surface, the air pressure drops by a factor of 10; thus, the OH mixing ratio strongly increases with altitude. The realistic NO and the HO_2/OH ratio in our model corroborate the accurate representation of radical recycling (Fig. 1). Another example of the high cleansing efficiency of the monsoon is the removal of pollutants and their oxidation products by precipitation. We calculate that, from all reactive sulfur emissions in South Asia, mostly as SO_2, ~80% are removed by precipitation, largely as sulfate (fig. S4). By turning off wet removal in our model, sulfate concentrations in the upper troposphere increase by three orders of magnitude.

Because of the high oxidation capacity, particulate organic carbon (OC) builds up during upward transport, formed from reactions with VOCs and increasing from about 200 to 300 pptv between 200 and 100 hPa in our model, whereas the particle number concentration decreases by a factor of two owing to coagulation (figs. S9 to S12). Although it is expected that monsoon rains remove particulate pollutants, the West African monsoon, in particular, transports much black carbon (BC) and OC upward (Fig. 2); however, the BC and OC transported by the West African monsoon has a much lower potential to reach the stratosphere than that transported by the South Asian monsoon (fig. S12). Within the anticyclone, we additionally find a large contribution by ammonium (NH_4^+), indicating that sulfate and nitrate are neutralized through agricultural ammonia emissions in South Asia. A comparison of pollution concentrations at 200 and 100 hPa (figs. S6 to S12) implies that a considerable part enters the stratosphere. Our model results corroborate recent studies, showing that, subsequent to convective transport into the anticyclone at 200 hPa, about 25% ascends through the tropical tropopause at 100 hPa, whereas the remainder returns to the troposphere in roughly equal parts over the monsoon region, the Pacific and North America, Africa, and the Mediterranean, thus contributing to global air pollution (*22*, *23*). About one-third of the upward fraction continues deeply into the stratosphere, and two-thirds travels poleward in the lower stratosphere (*23*).

It was proposed by Hofmann *et al.* (*24*) that SO_2 from large-scale coal burning in China is a source of stratospheric sulfate, which backscatters sunlight and influences climate, and forms the condensation nuclei for clouds that catalyze ozone destruction in polar regions (*25*). Recently, it was suggested that growing SO_2 emissions in India may also contribute (*26*). Even though the monsoon outflow provides an oxidizing environment, the reaction of SO_2 with OH in the gas phase is relatively slow, leading to a lifetime of several weeks. On shorter time scales, SO_2 can be oxidized in clouds (e.g., by H_2O_2, and removed by precipitation), but our results show that a substantial fraction of SO_2, up to 100 pptv, plus twice that amount of sulfate escapes the cloud convection into the monsoon anticyclone. Space-borne observations since the 1990s indicate an increase of stratospheric aerosol concentrations (*25*, *26*). The relative contributions of volcanoes, anthropogenic pollution, and other sources have been the subject of debate (*25*, *27*).

The SO_2 concentrations within the anticyclone are 5 to 10 times higher than those measured elsewhere in the tropics (*28*), which is explained by emissions from South Asia. We compared these results with model calculations that account for the recent eruptions of the Kelut, Fogo, and Calbuco volcanoes (*27*) and found a negligible influence on sulfur species compared to anthropogenic emissions. During upward transport into the stratosphere, which takes about 1 to 2 months, the SO_2 is oxidized into particulate sulfate. Furthermore, our model results indicate large contributions by OC and BC, together more than a factor of two in excess of sulfate (Fig. 2 and figs. S9 to S12). This is consistent with aircraft measurements near the tropical tropopause, showing a major contribution by compounds other than sulfate, and a large carbonaceous fraction (*26*, *28*–*31*). In the upper troposphere and lower stratosphere, OC is in a glassy, solid-phase state, with yet-unknown consequences for particle and cloud microphysics and heterogeneous processes that affect ozone chemistry (*30*, *32*).

We conclude that South Asian emissions dominate pollution concentrations in the anticyclone. Yet, the monsoon has two faces, like a Janus head—transferring pollutants from the surface upward while sustaining an effective cleansing mechanism that curbs the impacts. Once in the upper troposphere, in the absence of deposition processes, pollutants accumulate and are chemically processed in a reactive reservoir for weeks to more than a month, from which carbon-, sulfur-, nitrogen-, and halogen-containing reaction products disperse globally, including to the stratosphere. It is expected that the rapidly increasing South Asian emissions will intensify the flux of pollutants through the anticyclone in the years to come.

REFERENCES AND NOTES

1. V. Ramanathan *et al.*, *J. Geophys. Res.* **106** (D22), 28371–28398 (2001).
2. J. Lelieveld *et al.*, *Science* **291**, 1031–1036 (2001).
3. V. Ramanathan *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **102**, 5326–5333 (2005).
4. S. Lal *et al.*, *J. Atmos. Chem.* **60**, 189–204 (2008).
5. K. K. Moorthy, S. K. Satheesh, S. S. Babu, C. B. S. Dutt, *J. Earth Syst. Sci.* **117** (S1), 243–262 (2008).
6. T. N. Krishnamurti *et al.*, *J. Geophys. Res.* **114** (D6), D06213 (2009).
7. B. P. Kumari, B. N. Goswami, *Geophys. Res. Lett.* **37**, L06703 (2010).
8. M. G. Lawrence, J. Lelieveld, *Atmos. Chem. Phys.* **10**, 11017–11096 (2010).
9. V. S. Nair *et al.*, *J. Geophys. Res.* **115** (D21), D21201 (2010).
10. S. D. Ghude *et al.*, *J. Geophys. Res.* **118**, 1075–1089 (2013).
11. S. Lal, S. K. Peshin, M. Naja, S. Venkataramani, in *Observed Climate Variability and Change over the Indian Region*, M. R. Nair, S. Nayak, Eds. (Springer, 2017), pp. 249–269.
12. N. A. Krotkov *et al.*, *Atmos. Chem. Phys.* **16**, 4605–4629 (2016).

13. International Energy Agency (IEA), CO_2 emissions from fuel combustion (IEA, Paris, 2017).
14. S. Fueglistaler, M. Bonazzola, P. H. Haynes, T. Peter, *J. Geophys. Res.* **110**, D08107 (2005).
15. R. Fu *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **103**, 5664–5669 (2006).
16. M. Park *et al.*, *Atmos. Chem. Phys.* **8**, 757–764 (2008).
17. W. J. Randel *et al.*, *Science* **328**, 611–613 (2010).
18. M. L. Santee *et al.*, *J. Geophys. Res.* **122**, 5491–5514 (2017).
19. N. K. Heath, H. E. Fuelberg, *Atmos. Chem. Phys.* **14**, 2055–2070 (2014).
20. S. Fadnavis *et al.*, *Atmos. Chem. Phys.* **14**, 12725–12743 (2014).
21. A. E. Bourassa *et al.*, *Science* **337**, 78–81 (2012).
22. A. Rauthe-Schöch *et al.*, *Atmos. Chem. Phys.* **16**, 3609–3629 (2016).
23. F. Ploeger, P. Konopka, K. Walker, M. Riese, *Atmos. Chem. Phys.* **17**, 7055–7066 (2017).
24. D. Hofmann, J. Barnes, M. O'Neill, M. Trudeau, R. Neely, *Geophys. Res. Lett.* **36**, L15808 (2009).
25. S. Kremser *et al.*, *Rev. Geophys.* **54**, 278–335 (2016).
26. J.-P. Vernier *et al.*, *J. Geophys. Res. Atmos.* **120**, 1608–1619 (2015).
27. C. Brühl, J. Lelieveld, H. Tost, M. Höpfner, N. Glatthor, *J. Geophys. Res.* **120**, 2103–2118 (2015).
28. A. W. Rollins *et al.*, *Geophys. Res. Lett.* **44**, 4280–4286 (2017).
29. S. Borrmann *et al.*, *Atmos. Chem. Phys.* **10**, 5573–5592 (2010).
30. D. M. Murphy, K. D. Froyd, J. P. Schwarz, J. C. Wilson, *Q. J. R. Meteorol. Soc.* **140**, 1269–1278 (2014).
31. P. Yu, O. B. Toon, R. R. Neely, B. G. Martinsson, C. A. M. Brenninkmeijer, *Geophys. Res. Lett.* **42**, 2540–2546 (2015).
32. M. Shiraiwa *et al.*, *Nat. Commun.* **8**, 15002 (2017).

ACKNOWLEDGMENTS

We are grateful to the OMO and HALO teams, especially the scientists, pilots, and engineers; the Cyprus Institute; and EDT Hangar Services in Cyprus for excellent logistical and operational support of the aircraft measurement campaign. We also thank N. Ojha for modeling support. **Author contributions:** J.L. conceived and, together with H.H. and supported by F.H., coordinated the project. E.B., H.Fi., H.Fu., A.H., F.H., H.H., D.M., M.N., H.S., J.W., A.Z., and H.Z. were responsible for the measurements and A.P. and C.B for the modeling. J.L. wrote the manuscript. All authors contributed to the data analysis and the manuscript. **Competing interests:** None declared. **Data and materials availability:** Data and models are available on request.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/361/6399/270/suppl/DC1
Supplementary Text
Figs. S1 to S13
References (*33*–*48*)

18 October 2017; accepted 30 May 2018
Published online 14 June 2018
10.1126/science.aar2501

Science

The South Asian monsoon—pollution pump and purifier

J. Lelieveld, E. Bourtsoukidis, C. Brühl, H. Fischer, H. Fuchs, H. Harder, A. Hofzumahaus, F. Holland, D. Marno, M. Neumaier, A. Pozzer, H. Schlager, J. Williams, A. Zahn and H. Ziereis

Science **361** (6399), 270-273.
DOI: 10.1126/science.aar2501originally published online June 14, 2018

South Asian monsoon and pollution

Air pollution is growing fastest in monsoon-impacted South Asia. During the dry winter monsoon, the fumes disperse toward the Indian Ocean, creating a vast pollution haze. The fate of these fumes during the wet summer monsoon has been unclear. Lelieveld *et al.* performed atmospheric chemistry measurements by aircraft in the Oxidation Mechanism Observations campaign, sampling the summer monsoon outflow in the upper troposphere between the Mediterranean and the Indian Ocean. The measurements, supported by model calculations, show that the monsoon sustains a remarkably efficient cleansing mechanism in which contaminants are rapidly oxidized and deposited on Earth's surface. However, some pollutants are lofted above the monsoon clouds and chemically processed in a reactive reservoir before being redistributed globally, including to the stratosphere.

Science, this issue p. 270