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# Attribution of surface ozone to $NO_x$ and volatile organic compound sources during two different high ozone events

**Aurelia Lupaşcu et al.**

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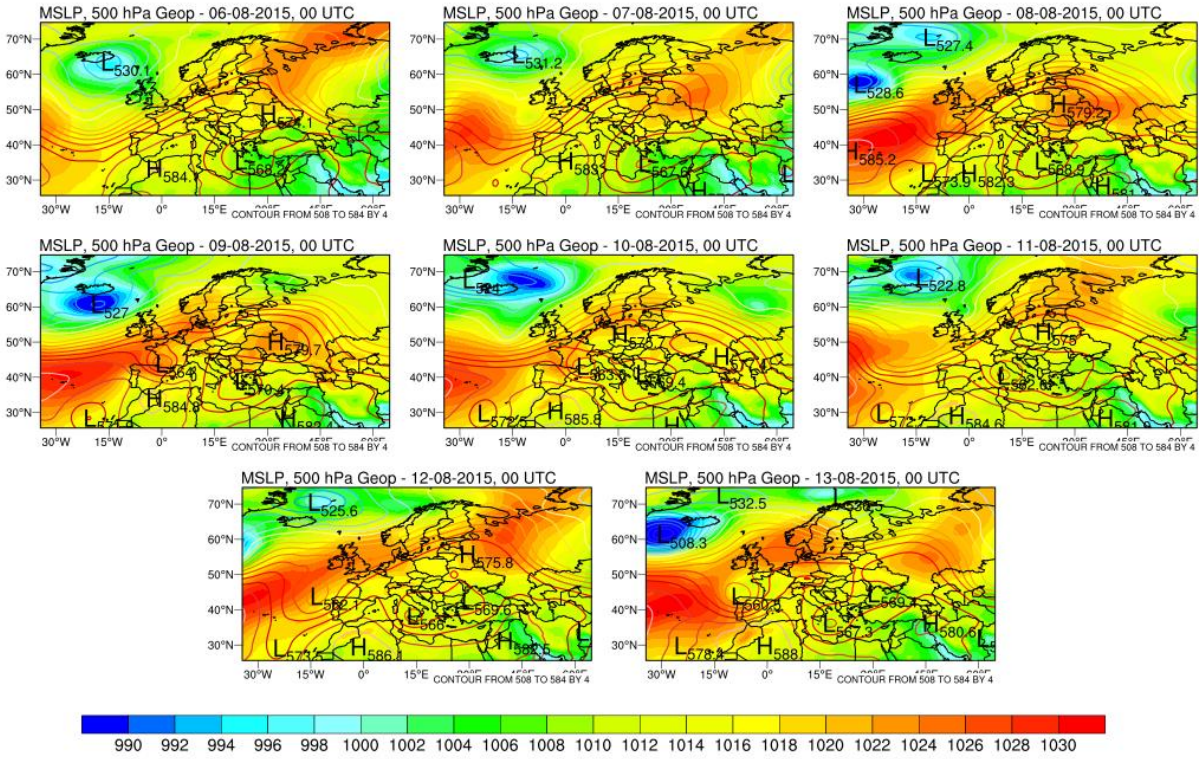


**Figure S1. Mean sea level pressure (filled colors) and geopotential heights (contours) at 500 hPa for the 6-13 August 2015 period, 00 UTC.**

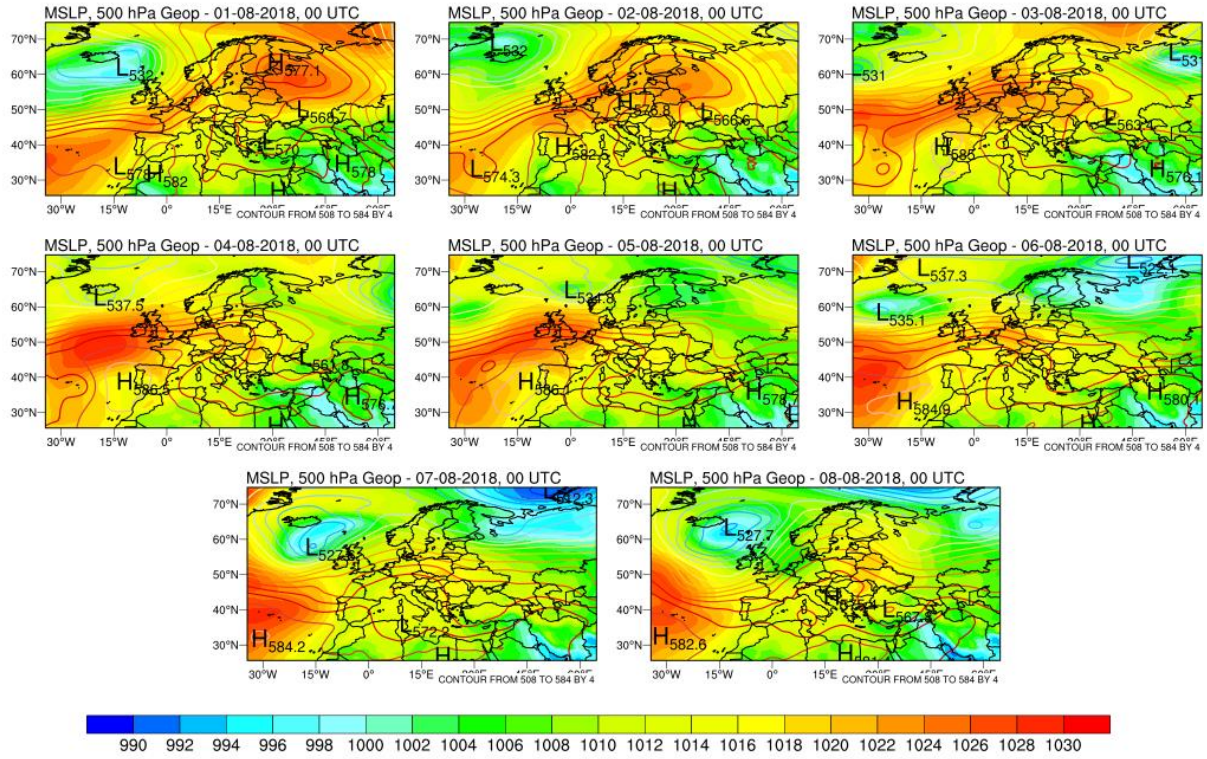


**Figure S2. Mean sea level pressure (filled colors) and geopotential heights (contours) at 500 hPa for the 1-8 August 2015 period, 00 UTC.**

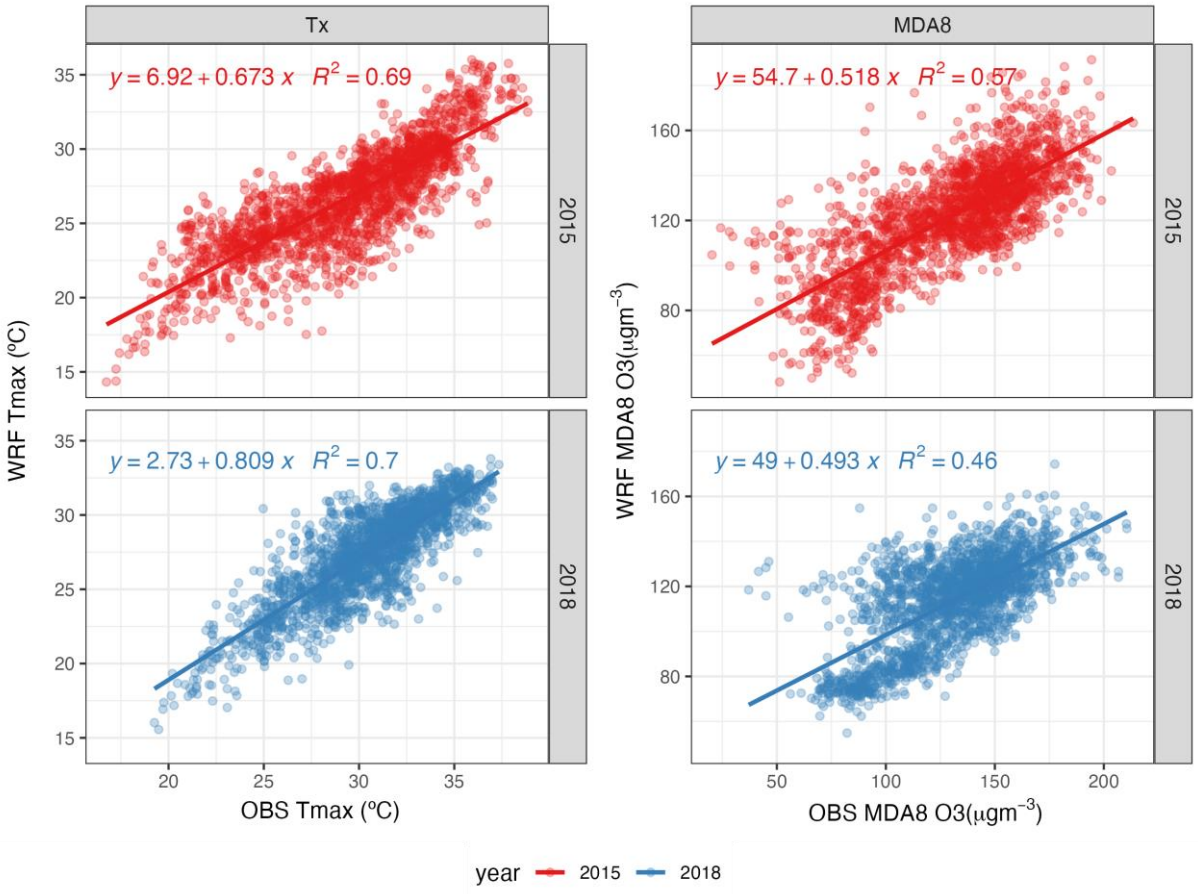


**Figure S3. Scatter plots showing the modeled versus observed MDA8 $O_3$ and T2MAX for 2015 (red dots) and 2018 (blue dots) for all analyzed stations. The left panels depict the observed vs modeled T2MAX, while the right panels exhibit the observed vs modeled MDA8 $O_3$. The solid lines are the lines of best fit.**

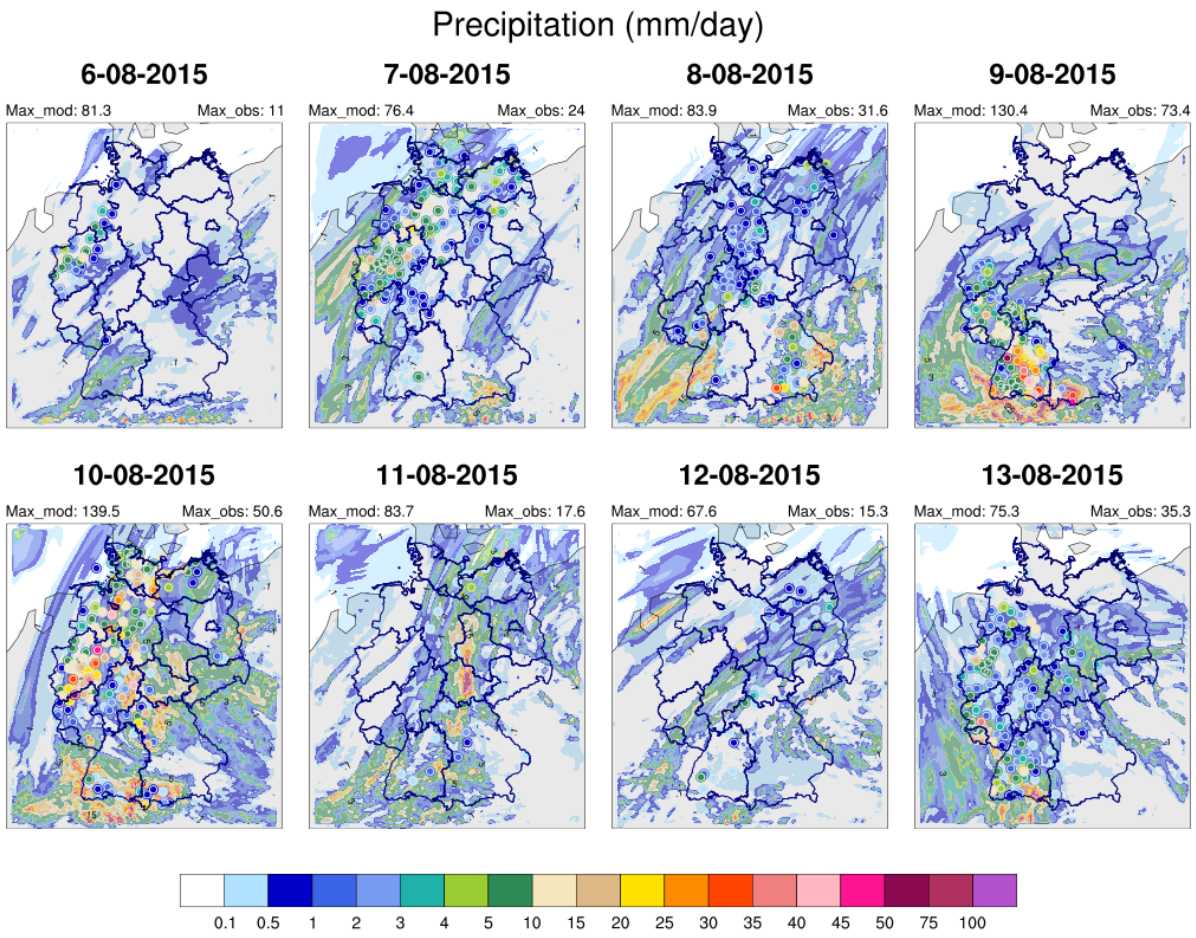


**Figure S4. Accumulated daily precipitation for the 6 – 13 August 2015 period. Colored dots represent the observed accumulated precipitation.**

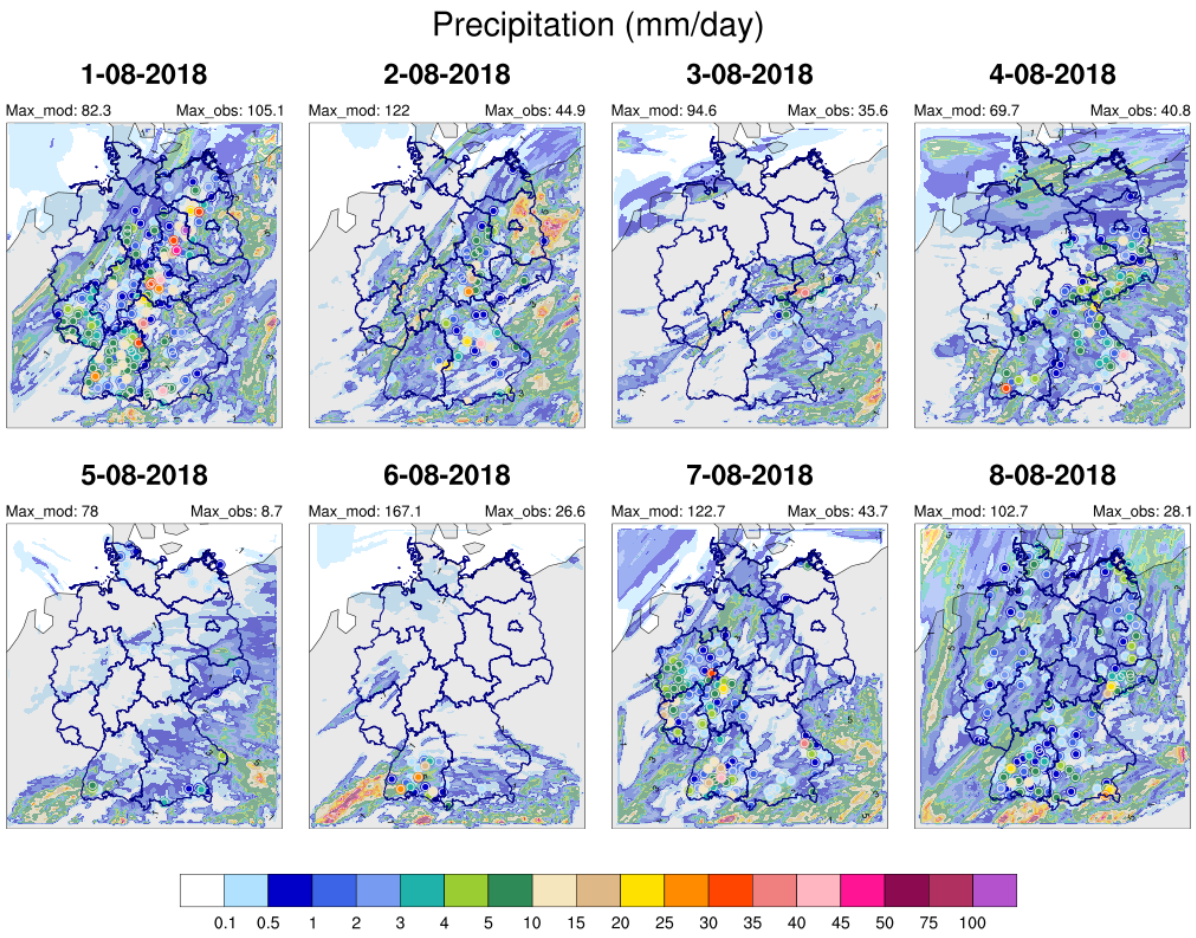


**Figure S5. Accumulated daily precipitation for the 1 – 8 August 2018 period. Colored dots represent the observed accumulated precipitation.**

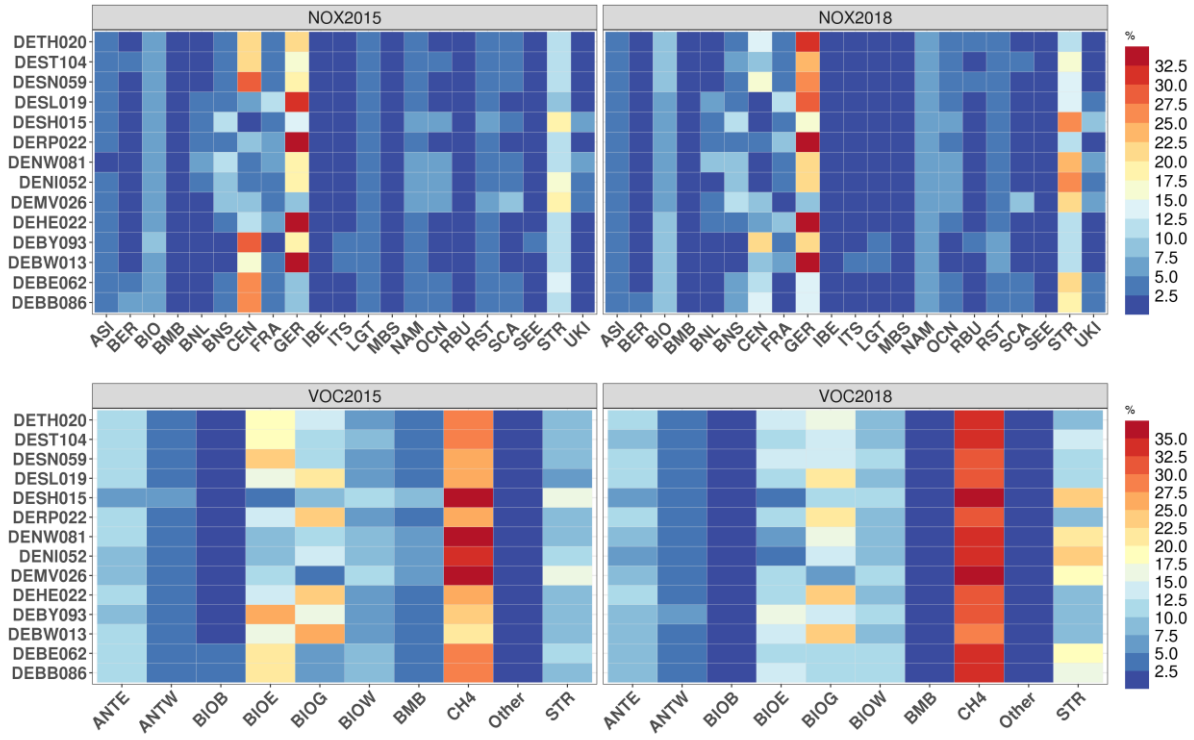


**Figure S6. Relative contribution to mean surface $O_3$ at 14 receptor stations from local and other European sources, HTAP2 sources, and other global sources. The upper panels denote the mean contribution of $NO_x$ precursor to total $O_3$ during 6 – 13 August 2015 (left) and 1 – 8 August 2018 (right). The bottom panels denote the mean contribution of VOC precursors to total $O_3$ during 6 – 13 August 2015 (left) and 1 – 8 August 2018 (right).**

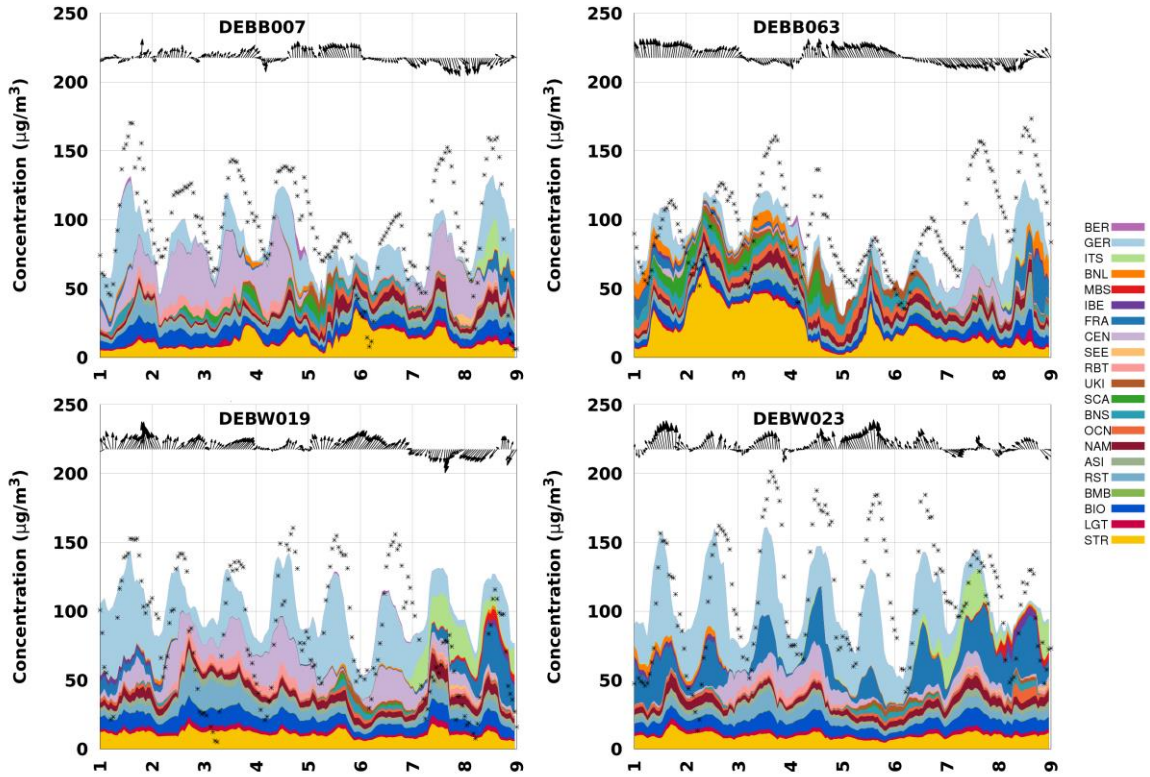


**Figure S7. Contribution to hourly $O_3$ concentrations of local and other European sources, HTAP2 source regions, and other global source types at each station during the 1-8 August 2018 period at two stations located in north and south of Brandenburg and at two stations located in east and west of Baden-Württemberg. In addition, this plot includes simulated wind speed and direction.**

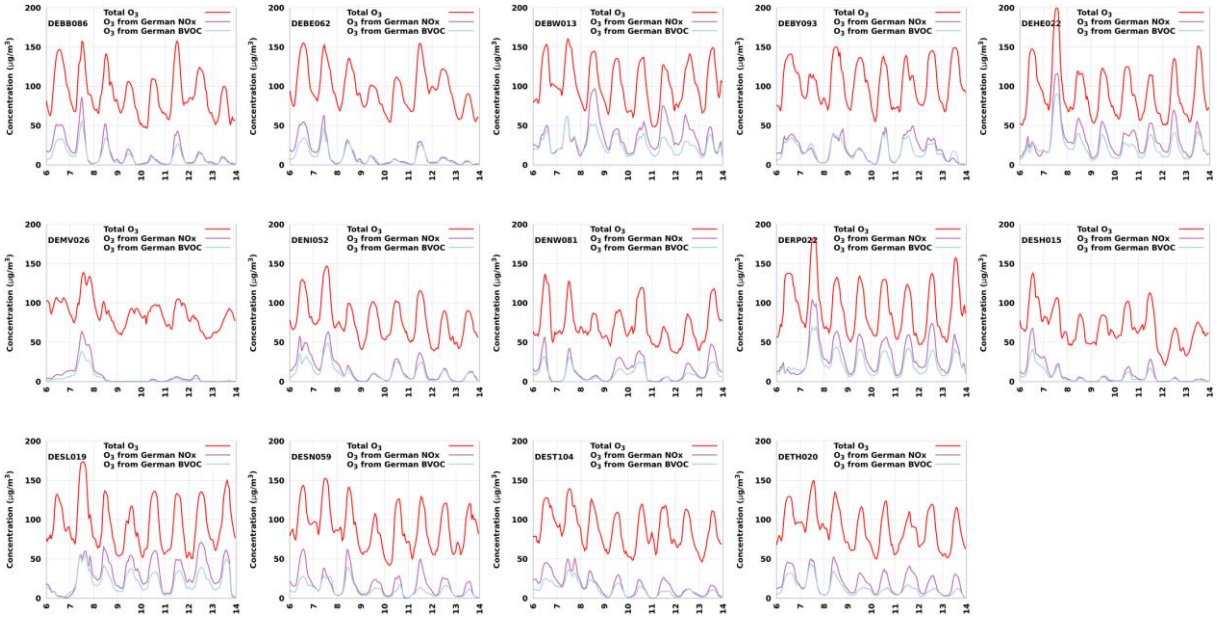


**Figure S8. Diurnal variation of total modeled ozone and of the ozone attributed to the German NOx and BVOC emissions at each station for 6 – 13 August 2015**

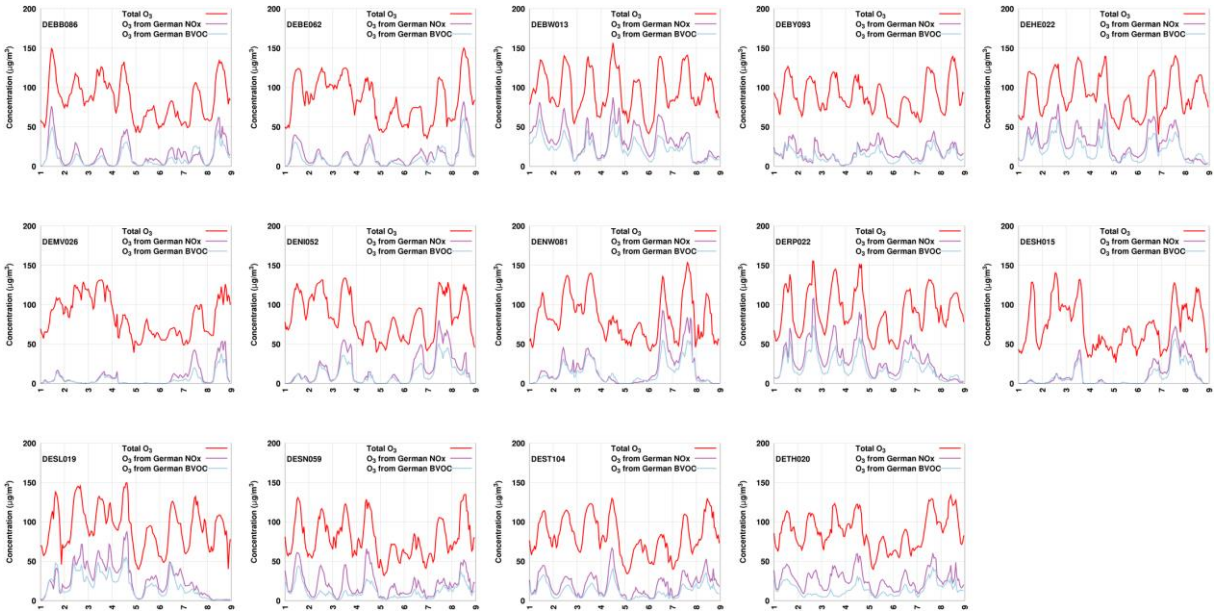


**Figure S9. Diurnal variation of total modeled ozone and of the ozone attributed to the German NOx and BVOC emissions at each station for 1 – 8 August 2018.**

**S1. Surface ozone origin attributed to NOx or VOC sources during two different high ozone peak events**

Figures S10 to S13 depict the contribution of each tagged source region and type to modeled MDA8 $O_3$ values for both the $NO_x$ and VOC tagged simulations in 2015 and 2018 for 14 German states. Results are averaged over each grid cell defined as a certain German state (see Table 7).

When we attribute ozone to VOC emissions, we noticed a high contribution of biogenic VOCs (on average 39.86 and 35.4 µg/m$^3$ in 2015 and 2018, respectively) compared to anthropogenic VOCs (on average 14.7 and 12.7 µg/m$^3$ in 2015 and 2018) on total ozone production. Previous studies (Safieddine et al., 2017, Glasius and Goldstein, 2016, Guenther et al., 2012) showed that biogenic VOC emissions are at least one order of magnitude higher than anthropogenic VOC emissions on a global scale and that BVOCs are also more reactive than the anthropogenic VOC (Atkinson and Arey, 2003). We see that during the high-ozone episodes, our model shows an enhancement of up to 60 µg/m$^3$ in the MDA8 $O_3$ concentration due to German biogenic VOCs, partly due to chemistry and partly due to the stagnant conditions that confine the pollutants near the ground. This is comparable to Churkina et al. (2017), in which, by switching on and off the biogenic emissions, it was shown that the ozone response to VOC emissions (both local and regional) reached a maximum of 60% during a heatwave period in July 2006. Karamchandani et al. (2017), using the OSAT (ozone source apportionment technology) tagged species methods in CAMx version 6.1, also indicated biogenic VOC emissions to be an important contributor to the high end of $O_3$ for most of the European cities selected for their work, explaining up to 33% of MDA8 $O_3$. In general, the contribution of European and German biogenic emissions to MDA8 $O_3$ is higher in 2015 (18.3 and 21.1 µg/m$^3$, respectively) than in 2018 (13.2 and 20.2 µg/m$^3$, respectively).

Methane also has an important contribution to $O_3$ formation, being most of the time the second-largest contributor after biogenic VOCs. $CH_4$ is coming mostly from lateral boundary concentration, and, due to its long lifetime, our results show a constant contribution of methane to total ozone ~32.4±3.4 µg/m$^3$ (up to 50% of total MDA8 $O_3$) similar to Butler et al., 2018, 2020, Fiore et al. 2008.

The $NO_x$- and VOC-tagged simulations revealed that for some of the German states, the ozone concentration during peak days seems not to be dominated by German emissions, but rather largely influenced by ozone transported from other countries. The contribution of German anthropogenic $NO_x$ precursor emissions to modeled MDA8 $O_3$ in different regions is lying between 2.1 to 76.6 µg/m$^3$ in 2015 and between 1.8 to 81.8 µg/m$^3$ in 2018 (see Figs. S5-S8), while the contribution of German biogenic VOC emissions in different German states varies between 1.8 and 57.1 µg/m$^3$ in 2015 and between 1 to 51.4 µg/m$^3$ in 2018. These findings emphasize that the contribution of German emissions shows a heterogeneous spatial and temporal behavior in the analyzed receptor regions. In Baden-Württemberg, Bavaria, Hesse, Rhineland-Palatinate, and Saarland, days with elevated MDA8 $O_3$ (above the WHO target limit of 100 µg/m$^3$) are driven by German sources (anthropogenic $NO_x$ or biogenic VOC) which explain more than 50% of modeled MDA8 $O_3$, thus highlighting the importance of German emissions combined with enhanced photochemical activity. Conversely, periods of low ozone concentration (under the WHO target limit of 100 µg/m$^3$) are driven by inter-regional and intercontinental transport combined with a large contribution of $O_3$ from the upper troposphere, while the contribution of German sources is small.

Intercontinental transport of ozone from anthropogenic and biogenic $NO_x$ and VOC sources apart from methane has little effect on the total MDA8 $O_3$ concentrations in the episodes studied here compared to the contribution of European $NO_x$ and VOC precursors. This is in agreement with previous findings of Fiore et al., 2009, Lupaşcu and Butler, 2019, Butler et al., 2020, and the reference therein that showed during summer the surface ozone has a stronger sensitivity to local and European emissions than in the other seasons.

As for the individual station analyzed, the ozone transported from other European regions has a significant contribution to the total MDA8 $O_3$. In both years, major upwind regions that dominate the ozone concentrations in different German receptor regions are central Europe (CEN) (up to 61.5 µg/m$^3$ in 2015 and 42.2 µg/m$^3$ in 2018), France (up to 65.1 µg/m$^3$ in 2015 and 50.3 µg/m$^3$ in 2018), Benelux (up to 18.6 µg/m$^3$ in 2015 and 26.4 µg/m$^3$ in 2018), United Kingdom and Ireland (up to 14.7 µg/m$^3$ in 2015 and 18.9 µg/m$^3$ in 2018) and the Scandinavian Peninsula (up to 18.3 µg/m$^3$ in 2015 and 18.2 µg/m$^3$ in 2018). As in the case of the individual stations, these findings strengthen the idea that a reduction of high $O_3$ pollution could not be achieved without a regional collaboration of controlling emissions sources within Europe.

Shipping activities in the Baltic and North Seas also have a relatively high contribution to the MDA8 $O_3$ calculated in the German receptor regions, up to 15.4 µg/m$^3$ in 2015 and up to 14.7 µg/m$^3$ in 2018 i.e., Schleswig-Holstein. This is consistent with previous work (i.e., Lupaşcu and Butler, 2019, Pay et al., 2019, Aksoyoglu et al., 2016, Jonson et al., 2020) that highlighted the impact of shipping on ozone production near coastal regions. As we saw when we analyze the contribution of shipping for individual stations in Bavaria and Baden-Württemberg, the Baltic and North Seas emissions can contribute to a peak of 1.9 µg/m$^3$ in 2015 and 4.3 µg/m$^3$ in 2015, reinforcing the role of the shipping on ozone predicted in coastal areas as well as the role of meteorology that transports the $O_3$ from these emissions further inland.

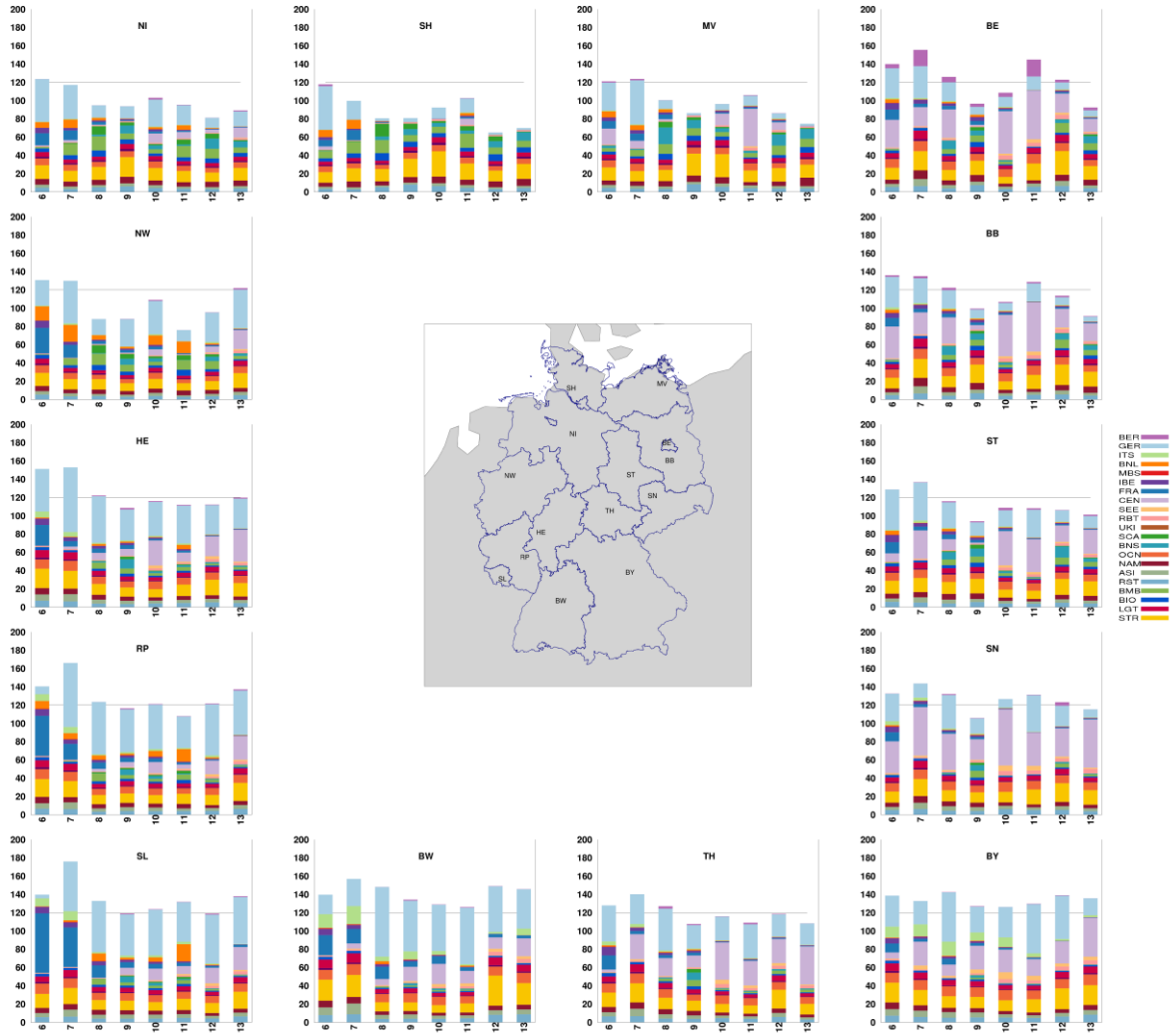


**Figure S10. Mean modeled MDA8 $O_3$ concentration for each German state from different emission sources and types during the 6-13 August 2015 period. In each case, the contributions of $NO_x$-tagged sources to the total MDA8 $O_3$ are shown.**

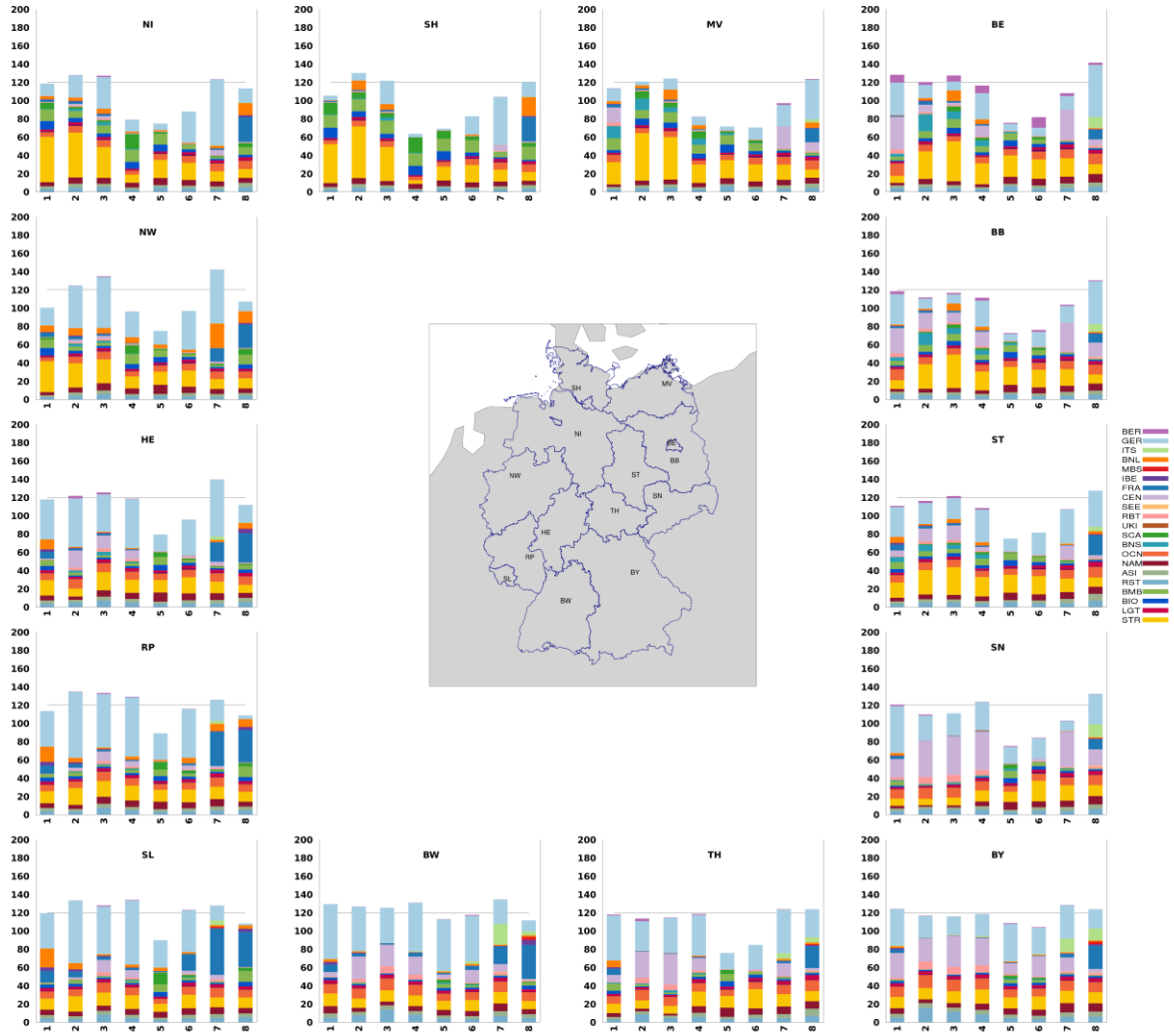


**Figure S11. Mean modeled MDA8 $O_3$ concentration for each German state from different emission sources and types during the 1-8 August 2018 period. In each case, the contributions of $NO_x$-tagged sources to the total MDA8 $O_3$ are shown.**

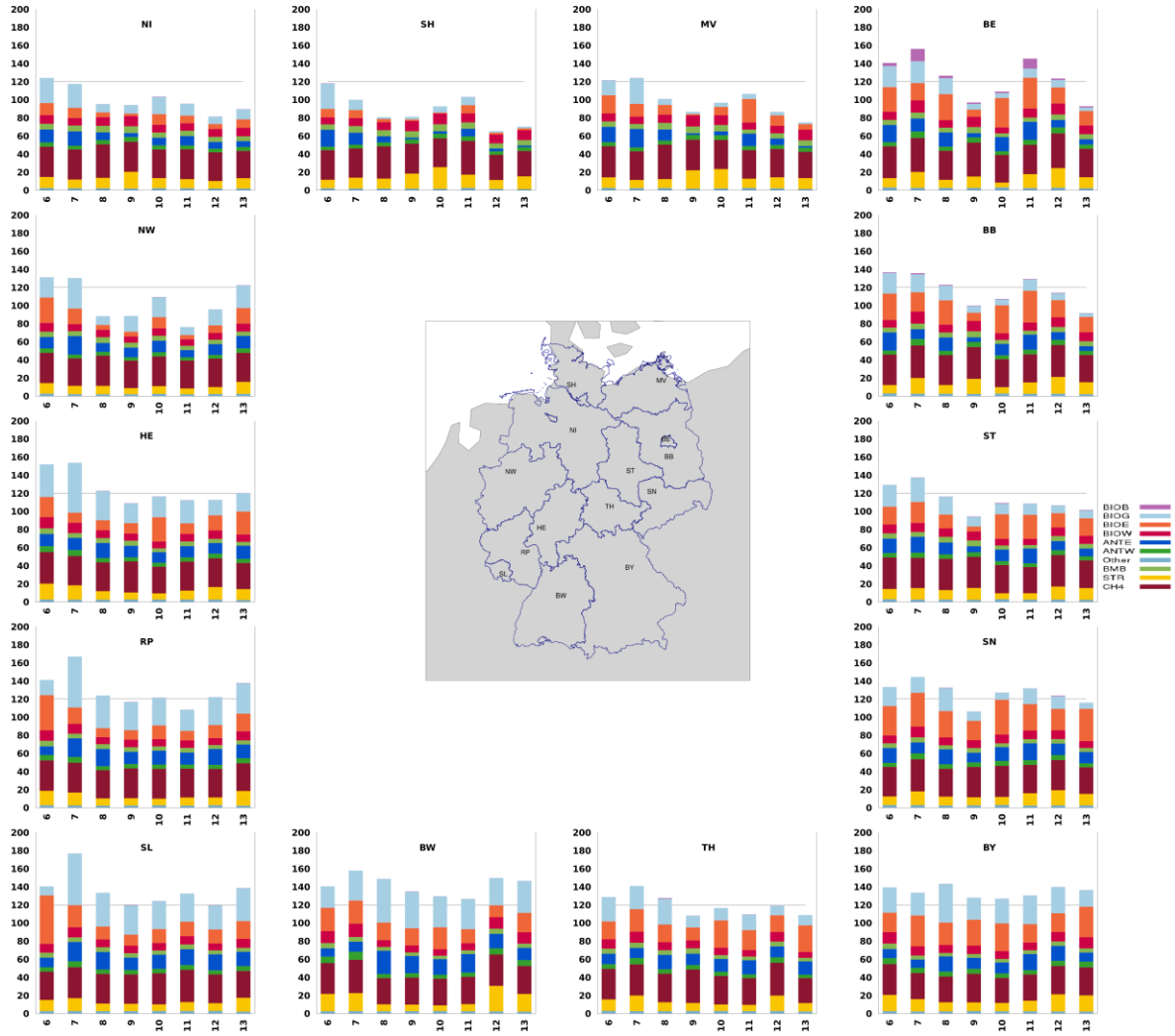


**Figure S12. Mean modeled MDA8 $O_3$ concentration for each German state from different emission sources and types during the 6-13 August 2015 period. In each case, the contributions of VOC-tagged sources to the total MDA8 $O_3$ are shown.**

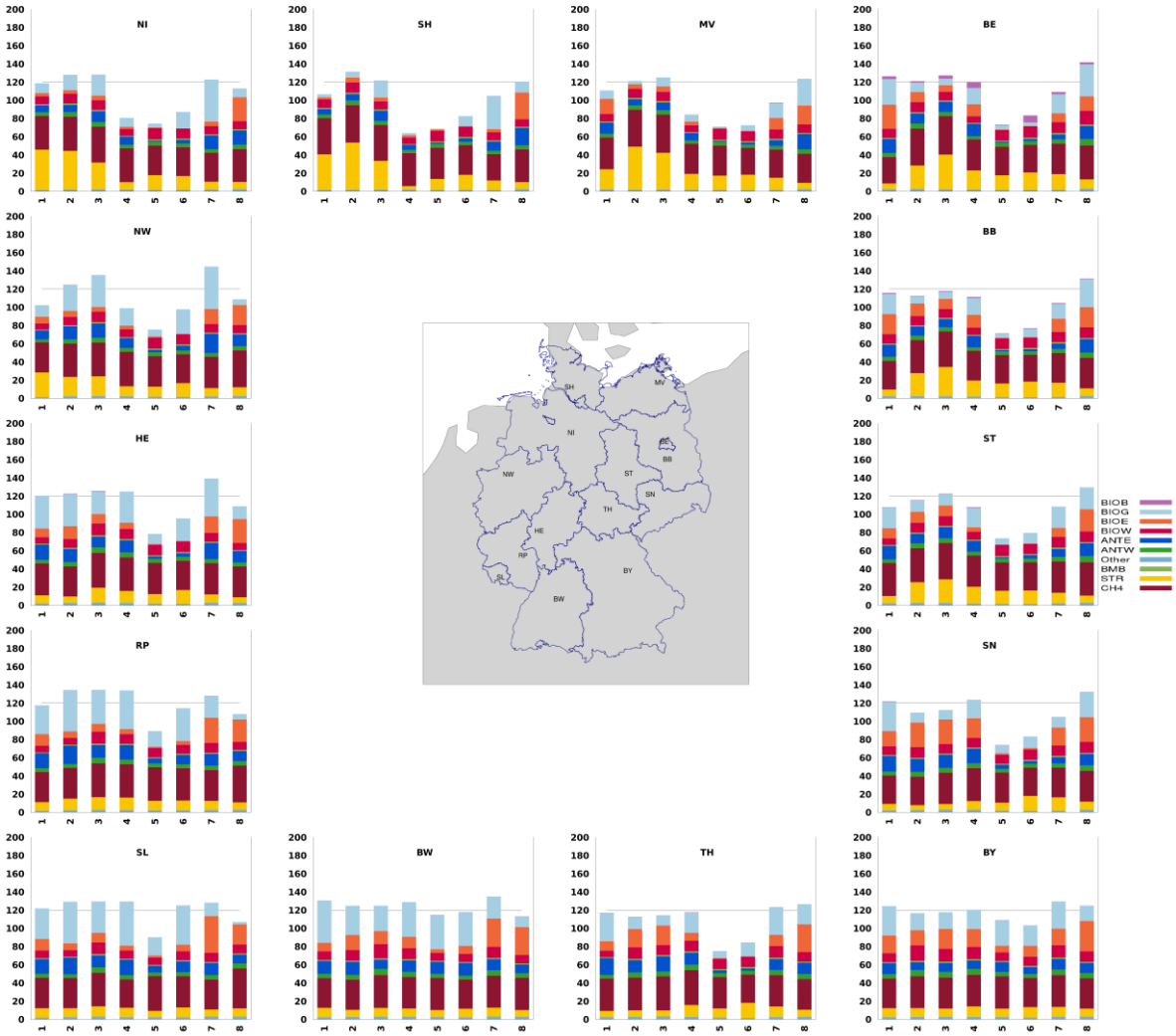


**Figure S13. Mean modeled MDA8 $O_3$ concentration for each German state from different emission sources and types during the 1-8 August 2018 period. In each case, the contributions of VOC-tagged sources to the total MDA8 $O_3$ are shown.**