Stable Carbon Isotope Ratios in Atmospheric VOC during the EMeRGe-EU and ASIA campaigns

M. Krebsbach [1], R. Koppmann[1]

[1]University of Wuppertal, Institute for Atmospheric and Environmental Research, Gaußstr. 20, 42119 Wuppertal, Germany

e-mail: m.krebsbach@ uni-wuppertal.de, koppmann@ uni-wuppertal.de

VOC (volatile organic compounds) play a critical role in the chemistry of the atmosphere. The formation of many important secondary pollutants in the atmosphere, such as ozone, peroxides, aldehydes, and peroxyacyl nitrates and secondary organic particulate matter depends critically on the availability of VOC as their precursors. Many of them have strong direct adverse effects on our environment. The assessment of the impact of VOC on the atmosphere can be significantly improved by measuring their stable carbon isotope ratios. The isotopic composition of compounds emitted by natural or anthropogenic activities vary for emissions from different sources. In almost all atmospheric processes, e.g. chemical reactions, photolytic processes, transport and dilution, diffusion, and phase transitions, the isotopic ratio in VOC is altered. Studying the isotope ratios of both precursors and products makes it possible to distinguish between freshly emitted VOC and photochemically processed compounds, to increase our knowledge of transport versus chemistry, to study the ultimate fate of oxidation products, and to help assess the impact of emissions, e.g. from large population centres (MPCs), on local, regional and even global pollution.

The automated high volume air sampling system MIRAH has been deployed during several missions with the German High Altitude – Long-range research aircraft (HALO). Here we focus on the campaigns EMeRGe-EU and -ASIA (Effect of Megacities on the transport and transformation of pollutants on the Regional and Global scales). The objectives were to measure the pollution emitted, transported and transformed from the MPCs London, BeNeLux, Rhine-Ruhr and Po Valley for the European Part. The second part of EMeRGe was conducted from Taiwan with the goal to investigate the pollution outflow from Asian MPCs such as Taipei, Hongkong, Shanghai, Beijing, Manila, Seoul and Tokio. In both parts a key experiment was the identification of the source of the air masses by collecting whole air samples on ground prior and during particular flights in specific metropolitan regions. On 7 flights in Europe and 12 flights in Asia, mostly below 6 km altitude, more than 140 air samples were collected on HALO during each campaign, and additional 46 samples at specific ground sides. The whole air samples were analysed for mixing ratios and stable carbon isotope ratios of selected aldehydes, ketones, alcohols, and aromatics. This allowed investigating air masses of different origin, characteristic, and atmospheric processing. In this presentation we will give an overview of the data and show exemplary results.

Example for EMeRGe-EU

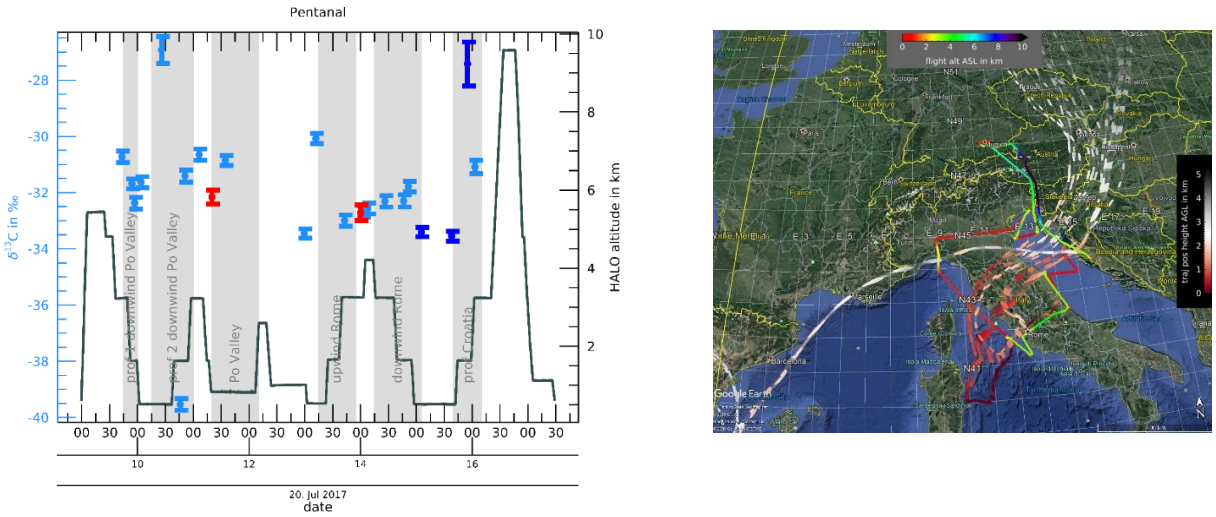


Fig 1.: The right figure shows the HALO flight track on 20th July, 2017, together with 5 days HYSPLIT backward trajectories for the dark blue coloured (left figure) samples downwind of Rome. The flight altitude as well as $\delta^{13}C$ values in Pentanal for the HALO samples (blueish) and for whole air samples on ground collected in Milan and Rome on that day (red) are illustrated in the left figure.

Fig. 1 shows an example for the European part of EMeRGe. Lower carbon isotope ratios indicate fresh emissions, whereas higher values are linked to chemical ageing. During the flight leg up- and downwind of Rome an evolution from lower towards higher $\delta^{13}C$ values in Pentanal is apparent. Moreover, the selected backward trajectories nicely show the different origin (and mean photochemical age) of air masses downwind of Rome. The $\delta^{13}C$ values in Pentanal of the ground site samples (representative source values for Milan and Rome) match with rather fresh emissions encountered downwind of Rome and during the profiles downwind of the Po Valley.

Example for EMeRGe-ASIA

On March 20, 2018, a transport strike took place in protest against the government's environment-friendly transport modernisation program, which mandates that "Jeepney" units aged 15 years and older be replaced by electric-powered or Euro 4-compliant vehicles. Therefore, rather unusual atmospheric conditions were encountered, which could be characterized as relatively "cleaner" in terms of black carbon and diesel exhausts.

The following figure shows an example chromatogram for a whole air sample taken in the Manila boundary layer on that day. In contrast to analyses of air samples taken in Europe, peaks of several compounds are significantly more pronounced.

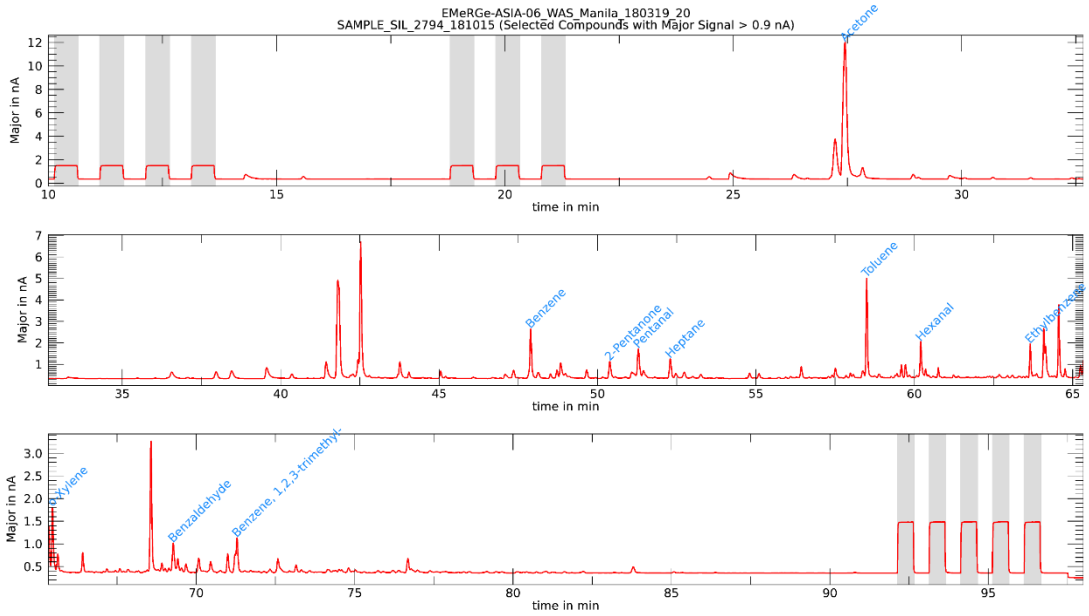
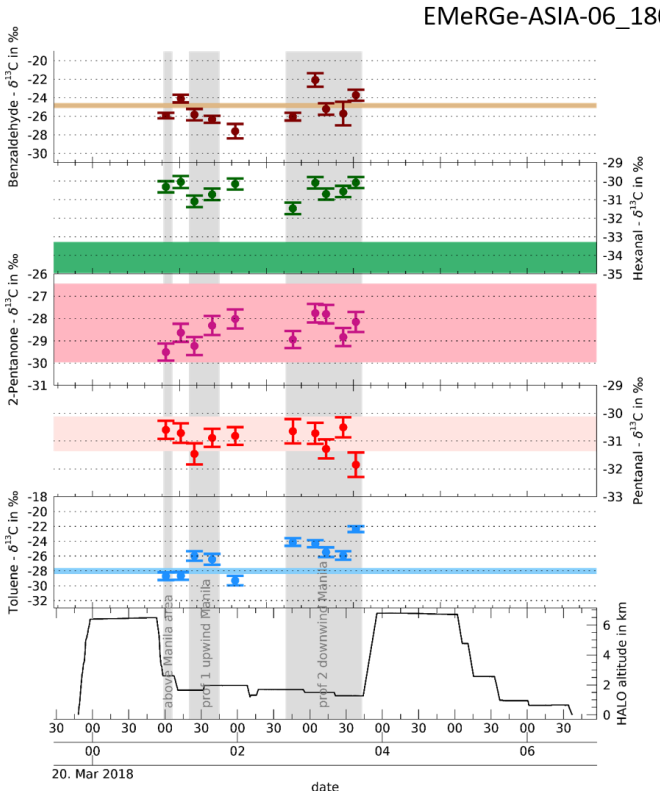


Fig. 2: The figure shows the major signal chromatogram of isotope ratio mass spectrometer for a whole air sample sampled on the One Corporate Center (OCC) building, Julia Vargas corner Meralco Ave. in Pasig City Metro Manila at a rooftop height of 185 m above ground (EMeRGe-ASIA-06_180320).



Toluene: $t \approx 15 - 30\ h$
@ [OH] = 10^6 cm^{-3}

Hexanal: $t \approx 18 - 32\ h$
@ [OH] = 10^6 cm^{-3}

One Corporate Center (OCC) building, Julia Vargas corner Meralco Ave. in Pasig City Metro Manila at a rooftop height of 185 m above ground

Ground based Air Samples: Toluene

Time in UTC	Mixing ratio in ppbv	$\delta^{13}C$ in ‰
19.03.2018		
04:50	594 +/- 9	-29.1
05:05	503 +/- 8	-28.0
06:15	957 +/- 12	-27.4
20.03.2018		
04:40	1463 +/- 16	-26.6
05:00	1426 +/- 16	-27.5

Fig. 3: Carbon isotope ratios in Benzaldehyde, Hexanal, 2-Pentanone, Pentanal and Toluene (left) taken on EMeRGe-ASIA-06_180320 up and downwind of Manila are shown on the left. The table gives the estimated mixing ratios and $\delta^{13}C$ values for toluene of the ground based measurements (source values).

An estimation of the average atmospheric residence (transport) times results in 15-30 h for Toluene and 18-32 h for Hexanal.

Eight days later (EMeRGe-ASIA-10_180328) whole air samples were collected at the Institute of Environmental Science and Meteorology (IESM) building (14.648054 N, 121.070255 E) at a rooftop height of 75.4 m above sea level in Manila. On that day, rather “normal conditions” were encountered.

A glance at the scale shows the significantly higher values for special compounds. Toluene even exceeds the detection capacity of the IRMS. Consequently, air samples taken on the HALO aircraft show much higher concentrations than during the campaign in Europe.

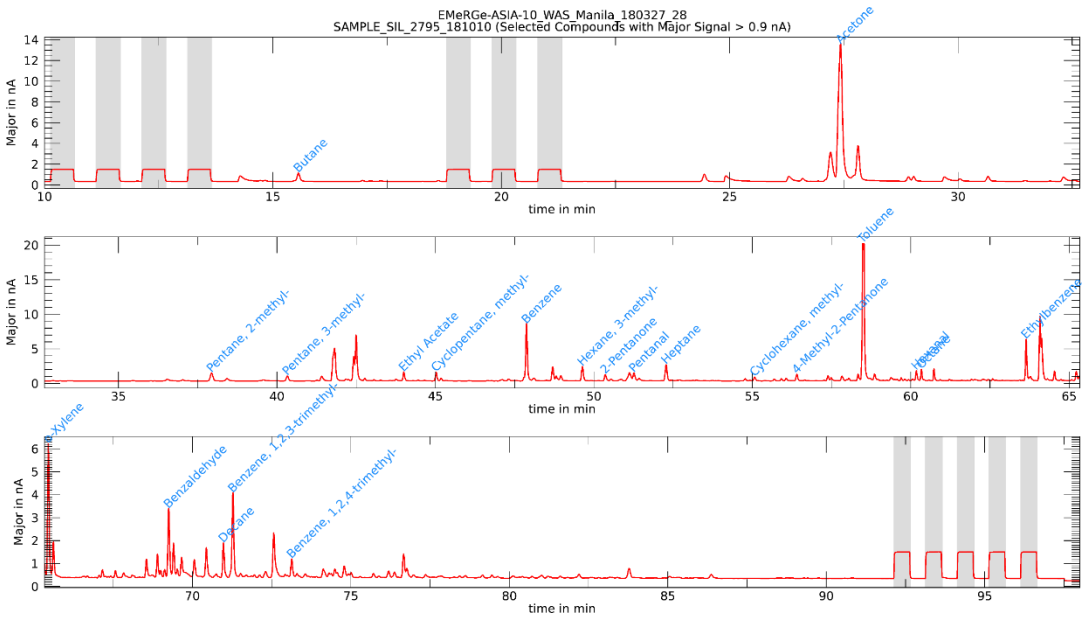


Fig. 4: As the previous figure but for a whole air sample sampled at the Institute of Environmental Science and Meteorology (IESM) building (14.648054 N, 121.070255 E) at a rooftop height of 75.4 m above sea-level in Manila (EMeRGe-ASIA-10_180328).

In the following figure, $\delta^{13}C$ values for Pentanal and Toluene are shown together with the HALO flight track for that day.

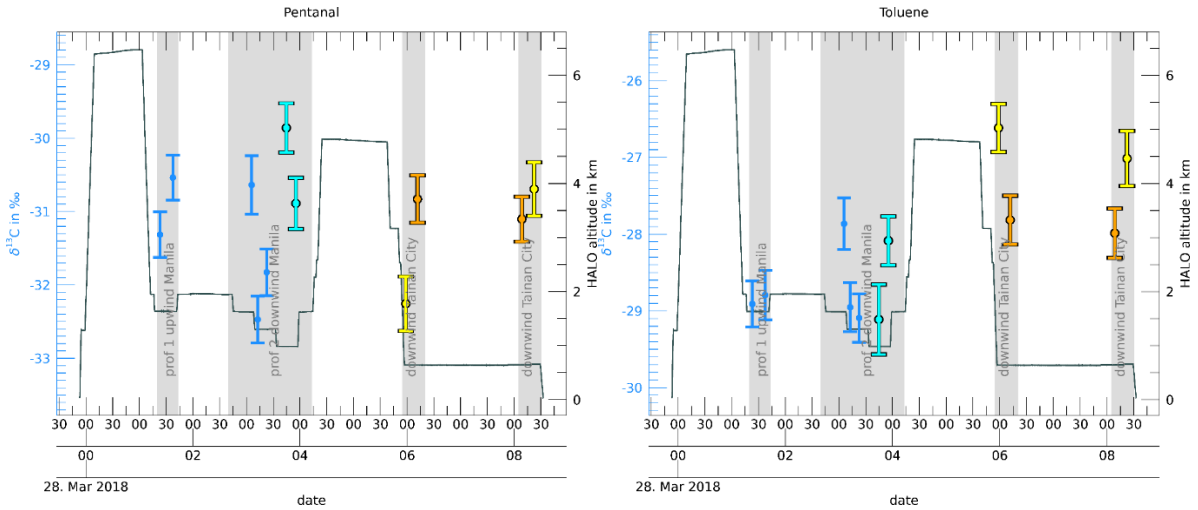


Fig. 5: Carbon isotope ratios in Toluene (left) and Pentanal (right) taken on EMeRGe-ASIA-10_180328 up and downwind of Manila as well as downwind of Tainan City.

$\delta^{13}C$ values for both compounds (Pentanal and Toluene) show the same structure for the blue and orange marked air data points. The consecutive measurements for the cyan and yellow data points is anticorrelated. The $\delta^{13}C$ values of Toluene and Pentane are in the same range as in the European sector but mixing ratios are significantly enhanced.

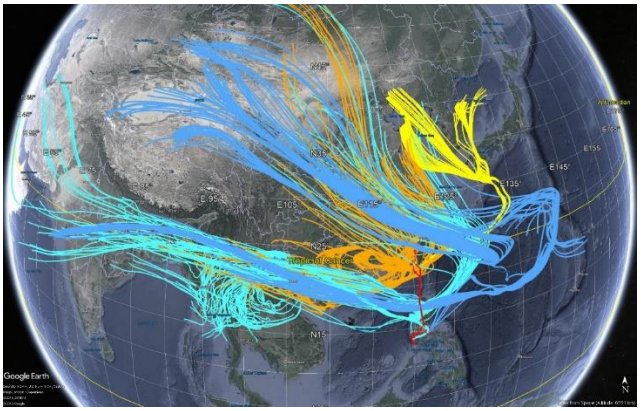


Fig. 6: HALO track on 28th Mar 2018 together with 7 days HYSPLIT backward trajectories for the colour coded samples in Fig. above

Short summary

The analysis of the chromatograms is tricky and very time consuming. Especially during the EMeRGe-ASIA part there seems to be a lot of mixing of processed air masses and fresh emissions. We have to find the right tracers to identify local pollution. With the right values for the kinetic isotope effect of selected compounds, we have to calculate atmospheric residence or transport times of the compounds of interest. The interpretation of the isotope ratios in the current stage is a very big challenge. However, a first rough estimate of the analyses of certain flight segments illustrates the value of the additional information provided by isotope ratios. We still have a lot of work to do.

This work was supported by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG Priority Program SPP 1294) under grant-No. KR3861/1-1.