

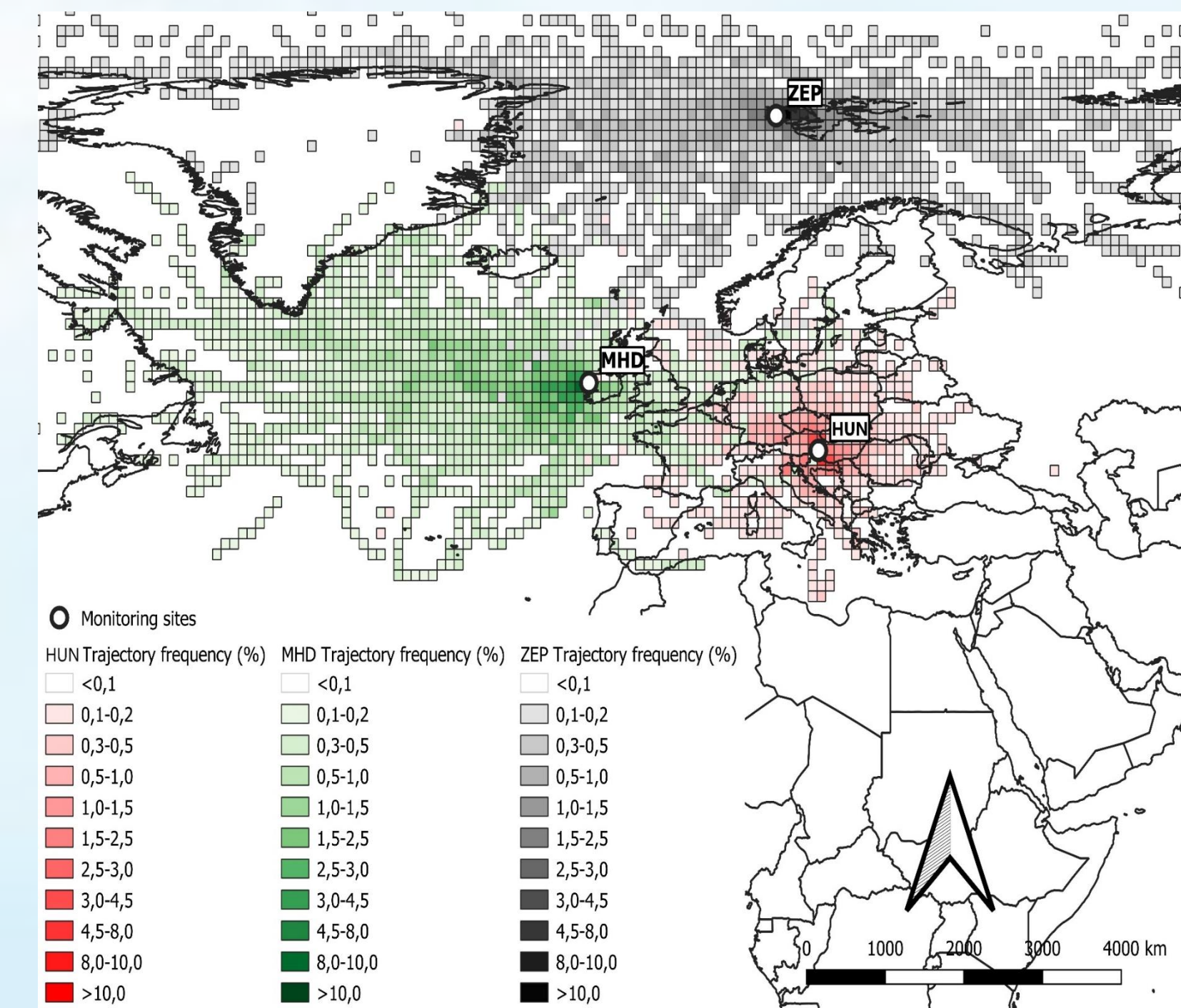
Identification of potential methane source regions in Europe using $\delta^{13}\text{C}_{\text{CH}_4}$ measurements and trajectory modeling

Tamás Varga^{1,2}, László Haszpra³, István Major¹, Euan G. Nisbet⁴, David Lowry⁴, Rebecca E. Fisher⁴, A.J. Timothy Jull^{1,5,6}, Mihály Molnár¹, Elemér László^{1*}

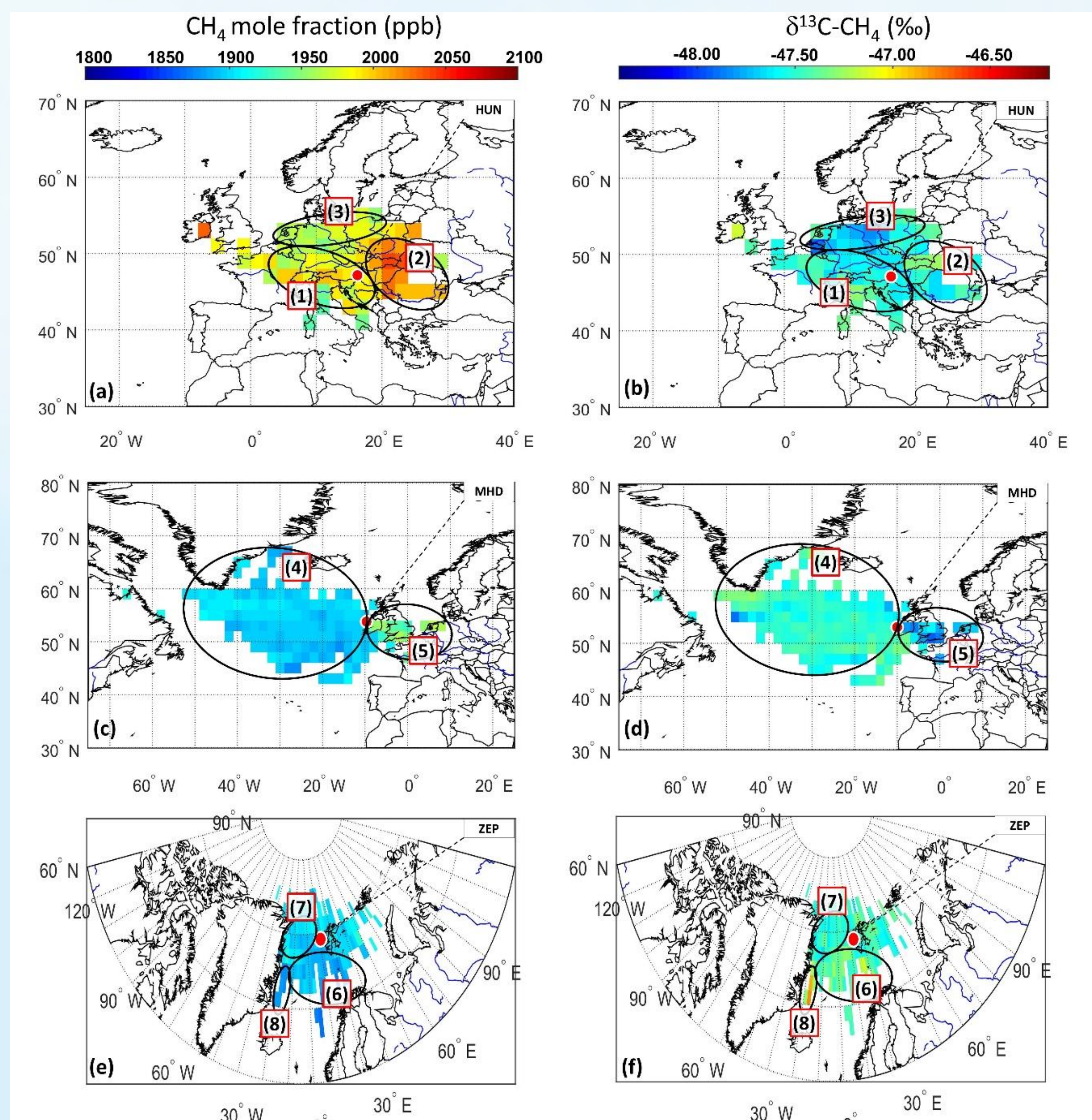
¹Isotope Climatology and Environmental Research Centre (ICER), Institute for Nuclear Research, Hungarian Academy of Sciences, Debrecen, 4026, Hungary ²University of Debrecen, Doctoral School of Physics, Debrecen, Hungary ³Research Centre for Astronomy and Earth Sciences, Geodetic and Geophysical Institute, Sopron, Hungary ⁴Royal Holloway, University of London, Department of Earth Sciences, Egham, Surrey, UK ⁵Department of Geosciences, University of Arizona, Tucson, AZ 85721 USA ⁶University of Arizona AMS Laboratory, Tucson, AZ 85721 USA

Abstract

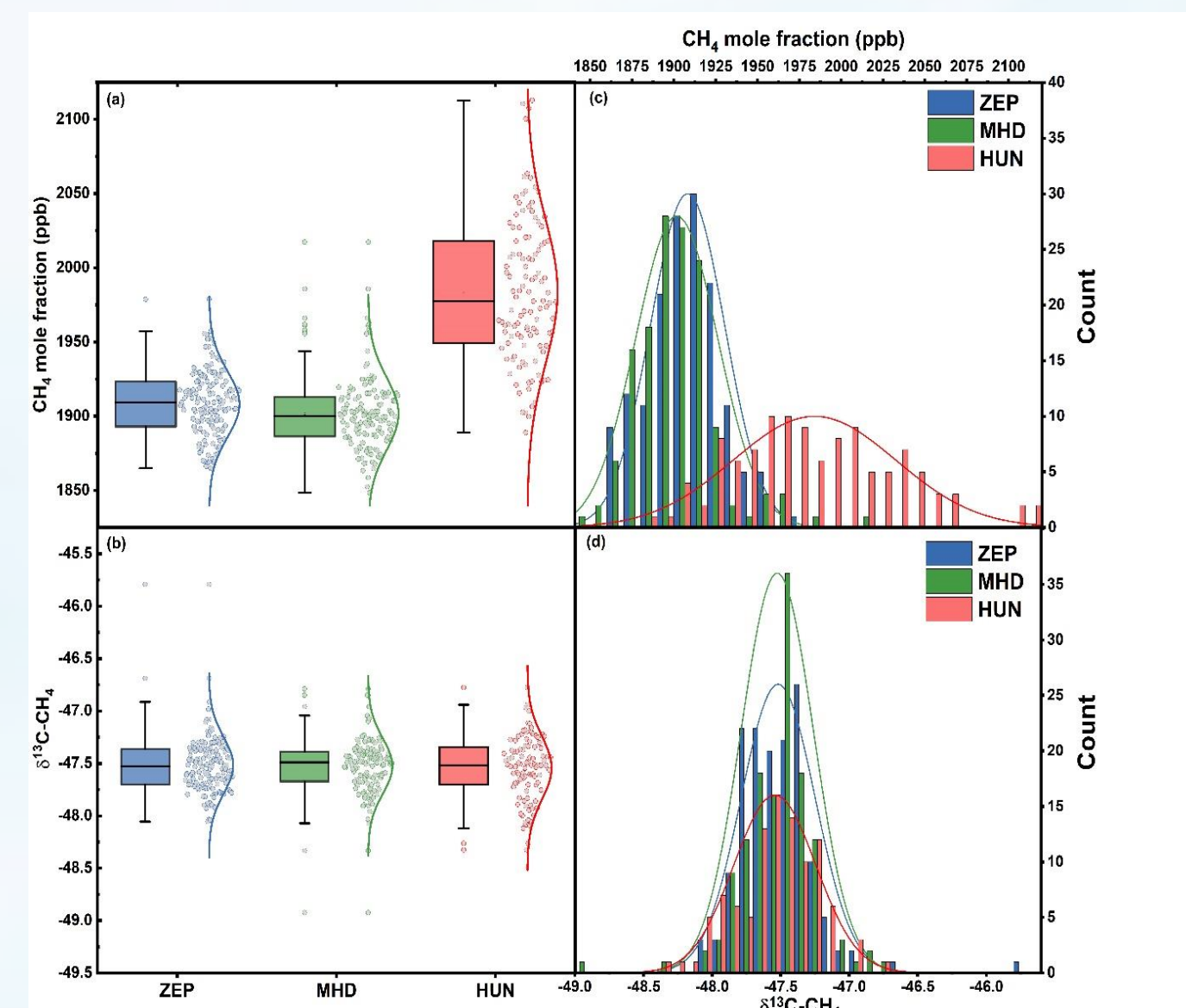
- Discrete sampling in a central European sampling site (Hegyhátsál/Hungary/HUN) for CH_4 mole fraction and $\delta^{13}\text{C}_{\text{CH}_4}$ measurement
- Comparison with two NOAA sampling site (Mace Head/Ireland/MHD, Zeppelin/Svalbard/ZEP)
- Cross-wavelet transform analysis for the determination of the phase shift between the mole fraction and stable isotope time series
- HYSPLIT air mass trajectory and concentration weighted source area modeling for the determination of potential CH_4 source areas in Europe



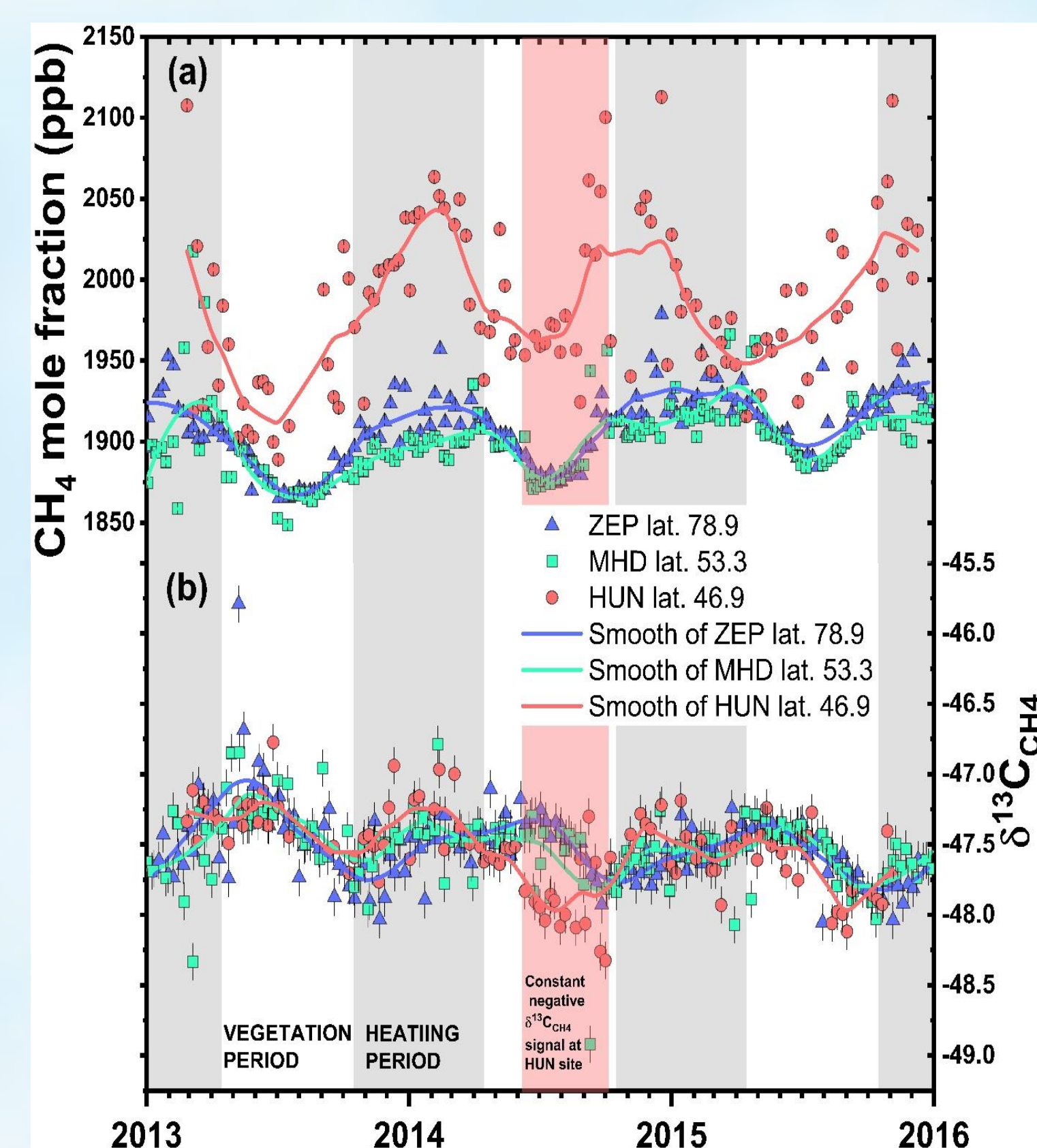
Potential source area analysis



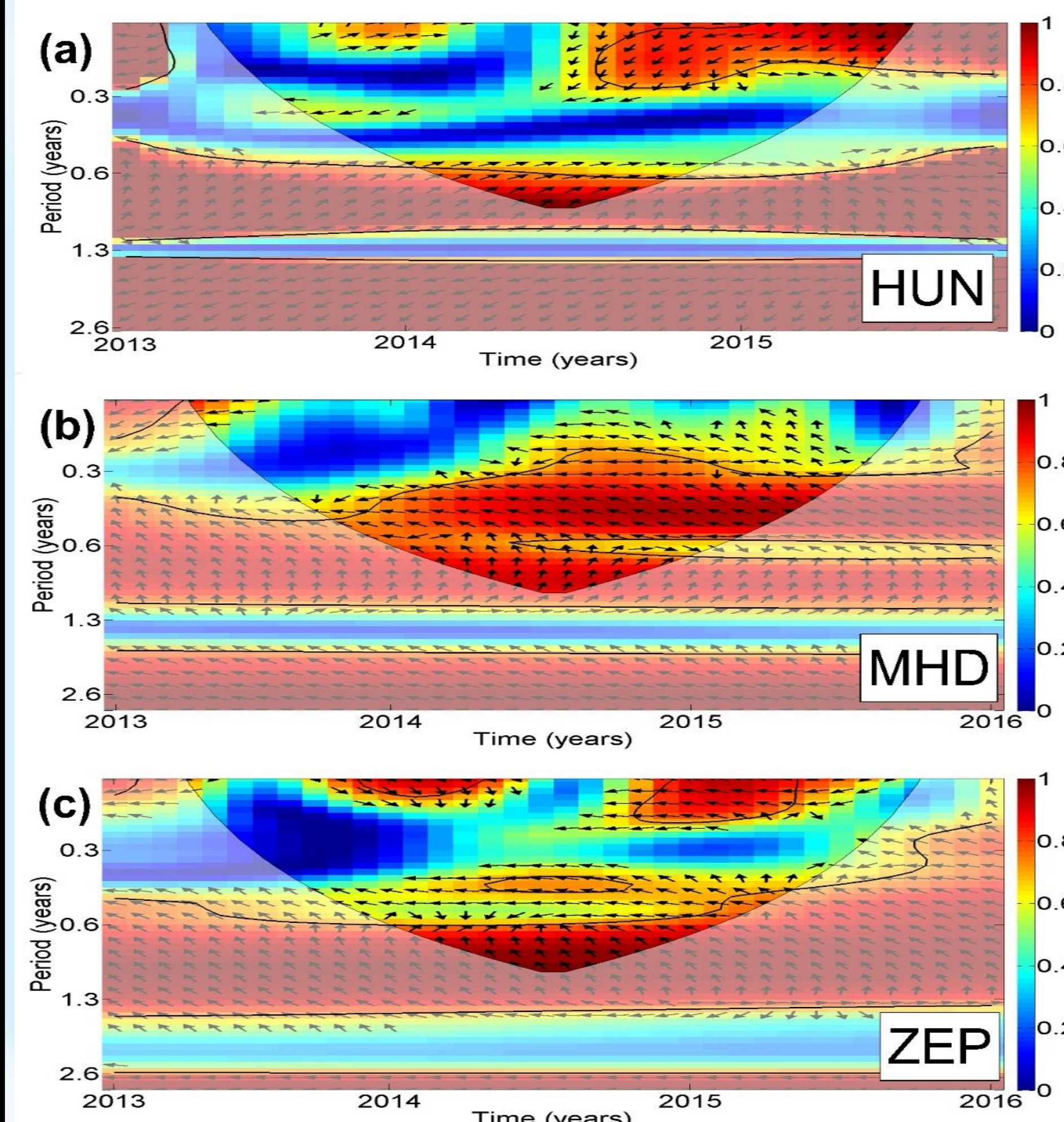
Temporal and spatial variation of CH_4 mole fraction and $\delta^{13}\text{C}_{\text{CH}_4}$ values



- Between 2013-2016, the mean CH_4 mole fraction was 1984 ± 48 ppb at the HUN station, 1908 ± 22 ppb at MHD and 1901 ± 22 ppb at ZEP.
- The distribution of the measured CH_4 mole fraction values covers a wider range at the HUN site.
- CH_4 mole fraction higher than 2000 ppb at HUN station is often observed during the monitoring campaign.
- The amplitude of seasonal variation is much higher at the HUN site than at the coastal or polar area, as a result of the proximity of several seasonally-intensive methane emission sources, and also because of the planetary boundary layer (PBL) varies more intensely in the HUN continental interior site.
- $\delta^{13}\text{C}_{\text{CH}_4}$ values of the HUN site fit in well the regional range and temporal variation, although high values can be observed at every site.
- During the vegetation period of 2014 and 2015, when the activity of biogenic sources, such as wetlands and microbial activity at the continental area (at HUN site) enhanced, with strongly negative carbon stable isotopic composition, the $\delta^{13}\text{C}_{\text{CH}_4}$ trended more negative compared to the ZEP and MHD sites.
- This period shows that there was a significant biogenic emission in central Europe, compared to the marine background



Cross-Wavelet transformation for CH_4 mole fraction - $\delta^{13}\text{C}_{\text{CH}_4}$ time series



Coherences with 1-year periodicity at HUN, MHD, and ZEP stations can be identified. The $\delta^{13}\text{C}_{\text{CH}_4}$ follows the CH_4 mole fraction changes with different phase shifts, indicated by the arrows in figure. The 45° phase shift indicates that the changes in the $\delta^{13}\text{C}_{\text{CH}_4}$ stable-isotope ratio follow the CH_4 mole fraction changes with ~ 2 -months delay at the HUN station, while the 85° and 95 - 100° phase shifts indicate ~ 6 and ~ 7 months delay at the MHD and ZEP stations.

Hegyhátsál
Hungary (HUN)
Mace Head
Ireland (MHD)
Zeppelin
Svalbard (ZEP)

- Source regions were identified in the continental, marine, and polar areas.
- The western European region is densely populated with significant industrial activity. This area could be affected by the northern Italian industrial region or more distant western areas.
- The eastern region, with a higher CH_4 mixing ratio (< 2000 ppb) coupled with bulk or slightly depleted, below -47.5 ‰ $\delta^{13}\text{C}$ signal. This region includes the largest river wetland in Europe, the Danube Delta. The eastern areas, between the Carpathian Basin and the Black Sea, have significant natural gas production and also geological seeps.
- The middle and northeast Carpathian Basin region is affected by industrial activity, also affected by the multiple emission sources in the region of the capital city of Hungary, Budapest.
- The northwestern and northern central European region, the $\delta^{13}\text{C}_{\text{CH}_4}$ isotopic signal is depleted compared to the surrounding area (> -47.6 ‰ $\delta^{13}\text{C}_{\text{CH}_4}$). This area has significant industrial activity and it is surrounded by intensively cultivated areas, population with high ruminant numbers, and significant pig manure emission.
- Atlantic Ocean region, that has a low CH_4 mole fraction with a bulk carbon isotopic ratio (~ -47.5 ‰ $\delta^{13}\text{C}_{\text{CH}_4}$).