

Electronic Supplementary Information (ESI) to
Remarkably constant PAH concentrations in Swiss soils over the last 30 years

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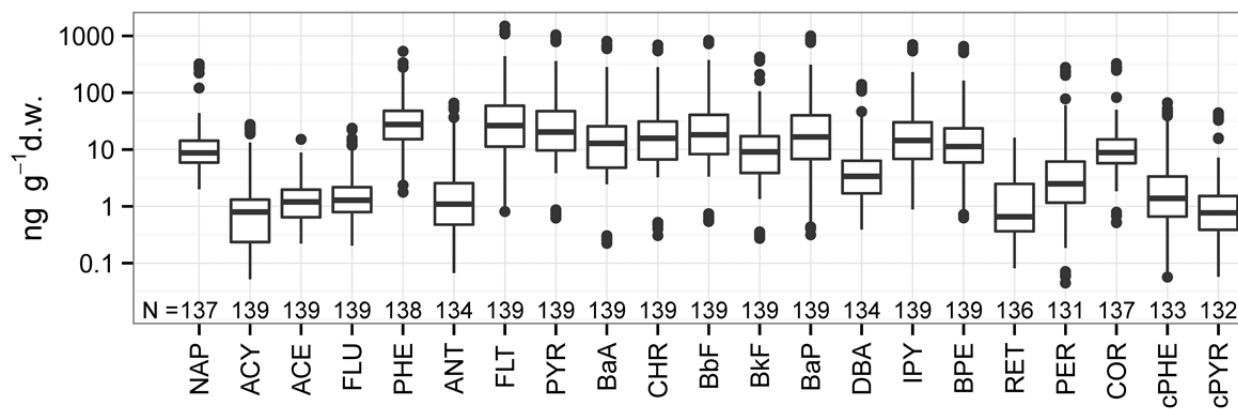


Figure S1. Boxplots of mean concentrations per site and campaign for PAH substances. Abbreviations: ACE: acenaphthene; ACY: acenaphthylene; ANT: anthracene; BaA: benz[a]anthracene; BaP: benzo[a]pyrene; BbF: benzo[b]fluoranthene; BkF: benzo[k]fluoranthene; BPE: benzo[ghi]perylene; CHR: chrysene; COR: coronene; cPHE: 4-H-cyclopenta[def]phenanthrene; cPYR: cyclopenta[cd]pyrene; DBA: dibenz[a,h]anthracene; FLT: fluoranthene; FLU: fluorene; IPY: indeno[1,2,3-cd]pyrene; NAP: naphtalene; PER: perylene; PHE: phenanthrene; PYR: pyrene; RET: retene.

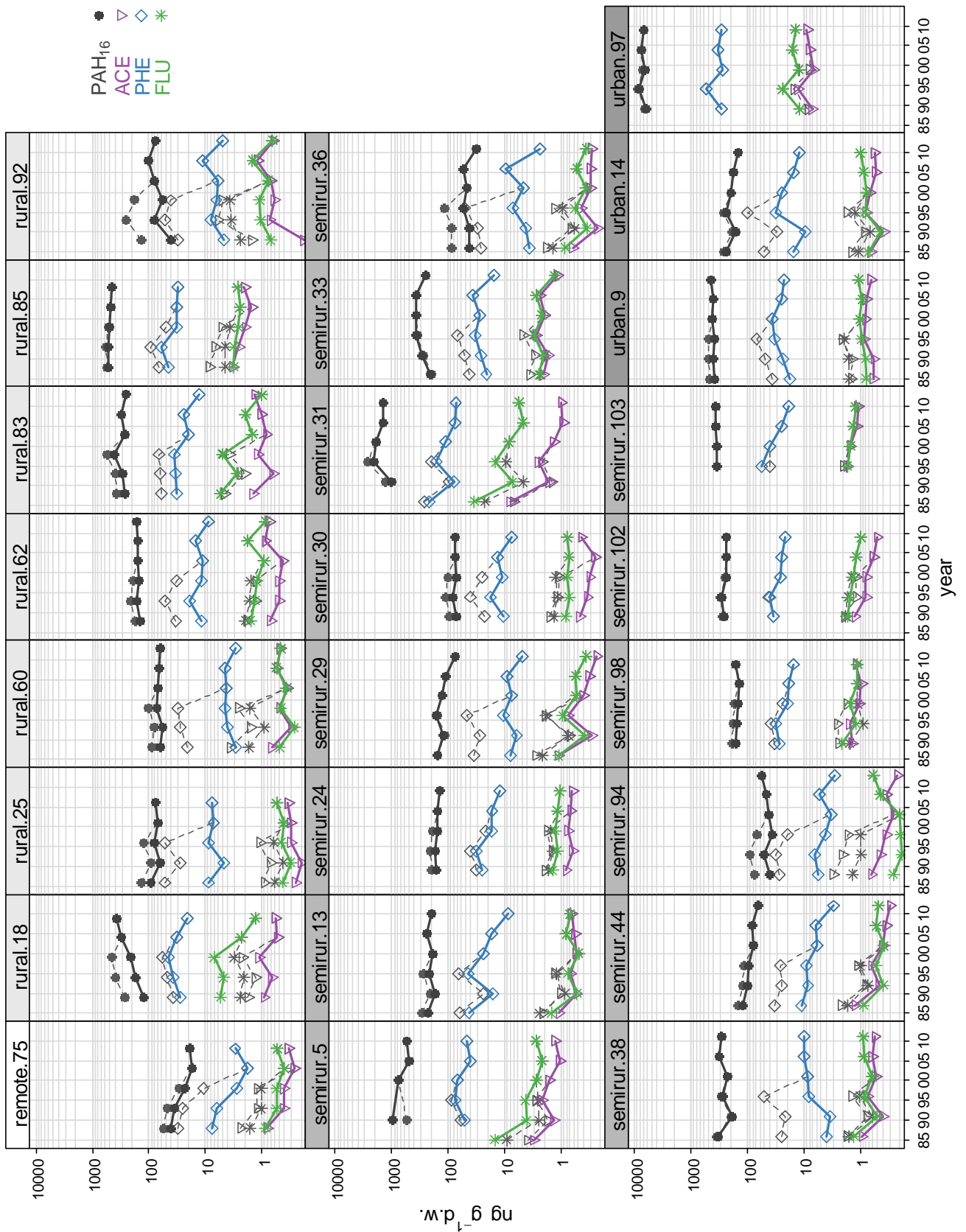


Figure S2. Temporal evolutions of the sum of 16 PAH (ΣPAH_{16}), acenaphthene (ACE), phenanthrene (PHE), and fluorene (FLU) with (coloured lines and symbols) and without correction (grey lines and symbols) of artefacts introduced by sample preparation.

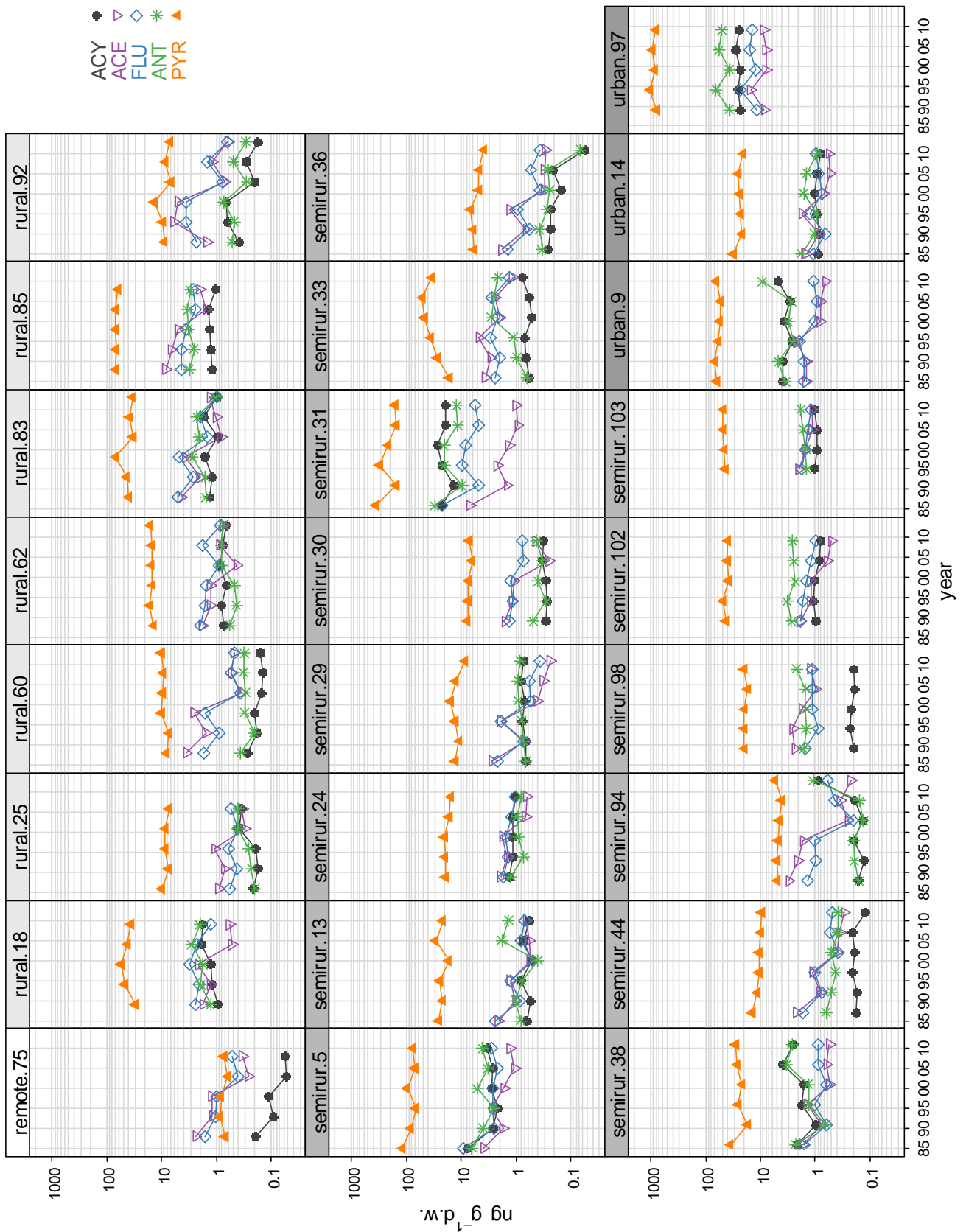


Figure S3. Temporal evolutions 1985-2013 for topsoil 0-20 cm of acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), anthracene (ANT), and pyrene (PYR) for long-term monitoring sites. Displayed values represent mean values of two measurements per site and sampling.

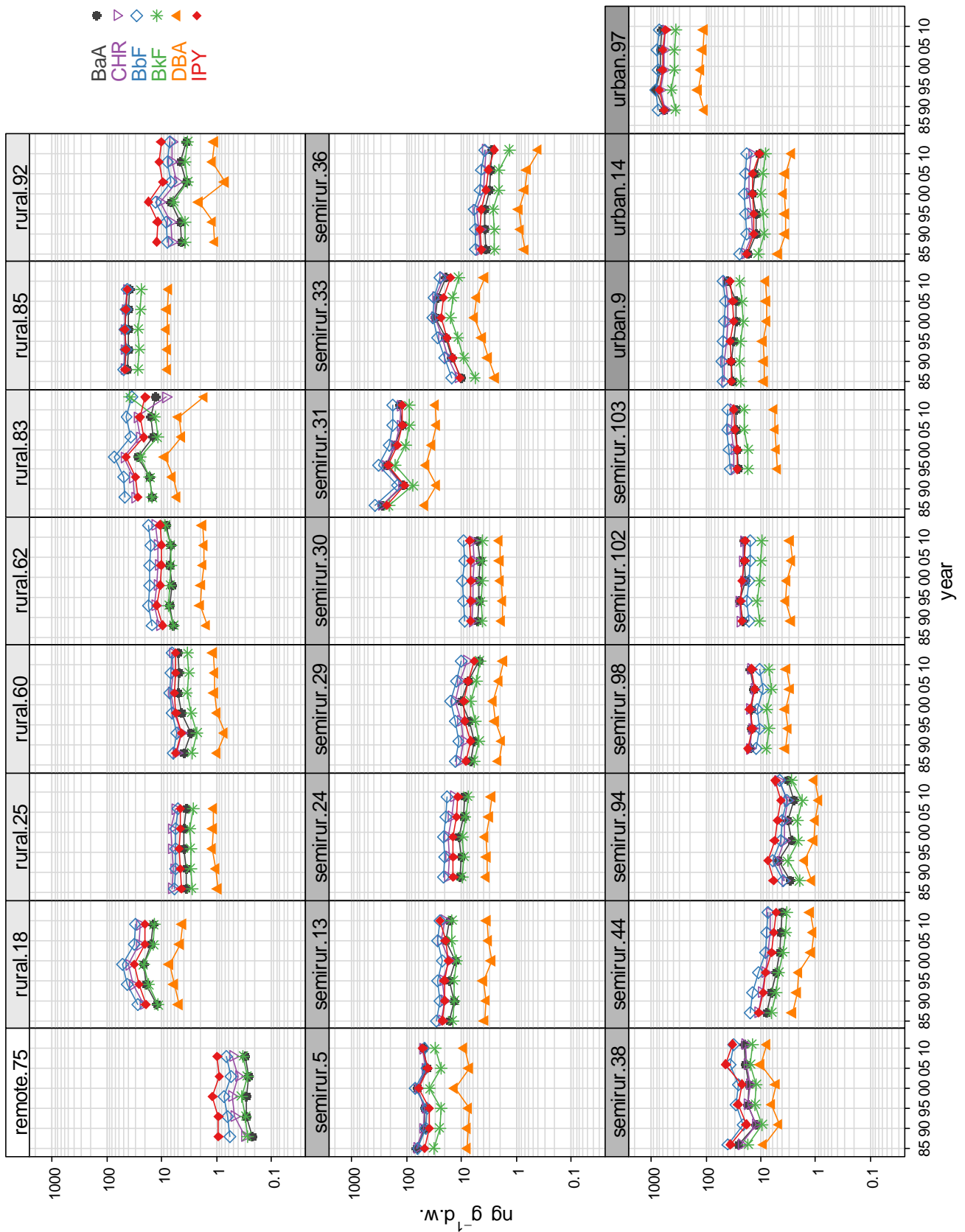


Figure S4. Temporal evolutions 1985-2013 for topsoil 0-20 cm of benz[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), dibenz[*a,h*]anthracene (DBA), and indeno[1,2,3-*cd*]pyrene (IPY) for long-term monitoring sites. Displayed values represent mean values of two measurements per site and sampling.

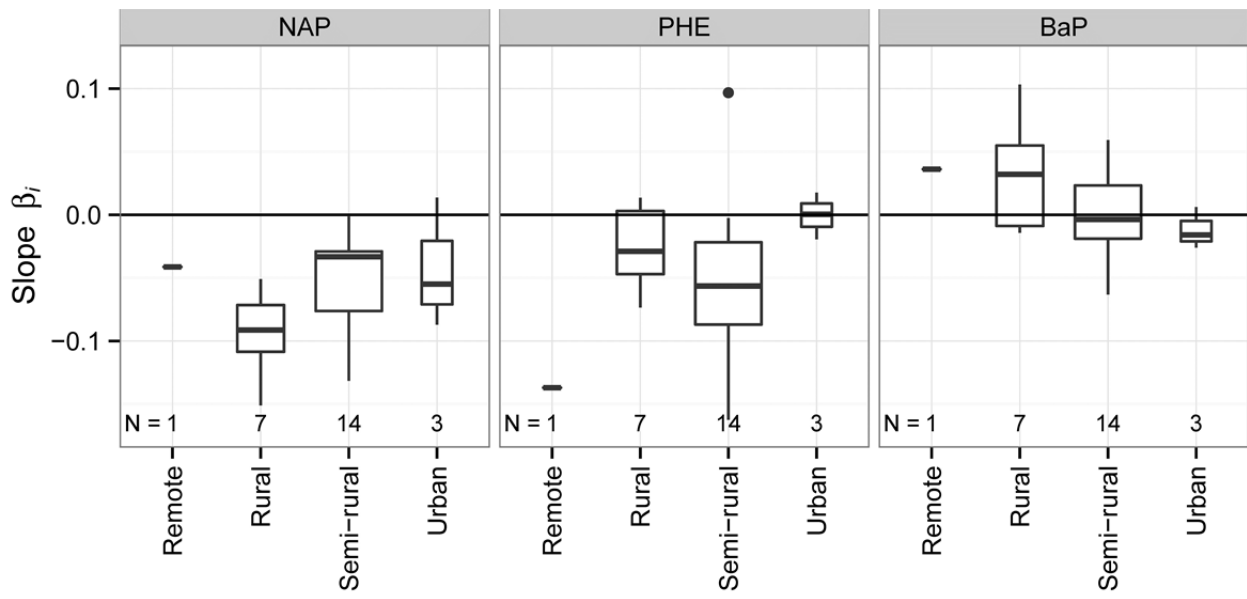


Figure S5. Slopes β of naphthalene (NAP), phenanthrene (PHE), and benzo[*a*]pyrene (BaP) with respect to exposure classes (remote, rural, semi-rural, and urban).

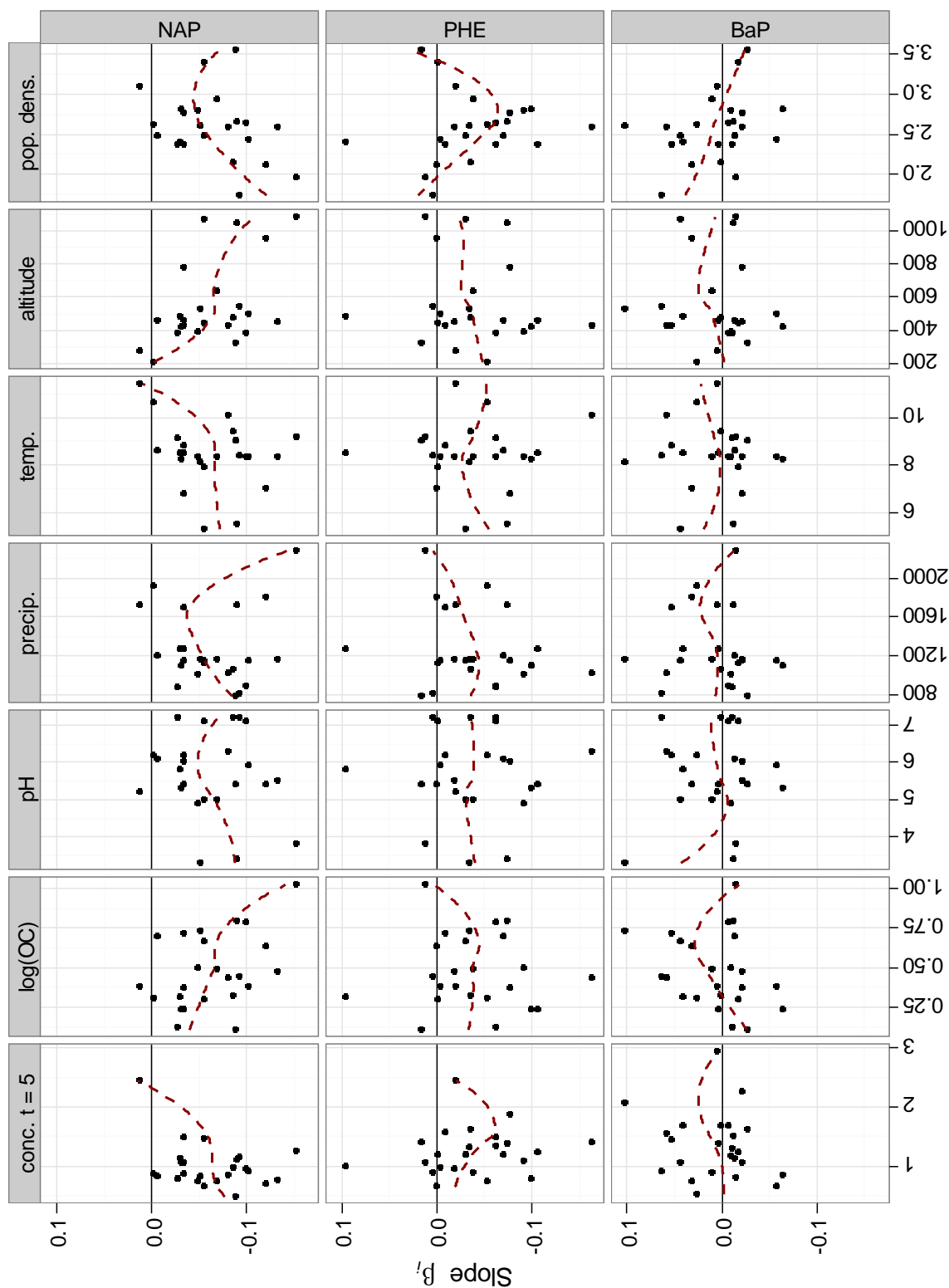


Figure S6. Slopes β per site for naphthalene (NAP), phenanthrene (PHE), and benzo[a]pyrene (BaP) compared with the site characteristics: concentration in fifth sampling campaign (conc. t = 5), \log_{10} of organic carbon (mean over time series; log(OC)), soil acidity (pH), annual mean precipitation (mm; precip.), annual mean temperature ($^{\circ}$ C; temp.), altitude (m above sea level), and population density (inhabitants per square km within a radius of 5 km around the monitoring site; op. dens.). The remote site 75 was excluded due to its outlying characteristics.

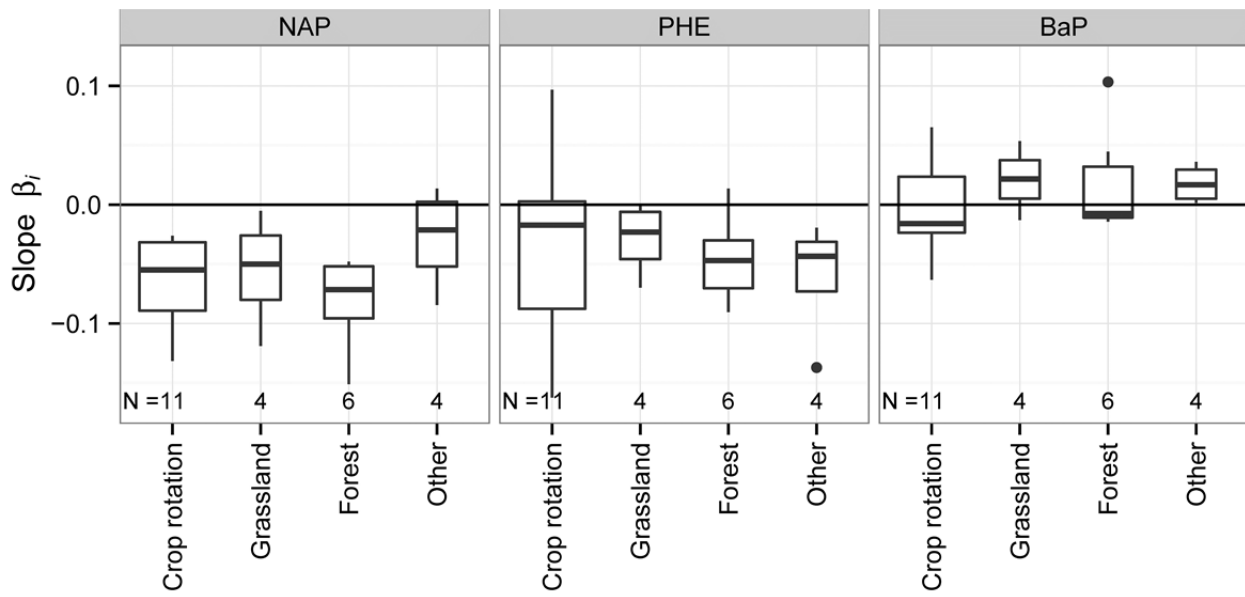


Figure S7. Slopes β of naphthalene (NAP), phenanthrene (PHE), and benzo[*a*]pyrene (BaP) with respect to land use (crop rotation, permanent grassland, forest, and other).

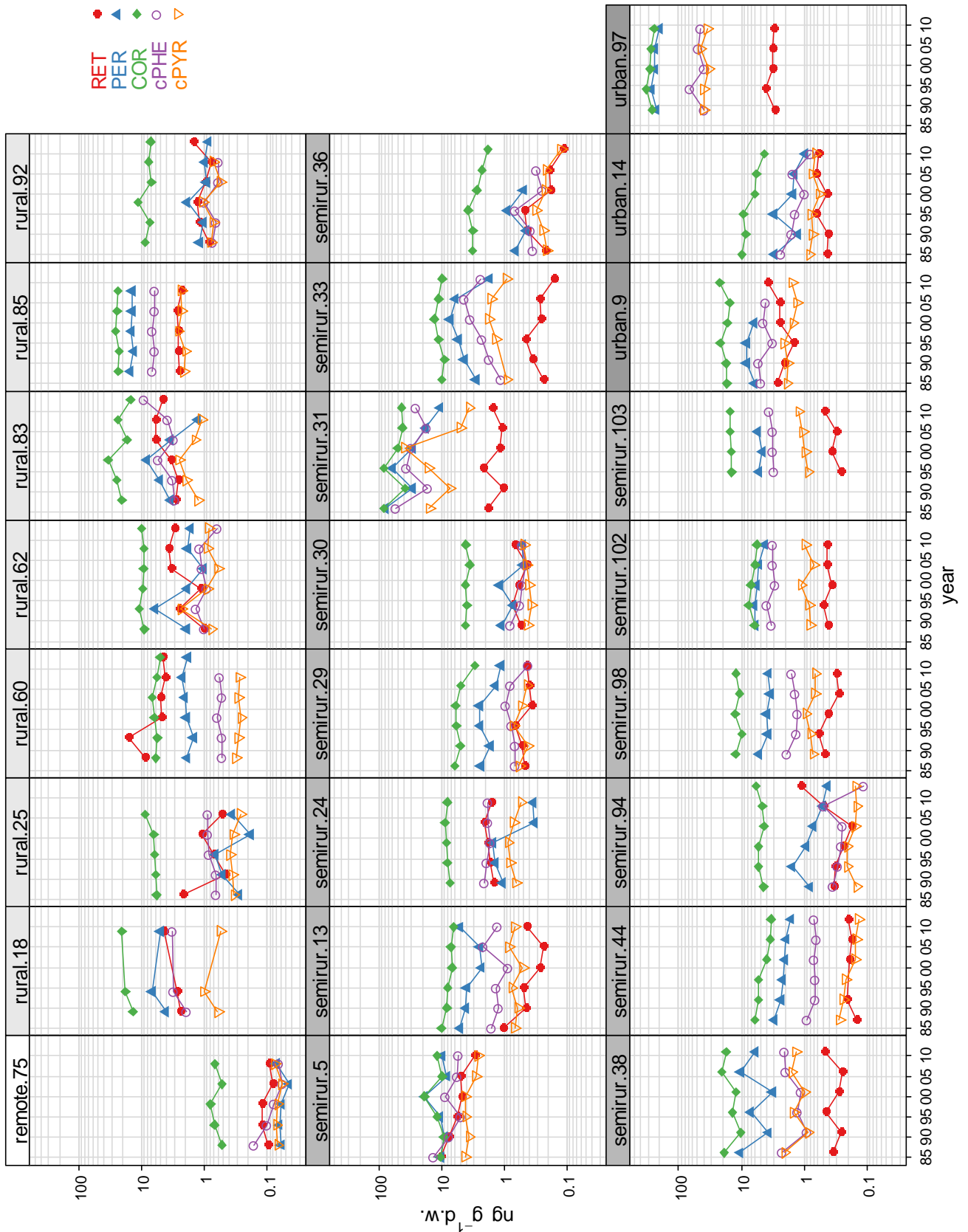


Figure S8. Temporal evolutions 1985-2013 of the marker substances coronene (COR), 4-H-cyclopenta[def]phenanthrene (cPHE), cyclopenta[cd]pyrene (cPYR), perylene (PER), and retene (RET) for topsoil 0-20 cm of long-term monitoring sites. Displayed values represent mean values of two measurements per site and sampling.

1 Additional information regarding specific monitoring sites

1.1 Site 75

The remote site 75 located within the Swiss National Park near Zernez showed the lowest $\sum\text{PAH}_{16}$ contents of all sites considered for the present study. Concentrations declined from 54 ng g⁻¹ d.w. in 1988 to 19 ng g⁻¹ d.w. in 2008. While concentration levels for the light congeners NAP, ACE, FLU, and PHE are comparable to those found at rural and semi-rural sites, concentrations for the remaining PAH (including markers) were ten times smaller, at least. In 1988, NAP and PHE contributed 25 and 58%, respectively, to $\sum\text{PAH}_{16}$. In 2008, their contributions were 49 and 16%, respectively. The high portions of light PAH relative to $\sum\text{PAH}_{16}$ are attributed to the remoteness of the site, as light PAH are transported over much longer ranges than heavy PAH.¹ Concentrations of heavy PAH stagnated at low levels over the whole observation period, whereas all light PAH from ACY to PHE as well as cPHE decreased considerably (for ANT and DBA, no data are available due to very low concentrations). From 1988 until 2008, NAP and PHE concentrations decreased from 13 to 9 and from 31 to 3 ng g⁻¹ d.w., respectively. While NAP was declining linearly over the whole period, very pronounced declines between 1998 and 2003 followed by slight re-rises were observed for ACY, ACE, FLU, and PHE. The samples for the fourth sampling were collected at the end of summer in 2003 that was an extraordinary hot year. For this region (Engadin, meteorological station of Segl-Maria), an annual mean temperature elevated by almost 2°C compared to the average per ten years (1998 until 2008) and 25% less precipitation were recorded.² Hence, reduced wet deposition and enhanced degradation and re-volatilisation of semi-volatile PAH are assumed for 2003.

1.2 Site 97

Site 97 is located at an urban park near the lake in the city centre of Lugano. It exhibits elevated PAH concentrations that remained unchanged over the whole observation period from 1989 to 2009 (around 7000-8000 and 800-900 ng g⁻¹ d.w. for $\sum\text{PAH}_{16}$ and BaP, respectively). The origin of the PAH remains unclear. Besides the common immisions related to the urban location and those from large passenger boats stopping at a near-by shipping pier, historical direct inputs are thinkable. Comparing the found PAH distribution with profiles provided by Brändli et al. (SI)³ suggests wood ash, asphalt binders, coal tar, and soot from diesel and gasoline as possible sources. (Besides, the site features elevated contents in heavy metals with concentrations of 140, 55, and 120 mg g⁻¹ d.w. for zinc, copper, and lead.) Data collected closed to the monitoring site (but in a larger distance to the lake) revealed PAH air concentrations comparable to other cities and semi-rural sites.⁴

1.3 Site 103

Based on inventory data,⁵ we concluded in the main text that PAH emissions from traffic are of minor importance compared to those from biomass combustion. Nevertheless, we assume traffic as the main reason for the increases of heavy PAH (PYR to BPE) and ANT observed at site 103, e.g. topsoil concentrations of BaP increased from 29 up to 44 ng g⁻¹ d.w. between 1995 and 2010. This site is located near Härkingen in a distance of only 15 m to a much frequented highway (on average 85'000 vehicles per day in 2010).⁶ Data of the National Air Pollution Monitoring Network (NABEL)⁴ measured at the same site showed no particularities; concentrations in air and the relative proportions of single PAH were comparable to other semi-rural and urban locations. The site has been used as cropland, but as stated in the main text, PAH inputs via manure and sewage sludge are not expected to cause increases of that magnitude.

References

- 1 I. J. Keyte, R. M. Harrison and G. Lammel, *Chem. Soc. Rev.*, 2013, **42**, 9333–9391.
- 2 MeteoSwiss, Homogeneous data - Monthly homogenized values of the station Segl-Maria, http://www.meteoschweiz.admin.ch/product/output/climate-data/homogenous-monthly-data-processing/data/homog_mo_SIA.txt, (accessed June 2015).
- 3 R. C. Brändli, T. D. Bucheli, S. Ammann, A. Desaulles, A. Keller, F. Blum and W. A. Stahel, *J. Environ. Monit.*, 2008, **10**, 1278–1286.

- 4 R. Gehrig, Polyzyklische aromatische Kohlenwasserstoffe im PM10 an ausgewählten Stationen des NABEL sowie kantonalen Stationen, Düberdorf, Switzerland, 2013.
- 5 Federal Office for the Environment (FOEN), *Switzerland's Informative Inventory Report 2014*, Bern, 2014.
- 6 Federal roads office (FEDRO), *Schweizerische automatische Strassenverkehrszählung (SASVZ). Ergebnisse 2007-2013*, <http://www.portal-stat.admin.ch/sasvz/>, (accessed February 2015).