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Global distribution of oxygenated polycyclic aromatic hydrocarbons in mineral topsoils

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Abstract

Hazardous oxygenated polycyclic aromatic hydrocarbons (OPAHs) originate from combustion (primary sources) or postemission conversion of polycyclic aromatic hydrocarbons (PAHs) (secondary sources). We evaluated the global distribution of up to 15 OPAHs in 195 mineral topsoils from 33 study sites (covering 52° N–47° S, 71° W–118 °E) to identify indications of primary or secondary sources of OPAHs. The sums of the (frequently measured 7 and 15) OPAH concentrations correlated with those of the Σ16EPA-PAHs. The relationship of the Σ16EPA-PAH concentrations with the Σ7OPAH/Σ16EPA-PAH concentration ratios (a measure of the variable OPAH sources) could be described by a power function with a negative exponent <1, leveling off at a Σ16EPA-PAH concentration of approximately 400 ng g^{-1}. We suggest that below this value, secondary sources contributed more to the OPAH burden in soil than above this value, where primary sources dominated the OPAH mixture. This was supported by a negative correlation of the Σ16EPA-PAH concentrations with the contribution of the more readily biologically produced highly polar OPAHs (log octanol-water partition coefficient <3) to the Σ7OPAH concentrations. We identified mean annual precipitation (Spearman $\rho = .33$, $p < .001$, $n = 143$) and clay concentrations ($\rho = .55$, $p < .001$, $n = 33$) as important drivers of the Σ7OPAH/Σ16EPA-PAH concentration ratios. Our results indicate that at low PAH contamination levels, secondary sources contribute considerably and to a variable extent to total OPAH concentrations, whereas at Σ16EPA-PAH contamination levels >400 ng g^{-1}, there was a nearly constant Σ7OPAH/Σ16EPA-PAH ratio (0.08 ± 0.005 [SE], $n = 80$) determined by their combustion sources.

Abbreviations: ASE, accelerated solvent extractor; C_{org}, soil organic carbon; K_{OW}, octanol-water partition coefficient; MAP, mean annual precipitation; MAT, mean annual temperature; OPAH, oxygenated polycyclic aromatic hydrocarbon; PAC, polycyclic aromatic compound; PAH, polycyclic aromatic hydrocarbon.

1 | INTRODUCTION

Oxygenated polycyclic aromatic hydrocarbons (OPAHs) are released from combustion processes together with other polycyclic aromatic compounds (PACs), like the intensely studied polycyclic aromatic hydrocarbons (PAHs), but can have additional sources, mainly from transformation of PAHs by biological (microbial, enzymatic) and abiotic (photochemical, thermal, photolytic) reactions (Fatiadi, 1967; Habe & Omori, 2003; Kanaly & Harayama, 2010; Lundstedt et al., 2007; Mallick et al., 2011; Marquès et al., 2017; Peng et al., 2008; Wilcke, Kiesewetter, et al., 2014). Many OPAHs and PAHs are persistent, bioaccumulative, and (eco)toxic. They can therefore adversely affect microbial, animal, and human health and can damage ecosystems (Arp et al., 2014; IARC, 2010; Lundstedt et al., 2007). Some OPAHs are reported to show higher toxicity (Lampi et al., 2006; Lundstedt et al., 2014), bioavailability (Matscheko et al., 2002), and mobility (Lundstedt et al., 2007; Weigand et al., 2002) in soil than their related parent-PAHs.

Recent research has shown that the ubiquitous PAH contamination of soils is always associated with OPAHs (Bandowe et al., 2010, 2011, 2014; Wilcke, Bandowe, et al., 2014). However, up to now correlation analyses between the concentrations of PAHs and OPAHs were restricted to small, homogeneous study areas (i.e., the cities of Bratislava [Bandowe et al., 2011] and Bangkok [Bandowe et al., 2014]) or to the industrial area of Angren in Uzbekistan (Bandowe et al., 2010). Therefore, it is unknown whether there is a global general relationship of PAH with OPAH concentrations. The knowledge of such a relationship would be helpful because the measurement of PAH concentrations is well established and there is a broad data basis of PAH concentrations available, whereas OPAH concentrations have comparatively rarely been measured. With the establishment of a relationship of PAH with OPAH concentrations, OPAH concentrations could be estimated from available data for a large number of soils.

Understanding and predicting concentrations of OPAHs in soils to assess their potential harm to ecosystems requires knowledge of their sources and formation processes. The concentrations of primary OPAHs in soil are mainly determined by their proximity to the OPAH sources (Bandowe et al., 2010; Bandowe, Wei, et al., 2019; Wilcke, Bandowe, et al., 2014). The drivers of secondary OPAH concentrations in soils are more complex. One possibility of the formation of secondary OPAHs is the photochemical transformation of parent-PAHs during transport in the atmosphere (Alam et al., 2014; Eiguren-Fernandez et al., 2008; Keyte et al., 2013; Kojima et al., 2010; McKinney et al., 1999). The contribution of photochemically derived OPAHs in soil therefore depends on the transport distance of PAHs in the atmosphere and other factors, such as the intensity of radiation, ambient temperature, relative humidity, and concentration of atmospheric oxidants. In line with this, Wilcke, Bandowe, et al. (2014) attributed the lack of a correlation between PAH and OPAH concentrations along a 2,500-km north–south climosequence in Argentina, where the primary sources of PAHs and OPAHs were concentrated in the north, partly to photochemical oxidation of PAHs during atmospheric transport. Another study by Shrivastava et al. (2017) concluded that the formation of oxidized derivatives of benzo(a)pyrene from its photochemical transformation is more pronounced during atmospheric transport in the tropics than in the high and mid-latitudes. Moreover, secondary OPAHs can be formed by microbial oxidation of PAHs in soil after their deposition from the atmosphere, which is driven by the microbial activity in soil (Bandowe, Leimer, et al., 2019; Wilcke, Bandowe, et al., 2014, Wilcke, Kiesewetter, et al., 2014). A previous study found higher OPAH/PAH concentration ratios in tropical than in temperate soils (Bandowe et al., 2014). This finding was attributed to the stronger insolation, higher temperatures, and higher microbial activity in the tropics than in the temperate zone, which results in enhanced transformation of PAHs to OPAHs (Bandowe et al., 2014). It can therefore be hypothesized that the degree of soil contamination with PAHs, remoteness (i.e., the distance to primary OPAH sources), climatic conditions, and soil properties driving the microbial activity play an important role in the explanation of OPAH concentrations in soils (Bandowe et al., 2014; Johnsen & Karlson, 2005, 2007; Wilcke, Bandowe, et al., 2014).

Climatic conditions are known to influence the microbial activity via soil moisture and temperature (Aerts, 1997; Grayston et al., 2001). Furthermore, soil properties that control microbial community composition and related enzyme activities in mineral soils, including organic carbon (C_{org}) concentrations, pH, clay content, nutrient availability, and substrate quality (Aerts, 1997; Sinsabaugh et al., 2008),

Core Ideas

- Some oxygenated PAHs are more hazardous to the environment and human health than PAHs.
- OPAHs can originate from combustion or postemission conversion from PAHs.
- At low PAH concentrations, secondary OPAHs dominate the OPAHs mixture.
- The concentration ratio of combustion-derived OPAHs to PAHs appears to be almost constant.
- The OPAH/PAH concentration ratios in topsoils at low PAH concentrations correlate with rainfall and clay content.

TABLE 1 Overview of the location and number of study sites, latitude, longitude, literature source, and number of measured oxygenated polycyclic aromatic hydrocarbons (OPAHs) included in this review and ordered from north to south

Sites	Latitude (°)	Longitude (°)	Reference	No. of OPAHs
Germany, city of Dortmund, two sites	51.51	7.47	this study	14
Germany, city of Jena, 80 sites	50.92	11.58	Bandowe, Leimer, et al., 2019	15
Germany, city of Mainz, one site	49.99	8.25	Bandowe & Wilcke, 2010	7
Switzerland, city of Aesch, one site	47.48	7.61	this study	14
Switzerland, city of Berne, three sites	48.78	7.44	Wilcke, Kiesewetter, et al., 2014;two sites, this study	14
Slovakia, city of Bratislava, 11 sites	48.08–48.19	16.98–17.18	Bandowe et al., 2011	9
Uzbekistan, industrial area of Angren, 11 sites	40.95–41.97	69.95–70.17	Bandowe et al., 2010	7
China, Qinghai-Tibetan Plateau (Qinghai lake area), nine sites	36.58–37.28	99.50–100.72	Bandowe, Wei, et al., 2019	15
China, temperate (Xi'an + rural), 12 sites	33.92–34.47	108.38–109.10	Bandowe, Wei, et al., 2019	15
China, subtropical (Chao lake area, nine sites)	31.50–31.64	117.35–117.80	Bandowe, Wei, et al., 2019	15
China, tropical (Huguangyan Marr lake area), seven sites	21.14–21.15	110.27–110.29	Bandowe, Wei, et al., 2019	15
Thailand, city of Bangkok, 28 sites	13.63	100.45	Bandowe et al., 2014	15
Brazil, Amazon basin, one site	−2.98	−59.98	Bandowe & Wilcke, 2010	7
Argentina, 20 sites along a 2,500-km climosequence	−32.77 to −47.41	−58.64 to −70.69	Wilcke Bandowe, et al., 2014	15

might determine the secondary formation of OPAHs from parent-PAHs (Bandowe, Leimer, et al., 2019; Wilcke, Bandowe, et al., 2014). The microbial degradation of PAHs and the resulting formation and accumulation of OPAHs in soils could be diminished in highly contaminated industrial and urban soils because the high concentration of toxic substances in these soils could negatively affect the activity of soil fauna, microbes, and enzymes (Cerniglia & Sutherland, 2010; Thavamani, Malik, et al., 2012; Welp & Brümmer, 1997). The degraded soil physical and chemical properties as well as the reduced bioavailability of PAHs in such highly contaminated industrial and urban soils might also limit microbial turnover of PAHs (Bamforth & Singleton, 2005; Reichenberg et al., 2010).

Our overall goal was to improve our understanding of the relationship of PAH with OPAH concentrations and the contributions of primary and secondary OPAH sources to the OPAH mixtures in soils. Our specific objectives were (a) to determine whether there is a unique global relationship of PAH with OPAH concentrations (i.e., whether the OPAH concentrations can be estimated from those of the PAHs), (b) to evaluate the OPAH/PAH concentration ratios as indicators of the contributions of OPAHs from various primary and secondary sources, and (c) to explore site conditions, including climate and soil properties, as potential drivers of the ratios of the sums of OPAH concentrations to those of PAHs. If primary OPAH sources, mainly originating from high-temperature combustion processes, dominated the global distribution of OPAHs, we would expect little variation in OPAH/PAH concentration ratios. On the contrary, a large variation of the OPAH/PAH concentration ratios could be attributable to a large variety of different combustion sources (low and high temperature) or might indicate a more prominent contribution of secondary sources to the OPAHs in soils. Because the secondary sources of OPAHs in soil have been shown to be related to biological oxidation of parent-PAHs (Grayston et al., 2001; Wilcke, Kiesewetter, et al., 2014), we would expect a correlation of OPAH/PAH ratios with drivers of microbial activity, including climate, soil nutrient status, and organic matter concentrations. We evaluated the largest currently available data set collected with the same analytical method (Bandowe & Wilcke, 2010), including 195 soil samples with latitudinal coverage from 52° N to 47° S and longitudinal coverage from 71° W to 118° E (Table 1). Supplemental Figure S1 shows the relationship of the locations of all 195 soil samples included in this study with their Σ7OPAHs concentrations (i.e., the minimum number of OPAHs determined in all samples).

2 | MATERIALS AND METHODS

2.1 | Soil samples and chemical analyses

The concentrations of 16 EPA-PAHs and up to 15 OPAHs were taken from the literature as listed in Table 1 or specifically analyzed for this study using the method briefly described below. In the various cited studies from which the data originated and in our new sampling in Germany and Switzerland, topsoils were sampled in a way representative for the A horizon (Argentina, China, Slovakia) at 0–0.05 m depth (Switzerland [two sites], Thailand), 0–0.1 m depth (Brazil, Germany, Uzbekistan, Switzerland [one site]), or 0–0.15 m depth (Switzerland [one site]). The soil samples were frozen in field-fresh state or air/freeze-dried, sieved to <2 mm, and stored at –20 ˚C before analysis. pH was measured with a glass electrode in H_2O, 0.01 M $CaCl_2$, or 1 M KCl at a soil/solution ratio of 1:2.5. Clay concentrations were determined with the pipette method after removal of carbonates with HCl, organic matter with H_2O_2, and Fe oxides with dithionite-citrate-hydrogencarbonate and wet sieving <50 µm. An aliquot of each soil sample was milled, and the total C concentrations were determined with an elemental analyzer (vario EL cube, Elementar Analysensysteme GmbH). The inorganic C concentration of each sample was also determined from an aliquot of soil after combusting C_{org} in a muffle oven (550 ˚C, 2 h). The C_{org} concentration was quantified as the difference between the total C and inorganic C concentrations. Although our data set did not cover all continents, we consider it as global because it covers a wide range of latitudes and longitudes (Supplemental Figure S1).

At all study sites, the concentrations of the 16 EPA-PAHs we used here and of up to 15 OPAHs (see Supplemental Table S1) in topsoils, European Reference Material (ERM-CC013a), and procedural blanks (inert sorbent, Isolute HM-N [Biotage] or diatomaceous earth [Dionex]) were determined using previously published methods (Bandowe & Wilcke, 2010; Bandowe et al., 2010; Lundstedt et al., 2014). In brief, soils (10–20 g) were mixed with Isolute HM-N or diatomaceous earth and transferred to 33-ml accelerated solvent extractor (ASE) cells. Each sample was spiked with a mixture of deuterated PAHs (6–11 compounds) and two deuterated OPAHs. Each sample was extracted twice by pressurized liquid extraction with an ASE (ASE 200, Dionex). Dichloromethane was used for the first extraction, followed by acetone/dichloromethane/1% trifluoroacetic acid (250:125:1 v/v/v) for the second extraction. An acidified solvent mixture was used in the second step to improve the extraction of hydroxyl-PAHs and carboxyl-PAHs, which were part of the target compound list in some of the previous studies (Bandowe & Wilcke, 2010; Bandowe et al., 2010, 2011) but were not considered here. The instrumental conditions for the ASE were the same as in Bandowe and Wilcke (2010), where more details of the used method are given.

Extracts from each sample were combined, passed through Na_2SO_4, spiked with hexane, and rotary evaporated until <1 ml remained. Extracts were transferred to 3 g silica gel (10% deactivated) in an 8-ml glass column. Each sample was eluted with hexane/dichloromethane (5:1 v/v; Fraction a) and dichloromethane followed by acetone (Fraction b). Fractions a and b, which contained PAHs and OPAHs, respectively, were collected in separate flasks. Each flask was spiked with drops of toluene and then rotary evaporated to <1 ml before being transferred to 2-ml vials to determine the concentrations of target PACs. Polycyclic aromatic hydrocarbons and OPAHs were determined in two different runs with an Agilent 7890 A gas chromatograph coupled to Agilent 5975 C mass spectrometer. The gas chromatograph–mass spectrometer was operated in the electron ionization mode with selected ion monitoring of target PACs. As a check of the accuracy of our analytical procedure, we simultaneously analyzed aliquots of the European Reference Material ERM-CCO13a (Polycyclic Aromatic Hydrocarbons in Soil) from the Federal Institute of Materials Research and Testing, Berlin, Germany. Procedural blanks (inert bulk sorbent: Isolute HM-N or diatomaceous earth) were also extracted and analyzed with the same methods as the samples and reference materials. Concentrations of target compounds were determined by the internal standard procedure. The average mass of target compounds in blanks was deducted from that in the samples before calculating the final concentrations per dry mass of extracted soil. Further details of quality control procedures are specified elsewhere (Bandowe & Wilcke, 2010; Bandowe et al., 2010; Lundstedt et al., 2014). Supplemental Table S1 lists the names and abbreviations of all analyzed compounds. Results of our quality control procedures are reported in the Supplemental Material, and Supplemental Table S2 reports the OPAH and PAH concentrations in all considered individual soil samples along with important soil properties.

2.2 | Calculations and statistical analyses

The sum of the concentrations of 16 PAHs defined by the USEPA as priority pollutants is designated as Σ16EPA-PAH, and the sums of the concentrations of the seven OPAHs (i.e., 1-indanone, 1,4-naphthoquinone, 1-naphthaldehyde, 2-biphenyldicarboxaldehyde, 9-fluorenone, 1,2-acenaphthenequinone, and 9,10-anthracenedione), which have been determined in all samples, and 15 OPAHs (Supplemental Table S1) are designated as Σ7OPAH and Σ15OPAH, respectively. To roughly convert pH values measured in H_2O or 0.01 M $CaCl_2$ to the pH in 1 M KCl, we lowered the pH (H_2O) by 1 unit and the pH (0.01 M $CaCl_2$) by 0.5 units to account for the different ionic strengths of the various commonly used equilibrium solutions. Because the data were usually not normally distributed and could not be brought to normal distribution by square root or $\ln(x + 1)$ transformations, we used the nonparametric Spearman correlation analysis in the software package STATISTICA (Statsoft Inc.). Octanol water partition coefficients (K_{OW}) for OPAHs (Supplemental Table S1) were estimated according to the USEPA KOWWINTM module of Estimation Programs Interface Suite for Microsoft Windows, v 4.11 (https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface).

3 | RESULTS AND DISCUSSION

3.1 | Relationship of PAH with OPAH concentrations

The Σ7OPAH concentrations ranged from not detected to 1,850 ng g^{-1} (median, 39.5 ng g^{-1}; mean, 93.7 ng g^{-1}; n = 195) (Supplemental Figure S1A; Supplemental Table S2). The mixtures of these seven OPAHs were dominated by 9,10-anthraquinone (41 ± 20% [SD]) > 9-fluorenone (27 ± 11%) > 1-indanone (14 ± 18%) (Supplemental Figure S2A). The Σ15OPAH concentrations ranged from 0.05 to 405 ng g^{-1} (median, 98.2 ng g^{-1}; mean, 112 ng g^{-1}; n = 165) (Supplemental Figure S1B). The mixtures of these 15 OPAHs were dominated by 9,10-anthraquinone (16 ± 11%) > 2-methyl-9,10-anthraquinone (12 ± 16%) > 6H-benzo(c,d)pyren-6-one (11 ± 11%) (Supplemental Figure S2B). The range of the Σ15OPAH concentrations was smaller than that of the Σ7OPAH concentrations because the 15 OPAHs were measured at comparatively less-contaminated sites. The quantitative dominance of 9,10-anthraquinone and the fact that its concentrations correlated with the Σ7OPAH concentrations (Spearman ρ = .91, p < .001, n = 195) and the Σ15OPAH concentrations (ρ = .78, p < .001, n = 165) (Supplemental Figure S3) renders this compound a suitable indicator for total OPAH concentrations, similar to benzo(a)pyrene for the total PAH concentrations (Wilcke, 2000). We therefore suggest that 9,10-anthraquinone should be included in the priority compound list if this list were to be amended to include OPAHs.

The Σ16EPA-PAH concentrations ranged from 1.71 to 232,000 ng g^{-1} (median, 374 ng g^{-1}; mean, 2,080 ng g^{-1}). The range of Σ16EPA-PAH concentrations was wider than in the global data set of Wilcke (2007), which included soils with Σ16EPA-PAH concentrations from 306 to 170,000 ng g^{-1}, illustrating that our data set included even more extreme sites both at the low background and at the extreme contamination ends. One site—the chemical waste dump in Bratislava—had an extreme Σ16EPA-PAH concentration of 232,000 ng g^{-1}, whereas the Σ7OPAH concentration of 1,080 ng g^{-1} was not an outlier relative to the concentrations of all 195 study sites (Bandowe et al., 2011). Omitting the extreme Bratislava sample reduced the upper end of the Σ16EPA-PAH concentration range to 34,000 ng g^{-1}, the median slightly to 373 ng g^{-1}, and the mean to 898 ng g^{-1} but had no impact on the PAH patterns. The mixtures of the 16EPA-PAHs were dominated by the benzo(b+j+k)fluoranthenes, which we could not separate with our method, (16 ± 6.8%) > phenanthrene (15 ± 6.6%) > pyrene (12 ± 5.2%). The dominance of phenanthrene, pyrene, fluoranthene, and benzo(b+j+k)fluoranthenes is typical of soils in the industrialized temperate zone and reflects the dominance of such soils in our data set (Arp et al., 2014; Desaules et al., 2008; Gras et al., 2000; Maliszewska-Kordybach et al., 2008; Wang et al., 2010; Wilcke, 2000). Phenanthrene is also a major compound in soils of the industrialized temperate zone but contributes even more in remote soils and is one of the dominant PAHs in tropical soils (Daly et al., 2007; Wilcke, 2007).

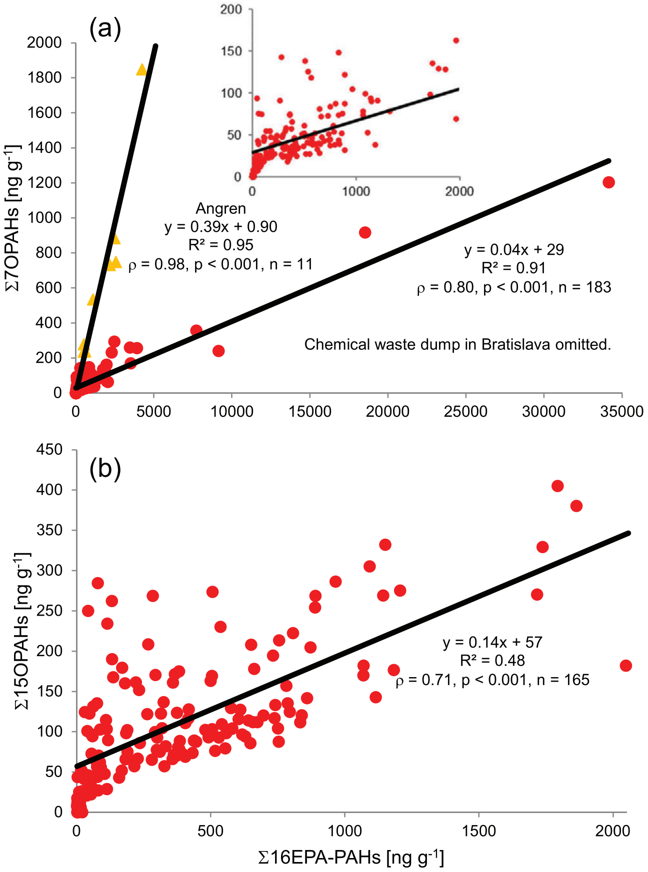

FIGURE 1 Relationship of the concentrations of Σ16EPA-PAHs with those of (a) the Σ7OPAHs in 183 topsoils and (b) the Σ15OPAHs in 165 topsoils from a global data set (the chemical waste dump in Bratislava with a Σ16EPA-PAH concentration of 230,000 ng g^{-1} was omitted). The 11 samples from an industrial area in Angren, Uzbekistan, showed a different relationship of the Σ16EPA-PAH with the Σ7OPAH concentrations and are therefore shown separately with triangles. The inlet figure magnifies the lower Σ16EPA-PAH concentration range. The axes of the inlet figure have the same legends as those of the main figure. Note the different axis scalings

The Σ7OPAH and Σ15OPAH concentrations correlated significantly with the Σ16EPA-PAH concentrations (Figure 1). There was a global regression line of the Σ7OPAH concentrations on the Σ16EPA-PAH concentrations for all study sites, except for the Angren industrial area in Uzbekistan (Figure 1). At Angren, only seven OPAHs have been measured.

The regressions of the different sums of OPAH concentrations on the frequently measured Σ16EPA-PAH concentrations suggest that the OPAH concentrations can usually be predicted based on PAH measurements (Figure 1).

However, in the industrial area of Angren, Uzbekistan, we found a different relationship of the Σ16EPA-PAH with the Σ7OPAH concentrations than at all other study sites (Figure 1) (Bandowe et al., 2010). At Angren, a coal mine, a rubber plant, a gold refinery, and a power plant emitted PAHs and OPAHs to the surrounding soils (Bandowe et al., 2010). One possible explanation for this different relationship of the Σ16EPA-PAH with the Σ7OPAH concentrations might be that the local emissions contained a higher OPAH/PAH ratio than all other sites of our study. Alternatively, pronounced photochemical reactions in this semi-arid region might have produced more OPAHs than in the other study regions (Marquès et al., 2016, 2017; Marusenko et al., 2011). On the other hand, the topsoil of the extremely PAH-contaminated chemical waste dump at Bratislava had a particularly low Σ7OPAH/Σ16EPA-PAH concentration ratio (Bandowe et al., 2011), likely because of unusually large PAH sources, which might have originated from PAH-rich industrial waste materials (e.g., industrially produced soot used for tires can contain high PAH concentrations). In our data set, the soil samples from Angren, which did not fall on the joint regression line between PAH and OPAH concentrations, accounted for 6.2% of the overall 195 samples, implying that the sum of OPAH concentrations can be predicted from the Σ16EPA-PAH concentrations in >90% of the soil samples considered in our study. The study from the Angren region was the only one from a semi-arid climate in our data set. It can therefore be speculated that dry climatic conditions modify the relationship of PAH with OPAH concentrations. Unfortunately, the semi-arid and arid climate zones are heavily underexplored with respect to their soil contamination with PAHs and OPAHs. We do not know of any other published work from a semi-arid or arid region beyond that from Angren that simultaneously determined PAH and OPAH concentrations in soils. Thus, future work should cover all climatic zones of the world to determine the potential influence of extreme climates on the relationship of PAH with OPAH concentrations.

Because the distribution of the individual soil samples among the various study regions was uneven, with a particularly high contribution of the alluvial floodplain in Jena, Germany (Table 1) (Bandowe, Leimer, et al., 2019), we calculated regression lines of the regional mean Σ7OPAH and Σ15OPAH concentrations for all soils with the same climate on the Σ16EPA-PAH concentrations (Supplemental Figure S4). The significant correlations between the Σ16EPA-PAH concentrations and the Σ7OPAH and Σ15OPAH concentrations persisted, and the slopes of the regression lines were similar. Thus, the possibly lacking spatial independence of the samples from the same study region did not substantially influence the relationships.

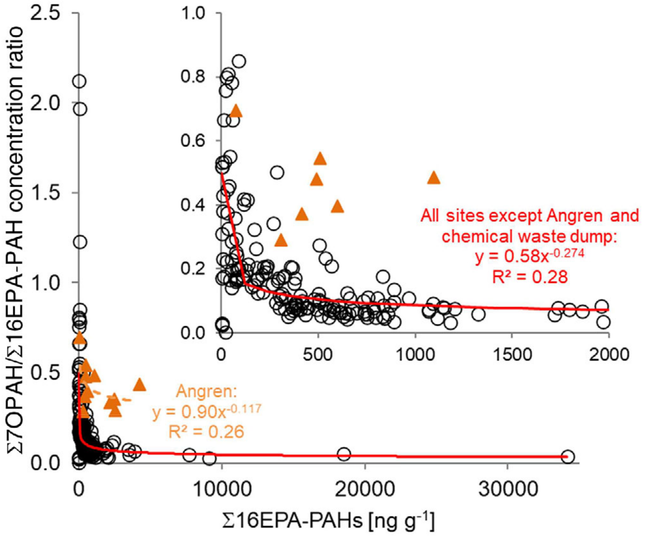

FIGURE 2 Relationship of the Σ16EPA-PAH concentrations with the Σ7OPAH/Σ16EPA-PAH concentration ratios and its best fit (red continuous line). The chemical waste dump in Bratislava was omitted because of its extreme Σ16EPA-PAH concentrations and small Σ7OPAHs/Σ16EPA-PAH concentration ratios. The data from Angren, Uzbekistan, are shown separately with triangles because of their deviating Σ7OPAH/Σ16EPA-PAH concentration ratios (see also Figure 1) and were fit with a different function (orange broken line). The inlet figure magnifies the lower Σ16EPA-PAH concentration range. The axes of the inlet figure have the same legends as those of the main figure. Note the different axis scalings

3.2 | OPAH/PAH concentration ratios as indicators of primary vs. secondary sources

The relationship of the Σ16EPA-PAH concentrations with the Σ7OPAH/Σ16EPA-PAH concentration ratios, which we assume to be an indicator of the various sources of OPAHs, could be best described with a power function (Figure 2). Again, the soils of the Angren area did not fit into the general relationship of all other study sites because of their elevated Σ7OPAH/Σ16EPA-PAH concentration ratios. However, the Angren data could also be fit with a power function leveling off at a higher Σ16EPA-PAH concentration of approximately 2,000 ng g^{-1} (Figure 2). The chemical waste dump in Bratislava had a low Σ7OPAH/Σ16EPA-PAH concentration ratio of 0.005 and was omitted from Figure 2. At soil concentrations of Σ16EPA-PAHs >400 ng g^{-1}, the ΣOPAH/Σ16EPA-PAH concentration ratios were nearly constant at 0.08 ± 0.005 (SE) (Σ7OPAHs, $n = 80$) or 0.21 ± 0.01 (Σ15OPAHs, $n = 64$). At soil concentrations of Σ16EPA-PAHs <400 ng g^{-1}, the Σ7OPAH/Σ16EPA-PAH concentration ratios showed a wide variation from <0.01 to 2.12 (mean, 0.30 ± 0.03; $n = 96$), and the Σ15OPAH/Σ16EPA-PAH concentration ratios varied from 0.02 to 11.9 (mean, 1.22 ± 0.18; $n = 97$). The relationships of individual parent-PAH concentrations with the concentration ratios of the related OPAHs to parent-PAHs had a generally similar shape as in Figure 2, although they were less close for the individual ratios than for the ratios of the sum of concentrations (Supplemental Figure S5). We attribute the less close relationships mainly to the smaller data sets for individual compound ratios (Supplemental Figure S5) than for the ratios of the sum of concentrations (Figure 2) because not all individual compounds were detected in all soils.

The reason for higher Σ7OPAH/Σ16EPA-PAH concentration ratios at sites with low Σ16EPA-PAH concentrations might be that the soils at these mostly remote sites in south Argentina and rural China receive PAC mixtures containing higher concentrations of OPAHs relative to PAHs because of the photochemical transformation of PAHs to OPAHs during transport in the atmosphere. With increasing atmospheric transport distance, an increasing proportion of the PAH concentrations is photochemically transformed to OPAHs (Alam et al., 2014). In line with this, a high 9,10-anthraquinone/anthracene ratio in remote marine sediments relative to sediments at contaminated sites has also been discussed as an indicator of a pronounced atmospheric transformation during transport to the remote sites (McKinney et al., 1999). Differing distances of remote sites to the locations where PACs are emitted into the atmosphere would then result in a variation of the Σ7OPAH/Σ16EPA-PAH ratios. For tropical soils in Bangkok and near Manaus with low PAH concentrations, the elevated Σ7OPAH/Σ16EPA-PAH concentration ratios are likely also related to enhanced production of OPAHs from photochemical transformation of PAHs because of the strong insulation in the tropics (Bandowe et al., 2014).

Alternatively, at low PAH concentrations in soil, the formation and accumulation of OPAHs from microbial transformations of PAHs might contribute more to the total OPAH concentrations than at sites with high PAH concentrations that also contain high OPAH concentrations from primary emissions. We speculate that soils at these remote sites are less degraded (low/absence of soil compaction, erosion of topsoils, or contamination with toxic chemicals). The good soil health at these remote sites could have favored the microbial community, thereby promoting the biodegradation of PAHs (Bamforth & Singleton 2005; Cerniglia, 1992; Cerniglia & Sutherland, 2010; Ghosal et al., 2016; Sandrin & Maier, 2003; Thavamani, Malik, et al., 2012). Such background sites might also show a higher PAH bioavailability because of the lower concentrations of anthropogenic pyrogenic or "hard-carbon"–derived compounds (e.g., coal particles) and shorter ageing time than the soils from urban and highly contaminated sites. Similarly, Wilcke (2007) reported that, in his evaluated global data set of PAH concentrations, the low-contaminated soils showed a dominance of naphthalene, phenanthrene, and perylene, for which biological sources are known, whereas the PAH mixtures in more contaminated soils were dominated by higher-molecular-weight PAHs (with four to six aromatic rings), which are thought to be indicative of high-temperature combustion of fossil fuels. This was similarly attributed to a greater soil health associated with a high microbial activity. Moreover, a large part of low-molecular-weight PAHs (two or three rings) in air are partitioned into the gaseous phase and are hence further spread in the atmosphere from their point of emission (Keyte et al., 2013). After deposition to soils, the low-molecular-weight PAHs are usually more bioavailable and are thus more quickly transformed than the high-molecular-weight PAHs (Bamforth & Singleton, 2005; Peng et al., 2008; Wilcke, 2000). The latter might also contribute to higher Σ7OPAH/Σ16EPA-PAH concentration ratios at low-contaminated sites. Varying degradation rates for parent-PAHs in background soils diffusely contaminated with PAHs could partially explain a strong variation in the Σ7OPAH/Σ16EPA-PAH ratios.

At high PAH concentrations, most of the OPAHs occurring at a nearly constant ratio to the PAHs likely originate from primary production by high-temperature combustion processes of fossil fuels. In our data set, high PAH concentrations occurred in urban areas of central Europe (Aesch, Berne, Bratislava, Dortmund, Mainz, Jena) and of China (Xi'an) for which long-lasting pronounced emissions of PAHs from the combustion of fossil fuels are known (Baek et al., 1991; Lima et al., 2005; Wilcke, 2000, 2007) (Figure 2). The apparent threshold value of Σ16EPA-PAH concentrations of approximately 400 ng g^{-1}, above which the corresponding Σ7OPAH/Σ16EPA-PAH ratios were almost constant, was higher than the mean Σ16EPA-PAH concentrations of arable and grassland soils reported in the review of Wilcke (2000). Concentrations of Σ16EPA-PAHs >400 ng g^{-1} frequently occur in urban areas and in some forest soils that are rich in organic matter. We therefore speculate that there are two possible explanations for the small variation in Σ7OPAH/Σ16EPA-PAH ratios that might operate in combination. First, soils with high Σ16EPA-PAH concentrations might have received such a high load of mainly primary OPAHs that would overwhelm the comparatively small microbial production, maintaining the minimal variation among the primary OPAH/PAH concentration ratios. Soils that are strongly contaminated with Σ16EPA concentrations far above approximately 400 ng g^{-1} also contain co-occurring toxic substances (e.g., trace metals and toxic organic compounds) that might inhibit the abundance and activity of microbes and enzymes that degrade PAHs in soils (Arp et al., 2014; Andreoni et al., 2004; Cerniglia & Sutherland, 2010; Kandeler et al., 1996; Maliszewska-Kordybach & Smreczak, 2003; Sandrin & Maier, 2003; Thavamani, Malik, et al., 2012). Mixtures of PAHs at these more strongly contaminated sites may also be particularly recalcitrant because they contain higher proportions of high-molecular-weight PAHs that are frequently strongly sorbed by aromatic moieties of the soil organic matter or black carbon and are hence inaccessible for microbial degradation (Reichenberg et al., 2010). To test our suggestions would require more detailed studies elucidating the drivers of biological OPAH formation in soil and determining the ecotoxicological thresholds of PAH (and co-contaminant) mixtures for microorganisms that degrade PAHs (Cerniglia, 1992; Cerniglia & Sutherland, 2010; Ghosal et al., 2016; Sandrin & Maier, 2003; Thavamani, Megharaj, et al., 2012; Peng et al., 2008).

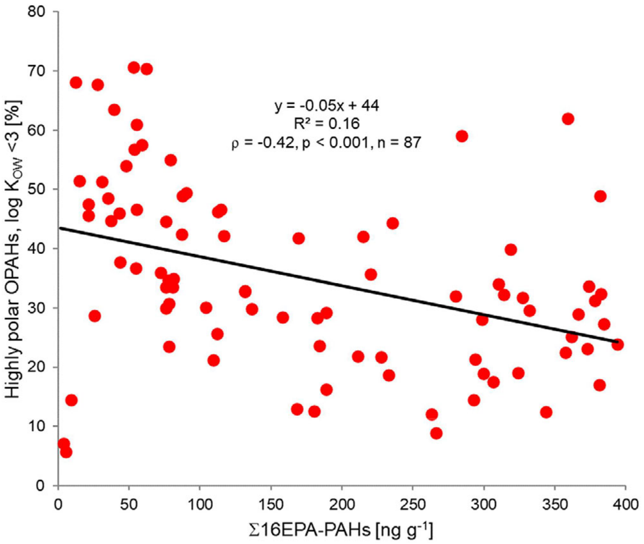

FIGURE 3 Relationship of the Σ16EPA-PAH concentrations with the contributions of highly polar OPAHs (log K_{OW} <3; i.e., 1-indanone, 1,4-naphthoquinone, 1-naphthaldehyde, and 1,2-acenaphthenequinone) to the Σ7OPAHs for soils with Σ16EPA-PAH concentrations <400 ng g^{-1}. Sites at which either no highly polar or no medium polar OPAH was detected were omitted because we considered 0 or 100% of one polarity class analytical artifacts attributable to the low sensitivity of the analysis method

We considered the relationship of the Σ16EPA-PAH concentrations with the contributions of the highly polar OPAHs (log K_{OW} <3) and the medium polar OPAHs (log K_{OW} >3; see Supplemental Table S1) to the Σ7OPAH concentrations separately. Our definition of the different polarity classes of OPAHs is arbitrary and was chosen because the highly polar OPAHs were to a larger extent produced biologically than the medium polar OPAHs in a short-term soil incubation (Wilcke, Kiesewetter, et al., 2014). Therefore, the sum of the contributions of highly and medium polar OPAH concentrations to the Σ7OPAH (or Σ15OPAH) concentrations was always 100%. For the soils with a Σ16EPA-PAH concentration <400 ng g^{-1}, there was a negative correlation of the Σ16EPA-PAH concentrations with the sum of the contributions of highly polar OPAHs (log K_{OW} <3) and a positive correlation with that of medium polar OPAHs (log K_{OW} >3, not shown) to the Σ7OPAH concentrations (Figure 3). We suggest that the negative relationship of the Σ16EPA-PAH concentrations with the sum of the contributions of the highly polar OPAHs to the Σ7OPAH concentrations indicates an increasingly higher contribution of biologically produced OPAHs to the total OPAH concentrations with decreasing PAH concentrations. The four highly polar OPAHs (1-indanone, 1,4-naphthoquinone, 1-naphthaldehyde, and 1,2-acenaphthenequinone) are known metabolic products of microbial degradation of the PAHs fluorene, naphthalene, 1-methylnaphthalene, acenaphthene, and acenaphthylene, respectively (Casellas et al., 1997; Cerniglia & Sutherland, 2010; Cerniglia, 1992; Ghosal et al., 2016; Habe & Omori, 2003; Mahajan et al., 1994; Mallick et al., 2011; Peng et al., 2008). Wilcke, Kiesewetter, et al. (2014) observed in an incubation experiment that particularly highly polar OPAHs can be produced in soils in a short time of a few weeks. Similarly, Bandowe, Leimer, et al. (2019) found that the highly polar OPAHs 1-indanone, 1-naphthaldehyde, and 1,2-acenaphthenequinone, together with the medium polar 2-biphenylcarboxaldehyde, were preferentially microbially produced in an urban grassland soil. Because the medium polar OPAH contributions to the Σ7OPAHs concentrations increased with increasing PAH concentrations complementarily to the decreasing contributions of the highly polar OPAHs, we suggest that in our data set 9-fluorenone, 9,10-anthraquinone, and 2-biphenylcarboxaldehyde have a higher share of primary sources derived from high-temperature combustion processes together with the PAHs than of secondary sources. The relationship of the Σ16EPA-PAH concentrations <400 ng g^{-1} with the sum of the contributions of highly polar OPAHs to the Σ15OPAH concentrations showed a similar negative trend, although this trend was not significant ($\rho = -.17$, $p = .12$, $n = 86$; sites at which either no highly polar or no medium polar OPAH was detected were omitted).

3.3 | Climatic and soil-related drivers of OPAH/PAH concentration ratios

To find explanations for the variation in the Σ7OPAH/Σ16EPA-PAH concentration ratios, we explored the role of climate and selected soil properties on the Σ7OPAH/Σ16EPA-PAH concentration ratios. Mean annual precipitation (MAP) was positively correlated with the Σ7OPAH/Σ16EPA-PAH concentration ratios (Figure 4a). For those sites, which were so close to each other that the climate did not differ, we used the regional means for the regression. However, in our data set MAP and mean annual temperature (MAT) were correlated ($\rho = .45$, $p = .08$, $n = 33$), so it is impossible to separate the moisture effect from a temperature effect. The positive influence of MAP (and the closely interrelated MAT) on the Σ7OPAH/Σ16EPA-PAH concentration

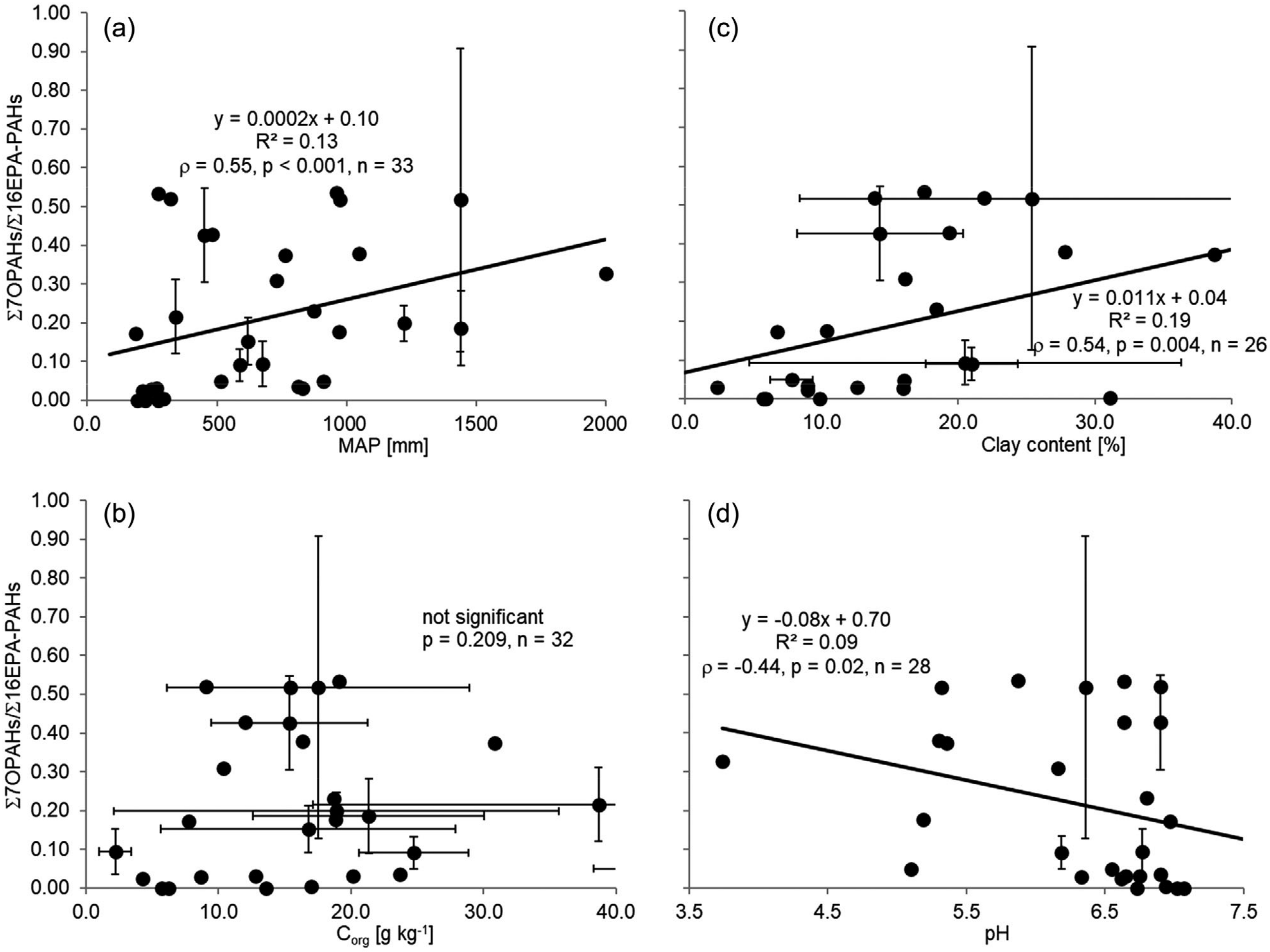

FIGURE 4 Relationship of (a) mean annual precipitation (MAP), (b) organic C concentrations (C_{org}), (c) clay contents, and (d) pH with the Σ7OPAH/Σ16EPA-PAH concentration ratios. The results of the sites with the same climate were averaged. Error bars show SD

ratios supports the earlier suggestion that the inner-tropical moist and hot climate enhances the formation of OPAHs from PAH transformation in air and soils via abiotic and biological processes (Bandowe et al., 2014; Shrivastastava et al., 2017).

When we considered the regional means of the sites with the same climate, the C_{org} concentrations did not influence the Σ7OPAH/Σ16EPA-PAH concentration ratios (Figure 4b). When all study sites were individually considered, C_{org} concentrations had a weak but significant negative influence (Supplemental Figure S6A). Because C_{org} concentrations were reported to correlate positively with microbial biomass (measured as the sum of phospholipid fatty acids) and the total number of bacteria (Crampon et al., 2014; Herold et al., 2014; Zeller et al., 2001), it could have been expected that C_{org} concentrations and the Σ7OPAH/Σ16EPA-PAH concentration ratios correlated positively. We attribute the discrepancy between our finding and the literature to the fact that not only total C_{org} concentrations but also organic matter quality influence soil organic matter decomposition (Aerts, 1997) and likely also the associated biodegradation of PAHs (Cerniglia, 1992; Cerniglia & Sutherland, 2010; Ghosal et al., 2016; Kanaly & Harayama, 2010; Mallick et al., 2011; Peng et al., 2008). Moreover, increasing C_{org} concentrations, particularly if associated with highly aromatic compounds such as soot or coal particles, could result in a more exhaustive sorption of PAHs, which reduces their bioavailability and thus their transformation to OPAHs (MacLeod & Semple, 2002).

The clay contents correlated positively with the Σ7OPAH/Σ16EPA-PAH concentration ratios, both for the averages per climatic region and for individual sites (Figure 4c; Supplemental Figure S6B). The positive influence of the clay concentrations on the Σ7OPAH/Σ16EPA-PAH concentration ratio cannot be attributed to the organic matter concentrations. Although organic matter concentrations in soil are frequently reported to be correlated with clay concentrations, this was not true in our data set. Instead, we suggest that the higher cation exchange capacity usually associated with a high clay mineral concentration in the clay fraction and the resulting positive effect of the supply of nutrients on microbial activity explain the relationship shown in Figure 4c and Supplemental Figure S6B. This assumption is corroborated by the close correlation of the clay concentrations with the effective cation exchange capacity in the 48 samples, for which both values were available ($\rho = .61$, $p < .001$).

The pH had a negligible influence on the Σ7OPAH/Σ16EPA-PAH concentration ratios, although it was statistically significant (Figure 4d). If the sites were considered individually, there was no relationship between pH and the Σ7OPAH/Σ16EPA-PAH concentration ratios (Supplemental Figure S6C).

4 | CONCLUSIONS

Our study demonstrated that OPAH concentrations are closely related with those of PAHs in all mineral topsoils. We found a unique relationship between PAH and OPAH concentrations at most study sites, which suggests that the total OPAH concentrations can be predicted from PAH concentrations in >90% of the studied 195 soil samples. However, at an industrial site in a semi-arid region, the OPAH/PAH concentration ratios deviated from the general relationship either because of site-specific particularly high OPAH/PAH ratios or fast PAH turnover processes. The OPAH 9,10-anthraquinone was ubiquitously present and showed a close correlation with the sum of OPAH concentrations, suggesting that it can serve as an indicator compound for OPAHs similar to benzo(a)pyrene for PAHs.

At soil concentrations of Σ16EPA-PAHs >400 ng g^{-1}, the ΣOPAH concentrations occurred with a nearly constant ratio to PAH concentrations, again except at the semi-arid site, where the OPAH/PAH concentration ratios were generally higher. In contrast, the ΣOPAH/Σ16EPA-PAH concentration ratios varied over a broad range at Σ16EPA-PAH concentrations <400 ng g^{-1}, possibly reflecting different degrees of OPAH formation during atmospheric transport and in terrestrial ecosystems.

The ΣOPAH/Σ16EPA-PAH concentration ratios were driven by climatic conditions (MAP and MAT) and clay content. We suggest that this finding supports a bigger role of microbial transformation of PAHs to OPAHs in soil at low PAH concentrations and broadly varying ΣOPAH/Σ16EPA-PAH concentration ratios because both identified drivers influence the microbial activity strongly and thus also the biodegradation of PAHs in soil.

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AUTHOR CONTRIBUTIONS

Wolfgang Wilcke, Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Project administration, Writing-original draft; Moritz Bigalke, Investigation, Writing-review & editing; Chong Wei, Investigation, Methodology, Writing-review & editing; Yongming Han, Conceptualization, Funding acquisition, Writing-review & editing; Benjamin A. Musa Bandowe, Conceptualization, Data curation, Investigation, Methodology, Validation, Writing-review & editing.

CONFLICT OF INTEREST

We declare no conflict of interest.

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SUPPORTING INFORMATION

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