

CLICK ANYWHERE on THIS PAGE to RETURN TO INFORMATION ON MOTHBALL ODORS and NAPHTHALENE at InspectApedia.com

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/268212198>

Persistent organic pollutants in soil: sources, concentrations, and fate

Conference Paper · February 2011

CITATIONS

0

READS

69

2 authors:



[Wolfgang Wilcke](#)

Karlsruhe Institute of Technology

291 PUBLICATIONS 7,596 CITATIONS

[SEE PROFILE](#)



[Benjamin Bandowe](#)

Karlsruhe Institute of Technology

68 PUBLICATIONS 669 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



NUMEX - the Ecuadorian NUtrient Manipulation EXperiment [View project](#)



MISOTRAG [View project](#)

Persistent organic pollutants in soil: sources, concentrations, and fate

Wolfgang Wilcke and Benjamin Bandowe

Geographisches Institut, Universität Bern, Hallerstrasse 12, 3012 Bern

Abstract

Persistent organic pollutants (POPs) are a legacy of industrialization resulting in long-term contamination of the environment. The purpose of our paper is mainly to describe open questions in the understanding of the fate of POPs in the soil environment and the resulting future research directions. Based on our own work, we focus on polycyclic aromatic hydrocarbons (PAHs), a large group of several 100 compounds which are produced unintentionally in combustion processes, with a broad range of physico-chemical properties, representative of most other POPs. We have structured our presentation into sources, distribution and fate of PAHs. We describe recently detected biological sources of PAHs and compound-specific isotope ratio approaches to separate combustion from biologically derived PAHs. Then, the global distribution of PAHs is addressed. Finally we assess bioavailability of PAHs and the occurrence of oxidized derivatives.

Zusammenfassung:

Persistente Organische Schadstoffe im Boden: Quellen, Gehalte und Verbleib

In diesem Manuskript beschreiben wir neu entdeckte biologische Quellen von polyzyklischen aromatischen Kohlenwasserstoffen (PAK), einer Substanzklasse, die überwiegend in Verbrennungsprozessen entsteht und eine breite Spanne physiko-chemischer Eigenschaften überstreicht, die typisch sind für persistente organische Schadstoffe. Insbesondere stellen wir substanzspezifische Isotopenansätze zur Unterscheidung von Verbrennungs- und biologischen Quellen der PAK dar. Danach behandeln wir die globale Verteilung von PAK und schließlich die Bioverfügbarkeit von PAK und das Vorkommen von oxidierten Derivaten.

Keywords: persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs), oxygen-containing polycyclic aromatic hydrocarbons (OPAHs), sources, global distribution

1. Introduction

It was in the year 1962, when Rachel Carson's "Silent Spring" appeared, that the broader public became aware of persistent organic pollutants (POPs) and their detrimental effects on the environment and human health. It lasted, however, decades of research and a long political process until the international Stockholm Convention on Persistent Organic Pollutants regulating the production and environmental release of the "dirty dozen", twelve (classes of) compounds considered as dangerous for the environment became effective and since 2010 the list of compounds is further expanded by nine more compound (classes).

The POPs are either intentionally produced for different purposes (e.g., many halogenated compounds for plant protection or industrial use) or unintentionally as industrial by-product or after accidents (like the dioxins and furans which are produced when halogenated compounds burn). The production of other POPs like the polycyclic aromatic hydrocarbons (PAHs) can even not be avoided because these compounds are formed in any incomplete combustion process of organic matter (SIMS and OVERCASH 1983). We focus on the PAHs because this is an ubiquitously occurring class of toxic compounds spanning a wide range of physico-chemical properties typical

of POPs that will also in future impact our environment (WILCKE 2000, 2007). The general line of progress of our knowledge and some likely near-future major directions of research will probably be similar for other POPs.

The PAHs are a class of several hundred individual compounds containing at least two condensed rings. Today, anthropogenic combustion of fossil fuels is thought to be the most important source of PAH inputs to the environment. This knowledge is derived from sediment archives showing a strong increase in deposition rates with the beginning industrialization and a maximum in the 70s of the 20th century. Although emissions decreased thereafter, contemporary deposition rates are still clearly elevated compared with the pre-industrial background (SANDERS et al. 1993). The largest environmental reservoir of PAHs is the soil (WILD und JONES 1995). Polycyclic aromatic hydrocarbons have received much attention since they were found in soils for the first time in 1961 (BLUMER 1961) because of their potentially harmful effects on ecosystems, bioaccumulation in the food chain, and humans. Our understanding of the PAH sources, their distribution in the environment, and their fate (i.e. sorption, transport, degradation) is far advanced

(WILCKE 2000). However, important knowledge gaps still need to be tackled.

Our understanding of the global distribution of POPs is currently challenged in the light of new findings of biological POP production (CHEN et al. 1998a, WILCKE et al. 2000, 2003). Separating anthropogenic and natural sources of POPs (even halogenated POPs can e.g., be produced biologically or during natural forest fires, ÖBERG 2002) requires new approaches of which the compound-specific stable isotope analysis is a promising one which will certainly be further expanded in the future (HOFSTETTER et al. 2008). Another important issue concerns the turnover and bioavailability of the persistent but not entirely unreactive compounds under real-world conditions in soils in which the POPs are already "aged", i.e. resided for some time). Such turnover times can be assessed in various ways including direct observation (perhaps making use of soil archives), laboratory incubations or possibly via the concentrations of POP-derived metabolites (which themselves can be similarly or even more toxic than their parent compounds). Furthermore, the occurrence and fate of such metabolites in the environment is considerably underexplored. Oxygenated derivatives and metabolites of PAHs (OPAHs) are not part of any legal regulation of POPs in spite of their known environmental risks.

We will present results of our work on the sources and fate of PAHs and OPAHs in the environment, with a global perspective.

2. Sources of PAHs

In recent literature, there are strong indications for biological sources of the three PAHs naphthalene, phenanthrene, and perylene in addition to their production in combustion processes. Evidence for a biological production of naphthalene has been derived from its presence in *Magnolia* flowers, flower scents of different Annonaceae species, and fungi (AZUMA et al. 1996, JÜRGENS et al. 2000, DAISY et al. 2002). High naphthalene concentrations in *Coptotermes formosanus* termite nests of subtropical North America where the termite species was imported from East Asia (CHEN et al. 1998a, b) and nests of various termite genera from tropical Brazil (WILCKE et al. 2000, 2003) suggested a naphthalene synthesis by termites or associated microorganisms which was directly proven in a microcosm experiment with termites (BANDOWE et al. 2009). WILCKE et al. (2004) roughly estimated the storages of naphthalene and phenanthrene in the Brazilian Cerrado, a $2 \times 10^6 \text{ km}^2$ -large area. The total storages in this little industrialized region were equivalent to 7300 years (naphthalene) and 400 years (phenanthrene) of the published annual emissions in the UK, respectively. This estimate supports our view that

there must be other sources of naphthalene and phenanthrene than the combustion of fossil fuels from which PAHs in the UK are mainly derived. There were early indications that phenanthrene can be produced biologically from alkyl-phenanthrene precursors in plant debris (SIMS and OVERCASH 1983). For perylene, biological production in anaerobic environments in soils and sediments is known (VENKATESAN 1988, GUGGENBERGER et al. 1996).

In the last decade, the C isotope signature of individual PAHs has been used to determine the contribution of different sources to the PAH burden of soils and sediments (e.g., O'MALLEY et al. 1994; SMIRNOV et al. 1998, MCRAE et al. 2000). Enzymatically catalyzed biological processes usually discriminate ^{13}C resulting in a shift of the $\delta^{13}\text{C}$ value (i.e. the $^{13}\text{C}/^{12}\text{C}$ ratio relative to a standard) from the atmospheric CO_2 to more negative, ^{13}C -depleted values. For plants following the C_3 photosynthetic pathway, the sources of fossil fuels, $\delta^{13}\text{C}$ values of -32‰ to -22‰ are common in bulk biomass with a mean of -27‰ (BOUTTON 1996). The combustion-derived PAHs resemble the $\delta^{13}\text{C}$ signal of the fuel, depending on combustion conditions. For coal combustion and gasification processes, high combustion temperatures lead to PAHs depleted in ^{13}C compared to parent materials, while for low temperatures the $\delta^{13}\text{C}$ values of PAHs are close to those of the parent coals (MCRAE et al. 1999). WILCKE et al. (2002) were able to prove biological production of perylene in tropical soils and termite nests with the help of the $\delta^{13}\text{C}$ value of perylene which was more negative than that of other (combustion-derived) PAHs (Fig. 1).

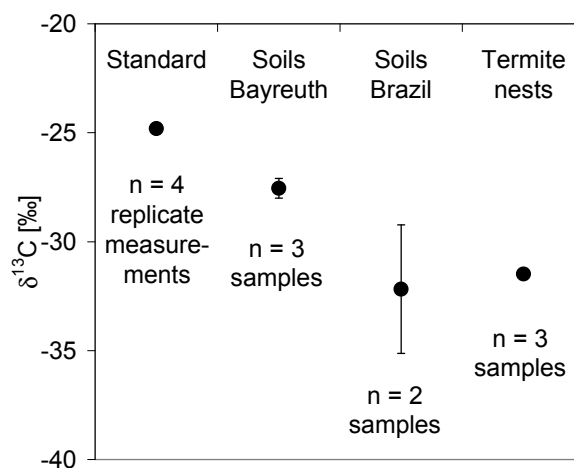


Figure 1: Mean $\delta^{13}\text{C}$ values of perylene in a standard from mineral oil spiked to a Ferralsol sample, urban soils of the city of Bayreuth, Germany and forest soils and termite nest material of the termite genus *Nasutitermes* from the Amazon region in Brazil. Error bars represent standard errors of replicate measurements (standard) or samples (WILCKE et al. 2002).

3. Global distribution of PAHs

Persistent organic pollutants have been detected around the world even at sites which are located far from industrial activity such as the polar regions (WANIA and MACKAY 1996). As the polar regions are far from all industrial sources, most anthropogenic PAHs could only have reached them by long-range transport. According to the “Global Distillation” hypothesis of WANIA and MACKAY (1996) this should result in a fractionation of the PAH pattern according to the volatility of the individual compounds. In a study of soils along a climosequence in the North American prairie, indications for such a fractionation were found for naphthalene – the most volatile PAH – but not for any other PAH (WILCKE and AMELUNG 2000). The contribution of naphthalene to the sum of 20 PAHs increased with decreasing mean annual temperature (Fig. 2).

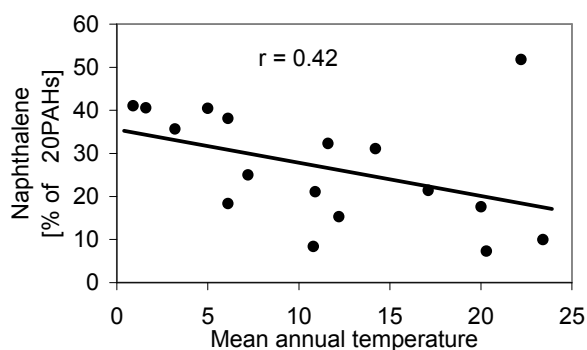


Fig. 2: Relationship between mean annual temperature and contribution of naphthalene to the sum of 20 PAH concentrations in soils along a climosequence in the North American prairie (WILCKE and AMELUNG 2000).

Recently, VON WALDOW et al. (2011), however, demonstrated that the latitudinal distribution of PCB concentrations in the atmosphere over Europe to the Arctic can also be explained as controlled by the remoteness index (RI), i.e. the distance to the sources. In their combined modelling and empirical analysis, the latitudinal distribution of polychlorinated biphenyls (PCBs) was independent of the temperature – the major driver of POP distribution in the “Global Distillation” model – which covaries with RI, a fact that seems to have been overlooked in earlier analyses. VON WALDOW et al. (2011) postulate that the latitudinal distribution of POPs is mainly driven by differential removal of individual compounds because of compound-specific degradation via OH radical-mediated oxidation or deposition to land and water surfaces and put forward the “Differential Removal” hypothesis. Similar to the hypothesis of VON WALDOW et al. (2011) to explain the global distribution of POPs,

PAH fractionation can also occur at the local scale along short-distance transects from point emitters of PAHs because of differential removal along deposition gradients in the scale of a few kilometers (WILCKE et al. 1996; MEHARG et al. 1998). Neither the “Global Distillation” nor the “Differential Removal” Models, however, take into consideration the fact that there might be biological sources of POPs, which in the case of PAHs may even be the dominant sources of PAHs in remote areas (WILCKE 2000, 2007). To assess the influence of local biological PAH production on the global distribution of PAHs, data from a large number of sites all over the world were evaluated (WILCKE 2007). The results reveal that there is a close negative correlation between the contributions of the sum of naphthalene and phenanthrene concentrations with the sum of eight high-molecular weight, presumably mainly anthropogenic PAHs (including benz[a]anthracene, chrysene, benzo[b(+j)]-fluoranthene, benzo[k]fluoranthene, benzo(a)-pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]-anthracene, and benzo(ghi)perylene, Fig. 3). Furthermore, there is a significant negative correlation between the sum of naphthalene and phenanthrene contributions to the sum of 16 EPA PAHs and the sum of concentrations of these 16 EPA PAHs ($r = -0.59$) if only the subset of 12 regions in which PAH concentrations were determined by our working group is considered. This correlation still remains significant if all 32 regions shown in Fig. 3 are included ($r = -0.32$). Thus, the less contaminated a soil is, the more contribute the partly biogenic compounds naphthalene and phenanthrene to the total PAH concentrations.

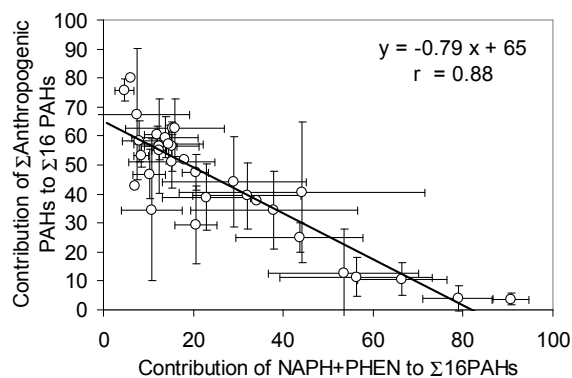


Fig. 3: Relationship between the contributions of naphthalene (NAPH) and phenanthrene (PHEN) to the sum of concentrations of the 16 EPA PAHs in 32 study regions all over the world. The figure includes data shown in WILCKE (2007) where also a complete list of references is given plus additional more recent data of CAI et al. (2007), DALY et al. (2007), HONDA et al. (2007), PING et al. (2007), and BOLL et al. (2008).

4. Fate of PAHs

The research into the fate of PAHs in the past focussed on bioavailability, transport, and dissipation (WILCKE 2000), while relatively little effort was placed on the concentrations of oxygenated derivatives of POPs such as the OPAHs.

The available studies of OPAH concentrations in the environment focus on atmospheric samples (aerosols and gas phase, ALLEN et al. 1997, ALBINET et al. 2006, LINTELMANN et al. 2006, DELHOMME et al. 2008), waste water (POJANA and MARCOMINI 2007), sediments (MCKINNEY et al. 1999), sewage sludge (BODZEK et al. 1997), human and animal fluids (SMITH et al. 2002, GROVA et al. 2005), and fish bile (JOHNSON-RESTREPO et al. 2008). The few studies of soils are limited to highly contaminated soils (creosote/gaswork/wood impregnation/coke production sites) or spiked soils at concentration levels of $\mu\text{g g}^{-1}$ - mg g^{-1} (WISCHMANN et al. 1996, MEYER et al. 1999, LUNDSTEDT et al. 2006). In these studies only few OPAHs were determined frequently not including hydroxyl-/carboxyl-OPAHs. To the best of our knowledge only one study in Europe has reported the OPAH concentrations in background soils, again only including carbonyl- but not hydroxyl-/carboxyl-OPAHs (NIEDERER 1998).

We therefore studied the PAH and OPAH concentrations in an industrial area in Uzbekistan (Angren) and urban soils of Bratislava, the capital of Slovakia (BANDOWE et al. 2010b, 2011) using a newly developed gas chromatography/mass spectrometry-based method (BANDOWE et al. 2010a). The $\Sigma 14$ OPAHs concentrations in soil ranged 62-2692 ng g^{-1} and those of $\Sigma 34$ PAHs 842-244870 ng g^{-1} . The carbonyl-OPAHs had higher concentrations than the hydroxyl-OPAHs. The most abundant carbonyl-OPAHs were consistently 9-fluorenone (9-FLO), 9,10-anthraquinone (9,10-ANQ), 1-indanone (1-INDA) and benzo[a]anthracene-7,12-dione and the most abundant hydroxyl-OPAH was 2-hydroxybenzaldehyde. The concentrations of carbonyl-OPAHs were frequently higher than those of their parent-PAHs (e.g., 9-FLO/fluorene >100 near a rubber factory in Angren, Fig. 4).

The concentrations of OPAHs like those of their alkyl/parent-PAHs were higher at locations closer to point sources and the OPAH and PAH concentrations were correlated suggesting joint sources. Only for 1-INDA and 2-biphenylcarboxaldehyde (2-BPCD), sources other than combustion seem to dominate because the concentrations of these compounds were not significantly correlated with those of the parent PAHs. Similar to parent/alkyl-PAHs, OPAH concentrations were higher in topsoils than subsoils. Evidence of higher mobility of OPAHs than their

parent-PAHs was provided by greater subsoil:topsoil concentration ratios of carbonyl-OPAHs (0.41-0.82) than their parent-PAHs (0.41-0.63) in Uzbekistan. This was further backed by the consistently higher contribution of more soluble 9-FLO and 1-INDA to the Σ carbonyl-OPAHs in subsoil than topsoil at the expense of 9,10-ANQ, 7,12-B(A)A and higher OPAH/parent-PAH concentration ratios in subsoil than topsoil in Bratislava.

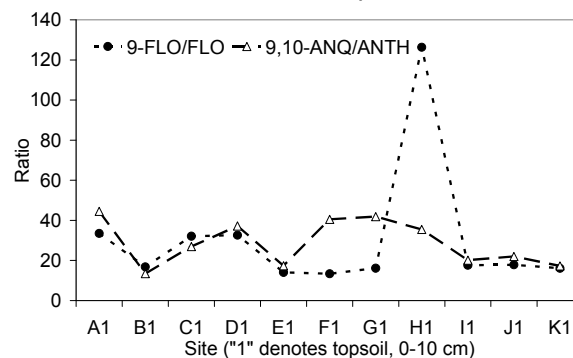


Fig. 4: Concentration ratios of the two most abundant OPAHs; 9-FLO and 9,10-ANQ to fluorene (FLO) and anthracene (ANTH) in 11 topsoils from the Angren industrial region, Uzbekistan (BANDOWE et al. 2010b).

5. Conclusions

In the past, important knowledge concerning sources, global distribution, and fate of PAHs – a class of persistent organic pollutants (POPs) was produced. Nevertheless, there are still several open questions which center around the separation of biological and anthropogenic sources of POPs, the reconciliation of the various models of global POP distribution, and the fate of POPs with a special focus on oxygenated derivatives which can be produced together with the PAHs or during microbial degradation of PAHs in soil.

6. Acknowledgments

We acknowledge the important support of (in alphabetical order) Wulf Amelung, Miguel Ayarza, Ademar Bandeira, Andrea Bergmann, Ludolf Eusterbrock, Alexej Fokin, Marco Garcia, Nualsri Kanchanakool, Martin Kaupenjohann, Michael Kersten, Jozef Kobza, Martin Krauss, Julia Lilienfein, Christopher Martius, Silke Müller, Chalinee Niamskul, Grigorij Safronov, Jaroslava Sobocka, Nosir Shukurov, and Wolfgang Zech. We furthermore thank the Bayerische Staatskanzlei and the Deutsche Forschungsgemeinschaft for funding our research.

7. Literature

- Albinet, A., E. Leoz-Garziandia, H. Budzinski and E. Villenave (2006): Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust) and on natural ambient air samples by gas chromatography-mass spectrometry with negative ion chemical ionisation. *Journal of Chromatography A* 1121, 106-113.
- Allen, J.O., N.M. Dookeran, K. Taghizadeh, A.L. Lafleur, K.A. Smith and A.F. Sarofim (1997): Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. *Environmental Science & Technology* 31, 2064-2070.
- Azuma, H., M. Toyota, Y. Asakawa and S. Kawano (1996): Naphthalene – a constituent of Magnolia flowers. *Phytochemistry* 423, 999-1004.
- Bandowe, B.A.M., D. Rückamp, M.A.L. Bragança, V. Laabs, W. Amelung, C. Martius and W. Wilcke (2009): Naphthalene production by microorganisms associated with termites: evidence from a microcosm experiment. *Soil Biology & Biochemistry* 41, 630-639.
- Bandowe, B.A.M. and W. Wilcke (2010a): Analysis of polycyclic aromatic hydrocarbons and their oxygen-containing derivatives and metabolites in soils. *Journal of Environmental Quality* 39, 1349-1358.
- Bandowe, B.A.M., N. Shukurov, M. Kersten, and W. Wilcke (2010b): Polycyclic aromatic hydrocarbons (PAHs) and their oxygen-containing derivatives (OPAHs) in soils from the Angren industrial area, Uzbekistan. *Environmental Pollution* 158, 2888-2899.
- Bandowe, B.A.M., J. Sobocka and W. Wilcke (2011): Oxygen-containing polycyclic aromatic hydrocarbons (OPAHs) in urban soils of Bratislava, Slovakia: patterns, relation to PAHs and vertical distribution. *Environmental Pollution* 159, 539-549.
- Blumer, M. (1961): Benzopyrenes in soil. *Science* 134, 474-475.
- Bodzek, D., B. Janoszka, C. Dobosz, L. Warzecha and M. Bodzek (1997): Determination of polycyclic aromatic compounds and heavy metals in sludges from biological sewage treatment plants. *Journal of Chromatography A* 774, 177-192.
- Boutton, T.W. (1996): Stable carbon isotope ratios of soil organic matter and their use as indicators of vegetation and climate change. pp. 47-82. In: Boutton, T.W. & Shin-ichi Yamasaki (eds.), *Mass Spectrometry of Soils*. Marcel Dekker, New York.
- Boll, E.S., J.H. Christensen and P.E. Holm (2008): Quantification and source identification of polycyclic aromatic hydrocarbons in sediment, soil, and water spinach from Hanoi, Vietnam. *Journal of Environmental Monitoring* 10, 261-269.
- Cai, Q.-Y., C.-H. Mo, Q.-T. Wu, a. Katsoyiannis and Q.-Z. Zeng (2007): The status of soil contamination by semivolatiles organic chemicals in China: a review. *The Science of the Total Environment* 389, 209-224.
- Chen, J., G. Henderson, C.C. Grimm, S.W. Lloyd and R.A. Laine (1998a): Termites fumigate their nests with naphthalene. *Nature* 392, 558.
- Chen, J., G. Henderson, C.C. Grimm, S.W. Lloyd and R.A. Laine (1998b): Naphthalene in Formosan subterranean termite carton nests. *Journal of Agricultural and Food Chemistry* 46, 2337-2339.
- Daisy, B.H., G.A. Strobel, U. Castillo, D. Ezra, J. Sears, D.K. Weaver and J.B. Runyon (2002): Naphthalene, an insect repellent, is produced by *Muscodora vitigenus*, a novel endophytic fungus. *Microbiology* 148, 3737-3741.
- Daly, G.L., Y.D. Lei, L.E. Castillo, D.C.G. Muir and F. Wania (2007): Polycyclic aromatic hydrocarbons in Costa Rican air and soil: a tropical/temperate comparison. *Atmospheric Environment* 41, 7339-7350.
- Delhomme, O., M. Millet and P. Herckes (2008): Determination of oxygenated polycyclic aromatic hydrocarbons in atmospheric aerosol samples by liquid chromatography-tandem mass spectrometry. *Talanta* 74, 703-710.
- Galceran, M.T. and E. Moyano (1996): Determination of hydroxy polycyclic aromatic hydrocarbons by liquid chromatography-mass spectrometry. Comparison of atmospheric chemical ionization and electrospray. *Journal of Chromatography A* 731, 75-84.
- Grova, N., F. Monteau, B. Le Bizec, C. Feidt, F. Andre and G. Rychen (2005): Determination of phenanthrene and hydroxyphenanthrenes in various biological matrices at trace levels using gas chromatography-mass spectrometry. *Journal of Analytical Toxicology* 29, 175-181.
- Guggenberger, G., M. Pichler, R. Hartmann and W. Zech (1996): Polycyclic aromatic hydrocarbons in different forest soils: mineral horizons. *Zeitschrift für Pflanzenernährung und Bodenkunde* 159, 565-573.
- Hofstetter, T.B., R. P. Schwarzenbach and S.M. Bernasconi (2008): Assessing transformation processes of organic compounds using stable isotope fractionation. *Environmental Science & Technology* 42, 7737-7743.
- Honda, K., M. Mizukami, Y. Ueda, N. Hamada and N. Seike (2007): Residue level of polycyclic aromatic hydrocarbons in Japanese paddy soils from 1959-2002. *Chemosphere* 68, 1763-1771.
- Johnson-Restrepo, B., J. Olivero-Verbel, S.J. Lu, J. Guette-Fernandez, R. Baldiris-Avila, I. O'Byrne-Hoyos, K.M. Aldous, R. Addink and K. Kannan (2008): Polycyclic aromatic hydrocarbons and their hydroxylated metabolites in fish bile and sediments from coastal waters of Colombia. *Environmental Pollution* 151, 452-459.
- Jürgens, A., A.C. Webber and G. Gottsberger (2000): Floral scent compounds of Amazonian Annonaceae species pollinated by small beetles and thrips. *Phytochemistry* 55, 551-558.
- Lintelmann, J., K. Fischer and G. Matuschek (2006): Determination of oxygenated polycyclic aromatic hydrocarbons in particulate matter using high-performance liquid chromatography-tandem mass spectrometry *Journal of Chromatography A* 1133, 241-247.
- Lundstedt, S., P. Haglund and L. Öberg (2006): Simultaneous extraction and fractionation of polycyclic aromatic hydrocarbons and their oxygenated derivatives in soil using selective pressurized liquid extraction. *Analytical Chemistry* 78, 2993-3000.

- Meharg, A.A., J. Wright, H. Dyke and D. Osborn (1998): Polycyclic aromatic hydrocarbon (PAH) dispersion and deposition to vegetation and soil following a large-scale chemical fire. *Environmental Pollution* 99, 29-36.
- McKinney, R.A., R.J. Pruell and R.M. Burgess (1999): Ratio of the concentration of anthraquinone to anthracene in coastal marine sediments. *Chemosphere* 38, 2415-2430.
- McRae, C., C.E. Snape, C.-G. Sun, D. Fabbri, D. Tartari, C. Trombini and A.E. Fallick (2000): Use of compound-specific stable isotope analysis to source anthropogenic natural gas-derived polycyclic aromatic hydrocarbons in a lagoon sediment. *Environmental Science & Technology* 34, 4684-4686.
- Meyer, S., S. Cartellieri and H. Steinhart (1999): Simultaneous determination of PAHs, hetero-PAHs (N, S, O) and their degradation products in creosote-contaminated soils. Method development, validation and application to hazardous waste sites. *Analytical Chemistry* 71, 4023-4029.
- Niederer, M. (1998): Determination of polycyclic aromatic hydrocarbons and substitutes (nitro-,oxy-PAHs) in urban soil and airborne particulate by GC-MS and NCI-MS/MS. *Environmental Science & Pollution Research* 5, 209-216.
- Öberg, G. (2002): The natural chlorine cycle – fitting the scattered pieces. *Applied Microbiology and Biotechnology* 58, 565-581.
- O'Malley, V.P., T.A. Abrajano Jr. and J. Hellou (1994): Determination of the $^{13}\text{C}/^{12}\text{C}$ ratios of individual PAH from environmental samples: can PAH sources be apportioned? *Organic Geochemistry* 21, 809-821.
- Ping, L.F., Y.M. Luo, H.B. Zhang, Q.B. Li and L.H. Wu (2007): Distribution of polycyclic aromatic hydrocarbons in thirty typical soil profiles in the Yangtze River delta region, east China. *Environmental Pollution* 147, 358-365.
- Pojana, G. and A. Marcomini (2007): Determination of monohydroxylated metabolites of polycyclic aromatic hydrocarbons (OH-PAHs) from wastewater-treatment plants. *International Journal of Environmental Analytical Chemistry* 87:627-636.
- Sanders, G., K.C. Jones, J. Hamilton-Taylor and Helmut Dörr (1993): Concentrations and deposition fluxes of polynuclear aromatic hydrocarbons and heavy metals in the dated sediments of a rural English lake. *Environmental Toxicology and Chemistry* 12, 1567-1581.
- Sims, R.C. and M.R. Overcash (1983): Fate of polynuclear aromatic compounds (PNAs) in soil-plant systems. *Residues Review* 88, 1-68.
- Smirnov, A., T.A. Abrajano Jr., A. Smirnov and A. Stark (1998): Distribution and sources of polycyclic aromatic hydrocarbons in the sediments of Lake Erie, Part I. Spatial distribution, transport and deposition. *Organic Geochemistry* 29, 1813-1828.
- Smith, C.J., C.J. Walcott, W.L. Huang, V. Maggio, J. Grainger and D.G. Patterson (2002): Determination of selected monohydroxy metabolites of 2-, 3- and 4-ring polycyclic aromatic hydrocarbons in urine by solid-phase microextraction and isotope dilution gas chromatography-mass spectrometry. *Journal of Chromatography B* 778, 157-164.
- Venkatesan, M.I. (1988): Occurrence and possible sources of perylene in marine sediments – a review. *Marine Chemistry* 25, 1-27.
- Waldow, von, H., M. Macleod, K. Jones, M. Scheringer and K. Hungerbühler (2010): Remoteness from emission sources explains the fractionation pattern of polychlorinated biphenyls in the northern hemisphere. *Environmental Science & Technology* 44, 6183-6188.
- Wania, F. and D. Mackay (1996): Tracking the distribution of persistent organic pollutants. *Environmental Science & Technology* 30, A390-A396.
- Wilcke, W. (2000): Polycyclic aromatic hydrocarbons (PAHs) in soil – a review. *Journal of Plant Nutrition and Soil Science* 163, 229-248.
- Wilcke, W. 2007. Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. *Geoderma* 141:157-166.
- Wilcke, W. and W. Amelung (2000): Persistent organic pollutants (POPs) in native grassland soils along a climosequence in North America. *Soil Science Society of America Journal* 64, 2140-2148.
- Wilcke, W., W. Zech and J. Kobza (1996): PAH pools in soils along a PAH deposition gradient. *Environmental Pollution* 92, 307-313.
- Wilcke, W., W. Amelung, C. Martius, M.V.B. Garcia and W. Zech (2000): Biological sources of polycyclic aromatic hydrocarbons (PAHs) in the Amazonian rain forest. *Journal of Plant Nutrition and Soil Science* 163, 27-30.
- Wilcke, W., M. Krauss and W. Amelung. 2002. Carbon isotope signature of polycyclic aromatic hydrocarbons (PAHs): evidence for different sources in tropical and temperate environments? *Environmental Science & Technology* 36: 3530-3535.
- Wilcke, W., W. Amelung, M. Krauss, C. Martius, A. Bandeira and M. Garcia (2003): Polycyclic aromatic hydrocarbon (PAH) patterns in climatically different ecological zones of Brazil. *Organic Geochemistry* 34, 1405-1417.
- Wilcke, W., M. Krauss, J. Lilienfein and W. Amelung (2004): Polycyclic aromatic hydrocarbon storage in a typical Cerrado of the Brazilian Savanna. *Journal of Environmental Quality* 33, 946-955.
- Wischmann, H., H. Steinhart, K. Hupe, G. Montresori and R. Stegmann (1996): Degradation of selected PAHs in soil/compost and identification of intermediates. *International Journal of Environmental Analytical Chemistry* 64, 247-255.
- Wild, S.R. and K.C. Jones (1995): Polynuclear aromatic-hydrocarbons in the United-Kingdom environment - a preliminary source inventory and budget. *Environmental Pollution* 88, 91-108.