Originalbeiträge

POP cycling in India - influenced by the monsoon

Gerhard Lammel [1,2*], Céline Degrendele [2], Sachin S. Gunthe [3], Qing Mu [1], Akila Muthalagu [3], Ondřej Audy [2], Petr Kukučka [2], Marie D. Mulder [2], Mega Octaviani [1], Petra Příbylová [2], Pourya Shahpoury [1], Irene Stemmler [4], Aswathy E. Valsan [3]

[1] Max Planck Institute for Chemistry, Multiphase Chemistry Department, Hahn-Meitner-Weg 1, 55128 Mainz, Germany
[2] Masaryk University, Research Centre for Toxic Compounds in the Environment, Kamenice 5, 62500 Brno, Czech Republic
[3] Indian Institute of Technology Madras, Environmental and Water Resources Engineering Division, Chennai 600036, India
[4] Max Planck Institute for Meteorology, Ocean in the Earth System Department, Bundesstr. 53, 20146 Hamburg, Germany

Abstract
Persistent organic pollutants that have accumulated in soils can be re-mobilised by volatilisation in response to chemical equilibrium with the atmosphere. Clean air masses from the Indian Ocean, advected with the onset of the summer monsoon, are found to reduce concentrations of hexachloro-cyclohexane (HCH), dichlorodiphenyltrichloroethane (DDT) and its derivatives, endosulfan and polychlorinated biphenyls (PCBs) in air (all in the range 5-20 pg m^{-3}) at a southern Indian mountain site by 77, 70, 82 and 45%, respectively. The analysis of fugacities in soil and air suggest that such a concentration drop triggers net volatilisation or enhances on-going re-volatilisation of the now-adays banned chemicals HCH and PCBs from the soil. Model simulations show that the response of the air-soil chemical equilibrium is such that the air is increasingly polluted from the soil with the northward propagation of the monsoon. Multi-decadal modelling shows that air-surface exchange of HCH and DDT have declined since the ban of these substances from agriculture, but re-mobilisation of higher chlorinated PCBs may have reached a historical high, 40 years after peak emission.

1. Introduction

Persistent organic pollutants pose a hazard to humans and wildlife as they may reach harmful concentrations in biota upon accumulation along food chains. Semivolatile substances (i.e., vapour pressure at 293 K in the range $10^{-6} – 10^{-2}$ Pa) are diffusing across air-sea and air-land interfaces in both directions. They tend to net volatilise from land and sea surfaces to which they had previously been deposited, once a level of contamination in chemical equilibrium with air pollution is reached (Bidleman, 1999; Cousins et al., 1999). The potential to re-volatilise is relevant to assess risks from chemicals as it enhances the long-range transport potential, hence, facilitates transport to and accumulation in remote areas, which are pristine with regard to primary (direct) contamination (Wania and Mackay, 2008; Semeena and Lammel, 2005). Air-soil dynamics occurs on various time scales, from multi-year long-term trends (Lammel and Stemmler, 2012) to seasonal cycling and short-term fluctuations (Bidleman, 1999). Vertical fluxes at the air-soil interface are driven by substance fugacities in either phase (Bidleman, 1999), apart from the wet deposition flux.

South Asia is a region, where persistent organic pollutants, in particular the organochlorine pesticides (OCPs) DDT and hexachlorocyclohexane (HCH) have been heavily used (Sharma et al., 2014). In India, air pollution levels are expected to drop with the onset of the summer monsoon. Triggered by the seasonal shift of the intertropical convergence zone, the large-scale advection pattern switches from regional (South Asia and adjacent seas) to intercontinental (from the Indian Ocean with influence from the relatively clean southern hemisphere).

Here we study air and soil pollution in India, first time with focus on the impact of the summer monsoon on air-surface exchange. The hypothesis is tested, whether drop of concentrations in air at the onset of the summer monsoon mobilizes pollutants stored in soils. To this end, (1) field observations in background soils in the Western Ghats, the first highlands that the southwest monsoon winds encounter, were performed before and during the onset of the monsoon (May-June 2014). These were complemented by (2) regional scale chemistry-transport modelling of the monsoon onset on the Indian subcontinent using a 3D air pollution model, WRF-Chem, coupled to a soil compartment. Finally, (3) the long-term chemodynamics is assessed by multi-media mass balance modelling, forced by climate and 3D modelling data.

2. Methods

2.1 Sites and sampling

Air samples were collected from 5 May – 10 June, 2014, 90 km inland from the Arabian Sea coast, on a slope oriented southwest in the northern outskirts of the town Munnar (10.093°N/77.068°E, Fig. 4) at 1600 m a.s.l., with the mountain ridge's elevation in the area ranging from 1950 – 2450 m a.s.l. The site is reached freely, i.e. without topographic obstacles, by air masses that are advected through the sector 180-360°N. It is directly adjacent to tea plantations (south to west) and deciduous forest (northwest to northeast). Additional land cover includes shrubs (south, east) and, to a lesser extent, agri-cultural fields and residential areas (south to southeast). For air sampling a high volume sampler equipped with a quartz fibre filter and 2 polyurethane foam (PUF) plugs was used. Soil samples were taken from each one plot in the tea plantation, in shrubs and in forest, at distances within 1 km from each other. The uppermost 5 cm soil was collected (using spade, Edelman auger and sieve). Each soil sample is a composite (pooled

sample), produced from equal amounts of soil collected from 6 individual spots at distances of 1 m from each other. Three replicates of each composite sample were analysed. At all plots the samples were nitisol, horizon A, which was brownish, loose, single grain structure, with fine roots in the shrubs and forest. Soil samples were homogenized by sieving and mixing. PUF samples were spiked to control analyte losses during handling, shipping and storage.

2.2 Chemical and data analysis

For organic analysis all samples were extracted with dichloromethane in an automatic extractor. Surrogate extraction standards were spiked on each sample prior to extraction. Samples were analysed using a gas chromatograph coupled with a tandem mass spectrometer for HCHs (4 isomers), DDE, DDD and DDT (DDX compounds, each 2 isomers), penta- and hexachlorobenzene (PeCB, HCB), 7 indicator PCBs, aldrin, dieldrin, endrin, α- and γ-chlordan, α- and β-endosulfan, endosulfan sulphate, and mirex.

The pollutant fugacities (Harner et al., 2001) were derived from measured concentrations in soil and air. The onset of the monsoon on site was dated with high temporal resolution based on air parcel history (back trajectory analysis). More QA/QC related details, blank levels and LOQ are given in Lammel et al., 2018.

2.3 Modelling atmospheric transport, chemistry and air-soil exchange

The response of air-soil exchange to the drop in air concentration, subsequent to the monsoon onset, was studied by the regional scale simulation of meteorology and chemistry using a regional-scale chemistry-transport model with a single layer soil compartment coupled to the atmosphere, WRF-Chem-PAH/POP (Mu et al., 2018; Lammel et al., 2018). The simulation of the period 1-30 June 2014, with a spatial resolution of 27×27 km^2; and a time step of 150 s of the South Asian domain (5-$32°$N/69-$89°$E), was driven by NCEP re-analyses (6-hourly, $1° \times 1°$ resolution). Physical and chemical spin-up time was 4 days. Primary emissions were considered for DDT and PCBs, while the secondary emissions were modelled based on initializing the soils of India uniformly by the observed levels in background soils (shrub, forest, section 2.1). Non-zero air concentrations, observed before and during monsoon at the site (see above), were advected continuously at all boundaries of the domain. In the model experiment pre-monsoon levels were continuously replaced by monsoon levels according to the northward propagation of the monsoon, while in the control run pre-monsoon levels were kept constant at the boundaries.

2.4 Multi-decadal simulation of pollution of air and soil in India

The air–soil mass exchange flux of the semivolatile organic compounds studied were simulated by a non-steady state one-dimensional (series of 7 two-boxes) model of inter-compartmental mass exchange (multi-media mass balance model; Lammel, 2004; Lammel et al., 2018). The boxes represent 7

zones in the north-south direction in India, 7.4-$33.4°$N, each $3.75°$ wide. For each box the mass balances for the two compartments planetary boundary layer and top soil were solved. The processes considered in air are wet and dry (particle) deposition, chemical removal from air by reaction with the hydroxyl radical, air-surface mass exchange flux (dry gaseous deposition and volatilisation), and loss by transport to the free troposphere, while in the soil atmospheric deposition fluxes, air-surface mass exchange flux, and degradation (as first order process) were considered. In addition to a 50-year model run, the sensitivity of soil pollution to a number of input parameters as well as under a hypothetic no-monsoon scenario was studied.

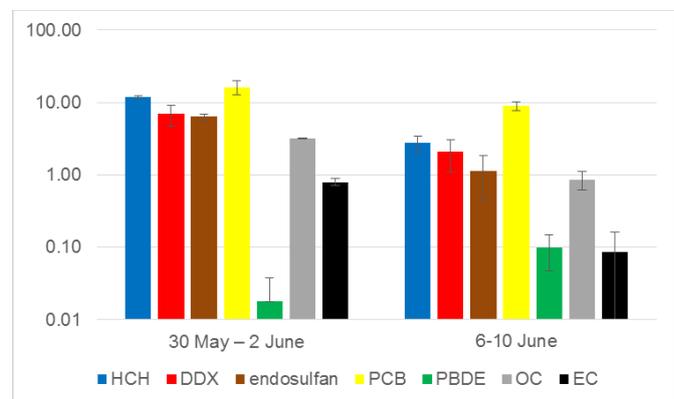**3. Results**

3.1 Field observations

Fig. 1. Observed concentrations in air, c_a, of pesticides (Σ_4HCH, Σ_6DDX, Σ_3Endosulfan), Σ_7PCB, Σ_9PBDEs (pg m^{-3}), OC and EC (µg m^{-3}) before and after onset of southwest monsoon in Munnar, India, 2014. Error bars reflect standard deviations. All concentration changes are significant (p < 0.05 level, t-test), except for PBDEs.

Relatively low pollution levels in soils (0.07-0.11 ng g^{-1} for Σ_4HCH, 0.18-0.43 ng g^{-1} for Σ_6DDX, 0.25-0.28 ng g^{-1} for Σ_7PCB, and 8.1-12.7 pg g^{-1} for Σ_9PBDEs) confirm the classification as "background" site. Actually, these HCH and DDX levels are lower than ever reported from soils in India (Sharma et al., 2014; Li et al., 2016). The soil sample from a tea plantation showed elevated levels of DDT and its metabolites (27.9 ng g^{-1} Σ_6DDX), pointing to previous application.

Indeed, measured air concentrations of carbonaceous aerosol and organic pollutants reach a distinctly lower level during the monsoon, dropping by a factor of 2-10, except for PBDEs, which apparently increased (Fig. 1). These concentration changes i.e., 77, 70, 82 and 45 % for Σ_4HCH, Σ_6DDX, Σ_3Endosulfan and Σ_7PCBs from before to after (Fig. 1) were all significant on the p < 0.05 level, most on the p < 0.01 level, except for PBDEs which was insignificant, even on the p < 0.1 level (unpaired Student t-test). Precipitation increased by a factor of ≈2 upon the monsoon onset (from 3.8 to 8.0 mm day^{-1}), associated with convective activity. With 2.3-17.7 pg m^{-3} Σ_4HCH and 0.36-10.4 pg m^{-3} Σ_6DDX the measurements at Munnar range at the lower end of the range reported from rural

sites in India in years after ban in agriculture. 1.3-8.5 pg m^{-3} endosulfan (including endosulfan sulfate) measured in Munnar in 2014, shortly after the ban of the pesticide is 3 orders of magnitude below what was reported 2006-07 (i.e., 1000-9200 pg m^{-3} at rural locations of South India; Pozo et al., 2011).
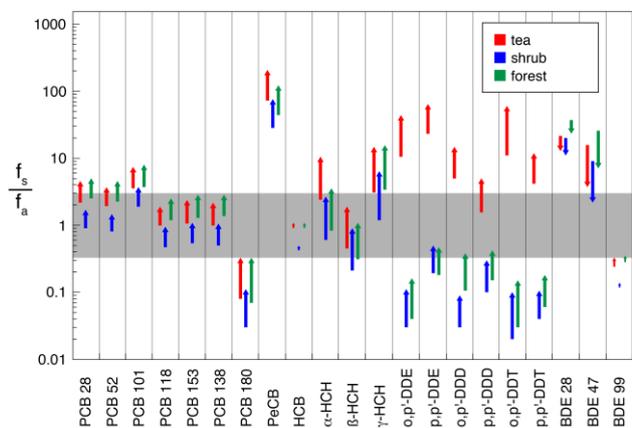

Fig. 2: Change of air-soil chemical equilibrium with the monsoon onset. Arrows denote direction and amount of change of fugacity ratio, f_s/f_a, over various soils from prior to posterior onset. $f_s/f_a < 1$ denotes downward (net-deposition), while $f_s/f_a > 1$ denotes upward (net-volatilisation) flux. The shaded zone ($0.33 < f_s/f_a < 3$) indicates insignificance of deviation from 1 due to input data uncertainties.

The direction of net gas exchange is determined by the fugacity ratio f_s/f_a. These calculations indicate both downward (PCB180, DDT and metabolites over forest and shrub soils, BDE99; $f_s/f_a < 1$) and upward (PCB101, PeCB, DDT and metabolites over tea garden soils, BDE28, BDE47; $f_s/f_a > 1$; Fig. 2) diffusive air-soil exchange fluxes prior to the monsoon. With the monsoon onset f_s/f_a generally increases, except for PBDEs. This triggers a change of flux direction for the tri- to hexachlorinated PCBs and α- and β-HCH (Fig. 2). For example α- and γ-HCH were close to phase equilibrium before onset, but net-volatilisation occurred during monsoon, while β-HCH changed from net-depositional to near phase equilibrium.

3.2 Response of air-soil gas exchange of pollutants to monsoon onset

According to the WRF-Chem-PAH/POP model simulations, within a few days after monsoon onset in southern India, the advection of air from the Indian Ocean has reduced HCH and PCBs' atmospheric levels over southern India and the Bay of Bengal, and to a lesser extent over central India (Fig. 3, centre panels). Three weeks after onset in southern India, the northern monsoon boundary has passed over India except the northwestern states Gujarat and Rajastan (i.e., north of ≈22°N and west of ≈77°E), but the distributions of HCH and PCB in air maintain significant gradients with high, i.e. only moderately reduced (by < 1 pg m^{-3}) levels in the north and east, and low levels after a decline of > 3 pg m^{-3} of HCH isomers and > 5 pg m^{-3} of PCB28, respectively, in the south and southwest.
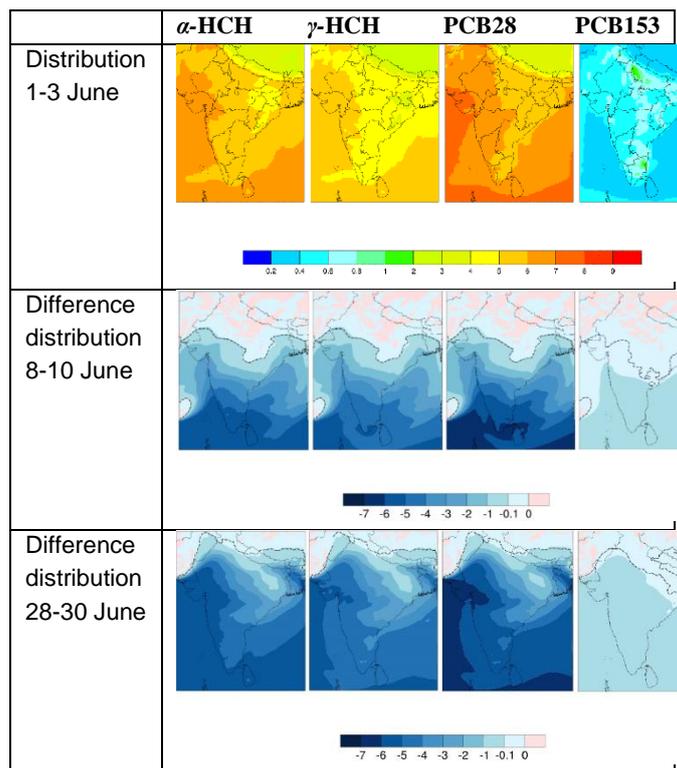

Fig. 3: Air pollutant distributions. α-HCH, γ-HCH, PCB28, and PCB153 (pg m^{-3}) predicted concentrations in near-ground air prior to monsoon onset (1-3 June, top panels) and difference distribution due to monsoon advection (experiment – control; centre panels: 8-10 June, bottom panels: 28-30 June 2014). The difference is significant (P < 0.05, t-test) south of the dotted line.

The response of the air-soil system subject to the monsoon leads to a spatially inhomogeneous distribution of pollutants across India. It is dominated by clean air advection in the south and southwest, but only moderately decreased air pollution in northern and eastern parts of the sub-continent, as the air has received secondary emissions from the soils. The latter increases with distance from the coasts after monsoon onset. The differences in concentrations before and during monsoon are significant (P < 0.05, t-test) in south, central and parts of northern India (Fig. 3). The model results show that HCH isomers and PCB28 concentrations drop by ≈80%, ≈20% and ≈4% at 9, 22 and 29°N, respectively, PCB153 by ≈40% and ≈10% at 9° and 22°N, respectively, while they increase by ≈1% at 29°N. The model realistically reproduces the decline of atmospheric concentration at the field site (Southern India, 9°N). In the model, the HCH and PCB volatilisation fluxes are enhanced in the south (by 0.02-0.78 pg m^{-2} h^{-1} i.e., 3-11%) by the drop in air pollution, and to a lesser degree in central India (0.002-0.19 pg m^{-2} h^{-1}), and even less or negligible at a northern India site (<0.0001-0.007 pg m^{-2} h^{-1}).

3.3 Multidecadal air-surface cycling of POPs and historic trends

As a result of historical applications in agriculture and industry, POPs have been accumulating in soils in India over decades, partly continuing beyond peak emission. The atmospheric concentrations of PCBs have decreased since ≈1974, and α-

HCH and DDT since ≈1989, but soil concentrations only decreased for p,p'-DDT, while they have levelled off for α-HCH, or are even still on the rise (PCB153). Apart from changes over time, in general related to substance usage, the spatial variation of the pollutants' concentrations in mostly agricultural soils in India is very large i.e., ≥ 2 orders of magnitude. No data from background sites are available, though. The simulated pesticide levels, 0.5-20 ng g^{-1} α-HCH and 50-5000 and 1-200 ng g^{-1} DDT in the 1990s and 2000s, respectively, fall into the ranges spanned by observations (Sharma et al., 2014, besides others).

A north-south gradient is predicted for the pollutants, which is certainly influenced by the emission distribution (maximum in North India, in the Indo-Gangetic Plain) as well as by the direction of advection in air (prevailing westerly, with northerly component). While PCB28 have turned net-volatilisational after a few years upon release into the environment, this was much later for the highly lipophilic PCB153, ≈1 decade in southern India, ≈2 decades in central and even later in northern India (Fig. 4d). Nowadays, the diffusive air-surface exchange flux of the pesticides α-HCH and DDT is expected in the 0.1-1 fg m^{-2} h^{-1} range, several orders of magnitude lower than before or shortly after the ban (Fig. 4a-b). In contrast and related to on-going emissions from old industrial facilities, the strong decrease in PCB usage did not strongly impact air-surface cycling. The magnitude of fluxes remained within the same order of magnitude, 0.1-1 fg m^{-2} h^{-1}, being even on the rise in the case of PCB153 (Fig. 4c-d). The air-ground flux fluctuations are expectedly mediated by storage of part of the pollutant burden in vegetation, not resolved in the model.

The results of simulation of a fictive no-monsoon scenario suggest that the effects of monsoon have been limiting pollution of soils by HCH and PCB28 somewhat (<20% in 2014), while they have been contributing to DDT and PCB153 in soils by ≈50% and ≈10%, respectively. This suggests that monsoon's effect on re-volatilisation of soil burdens in response to drop in air concentrations at the onset of the mon-soon is a secondary effect for DDT and PCB153, while mon-soon's enhancement of air-to-soil transfer by wet deposition is the primary effect. This trend could be explained by the higher significance of wet deposition for DDT and PCB153, which are more partitioning to the particulate phase than HCH and PCB28, whereas the efficiency of gas scavenging is generally low for POPs.
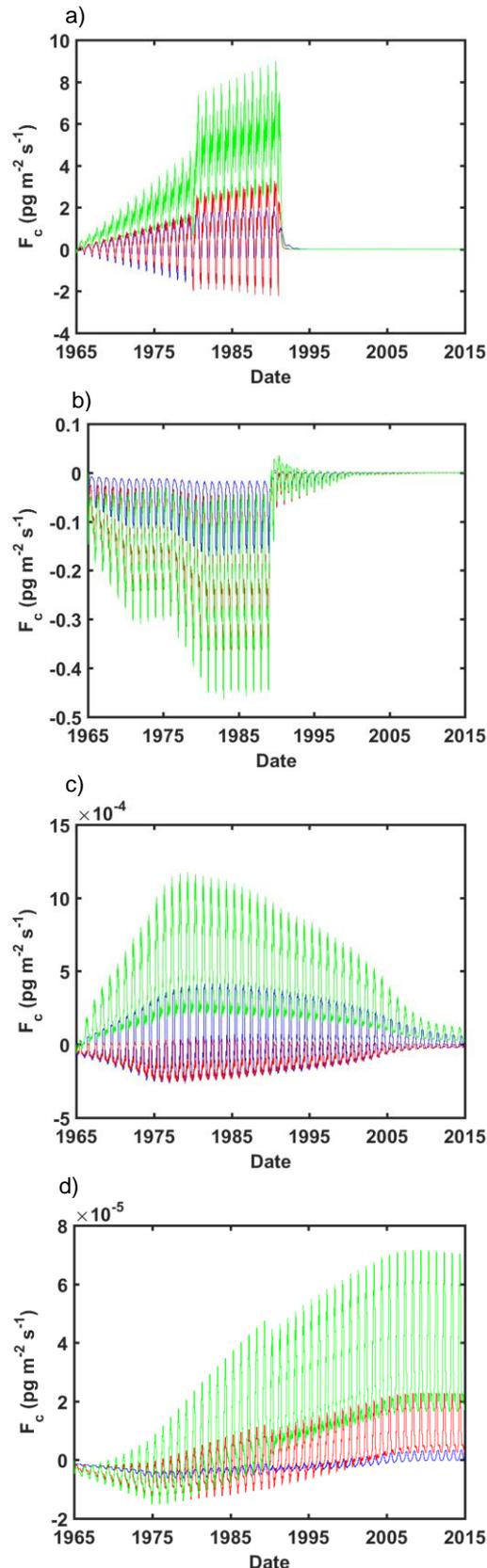

Fig. 4. Predicted multidecadal diffusive air-surface exchange fluxes. 1D model. F_c (positive = upward, negative = downward; lower) of (a) *α*-HCH, (b) *p,p'*-DDT, (c) PCB28, (d) PCB153 in the northern (29.7-33.4°N, blue), central (18.5-22.3°N, red) and southern (7.4-11.2°N, green) zones of India during 1965 – 2014.

Originalbeiträge

4. Discussion and conclusions

The results of both the field measurements and the modelling indicate a so far overlooked mechanism of pollutant cycling over the Indian subcontinent, i.e. monsoon-driven mobilisation of POPs from previously contaminated soils. The decline of POP levels in the southwesterly flow upon monsoon onset is partly related to the advection of clean air from the Indian Ocean (seasonal shift of the ITCZ), and partly by the washout of particulate pollutants (Fig. 5), as well as deepening of the planetary boundary layer. During transport over the Indian subcontinent near the surface, air masses collect pollution emitted from primary and secondary sources at the ground in urban and rural areas.

The secondary pollutant sources found correspond to a seasonal decrease of the soil burden by a few percent relative to the annual mean. This secondary source (re-volatilisation) weakens as a function of distance from the coast, as the monsoon advection propagates across the subcontinent (Fig. 5).
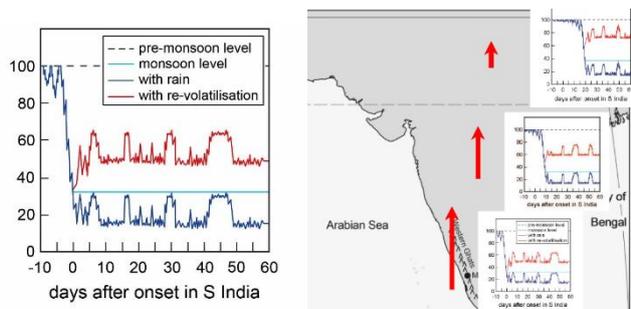

Fig. 5. Illustration of temporal (left) and spatial (right) variation of semivolatile and persistent substances' advection and re-volatilisation (red arrows) over southern, central and northern India in response to the monsoon onset and its northward propagation. Field site Munnar.

Secondary emissions, originating from past deposition to soils, also contribute to the long-range transport of atmospheric POPs to remote areas in central Asia (Sheng et al., 2013). This study confirms and quantifies the understanding that fluctuation of air pollution levels in general does enhance regional POP cycling. A similar trend of pollutant release from soils can be expected for other semivolatile organic substances in the region, such as polycyclic aromatic hydrocarbons (actually indicated by observations on site, not reported here) and brominated chemicals, as well as for other terrestrial or marine (Mulder et al., 2014) environments subject to other kind of seasonal drop in air pollution level.

References

Bidleman, T.F. (1999) Atmospheric transport and air-surface exchange of pesticides, Water Air Soil Pollut. 115, 115-166.

Cousins, I.T., Beck, A.J., Jones, K.C. (1999) A review of the processes involved in the exchange of semivolatile organic compounds (SVOC) across the air-soil interface, Sci. Total Environ. 228, 5-24.

Harner, T., Bidleman, T.F., Jantunen, L.M.M., Mackay, D. (2001) Soil-air exchange model of persistent pesticides in the U.S. Cotton Belt, Environ. Toxicol. Chem. 20, 1612–1621.

Lammel, G. (2004) Effects of time-averaging climate parameters on predicted multicompartmental fate of pesticides and POPs, Environ. Pollut. 128, 291-302.

Lammel, G., Stemmler, I. (2012) Fractionation and current time trends of PCB congeners: Evolvement of distributions 1950-2010 studied using a global atmosphere-ocean general circulation model, Atmos. Chem. Phys. 12, 7199-7213.

Lammel G., Degrendele C., Gunthe S.S., Mu Q., Muthalagu A., Audy O., Biju C.V., Kukučka P., Mulder M.D., Octaviani M., Příbylová P., Shahpoury P., Stemmler I., Valsan A.E. (2018) Re-volatilisation of soil accumulated pollutants triggered by the summer monsoon in India, Atmos. Chem. Phys. 18, 11031-11040.

Mu, Q., Shiraiwa, M., Octaviani, M., Ma, N., Ding, A.J., Su, H., Lammel, G., Pöschl, U., Cheng, Y.F. (2018) Temperature effect on phase state and reactivity controls atmospheric multiphase chemistry and transport of PAHs, Sci. Adv. 4, aap7314.

Mulder M.D., Heil A., Kukučka P., Klánová J., Kuta J., Prokeš R., Sprovieri F., Lammel G. (2014) Air-sea exchange and gas-particle partitioning of polycyclic aromatic hydrocarbons in the Mediterranean, Atmos. Chem. Phys. 14, 8905-8915.

Pozo, K., Harner, T., Lee, S.C., Sinha, R.K., Sengupta, B., Loewen, M., Geethalakshmi, V., Kannan, K., Volpi, V. (2011) Assessing seasonal and spatial trends of persistent organic pollutants (POPs) in Indian agricultural regions using PUF disk passive air samplers, Environ. Pollut. 159, 646-653.

Semeena, V.S., Lammel, G. (2005) The significance of the grasshopper effect on the atmospheric distribution of persistent organic substances, Geophys. Res. Lett. 32, L07804.

Sharma, B.M., Bharat, G.K., Tayal, S., Nizzetto, L., Čupr, P., Larssen, T. (2014) Environment and human exposure to persistent organic pollutants (POPs) in India: A systematic review of recent and historical data, Environ. Int. 66, 48-64.

Sheng, J.J., Wang, X.P., Gong, P., Joswiak, D.R., Tian, L.D., Yao, T.D., Jones, K.C. (2013) Monsoon-driven transport of organochlorine pesticides and polychlorinated biphenyls to the Tibetan Plateau: Three years atmospheric monitoring study, Environ. Sci. Technol. 47, 3199-3208.

Wania, F., Mackay, D. (1993) Global fractionation and cold condensation of low volatile organic chlorine compounds in polar regions, Ambio 22, 10-18.

Korrespondenzadresse

Gerhard Lammel
Max-Planck-Institut für Chemie
Abteilung für Multiphasenchemie
Hahn-Meitner-Weg 1
55128 Mainz