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Revolatilisation of soil-accumulated pollutants triggered by the summer monsoon in India

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Abstract. Persistent organic pollutants that have accumulated in soils can be remobilised 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 hexachlorocyclohexane (HCH), dichlorodiphenyltrichloroethane (DDT) and its derivatives, endosulfan and polychlorinated biphenyls (PCBs) in air at a mountain site (all in the range 5–20 pg m^{-3}) by 77 %, 70 %, 82 % and 45 %, respectively. The analysis of fugacities in soil and air suggest that the arrival of summer monsoon triggers net volatilisation or enhances ongoing revolatilisation of the now-banned chemicals HCH and PCBs from background soils in southern India. The response of the air–soil exchange was modelled using a regional air pollution model, WRF-Chem PAH/POP. The results suggest that the air is increasingly polluted during transport by the south-westerly monsoon winds across the subcontinent. Using a multidecadal multimedia mass balance model, it is found that air–surface exchange of HCH and DDT have declined since the ban of these substances from agriculture, but remobilisation 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. Semi-volatile substances (i.e. vapour pressure at 293 K in the range 10^{-6}–10^{-2} Pa) diffuse across air–sea and air–land interfaces in both directions. They tend to net volatilise from land and sea surfaces on which they had previously been deposited once a level of contamination in chemical equilibrium with air pollution was reached (Bidleman, 1999; Cousins et al., 1999; Meijer et al., 2003; Kurt-Karakus et al., 2006; Wong et al., 2007; Růžičková et al., 2008; Degrendele et al., 2016). The potential to revolatilise is relevant to assessing risks from chemicals as it enhances the long-range transport potential and hence facilitates transport to and accumulation in remote areas, which are pristine with regard to primary (direct) contamination (Wania and Mackay, 1993; Semeena and Lammel, 2005; Wania and Westgate, 2008; Lammel and Stemmler, 2012). In the terrestrial environment, soils represent the main reservoir of the more lipophilic substances (log $K_{oa} \gtrsim 6$), while smaller mass fractions are stored in the atmosphere, vegetation and freshwater sources as suggested by field studies (Meijer et al., 2003) and modelling (Wania, 2006; Lammel et al., 2007; Lammel and Stemmler, 2012). Thus, understanding the dynamics of soil contamination and exchange with the overlying air is important for assessing spatio-temporal scales of the distribution and impact of local

pollution. Air–soil dynamics occurs on various timescales, from multi-year long-term trends (Lammel and Stemmler, 2012) to seasonal cycling and short-term fluctuations (Bidleman, 1999). One key region, where persistent organic pollutants have been heavily used, is southern Asia. In India, high levels of organochlorine pesticides (OCPs) were found in both abiotic (Ramesh et al., 1989, 1991; Kumari et al., 1996; Rajendran et al., 1999; UNEP, 2002; Shunthirasingham et al., 2010; Pozo et al., 2011, Chakraborty and Zhang, 2012; Bajwa et al., 2016) and biotic (Ramesh et al., 1990, 1992; Senthilkumar et al., 2001; UNEP, 2002) environmental samples. The country is considered a hotspot for DDT and hexachlorocyclohexane (HCH) with no evidence of decline (Sharma et al., 2014). Besides OCPs, polychlorinated biphenyls (PCBs) and polybrominated diphenylethers (PBDEs) are of relevance in southern Asia, where they were used as flame retardants. High levels of PBDEs were reported in India (Zhang et al., 2008) and waste might be a significant ongoing source of penta- and hexachlorobenzene (PeCB, HCB), PCBs (Senthilkumar et al., 2001; Wong et al., 2010; Zhang et al., 2011; Sharma et al., 2014) and PBDEs (Breivik et al., 2012; Sharma et al., 2014). Thus far, studies on the environmental exposure of the Indian subcontinent have been mostly limited to urban areas (Chakraborty and Zhang, 2012; Sharma et al., 2014; Chakraborty et al., 2015), while the continental background was scarcely addressed. The air–soil dynamics of OCPs or other semi-volatile substances related to the monsoon have not been studied yet. 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 (southern Asia and adjacent seas) to intercontinental (from the Indian Ocean with influence from the relatively clean Southern Hemisphere (IMD, 2014).

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 mobilises pollutants stored in soils. To this end, (1) field observations in background soils in the Western Ghats, the first highlands that the south-westerly 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 3-D air pollution model coupled to a soil compartment (3-D model WRF-Chem PAH/POP). Finally, (3) the long-term chemodynamics is assessed by multimedia mass balance modelling, forced by climate and 3-D modelling data (1-D model, series of two boxes).

2 Methods

2.1 Sites and sampling

Air samples were collected from 5 May to 10 June 2014, 90 km inland from the Arabian Sea coast, on a slope oriented south-west 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 to 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 (north-west to north-east). Additional land cover includes shrubs (south, east) and, to a lesser extent, agricultural fields and residential areas (south to south-east). Twenty-four air samples were collected. The 2014 monsoon season in the area was characterised by scattered rainfall at the monsoon onset, after which rainfall became persistent from the last week of June (Valsan et al., 2016).

For air sampling a high volume sampler (Digitel DH-77) equipped with a quartz-fibre filter and two polyurethane foam (PUF) plugs (Gumotex Břeclav, density 0.030 g cm^{-3}, 100 mm diameter, total depth 12 cm, cleaned by extraction in acetone and dichloromethane) was used. Soil samples were taken from one plot each in the tea plantation, in shrubs and in forest, at distances within 1 km from each other. The uppermost 5 cm of soil was collected (using a spade, Edelman auger and sieve). Each soil sample is a composite (pooled sample), produced from equal amounts of soil collected from six 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 (GOI, 1985; FAO, 2014), horizon A, which had a brownish, loose, single grain structure, with fine roots in the shrubs and forest. Soil samples were homogenised 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 (Büchi B-811). Surrogate extraction standards (PCB30, PCB185,^{13}C BDEs 28, 47, 99, 100, 153, 154, 183, 209) were spiked on each sample prior to extraction. The volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and clean-up was achieved on a Florisil column. Samples were analysed using a GC-MS/MS (gas chromatograph coupled with a tandem mass spectrometer) Agilent 7890 coupled to Agilent 7000B with a SGE HT-8 column (60 m × 0.25 mm × 0.25 μm) for α-, β-HCH, γ- and δ-HCH (i.e. four HCH isomers), o, p'- and p, p'-DDE, -DDD and -DDT (six DDX compounds), penta- and hexachlorobenzene (PeCB, HCB), PCB28, −52, −101, −118, −153, −138 and

−180 (i.e. seven indicator PCBs), aldrin, dieldrin, endrin, α-and γ-chlordan, α- and β-endosulfan, endosulfan sulfate and mirex. More details are given in the Supplement Sect. S1.1.

The mean of three field blank values was subtracted from the air sample values. Values below the mean + 3 standard deviations of the field blank values were considered to be < LOQ. Field blank values of a number of analytes in air samples were below the instrument limit of quantification (ILOQ), which corresponded to 0.006–0.012 pg m^{-3} for PCB/OCPs and 0.50–5.2 pg m^{-3} for PBDEs (Table S1 in the Supplement). LOQs ranged 0.006–0.06 pg m^{-3} for PCBs, 0.006–0.12 pg m^{-3} for OCPs (with few exceptions higher) and 0.001–0.01 pg m^{-3} for PBDEs (Supplement Sect. S1.1, Table S1).

Organic and elemental carbon in filter samples, as well as total organic carbon in soil was determined by a thermal-optical method (Sunset Lab., USA; EUSAAR protocol).

The pollutant fugacities (Harner et al., 2001) have been derived from concentrations in soil and air (details in Supplement Sect. S1.2). The onset of the monsoon on site was dated with high temporal resolution based on air parcel history (back trajectory analysis, Supplement Sect. S1.3).

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 the WRF-Chem PAH/POP model. The WRF-Chem PAH/POP has been recently extended from the regional model WRF-Chem version 3.6.1 (Grell et al., 2005; Mu et al., 2018), to also represent the chemistry, in- and below-cloud scavenging, gas-particle partitioning and surface gas exchange of semi-volatile organics (described in Supplement Sect. S1.4.1, input data in S1.4.3). 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 southern Asian domain (5–32° N, 69–89° E), was driven by NCEP reanalyses (6 h, 1° × 1° resolution). Physical and chemical spin-up time was 4 days. Primary emissions were considered for DDT and PCBs (Supplement Sect. S1.4.1), while the secondary emissions were modelled based on initialising the soils of India uniformly by the observed levels in background soils (shrub, forest, Sect. 2.1). Non-zero air concentrations, observed before and during the monsoon at the site (see above), were advected continuously at all boundaries of the domain (Supplement Sect. S1.4.1). 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 semi-volatile organic compounds studied were simulated by a non-steady state one-dimensional (series of 7 two-boxes) model of inter-compartmental mass exchange (multimedia mass balance model (Lammel, 2004; Fig. S1 in the Supplement). 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 (Supplement Sect. S1.4.2, input data in Sect. S1.4.3). 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

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 a background site (Table 1). Actually, these HCH and DDX levels are lower than ever reported from soils in India, which previously ranged 1.6–835 for HCH (excluding hotspots; Sharma et al., 2014), 14–934 ng g^{-1} for DDX (Sharma et al., 2014) and 30 (0–149) pg g^{-1} (rural sites, same congeners; 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 (Table S2).

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, Table S3). 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 were insignificant even on the $p < 0.1$ level (unpaired Student t test). Precipitation increased by a factor of ≈ 2 at the monsoon onset (from 3.8 to 8.0 mm day^{-1}), associated with convective activity (Valsan et al., 2016). With 2.3–17.7 pg m^{-3} Σ_4HCH and 0.36–10.4 pg m^{-3} Σ_6DDX (Table S3) the measurements at Munnar range at the lower end of the range reported from rural sites in India in years after a ban in agriculture (listed in Table S6c). 1.3–8.5 pg m^{-3} endosulfan (including endosul-

Table 1. Observed concentrations in soil, c_s (ng g^{-1}; together with standard deviation based on 3 replicates) of **(a)** pesticides, **(b)** PCBs and **(c)** PBDEs (quantified species only). TOC is total organic carbon content (% of dry mass).

Land use	Tea plantation	Shrubs	Forest
(a)			
TOC	4.4	10.75	4.0
PeCB	0.018 ± 0.001	0.017 ± 0.002	0.010 ± 0.000
HCB	0.021 ± 0.001	0.023 ± 0.005	0.019 ± 0.000
α-HCH	0.036 ± 0.005	0.020 ± 0.001	0.010 ± 0.000
β-HCH	0.016 ± 0.000	0.019 ± 0.000	<0.010
γ-HCH	0.054 ± 0.011	0.055 ± 0.001[a]	0.055 ± 0.003
δ-HCH	<0.010	<0.010	<0.010
ε-HCH	<0.010	<0.010	<0.010
o,p'-DDE	1.83 ± 0.12	0.012 ± 0.001	0.006 ± 0.000
p,p'-DDE	12.13 ± 0.50	0.22 ± 0.05	0.077 ± 0.004
o,p'-DDD	0.49 ± 0.03	0.007 ± 0.001	<0.010
p,p'-DDD	0.17 ± 0.01	0.025 ± 0.002[a]	0.14 ± 0.00
o,p'-DDT	11.34 ± 0.71	0.044 ± 0.001[a]	0.025 ± 0.003
p,p'-DDT	1.90 ± 0.14	0.12 ± 0.00[a]	0.060 ± 0.026
(b)			
PCB28	0.054 ± 0.008	0.055 ± 0.000[a]	0.060 ± 0.002
PCB52	0.048 ± 0.022	0.050 ± 0.005[a]	0.053 ± 0.007
PCB101	0.043 ± 0.009	0.050 ± 0.007[a]	0.051 ± 0.004
PCB118	0.021 ± 0.005	0.025 ± 0.002	0.026 ± 0.003
PCB153	0.034 ± 0.008	0.040 ± 0.007	0.038 ± 0.008
PCB138	0.031 ± 0.008	0.037 ± 0.005	0.038 ± 0.005
PCB180	0.015 ± 0.004	0.014 ± 0.001	0.013 ± 0.008
(c)			
BDE28	<0.35	0.77 ± 0.22	0.54 ± 0.38
BDE47	5.09 ± 0.53	7.83 ± 0.01[a]	7.69 ± 0.38
BDE66	0.96 ± 0.14	0.55 ± 0.52	<0.70
BDE100	0.32 ± 0.04	<0.81	0.71 ± 0.18
BDE99	1.77 ± 0.05	1.99 ± 0.08[a]	1.81 ± 0.34
BDE85	<0.27	<1.50	<0.32
BDE154	<0.31	<0.25	<0.25
BDE153	<0.68	<0.40	<0.43
BDE183	<0.48	1.58 ± 0.09	<0.88

[a] Based on two replicates.

Figure 1. Observed concentrations in air, c_a, of pesticides (Σ_4HCH, Σ_6DDX, Σ_3Endosulfan), Σ_7PCB, Σ_9PBDE (pg m^{-3}), OC and EC (μg m^{-3}) before and after the onset of the south-westerly monsoon in Munnar, India, 2014. Error bars reflect standard deviations. All concentration changes are significant ($p < 0.05$ level, t test) except for PBDE.

diffusive air–soil exchange fluxes prior to the monsoon. With the monsoon onset f_s/f_a generally increases (except for PB-DEs, for which concentrations in monsoon air were somewhat elevated compared to pre-monsoon air; Table S3). This can trigger a change in flux direction for the tri- to hexachlorinated PCBs (i.e. all targeted except PCB180) and $\alpha-$ and β-HCH (Fig. 2). For example, $\alpha-$ and γ-HCH were close to phase equilibrium before onset, but net volatilisation occurred during the 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

Findings from the field campaign were used to constrain the regional WRF-Chem model simulations for the Indian subcontinent. In the model experiment the pre-contaminated soil (as observed at the background site, mean of soil samples) is exposed to a drop of atmospheric concentrations, forced from the domain boundaries along with the monsoon onset and its northward propagation. In a control experiment pre-monsoon air concentrations are prescribed at the boundaries throughout the simulation (detailed in Methods and Supplement Sect. S1.4.1).

Within a few days after the monsoon onset in southern India, the advection of air from the Indian Ocean reduced atmospheric levels of HCH and PCB 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 north-western states of Gujarat and Rajasthan (i.e. north of $\approx 22°$ N and west of $\approx 77°$ E; Valsan et al., 2016), 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 af-

fan sulfate) measured in Munnar in 2014, shortly after the ban of the pesticide is 3 orders of magnitude below what was reported from 2006 to 2007 (i.e. 1000–9200 pg m^{-3} at rural locations in southern India; Pozo et al., 2011). Similarly, the range of 2.8–70 pg m^{-3} Σ_7PCBs measured in 2014 at Munnar lies distinctly below 32–440 pg m^{-3}, reported for the same substances at rural coastal sites in 2006 (Zhang et al., 2008).

The fugacity ratio f_s/f_a is used to characterise air–soil exchange (Supplement Sect. S1.2). Calculations indicate both downward (PCB180, DDT and metabolites over forest and shrub soils, BDE99) and upward (PCB101, PeCB, DDT and metabolites over tea garden soils, BDE28, BDE47; Fig. 2)
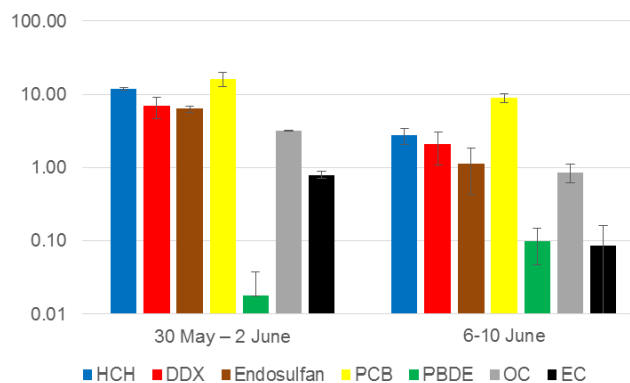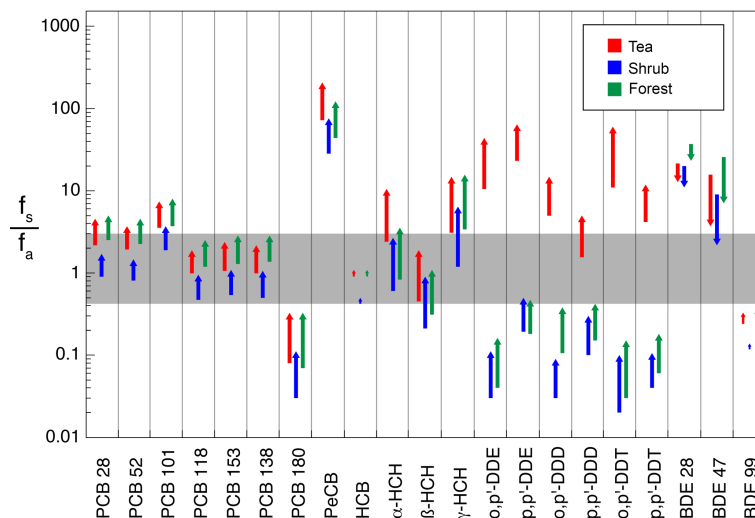
Figure 2. Change in air–soil chemical equilibrium with the monsoon onset. Arrows denote direction and amount of change in the fugacity ratio, f_s/f_a, over various soils from prior to posterior onset. $f_s/f_a < 1$ denotes downward (net deposition) while $f_s/f_a > 1$ denotes upward (net volatilisation) flux. The shaded zone ($0.33 < f_s/f_a < 3$) indicates insignificance of deviation from 1 due to input data uncertainties.

ter a decline of $> 3\,\mathrm{pg\,m^{-3}}$ of HCH isomers and $> 5\,\mathrm{pg\,m^{-3}}$ of PCB28, respectively, in the south and south-west. The response of the air–soil system 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 subcontinent, as the air receives secondary emissions from the soils. The secondary emissions increase with distance from the coasts after the monsoon onset. The differences in concentrations before and during the monsoon are significant ($p < 0.05$, t test) in southern and central India and parts of the north (Fig. 3). The model results show that HCH isomers and PCB28 concentrations drop by $\approx 80\,\%$, $\approx 20\,\%$ and $\approx 4\,\%$ at 9, 22 and 29° N, respectively, PCB153 by $\approx 40\,\%$ and $\approx 10\,\%$ at 9 and 22° N, respectively, while they increase by $\approx 1\,\%$ at 29° N (Table S5a). The model realistically reproduces the decline in atmospheric concentration at the field site (southern India, 9° N; Table S6a, b). In the model, the HCH and PCB volatilisation fluxes are enhanced in the south (by 0.02–$0.78\,\mathrm{pg\,m^{-2}\,h^{-1}}$ i.e. 3–11 %; Table S5b) by the drop in air pollution, to a lesser degree in central India (0.002–$0.19\,\mathrm{pg\,m^{-2}\,h^{-1}}$), and by an even smaller or negligible amount at a site in northern India (< 0.0001–$0.007\,\mathrm{pg\,m^{-2}\,h^{-1}}$).

The south-westerly summer monsoon is associated with strong convection that effectively lifts air pollution to high altitudes in the troposphere. The monsoon outflow from India is predominantly directed towards western Asia, Africa and the Mediterranean, while a smaller fraction is transported towards eastern Asia (Lawrence and Lelieveld, 2010).

3.3 Multidecadal air–surface cycling of POPs and historic trends

To put the above described seasonal feature into historical context, with long-term trends of air–soil contamination, a multimedia mass balance box model was developed and applied to several measured contaminants.

As a result of historical applications in agriculture and industry, POPs have been accumulating in soils in India over decades (Fig. S3), partly continuing beyond peak emission. The atmospheric concentrations of PCBs have decreased since ≈ 1974 and those of α-HCH and DDT since ≈ 1989, but soil concentrations only decreased for p, p'-DDT and levelled off for α-HCH (Fig. S3a, b), or are even still on the rise (PCB153; Fig. S3d). Apart from changes over time, in general related to substance usage, the spatial variation in the concentrations of pollutants in mostly agricultural soil in India (Ramesh et al., 1991; Kumari et al., 1996; Sharma et al., 2014) is very large, i.e. ≥ 2 orders of magnitude. No data from background sites are available (Table S6c). The simulated pesticide values, 0.5–$20\,\mathrm{ng\,g^{-1}}$ α-HCH and 50–5000 and 1–$200\,\mathrm{ng\,g^{-1}}$ DDT in the 1990s and 2000s, respectively (Fig. S2), fall into the ranges spanned by the observations (Table S6c). For PCBs, no soil data were reported (UNEP, 2002).

A north–south gradient is predicted for the pollutants (Fig. S3), which is certainly influenced by the emission distribution (maximum in northern India, in the Indo-Gangetic Plain) as well as the direction of advection in air (prevailing westerly, with northerly component). For α-HCH, this gradient was also reflected in soil distributions in India, which were based on a gridded mass balance model (Xu et al., 2013). While PCB28 had net volatilisation after a few years
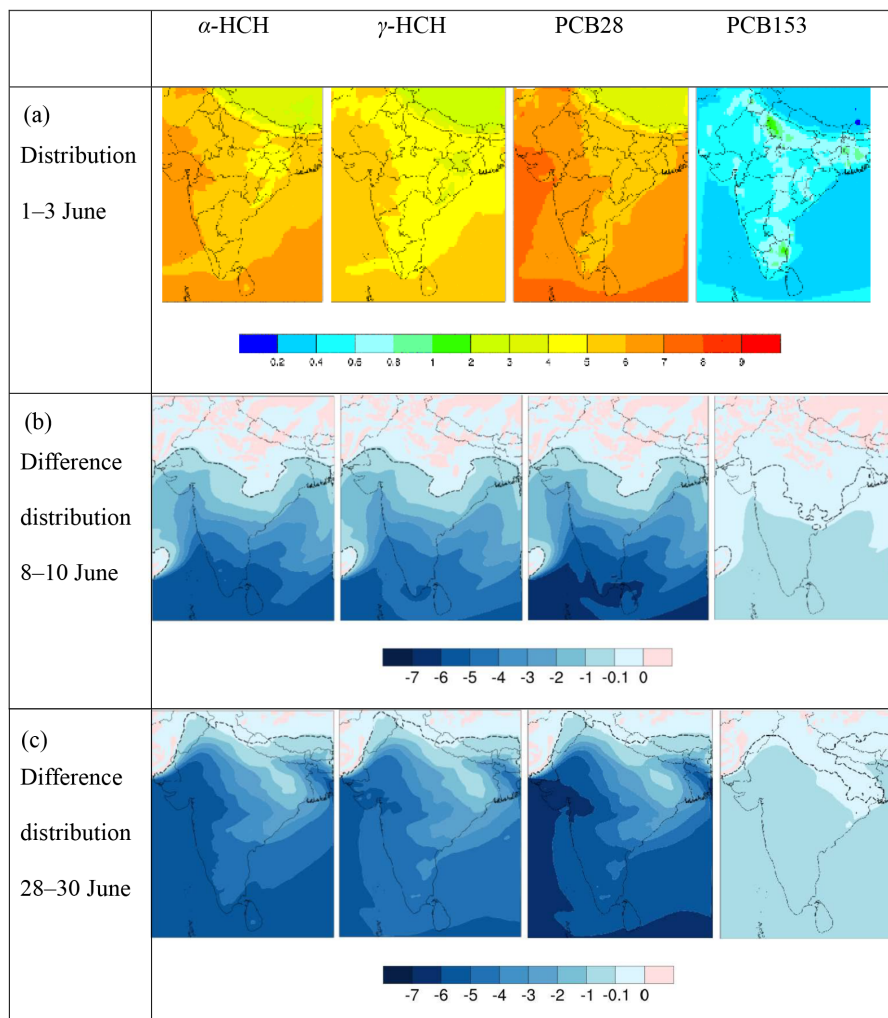
Figure 3. Air pollutant distributions. α-HCH, γ-HCH, PCB28 and PCB153 (pg m^{-3}) predicted concentrations in near-ground air prior to monsoon onset (1–3 June, **a**) and difference distributions due to monsoon advection (experiment – control; **b**: 8–10 June, **c**: 28–30 June 2014). The difference is significant ($p < 0.05$, t test) south of the dotted line.

upon release into the environment, this was much later for the highly lipophilic PCB153, with ≈ 1 decade in southern India, ≈ 2 decades in central and even longer 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 ongoing 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 fluctuations are expectedly mediated by the storage of part of the pollutant burden in vegetation (not resolved in the model).

The results of a simulation of a fictive no-monsoon scenario suggest that the effects of the monsoon have been limit-

ing pollution of soils by HCH and PCB28 somewhat ($< 20\%$ in 2014), while they have been contributing to DDT and PCB153 in soils by $\approx 50\%$ and $\approx 10\%$, respectively (Supplement Sect. S2.2.3, Table S8). This suggests that the monsoon's effect on revolatilisation of soil burdens in response to drop in air concentrations at its onset is a secondary effect for DDT and PCB153, while the monsoon'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 partition the particulate phase more than HCH and PCB28, whereas the efficiency of gas scavenging is generally low for POPs (Atlas and Giam, 1988; Bidleman, 1988; Shahpoury et al., 2015).
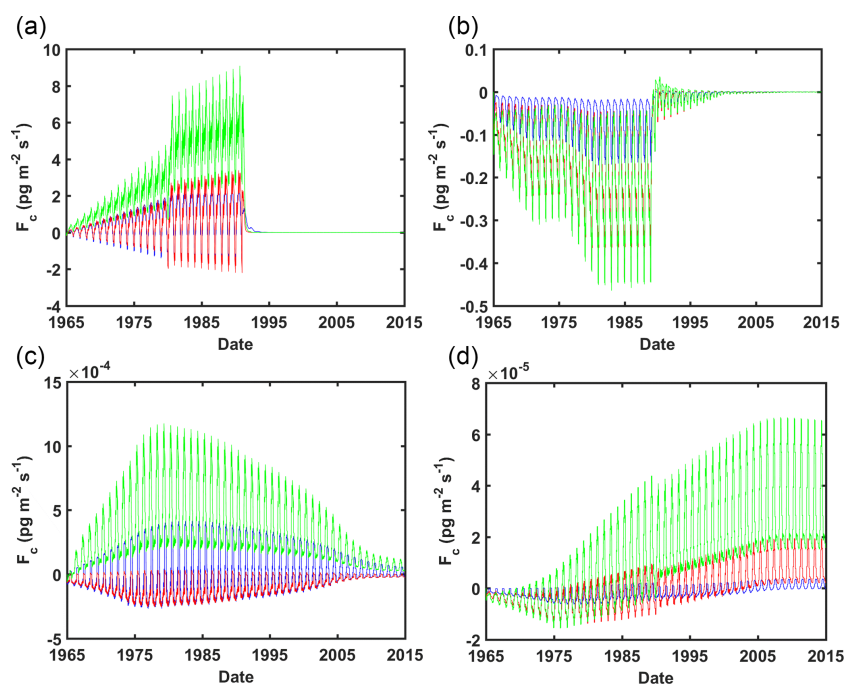
Figure 4. Predicted multidecadal diffusive air–surface exchange fluxes. 1-D model. F_c (positive is upward, negative is downward; lower) of **(a)** α-HCH, **(b)** p, p'-DDT, **(c)** PCB28, **(d)** PCB153 in the northern (29.7–33.4° N, blue), central (18.5–22.3° N, red) and southern (7.4–11.2° N, green) zones of India during 1965–2014. Predicted concentrations in air and soil are shown in Fig. S3 in the Supplement.
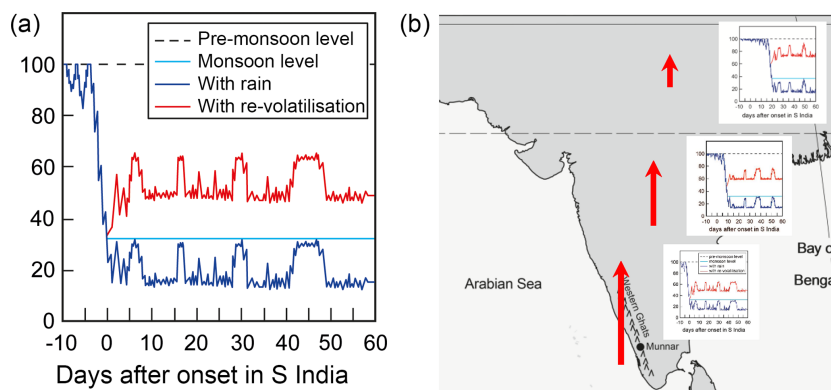

Figure 5. Illustration of temporal **(a)** and spatial **(b)** variation in semi-volatile and persistent substance advection over southern, central and northern India in response to the monsoon onset and its northward propagation. Field site is Munnar.

4 Discussion

Both the field measurements and modelling results of this study 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 south-westerly flow at the 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. In contrast, washout of gaseous organic pollutants is very limited,

because of low water solubility (Atlas and Giam, 1988; He and Balasubramanian, 2010; Shahpoury et al., 2015). Because of the convective vertical transport during the monsoon, pollutants can be released at the cloud top and subsequently undergo long-range transport in the upper troposphere over and beyond southern Asia. 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. We have shown here that secondary sources are partly triggered by the low concentrations in relatively pristine air, which are most pronounced in areas that receive marine background air, i.e. in south-

western India. This corresponds to a seasonal decrease in the soil burden by a few percent relative to the annual mean. This secondary source (revolatilisation) weakens as a function of distance from the coast, as the monsoon advection propagates across the subcontinent (Table S4b, Fig. 5). The 2014 south-westerly monsoon was relatively weak (South Asian summer monsoon index; Li and Zeng, 2002) compared to the long-term mean. For strong monsoon events, more efficient air-to-soil transfer of pollutants by wet deposition could result. The simulation under a no-monsoon scenario suggests that the latter process dominates for the least water soluble and least volatile (high partitioning to the particulate phase) pollutants. Scavenging and air-to-soil transfer of POPs under monsoon rain had hardly been studied in the field and should be addressed.

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; Gong et al., 2015). A similar trend of pollutant release from soils can be expected for other semi-volatile organic substances such as polycyclic aromatic hydrocarbons (actually indicated by observations on site, not reported here) and brominated chemicals.

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