Response to reviewers' comments

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Title: Re-volatilisation of soil accumulated pollutants triggered by the summer monsoon in India
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We would like to thank the reviewers for their thoughtful reading, comments and questions, which considerably helped to improve this manuscript. We have addressed all comments below and have indicated the corresponding modifications in the revised version of the manuscript which is attached to this response (changes highlighted).

Colour coding below:
(1) comments from Referees,
(2) author's response,
(3) author's changes

Anonymous Referee #1

Does modeling study point a specific region as a source of re-volatilised pesticides in the study area?

Under on-going primary emissions (which applies for PCBs and DDT until present day, and for α-HCH until 1980s), the highest absolute air-soil exchange fluxes, F_c, are simulated for southern India, somewhat lower for northern, and least for central India (see also Fig. 4). The -HCH air-soil exchange flux, which remains long after the ban, is found higher in the northernmost zone than in southern and central India, corresponding to a somewhat higher soil burden in the north (Fig. S3a). (Multi-decadal simulation using the 1D multimedia mass balance model, Sections 2.3 and S1.4.2).

The exchange fluxes are resulting from a combination of the historical emission distributions and fate, the latter latitudinal dependence being dominated by differences in climate across latitudinal zones.

Anonymous Referee #2

The authors discussed the re-volatilisation of the nowadays-banned POPs accumulated in soils. The abstract is too simple; there was not description on the data, the methods, and models used. The way of the method validation is also not very clear.

Abstract now extended, including quantification of concentrations in air and drop of these, identification of models used. sentences to abstract. 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 enhance on-going re-volatilisation… (after the first sentence of the abstract) The response of the air-soil exchange was modelled using a regional air pollution model, WRF-Chem-PAH/POP. The results suggest that… (before the last sentence) Using a multidecadal multi-media mass balance model, it is found that… (beginning of the last sentence of the abstract)

Quantified the drop in air concentration in the text (Section 3.1, lines 168-169) using the same metrix: concentration changes i.e., 77, 70, 82 and 45 % for Σ_4HCH, Σ_6DDX, Σ_3Endosulfan and Σ_7PCBs

Specific Comments:

Line 18: Clean air masses from the Indian Ocean, advected with the onset of the summer monsoon, are found to trigger or enhance re-volatilisation of the nowadays banned chemicals hexachlorocyclohexane (HCH) and polychlorinated biphenyls (PCBs) from background soils in southern India.
Comments: Re-volatilisation of the chemicals in soil always exists at the boundary between soil and air, and cannot triggered by clean air masses from the Indian Ocean.
True. rephrased accordingly (line 19-20)

Line 29: Semivolatile substances (i.e., vapour pressure at 293 K in the range 10^{-6} –10^{-2} Pa) tend to re-volatilise from land and seasurfaces to which they had previously been deposited, once a level of contamination in chemical equilibrium with air pollution is reached.
Comments: This statement is not correct since both the deposition and re-volatilisation co-exist regardless if the equilibrium is reached or not.
Thnaks, corrected accordingly (line 29-30)

Line 56: Thus far, studies on 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.
Comments: The following three published papers should be addressed in the manuscript, since these three papers studied the SVOCs in Indian air and soil on a national scale.
Li, W. L., Ma, W. L., Zhang, Z. F., Liu, L. Y., Song, W. W., Jia, H. L., Ding, Y. S., Nakata, H., Minh, N. H., Sinha, R. K., Moon, H. B., Kannan, K., Sverko, E., Li, Y. F., 2017, Occurrence and Source Effect of Novel Brominated Flame Retardants (NBFRs) in Soils from Five Asian Countries and Their Relationship with PBDEs, Environmental Science & Technology, 51, 11126-11135
Li, Wenlong, Ma Wan-Li, Jia Hongliang, Hong Wenjun, Moon Hyo-Bang, Nakata Haruhiko, Minh Nguyen Hung, Sinha Ravindra Kumar, Chi Kai Hsien, Kannan Kurunthachalam, Sverko Ed, Li Yi-Fan, (2016). Polybrominated Diphenyl Ethers (PBDEs) In Surface Soils across Five Asian Countries: Levels, Spatial Distribution and Source Contribution. Environmental Science & Technology. 2016, 50 (23), 12779–12788
Hong, Wen-Jun, Hongliang Jia, Wan-Li Ma, Ravindra Kumar Sinha, Hyo-Bang Moon, Haruhiko Nakata, Nguyen Hung Minh, Kai Hsien Chi, Wen-Long Li, Kurunthachalam Kannan, Ed Sverko, and Yi-Fan Li, 2016, Distribution, fate, inhalation exposure and lung cancer risk of atmospheric polycyclic aromatic hydrocarbons in some Asian countries, Environmental Science & Technology. 2016, 50 (13), 7163–7174
Thanks, included results and citation Li et al. 2016 (lines 156-160). The other two papers address pollutants not studied here.

Page 205: The differences in concentrations before and during monsoon are significant ($P < 0.05$, t-test) in south, central and parts of northern India (Fig. 3b,c).
Comments: In Fig. 3, there is no Panels b and c indicated!
Corrected (line 209)

Line 225: 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, Fig. S4).
Comments: There is no Fig. S4!
Corrected (line 229)

Line 260: Both, field measurements and modelling results reveal a thus far overlooked mechanism of pollutant cycling over the Indian subcontinent, i.e. monsoon-driven mobilization from previously contaminated soils.
Comments: Rewrite the sentence.
Followed for better clarity, and corrected "The results of 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."

Re-volatilisation 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 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 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 enhance on-going re-volatilisation of the nowadays 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 southwesterly monsoon winds across the subcontinent. Using a multidecadal

multi-media 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 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 (Bidelman, 1999; Cousins et al., 1999; Meijer et al., 2003; Kurt-Karakus et al., 2006; Růzičková et al., 2008; Wong et al., 2007; Degrendele et al., 2016). 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; 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 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 time scales, 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 South

Asia. In India, high levels of organochlorine pesticides (OCPs) were found in both abiotic (Ramesh et al., 1989, 1991; Shunthirasingham et al., 2010; Rajendran et al., 1999; Kumari et al., 1996; UNEP, 2002; 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 as a hot spot for DDT and hexachlorocyclohexane (HCH) with no evidence of decline (Sharma et al., 2014). Besides OCPs, also polychlorinated biphenyls (PCBs) and polybrominated diphenylethers (PBDEs) are of relevance in South 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 on-going 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 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 semivolatile substances related to monsoon has 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 (South 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 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, agricultural fields and residential areas (south to southeast). 24 air samples were collected. The 2014 monsoon season in the area was characterized 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 2 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 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 (GOI, 1985; FAO, 2014), 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 (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 x 0.25 mm x 0.25 µm) for α-, β-HCH, γ-, and δ-HCH (i.e., 4 HCH isomers), *o,p'*- and *p,p´*-DDE, -DDD and –DDT (6 DDX compounds), penta- and hexachlorobenzene (PeCB, HCB), PCB28, -52, -101, -118, -153, -138 and -180 (i.e., 7 indicator PCBs), aldrin, dieldrin, endrin, α- and γ-chlordan, α- and β-endosulfan, endosulfan sulphate, and mirex. More details are given in the Supplementary Information, S1.1.

The mean of 3 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). 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 (SI 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 Supporting Information S1.2). The onset of the monsoon on site was dated with high temporal resolution based on air parcel history (back trajectory analysis, Supporting Information 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 semivolatile organics (described in Supporting Information 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 South Asian domain (5-32°N/69-89°E), was driven by NCEP re-analyses (6-hourly, 1° × 1° resolution). Physical and chemical spin-up time was 4 days. Primary emissions were considered for DDT and PCBs (SI S1.4.1), 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 (SI 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.

2.3 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; SI Fig. S1). 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 (Supporting Information S1.4.2, input data in 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 "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 hot spots; 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 Σ_9PBDEs, 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 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 (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 ban in agriculture (listed in Table S6c). 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). 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 characterize air-soil exchange (Supplementary, Text 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) diffusive air-soil exchange fluxes prior to the monsoon. With the monsoon onset f_s / f_a generally increases (except for PBDEs, of which concentrations in monsoon air were somewhat elevated compared to pre-monsoon air; Table S3). This can trigger a change of flux direction for the tri- to hexachlorinated PCBs (i.e., all targeted except PCB180) 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

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 Supporting Information, S1.4.1).

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; 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 after a decline of > 3 pg m^{-3} of HCH isomers and > 5 pg m^{-3} of PCB28, respectively, in the south and southwest. 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 (Table S5a). The model realistically reproduces the decline of 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 pg m^{-2} h^{-1} i.e., 3-11%; Table S5b) 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}).

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

227 **3.3 Multidecadal air-surface cycling of POPs and historic trends**

228 To put the above described seasonal feature into historical context, with long-term trends of
229 air/soil contamination, a multi-media mass balance box model was developed and applied for
230 several measured contaminants.

231 As a result of historical applications in agriculture and industry, POPs have been accumulating in
232 soils in India over decades (Fig. S3), partly continuing beyond peak emission. The atmospheric
233 concentrations of PCBs have decreased since ≈1974, and α-HCH and DDT since ≈1989, but soil
234 concentrations only decreased for *p,p'*-DDT, while they have levelled off for α-HCH (Fig.
235 S3a,b), or are even still on the rise (PCB153, Fig. S3d). Apart from changes over time, in general
236 related to substance usage, the spatial variation of the pollutants' concentrations in mostly
237 agricultural soil in India (Ramesh et al., 1991; Kumari et al., 1996; Sharma et al., 2014) is very
238 large i.e., ≥ 2 orders of magnitude. No data from background sites are available (Table S6c). The
239 simulated pesticide values, 0.5-20 ng g^{-1} α-HCH and 50-5000 and 1-200 ng g^{-1} DDT in the 1990s
240 and 2000s, respectively (Fig. S2), fall into the ranges spanned by the observations (Table S6c).
241 For PCBs, no soil data were reported (UNEP, 2002).
242
243 A north-south gradient is predicted for the pollutants (Fig. S3), which is certainly influenced by
244 the emission distribution (maximum in North India, in the Indo-Gangetic Plain) as well as to the

direction of advection in air (prevailing westerly, with northerly component). For α-HCH, such a gradient was also reflected in soil distributions in India which were based on a gridded mass balance model (Xu et al., 2013). 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 (SI S2.2.3, Table S8). This suggests that monsoon's effect on re-volatilisation of soil burdens in response to drop in air concentrations at the onset of the monsoon is a secondary effect for DDT and PCB153, while 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 are more partitioning to the particulate phase 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).

4. Discussion

The results of 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 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. 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 South 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, most pronounced in areas that receive marine background air, i.e. in southwestern India. This corresponds 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 (Table S4b, Fig. 5). The 2014 southwesterly 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 rains 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 semivolatile organic substances such as polycyclic aromatic hydrocarbons (actually indicated by observations on site, not reported here) and brominated chemicals.

Associated content:

Supporting Information Fugacity calculations, air mass history analysis and model descriptions and input data. Field data, model results and sensitivities.

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Notes The authors declare no competing financial interest.

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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 = total organic carbon content (% of dry mass).

a.

Land use	Tea plantation	Shrubs	Forest
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.

	Tea plantation	Shrubs	Forest
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.

	Tea plantation	Shrubs	Forest
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 2 replicates

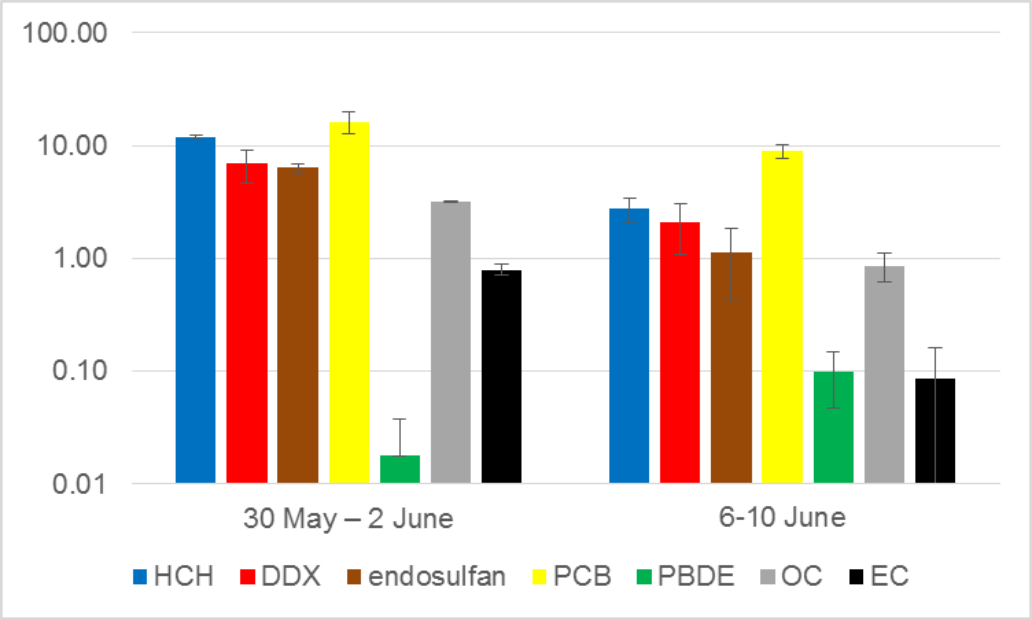
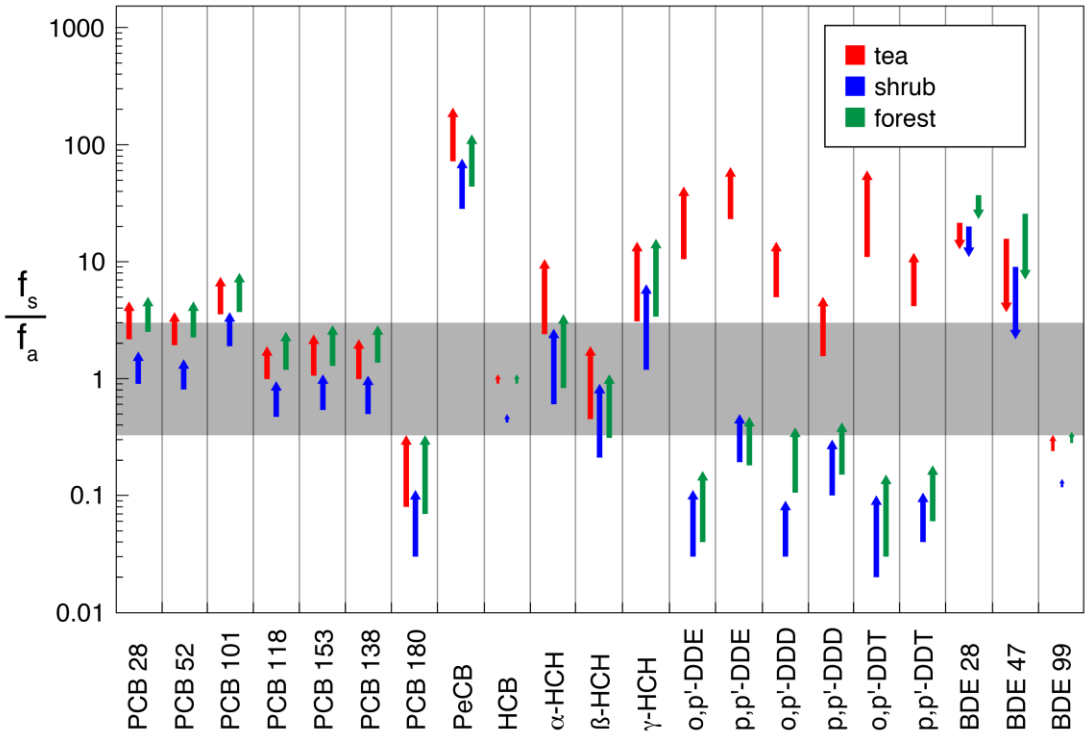


Fig. 1. Observed concentrations in air, c_a, of pesticides (Σ_4HCH, Σ_6DDX, Σ_3Endosulfan), Σ_7PCB, Σ_9PBDEs (pg m^{-3}), OC and EC (µg m^{-3}) before and after onset of southwest monsoon in Munnar, India, 2014. Error bars reflect standard deviations. All concentration changes are significant ($p < 0.05$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

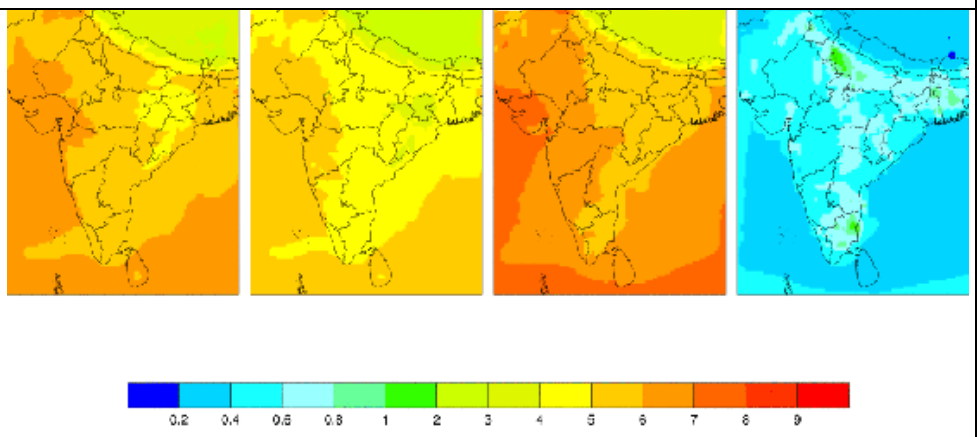
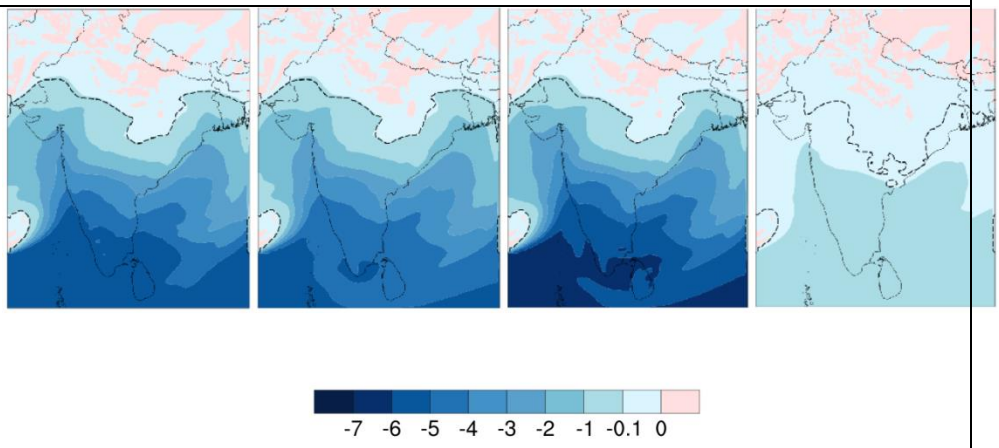


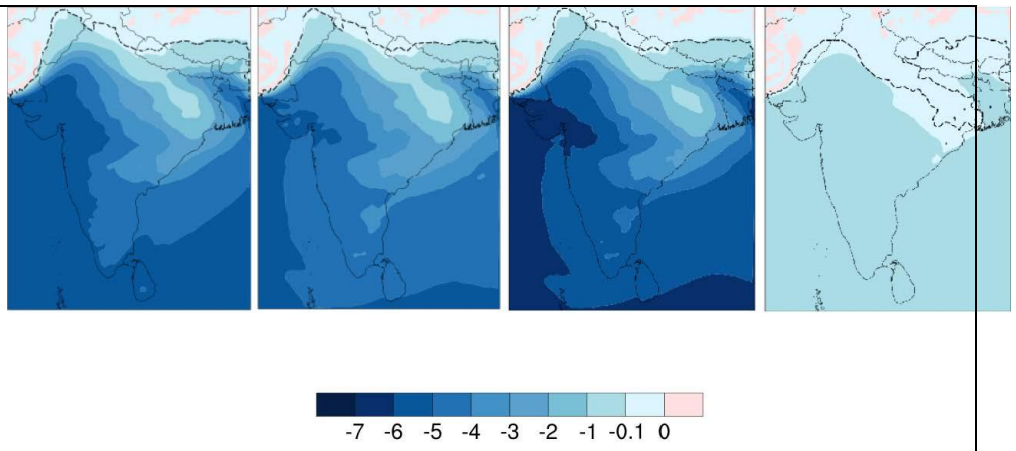
456

457 **Fig. 2**: Change of air-soil chemical equilibrium with the monsoon onset. Arrows denote direction
458 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)
460 flux. The shaded zone ($0.33 < f_s/f_a < 3$) indicates insignificance of deviation from 1 due to input
461 data uncertainties.

462

463

	α-HCH	γ-HCH	PCB28	PCB153
Distribution 1-3 June				
Difference distribution 8-10 June				

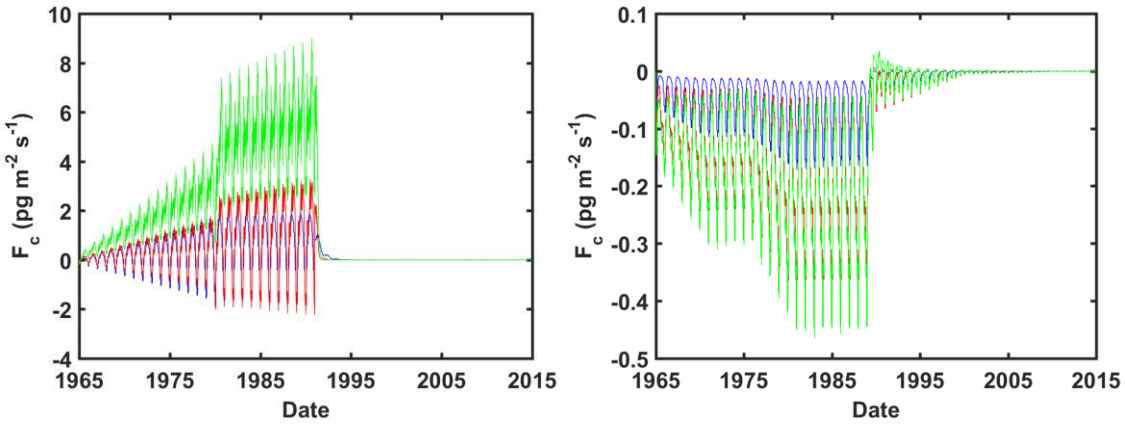
Difference distribution 28-30 June	

464

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

469

a. b.



c. d.

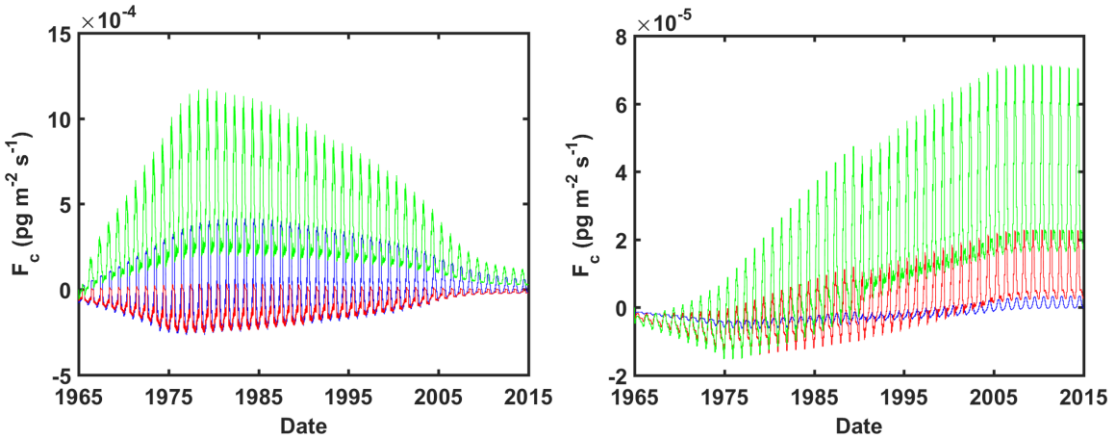
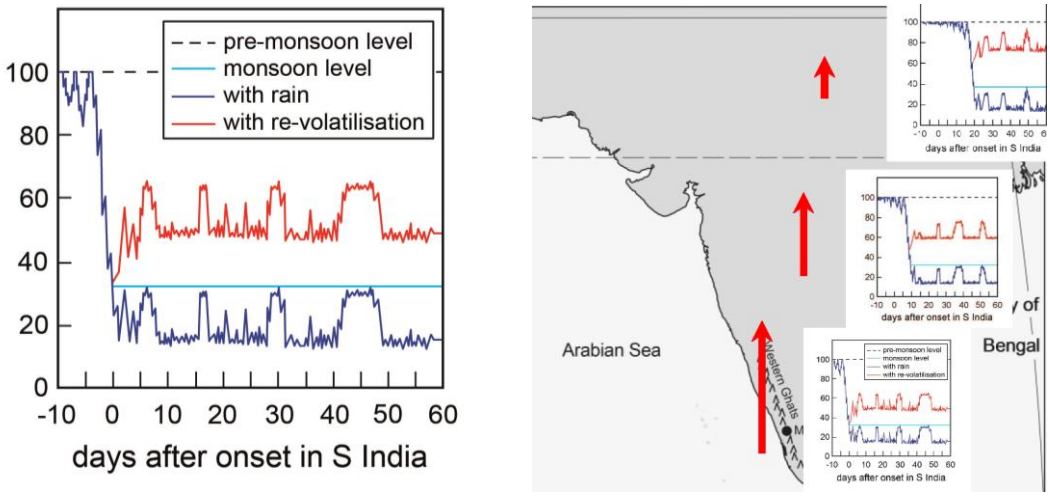


Fig. 4. Predicted multidecadal diffusive air-surface exchange fluxes. 1D model. F_c (positive = upward, negative = downward; lower) of (a) *α*-HCH, (b) *p,p'*-DDT, (c) PCB28, (d) PCB153 in the northern (29.7-33.4°N, blue), central (18.5-22.3°N, red) and southern (7.4-11.2°N, green) zones of India during 1965 – 2014. Predicted concentrations in air and soil are shown in SI, Fig. S4.



480

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