

1 **Re-volatilisation of soil accumulated pollutants triggered by the summer monsoon in India**

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15

16 **Abstract**

17 Persistent organic pollutants that have accumulated in soils can be re-mobilised by volatilisation
18 in response to chemical equilibrium with the atmosphere. Clean air masses from the Indian
19 Ocean, advected with the onset of the summer monsoon, are found to reduce concentrations of
20 hexachlorocyclohexane (HCH), dichlorodiphenyltrichloroethane (DDT) and its derivatives,
21 endosulfan and polychlorinated biphenyls (PCBs) in air at a mountain site (all in the range 5-20
22 pg m^{-3}) by 77, 70, 82 and 45 %, respectively. The analysis of fugacities in soil and air suggest
23 that the arrival of summer monsoon triggers net volatilisation or enhance on-going re-
24 volatilisation of the nowadays banned chemicals HCH and PCBs from background soils in
25 southern India. The response of the air-soil exchange was modelled using a regional air pollution
26 model, WRF-Chem-PAH/POP. The results suggest that the air is increasingly polluted during
27 transport by the southwesterly monsoon winds across the subcontinent. Using a multidecadal

28 multi-media mass balance model, it is found that air-surface exchange of HCH and DDT have
29 declined since the ban of these substances from agriculture, but re-mobilisation of higher
30 chlorinated PCBs may have reached a historical high, 40 years after peak emission.

31 **1. Introduction**

32 Persistent organic pollutants pose a hazard to humans and wildlife as they may reach harmful
33 concentrations in biota upon accumulation along food chains. Semivolatile substances (i.e.,
34 vapour pressure at 293 K in the range $10^{-6} - 10^{-2}$ Pa) are diffusing across air-sea and air-land
35 interfaces in both directions. They tend to net volatilise from land and sea surfaces to which they
36 had previously been deposited, once a level of contamination in chemical equilibrium with air
37 pollution is reached (Bidleman, 1999; Cousins et al., 1999; Meijer et al., 2003; Kurt-Karakus et
38 al., 2006; Růžicková et al., 2008; Wong et al., 2007; Degrendele et al., 2016). The potential to re-
39 volatilise is relevant to assess risks from chemicals as it enhances the long-range transport
40 potential, hence, facilitates transport to and accumulation in remote areas, which are pristine with
41 regard to primary (direct) contamination (Wania and Mackay, 2008; Semeena and Lammel,
42 2005; Wania and Westgate, 2008; Lammel and Stemmler, 2012). In the terrestrial environment,
43 soils represent the main reservoir of the more lipophilic substances ($\log K_{oa} \gtrsim 6$), while smaller
44 mass fractions are stored in the atmosphere, vegetation and freshwater as suggested by field
45 studies (Meijer et al., 2003) and modelling (Wania, 2006; Lammel et al., 2007; Lammel and
46 Stemmler, 2012). Thus, understanding the dynamics of soil contamination and exchange with the
47 overlying air is important for assessing spatio-temporal scales of the distribution and impact of
48 local pollution. Air-soil dynamics occurs on various time scales, from multi-year long-term
49 trends (Lammel and Stemmler, 2012) to seasonal cycling and short-term fluctuations (Bidleman,

50 1999). One key region, where persistent organic pollutants have been heavily used, is South
51 Asia. In India, high levels of organochlorine pesticides (OCPs) were found in both abiotic
52 (Ramesh et al., 1989, 1991; Shunthirasingham et al., 2010; Rajendran et al., 1999; Kumari et al.,
53 1996; UNEP, 2002; Pozo et al., 2011; Chakraborty and Zhang, 2012; Bajwa et al., 2016) and
54 biotic (Ramesh et al., 1990, 1992; Senthilkumar et al., 2001; UNEP, 2002) environmental
55 samples. The country is considered as a hot spot for DDT and hexachlorocyclohexane (HCH)
56 with no evidence of decline (Sharma et al., 2014). Besides OCPs, also polychlorinated biphenyls
57 (PCBs) and polybrominated diphenylethers (PBDEs) are of relevance in South Asia, where they
58 were used as flame-retardants. High levels of PBDEs were reported in India (Zhang et al., 2008)
59 and waste might be a significant on-going source of penta- and hexachlorobenzene (PeCB,
60 HCB), PCBs (Senthilkumar et al., 2001; Wong et al., 2010; Zhang et al., 2011; Sharma et al.,
61 2014) and PBDEs (Breivik et al., 2012; Sharma et al., 2014). Thus far, studies on environmental
62 exposure of the Indian subcontinent have been mostly limited to urban areas (Chakraborty and
63 Zhang, 2012; Sharma et al., 2014; Chakraborty et al., 2015), while the continental background
64 was scarcely addressed. The air-soil dynamics of OCPs or other semivolatile substances related
65 to monsoon has not been studied yet. In India, air pollution levels are expected to drop with the
66 onset of the summer monsoon. Triggered by the seasonal shift of the intertropical convergence
67 zone, the large-scale advection pattern switches from regional (South Asia and adjacent seas) to
68 intercontinental (from the Indian Ocean with influence from the relatively clean southern
69 hemisphere (IMD, 2014).

70 Here we study air and soil pollution in India, first time with focus on the impact of the summer
71 monsoon on air-surface exchange. The hypothesis is tested, whether drop of concentrations in air
72 at the onset of the summer monsoon mobilizes pollutants stored in soils. To this end, (1) field

73 observations in background soils in the Western Ghats, the first highlands that the southwest
74 monsoon winds encounter, were performed before and during the onset of the monsoon (May-
75 June 2014). These were complemented by (2) regional scale chemistry-transport modelling of the
76 monsoon onset on the Indian subcontinent using a 3D air pollution model, WRF-Chem, coupled
77 to a soil compartment. Finally, (3) the long-term chemodynamics is assessed by multi-media
78 mass balance modelling, forced by climate and 3D modelling data.

79

80 **2. Methods**

81 **2.1 Sites and sampling**

82 Air samples were collected from 5 May – 10 June, 2014, 90 km inland from the Arabian Sea
83 coast, on a slope oriented southwest in the northern outskirts of the town Munnar
84 (10.093°N/77.068°E, Fig. 4) at 1600 m a.s.l., with the mountain ridge's elevation in the area
85 ranging from 1950 – 2450 m a.s.l.. The site is reached freely, i.e. without topographic obstacles,
86 by air masses that are advected through the sector 180-360°N. It is directly adjacent to tea
87 plantations (south to west) and deciduous forest (northwest to northeast). Additional land cover
88 includes shrubs (south, east) and, to a lesser extent, agricultural fields and residential areas (south
89 to southeast). 24 air samples were collected. The 2014 monsoon season in the area was
90 characterized by scattered rainfall at the monsoon onset, after which rainfall became persistent
91 from the last week of June (Valsan et al., 2016).

92 For air sampling a high volume sampler (Digital DH-77) equipped with a quartz fibre filter and 2
93 polyurethane foam (PUF) plugs (Gumotex Břeclav, density 0.030 g cm⁻³, 100 mm diameter, total

94 depth 12 cm, cleaned by extraction in acetone and dichloromethane) was used. Soil samples were
95 taken from each one plot in the tea plantation, in shrubs and in forest, at distances within 1 km
96 from each other. The uppermost 5 cm soil was collected (using spade, Edelman auger and sieve).
97 Each soil sample is a composite (pooled sample), produced from equal amounts of soil collected
98 from 6 individual spots at distances of 1 m from each other. Three replicates of each composite
99 sample were analysed. At all plots the samples were nitisol (GOI, 1985; FAO, 2014), horizon A,
100 which was brownish, loose, single grain structure, with fine roots in the shrubs and forest. Soil
101 samples were homogenized by sieving and mixing. PUF samples were spiked to control analyte
102 losses during handling, shipping and storage.

103 **2.2 Chemical and data analysis**

104 For organic analysis all samples were extracted with dichloromethane in an automatic extractor
105 (Büchi B-811). Surrogate extraction standards (PCB30, PCB185, ¹³C BDEs 28, 47, 99, 100, 153,
106 154, 183, 209) were spiked on each sample prior to extraction. The volume was reduced after
107 extraction under a gentle nitrogen stream at ambient temperature, and clean-up was achieved on
108 a Florisil column. Samples were analysed using a GC-MS/MS (gas chromatograph coupled with
109 a tandem mass spectrometer) Agilent 7890 coupled to Agilent 7000B with a SGE HT-8 column
110 (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
111 *p,p'*-DDE, -DDD and -DDT (6 DDX compounds), penta- and hexachlorobenzene (PeCB, HCB),
112 PCB28, -52, -101, -118, -153, -138 and -180 (i.e., 7 indicator PCBs), aldrin, dieldrin, endrin, α -
113 and γ -chlordan, α - and β -endosulfan, endosulfan sulphate, and mirex. More details are given in
114 the Supplementary Information, S1.1.

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

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

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

127 **2.3 Modelling atmospheric transport, chemistry and air-soil exchange**

128 The response of air-soil exchange to the drop in air concentration, subsequent to the monsoon
129 onset, was studied by the regional scale simulation of meteorology and chemistry using the
130 WRF-Chem-PAH/POP model. The WRF-Chem-PAH/POP has been recently extended from the
131 regional model WRF-Chem version 3.6.1 (Grell et al., 2005; Mu et al., 2018), to also represent
132 the chemistry, in- and below-cloud scavenging, gas-particle partitioning and surface gas
133 exchange of semivolatile organics (described in Supporting Information S1.4.1, input data in
134 S1.4.3). The simulation of the period 1-30 June 2014, with a spatial resolution of $27 \times 27 \text{ km}^2$; and
135 a time step of 150 s of the South Asian domain ($5\text{-}32^\circ\text{N}/69\text{-}89^\circ\text{E}$), was driven by NCEP re-

136 analyses (6-hourly, $1^\circ \times 1^\circ$ resolution). Physical and chemical spin-up time was 4 days. Primary
137 emissions were considered for DDT and PCBs (SI S1.4.1), while the secondary emissions were
138 modelled based on initializing the soils of India uniformly by the observed levels in background
139 soils (shrub, forest, section 2.1). Non-zero air concentrations, observed before and during
140 monsoon at the site (see above), were advected continuously at all boundaries of the domain (SI
141 S1.4.1). In the model experiment pre-monsoon levels were continuously replaced by monsoon
142 levels according to the northward propagation of the monsoon, while in the control run pre-
143 monsoon levels were kept constant at the boundaries.

144 **2.3 Multi-decadal simulation of pollution of air and soil in India**

145 The air–soil mass exchange flux of the semivolatile organic compounds studied were simulated
146 by a non-steady state one-dimensional (series of 7 two-boxes) model of inter-compartmental
147 mass exchange (multi-media mass balance model (Lammel, 2004; SI Fig. S1). The boxes
148 represent 7 zones in the north-south direction in India, $7.4\text{--}33.4^\circ\text{N}$, each 3.75° wide. For each
149 box the mass balances for the two compartments planetary boundary layer and top soil were
150 solved. The processes considered in air are wet and dry (particle) deposition, chemical removal
151 from air by reaction with the hydroxyl radical, air-surface mass exchange flux (dry gaseous
152 deposition and volatilisation), and loss by transport to the free troposphere, while in the soil
153 atmospheric deposition fluxes, air-surface mass exchange flux, and degradation (as first order
154 process) were considered (Supporting Information S1.4.2, input data in S1.4.3). In addition to a
155 50-year model run, the sensitivity of soil pollution to a number of input parameters as well as
156 under a hypothetical no-monsoon scenario was studied.

157

158 3. Results

159 3.1 Field observations

160 Relatively low pollution levels in soils (0.07-0.11 ng g⁻¹ for Σ_4 HCH, 0.18-0.43 ng g⁻¹ for Σ_6 DDX,
161 0.25-0.28 ng g⁻¹ for Σ_7 PCB, and 8.1-12.7 pg g⁻¹ for Σ_9 PBDEs) confirm the classification as
162 “background” site (Table 1). Actually, these HCH and DDX levels are lower than ever reported
163 from soils in India, which previously ranged 1.6-835 for HCH (excluding hot spots; Sharma et
164 al., 2014), 14-934 ng g⁻¹ for DDX (Sharma et al., 2014), and 30 (0-149) pg g⁻¹ (rural sites, same
165 congeners; Li et al., 2016). The soil sample from a tea plantation showed elevated levels of DDT
166 and its metabolites (27.9 ng g⁻¹ Σ_6 DDX), pointing to previous application (Table S2).

167 Indeed, measured air concentrations of carbonaceous aerosol and organic pollutants reach a
168 distinctly lower level during the monsoon, dropping by a factor of 2-10, except for PBDEs,
169 which apparently increased (Fig. 1, Table S3). These concentration changes i.e., 77, 70, 82 and
170 45 % for Σ_4 HCH, Σ_6 DDX, Σ_3 Endosulfan and Σ_7 PCBs from before to after (Fig. 1) were all
171 significant on the p < 0.05 level, most on the p < 0.01 level, except for PBDEs which was
172 insignificant, even on the p < 0.1 level (unpaired Student t-test). Precipitation increased by a
173 factor of ≈ 2 upon the monsoon onset (from 3.8 to 8.0 mm day⁻¹), associated with convective
174 activity (Valsan et al., 2016). With 2.3-17.7 pg m⁻³ Σ_4 HCH and 0.36-10.4 pg m⁻³ Σ_6 DDX (Table
175 S3) the measurements at Munnar range at the lower end of the range reported from rural sites in
176 India in years after ban in agriculture (listed in Table S6c). 1.3-8.5 pg m⁻³ endosulfan (including
177 endosulfan sulfate) measured in Munnar in 2014, shortly after the ban of the pesticide is 3 orders
178 of magnitude below what was reported 2006-07 (i.e., 1000-9200 pg m⁻³ at rural locations of

179 South India; Pozo et al., 2011). Similarly, the range of 2.8-70 pg m^{-3} $\Sigma_7\text{PCBs}$ measured in 2014
180 at Munnar lies distinctly below 32-440 pg m^{-3} reported for the same substances at rural coastal
181 sites in 2006 (Zhang et al., 2008).

182 The fugacity ratio f_s/f_a is used to characterize air-soil exchange (Supplementary, Text S1.2).
183 Calculations indicate both downward (PCB180, DDT and metabolites over forest and shrub
184 soils, BDE99) and upward (PCB101, PeCB, DDT and metabolites over tea garden soils, BDE28,
185 BDE47; Fig. 2) diffusive air-soil exchange fluxes prior to the monsoon. With the monsoon onset
186 f_s / f_a generally increases (except for PBDEs, of which concentrations in monsoon air were
187 somewhat elevated compared to pre-monsoon air; Table S3). This can trigger a change of flux
188 direction for the tri- to hexachlorinated PCBs (i.e., all targeted except PCB180) and α - and β -
189 HCH (Fig. 2). For example α - and γ -HCH were close to phase equilibrium before onset, but net-
190 volatilisation occurred during monsoon, while β -HCH changed from net-depositional to near
191 phase equilibrium.

192

193 **3.2 Response of air-soil gas exchange of pollutants to monsoon onset**

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

199 the boundaries throughout the simulation (detailed in Methods and Supporting Information,
200 S1.4.1).

201 Within a few days after monsoon onset in southern India, the advection of air from the Indian
202 Ocean has reduced HCH and PCBs' atmospheric levels over southern India and the Bay of
203 Bengal, and to a lesser extent over central India (Fig. 3, centre panels). Three weeks after onset
204 in southern India, the northern monsoon boundary has passed over India except the northwestern
205 states Gujarat and Rajasthan (i.e., north of $\approx 22^\circ\text{N}$ and west of $\approx 77^\circ\text{E}$; Valsan et al., 2016), but the
206 distributions of HCH and PCB in air maintain significant gradients with high, i.e. only
207 moderately reduced (by $< 1 \text{ pg m}^{-3}$) levels in the north and east, and low levels after a decline of
208 $> 3 \text{ pg m}^{-3}$ of HCH isomers and $> 5 \text{ pg m}^{-3}$ of PCB28, respectively, in the south and southwest.
209 The response of the air-soil system subject to the monsoon leads to a spatially inhomogeneous
210 distribution of pollutants across India. It is dominated by clean air advection in the south and
211 southwest, but only moderately decreased air pollution in northern and eastern parts of the sub-
212 continent, as the air has received secondary emissions from the soils. The latter increases with
213 distance from the coasts after monsoon onset. The differences in concentrations before and
214 during monsoon are significant ($P < 0.05$, t-test) in south, central and parts of northern India (Fig.
215 3). The model results show that HCH isomers and PCB28 concentrations drop by $\approx 80\%$, $\approx 20\%$
216 and $\approx 4\%$ at 9° , 22° and 29°N , respectively, PCB153 by $\approx 40\%$ and $\approx 10\%$ at 9° and 22°N ,
217 respectively, while they increase by $\approx 1\%$ at 29°N (Table S5a). The model realistically reproduces
218 the decline of atmospheric concentration at the field site (Southern India, 9°N ; Table S6a, b). In
219 the model, the HCH and PCB volatilisation fluxes are enhanced in the south (by $0.02\text{-}0.78 \text{ pg m}^{-2}$
220 h^{-1} i.e., 3-11%; Table S5b) by the drop in air pollution, and to a lesser degree in central India

221 (0.002-0.19 $\text{pg m}^{-2} \text{h}^{-1}$), and even less or negligible at a northern India site (<0.0001 - 0.007 pg m^{-2}
222 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
245 direction of advection in air (prevailing westerly, with northerly component). For α -HCH, such a
246 gradient was also reflected in soil distributions in India which were based on a gridded mass
247 balance model (Xu et al., 2013). While PCB28 have turned net-volatilisation after a few years
248 upon release into the environment, this was much later for the highly lipophilic PCB153, ≈ 1
249 decade in southern India, ≈ 2 decades in central and even later in northern India (Fig. 4d).
250 Nowadays, the diffusive air-surface exchange flux of the pesticides α -HCH and DDT is expected
251 in the $0.1-1 \text{ fg m}^{-2} \text{ h}^{-1}$ range, several orders of magnitude lower than before or shortly after the
252 ban (Fig. 4a-b). In contrast and related to on-going emissions from old industrial facilities, the
253 strong decrease in PCB usage did not strongly impact air-surface cycling. The magnitude of
254 fluxes remained within the same order of magnitude, $0.1-1 \text{ fg m}^{-2} \text{ h}^{-1}$, being even on the rise in
255 the case of PCB153 (Fig. 4c-d). The air-ground flux fluctuations are expectedly mediated by
256 storage of part of the pollutant burden in vegetation, not resolved in the model.

257 The results of simulation of a fictive no-monsoon scenario suggest that the effects of monsoon
258 have been limiting pollution of soils by HCH and PCB28 somewhat ($<20\%$ in 2014), while they
259 have been contributing to DDT and PCB153 in soils by $\approx 50\%$ and $\approx 10\%$, respectively (SI S2.2.3,
260 Table S8). This suggests that monsoon's effect on re-volatilisation of soil burdens in response to
261 drop in air concentrations at the onset of the monsoon is a secondary effect for DDT and
262 PCB153, while monsoon's enhancement of air-to-soil transfer by wet deposition is the primary
263 effect. This trend could be explained by the higher significance of wet deposition for DDT and
264 PCB153, which are more partitioning to the particulate phase than HCH and PCB28, whereas the

265 efficiency of gas scavenging is generally low for POPs (Atlas and Giam, 1988; Bidleman, 1988;
266 Shahpoury et al., 2015).

267 **4. Discussion**

268 The results of both the field measurements and modelling results of this study indicate a so far
269 overlooked mechanism of pollutant cycling over the Indian subcontinent, i.e. monsoon-driven
270 mobilisation of POPs from previously contaminated soils. The decline of POP levels in the
271 southwesterly flow upon monsoon onset is partly related to the advection of clean air from the
272 Indian Ocean (seasonal shift of the ITCZ), and partly by the washout of particulate pollutants
273 (Fig. 5), as well as deepening of the planetary boundary layer. In contrast, washout of gaseous
274 organic pollutants is very limited, because of low water solubility (Atlas and Giam, 1988; He and
275 Balasubramanian, 2010; Shahpoury et al., 2015). Because of the convective vertical transport
276 during the monsoon, pollutants can be released at the cloud top and subsequently undergo long-
277 range transport in the upper troposphere over and beyond South Asia. During transport over the
278 Indian subcontinent near the surface, air masses collect pollution emitted from primary and
279 secondary sources at the ground in urban and rural areas. We have shown here that secondary
280 sources are partly triggered by the low concentrations in relatively pristine air, most pronounced
281 in areas that receive marine background air, i.e. in southwestern India. This corresponds to a
282 seasonal decrease of the soil burden by a few percent relative to the annual mean. This secondary
283 source (re-volatilisation) weakens as a function of distance from the coast, as the monsoon
284 advection propagates across the subcontinent (Table S4b, Fig. 5). The 2014 southwesterly
285 monsoon was relatively weak (South Asian summer monsoon index; Li and Zeng, 2002)
286 compared to the long-term mean. For strong monsoon events, more efficient air-to-soil transfer

287 of pollutants by wet deposition could result. The simulation under a no-monsoon scenario
288 suggests that the latter process dominates for the least water soluble and least volatile (high
289 partitioning to the particulate phase) pollutants. Scavenging and air-to-soil transfer of POPs
290 under monsoon rains had hardly been studied in the field and should be addressed.

291 Secondary emissions, originating from past deposition to soils, also contribute to the long-range
292 transport of atmospheric POPs to remote areas in central Asia (Sheng et al., 2013; Gong et al.,
293 2015). A similar trend of pollutant release from soils can be expected for other semivolatile
294 organic substances such as polycyclic aromatic hydrocarbons (actually indicated by observations
295 on site, not reported here) and brominated chemicals.

296

297

298 **Associated content:**

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

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441

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

445 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

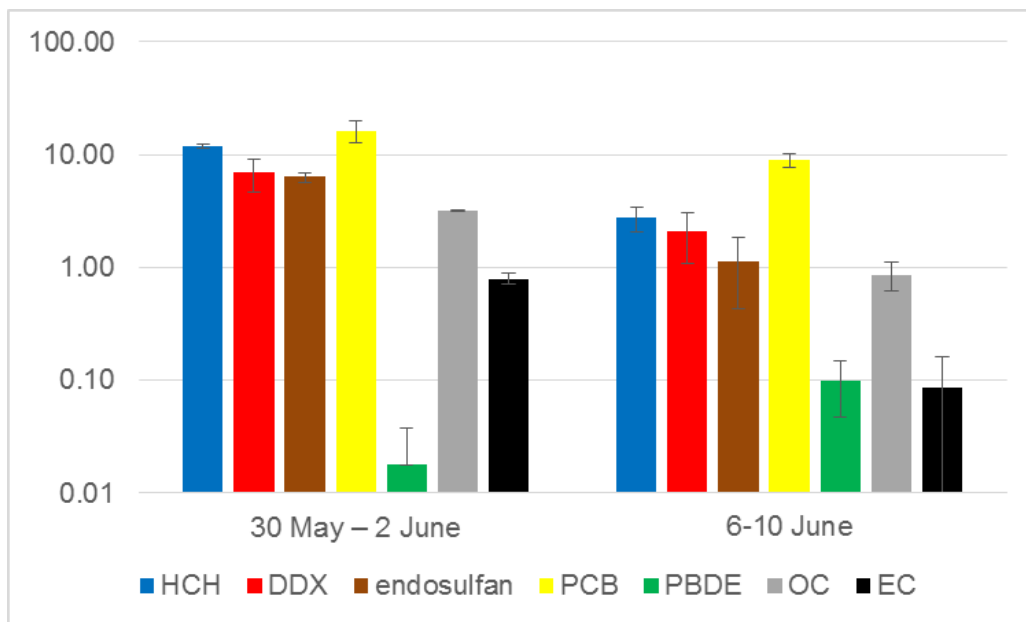
446 b.

	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

447 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

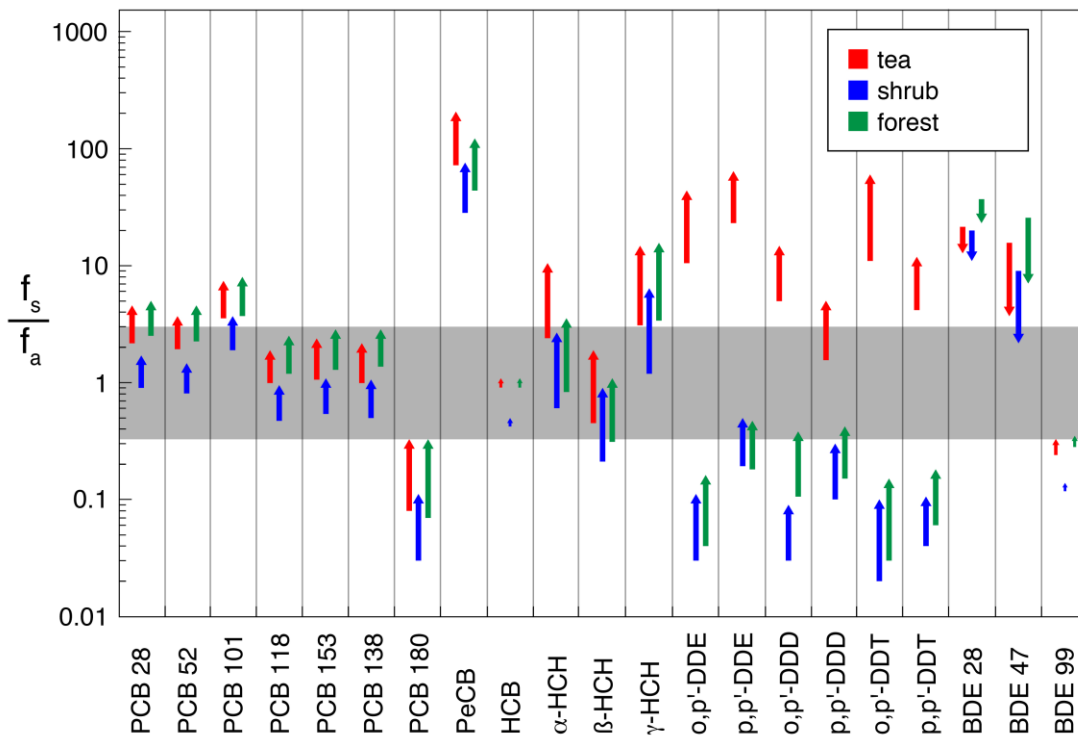
448 ^a based on 2 replicates
449



450

451 **Fig. 1.** Observed concentrations in air, c_a , of pesticides (\sum_4 HCH, \sum_6 DDX, \sum_3 Endosulfan),
 452 \sum_7 PCB, \sum_9 PBDEs ($\mu\text{g m}^{-3}$), OC and EC ($\mu\text{g m}^{-3}$) before and after onset of southwest monsoon in
 453 Munnar, India, 2014. Error bars reflect standard deviations. All concentration changes are
 454 significant ($p < 0.05$ level, t-test), except for PBDEs.

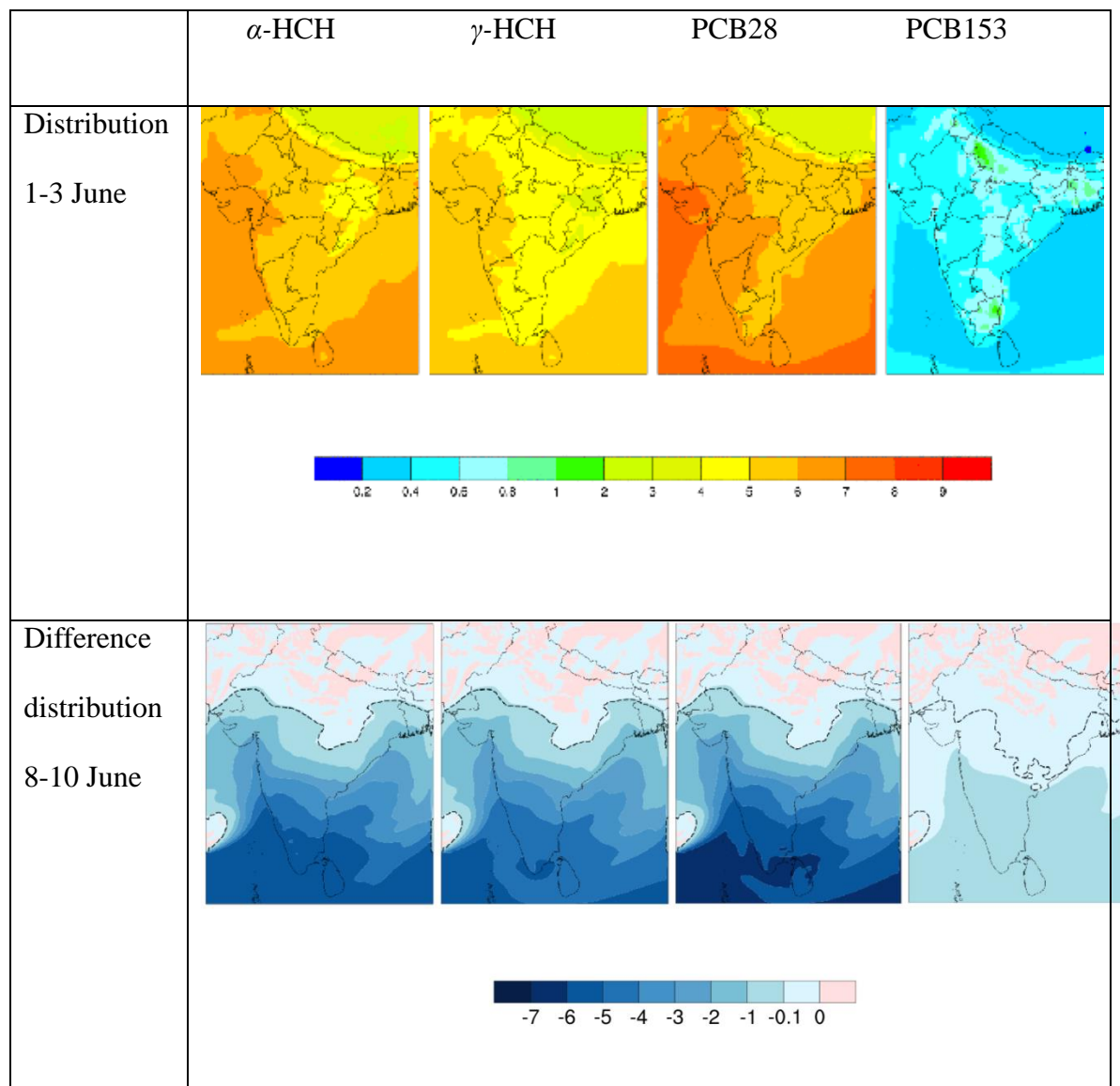
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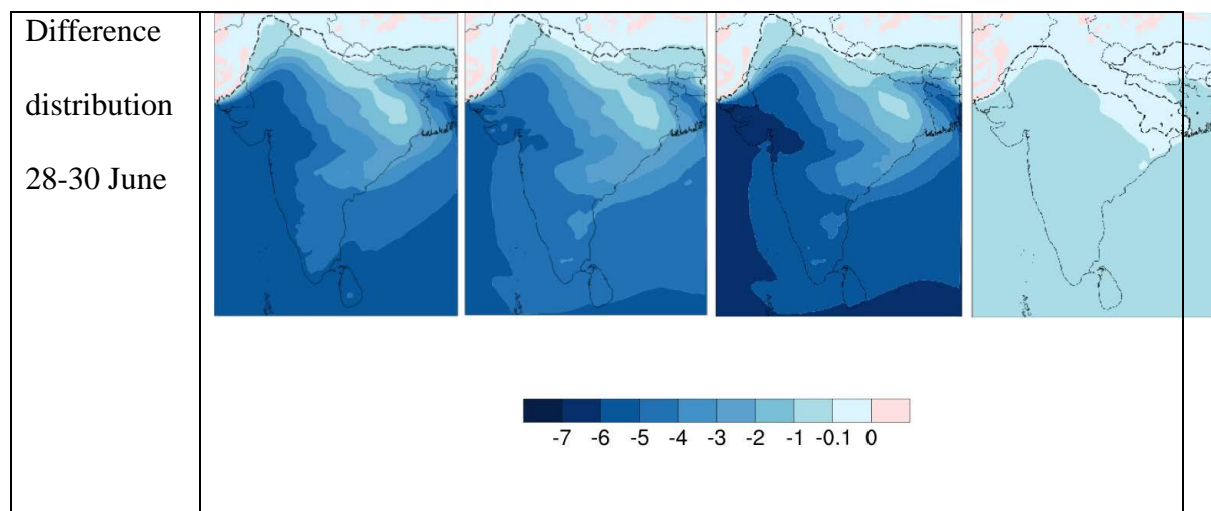


456

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. $f_s/$
 459 $f_a < 1$ 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





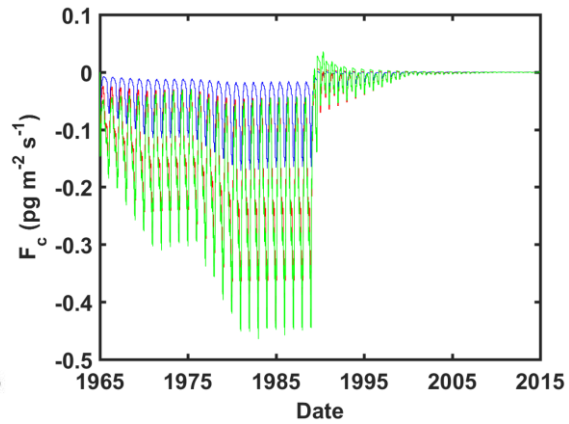
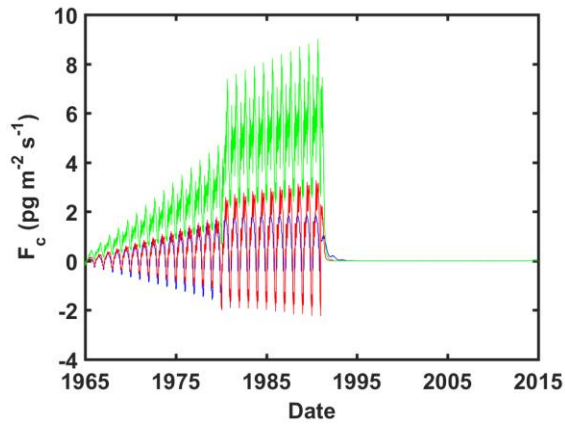
464

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

470 a.

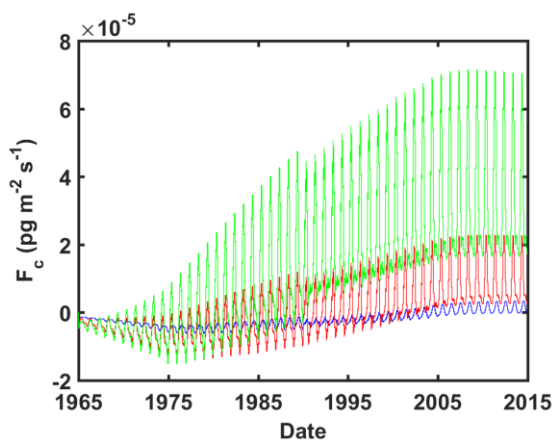
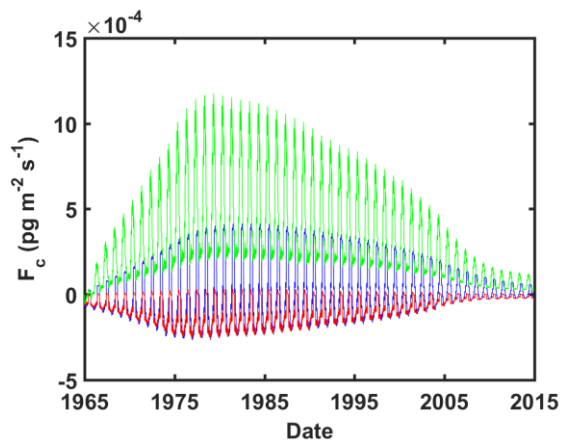
b.



471

472 c.

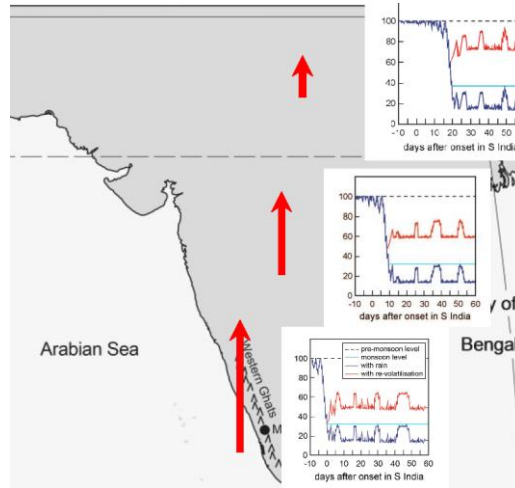
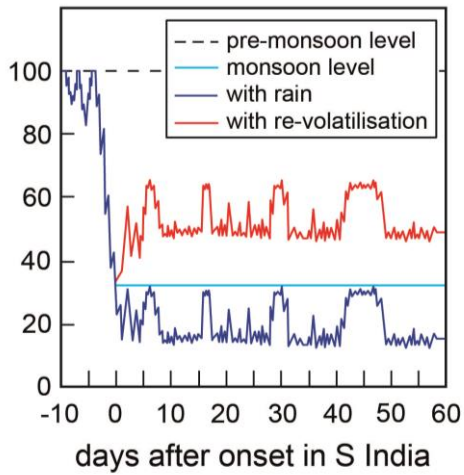
d.



473

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

479



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.