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Does an analysis of polychlorinated biphenyl (PCB) distribution in mountain soils across China reveal a latitudinal fractionation paradox?

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ABSTRACT

Organic and mineral soil horizons from forests in 30 mountains across China were analysed for polychlorinated biphenyl (PCB). Soil total organic carbon (TOC) content was a key determinant of PCB distribution explaining over 90% of the differences between organic and mineral soils, and between 30% and 60% of the variance along altitudinal and regional transects. The residual variance (after normalization by TOC) was small. Tri- to tetra-CB levels were higher in the South in relation to high source density and precipitation. Heavier congeners were instead more abundant at mid/high-latitudes where the advection pattern was mainly from long range transport. This resulted in a latitudinal fractionation opposite to theoretical expectations. The study showed that exposure to sources with different characteristics, and possibly accumulation/degradation trends of different congeners in soils being out-of-phase at different latitudes, can lead to an unsteady large scale distribution scenario conflicting with the thermodynamic equilibrium perception.

1. Introduction

Persistent organic pollutants (POPs) have been the focus of research and regulation due to their persistence, ubiquitous distribution and bioaccumulative and toxic properties (Aichner et al., 2013; Jones and de Voogt, 1999; Klanova et al., 2011; Zhang et al., 2008b). Polychlorinated biphenyls (PCBs) represent a class of POPs with a broad range of physical–chemical properties (Bozlaker et al., 2008), ideal for investigating the mechanisms involved in the control of fate and global distribution of POPs in general (Aichner et al., 2013).

Although PCBs are banned in most parts of the world, primary emissions continue mostly from old equipment and inadequate waste management (Breivik et al., 2002; Li et al., 2009). Secondary emissions from environmental reservoirs such as soils, vegetation and oceans hosting PCBs burdens emitted during the past, also significantly contribute in feeding long-range atmospheric transport (e.g. (Lammel and Stemmler, 2012)).

Predicting the future of POP exposure requires understanding the dynamic balance between atmospheric sources, atmospheric depositions, environmental degradation and remobilization from environmental reservoirs. Analyzing the current regional and global distribution of the environmental burden of POPs in the major reservoir compartments (such as soils) represent an effective approach to gather information useful for predicting possible future exposure conditions (Meijer et al., 2003).

China has 134 million hectares of forested land including a range of different biomes including subtropical forests, boreal forests, and semi-arid environments (Fang et al., 2001). Large geographic scale, climate variability, complex topography, ecosystem diversity, and

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densely populated conglomerates in well-defined areas make China a very interesting case study (Jiang et al., 1999).

In order to provide an assessment of anthropological and environmental controls on POP distribution, the patterns of PCBs in forest soils of several mountain sites in China were investigated in this study, considering gradients such as soil depth, soil type, altitude, latitude and distance from urban/industrial clusters.

2. Materials and methods

2.1. Monitoring design

Thirty mountain sites across China were chosen (shown in Fig. 1). In each mountain site, up to four sampling locations were selected along the same aspect on the altitudinal transect. In total 159 forest-soil samples were collected in 82 locations from the 16th of May 2012 to the 15th of March 2013. Major gradients included: latitude ranging between 21° and 53°; altitude ranging between 200 m and 3800 m; yearly mean temperature (*ymt*) and averaged total yearly precipitation (*typ*) ranging −6 °C–21 °C and 245 mm–2129 mm, respectively; distance from the major urbanized areas (assumed here as proxy of major primary sources locations) ranging between a few tenths to several hundred km.

The monitoring plan was defined taking into consideration the need of sampling in all major accessible mountain areas of China, achieving homogeneous geographical distribution, and collecting multiple samples along slopes at locations differing at least 200 m in elevation.

2.2. Sampling of soil

Three small trenches located at about 5 m distance from each other were excavated at the depth of 30 cm in each individual altitude location. Vegetation litter was carefully removed and a preliminary classification of the soil layers was performed in-situ based on colour and structure of the material present in each horizon. Samples from the O- (organic) and A- (mineral) horizons were collected separately from each trench using a metal spoon, folded in aluminium foil, placed in polyethylene zip-bags, cooled and transported to the laboratory where their mass, water content, bulk density and total organic carbon (TOC) content were determined. The samples were then freeze dried and stored at −20 °C for maximum 3 months before chemical analysis began.

2.3. Chemical analysis

Dry samples were sieved in order to remove stones and aggregates larger than 2 mm. The samples from each trench were homogeneously mixed to create aggregated samples of the O-horizon and A-horizon reflecting average conditions of the sampling location at the selected altitude. Sample extraction and preparation, instrumental analysis and adopted quality assurance and control methods were consistent with those described in a previous study (Huang et al., 2013). Details on analytical methods are also reported in the Supplementary information (SI) available on line.

2.4. Geographic information

A set of spatially explicit datasets were used in this study to feed the exploratory analysis performed in order to assess physical and anthropogenic influences on contaminant distribution. Geo-referenced datasets of elevation, *ymt*, *typ* (0.5′ resolved) and human population counts (2.5′ resolved) were obtained from WorldClim (Jurado et al., 2004; WORLDCLIM) and CIESIN (CIESIN; Gioia et al., 2006). Geographic information was elaborated using ArcGIS Desktop software. Multiannual averaged *ymt* of individual sites was calculated using monthly averages of time series (1950–2000). The information on human population distribution was used as

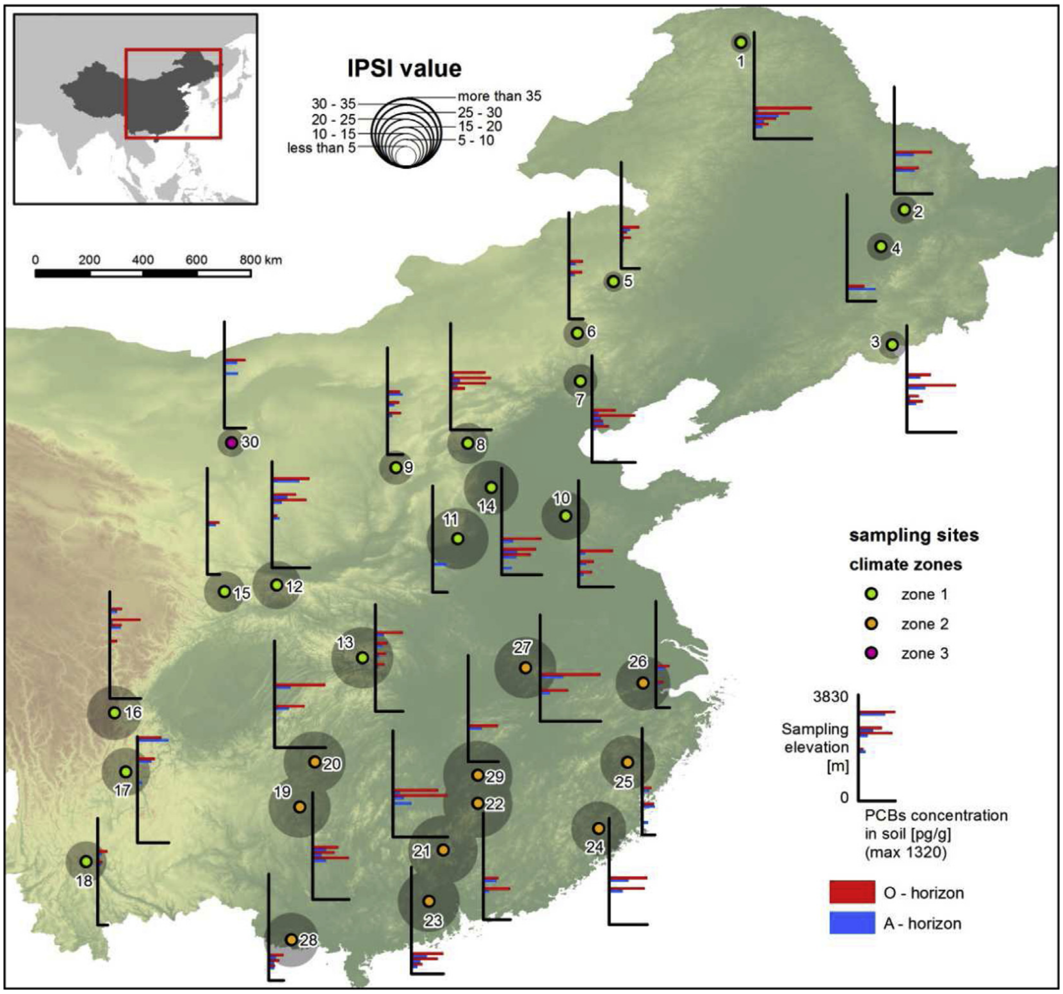

Fig. 1. Altitudinal and regional distribution of PCBs in organic (red bars) and mineral (blue bars) soil horizons, and the index of potential source influence (IPSI) (defined in Section 2.6). Different climate zones are represented by points with different colors: green: Climate zone 1: humid continental climate; orange: Climate zone 2: humid subtropical climate; purple: Climate zone 3: semiarid continental climate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

proxy for the distribution of PCB primary atmospheric sources in China, as further discussed in Section 2.6 of this paper.

2.5. Atmospheric back trajectories analysis

Atmospheric back trajectories were analysed using Hysplit (Draxler and Hess, 1998) to evaluate, on an annual base, the main origin of air masses reaching individual sampling sites. For each sampling site, a total of 360 ten-days backward trajectories were computed covering the full year preceding the sampling. Back trajectories were released from an altitude of 100 m above ground level every 2 days at 6 and 18 UTC (2 and 14 Beijing time (CST)) in order to take into account the day/night variation of the depth of the (mixed) planetary boundary layer (BL). The information on air mass trajectory was elaborated to obtain maps of back trajectories density. The back trajectory density $f_{x,i}$ value for a given point in space i (identified by the area delimited by grid cells with 2.5' resolution) was calculated in relation to each sampling location x as:

$$f_{x,i} = \frac{BTn_{x,i}}{360}$$

where $BTn_{x,i}$ is the number of times a back trajectory originated from site x was passing over location i during the year preceding the sampling, and 360 is the total number of computed back trajectories. The rationale of such an elaboration was to obtain aggregated information showing the areas surrounding the sampling locations with the highest potential to serve as source of airborne PCBs for the selected sampling areas. For example, emissions of contaminants from locations with low $f_{x,i}$ value are likely to have little influence on the contamination profile of site x.

2.6. Index of potential source influence

In order to further parameterize the potential influence of primary urban sources on the regional distribution of PCBs in China, a numerical index of potential source influence (IPSI) was defined combining the information on back trajectories density and human population distribution. More specifically IPSI was calculated as:

$$\mathrm{IPSI}_x = 10^{-8} \sum_i \left(f_{x,i} \cdot p_i \right)$$

where p_i is the human population residing within a generic point in space i, and the numerical parameter is simply a scaling factor. IPSI for a given sampling site x is proportional to the product of back trajectory density and human population counts calculated for a circular geographical area (6000 km diameter) centred in x.

In the definition of IPSI it is implicitly assumed that the geographical distribution of human population reflects the distribution of PCBs primary sources. PCBs were used in China mainly in electric equipment and painting (SEPA, 2003). Similarly to other parts of the world (Motelay-Massei et al., 2005; Yeo et al., 2004; Zhang et al., 2008a), previous assessment of PCBs distribution in soils and other environmental compartments in China evidenced the existence of an urban-rural gradient with highly populated urban and industrial districts representing the areas with highest density of potential primary atmospheric sources (Cui et al., 2013; Ren et al., 2007; Xing et al., 2005; Zheng et al., 2010). In China industrial and major urban clusters closely overlap (Xing et al., 2005). For this reason population count is an adequate proxy for describing potential PCB usage and primary source location while the associated back-trajectory density value weights different locations influence based on how often they were upwind the sampling point. The IPSI values defined here represent therefore a strategy to rank the influence of potential primary source areas on the contamination pattern in the receiving mountain soils. In addition, IPSI can be considered as an index of potential influence from sources in the subregional/local domain rather than from long-range transport. This derives from the fact that $f_{x,i}$ values, which obviously tend to be higher in proximity of the back trajectory origin, were not weighted for the effect of distance. The potential influence of long-range transport was instead assessed by computing the fraction of time air masses were traveling above the BL using the Hysplit outputs for BL height and back trajectory elevations.

2.7. Statistical analysis

Multivariate statistical analysis was carried out using principal component analysis (PCA). Principal components were calculated based on correlation matrixes using normalized, standardized and centred data. Raw data of contamination and *typ* data were normalized by natural logarithm transformation. All variables were standardized by dividing by one standard deviation and centred by subtracting the mean. Non-parametric rank correlation (Spearman) analysis was performed on raw or transformed data, to elucidate significance of observed co-linearity.

3. Results and discussion

3.1. Air mass patterns and index of potential source influence (IPSI)

The dominant large-scale air mass advection pathway into the BL of China at locations above 30°N is from northwest. In winter, air from Europe and Central Asia moves eastwards and turns south under the influence of a large semi-permanent high pressure system. Advection from west is prominent for upper tropospheric levels eventually intersecting high altitude sites in western China. In summer, there is a semi-permanent low pressure system above Central Asia, with air masses flowing mainly from the North-Northwest and less frequently from the Northeast toward the low pressure system.

IPSI values for different sampling sites ranged between 1 and 37 (Fig. 1) following a negatively skewed distribution with most frequently observed values around 25. The highest IPSI values are observed in the South-East reflecting the distribution of highly populated areas. The trajectories arriving at sampling locations in this part of China (in particular sites 21–23) are estimated to have spent a considerable fraction of the last 5 days before arrival to the sampling site within the BL. These were the locations which likely received the highest contribution from local sources. In contrast, sites located in the South-West (Yunnan province), despite frequently receiving air masses from highly populated areas in Northern India, scored with intermediate IPSI values, reflecting relatively low population density in the local-regional domain.

The lowest IPSI values were observed in the Northern part of China and along the Greater Khingan range in Inner Mongolia (NorthEast), due to relatively low population in this region of China. These sites too, received often air masses from large scale advection carrying contamination signals from long range transport.

Unfortunately *typ* and IPSI geographical distribution co-varied ($p < 0.05$). This was essentially due to the fact that human population in China is concentrated in the Southern and Western provinces experiencing higher precipitations, while sampling sites in populated region of northern and eastern China are located mostly upwind of conurbations. Because of this covariance, it was not possible to separate IPSI and *typ* during exploratory and regression statistical analysis to assess their individual influence on PCB distribution.

3.2. Summary of PCB concentration results

Measured total PCB concentrations are displayed in Fig. 1 individually for O-horizon and A-horizon. The full dataset including individual congener results is reported in Table S3.

The total concentrations of PCBs ($\sum_{29}$PCBs) averaged over all O- and A-horizon samples were 510 ng kg^{-1} (57–1320 ng kg^{-1}) and 227 ng kg^{-1} (36–679 ng kg^{-1}), respectively. These concentration ranges are consistent with those reported by a previous study on background soil contamination in Asia (Li et al., 2009). PCB contaminations in Chinese background soil appeared to be considerably lower than in North America (mean 4300 ng kg^{-1}) South America (mean 1400–4300 ng kg^{-1}) (Li et al., 2009), and Europe (e.g. UK (mean 4500 ng kg^{-1}) (Meijer et al., 2002) and forest soils in Germany (mean 24,700 ng kg)(Aichner et al., 2013)). This reflects lower historical usage of PCBs in China compared to the western countries (Breivik et al., 2002). Seven indicator congeners (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180) accounted for approximately 49.8% of $\sum_{29}$PCBs, while PCB -28, -138 and -153 were the main contributors.

The differences between the highest and lowest concentrations were within a factor of 20. When considering dry weight based concentration data, no outliers were found. TOC normalized concentration data showed instead a considerably lower variance (i.e. a factor of 10 between the highest and the lowest measured values). In this case only a single outlier was found. This was the Dinghu Mountain in the south of Guangdong province (Site 23) with TOC normalized concentrations about 2–3 times higher compared to the maximum of any other site (consistently for all sampled elevations). Site 23 was among the locations with the highest IPSI value, suggesting significant impact from local sources, while its soil had the lowest TOC content observed in this study.

3.3. *Distribution across soil layers*

Concentrations in the O-horizon were generally higher (average factor of 2.2) compared to the A-horizon. This difference nearly completely disappeared when TOC normalized data were compared. After TOC normalization, the residual difference between O-horizon and A-horizon concentrations scattered following a normal distribution with mean approaching 0 (Fig. S3). Such a residual variance could not be explained by any environmental factor considered in this study. TOC normalized concentrations were consistent and significantly correlated ($p < 0.01$) between the two soil horizons (Fig. S2) confirming the expected pivotal control of soil layer specific TOC content on the vertical distribution of POPs (Moeckel et al., 2008), and showing lack of significant influence of other potential drivers (e.g. climate, altitude, soil type, distance from sources) over such a control.

3.4. *Distribution along the altitudinal gradient*

The analysis of the altitudinal trends was based on selected 20 sites (86% of the entire data set), as, obviously, mountain sites with only one location sampled along the altitudinal gradient and sites with two sampling locations less than 500 m apart in altitude were excluded.

An increasing trend of TOC normalized concentrations of penta-CBs or higher chlorinated congeners was observed at increasing altitude in 16 sites out of 20. In order to assess the relevance of this result from a statistical point of view, the significance of the observed trend was estimated from the p-value of the correlation analysis between the scaled values of concentration and altitude of all the 20 considered sites. Scaling was performed by dividing individual data points of concentration and altitude by their median value at each respective mountain transect. The occurrence of a significant ($p < 0.05$) positive correlation between TOC normalized concentrations in soil and altitude was confirmed for all penta-CBs and higher chlorinated congeners (Fig. 2).

The present result highlights the tendency of enrichment of heavier PCBs in high altitude soils. This trend was consistent across sites with different climates and conditions and confirms some previous evidences of orographic cold trapping collected in Chinese high mountains (Chen et al., 2008; Wang et al., 2009) and other regions of the world.

Many physical, ecological and anthropological factors can contribute to determine the observed altitudinal distribution pattern. Although the present dataset does not allow a detailed analysis of the influence of individual drivers due to co-linearity (e.g. temperature, precipitation, vegetation type, and potential exposure to local sources co-varied, as expected, with altitude), temperature and wet deposition are suggested as pivotal variables. These were in fact the only variables significantly ($p < 0.05$) correlated with PCBs enrichment trends along the slopes. Such a result is consistent with theoretical expectations of altitudinal cold trapping. Orographic cold trapping is expected to mainly derive from different magnitude of wet depositions along altitudes (Wania and Westgate, 2008). A number of other factors can also contribute to the observed pattern, including higher capacity of fugacity of soils and slower bio-degradation processes at lower temperature/high altitude soils. Differential wet deposition along altitude, however, specifically results in a more effective entrapment of compounds with values of the scavenging ratio (at 25 °C) between $10^{3.5}$ and $10^{5.5}$ represented here by penta- and heavier-CB congeners (Wania and Westgate, 2008). Coincidently these were also the congeners for which significant altitudinal trends were observed in the present dataset.

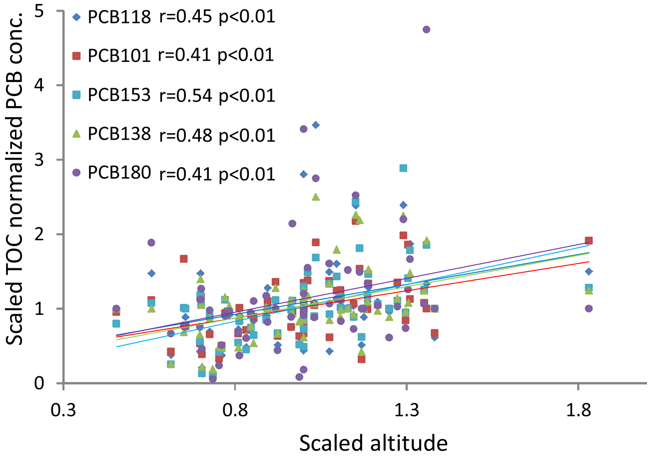

Fig. 2. Correlation between scaled TOC normalized PCB concentrations of tetra- and higher congeners and scaled altitude. *r* values are Spearman's rank correlation coefficients.

Unlike previous observations from other few mountain sites in China (Chen et al., 2008; Wang et al., 2009), the influence from local PCB sources at lower altitudes was visible here only in few cases (sites 9, 14, 25 and 26). Here in fact, TOC normalized concentrations of heavier PCBs had maxima at lower altitudes. Coincidently these sites had IPSI values in the medium-to-high range (13.5, 28.1, 25.6 and 27.4, respectively); they were exposed to air masses with relatively high residence time in the BL; and were located in proximity (e.g. less than 100 km apart) of major conurbations.

3.5. *Soil TOC influence on regional distribution*

The exploratory analysis of factors controlling regional distribution of PCBs was performed here considering the following set of uncorrelated (when considering the entire dataset) environmental variables: *ymt*, altitude, TOC and *typ*. It is recalled that *typ* has to be regarded here also as a proxy of IPSI owing to the significant positive correlation ($p < 0.05$) between these two variables (Table S4). TOC content explained large part of the variance of PCB concentrations (expressed on soil dry weight) for both the O-horizon and A-horizon as illustrated by the biplot in Fig. S4. Covariance is showed here by the similar orientation of the vectors representing $\sum_{29}$PCBs and TOC.

Several previous studies had provided parameterizations for the relationship between PCB concentrations and TOC using data from global and regional scale surveys (Meijer et al., 2003; Salihoglu et al., 2011). TOC in the O-horizon and A-horizon ranged 3.9–44.6% with mean 26.8% and 2.0–26.4% with mean 10.9%, respectively. The relationship between PCB concentrations and TOC was analyzed individually here for O-horizon and A-horizon. In order to perform such an analysis, PCB concentrations ([PCB]) and TOC were log-transformed. As expected, a significant ($p < 0.05$) positive relationship between log TOC and log [PCB] was observed. Table 1 reports correlation coefficients and slope values of the regression curve for selected representative congeners. Regression parameters are generally consistent with previous observations (Meijer et al., 2003). PCBs high thermodynamic affinity for organic matter, as described by the very high values of the octanol–air and octanol–water equilibrium partitioning (Li et al., 2003), and elevated persistence in soil solids bounded phase, underpin such a strong relationship.

Table 1
Spearman correlation coefficient (*r*) and regression line slopes describing the relationship between PCB concentrations and soil TOC. Data are reported for the analysis including the full dataset and grouped climate type. Bold numbers highlight correlation coefficients of significant ($p < 0.05$) relationships.

	∑PCBs		PCB 8		PCB 28		PCB 52		PCB 101		PCB 118		PCB 153		PCB 138		PCB 180	
	r	Slope	*r*	Slope	*r*	Slope	*r*	Slope	*r*	Slope	*r*	Slope	*r*	Slope	*r*	Slope	*r*	Slope
O-horizon																		
Global	**0.47**	0.48	0.18	0.26	**0.35**	0.33	**0.42**	0.54	**0.45**	0.71	**0.47**	0.48	0.18	0.26	**0.35**	0.33	**0.42**	0.54
Group 1 (Temperate)	**0.41**	0.81	0.12	0.28	**0.37**	0.68	**0.41**	0.95	**0.34**	1.02	**0.41**	0.81	0.12	0.28	**0.37**	0.68	**0.41**	0.95
Group 2 (Subtropical)	**0.66**	0.37	0.41	0.26	0.42	0.37	**0.62**	0.52	**0.59**	0.45	**0.66**	0.37	0.41	0.26	0.42	0.37	**0.62**	0.52
A-horizon																		
Global	**0.50**	0.48	0.17	0.18	**0.28**	0.34	**0.28**	0.29	**0.44**	0.60	**0.50**	0.48	0.17	0.18	**0.28**	0.34	**0.28**	0.29
Group 1 (Temperate)	**0.52**	0.55	**0.32**	0.32	**0.44**	0.56	0.21	0.26	**0.37**	0.59	**0.52**	0.55	**0.32**	0.32	**0.44**	0.56	0.21	0.26
Group 2 (Subtropical)	**0.56**	0.35	0.06	0.14	0.14	0.04	0.39	0.32	**0.63**	0.48	**0.56**	0.35	0.06	0.14	0.14	0.04	0.39	0.32

The analysis of the present dataset, including observations performed across the boundaries of different climate zones, can contribute to establish a relationship on how the relationship between soil organic matter and POP distribution is modulated in different environmental and ecological conditions. To this end, sampling locations were divided into 3 climate zones individuated based on *typ* and *ymt* values. These zones are: Climate type 1 with *ymt* and *typ* of 4.8 °C, and 736 mm, respectively, identified as the humid continental climate zone; type 2 with $ymt = 13.7$ °C and $typ = 1700$ mm identified as the subtropical climate zone; and type 3 (cold semi-arid climate zone) with $ymt = 4.2$ °C and $typ = 255$ mm which only included a single site (#30). Sampling sites grouped based on their climate zone are shown in Fig. 1 and Table S2. PCB concentrations were correlated to TOC ($p < 0.05$) for most of the congeners (with the exception of PCB 8) also when climate specific sub-datasets of data were considered. Slope values for the regression between OC and PCB concentrations (in case of O-horizons) were generally lower by a factor of 2–10 in the subtropical climate (zone 2) compared to the temperate climate (Table 1). This behavior is consistent with previous observations of lower dependence of PCB concentration on soil organic matter content at lower latitudes (Meijer et al., 2003). Interestingly, the same behavior was not observed for the A-horizon dataset. This possibly reflects the influence of different characteristics of soil organic matter or even a higher influence of precipitation and temperature, which had consistently higher values in the subtropical China. Less acidic constituents in vegetation litter and higher soil organic matter turn-over are important distinguishing characteristics of subtropical soils (compared to soils in temperate areas). These properties are both dependent on temperature and precipitation and might have an influence in determining the lower slope values observed here in climate zone 2. Recent experimental evidences seem in fact to suggest a relationship between fast turnover of labile organic matter and rapid remobilization of hydrophobic contaminants from soils (Liu et al., 2013; Wong and Bidleman, 2011). The detailed study of the dynamic coupling between soil organic matter turn-over and remobilization of POPs from soils is however still in its early stages.

3.6. Residual variance of TOC normalized concentrations

After normalization by TOC content, the residual variance of the dataset considerably dropped (factor of 2) making difficult to find significant relationships with possible environmental or anthropological drivers. However some spatial distribution trend could be observed. For example (Fig. 3), TOC normalized concentrations of more volatile congeners tended to be higher at lower latitudes, especially in relation to the more populated areas in the subtropical humid climate zone. Altogether up to 20–40% of the residual variance of lighter congeners could potentially be associated to precipitation and IPSI which both had the highest values in the southern part of China (e.g. PCB 28: $p < 0.01$, $r = 0.41$, and $p = 0.06$, $r = 0.22$, for *typ* and IPSI respectively). In contrast heavier congeners did not display such dependence but when only the temperate humid climate zone dataset was considered they tended to increase their abundance at northern latitudes. These trends for the heavier congeners were poorly significant or non-significant (e.g. PCB 180: $p = 0.056$, $r = 0.27$).

3.7. Latitudinal fractionation

Latitudinal cold trapping is a process expected to influence phase distribution equilibrium of semivolatile chemicals between the atmosphere and earth's surface resulting in varying contaminant patterns along the latitudinal temperature gradient (Wania and MacKay, 1996). Experimental evidences of cold trapping driven latitudinal fractionation of POPs were reported by previous studies in a range of geographical scales and locations and in relation to different environmental matrixes, including vegetation (Calamari et al., 1991) and soils (Meijer et al., 2002). In agreement with thermodynamics-based predictions these results show that

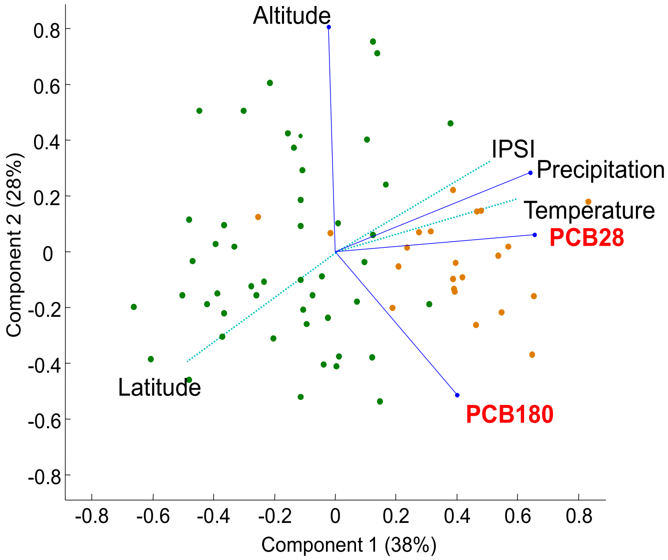

Fig. 3. Biplots from the Principal Component Analysis depicting relationships between TOC normalized PCB 28 and PCB 180 (taken as examples) concentration patterns and environmental descriptors. Light blue vectors in the biplots represent auxiliary variable which were correlated with one of the variables included in the analysis and for this reason not directly included in the computation of principal components. Vectors having similar orientation indicate covariance between the associated variable. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the lighter congeners tend to increase their relative abundance at high latitudes (low *myt*) in the condensed phase (e.g. soil) while heavier congeners are more abundant in the south (high *myt*) (Gouin and Wania, 2007; Wang et al., 2012). Latitudinal fractionation of PCBs was investigated here by calculating the ratio between the concentrations of selected congeners representative of different homologue groups and $\sum_{29}$PCBs. Results are plotted in Fig. 4. When the full dataset is included in the analysis a progressive decline of relative abundance of tri- and tetra-congeners could be observed at increasing latitude ($p < 0.05$), while penta- and hexa-congeners were more abundant in the north (both in relative and absolute terms ($p < 0.05$)). Fractionation trends were not significant for PCB 138 and PCB 180 (Fig. 4). In order to reduce the possible confounding factor associated to source proximity to the sites located in the southern part of China, the analysis was repeated considering only high altitude sites (e.g. >1500 m). These sites were more prone to receive air masses with a shorter residence time in BL and therefore less influenced by local sources. Fractionation trends of tri- to hexa-CBs for this subset of data were consistent with those obtained considering the entire dataset. In this case, however dependence on latitude was higher with correlation coefficients higher of a factor of 2) (Table S5). Increasing trends of heavier congeners (PCB 138 and 180) relative abundance were observed too, however they were still not significant from a statistical point of view (Table S5).

The PCB fractionation displayed in Fig. 4 is opposite to that expected from the cold trapping theory (Wania and MacKay, 1996) and previously observed from other global scale surveys (Meijer et al., 2002). As highlighted in Section 3.6 considerably higher precipitations and proximity to PCBs sources have likely determined the higher levels of di- to tetra-chlorinated PCBs in Southern China forested soils. The latitudinal pattern displayed by lighter congeners had a strong influence in determine the general fractionation results. The relative importance of heavier congeners (or, in other terms, the relatively lower abundance of lighter PCBs) in Northern China could not be ascribed to the influence of different

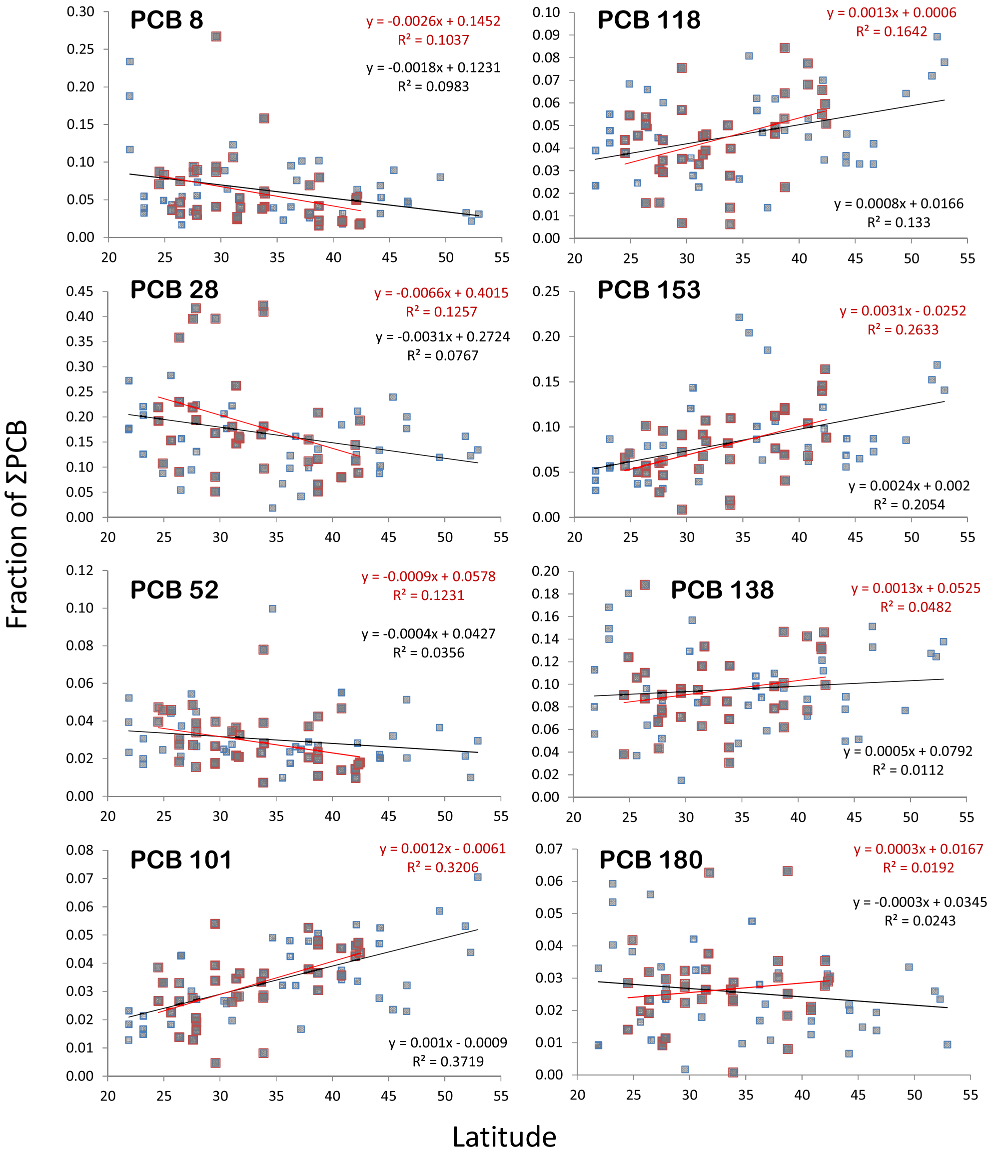

Fig. 4. "Inverse" latitudinal fractionation of PCB congeners in Chinese soils. Blue data points and black trend line and regression parameters refer to the full dataset. Data points highlighted in red and red trend lines and regression parameters refer to the high altitude (i.e. locations above 1500 m) subset of data (see Section 3.6). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

types of local sources since all the sites in this region scored with low values of IPSI (Fig. 1). Sites in the Northern China (especially those located at the higher altitudes) were instead more prone to receive contamination signals associated to long range atmospheric transport from North-West (as described in Section 3.1). It is likely these signals carried a different PCB profile compared to that expressed by local sources in Southern China. Higher abundance of low chlorinated congeners in commercial mixtures are in fact a peculiarity of PCB usage in China (Ren et al., 2007; Xing et al., 2005).

Some considerations on soil exposure dynamics may also contribute to explain the apparent inverse fractionation pattern displayed by the present data. Spatially resolved multicompartment modeling (Lammel and Stemmler, 2012) highlighted that temporal trends of different PCB congeners in soils are out of phase, with declining burdens of the less chlorinated, peaking burdens of mid chlorinated, and still increasing burdens of high chlorinated congeners in soils of east Asia in 2001–2010. Hereby, peaking of heavier congeners in north China soils is expected to lag 5–15 years behind south China soils, while lighter congeners might start declining earlier by means of their considerably shorter degradation half-lives in soil. The combined effect of different degradation rates, accumulation from the atmosphere, and exposure to sources could have therefore contributed, in this decade and region, to the definition of an unsteady scenario which resulted in fractionation trends inverse to the thermodynamic global-scale perception.

3.8. Conclusions

This regional-scale analysis of POP distribution in eastern Asia highlighted that soil TOC plays a controlling role in the vertical (across soil layers), altitudinal and regional distribution of PCBs. Between 37% and 60% of the total variance of concentrations data was explained by the variance of TOC. TOC also explained nearly 90% of the differences of PCBs levels between O- and A-horizons.

The residual limited variance could not be clearly related to any of the considered environmental and anthropological drivers. PCB contaminations of mountain soil of China reflect exposure to background atmospheric levels which are quite uniform throughout China. Under these conditions a strong direct influence of primary sources could not be clearly detected in most of the selected sites. Conversely, the influence of environmental factors (especially temperature and rainfall) emerged from the observed trends of orographic enrichment in most of the sampled sites.

Enrichment of lighter congeners at lower latitudes determined a general latitudinal fractionation pattern opposite to that expected from merely thermodynamic considerations. Such a behavior was interpreted as the combined results of different factors, including in particular: exposure to sources with different characteristics in different regions (e.g. local sources vs remote sources) and accumulation/degradation trends of PCBs in soils being out of phase at different latitudes in this region. In summary, the study experimentally showed that different driving factors acting in different regions can produce PCB latitudinal distribution patterns opposite to expectations from the fractionation theory, even at relatively large geographical scales.

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Appendix A. Supporting information

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2014.08.021.

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