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Forest Filter Effect versus Cold Trapping Effect on the Altitudinal Distribution of PCBs: A Case Study of Mt. Gongga, Eastern Tibetan Plateau

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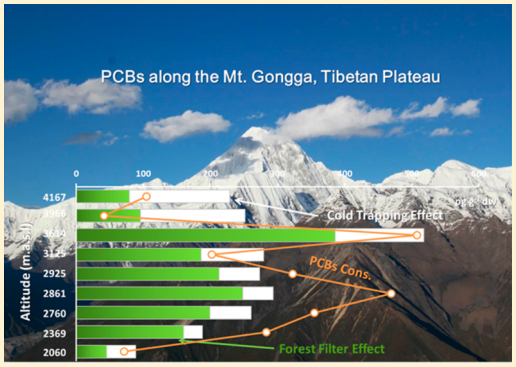
Supporting Information

ABSTRACT: Mountains are observed to preferentially accumulate persistent organic pollutants (POPs) at higher altitude due to the cold condensation effect. Forest soils characterized by high organic carbon are important for terrestrial storage of POPs. To investigate the dominant factor controlling the altitudinal distribution of POPs in mountainous areas, we measured concentrations of polychlorinated biphenyls (PCBs) in different environmental matrices (soil, moss, and air) from nine elevations on the eastern slope of Mt. Gongga, the highest mountain in Sichuan Province on the Tibetan Plateau. The concentrations of 24 measured PCBs ranged from 41 to 510 pg/g dry weight (dw) (mean: 260 pg/g dw) in the O-horizon soil, 280 to 1200 pg/g dw (mean: 740 pg/g dw) in moss, and 33 to 60 pg/m^3 (mean: 47 pg/m^3) in air. Soil organic carbon was a key determinant explaining 75% of the variation in concentration along the altitudinal gradient. Across all of the sampling sites, the average contribution of the forest filter effect (FFE) was greater than that of the mountain cold trapping effect based on principal components analysis and multiple linear regression. Our results deviate from the thermodynamic theory involving cold condensation at high altitudes of mountain areas and highlight the importance of the FFE.



INTRODUCTION

Persistent organic pollutants (POPs) in remote areas, particularly the Arctic and Antarctic, are a global issue, and the reasons for deposition in these areas have been hotly debated.[1,2] Mackay and Wania first proposed the "global distillation model," which suggests that semivolatile organic chemicals (SOCs) experience repeated cycles of deposition and evaporation at higher latitudes.[3,4] This process, called "polar cold trapping", is driven by temperature. However, other models and data have suggested that the thermodynamic effect might not be the sole determinant of the environmental fate of POPs.[5−7] A report by Dalla Valle[8] indicated that forested, and other carbon-rich, soils in the Northern Hemisphere retarded the movement of polychlorinated biphenyls (PCBs) to the Arctic.

Remote high mountains are similar to the polar regions in many ways, such as having low temperatures and deep snow cover, and previous studies have reported preferential accumulation of selected POPs at higher elevations on mountains.[9−12] Similar to "polar cold trapping," this effect has been termed "orographic" or "mountain cold trapping." However, mountains differ from polar areas in several key aspects that must be considered when estimating the distribution of POPs, such as closer proximity to emission sources, strong influence of local meteorological conditions (wind direction, temperature inversion, and precipitation gradients), and dramatic changes in ecological gradients across very short distances.[13] In addition, not all pollutants are enriched at high elevations, and a wide variety of deposition patterns exist.[14] For example, hexachlorobenzene (HCB) was not concentrated at higher elevations in the soils of the Andes Mountains.[15] The composition and concentrations of POPs differed between the Alps and the Andes, with greater deposition at higher elevations found only in the Alps.[13] The thermodynamic theory does not adequately explain mountain

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Table 1. Information, Climate Indices, and PCB Concentrations of the Sampling Sites

site	vegetation type	altitude (m a.s.l.[a])	longitude (°N)	latitude (°E)	precipitation (mm/yr)	AT[b]/ST[c] (°C)	Σ_{24}PCB air (pg/m^3)	Σ_{24}PCB moss (pg/g dw[d])	Σ_{24}PCB soil (pg/g dw)	SOC (%)
1	subtropical evergreen broad-leaved forest	2060	29°36′20″	102°04′25″	1200	10/12	33	550	71	17
2	coniferous and broad-leaved forest	2369	29°35′73″	102°02′65″	1600	8.7/11	40	870	280	37
3	coniferous and broad-leaved forest	2760	29°35′14″	102°01′52″	1900	7.6/6.8	49	970	360	30
4	subalpine conifer forest	2861	29°34′48″	102°00′31″	1900	6.6/8.6	59	790	470	40
5	subalpine conifer forest	2925	29°34′36″	102°00′06″	2100	5.7/7.6	40	630	320	38
6	subalpine conifer forest	3125	29°34′40″	101°59′32″	2200	4.9/6.8	51	540	200	30
7	subalpine conifer forest	3614	29°32′99″	101°58′11″	3200	3.1/5.4	60	840	510	38
8	alpine shrub meadows	3966	29°32′78″	101°57′66″	1900	0.54/2.4	37	1200	41	7.3
9	alpine shrub meadows	4167	29°32′66″	101°57′46″	1400	0.080/1.8	57	280	110	4.6

[a]a.s.l.: above sea level. [b]AT: air temperature. [c]ST: soil temperature. [d]dw: dry weight.

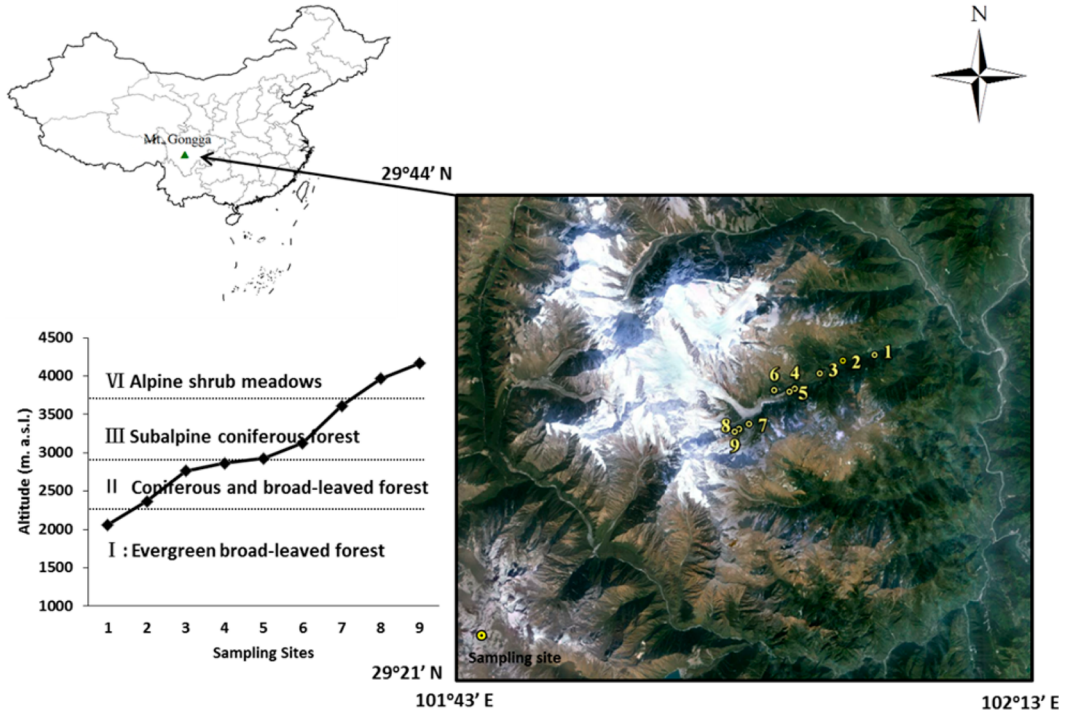

Figure 1. Geographic location, altitude, and forest type of sampling sites.

cold trapping, and the driving forces for the altitudinal distribution of POPs are still unclear.

Because high altitudes often have little vegetative cover, these areas may have little capacity to retain POPs with significant revolatilization and runoff during the snow-free season compared to lower elevations that are typically forested.[14] Forests can effectively attenuate the long-range atmospheric transport (LRAT) of POPs[16] and increase air-to-ground fluxes,[17−19] which is related to elevated atmospheric deposition to the forest canopy and high organic carbon content in foliage and soil.[20,21] The role of forests in filtering airborne organic pollutants from the atmosphere and transferring them to soil has been termed the "forest filter effect (FFE)."[18]

More work is needed to understand the key driving forces of the altitudinal distribution of POPs. We are skeptical of the temperature-driven theory, hypothesizing a more important role of forests in distribution of POPs in mountain areas. Mt. Gongga (29°20′−30°00′N, 101°30′−102°10′E), also known as Minya Konka, is in the transitional zone between the dry Tibetan Plateau and the humid Sichuan basin, in the Great Snow Mountain range of the Ganzi Tibetan Autonomous Prefecture west of Sichuan Province. Previous studies have found that Mt. Gongga has high atmospheric deposition of heavy metals.[22,23] Both heavy metals and POPs can be brought to remote mountain regions by LRAT and subsequently accumulated in the soil as wet and (or) dry deposition. Moreover, Mt. Gongga is relatively cold, largely forested with abundant precipitation, and far from intensive human activities. Plant and animal communities are simple here. Therefore, this area is likely sensitive to inputs of POPs and is well suited for examining their topographic distribution. Due to their wide physicochemical properties and years of prohibition, we chose to examine the distribution of PCBs. Little data exist on the environmental fate of POPs on Mt Gongga, and only a few studies of PCBs in the Tibetan Plateau are available.[12,24−32]

This study was conducted on the eastern slope of Mt. Gongga, along an altitudinal gradient from subtropical evergreen broad-leaved forest to alpine shrub and meadows.[33] We studied the dominant factors influencing levels and patterns of POPs in different environmental matrices (air, moss, and soil) at different elevations on the mountain. We evaluated the effects of environmental conditions, such as soil organic carbon (SOC) content and precipitation, as possible factors in the distribution of these POPs.

EXPERIMENTAL SECTION

Study Area and Sampling. The prevailing winds on the eastern slope of Mt. Gongga are from the east and southeast (East Asian Monsoon) and the south (Indian Monsoon).[34,35] Both East Asian Monsoons and Indian Monsoons bring precipitation to the region, resulting in a warm, humid climate. Climate indices, including soil temperature (ST), ambient air temperature (AT), and precipitation, were obtained from seven meteorological stations set up along an altitudinal gradient by the Alpine Ecosystem Observation and Experiment Station of Mt. Gongga. For sites without a meteorological station, we calculated climatic conditions by fitting equations based on yearly climatic data from the seven meteorological stations.[36] According to data (1988−2010) from the Hailuogou Observation Station [29°34′34.69″N, 101°59′55.08″E; 3,000 m above sea level (a.s.l.)], the mean annual precipitation is 1947.7 mm, concentrated in the summer season (May−October); the mean annual temperature is 4.2 °C with the minimum in January (−4.6 °C) and the maximum in July (12.5 °C).[35] Three distinct forest ecosystems occur below the tree line (Table 1): subtropical evergreen broad-leaved forest (1100−2200 m a.s.l.), coniferous and broad-leaved forest (2200−2800 m a.s.l.), and subalpine coniferous forest (2800−3600 m a.s.l.). Above 3600 m, an alpine shrub and meadow zone (3600−4200 m a.s.l.), an alpine frigid meadow zone (4200−4600 m a.s.l.), an alpine frigid sparse grass and desert zone (4600−4800 m a.s.l.), and an alpine ice/snow zone exist (above 4900 m a.s.l.).[33]

The sampling was performed in May 2012, along a transect which crosses through four biomes as shown in Figure 1. Nine elevations were selected between 2060 and 4167 m a.s.l. according to habitat type (forest, grassland) and accessibility. At each site, three soil pits (∼5 m apart) were hand-dug using a cleansed stainless steel spade. Soils were collected from the organic (O-) horizon, in which superficial litter, large roots, and any nonorganic material were removed to avoid interference. Composite moss cushions were collected from individual three or four rocks under forest canopies at each site. All samples were sealed in zippered plastic bags and placed in an insulated cooler with ice for transport to the laboratory where they were stored at −20 °C until extraction. Passive air sampling (PAS) was deployed at the same locations for 77 days from 15 May to 1 August, using a polyurethane foam (PUF) disk apparatus.[37,38] All PUF disks were pre-extracted consecutively with acetone (48 h) and dichloromethane (DCM) (48 h), then transferred to the sampling locations in sealed, solvent-cleansed metal tins. At the end of the deployment period, the PUF disks were retrieved, resealed in their original metal tins, and sent back for further analysis.

Sample Pretreatment and Analysis. Detailed descriptions of the sample pretreatment and analysis can be found in the Supporting Information (Text S1, Table S1). Briefly, the freeze-dried soil and moss samples (∼20 g) were spiked with PCB 30 and PCB 198 as recovery surrogates and Soxhlet extracted with acetone/hexane (1:3) for 48 h. The extracts were further washed with concentrated sulphuric acid, purified on a multilayer acidic silica gel column, and then treated with gel permeation chromatography (GPC). The PUF disks were spiked with the same surrogates, then extracted with DCM for 48 h and purified with the multilayer column method. Forty milliliters of DCM/hexane (1:1) was eluted to collect the PCB fraction. Under a gentle stream of nitrogen, the PCB fraction was reduced in volume and solvent exchanged to ∼50 μL of isooctane containing a known amount of ^{13}C-PCB 141 as an internal standard.

We performed PCB analysis using an Agilent 7890/7000 GC-MS/MS with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm; Agilent, Santa Clara, CA, USA) as in Huang et al.[39] SOC content was measured using a Vario EL III elemental analyzer (Elementar, Shanghai, China).

QA/QC. We analyzed laboratory and field blanks for PUF. The instrument detection limit (IDL) was calculated as the corresponding amount of compound that would generate a signal-to-noise ratio of 3:1. The method detection limit (MDL) was defined as the average of all blanks plus 3× the standard deviation or 3× the IDL, whichever was greater. The MDLs of PCBs were 0.31−6.0 pg/g, 0.93−18 pg/g, and 0.040−0.78 pg/m^3 for all congeners in O-horizon soils, mosses, and PUF disks, respectively (Tables S2-1−S2-3). The average recoveries from all environmental samples were 60% ± 11% and 105% ± 14% for PCB 30 and PCB198, respectively. All reported values are blank-corrected but not corrected for recovery rates.

Air Mass Back Trajectories. Air mass origins were determined using NOAA's HYSPLIT model.[40,41] The arrival height of air mass should be multiple within or just above the local atmospheric boundary layer (ABL) in order to get the air mass which reflects the possibility of LRAT.[42] The ABL is generally below 1 km in urban cities; however, it should be much higher and can even extend to almost 3 km above the ground surface in the Tibetan Plateau.[43] Consequently, 5 day back trajectories at the Hailuogou Station were calculated at 100, 500, and 3000 m above ground level at 12 h intervals for each day for more than a year (May 2011−July 2012, including the entire sampling period). The trajectories (n = 915) for each of the three heights clustered separately based on the percent change in total spatial variance (Figure S1).

RESULTS AND DISCUSSION

General Remark on PCBs. Data derived from PAS were converted to estimates of compound mass per unit air volume (e.g., pg/m^3) using an average sampling rate of 3.5 m^3/day based on previous calibration studies against active samplers.[38] Concentrations of PCBs in soils and mosses refer to dry weight unless otherwise stated. The data for quantified PCBs are summarized in Table 1, and the full data are shown in Tables S2-1−S2-3.

Air. The sum of the 24 measured PCBs (Σ_{24}PCBs) in the air ranged from 33 to 60 pg/m^3 with a mean value of 47 pg/m^3. These concentrations were similar to values found in the rural Italian Alps in 2003 (25−52 pg/m^3),[44] lower than the latest report by Gai et al.[24] (88−145 pg/m^3) in the Ruoergai Grassland (on the eastern edge of the Tibetan Plateau) in 2011, and within background levels for Asia (17−150 pg/m^3) and Europe (5.1−170 pg/m^3).[45] Tetra-CBs (46%) were the most abundant homologue group, followed by di- (25%) and tri-CBs (24%) (Figure S2-1). This differed from previous results for

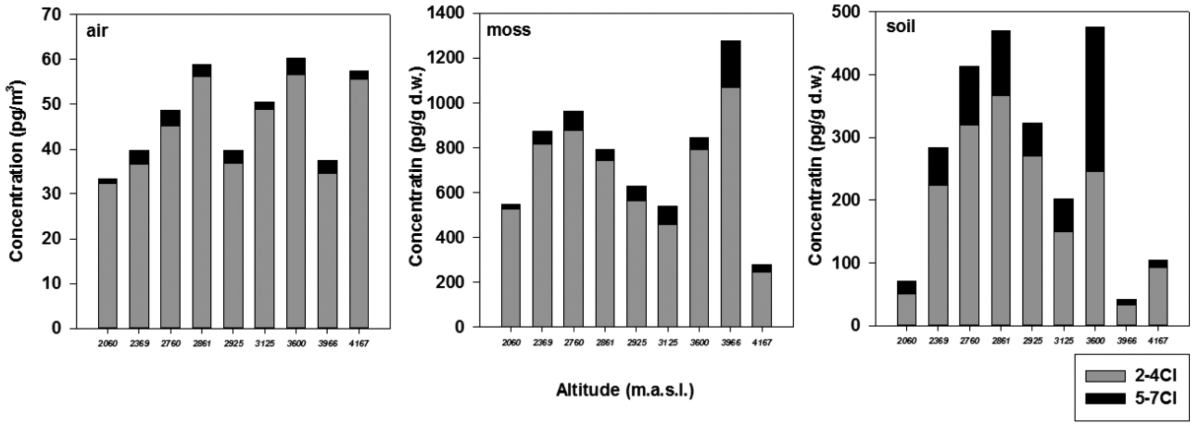

Figure 2. PCB concentrations of three environmental matrices along the altitude.

PCBs in other urban and background sites of China, where tri-CBs dominated.[38,46] The air composition on Mt. Gongga might be influenced by the southwesterly winds from India where tetra-CBs prevail at rural sites.[47] This result is in agreement with other work conducted over the Tibetan Plateau by PAS during 2007 and 2008.[27] The total concentration of seven indicative PCBs (Σ_7PCBs) (PCB 28, 52, 101, 118, 138/158, 153, and 180, identified by the International Council Exploration as markers of the degree of contamination) varied from 11 to 24 pg/m^3, and contributed 24−41% of the Σ_{24}PCBs. PCB28 was the predominant congener in all samples, which is consistent with other studies from the Tibetan Plateau.[24,31,32] The heavier congeners (101, 118, 138/158, 153, and 180) were always below 1 pg/m^3.

Moss. Because moss has no true roots, it takes up nutrients and pollutants primarily from the air and can accumulate them on or in its tissue.[48] Mosses are frequently used as biomonitors to evaluate airborne pollution from POPs. Moreover, the majority of studies have focused on the levels of polycyclic aromatic hydrocarbons (PAHs) in mosses,[49−51] and relatively few studies have been conducted on other POPs. Additionally, very few studies have been conducted at mid to low altitudes of remote areas, or directly related to concentrations in mosses with measured atmospheric concentrations.

We found a range of PCB concentrations in moss of 280−1200 pg/g, which is to our knowledge the first reported value for the Tibetan Plateau. The concentrations of Σ_7PCBs varied from 83 to 310 pg/g, accounting for 23−36% of the total PCBs. A most recent study in mosses from Antarctic Peninsula reported total PCBs in the range of 40−760 pg/g dw which was comparable with our result, although moss species were different.[52] In general, moss concentrations of total PCBs in the present study were an order of magnitude lower than previously reported in Norway,[53] Finland,[54] and East Antarctic,[55] the sampling campaigns of which were conducted more than 20 years ago. It is suggested that the reduction in the global use and manufacture of PCBs leads to decline of total PCBs sorbed by moss.[53,54] The order of abundance of PCBs in moss was similar to the distributions in air, with the order: tetra-CBs (33%) > di- (32%) > tri-CBs (26%) (Figure S2-2). The percentage of tetra-CBs and di-CBs were nearly equal in moss, whereas tetra-CBs were almost twice more abundant than di-CB in air samples. Despite being washed with deionized water to remove particles prior to PCB analysis, mosses were still capable of retaining heavy congeners (penta-, hex-, and hepta-CBs), showing 9.4% in moss compared to 5.5% in the atmosphere, indicating that moss tended to retain heavier PCBs more efficiently.

Soil. Soil concentrations of Σ_{24}PCBs (range: 41−510 pg/g, mean: 260 pg/g) in the present study were similar to those reported from the Tibetan Plateau (Mt. Sygera: 100−300 pg/g, Mt. Qomolangma: 47−423 pg/g),[26,30] but much lower than other remote regions (Pyrenees and Tatra mountains in Europe: 410−1500 pg/g, Norway and Italy background areas: 420−28 000 pg/g),[56,57] and concentrations in Asian (120−2900 pg/g) and European (47−97 000 pg/g) background soils.[45] Unlike the distributions in the atmosphere and moss, di-CBs (13%) in the soil ranked third behind tetra- (39%) and tri-CBs (25%) (Figure S2-3). In comparison to the air and moss matrices, O-horizon soil had a relatively higher proportion of Σ_7PCBs (35−48%), and PCB28 was the predominant congener.

In summary, PCB contamination on Mt. Gongga was generally low in a global perspective. This area is relatively pristine in terms of PCB contamination compared to other midlatitude sites in the Northern Hemisphere. The total of low-chlorinated congeners (di-, tri-, and tetra-CBs) dominated in all samples, indicating that lighter PCBs were more prone to LRAT.

Distribution of PCBs along the Altitudinal Gradient. Processes such as air advection, temperature-dependent air−soil exchange, and vertical mixing could play important roles in the short term variation of PCBs in ambient air of the region. We found that PCBs sequestered in the PAS did not change significantly with altitude by a variation factor of 21%, whereas it was 36% and 65% in moss and soil, respectively (Figure 2). Wang et al.[27,28] assessed the soil−air equilibrium state of POPs at 14 background sites across the Tibetan Plateau. They concluded that Tibetan soils were a "sink" for less volatile compounds, and light PCB congeners (28, 52) were close to equilibrium when the temperature increased from −5 to 15 °C. Obviously, temperature variation in our study was limited (Table 1), which implied that net volatilization of PCBs was unlikely to happen during sampling, and thus the process that PCBs was released from soil and subsequently trapped by PAS could be ignored. Southwesterly winds dominated the air circulation in 2012 (Figure S1), and back trajectory analysis revealed that air masses flowed primarily from India at all heights above ground (100, 500, or 3000 m), providing robust evidence that PCBs in the study area were mobilized by the

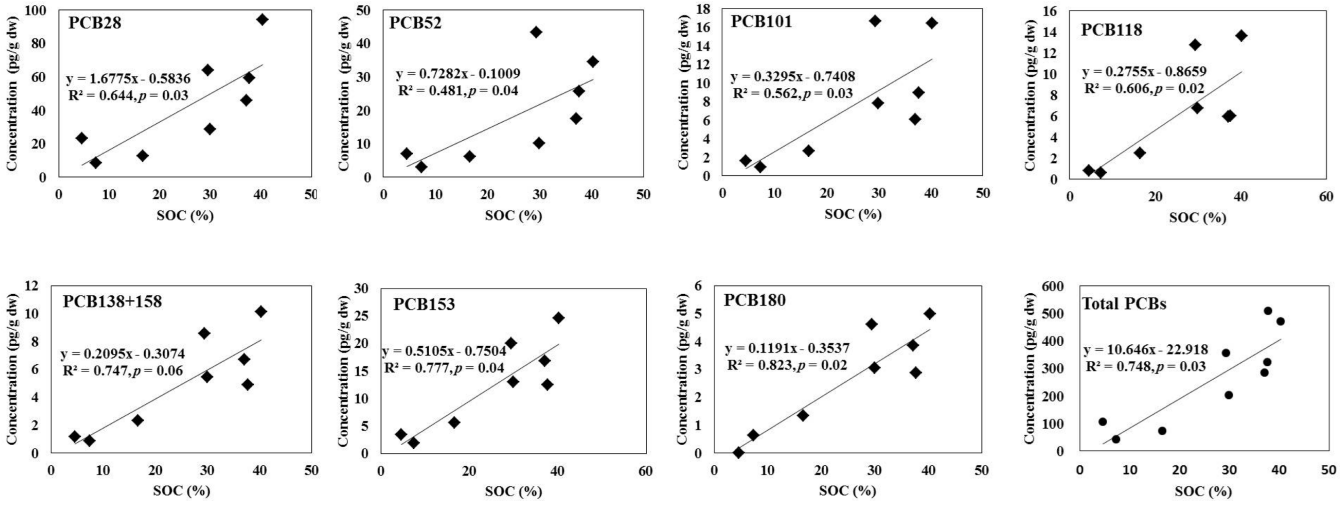

Figure 3. Regression plots and parameters between PCB concentration of O-horizon soil and SOC. The correlation plot of the individual congener versus SOC was processed for the sampling sites excluding the Site 7, while the correlation plot of the total PCBs versus SOC was processed for all the sampling sites.

Indian Summer Monsoons passing over Burma and Yunnan Province of China. The similarity of these trajectories indicates that convection in the atmospheric boundary layer was relatively consistent and that pollutants were well mixed.[28] Airborne PCBs at different elevations could come from air masses at different heights. Although it is difficult to determine precise values, this sort of discrepancy is unlikely to be responsible for the uniform dispersal of PCBs in the atmosphere among sampling sites. A more likely explanation is the high volatility and long atmospheric residence time of low-chlorinated biphenyls.[28,32]

PCBs in mosses showed no obvious trend with altitude (Figure 2). Each type of moss had its own physiological structure relating to absorption of PCBs. Because mosses have a large surface-area-to-volume ratio, they can trap more gaseous chemicals from dry and wet deposition, resulting in higher PCB concentrations and higher fractions of low-chlorinated congeners compared to soils. Moss is useful for sampling PCBs because it is widespread and easy to collect; however, the age and species of mosses are difficult to determine. We were not able to sample the same species of moss at each site (Table S3), and there are no data available on the age of moss in the study area. Thus, the irregular altitudinal distribution of PCBs that we found in mosses could have been due to differences among moss species or ages in their exposure time and absorption capacity of PCBs. Additionally, we noted that the PCB content in the moss at site 8 is very high, although the concentrations in the air and soil are relatively low. This is difficult to understand. Notably, the moss cushions we collected at site 8 grew much better (thicker) than those from the other sites, which indicated that they might be very rich in lipids, thus leading to a large capacity for PCBs.[52] We recommend additional field studies be done on the uptake efficiency (and loss) of organic pollutants by moss, which is helpful to evaluate such results.

The concentration of PCBs in soil showed the highest values at intermediate altitudes (Figure 2). As we expected, the average concentration of PCBs below the tree line was three times higher than that in the alpine shrub and meadow zones. The maximum concentration was found at Site 7 (3600 m a.s.l.), which was situated in the timberline forest. Site 7 also received the highest annual rainfall (>3000 mm/yr) and had a relatively higher SOC content of 38% (Table 1). Rainfall supplies water for plant growth, allowing plants to take up gaseous and particulate organic pollutants via atmospheric deposition (e.g., rain) and translocate these pollutants to forest soils. POPs in mountain soils from the Alps and Andes suggested a "precipitation effect" along altitudinal gradients.[13] Previous research conducted on Mt. Gongga indicated that more precipitation in the coniferous vegetation zone (2600–3600 m a.s.l) should result in higher atmospheric cadmium (Cd) deposition and higher Cd concentrations in the soil of coniferous forests.[23] PCBs have a high affinity to organic matter. Calculations by Nizzetto et al.[58] estimated that compared with other components of the forest, including primary producers, litter, and animals, soil humus could contain 96% of the total PCB153. Consequently, considering the uniform air concentrations along the transect (Figure 2), SOC coupled with precipitation could explain the results reported here. The percentage of dominant congener tetra-CBs did not change regularly with altitude, with values of 39 ± 8.0% below the tree line and 39 ± 4.0% above the tree line (Figure S2-3). We found that heavier PCBs were greatly enriched at Site 7 at 46%, while they averaged 21 ± 6.0% at the other sites (Figure S2-3). This suggests that precipitation should be the dominant deposition pathway, leading to more efficient scavenging from atmosphere and enrichment in soil for heavier organic compounds. The results also revealed that the concentration of total PCBs increased with altitude in the alpine meadow area (Figure 2). However, the increase became more distinct with the maximum occurrence at the highest elevation among all sampling sites after concentrations were normalized for SOC (Figure S3). SOC content and precipitation scavenging are clearly important variables that influence the distribution of POPs in mountain regions.[59,60]

Factors Influencing the Altitudinal Distribution of PCBs in Soils. To evaluate the possible influence of physicochemical drivers on the altitudinal distribution of PCBs, we initially tested soil PCB concentrations against each individual parameter for all sites. Independent variables included SOC, AT, and annual precipitation.

SOC ranged from 4.6 to 40%, which was a much wider range than previously reported values (~0−4.5%)[28] used for the investigation of an SOC effect in soils of the Tibetan Plateau. On average, SOC content in soils sampled below the tree line was ~5 times higher than above the tree line (Table 1). A strong relationship was observed between the total PCB concentration and SOC (p = 0.030, R^2 = 0.75; Figure 3), which was in agreement with previous studies.[12,30,61] This indicated that SOC plays an important role in controlling the sorption of organic compounds in soil. We also examined the correlations between SOC and the concentration of individual congeners and found this relationship to be notably stronger for heavier PCBs (Figure 3), except for one abnormal point. Data from Site 7 were excluded because of the probably strong influence of precipitation on the accumulation potential of heavier PCBs. The correlations between SOC and the precipitation-normalized concentration of individual congeners were hence calculated (Figure S4), and the results were consistent.

Factors other than temperature-dependent octanol−air and octanol−water partition coefficients (K_{OA}/K_{OW}) may partially govern the potential of mountain cold trapping. These factors include reduced degradation rates due to low temperatures and precipitation in the form of snow, which results in higher scavenging capacity.[14] Prior to correlation analysis with precipitation and the reciprocal of absolute AT, PCB concentrations were normalized by the SOC content and log-transformed. However, neither variable was statistically significant when their influence was assessed individually (Table S4), which suggests that trapping of POPs by mountain soils is affected by the integration of many factors, rather than just one. Precipitation and AT, in conjunction with SOC, jointly explained 89% of the total variation in the concentration of PCBs (p = 0.041, R^2 = 0.89).

Forest Filtering versus Mountain Cold Trapping. Principal components analysis (PCA) with multiple linear regression analysis (MLRA) has been used to apportion different sources of organic pollutants in the environment.[62,63] Because the purpose of PCA is dimension reduction, numerous indices can be synthesized to highlight the dominant factors. For example, Motelay-Massei et al. identified the meteorological parameters that controlled the variations in PAH concentration of bulk deposition at a suburban site of France.[64] Aichner et al. evaluated the influence of main environmental factors upon POP levels in forested soils of Germany.[5]

In our study, total variability of the original data (low-chlorinated PCBs, high-chlorinated PCBs, SOC, precipitation, and altitude) was first represented by a minimum number of linearly uncorrelated components during the PCA. The first two principal components (PCs), with eigenvalues greater than 1, accounted for 90% of the total variance in the data set. As shown in Table 2, PC1, which explained 61% of the total variance, was highly dominated by SOC and PCBs. It also had a large loading for precipitation. High SOC content, together with the capacity of global vegetation to accumulate organic pollutants, created conditions for forests to be an important storage or "retardation" compartment for POPs in the terrestrial environment.[19] A model predicted that the concentrations of some POPs in forested soils could increase by 28% compared to bare soil.[65] In addition, precipitation improves the growth of vegetation. The large vegetation coverage generally exhibits a strong effect of vegetation filtering organic compounds. Thus, this component might be highly indicative of the FFE. PC2 accounted for 29% of the total variance and was heavily weighted by altitude. Mountain cold trapping of organic chemicals is attributable to the difference in the temperature with increasing altitude,[59] and thus PC2 might be reflective of the mountain cold trapping effect (CTE).

MLRA was subsequently conducted on the PCA scores in order to obtain mass apportionment of the two effects to the total concentration of PCBs in the soils at various elevations. More information on the methodology can be found elsewhere.[62] Briefly, the two factor scores reflecting the FFE and the CTE, respectively, were regressed against the standard normalized deviate of total PCBs. Coefficients (Bi) of the factor scores were then determined with a stipulated minimum 95% confidence limit. Therefore, the mean percent contribution (defined as Bi/Σ Bi × 100%) was 67% for the FFE and 33% for the mountain CTE. The contribution of each effect i to the Σ_{24}PCBs value in each O-horizon soil sample was calculated as

$$\text{Contribution of effect } i \text{ (pg/g dw)} = \text{mean} \sum_{24} \text{PCBs} \times (\text{B}i/\sum \text{B}i) + \text{B}i\sigma_{\text{PCBs}}\text{FS}i$$

(see ref 62), where mean $\sum_{24}$PCBs was 260 pg/g dw, σ_{PCBs} was 170 pg/g dw, and FSi was the factor score for factor i.

As shown in Figure 4, the contribution of the CTE increased with altitude on the whole and explained 64% of the PCB

Table 2. Component Pattern for PCBs and Environmental Parameters in O-Horizon Soils

	PC1	PC2
low-chlorinated PCBs	0.88	−0.21
high-chlorinated PCBs	0.90	0.29
SOC	0.91	−0.37
precipitation	0.78	0.56
altitude	−0.18	0.93
loading (%)	61	29

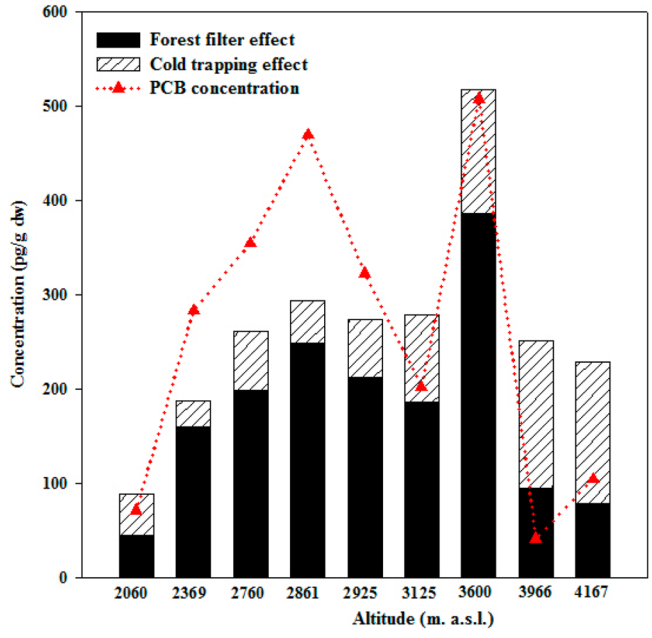

Figure 4. Patterns of PCBs in O-horizon soils by principal component analysis/multiple linear regression (PCA/MLR).

distribution in alpine shrub meadows. This was much lower than expected, partially owning to dwarf trees and grass reflected by SOC values. However, taking all of the sampling sites into consideration, FFE was the predominant factor controlling the accumulation of PCBs in soils along the eastern slope of Mt. Gongga. Because FFE is modulated by the differential leaf area index (LAI) (area of leaf/area of ground surface), LAI should be specified when relating soil concentration differences to the FFE among forest types. Luo et al.[66] quantified LAI from 1900 to 3700 m a.s.l. along the eastern slope of Mt. Gongga during 1999−2000. Their results perfectly supported ours, showing that LAI were higher at 2850 and 3700 m a.s.l. almost where O-horizon soils hosted higher amounts of PCBs and the contribution of the FFE were statistically greater. LAI generally increased with increasing precipitation. The lowest LAI was found at 1900 m a.s.l. Mt. Gongga is cold even at the bottom of the mountain. As a result, FFE contributed the least at 2060 m a.s.l. among forests with a percentage of 51%. The plot of calculated total PCBs were lower than measured in intermediate forests, and the opposite was observed in the alpine shrub and meadow zone. This finding can be interpreted by the fact that chemicals move from high altitudes to lowlands with runoff during the snow-free season. In summary, the study experimentally showed that the two effect acting in different elevations can produce PCB altitudinal distribution deviating from the thermodynamic theory. Elevated concentrations in forested soils can be explained by direct deposition and accumulation rather than by increased thermodynamic partitioning because of low temperatures. This is a very important finding, especially for modelers to make predictions of the fate and behavior of PCBs and other highly persistent SOCs in cold environments. It will not only help to prevent researchers from focusing too much on one effect but also guide the design of more comprehensive studies.

■ ASSOCIATED CONTENT

Supporting Information

Detailed description of laboratory procedures and additional tables and figures from data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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