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Polychlorinated biphenyls in a grassland food network: Concentrations, biomagnification, and transmission of toxicity

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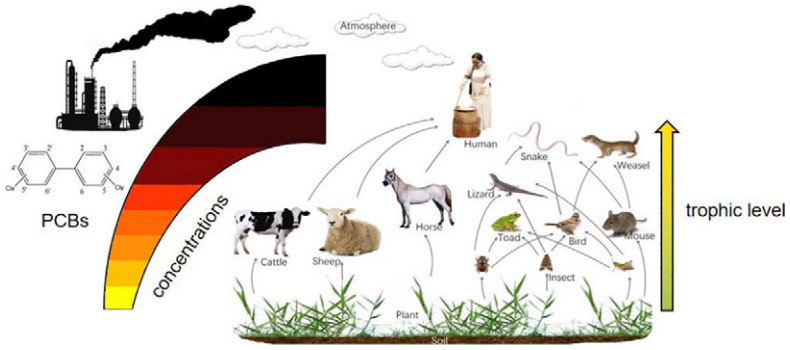
HIGHLIGHTS

- PCBs appeared to be enriched as the trophic level increased.
- Snake/quarry had BMFs as high as 5000 for PCB-114, -156, and 169.
- Up-PCBs (PCB-126, 169) had the highest TEQ concentrations in the organisms.

GRAPHICAL ABSTRACT



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ABSTRACT

The production of polychlorinated biphenyls (PCBs) is prohibited by the *Stockholm Convention* in 2001, but the unintentionally produced PCBs are still continuously discharged into the environment. In this study, the distributions, biomagnification and toxicity amplification in a grassland food network (including inorganic environment, animals and vegetation) were investigated. PCB concentrations in various samples were determined, and PCBs appeared to be enriched as the trophic level increased. The PCB concentrations in the inorganic environment samples ranged from below the detection limit to 0.329 ng g^{-1}, and the PCB concentrations in vegetation were 0.0829–4.45 ng g^{-1}. The PCB concentration in snake subcutaneous fat (8.74 ng g^{-1} lipid weight) was higher than the concentrations in other animal samples, and the next highest concentration was found in yellow weasel muscle (7.31 ng g^{-1} lipid weight). Biomagnification factors were calculated for different PCBs and different organisms. Biomagnification was most obvious for organisms at the top of the food chain (the snake/mouse biomagnification ratio was >1000). The PCB-126 toxic equivalent concentration increased markedly as the trophic level increased. The toxic equivalent concentrations were 1200 times higher for high trophic level biota than low trophic level biota. PCB-169 had the highest toxic equivalent concentrations for the animal hair samples (0.00001 pg toxic equivalents g^{-1}). However, PCB-81 had the highest toxicity equivalent concentrations for the herdsmen hair samples. PCBs found at relatively low concentrations and low toxic equivalent concentrations at low trophic levels can be biomagnified as they are transferred through the food chain and can reach high actual and toxic equivalent concentrations at high trophic levels.

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1. Introduction

Polychlorinated biphenyls (PCBs) are man-made chemicals that are chemically stable, have excellent thermal conductivity and insulation properties, and are not flammable (Wang et al., 2014).Because of these properties, PCBs have been widely used in heat exchange devices, in insulating oils in capacitors and transformers, and as lubricating agents, plasticizers, and additives in various types of coating (Li et al., 2007). PCBs were first synthesized in the laboratory in Germany in 1881 and started to be produced commercially in various countries in 1929 (Li et al., 2007). The properties of PCBs fit the criteria used to define persistent organic pollutants (POPs), and PCBs are included in the Stockholm Convention on POPs. PCB production around the world ceased from the 1970s onward (Zhao, 2008). It has been estimated that ~1×10^6 t of PCBs were produced globally between 1930 and 1993 (Zhao, 2008). PCB production in China started in 1965, but PCB production in China gradually ceased from 1974 (Meng et al., 2008). Dioxin-like PCB and toxic equivalent (TEQ) concentrations in serum from the general population of Weifang City (China) decreased between 2011 and 2017, but the decrease was not statistically significant. The concentrations of most individual dioxin-like PCB congeners decreased between 2011 and 2017, but the PCB-118 concentration increased. The dioxin-like PCB congener patterns in the samples collected in 2011 and 2017 were therefore clearly different (Liu, 2018). PCBs can persist in the environment for a long time, and can migrate in the atmosphere and accumulate at high latitudes and altitudes because of global fractionation (Zhang, 2010a, 2010b). It has been found that certain organic contaminants can reach high concentrations in organisms relative to the concentrations in the environment the organisms inhabit (Mackay and Fraser, 2004). Organisms consuming contaminated organisms (e.g., fish) can be exposed to high doses of toxic chemicals (Mackay and Fraser, 2004). PCBs can cause toxic symptoms such as skin damage and liver damage. People and animals will show lethargy, general weakness, loss of appetite, nausea, abdominal distention, abdominal pain, jaundice, hepatomegaly, etc. after they are poisoned. Low concentrations of PCBs will slowly invade the human body such as damaging the liver, kidney and heart. PCBs can even be incorporated into the DNA of cells, leading to the disorder of genetic factors and the generation of cancer (Chen and Fang, 1989). Many accidents about PCBs pollution in history such as PCBs pollution incident in Aniston, USA; PCBs pollution in Irish pork, Japan and Taiwan had caused great loss and pain to human beings (Chen and Fang, 1989). Therefore, PCB concentrations in the environment and the transfer of PCBs to biota need to be studied.

As mentioned above, PCBs are persistent, can accumulate in biota, and are toxic (Wang et al., 2014). PCBs are semi-volatile, so can be transported long distances in the atmosphere and then be deposited to the terrestrial environment. POPs can be transported from their sources to areas in which they have never been used (Lohmann et al., 2009), and tend to be deposited in areas with low temperatures (i.e., at high latitudes (particularly the poles) and altitudes). POPs have been found in the Arctic and have accumulated through Arctic food chains (MacDonald et al., 2000). POPs bioaccumulate in aquatic biota and biomagnify through aquatic food webs. Very high concentrations of POPs have been found in fish blood and liver (Hoekstra et al., 2002; Kelly and Gobas, 2003; Kelly and Gobas, 2001). POP concentrations in ambient air have been determined in many studies (Halsall et al., 1998; Su et al., 2006; Su et al., 2008), but POP concentrations in grass have been studied little. No comprehensive study of PCBs in complicated terrestrial food webs has been performed (Chen and Hale, 2010). Unintentional emissions of PCBs during industrial processes have become the main sources of PCBs to the environment, although PCB residues in environmental media from historic PCB use remains a problem. The effects of unintentional emissions of PCBs on PCB concentrations in remote areas and PCB transfer through terrestrial food chains are not yet clear (Kim et al., 2015; Vorkamp et al., 2015; Wolschke et al., 2015).

In this study, samples from a remote area, Xilingol Prairie in Inner Mongolia, were analysed. Samples representing a complete closed-loop food web were analysed to allow PCB concentrations in different biota at the same trophic level and the transfer and biomagnification of PCBs between biota at different trophic levels to be investigated.

2. Materials and methods

2.1. Sample collection

Samples were collected from three areas in Xilingol Prairie. One area was the 426×10^6 m^2 Maodeng Pasture (M.P.) National Nature Reserve (116.36° E, 44.24° N, 1010 m above sea level). Samples were collected from three private pastures in the second area, which was 40 km from the eastern part of Xilingol City. The three pastures were called herdsman household H.H.1, H.H.2, and H.H.3. This area was at 116.39° E, 44.19° N, and 970 m above sea level. Samples were also collected from two private pastures 80 km from the northern part of Xilingol City. These two pastures were called H.H.4 and H.H.5. This area was at 116.22° E, 44.63° N, and 1190 m above sea level. The sampling areas, sampling point locations, and relevant information on the samples are shown in Fig. 1. Samples of well water (500 mL per sample), surface soil (0–10 cm deep), and air (collected using passive air samplers) were collected between 4 April and 19 July 2018. Samples of vegetation (the first trophic level) were collected. The vegetation samples were of *Artemisia frigida*, *Agaricus tenuifolia*, *Leymus chinensis*, *Allium mongolicum*, and grass seeds. Insect (second trophic level) samples were collected during the night by attracting the insects to light. The insect species that were collected were *oriental migratory locust*, *Cnethodonta grisescens*, *Xylinophorus mongolicus* Faust, and *Cimex lectularius*. Samples of animals at the third trophic level killed on roads were collected, but mice were captured. The animals collected from roads were toads, snakes, and birds. No animals that are protected in China were harmed during the sampling process. The third trophic level samples that were collected were toad (*Bufo gargarizans*), lizard (*Phrynocephalus frontalis*), mouse (*Spermophilus erythrogenys*) muscle, mouse (*Lasiopodomys brandtii*) muscle, bird (in the genus *Passer*) muscle, bird (barn swallow) muscle, bird (*Cuculus canorus*) muscle, and Mongolian sheep (in the subfamily Caprinae) muscle. Fourth trophic level animal samples were also collected. These were snake (*Elaphe dione*) muscle, viscera, skin, and yellow weasel (*Mustela sibirica*) muscle. Hair was also collected from the backs of the necks of herdsmen. Wool was collected from the backs and tail ends of sheep. Hair was collected from the backs of the necks and from the tails of horses and from the tails of cattle. The samples were stored at a low temperature until they were analysed.

2.2. Pretreatment and extraction

2.2.1. Sample pretreatment

A 100 mL aliquot of a water sample was extracted with 200 mL of a 1:1 *v*/v mixture of *n*-hexane and acetone. The internal standards (0.64 ng of ^{13}C-labeled PCBs) were added, then the sample/extractant mixture was shaken for 1 h and then allowed to separate. A 50 mL aliquot of the upper layer was removed, then the extraction was repeated five times. The other samples were Soxhlet extracted. Before extraction, each solid sample was freeze-dried. The internal standards (0.64 ng of ^{13}C-labeled PCBs) were added to an aliquot of a sample, then the sample was Soxhlet extracted with 200 mL of a 1:1 *v*/v mixture of *n*-hexane and acetone for 24 h. The extract was then rotary evaporated and then transferred to a centrifuge tube and evaporated to dryness to determine the lipid content. The residue was then dissolved in 5 mL of a 1:1 v/v mixture of *n*-hexane and acetone.

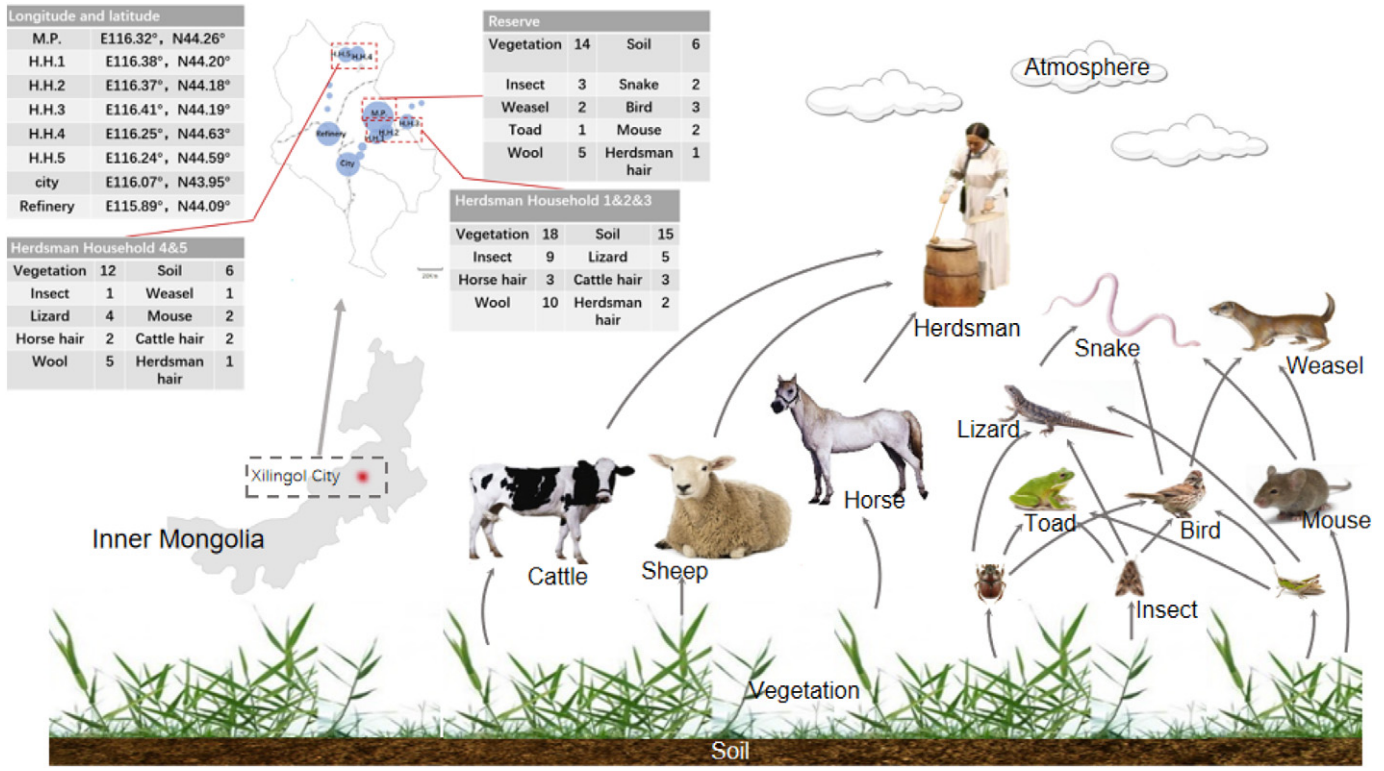

Fig. 1. Sampling information in Xilingol Prairie of China and a diagram of the food web.

Each extract was evaporated to 4 mL, then centrifuged and the impurities removed. The extract was then passed through a composite silica gel column containing, from bottom to top, 1.0 g of neutral silica gel, 4.0 g of alkaline silica gel, 1.0 g of neutral silica gel, 8.0 g of acidic silica gel, 2.0 g of neutral silica gel, and 4.0 g of anhydrous sodium sulfate. Once the sample extract had been applied, the column was eluted with 18.0 mL of *n*-hexane, which was discarded. The column was then eluted with 100.0 mL of a 97:3 *v*/v mixture of *n*-hexane and dichloromethane, which was collected. The solution was evaporated to a small volume, transferred to a sample vial containing 100 μL of nonane, and evaporated to 100 μL under a gentle stream of nitrogen. The extracts were then analysed by gas chromatography mass spectrometry.

2.2.2. Instrumental analysis

The gas chromatograph was fitted with a J&W DB-5 MS column (30 m length, 0.25 mm i.d., 0.1 μm film thickness; Agilent Technologies, Santa Clara, CA, USA). The oven temperature program started at 100 °C, which was held for 3 min, then increased at 5 °C min^{-1} to 250 °C. The injection port, ion source, and quadrupole temperatures were 300, 150, and 150 °C, respectively. The carrier gas flow rate was 1.0 mL min^{-1}. The sample injection volume was 1.0 μL, and splitless injection mode was used. The mass spectrometer was operated in negative chemical ionization mode and selected ion monitoring mode, and quantitative analysis was performed. The *m*/*z* ratios monitored were 256.0 and 186.0 for PCB-28; 290.0 and 292.0 for PCB-81,-77 and − 52; 326.0 and 328.0 for PCB-123, −118, −114, −105,-101 and − 126; 360.0 and 362.0 for PCB-169, −167, −157, and − 156; and 394.0 and 396.0 for PCB-189 and -180. The m/z ratios monitored for the $^{13}C_{12}$-labeled PCB internal standards were 12 units higher than the m/z ratios monitored for the corresponding unlabelled PCBs.

2.2.3. Quality control and assurance

Each item of glassware was rinsed 30 times with distilled water and 15 times with ultrapure water, then baked at 450 °C, and then rinsed three times with pesticide residue grade *n*-hexane before use. The target compounds were quantified using an isotope-labeled internal standard method using a five-point calibration. The calibration curve correlation coefficient r was >0.9999 for every analyte. The PCB concentrations in the samples were very low, so the limit of detection was defined as the concentration giving a signal-to-noise ratio of 3. The instrument detection limits were 0.05–2 pg, and the method detection limits were 0.1–10 pg g^{-1} lipid weight (l.w.).

Procedural blank and field blank were analysed with the real samples. The target compounds were not detected in the blanks. The recoveries for the inorganic environmental samples were 40%~110%. The recoveries for the plant samples were 30%~150%. The recoveries for the animal samples were 50%~200%. In this study, 121 samples were divided into eight groups for analysis. We randomly selected one sample from each group for duplicate test and RSDs of all duplicate products were between 4.47% and 15.2%.

3. Results and discussion

3.1. PCB concentrations and distributions in the grassland ecosystem

Xilingol Prairie is in a clean middle-latitude and high-altitude area. There are no records of PCBs being produced in the area. All sampling areas are mostly inaccessible places, so there are few man-made equipment in the prairie. The PCBs in the area will therefore have mainly been supplied through atmospheric deposition (Yu et al., 2013). The PCB concentrations in the samples are shown in Table 1. The concentrations of most of the PCB congeners in the water samples were below the detection limits. Hexachlorobiphenyls and heptachlorobiphenyls only accounted for <10% of the total PCBs in groundwater samples, while accounted for 31.3% of the total PCBs in soil samples. Soil was more likely than water to accumulate more-chlorinated PCBs. The tetrachlorobiphenyls contributed 30% of the total PCB concentrations in the soil samples. The sum of the PCB-28, −52, −77, −81, −101,

Table 1
Polychlorinated biphenyl (PCB) concentrations in environmental, vegetation, animal, and herdsmen hair samples from Xilingol Prairie.

Sample		Part	Total concentration range	Average concentration ± SD	Median concentration	ΣPCBs TEQ mean	ΣPCBs TEQ min	ΣPCBs TEQ max
			(ng g^{-1})	(ng g^{-1})	(ng g^{-1})	(pg WHO-TEQg^{-1})	(pg WHO-TEQg^{-1})	(pg WHO-TEQg^{-1})
PUF (air sampler)*			0.081	0.081	0.081	0.0459		
Water			<LOD	<LOD	<LOD			
Soil			(0.0350, 0.329)	0.0976 ± 0.104	0.0523	0.0466	0.000355	0.214
Vegetation	*Artemisia frigida*	Whole	(1.056, 4.448)	2.25 ± 1.33	1.74	4.31	0.0452	13.4
	Agaricus tenuifolia	Whole	(0.198, 3.021)	1.70 ± 0.944	2.01	24.4	0.00479	54.0
	Leymus chinensis	Whole	(0.499, 2.09)	1.13 ± 0.642	0.974	24.4	0.199	63.7
	Allium mongolicum	Whole	(0.083, 1.59)	0.695 ± 0.603	0.555	11.2	0.415	27.2
	Grass seeds*	Whole	1.04	1.04	1.04	0.0179		
	Mixed grass	Whole	(0.139, 0.311)	0.225 ± 0.0856	0.225	0.0202 (pg WHO-TEQg^{-1}l.w.)	0.00400 (pg WHO-TEQg^{-1}l.w.)	0.0365 (pg WHO-TEQg^{-1}l.w.)
Animals[a]	*Orental migratory locust*	Whole	(0.556, 1.01)	0.756 ± 0.187	0.709	0.269	0.00509	0.705
	*Cnethodonta grisescens**	Whole	0.761	0.761	0.761	0.186		
	*Xylinophorus mongolicus faust **	Whole	0.356	0.356	0.356	0.00558		
	Cimex lectularius	Whole	(0.860, 0.968)	0.914 ± 0.054	0.914	11.8	0.0114	23.7
	Hybrid insect *	Whole	1.61	1.61	1.61	0.0146		
	*Bufo gargarizans**	Whole	0.512	0.512	0.512	0.160		
	Phrynocephalus frontalis	Whole	(0.661, 3.50)	2.09 ± 0.967	2.20	0.830	0.00188	2.28
	Mongolia Citellus dauricus	Muscle	(0.762, 1.02)	0.891 ± 0.129	0.891	0.0135	0.00687	0.0201
	Lasiopodomys brandtii	Muscle	(0.403, 2.76)	1.58 ± 1.18	1.58	0.0478	0.00691	0.0887
	Passer	Muscle	(1.34, 1.44)	1.39 ± 0.0530	1.39	0.0122	0.0113	0.0131
	*Barn swallow**	Muscle	2.99	2.99	2.99	0.0679		
	*Cuculus canorus**	Muscle	2.24	2.24	2.24	0.0236		
	Sheep*	Muscle	5.17	5.17	5.17	0.0517		
		Muscle	(2.65 , 3.63)	3.14 ± 0.491	3.14	0.0349	0.00861	0.0612
		Viscera*	4.08	4.08	4.08	46.6		
	Snake	Skin *	8.74	8.74	8.74	2.83		
	Yellow weasel	Muscle	(4.29, 7.31)	6.23 ± 1.37	7.07	7.52	0.0466	18.6

Notes: water, soil, plant samples, units ngg^{-1}; animal samples, units ng g^{-1} lipid weight.
ΣPCBs = sum of the PCB-28, −52, −77, −81, −101, −105, −114, −118, −123, −126, −156, −157, −167, −169, −180, and −189 concentrations.
TEQ = toxic equivalent concentration, calculated using the WHO-05 toxic equivalence factors for PCB-77, −81, −105, −114, −118, −123, −126, −156, −157, −167, −169, and 189.
Limit of detection (LOD) 0.0026 ng g^{-1}.
[a] indicates that the concentration of pollutants in the animal body is calculated by lipid standardized concentration.
Samples with an asterisk represent less than three samples, and samples without an asterisk represent more than three.

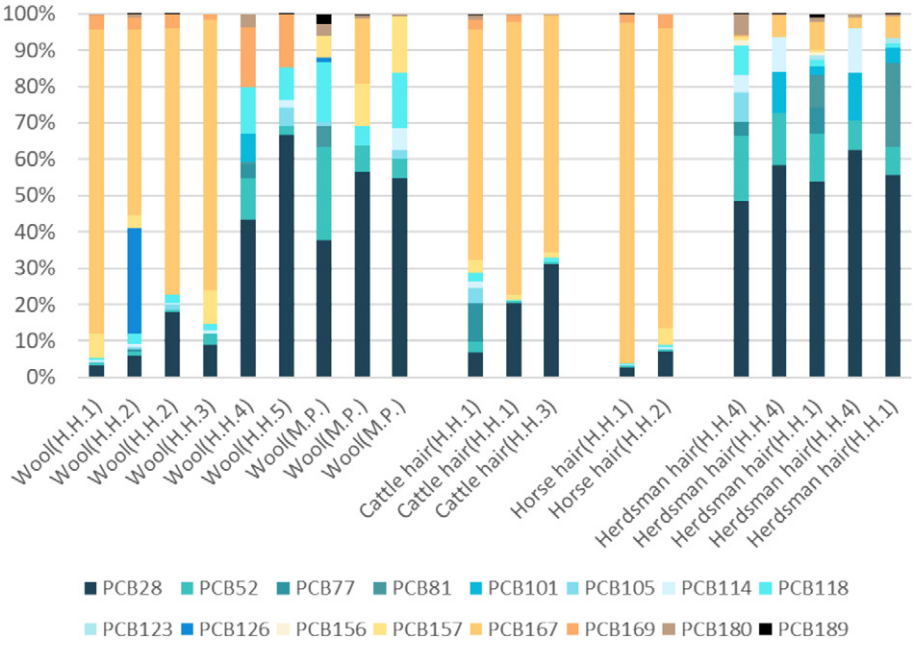

Fig. 2. Polychlorinated biphenyl (PCB) congener profiles in the animal hair samples.

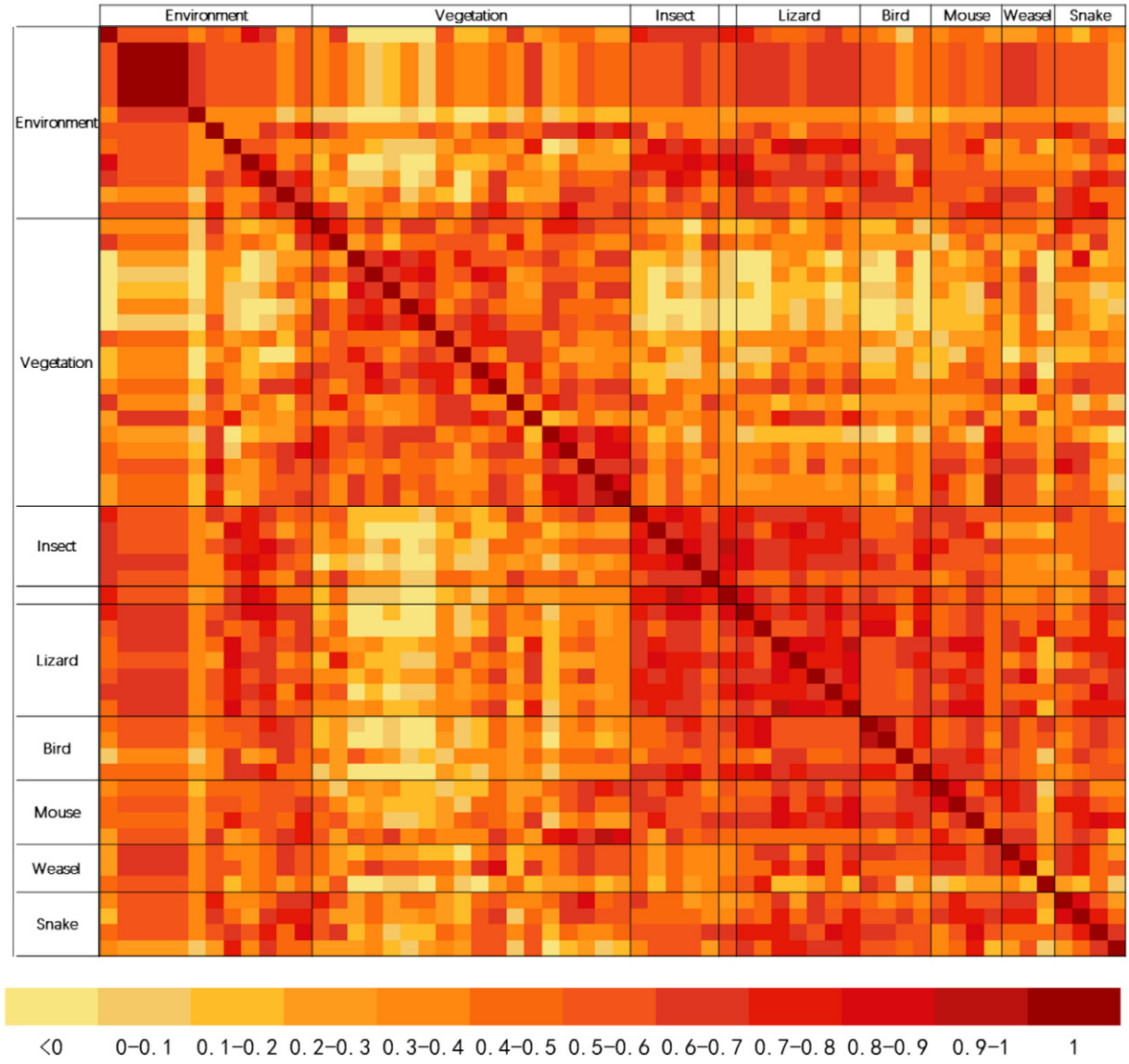

Fig. 3. Thermodynamic diagram of the correlations between polychlorinated biphenyl concentrations in different food web samples from the grassland sampling area.

−105, −114, −118, −123, −126, −156, −157, −167, −169, −180, and − 189 ($\sum_{16}$PCB) concentrations in the soil samples were 0.0350–-0.329 ng g − 1, and the median was 0.0523 ng g^{-1}. The concentration in the H.H.2 soil was the highest (0.329 ng g^{-1}) in the concentrations of all the soil samples. The concentration in the M.P. soil was the lowest (0.0350 ng g^{-1}) in the concentrations of all the soil samples. This indicated that the PCB concentrations in soil decreased as the distance from Xilingol City increased.

Vegetation samples from H.H.1–H.H.5 and M.P. were analysed. The PCB concentrations in the vegetation samples varied spatially in a similar way to the PCB concentrations in the soil samples. The PCB concentrations decreased as the distance from Xilingol City increased. The $\sum_{16}$PCB concentrations in the vegetation samples were 0.0829–4.45 ng g^{-1}. The highest $\sum_{16}$PCB concentration (4.45 ng g^{-1}) was found in *Artemisia frigida* from H.H.1, and the lowest concentration (0.0829 ng g^{-1}) was found in *Allium mongolicum* from H.H.5, which was far from Xilingol City. PCB-28 was the dominant PCB congener in the vegetation samples, and PCB-167 was the second most dominant. The PCB patterns in the different types of vegetation were different. The dominant PCB homolog in *Leymus chinensis* was the hexachlorobiphenyl homolog, the concentration of which was 0.993 ngg^{-1}.The hexachlorobiphenyls contributed 50% of the $\sum_{16}$PCB concentration. The more-chlorinated PCBs were dominant in every *Leymus chinensis* sample, but the less-chlorinated PCBs were found at very high concentrations in every *Allium mongolicum* sample. The trichlorobiphenyls contributed >40% of the $\sum_{16}$PCB concentrations, on average. This indicated clear differences in the PCB-enrichment characteristics of *Leymus chinensis*and *Allium mongolicum*.

Insect samples were collected in the M.P. and the five H.H.s (shown in Fig. 1). The $\sum_{16}$PCB concentration in *Cnethodonta grisescens* (0.761 ng g^{-1}) was higher than the concentrations in the other insects. The $\sum_{16}$PCB concentration in *Xylinophorus mongolicus* Faust (0.356 ng g^{-1}) was lower than the concentrations in the other insects. PCB-28 was the dominant PCB congener in the insects.

The $\sum_{16}$PCB concentrations in the other animal samples were 0.403–8.74 ng g^{-1} l.w. The $\sum_{16}$PCBconcentrationin snake subcutaneous fat (8.74 ng g^{-1} l.w.) was higher than the concentrations in the other animal samples. Snakes are the top predators in the sampling area. The $\sum_{16}$PCB concentrations in the snake tissues decreased in the order subcutaneous fat (8.74 ng g^{-1} l.w.) > liver (4.08 ng g^{-1} l.w.) > muscle (3.14 ng g^{-1} l.w.). The lipid contents of the snake tissues decreased in the order subcutaneous lipid > liver > muscle. It can be seen that PCB

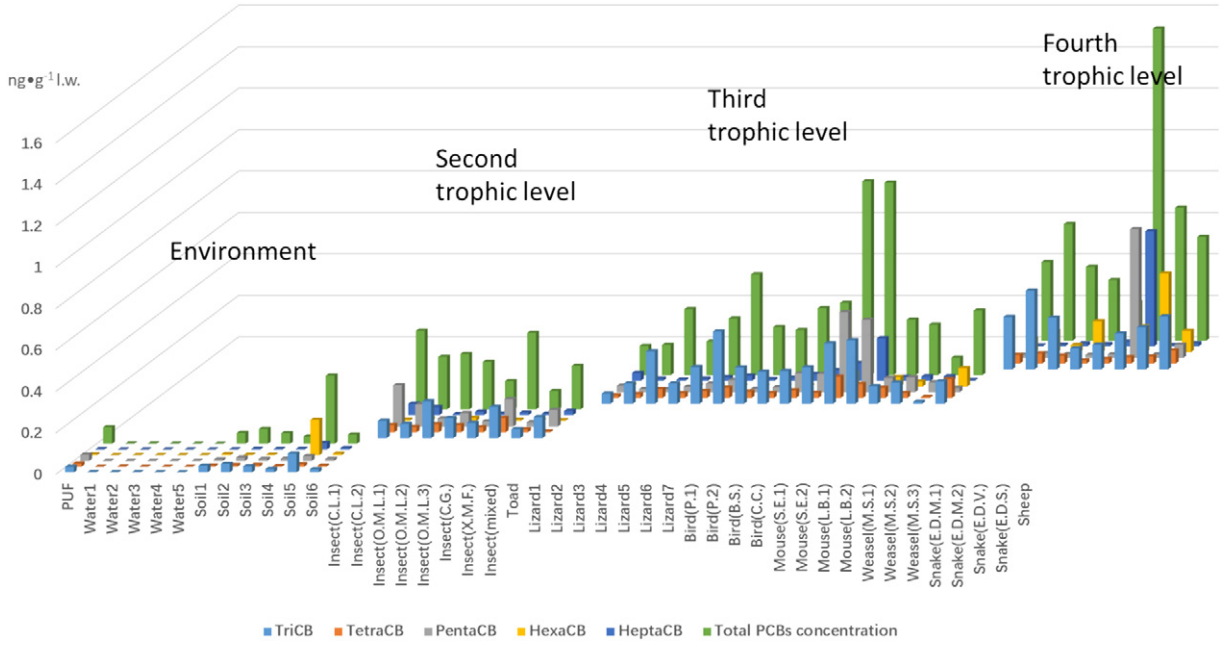

Fig. 4. Polychlorinated biphenyl homolog concentrations in the samples from Xilingol Prairie ng·g^{-1} l.w.

enrichment increased as the lipid content increased. In a previous study, perfluorocarbon concentrations were higher in the livers than the muscles and kidneys of reindeer in Yukon Territory, northern Canada (Claudia et al., 2011). The perfluoro carboxylic acid and perfluoro sulfonic acid concentrations in liver samples were 5–15 times higher than the concentrations in muscle samples from wolves from the same area in northern Canada (Claudia et al., 2011). The $\sum_{16}$PCB concentrations in reindeer or wolf subcutaneous fat were not determined in that study. In our study, the $\sum_{16}$PCB concentrations in the animal samples increased as the trophic level increased. For the second trophic level (which included oriental migratory locust, *Cnethodonta grisescens*, *Xylinophorus mongolicus* Faust, and *Cimex lectularius*), the trichlorobiphenyls contributed ~65% of the $\sum_{16}$PCB concentrations. For the third trophic level (which included *Bufo gargarizans*, *Phrynocephalus frontalis*, *Spermophilus erythrogenys* muscle, *Lasiopodomys brandtii* muscle, *Passer* muscle, *Barn swallow*muscle, *Cuculus canorus* muscle, and *Caprinae* muscle), the pentachlorobiphenyls were dominant. High pentachlorobiphenyl concentrations were generally found in the bird muscle samples. The highest pentachlorobiphenyl concentration in the bird muscle samples was 0.386 ng g^{-1} l.w. More-chlorinated PCBs were found in the fourth trophic level samples (snake and yellow weasel tissues). The hexachlorobiphenyl concentration in snake viscera was 0.556 ng g^{-1} l.w. These results indicated that less-chlorinated PCBs were dominant in the low trophic level samples and more-chlorinated PCBs were mainly found in the high trophic level samples. Very high PCB-126and −167 concentrations of 0.167 and 0.373 ng g^{-1} l.w., respectively, were found in the snake (top predator) samples.

The $\sum_{16}$PCB concentrations in the hair samples decreased in the order herdsman hair (median 2.07 ng g^{-1}) > horse hair (median 2.00 ng g^{-1}) > cattle hair (median 1.66 ng g^{-1}) > wool (median 0.987 ng g^{-1}). The dominant PCB homolog in the cattle hair and horse hair samples was the hexachlorobiphenyl homolog, which contributed >70% of the $\sum_{16}$PCB concentrations. The PCB-167 concentration contributed >63.4% of the $\sum_{16}$PCB concentration in cattle hair from H.H.1 and the other sampling sites and > 82.6% of the $\sum_{16}$PCB concentration in horse hair from H.H.4. The PCB congener profiles in the wool samples from different sites were different ($r < 0.5$, $p > .05$) (Fig. 2), but PCB-167 was the dominant PCB congener in the wool samples from H.H.1, H.H.2, and H.H.3, which were all near Xilingol City. PCB-28 was the dominant PCB congener in the wool samples from H.H.4 and H.H.5, which were far from Xilingol City. PCB-28 contributed >63.5% of the $\sum_{16}$PCB concentrations in these samples. The PCB patterns in the herdsmen hair samples and animal hair samples were different. The PCBs in the herdsmen hair samples were dominated by the less-chlorinated PCBs, and PCB-28 contributed ~50% of the $\sum_{16}$PCB concentrations. The PCB patterns in the herdsmen hair samples from different sites (H.H.1 and M.P.) were very similar ($r > 0.8$, $p = .03$). The pentachlorobiphenyls and less-chlorinated PCBs contributed >61.7% of the $\sum_{16}$PCB concentrations in these samples. The PCB patterns in samples from different sites were much less different for the herdsmen hair samples than for the cattle and horse hair and wool samples ($r > 0.8$, $p = .02$) (as shown in Fig. 2). It has previously been found that PCBs in human hair are mainly endogenous (Yuan et al., 2017), meaning the diets of the herdsmen would have been the main sources of PCBs to the herdsmen hair samples and that future changes in the PCB concentrations in the diets may affect the PCB concentrations in the herdsmen's hair.

The PCB patterns in the samples were assessed by performing Spearman's correlation analyses using SPSS 20.0 software. The results are shown as a correlation thermodynamic diagram in Fig. 3 with r values of 0–1 shown in different colours. The correlation coefficient r is higher when the colour is darker. No significant correlations ($r < 0.5$, $p > .05$) were found between the PCB patterns in the vegetation and inorganic environment samples (soil, water, and air) or between the PCB patterns in the vegetation and wool, cattle hair, and horse hair samples ($r < 0.4$, $p > .05$). The PCB concentrations in the vegetation samples from different areas were very different, but the concentrations in samples of the same vegetation species significantly correlated ($r > 0.8$, $p = .03$). Lizard (*Phrynocephalus frontalis*) samples were collected from sites H.H.1 and H.H.4, 100 km apart, but the PCB concentrations in the samples significantly correlated ($r > 0.75$, $p = .03$). There is no record of PCB production in Xilingol Prairie, so PCBs will mainly have entered the environment in the study area through atmospheric deposition (Yu et al., 2013). Significant correlations were found between the PCB concentrations in animals with predation relationships ($r > 0.8$, $p < .05$), such as snakes and mice ($r = 0.92$, $p = .03$) and yellow weasels

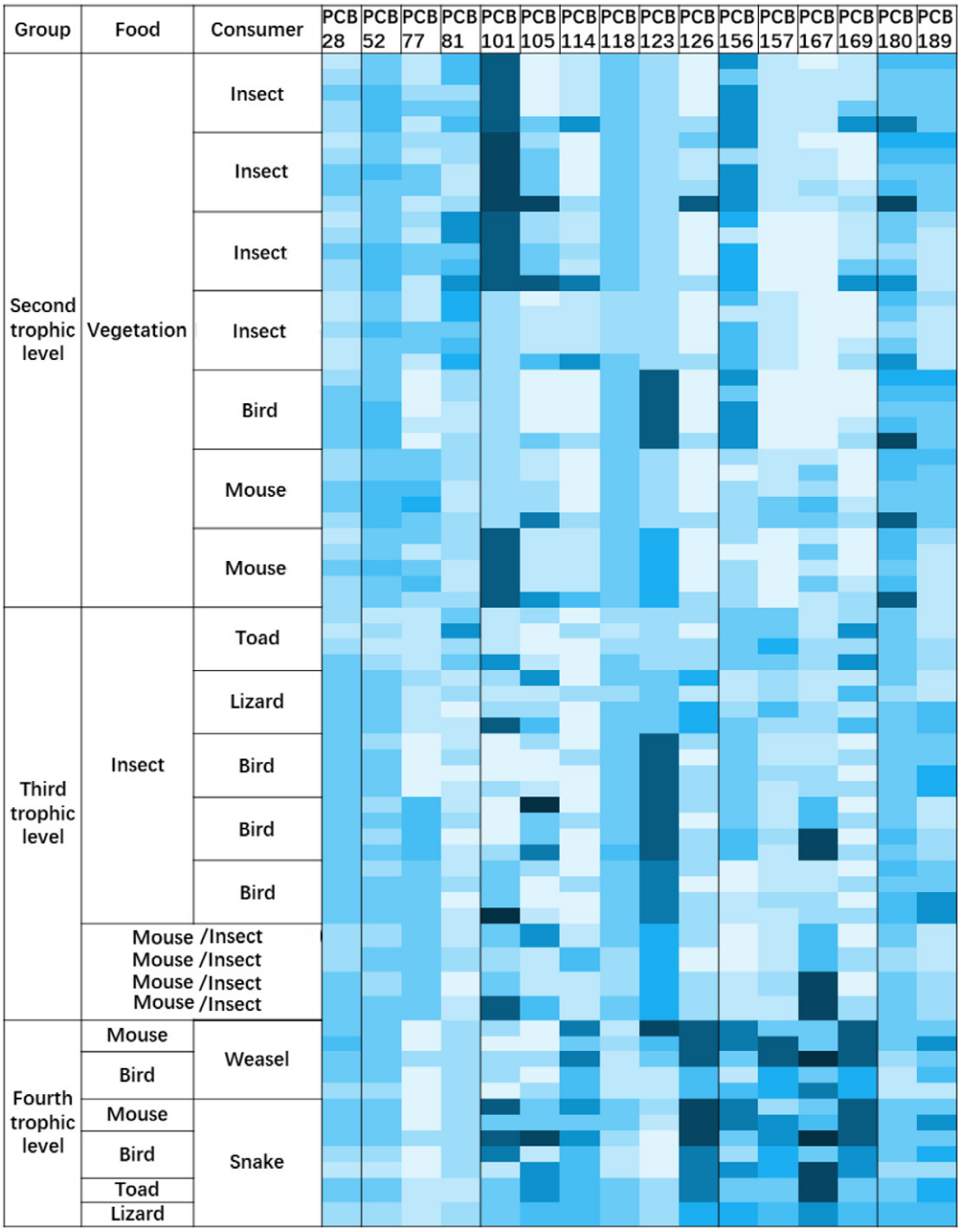

Fig. 5. Thermodynamic diagram for polychlorinated biphenyl biomagnification in the Xilingol Prairie ecosystem.

and *Passer* species ($r = 0.96$, $p = .03$). This indicated that PCBs were transmitted from prey to predator in animal.

3.2. PCB transfer and biomagnification in the grassland food web

The $\sum_{16}$PCB concentration generally increased as the trophic level increased (as shown in Fig. 4). The trichlorobiphenyl and tetrachlorobiphenyl concentrations were enriched uniformly as the trophic level increased, i.e., the PCB concentration increased each time the trophic level increased. The hexachlorobiphenyls were only enriched in the highest trophic level relative to the second highest trophic level, and the hexachlorobiphenyl concentrations in the other trophic levels were similar (i.e., no enrichment occurred). The pentachlorobiphenyl and heptachlorobiphenyl concentrations did not increase as the trophic level increased. This may be because some more-chlorinated PCBs can be biologically and chemically degraded to give less-chlorinated PCBs (Niimi and Oliver, 1988; Selck et al., 2003; Gewurtz, 2000).

We calculated BMFs for the samples, as recommended in a previous publication (Mackay and Fraser, 2004), using the lipid standardized PCB concentrations, to describe biomagnification of the PCB congeners. The calculations were performed taking the predation relationships in the grassland ecosystem and the trophic levels into consideration. The formula used to calculate the BMFs is shown in Eq. (1).

$$BMF = C_B/C_A \quad (1)$$

In Eq. (1), C_B is the PCB concentration in a predator sample and C_A is the PCB concentration in a prey sample. The results are shown in Fig. 5.

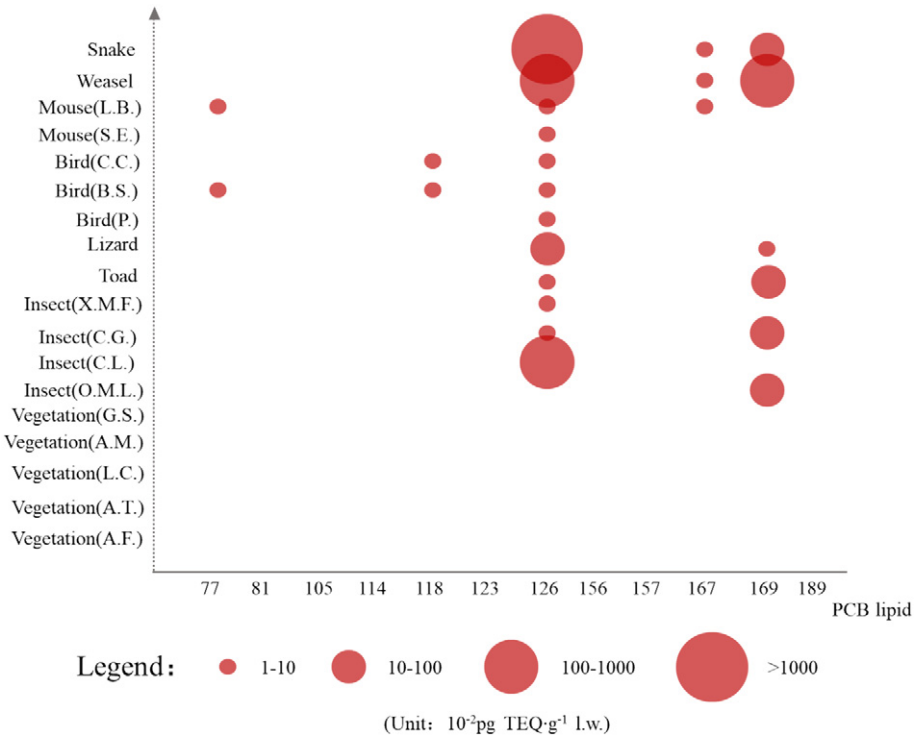

Fig. 6. Toxicities of different polychlorinated biphenyls in organisms in Xilingol Prairie.

Most of the PCB congeners were not clearly biomagnified by the second trophic level organisms, and the BMFs were relatively low. This may have been related to the short life cycles, simple metabolic mechanisms, and low subcutaneous fat contents of insects. However, PCB-101 and -123 were clearly biomagnified (by factors of 600–1000) by the second trophic level. The reason for this needs to be investigated further. Most of the PCB congeners were also not clearly biomagnified by the third trophic level organisms. Most of the BMFs were between 1 and 50. Toads and lizards did not biomagnify pentachlorobiphenyls. However, PCB-101, -105, and -123 were biomagnified by factors of 1000–1500 by birds relative to insects. We speculated that this was related to the PCBs being strongly biomagnified because of the low PCB concentrations in the insects and the high lipid contents of the bird muscles. Clear biomagnification was found at the fourth trophic level. The PCB-

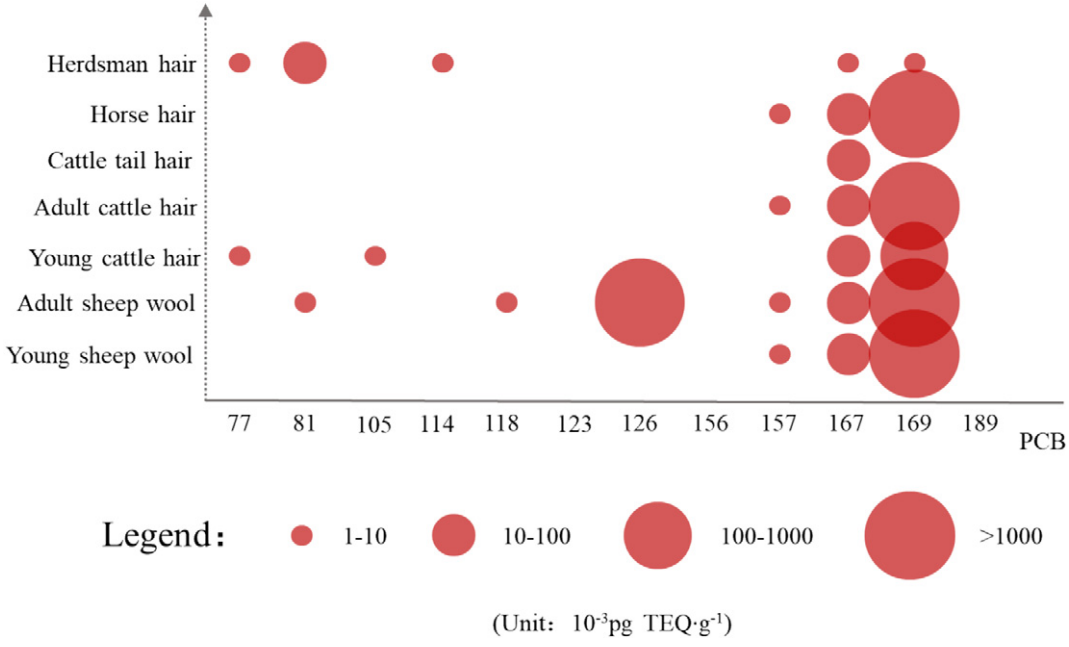

Fig. 7. Toxicities of different polychlorinated biphenyls in the animal hair and herdsmen hair samples from Xilingol Prairie.

114, -123, -126, -156, -157, -167, and -169 BMFs at the fourth trophic level were all >1500. Surprisingly, snakes had BMFs as high as 5000 for PCB-114, -156, and 169.

3.3. Estimating PCB toxicity in the grassland organisms

We calculated the PCB TEQs for the organisms to assess the PCB toxicities to the organisms. The formula used to calculate the toxicity is shown in Eq. (2).

$$TEQ = (Congener_i \times TEF_i) + \ldots + (Congener_n \times TEF_n) \quad (2)$$

In Eq. (2), the toxic equivalent is calculated by multiplying each congener concentration by their respective toxicity equivalency factors (TEF). The total toxic equivalent of all congeners is the Toxicity equivalent of the mixture. WHO-2005 standard was adopted for toxicity equivalent factor value (Jin et al., 2005). The results are shown in Table 1. As shown in Fig. 6, PCB-126 had a TEQ concentration of 0.1 pg TEQ g^{-1} l.w. and PCB-169 had a TEQ concentration of 0.00001 pg TEQ g^{-1} l.w. These were the highest TEQ concentrations for the organisms. This would have been because PCB-126 has a high toxic equivalence factor and the PCB-169 concentrations were higher than the concentrations of the other PCB congeners in almost all of the biological samples. PCB-126 had the highest TEQ concentrations at all of the trophic levels. The PCB-126 TEQ concentration increased markedly as the trophic level increased. The PCB-126 TEQ concentrations in high trophic level organisms (e.g., snake viscera,46.6 pg TEQg^{-1} l.w.) were as much as 3500 times higher than the PCB-126 TEQ concentrations in low trophic level organisms (e.g., Mongolian mouse muscle, 0.0135 pg TEQ g^{-1} l.w. and *Passer* muscle, 0.0122 pg TEQ g^{-1} l.w.). The PCB-77, -118, and -167 TEQ concentrations also increased as the trophic level increased. The tetrachlorobiphenyls and more-chlorinated PCB TEQ concentrations were higher than the less-chlorinated PCB TEQ concentrations in high trophic level organisms.

As shown in Fig. 7, PCB-169, -167, -157, -126, -118, -105, -81, and -77 had high TEQ concentrations in animal hair. PCB-169 had a high concentration in almost all of the animal hair samples (median > 0.987 ng g^{-1}), so the PCB-169 TEQ concentration (0.00001 pg TEQ g^{-1}) was higher than the other PCB TEQ concentrations in the animal hair samples. The highest TEQ concentrations in the herdsmen hair samples were for PCB-77, -81, -114, -167, and -169. The highest TEQ concentration was for PCB-81. PCB-77, -81, and -114 (less-chlorinated PCBs) were found at high concentrations in the herdsmen hair samples. However, the more-chlorinated PCBs PCB-167 and -169 have high toxicity factors, so had similar TEQ concentrations to the less-chlorinated PCBs even though the PCB-167 and -169 concentrations were low. The highest TEQ concentrations in the herdsmen hair samples were for PCB-81, but the highest TEQ concentrations in the other animal samples were for PCB-167 and -169. This was consistent with PCBs being transferred between the animals through the food chain. PCBs found at low concentrations and TEQ concentrations in low trophic level organisms were able to biomagnify and reach high TEQ concentrations in high trophic level organisms by being transmitted through the food chain (Nfon et al., 2008). For example, PCB-114 had a TEQ concentration below the detection limit in animal hair but had a detectable TEQ concentration in the herdsmen hair samples. A PCB at a low concentration in the environment could therefore have strong toxic effects in top predators such as humans.

4. Conclusions

The PCB concentrations in soil and vegetation from Xilingol Prairie decreased as the distance from Xilingol City increased. PCBs were enriched more in animal tissues and organs with high lipid contents than in tissues and organs with low lipid contents. Trichlorobiphenyls and tetrachlorobiphenyls were biomagnified through the food web, i.e., increased in concentration as the trophic level increased. Hexachlorobiphenyls were only biomagnified by the highest trophic level organisms. The pentachlorobiphenyl and heptachlorobiphenyl concentrations did not increase as the trophic level increased. PCB-101 and -123 were markedly biomagnified by the second and third trophic level organisms. PCB biomagnification was clearer at the fourth trophic level. PCB-126 and -169 had the highest TEQ concentrations in the organisms and may be the most harmful PCBs to top predators. These two congeners will be continually emitted by industrial plants in which PCBs are unintentionally produced, and they may have serious effects on grassland organisms. PCB-126 and -169 emissions therefore need to be controlled. The highest TEQ concentrations in the herdsmen hair samples were for PCB-81, but the highest TEQ concentrations in the other animal samples were for PCB-167 and -169. The PCB TEQ concentrations were lower for humans than for the other animals at the top of the food chain. The health risks posed by PCBs to both humans and other animals therefore need to be monitored.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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