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Distribution of organochlorine pesticides and polychlorinated biphenyls in Ny-Ålesund of the Arctic

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Abstract Sediment, moss and animal-dropping samples were collected from Ny-Ålesund of the Arctic to investigate the distribution of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in the Arctic area. OCPs and PCBs were analyzed using the capillary gas chromatography (GC-ECD). Recoveries of three surrogates were at a range of 69.5～92.2% (mean: 78.8%), 75.1～112.1% (98.5%) and 67.7～95.1% (79.5%), and the relative standard deviations were 6.7%, 8.0% and 11.3%, respectively. The major monomers of OCPs were hexachlorocyclohexanes (HCHs) and DDTs. Their concentrations were at a range of 0.86～4.50 ng/g (mean: 2.24 ng/g) and 0.22～1.09 ng/g (mean: 0.55 ng/g). The concentrations of PCBs were 0.20～3.25 ng/g (mean: 0.84 ng/g) and the major congeners were tetra-, penta-, and hexa-PCBs, which were up to 23.8%、26.7% and 32.3% of total PCBs, respectively. Based on the results of the ratio analysis and the principal component analysis, the atmospheric transport is believed be one of the major input ways of OCPs and PCBs in the Ny-Ålesund of the Arctic.

Key words POPs, Ny-Ålesund, PCBs, OCPs

1 Introduction

Svalbard Archipelago (74°-81°N, 10°-35°E) locates between the Barents Sea and the Greenland Sea. It consists of three major islands (Spitsbergen Island, Nordaustlandet Island and Edgeoya Island) and a group of small islands[1]. Ny-Ålesund, located in the west coast of Spitsbergen Island, is an important scientific window of the Arctic. To date, 11 countries have established bases for science investigation. The Chinese Yellow River Station in Ny-Ålesund was built in 2004.

Persistent organic pollutants (POPs) are common pollutants in the environment[2]. They have become an issue of increasing concern because of the large production and usage, especially organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs). These compounds are persistence, lipophilicity, semi-volatility and can be long-distance transported in the atmosphere. POPs are ubiquitous in different environmental matrices and a large number of studies have shown that such substances can migrate to the whole world through the transmission of atmosphere and ocean currents, and therefore the Arctic has become a sink of POPs[3,4]. The Arctic is an important area of the substance and energy exchange between atmosphere and ocean. Ny-Ålesund is on the border of converging area where the exchange of atmosphere and ocean occurred and it is mainly influenced by the North Atlantic circulation and the polar atmospheric circulation[3,4]. In this study, samples of surface sediments, moss and animal-droppings were collected from the area of Ny-Ålesund to investigate the distribution and contamination status of OCPs and PCBs in this area. It also discusses their primary sources in Ny-Ålesund.

2 Materials and methods

2.1 Samples collection and processing

Surface sediment, moss and animal-dropping samples were collected in Ny-Ålesund from July to August of 2007. The sampling sites (S1 to S20) are shown in Figure 1. All samples were packed in aluminum foil and stored at - 20℃. Before analysis, sediment and animal-dropping freeze-dried, ground and sieved (80 mesh).

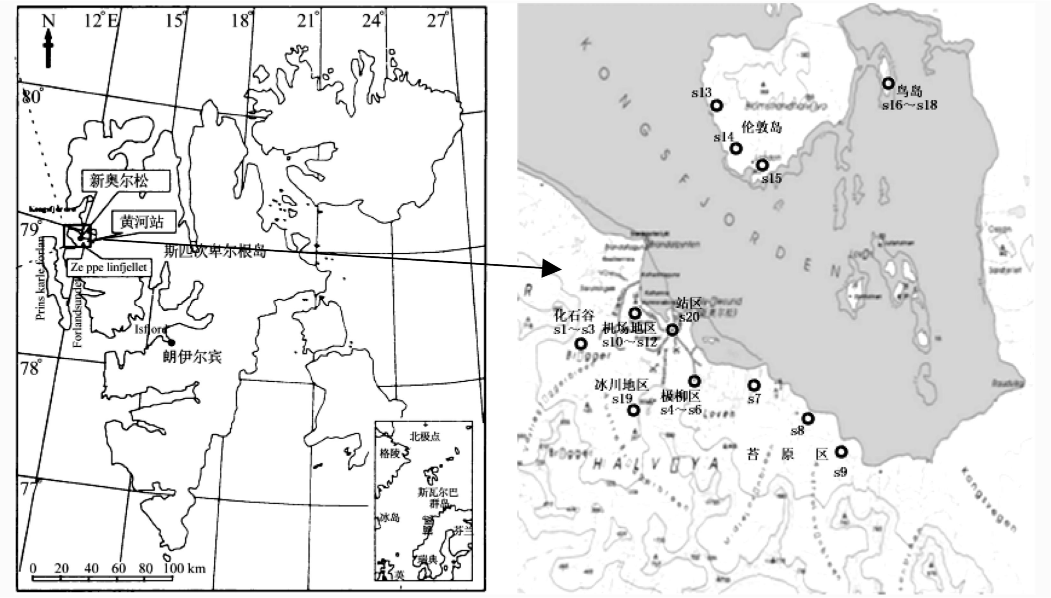


Fig 1 Sampling sites in Ny-Ålesund, Svalbard of the Arctic.

2.2 Materials, standards, and reagents

All solvents (including n-hexane, dichloromethane, acetone, nonane) were pesticide residue grade (TEDIA Company, Ohio, USA). Silica gel (0.063-0.100 mm) was obtained from Merck Company (Whitehouse Station, NJ). Florisil (60-100 mesh) was purchased from Floridin Company (Florida, U.S.A). The OCP standard solution including α-, β-, γ-, δ-HCH, *p, p′*-DDT, *o, p′*-DDT, *p, p′*-DDE, *p, p′*-DDD and HCB was purchased from Wellington Laboratories (Guelph, Canada). PCB reference materials (including CB-28, 52, 101, 112, 118, 138, 153, 155, 180 and 198) were obtained from Supelco (Pennsylvanian, USA). Injection standard solution tetrachloro-*m*-xylene (TCMX, 100 ng · mL^{-1}) and surrogate standard solution 4,4′-dibromoocta Fluorobiphenyl (4,4′-DOB, 100 ng · mL^{-1}), 4,4′-dibromobiphenyl (4,4′-DBB, 100 ng · mL^{-1}) and PCB209 (100 ng · mL^{-1}) were obtained from Cambridge Isotope Laboratories (USA).

2.3 *Samples pretreatment*

An aliquot of 10 g of sample, homogenized by 10 g anhydrous sodium sulfate, was spiked with the surrogate standards 4,4′-DOB, 4,4′-DBB and PCB209 and extracted triplicately in an ultrasonic bath for 30 min using hexane/acetone (1∶1, v∶v) of 40, 30 and 30 mL, respectively. The extracts were combined and rotary-evaporated to about 2 mL (sediment samples need to add activated copper powder to remove elemental sulfur). The concentrated extract was subjected to clean up by elution through a multi-layered column (30 cm length and 1 cm diameter) with 3 g Florisil and 3 g silica gel The column was precleaned by eluting 20 mL hexane prior to the transfer of the extract After the extract was loaded, the target analytes were eluted by 35 mL hexane and dichloromethane (7∶3, v∶v) and the effluent was concentrated through the K-D concentrator to about 1 mL. Then the volume of solution was concentrated to about 200 μL by a gentle stream of nitrogen gas Internal standard TCMX (10 μL) was added to the vial and mixed by vortexing prior to instrumental analysis

2.4 *Instrumental analysis*

Samples were quantified on a gas chromatograph coupled with an electron capture detector (GC-ECD, Shimadzu 2010) and a DB-5 capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). Oven temperature program: initial oven temperature was set at 80 ℃; then increased to 150 ℃ at a rate of 20 ℃/min and held for 3 min; after that, increased at a rate of 4 ℃/min to 250 ℃ and held for 1 min; and lastly increased at a rate of 20 ℃/min to 270 ℃ and held for 1 min The injection volume was 1 μL with the splitless mode, the detector temperature was 300 ℃ Nitrogen was used for carrier gas at a constant flow rate of 12.0 mL/min with the constant column pressure of 55.0 kPa

2.5 *QA/QC*

Strict quality controls were implemented to ensure the correct identification and accurate quantification of the target compounds Recoveries of all the samples and blanks determined by surrogate standards of 4,4′-DOB, 4,4′-DBB and PCB209 were 69.5%-92.2% (mean: 78.8%), 75.1%-112.1% (mean: 98.5%) and 67.7%-95.1% (mean: 79.5%), respectively, and the relative standard deviation were 6.7%, 8.0% and 11.3%, respectively. The limit of detection (LOD) was calculated as a signal-to-noise (S/N) ratio of 8 and they were 0.004, 0.004, 0.004 and 0.002 ng · g^{-1} for α-, β-, γ- and δ- isomer of HCHs, respectively. The LOD of other OCPs and PCBs were 0.005 ng · g^{-1}. The accuracy and sensitivity of this method all met the requirements specified in USEPA 8081 and 8082

Results of three groups of blank experiment showed that only a small amount of β-BHC, CB-52 and β-chlordane were higher than the detection limit (less than 5% of the minimum concentration of the samples). All experimental data in Table 1 had deducted the blank value and values which below the detection limit was labeled with "nd".

Table 1. Concentrations of OCPs and PCBs in soil, moss and dung (ng/g dw)

Location	Matrix	ΣBHC	ΣDDT	ΣOCP *	ΣPCB
Fossil valley	soil	2.24	0.29	0.63	1.59
	moss	4.50	0.30	0.83	1.75
	dung	1.77	0.65	1.52	1.52
Polar willow area	soil	3.12	0.22	0.35	1.68
	moss	2.67	0.67	1.03	1.39
	dung	1.55	0.34	1.32	1.56
Moss belt	soil	2.25	0.46	2.99	1.89
	moss	1.41	0.49	2.08	2.14
	dung	1.75	0.28	3.08	1.97
Airport area	soil	3.04	0.44	0.98	1.90
	moss	3.13	0.73	1.26	1.65
	dung	1.63	0.78	1.24	1.03
London island	soil	2.39	0.46	1.08	1.19
	moss	1.49	1.09	1.68	1.33
	dung	1.18	0.61	0.92	0.92
Bird island	soil	2.29	0.56	1.96	1.65
	moss	4.19	0.92	2.47	0.92
	dung	0.86	0.98	1.12	0.58
Glacier area	soil	1.09	0.34	0.05	0.62
Station area	soil	2.21	0.36	1.15	1.22

Note: ΣOCPs * refers to the total sum of OCPs with exception for ΣBHCs and ΣDDTs

3 Results and discussion

3.1 Organochlorine pesticides (OCPs)

3.1.1 Contamination status and composition

The detected ratios of OCPs in soil, moss and feces were 76.8%, 82.5% and 78.6%, respectively. The average concentrations of 20 OCPs in the three compartments were 5.01 ng · g^{-1}, 6.72 ng · g^{-1} and 5.12 ng · g^{-1} (dw), respectively. Among all OCPs, HCHs and DDTs were the dominant compounds (Fig 2) with the detected ratio of 100%, except for γ-HCH、*p, p'*-DDE, and *p, p'*-DDT which the detected ratios were 55.0%, 90.0%, and 80.0%, respectively. Other Organochlorine pesticide compounds were also detected in different levels with the detected ratio ranging from 27.3% to 90.9%, and Heptachlor epoxide compound was detected with the highest ratio and the highest concentration which was up to 0.32 ng · g^{-1} (dw). The concentrations of HCHs and DDTs were ranged from 0.86 ng/g to 4.50 ng · g^{-1} with the mean value of 2.24 ng/g and from 0.22 ng · g^{-1}

to 1. 09 ng · g^{-1} with the mean value of 0. 55 ng · g^{-1}, respectively (Fig 2). α- and β-HCH were the major isomers of HCHs, accounting for 81. 6 % of total HCHs *p, p'*-DDE and *p, p'*-DDD were the dominant isomers of DDT, which accounted for 77. 6 % of the total DDT. Endosulfan-II was not detected in all the samples

Besides HCHs and DDT, the detection rate and concentration of the heptachlor epoxide were the highest, which were up to 90. 9% and 0. 32 ng · g^{-1}, however, the detected ratio of the heptachlor was 50. 0% with an average concentration of 0. 05 ng · g^{-1}. The different characteristics of the heptachlor epoxide and the heptachlor in the three compartments can be explained with respect to the transformation trend of the heptachlor into the heptachlor epoxide in the environment

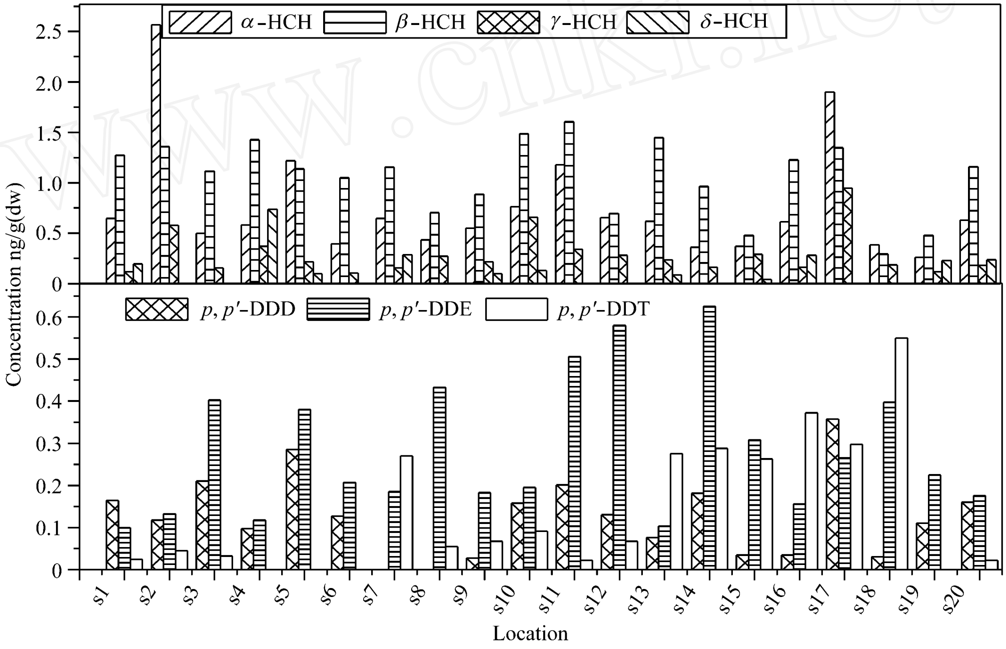


Fig 2 Concentrations and patterns of HCHs and DDTs at each site

3. 1. 2 Source analysis

It is generally believed that the use of OCPs in agriculture in developing countries of northern hemisphere in mid- and low-latitudes coupled with the function of atmospheric transportation and ocean currents are the major sources of OCPs in the Arctic[4]. As pointed in report of AMAP 2002, atmospheric transport was the fastest way to input the pollutants, but the ocean current transportation also played an important role especially for high water-solubility organic pollutants[5]. Li *et al* reported that β-HCH was carried into the Arctic area mainly through the way of ocean currents[6]. As stated above, Ny-Ålesund locates in north area of 74-81 °N and on the border of converging area of exchange between the atmosphere and ocean It was mainly influenced by the North Atlantic circulation and the polar atmospheric circulation and thus atmospheric transportation was one of the main ways for pollutants into this area[3,7].

It is well known that the proportion of four isomers of commercial HCH mixtures is certain: about 60-70% -HCH, 5-12% -HCH, 6-10% -HCH and 3-4% -HCH, while the dominant isomer of industrial Lindane is -HCH, which accounts for about 90% of total HCHs The concentration ratio of -HCH and -HCH was often used to identify the source of HCHs[4]. The ratio of α/γ-HCH in general industrial product ranged from 4 to 7, whereas the value of α/γ-HCH ratio closed to 1 could be used to indicate the input of Lindane[8]. In this study, the proportions of the four isomers α-, β-, γ- and δ-HCH were 32.4%, 49.2%, 12.9% and 5.5%, respectively. The mean values of concentration ratios of α/γ-HCH in soil, moss and dung ranged from 1.6 to 5.7, which indicated that the contamination of HCH in Ny-Ålesund was mainly from the use of general industrial products The reason why β-HCH isomer in this region had a higher level than other isomers might be that the molecular structure of β-HCH is much symmetrical and the chemical properties and physical properties of β-HCH are more stable than other isomers and it is more difficult to be degraded[9].

p, p'-DDT can be metabolized into *p, p'*-DDE under aerobic conditions and into *p, p'*-DDD under anaerobic conditions by microbial degradation. The concentration ratio of DDE/DDD is often employed to indicate the redox conditions during the degradation process of DDT[10]. The concentration ratio of (DDD + DDE)/DDD can be used to indicate the degradation degree of DDT and to identify the sources of DDT[11]. The average value of the ratio DDE/DDD in soil of Ny-Ålesund was 0.8, which suggested that transformation of DDT into *p, p'*-DDD occurred under anaerobic conditions by microbial degradation. The ratio of (DDD + DDE)/DDD were below 1 in most soil samples The result indicated that DDT had been experienced a long-term degradation in soil of Ny-Ålesund, whereas a high detectable ratio of DDTs indicated that there were still potential inputs of DDTs[12].

3.2 Polychlorinated Biphenyls (PCBs)

The concentrations of PCBs in soil, moss and dung ranged from 0.20 to 3.25 ng/g with the average value of 0.84 ng/g (Table 1). The major congeners of PCBs were tetra-, penta- and hexa-PCBs, which accounted for 23.8%, 26.7% and 32.3% of the total PCBs, respectively. The monomers with higher percentage were CB52, CB101, CB112, CB138 and CB155, which accounted for 23.8%, 10.4%, 11.1%, 16.3% and 32.3% of the total PCBs, respectively. The relative abundance of CB28 was low, which was mainly due to the high volatility of CB28 and prone to evaporation from soil into the atmosphere through the exchange interaction of soil-atmosphere.

Principal component analysis (PCA) was performed to investigate the distribution of PCBs Fig 4 depicts the factor loading plots and factor score plots for the PCBs concentration data. In Fig 4a, component 1 was highly correlated with moss samples and dung samples, which interpreted 57.8% of the total variance. Component 2 was correlated with soil samples, which interpreted 14.6% of the total variance. The concentrations of CB52 in moss and dung samples were relatively higher than those in soil The dominant congeners of PCBs in soil mainly were CB101, CB112, CB138 and CB155. Wendy *et al.*[13] considered that the source pathway of PCBs in soil were mainly through the dry/wet deposition and reported the similar patterns with the results obtained in this study. The different distribution characteristics of PCBs in soil, moss and dung was mainly caused by different enrichment ways of PCBs in the three compartments and the different physicochemical properties CB52 has a higher volatility (higher subcooled liquid vapor pressure p_L°), thus it mainly exist in gas phase[14]. The volatility of other monomers with high molecular weight was relatively low and therefore they were mainly present in particulate phase[15]. PCBs in soil were mainly from the wet/dry atmospheric deposition, and therefore the proportion of PCB congeners with high weight molecular was relatively high Moss, a typical passive air sampler of semi-volatile organic compounds in the atmosphere, enriched the pollutants of gas phase mainly through the process of "absorption", and thus, compared with soil, low molecular weight of PCBs were the dominant congeners in moss PCBs in dung were mainly from the body metabolites, and plants were the major food of deer, and thus the distribution characteristics of PCBs in dung were similar with that in moss

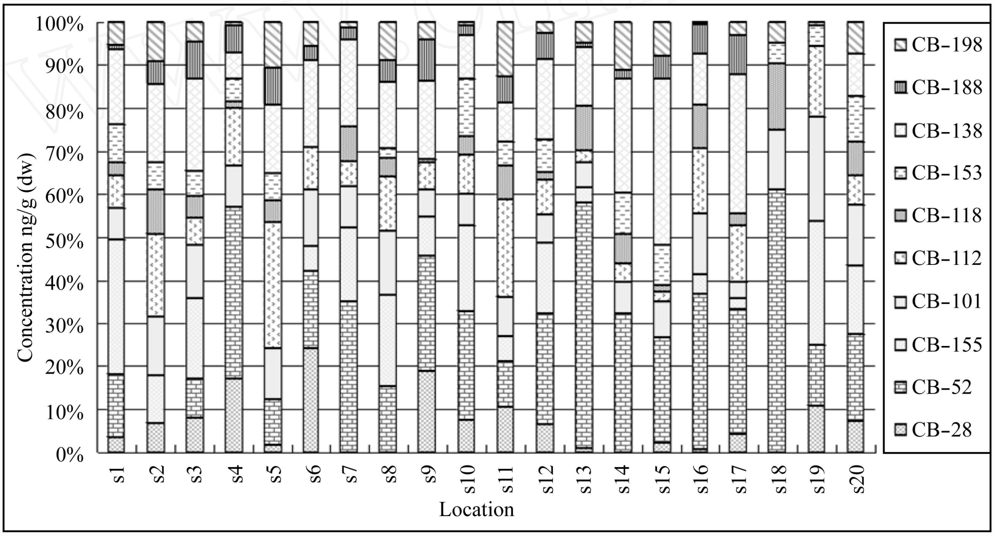
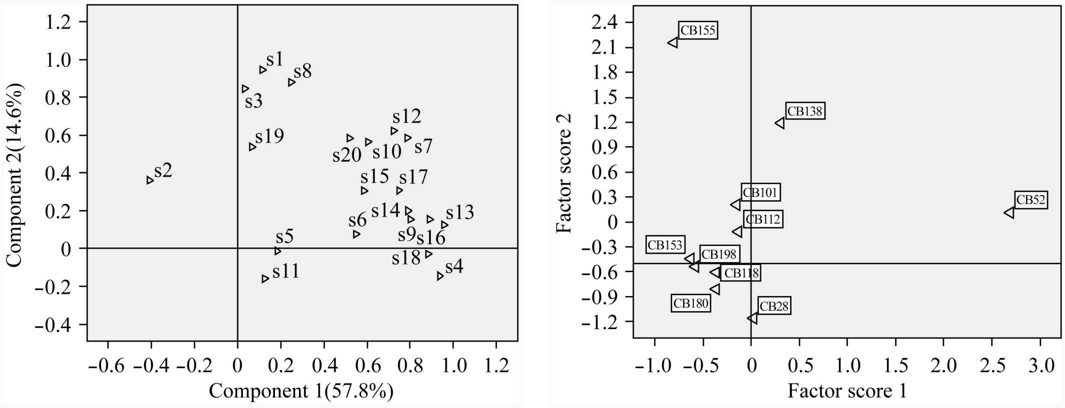


Fig 3 Congener patterns of PCBs in different samples



(a) Loading plots (b) Score plots

Fig 4 Loading and score plots of principal component analysis

3.3 Comparison with other studies

Results of HCHs, DDTs and PCBs in soil and moss of other works are summarized in Table 2 As can be seen in Table 2, the concentrations of these pollutants in soil of the Arctic were slightly high than those of Alaska and Russia, while the concentrations in moss were relatively low. The concentrations of DDT in the Arctic was relatively low compared with the above two regions Although the difference was obviously in soil, the difference in moss was not significant The PCB concentrations in both soil and moss were relatively low compared with the above two regions, but equivalent with the island Bjørnøya in Norway.

Previous studies showed that high concentrations of PCBs in the northern hemisphere mainly occurred in middle and low latitudes To date, the contamination status of PCBs had declined significantly due to many countries had implemented the action to restrict the use and disposal of PCBs The above results suggested that the concentration of PCBs had declined significantly compared with the high contamination areas in low latitudes[16], whereas the declined trend was not obvious compared with the relatively clean polar region.

Table 2. Concentrations of HCHs, DDTs and PCBs in different matrix of the Arctic (ng · g^{-1}, dw)

Matrix	Location sites	Concentration			Time	References
		∑HCHs	∑DDTs	∑PCBs		
soil	Alaska, USA	0.18 ±0.08	19.5 ±19.5	13.2 ±12.4	2000	Ford *et al*[17]
	Kola Peninsula	1.54 ±0.93	3.82 ±2.67	2.21 ±1.34		
	Lovozero, Russia	1.19 ±0.70	1.72 ±0.76	4.07 ±0.59	2001	RAIPON/AMAP/GEF[18]
	Bjørnøya, Norway	-	-	1.8 (mean)	2004	Anita E *et al*[19]
moss	Alaska, USA	4.23 ±0.32	0.03 ±0.01	4.09 ±0.71	2000	Ford *et al*[17]
	Kola Peninsula	6.26 ±0.78	0.34 ±0.09	2.56 ±0.26		
	Taymir Peninsula	7.98 ±0.83	0.18 ±0.02	8.41 ±1.27		
soil	Ny-Ålesund	2.33 ±0.62	0.39 ±0.11	1.47 ±0.43	2008	This study
moss		2.90 ±1.31	0.70 ±0.29	1.53 ±0.42		
feces		1.46 ±0.36	0.60 ±0.26	1.26 ±0.51		

4 Conclusions

Previous studies have indicated that the POPs can migrate to the whole world through transport of the atmosphere and the ocean currents, and the Arctic has become a sink area of POPs HCHs and DDTs were the major pollutants and the detectable ratios were up to 100% with exception of γ-HCH, p, p′-DDE and p, p′-DDT. Through the compositional ratio study of -HCH and -HCH isomer and DDTs isomers, and principal component analysis of PCBs homologue, it can be found that various POPs in Ny-Ålesund had the similar input pathway. Through the comparison of the concentrations in soil and moss with central Arctic areas, the declined trend of POPs was not obvious except for DDTs, and all over the Arctic region, persistent organic pollutants were trending to be a status of balance in whole

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