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## Hexachloro benzene in the Nanshan Karst systems, China

M. J. Alam<sup>3\*</sup>, Y. Daoxian<sup>1</sup>, S. Yachuan<sup>1</sup>, Y. J. Jiang<sup>1</sup>, M. E. Quayum<sup>2</sup>, L. J. Cheng<sup>1</sup>

<sup>1</sup>*School of Geographical Sciences, Institute of Karst Environment and Rock Desertification Rehabilitation, Southwest University, 400715, Beibei, Chongqing, P. R. China.*

<sup>2</sup>*Dept. of Chemistry, University of Dhaka.*

### Abstract

Karst areas have much higher ecological vulnerability and are easy to be contaminated with hexachlorinated benzene (HCB) which is introduced as health risk pollutants. HCB concentrations were used to understand the transport of HCB conducted in the Nanshan karst system, China. Water, sediments from the underground river and water, sediments and soil from the surface systems were collected monthly in 2011 - 2012 and HCB were analyzed. The levels of HCB were 19.9 ng L<sup>-1</sup> in underground waters and 11.6 ng g<sup>-1</sup> in underground sediments while 99.1 ng L<sup>-1</sup> in surface waters and 110.5 ng g<sup>-1</sup> in surface sediments and 2.8 ng g<sup>-1</sup> in soils. Seasonal variations were found in concentrations of HCB both in the waters and the sediments. HCB concentrations varied from 7.8 ng L<sup>-1</sup> in winter to 86.9 ng L<sup>-1</sup> in spring in the groundwaters and 0.3 ng g<sup>-1</sup> in autumn to 36.7 ng g<sup>-1</sup> in spring in the underground sediments. HCB concentrations varied from 38.6 ng L<sup>-1</sup> in autumn to 1019.8 ng L<sup>-1</sup> in spring in the surface waters, 0.7 ng g<sup>-1</sup> in autumn to 133.4 ng g<sup>-1</sup> in spring in the surface sediments and 2.5 ng g<sup>-1</sup> in autumn to 17.4 ng g<sup>-1</sup> in winter in soil. The substantial seasonal variation found between underground system and surface system which indicate that the surface systems play major role for the transport and contamination of HCB in the underground river systems due to karst features.

**Keywords** Pollutants; Karsts system; Water; Soil; Sediment

### Introduction

Hexachloro benzene (HCB) was used globally as a fungicide and an industrial synthetic material however it was banned several decades ago (Chena *et al.*, 2010). The extensive uses of HCB are to make organic materials such as rubber, dyes, wood preservatives, additive in explosives, and in electrode manufacture. HCB is unintentionally generated as a byproduct from the manufacture of the chlorinated pesticides (Anonymous, 2010; Bailey 2001). HCB was also used to make fireworks and ammunition (Anonymous, 2000). Because of the bioaccumulation, persistence and toxicity, HCB was classified as one of the organic pollutants by the United Nations Stockholm Convention. The contaminations of HCB have been found in many places in the world as the consequences of uncontrolled release in environment. HCB was extensively detected in the sediment and soils (Beurskens *et al.*, 1994; Prytula and Pavlostathis 1996; Rosenbrock *et al.*, 1997; Brigden *et al.*, 2003; Chen *et al.*, 2004; Anotai *et al.*, 2006). Karst groundwater is the drinking water supply for about ¼ of the population on the earth. Groundwater systems are particularly prone to contaminations because of their unique hydrogeological

characteristics. Due to the formation and development of rocky desertification, karst system often has little or no soil cover, which leads to poor filtration, poor pre-purification and rapid infiltration (this is not explicitly a karst water factor but definitely an incidental aggravating factor) (He *et al.*, 2010). In addition, flow in a karst system has been often conduit-dominated and the residence time is usually short, which further limits its ability for self-purification as well as for microorganisms to die off. Furthermore, large numbers of interconnected fissures can make pollutions spread quickly and widely in a karst system (Legrand 1984; Prohic 1989; Ford 1993; Prytula and Pavlostathis 1996). HCB was reported in soil and groundwater in karst area. Future improvements of drinking water quality in the underground river, it is necessary to know the levels, distribution, and transport of HCB for karst systems.

Therefore, in this study, we focus on the Nanshan karst system in southwest China, to investigate the contamination level, distribution, and transport of HCB.

\*Corresponding author: E-mail: [mira61031@yahoo.com](mailto:mira61031@yahoo.com); [jiangjyj@swu.edu.cn](mailto:jiangjyj@swu.edu.cn)

**Materials and methods**

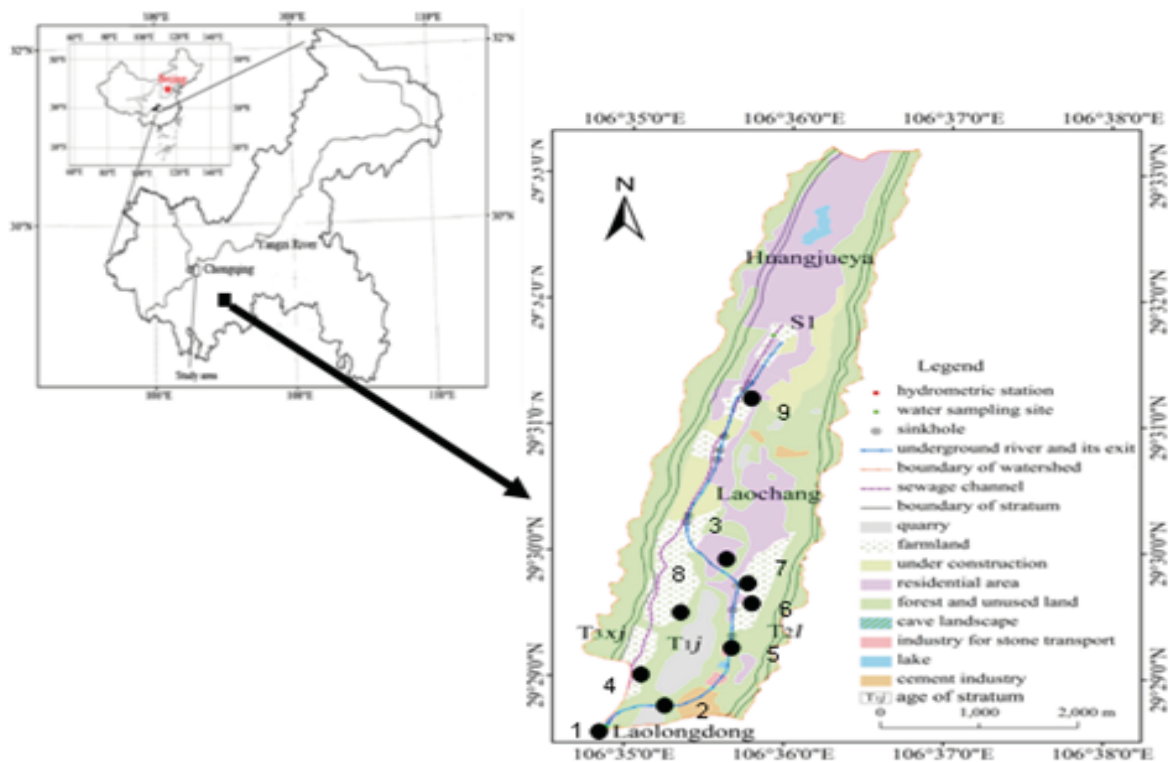
*Sampling sites*

The Laolongdong Underground River System (LURS) area is located at the center of Chongqing municipality, Southwest China (Fig. 1). The underground drainage area of the system is approximately 12.6 km<sup>2</sup>. The elevation of LURS is between 350~685 m above average sea level. The climate is primarily subtropical monsoonal with a mean annual precipitation of 1100 mm and a mean air temperature of 18.7 °C. The monsoonal climate results in a rainy season from May to October and a dry season from November to April. The Laolongdong Underground River originates from the core of

the karst trough valley and flows along anticlinal axis with a total length of 6 kilometers. The dominant types of soils are mainly limestone soils and yellow earth derived from carbonate rocks and sandstones, respectively.

*Geology and hydrology*

The outcrops are principally carbonated rocks (limestone), with Triassic strata being widespread. The strata of the anticlinal axis are carbonate rocks of the Lower Triassic Challenging Formation (T<sub>1j</sub>), with limestone being a major lithology, whereas anticlinal wings are carbonate rocks of the Middle Triassic Leikoupo Formation (T<sub>2l</sub>) and sandstones of the Upper Triassic Xujiahe Formation (T<sub>3xj</sub>). Precipitation is



Water samplings in underground river: 1-UG1, 2-UG2, Sediment samplings in underground river: 1-SeUG1, 2-SeUG2, Water samplings in farmlands: 5-FD, 7-FU, 8-FL, 4,9-sewch/Nsewch, Water samplings in sinkholes: 6-Shw, Seww, Water samplings in Well; 5-well, Sediments samplings in farmland: 5-seFD, 7-SeFU, 4-SeFL, 9-Sewch, Farmland samplings in Soils: 5-SFD, 7-SFU, 8-SFL, 9-Ssewch, Water samplings in sinkholes type ground water: 3-UG3, sediment sampling in underground type well:3-SeUG3

**Fig. 1. Location, land use, hydrological map and distribution of samples**

the major recharge source of the groundwater that ensures abundant groundwater resources.

A mixture of subtropical evergreen broadleaf needle forests is dominant, including Masson pine, fir, cedar, camphor and ficus virens. There are four land use categories (Figure.1): land use for residential construction with an area of 4.5 kilometers, 2.5 kilometers for factories, 2 kilometers for agriculture, 3 kilometers of forest and unused land, respectively. Residential areas are built in the center of the northern trough or on either side of the roads. Underground rivers and springs used to be the only one major source of water supply for the residents.

#### *Samples*

Water samples were collected monthly individually 1 L cleaned glass bottle in 2011-2012 from the underground river and its surface systems vertically from 5 cm (Fig.1). 100 g of sediment samples were collected in plastic bags from the underground river and surface systems. 500g of soil samples were collected in plastic bags from the surface systems. Sediments and soils samples were collected also vertically from 5 cm. Water samples were filtered with Whatman GF/F (0.45  $\mu\text{m}$  effective pore) pre combusted at 450  $^{\circ}\text{C}$  for 5 h. Surrogate standards (2 $\mu\text{l}$ ) were added into water samples after the filtration. The filtered water was then passed through solid phase extractor (SPE-DEX controller 4700/4790, Horizon Technology). Soil and sediment samples were air dried before analysis.

#### *Chemicals and analytical procedure*

2,4,5,6-tetrachloro-m-xylene (TCMX) and Hexachloro benzene standard was used as surrogate standard. Hexamethyl benzene was used as recovery standard. All standard were purchased from Supelco, USA. Silica gel (80–100-mesh) and neutral alumina (100–200-mesh) were extracted with dichloromethane for 72 h by using a extractor. Upon drying under room temperature conditions, silica gel and alumina were baked at 180 and 250  $^{\circ}\text{C}$  for 12 h respectively. Sodium sulfate was baked at 550  $^{\circ}\text{C}$  for 8 h and stored in sealed containers (Zhang et al. 2007). About 10 g soil and sediment dried samples were kept in a cleaned filter paper (for 72 h) and every sample including water samples were spiked with the surrogate standards and extracted for 24 h with dichloromethane. Activated Cu was added for desulphurization. The extract for each sample was concentrated and solvent-exchanged to hexane, and further

reduced to approximately 1 ml under vacuum rotary evaporator. Concentrated extracts were fractionated with a 1:2 alumina: silica gel glass column and 15 ml n-hexane, 70 ml 3:7 dichloro methane: n-hexane, successively. It was finally concentrated to 0.2 ml. The extracts of water samples were dried by anhydrous sodium sulphate and concentrated to 0.2ml with a gentle stream of purified nitrogen. Known quantities of internal standard were added to the sample prior to instrumental analysis. HCBs were measured using gas chromatograph (GC) (Agilent 7890A) equipped with a micro electron capture detector ( $\mu\text{-ECD}$ ) and an HP-5 MS silica fused capillary column (30 m x 0.32 mm; film thickness 0.25  $\mu\text{m}$ ). Additional details of the chromatographic and spectrometric conditions are provided elsewhere (Mai *et al* 2002). Quantification was performed using the internal calibration method based on five-point calibration curve for individual component. The reported results were surrogate corrected. Recoveries were 75-115% for HCBs of the certified values. For HCBs with a sample size of 1 l the detection limit ranged from 0.09-0.25 ng/l.

#### **Results and discussion**

##### *Levels of HCB in surface waters, ground waters, sediments and soils*

The levels (mean) of HCB in different samples are shown in table1. The level of HCB in groundwaters was 19.9 ng L<sup>-1</sup> and the level of HCB in underground sediments was 11.5 ng g<sup>-1</sup>. The level of HCB in surface waters was 99.1 ng L<sup>-1</sup>. The levels of HCB in sediments were 110.0 ng g<sup>-1</sup> and in soils of the surface was 2.8 ng g<sup>-1</sup>. (Anonymous, 1993) reported that the tolerance limit of HCB concentrations in drinking water is 1  $\mu\text{g/l}$ . According to the report, the waters of the Nanshan karst are far from the HCB pollution.

##### *Seasonal variations of HCB in different samples in the underground river systems*

Seasonal variations of HCBs in groundwaters, and sediments are shown in table 1, Fig. 2, and Fig.3.

HCB concentrations in groundwaters ranged from 13.3-39.6 ng L<sup>-1</sup> in autumn, 7.8-24.0 ng L<sup>-1</sup> in winter, 14.7- 86.9 ng L<sup>-1</sup> in spring. Seasonal variations in concentrations of HCB were found in groundwaters. HCB content in sediments of the underground river ranged from 0.3-7.2 ng g<sup>-1</sup> in autumn, 2.1 ng g<sup>-1</sup> in winter, 28.0- 36.7 ng g<sup>-1</sup> in spring. Seasonal variations were found substantial in underground sediments.

*Seasonal variations of HCB in different samples of the surface systems*

Seasonal variations of HCB in the waters, the sediments and the soils are shown in table 1, fig. 2, and fig.3. The concentration of HCB in surface waters ranged from 38.6-291.2 ng L<sup>-1</sup> in autumn, 330.4- 608.4 ng L<sup>-1</sup> in winter,

underground river waters in autumn and spring than winter (table 1, Fig. 2). Similarly, the contents of HCB in the sediments of the underground river were higher in autumn and spring than winter. The HCB concentrations in the surface waters were also higher in winter and spring than autumn (table 1). The higher concentrations of HCB similarly found in waters in spring both in underground systems and

**Table 1. Sampling sites, sampling period, mean values, seasonal variability, total concentrations, and percentage of HCB**

Sites	Autumn				Winter			Spring	
	September	October	November	December	January	February	March	April	May
UG1	39.6	13.3	-	7.8	8.4	6.2	40.1	5.6	6.8
UG2	-	-	-	-	15.6	3.3	46.8	38.1	7.9
FL	-	-	-	ND	6.2	4.4	44.2	11.9	417.6
FD	0.9	-	-	2.2	ND	1.8	0.7	3.9	ND
Well	1.5	166.8	-	ND	0.9	4.3	ND	0.9	ND
FU	12.5	-	-	5.2	4.4	123.7	ND	123.3	2.9
Shw	-	5.4	-	601.0	35.8	ND	19.3	142.0	7.3
Seww	9.7	119.0	-	-	284.0	136.0	205.0	250.0	428.0
Sewch/	14.0	-	-	-	-	ND	90.2	365.0	164.0
Nsewch									
UG3	-	-	-	-	50.7	ND	-	-	-
SeUG1	0.3	0.3	1.1	-	1.7	-	1.4	-	1.9
SeUG2	-	-	6.1	-	0.4	-	26.6	-	34.8
SeFL	-	0.8	-	9.2	-	-	-	15.3	-
SeFD	0.4	0.4	-	1.2	-	-	-	-	-
SeFU	-	0.3	-	11.9	-	-	-	118.1	-
Sesewch	0.3	0.3	-	23.1	-	-	-	-	-
SeUG3	-	-	-	8.7	24.2	1.3	-	-	-
SFL	-	-	-	-	-	1.7	-	-	-
SFD	0.8	-	-	-	-	2.6	-	-	-
SFU	1.2	-	-	-	-	2.7	-	-	-
Ssewch	0.5	-	-	-	-	10.4	-	-	-

ND-not detected

359.4-1019. ng L<sup>-1</sup> in spring. Seasonal variations in concentrations of HCB were found substantially in surface waters. The lowest HCB concentration in surface waters was 0.7 ng L<sup>-1</sup> in spring at FU and the highest was 601.0 ng L<sup>-1</sup> in winter in a sinkhole. HCB content in surface sediments were from 0.7-1.8 ng g<sup>-1</sup> in autumn, 1.3-54.1 ng g<sup>-1</sup> in winter, 133.4 ng g<sup>-1</sup> in spring and in soils varied from 2.5 ng g<sup>-1</sup> in autumn to 17.4 ng g<sup>-1</sup> in winter. The lowest HCB concentration in sediments was 0.3 ng g<sup>-1</sup> in autumn at SeFU and Sesewch and the highest was 118.1 ng g<sup>-1</sup> in spring at SeFU.

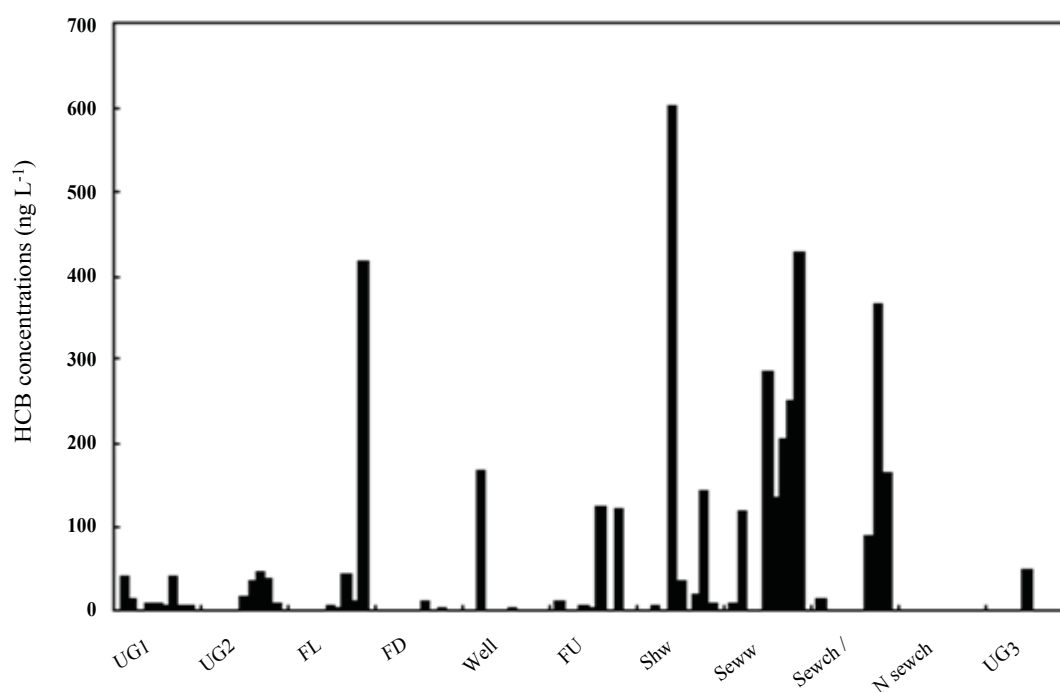
*Transport of HCB into underground river systems*

Higher concentrations of HCB were found in the

surface systems due to increase of microbial activity (Thurman 1985). The concentrations and content of HCB in winter in the surface systems were higher than those in the underground river systems. The higher magnitude in winter is not clearly known. The concentrations and content of HCB in autumn were higher than those in the surface systems might be related to own characteristics of the underground systems. The higher concentrations of HCB in waters in different seasons were found than those in sediments and soils both in the underground river and surface system due to higher soluble trend in waters like HCH and atmospheric deposition would be and important pathways for HCB to soluble in surface waters (Willet *et al* 1998; Alam *et al* 2014).

Comparatively higher concentrations of HCB found in sinkholes (Shw, Seww, Sewch/Nsewch) than those in farmlands probably related to lower evaporation and massive transport from nearby used sources directly. Substantial seasonal variations found in two systems indicate that the underground river system might be affected by the surface system (Fig.2 and Fig.3). Transport of HCB in underground river system could be interpreted by the percolation and leaching. These two processes are common phenomena in

Alam *et al* (2013) showed the transport of polycyclic aromatic hydrocarbons, organochlorine pesticides, and polychlorinated bi phenyls in underground river system from surface system of karst area through percolation and leaching processes. He *et al* (2010) reported that the underground rivers are major locations for the movement and deposition of karst waters. This also reported that the underground river system can be more easily polluted by agricultural activity, domestic effluents and industrial



**Fig. 2. Comparison in concentrations between underground waters and surface waters**

non karst surface system (Alam *et al.* 2007; 2012). The karst features subject to lot of fissures and porosity might enhance the percolation and leaching processes in karst area for the input of HCB towards the underground system from surface system (Fig.4). Much of human activities are continuing in the karst areas worldwide which would increase the transport of HCB in the underground system.

Evidently, seepage waters and drip waters are commonly found in a cave of the karst area which would be a pathway for the role of surface system towards the surface system (Baker and Fairchild 2012). Alam *et al* (2014) and

waste water through thin soils or via sink holes due to their unique hydrogeological characteristics. Another possibility of HCB input in the ground waters was from the underground sediment through re-suspension (Thurman 1985; Luo *et al* 2004).

The total HCB concentrations were 239.5 ng L<sup>-1</sup> in the underground waters, 74.1 ng g<sup>-1</sup> in the underground sediments, 3810.9 ng L<sup>-1</sup> in the surface waters, and 237.5 ng g<sup>-1</sup> in the surface sediments and soils. The HCB in the underground waters was 6.2 % of those of the surface waters and the HCB in the underground sediments was 31.2% of those of the surface soil and sediments.

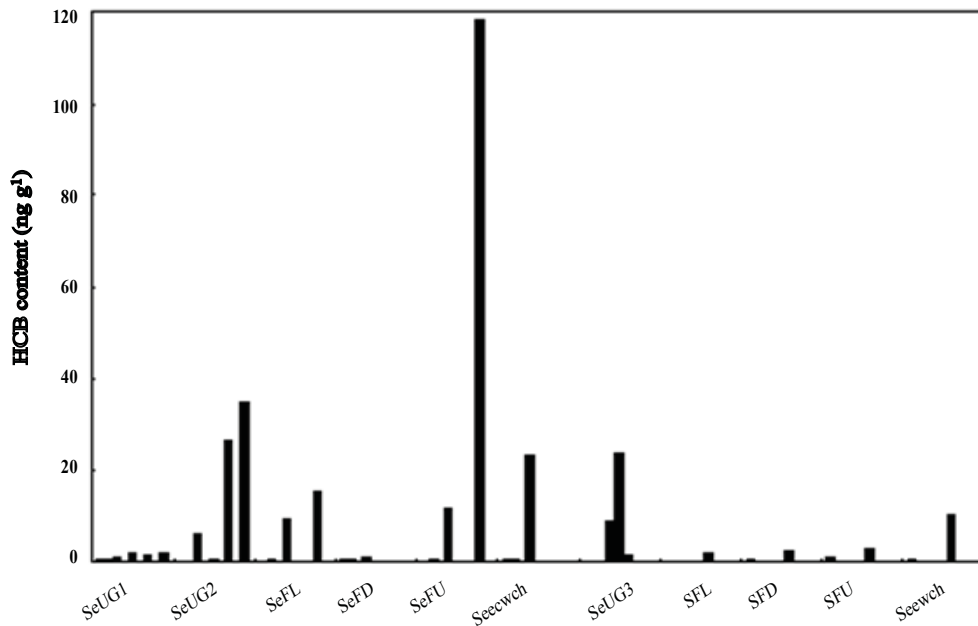


Fig. 3. Comparison in content between underground sediments and surface sediments and soils

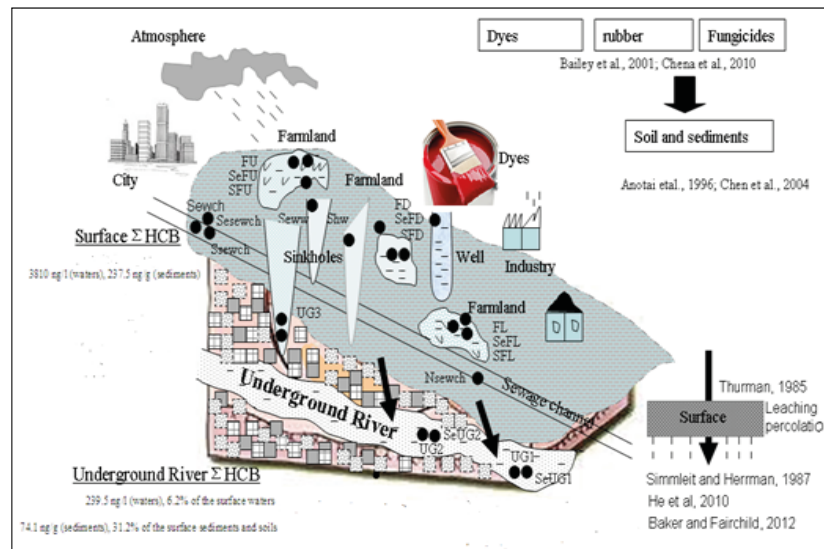


Fig. 4. Karst roles and transport of HCB in the underground river system

**Conclusion**

Waters, soils, and sediment samples were collected in the Nanshan karst system for several months. Detected HCB were used to understand the transport of HCB in the Nanshan karst system. HCB was dominantly found in waters than sediment

both in the underground river system and surface system. Seasonal variations substantially found between the underground and surface systems which indicate that surface system play major role for the accumulation and delivering of HCB in the underground river system and keep the threat of contamination of HCB. Eventually, it still had HCB

contamination due to air transfer, water filtration, and other processes. Karst features enhance the processes. The HCB in underground waters was about 6.2% delivered from the surface waters while the HCB in the underground sediments was 31.2% delivered from the surface sediments and the soils.

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