# Biogeochemical sulphur cycle in Haihe River Basin

## Liu Quanyou

Research Center for Eco - Environmental Sciences, Chinese Academy of Sciences, Beijing 100085

Abstract — The characteristics of biogeochemical sulphur cycle in Haihe River Basin were discussed in this paper basing on the storage and fluxes of sulphur in the hydrosphere, atmosphere, pedosphere and biosphere through a study on the distribution character and content in them.

Keywords: hydrosphere; pedosphere; atmosphere; biosphere; sulphur cycle.

## 1 Introduction

Sulphur is an essential element for the growth of plants and one of the principal elements to sustain human survivor on earth. It is very important to study the biogeochemical cycle of these elements in the pedosphere, hydrosphere, atmosphere and biosphere for protecting natural resources and improving the eco-environment.

# 2 The study area

The Haihe River Basin covers four rivers: Yongding River, Daqing River, Zhanghe River and Wenhe River, with an area of  $2.6 \times 105 \; \mathrm{km^2}$ . This area belongs to the warm temperate semi - humid physical geographical zone. The average annual temperature is around  $8^{\circ}\mathrm{C} - 12^{\circ}\mathrm{C}$ , and the annual rainfall is about  $500-700 \; \mathrm{mm}$ . The landform develops in steps from west to east in the following types: moderately high hill, basin, low hill, hillock, alluvial fan or terrace, alluvial plain, flooding plain and marine plain. The highest summit is about 2800 meters above sea level. The granite and schist outcrop extensively in the western mountain area, and the alluvium, lacustrine and marine deposits constitute the dominant surface material in the eastern part. The soils in this region are formed in three main types, the cinnamon soils, fluvo - aquatic soils and salinized fluvo - aquatic soils, and distributed in belt from west to east. The main stream flows into the Bohai Sea from northwest to southeast under the control of topographical feature (Liu, 1993).

### 3 Materials and methods

# 3. 1 The storage capacity of sulphur in hydrosphere

The content of sulphur and the amount of river runoff and underground water are calculat-

#### ed. The result is shown in Table 1 and Table 2.

	North	Yongding	Daqing	Ziya	East	Zhangwei	Main stream	Tuhai	
canal Ri		River	River	River Heilonggang River		canal	of Haihe River	River	
Run - off >	₹10 <sup>8</sup>					-			
m³/a	41.61	20. 29	41.7	40.41	9. 21	38. 81	1.57	15.24	
Average o	ontent of sul	phur			69. 26	9			
Total amo	unt				1.45 ×10	9kg/a			

Table 1 The storage capacity of sulphur in the river run - off

Table 2 The storage capacity of sulphur in underground water

	Run - off, $\times 10^8 \text{m}^3$							
	Bedflow	Leaching	Underflow	Spring	Mining	of sulphur	run - off	
North part of Haihe	20.8	9. 2		0, 30	1.76			
South part of Haihe	53. 14	11.27	1.57	1.173		13.45		
Whole basin	73. 22	20.47	1.57	1.473	1.76			
Total			98. 49				1. $31 \times 10^{8}$	

#### 3. 2 The storage capacity of sulphur in soil

Sulphur exists in soil with various specifications that are closely related to the soil type, microbe and some other factors. The storage capacity of sulphur in different forms can be obtained by finding the product of the content of sulphur and the volume of soil, which are listed in Table 3.

Table 3	The storag	ge capacity of sulphur in different	specifications of soil	Soil depth: 40 cm
Type of si	dobue	Content of sulphur, ug/g	Average value	Total amount of S kg

Type of sulphur	Content of sulphur, μg/g	Average value	Total amount of S., kg
Soluble sulphur	3. 98-54. 37	19.9	4.09 ×109
Insoluble sulphur	5. 55 <del>- 33. 78</del>	13.6	$2.79 \times 10^{9}$
HCI - soluble sulphur	90.71-920.40	398	8.18 ×10 <sup>10</sup>
Organic sulphur	39.51-666.0	205, 8	4.23 ×10 <sup>10</sup>
Total sulphur	382.0-1518.0	684. 3	1.41 ×10 <sup>11</sup>

#### 3. 3 The storage capacity of sulphur in the parent materials

The sulphur in soil was derived mainly from the weathering of plutonic rocks. Sulphide in primary minerals is released and oxidized to sulphate during the weathering process. The total amount of sulphur that exists in parent materials within 40 cm is about  $5.34 \times 10^{10}$  kg, which is based on the content (260 ppm carat) in crust estimated by Tailor in 1962 (Liu, 1984).

#### 3. 4 The amount of sulphur contained in the excrement of human and livestock

Human and livestock have a close relation with the soil. They absorb sulphur by eating plants and return it to the soil through excrement (Liu, 1994). The total amount of sulphur from the excrement is calculated on the basis of the population and livestock statistics (Table 4 and 5).

Table 4	The	amount	of	sulphur	from	human	excrement

Popula	tion - 8.	27×107

	Excrement,	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Percentage of	K <sub>2</sub> SO <sub>4</sub>	Percentage of	Total	Loss of	Remainder
	kg/(p, a)		S in (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>		S in K <sub>2</sub> SO <sub>4</sub>	sulphur,	sulphur,	of sulphur
						kg	61.8%	
Human excrement	90	37. 2	0. 25	5.8	0.183	9.7×10 <sup>5</sup>	6.67×10 <sup>5</sup>	4.17×10 <sup>5</sup>
Urine	700	144.7	0. 25	22. 9	0.183	1.09×10 <sup>5</sup>		

# 3.5 The amount of sulphur coming from the chemical fertilizers, green manure and crop straws returned to soil

#### 3. 5. 1 Chemical fertilizer

One important source of sulphur in soil is the application of sulphur chemical fertilizers and pesticides, which result in the increase of sulphur. Some controlling - release fertilizers can produce a S° cover on the vegetation, such as the sulphur - covering carbamide, about 20% of the sulphur was oxidized into SO<sub>4</sub><sup>2</sup>-by microorganism in soil (Ivanov, 1983). Knowing the annual amount of chemical fertilizer used in this region, the total amount of sulphur can be found (Table 6).

Table 5 The amount of sulphur in the excrement of livestock

Total number livestock	Excrement,	Total excrement,	Amount of $(NH_4)_2SO_4$ , 0. 25%	Amount of K <sub>2</sub> SO <sub>4</sub> , 18%	Loss of sulphur	Remainder of sulphur
3. 23 × 10 <sup>8</sup>	23979	8.1 ×10 <sup>10</sup>	2.01×10 <sup>8</sup> 1.45×10 <sup>8</sup> 3.46×10 <sup>8</sup>	2. 2×10 <sup>8</sup>	1.36×10 <sup>8</sup>	0. 92

Table 6 The amount of sulphur from the chemical fertilizers and pesitides

Applyment of	Net amount of	Loss of chemical	Amount remained,	Loss of sulphur,	Sulphur remained,
chemical f. *, kg	chemical f. *, kg	f. * , 15.5%	84.5%	kg	kg
6.89×10 <sup>9</sup>	1.76×10°	2. 73×10 <sup>8</sup>	1. $49 \times 10^9$	2.18×10 <sup>6</sup>	1.19×10 <sup>6</sup>

Note: f is the fertilizer

#### 3. 5. 2 Green manure

It is very helpful for increasing the content of organic matter in soil. It can raise the yield of fodder to a large extent for the livestock and produce much more protein for human and livestock. In this region, the area of green manure plants is about 24360 ha (Dai, 1988) with a product of 30000 kg/ha. Since the amount of sulphur content in organic matters is lacking the content of sulphur in grass ashes (about 1.81%) is used to calculate the total amount in green manure which is  $1.32\times10^7$  kg each year.

#### 3. 5. 3 The amount of sulphur returned to soil from the crop straw

Even though a great deal of crop straw was produced in this area each year, only a small part is used as green manure returning to farmland. The total amount of crop straws produced in Haihe basin is obtained by comparing the area of cultivated land between Haihe River basin (10.1 $\times$ 10<sup>6</sup> ha) and Hebei Province (6.59 $\times$ 10<sup>6</sup> ha), because the actual amount of crop straws yield is unavailable in this region and otherwise it is known in Hebei Province about 3.5 $\times$ 10<sup>10</sup>

kg. Thus the total amount of crop straws produced, in Haihe River basin each year is nearly  $5.36 \times 10^{10}$  kg. Supposing 30% of them is used to return to the farm field, then the total amount is about  $1.609 \times 10^{10}$  kg and the amount of sulphur it contains is about  $2.89 \times 10^8$  kg.

#### 3. 6 The amount of sulphur in urban garbage

The garbage produced by the people in the three big cities and fifteen medium - sized cities is listed in Table 7. The total amount of sulphur included in it reaches Ca 3.  $79 \times 10^6$  kg each year.

Besides those garbage which are taken to the disposal factory for reutilization, the organic matters, contained in the leaves, garbage from the open market and daily rubbish, are taken into account to calculate the amount of sulphur. Actually, only a small part of the garbage is disposed at present in China through three means, as much as 70% of them is used for filling materials, 25% is burnt and 5% is used as green manure. The amount of sulphur, contained in garbage disposed in above three means is about  $2.78 \times 10^5$  kg,  $9.93 \times 10^5$  kg and  $1.99 \times 10^5$  kg each year, respectively.

Items *	Beijing	Tianjin	Shijiazhuang	The other 15 cities* *	
population 7.	8×106	6.92 $\times 10^6$	2. 1×10 <sup>6</sup>	7.655 $\times 10^6$	
Total garbage,		72.66		27. 56	
$10^{10}  \text{kg/a}$		(1.2  kg/p. d)		(1 kg/p.d)	
Organic matter,		21.80		4. 68	26.48
1010 kg/a		(30%)		(17%)	
Amount of sulphur,		3. 27		0.70	3. 97
106 kg/a		(0.15%)		(0.15%)	
Sulphur contained in					
filling garbage			2.78×10 <sup>6</sup> kg/a (2	70%)	
Sulphur contained in burned	garbage		$9.93 \times 10^5 \text{ kg/a}(5)$	%)	
Sulphur in garbage for green	manure		1.99 $\times$ 10 $^{5}$ kg/a		
Total, 108kg			100.22		

Table 7 The amount of sulphur contained in the urban garbage

#### 3.7 The amount of sulphur in the flying ashes and falling dust

China, as one of the major countries in the world living on coal-combustion, emit Ca  $1.3 \times 10^6$  SO<sub>2</sub> each year. Among them, about  $3.3 \times 10^4$  kg is from Beijing,  $3.0 \times 10^4$  kg from Tianjin and  $8.6 \times 10^4$  kg is from Hebei Province. It will continue to increase with the development of energy industry, which will engender much influence on the air quality.

The amount of sulphur in flying ashes is obtained on the basis of the content collected by sampling in the big cities on coal -combustion in June of 1988 and the volume of air (Liu, 1994). The deposit rate of dry deposits defined by Chamberlain is the ratio between the amount of deposits and the content of certain gas or particle in the air, which can be expressed as follows:

- Flux = 
$$Vd.c$$
.

If the values of Vd and C are given, the total amount can be found easily. The dry deposit rate, at the height of 1-1. 5m above ground and 10-15m above sea level, released in the pub-

<sup>\* :</sup> according to "Compilation of data on disposal of garbage", compiled by the division of information of Southwest Academy of Engineering - design for Urban Construction in China, 1986;193-197

<sup>\* \*:</sup> according to the "Annual Economic Statistics", China Statistics Press, 1988

lished papers, is around 10-180 cm/s. It is changeable with the topographic nature. The results are shown in Table 8.

Deposit ratio,	. C	ontent of s	ulphur,µg/m	3	The percentage of vegetation,
cm/s	Langfang Nanpi Dingzhou Xizhou		%		
	12.56	13.61	15.4	17.99	
0.005	0.0195	0.0211	0.0239	0.0279	34.4 (leaves, Vd=89393 km²)
1	3.906	4.233	4.789	5. 595	2.6 (grass, $Vd = 6625 \text{ km}^2$ )
7	27.343	29,629	33.535	39.164	51.8 (larmland, Vd=10085 km²)
Average value		16.875	$1 \text{ g/m}^2$ a		$4.33 \times 10^6  \text{kg/a}$

Table 8 The amount of sulphur contained in flying ashes

The amount of sulphur in falling dust is calculated on the basis of the measured content collected in Dingzhou and Xinzhou cities (Table 9).

Table 9 The content of sulphur contained in falling dusts

	Dingzhou	Xinzhou	Dingzhou	Xinzhou	Total	kg/a
	1988	1988	1989	1989	area, km²	
Content of sulphur, kg/km². a	3, 76	0.54	3. 20	0.98	256869	5.51×10 <sup>8</sup>

Clearly, the sulphur content in falling dusts in the western mountain area is much higher than that in the eastern plain,

## 3. 8 The fluxes and storage of sulphur in plants

Plants can uptake sulphur directly from surrounding for growth. The sulphur content in different kinds of plants is quite different, even through for the same plant it is still varied widely with the different parts of plants (roots, trunks, leaves and fruits) and with the seasons. According to the types and area of the 62 plants in this region, the total amount of sulphur coming from plants is about  $2.71 \times 10^8$  kg and those still remain in vegetation is Ca  $3.16 \times 10^7$  kg.

For discussing the balance of input and output of sulphur from the ecosystem view - points, the calculated results of the crops, forests and grassland are summarized in Table 10 and Table 11.

Table 10 The flux and storage of sulphur in different plants

Type of vegetation	Area, ha	Output, kg/a	Input, kg/a
Crops	15269300	2. 48×10 <sup>8</sup>	3. 15×10 <sup>7</sup>
Forest	5565300	$3.40 \times 10^6$	
Grassland	3253300	1. $05 \times 10^7$	$1.59 \times 10^{5}$
Total ·	24587900	2.71×10 <sup>8</sup>	3. $16 \times 10^7$

#### 4 Result and discussion

Sulphur exists extensively in living organisms and is an imperative element for plant growth. Fig. 1 shows the amount contained and sulphur cycle in different compartments based on the above results.

#### 4. 1 Biogeochemcial cycle of sulphur (Fig. 1)

Unit: kg/a

 $1.19 \times 10^{6}$ 

 $2.18 \times 10^{6}$ 

2.  $78 \times 10^{6}$ 9.  $93 \times 10^{5}$ 

1. 99×10<sup>5</sup> 1. 32×10<sup>7</sup>

Remainder in chemical fertilizers

Loss with chemical fertilizers Garbage as filling materials

Garbage as green manure

Burnt garbage

Green manure

Table 11 The fluxes and storage of sulphur in different inventory in Haihe River basin

Storage of sulphur Compartments of sulphur 1.  $41 \times 10^{11}$ Soil 5.  $34 \times 10^{10}$ Parent materials  $4.17 \times 10^{5}$ Remainder in human urine Loss with human urine 6.67 $\times 10^{5}$ 1.36 $\times$ 108 Remainder in excrement of livestock Loss with excrement of livestock  $2.20 \times 10^{8}$  $2.48 \times 10^{8}$ Output of crops 3.  $15 \times 10^7$ Input of crops  $3.40 \times 10^{6}$ Output of forest Input of forest 1.05 $\times$ 167 Output of grassland Input of grassland  $1.59 \times 10^{5}$  $2.89 \times 10^{8}$ Returned from crop straws to farmland  $1.45 \times 10^9$ River run - off 1.  $31 \times 10^8$ Underground water 4.33 $\times$ 108 Flying ashes 5.51 $\times$ 108 Dry deposits 7.55 $\times$ 108 Wet deposit

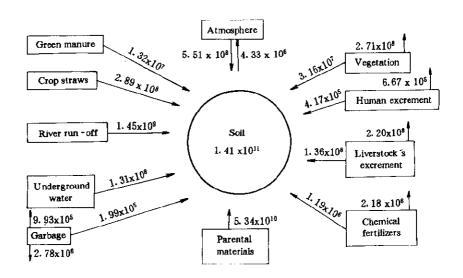


Fig. 1 Sketch map of cycle of sulphur in Haihe River Basii

#### 4.2 The balance of sulphur

The calculation of input and output of sulphur in Haihe River Basin is carried out by taking the agricultural ecosystem as the mainbody and the forest ecosystem and air - particle as the principal influencing factors to the cycle of sulphur. The total input, excluding the amount from parent materials, in agricultural ecosystem is about  $2.59 \times 10^9$  kg/a and the total output is Ca 6. 20  $\times 10^8$  kg/a, it indicates an accumulation process for the agricultural ecosystem (Fig. 2, Table 12).

Table 12 Comparison of input and output of sulphur in Haihe River Basin

Types of	Input of	Output of	Balance	Difference
ecosystem	sulphur	sulphur	comparison	
Agricultural	$2.59 \times 10^9$	6. $20 \times 10^8$	23. 9%	1. 97×10 <sup>9</sup>

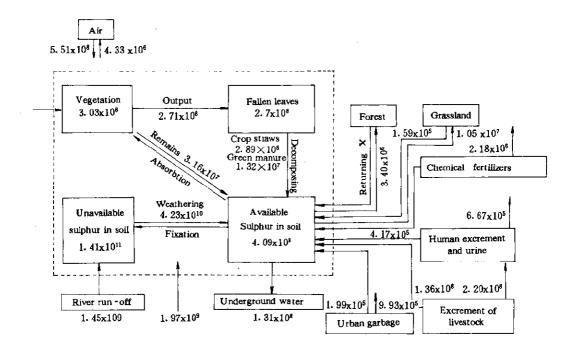


Fig. 2 The balance of sulphur in Haihe River Basin

It is concluded that the input of sulphur is much higher than the output of sulphur. The sulphur content in agricultural ecosystem is increasing with the time, this could result in the acidification of soil and hinder the growth of plants. Upon the above discussion, there are two large contributor for the increase of sulphur in soil.

The increase of the sulphur from the air deposits, which is up to  $5.51 \times 10^8 \text{ kg/a}$ , could be

the most important reason to cause the increase of sulphur in soil.

The increase of sulphur fixed and returned to soil by the plants is another reason of the increase in soil. The amount of sulphur returning to soil from the millet is about 46 kg/(ha. a) and the total amount is about  $2.89 \times 10^8 \text{ kg}$  each year in this region. The accumulation of sulphur in plant leaves is also very important, which accords with the phenomenon studied by Zhang Fuzhu (Zhang, 1991) on penis - tabulaeformis forest ecosystem in Huairou Mountain region.

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