博 士 論 文

STUDY ON DISTRIBUTION OF POLLUTION SOURCES AND REMOVAL OF TYPICAL POLLUTANTS IN SONGHUA RIVER BASIN

松花江流域の汚染源分布及び典型的な汚染物除去に関する研究

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谢 毅

YI XIE

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ABSTRACT

Songhua River Basin located in Northeast China, owning a total area of 55.68 square kilometers. the Songhua River Basin is the third largest basin in China, after the Yangtze River and the Yellow River. The water quality of Songhua River seriously affects the ecological environment of the basin. It is urgent to scientifically plan pollution sources, improve water quality and ensure residents' water safety according to the economic development of Songhua River Basin. Based on studying typical pollutant removal methods in Songhua River Basin, this paper studies the pollution source planning in Songhua River Basin. Finally, some suggestions are put forward to solve the pollution sources in Songhua River Basin. Two efficient removal methods of main pollutants are found in this paper, which are not limited to the Songhua River Basin, but also applicable to the pollution control of other waters.

In chapter 1, Research background and purpose of the study is present. This paper mainly focuses on the source distribution of persistent pollutants in water and sediments of Songhua River Basin and typical representative pollutants removal. The whole Songhua River Basin is selected as the research target. According to the density of industrial layout and regional population density, the basin is divided into Heyuan sub region (Changbaishan Tianchi Baishan reservoir), upstream sub region (Baishan reservoir Fengman) and middle and lower reaches sub region (Fengman Songnen intersection), which basically represents different regional environmental types of Songhua River Basin. Although there are many researches that report on Songhua River Basin, a small area or some sections of the river is studied, and there are few reports on the overall research of the basin. This paper studies the overall pollution source distribution.

In chapter 2, current situation of urban development and pollution source distribution in Songhua River Basin is present. The key factories in the Songhua River Basin mainly come from Heilongjiang and Jilin Provinces. The number of enterprises in the two Provinces accounts for 84% of the whole basin, and they are mainly located in 13 prefecture level cities, accounting for more than 80%. They are the main control areas. The key industries are agricultural and sideline processing, papermaking, beverage manufacturing and petrochemical industry. They are the main contributors of heavy metals and toxic organics in Songhua River, and the proportion of high-risk pollution sources is relatively high.

In chapter 3， Through the analysis of monitoring data, the main pollutants in Songhua River Basin are obtained. At the same time, the effective removal methods of main pollutants are studied

through experiments. Through the total amount control of pollution sources, the variation law of water quality in typical sections of Songhua River Basin is studied, and some suggestions on water environment protection are put forward. The experimental method and seasonal Kendall test mathematical model used in this paper are introduced. Monitoring Status And Data Of Water Pollution In Songhua River Basin. Research Route And Analysis Method. Based on the data of pH, DO, COD, heavy metals, NH_3-N and other water quality monitoring indicators of 11 sections in Songhua River Basin from 2016 to 2019, the trend, periodicity and fluctuation of water quality monitoring indicators and the contribution of water quality indicators to water quality categories are analyzed.

In chapter 4, Analysis And Removal Of Major Pollutants Heavy Metals.The content and pollution degree of heavy metals in surface sediments of Songhua River Basin in different periods (dry season, wet season and flat season) were compared and studied. It was proved that the addition of nano zero valent iron accelerated the removal of lead, chromium and nickel. The best removal efficiency of Cr reached 95.5%. The highest Pb and Ni removal is 89.63%, 96.64% when temperature is 40°C, reaction time is 540 s, and nano zero valent iron is 10 g/L.

In chapter 5， Analysis And Removal Of Main Pollutant Ammonia Nitrogen.Taking Songyuan City, a major city in Songhua River Basin, as an example, this chapter investigates and analyzes the main sources and removal methods of non-metallic pollutants.In this chapter, horse manure is selected as the main pollution source of ammonia nitrogen, The influence of alkali on the gasification of horse dung at 560°C, 25 MPa was investigated. The results show that LiOH addition increased H2 fraction and the gas yield. The precipitated alkali in the reactor still showed high catalytic effect on the subsequent gasification of horse dung without further adding the alkali. A novel 4-lump kinetic model for horse dung in SCWG including feedstock, CH4, CO, and CO2 lumps is proposed.

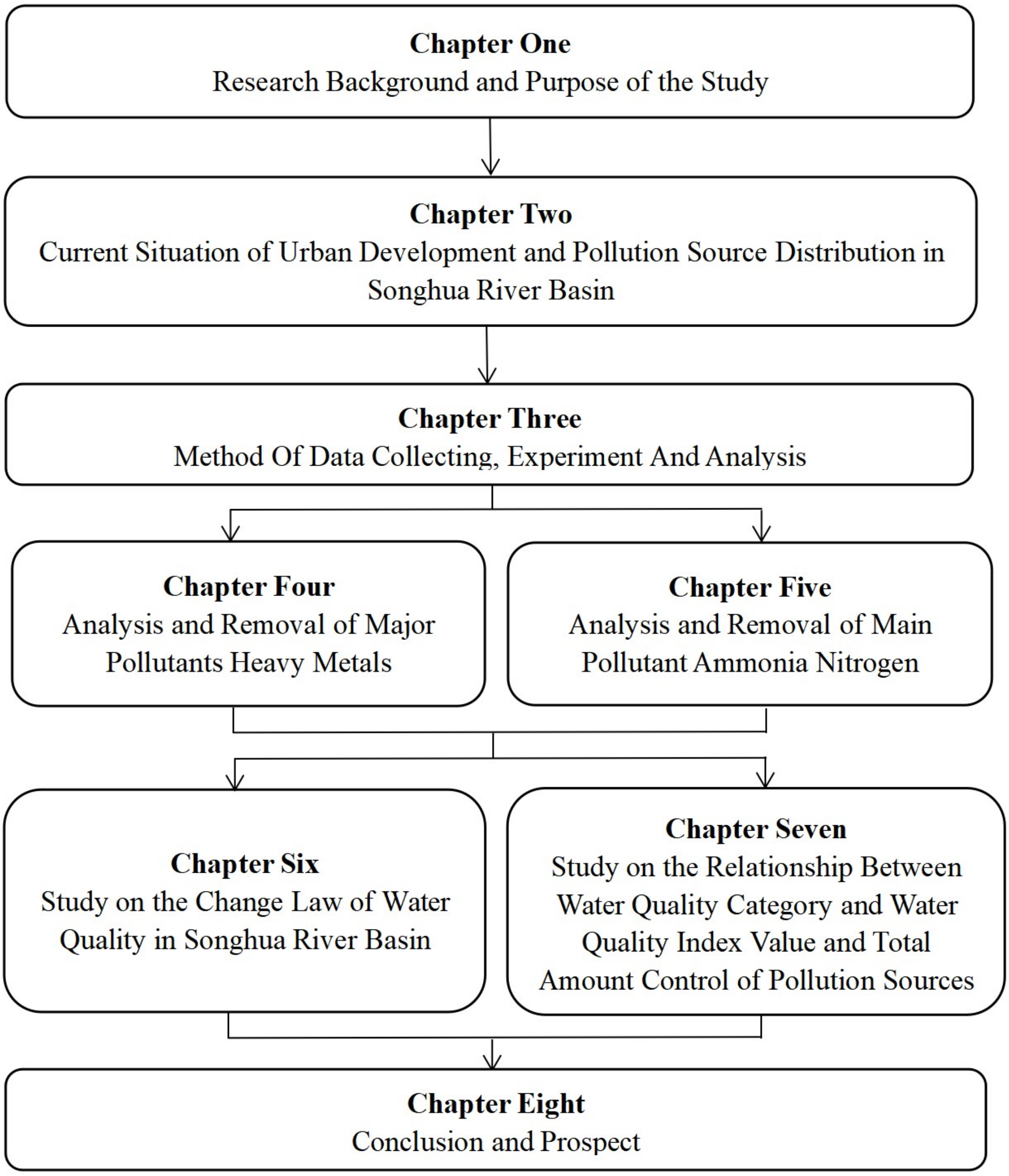
In chapter 6， Study On The Change Law Of Water Quality In Songhua River Basin.Based on the trend of water quality monitoring index values, it is found that the water quality of Songhua River Basin shows a good development trend as a whole during the study period; Through the periodic study of water quality monitoring index values, the periodic changes of pH, dissolved oxygen, permanganate index and ammonia nitrogen in a calendar year in Songhua River Basin are studied and expounded; Through the study on the fluctuation (randomness) of water quality monitoring index values, the probability distribution of four indexes in different periods is calculated, which can provide reference for the estimation and prediction of index values.

In chapter 7， Study On The Relationship Between Water Quality Category And Water Quality Index Value And Total Amount Control Of Pollution Sources.This chapter puts forward reasonable suggestions on pollution source control through the analysis of the contribution of water quality indicators to the change of water quality categories, the sensitivity analysis of water quality categories to water quality monitoring standards, the accessibility analysis of water quality objectives, the key points of water environment protection, the analysis of main pollution sources and the research on the total emission control of pollution sources.

In chapter 8, Conclusion And Prospect. The research conclusions and suggestions for the next work are put forward.

谢 毅　博士論文の構成

Study On Distribution Of Pollution Sources And Removal Of Typical Pollutants In Songhua River Basin



NOMENCLATURE

AIC annual investment cost ($/year)
ZMC annual maintenance cost ($/year)
AOC annual operating cost ($/kWh)
ATC annual total cost ($/year)
C cost ($/year)
CCHP combined cooling heating and power
CDE carbon dioxide emission
COP coefficient of performance
CO_2 carbon dioxide
CPI comprehensive performance index
CSR cost-saving ratio
E electricity demand(kWh)
F fuel consumption(m^3)
ETL following the thermal load
GA genetic algorithm
I investment cost ($)
KSPR Kitakyushu science and research park
M maintenance cost ($/year)
N capacity of the equipment (kWh)
PEC primary energy consumption
PECR primary energy consumption ratio
PGU power generation unit
Q heat (kWh)
SP separated production
STOU seasonal time-of-use
TOU time-of-use

Greek letter

η efficiency
μ CO_2 emission conversion factor
ω weight vector

Subscript

ab auxiliary boiler
ac absorption chiller
b boiler
c cooling
e electric chiller
ec electric chiller
f fuel
grid electricity grid
h heating
he heat exchanger
m equipment number
pgu power generation unit
r recovery heat
Rh recovery heat supplied to heat exchanger
t hours
total total amount of fuel
tr transmission of power grid

CONTENTS

Chapter 6. Study on the Change Law of Water Quality in Songhua River Basin

Chapter 7. Study on the Relationship Between Water Quality Category and Water Quality Index Value and Total Amount Control of Pollution Sources

Chapter 8. Conclusion and Prospect

CONTENTS OF FIGURES

CONTENTS OF TABLES

Chapter 1

RESEARCH BACKGROUND AND PURPOSE OF THE STUDY

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1.1 Research Background and Object

1.1.1 Research Background

Water is a basic and strategic resource, which supports all life activities and the lifeblood of the whole social and economic development. With the progress of society and the rapid development of economy, water resources have become indispensable for human development. China is one of the water-deficient countries in the world, and the per capita ownership of water resources is seriously insufficient. According to China water resources bulletin in 2018 issued by the Ministry of water resources, total amount of water resources in 2018 is 2.72×10^{12} m^3, the per capita water resources is about 1968.64 m^3, which is lower than 2000 m^3 that recognized "moderate water shortage" line. Correspondingly, water shortage and a large number of water pollution in many parts of China appeared. At present, very serious harm to the social economy and human health is caused, so the problem of water resources should be paid great attention to.

River is an important ecosystem that connects land and oceans, and it is also an important way of land water cycle, as well as an important way for terrestrial water cycles. As an open and sustainable ecosystem, rivers are an environment where many aquatic organisms can inhabit and survive. It plays an important role in regulating climate, material circulation, maintaining biodiversity and maintaining the ecological environment. Since the 1970s, China's economy has developed rapidly, but the awareness of environmental protection has been relatively backward. Large amounts of garbage are discharged into rivers in most areas of China, causing serious harm to ecological health. Therefore, it is an urgent task of environmental protection to carry out the prevention and control of water pollution and control the pollution of rivers and other water bodies.

1.1.2 Research Object

Songhua River has a total length of 1927 kilometers and a basin area of 545600 square kilometers, spanning Heilongjiang, Jilin and Inner Mongolia. Songhua River has two sources, north and south (Figure 1.1). Its southern source is the Songhua River, which originates from the Tianchi Lake of Changbai Mountain located in the southeast of Jilin Province. The north source is Nenjiang River, which originates from Yilehuli Mountain in Greater Khingan Range. The Songhua River flows northwest from the Tianchi Lake of Changbai Mountain, traverses Jilin Province, joins the Nenjiang River flowing from north to south at Sancha River in Fuyu County, and is hereinafter referred to as the Songhua River. From here, the river turns to the northeast, flows through the south of Heilongjiang Province, passes through the narrow valley at the south end of Xiao Hinggan Mountain, and then flows into the Sino Soviet border river Heilongjiang in Tongjiang town of Sanjiang lowland.

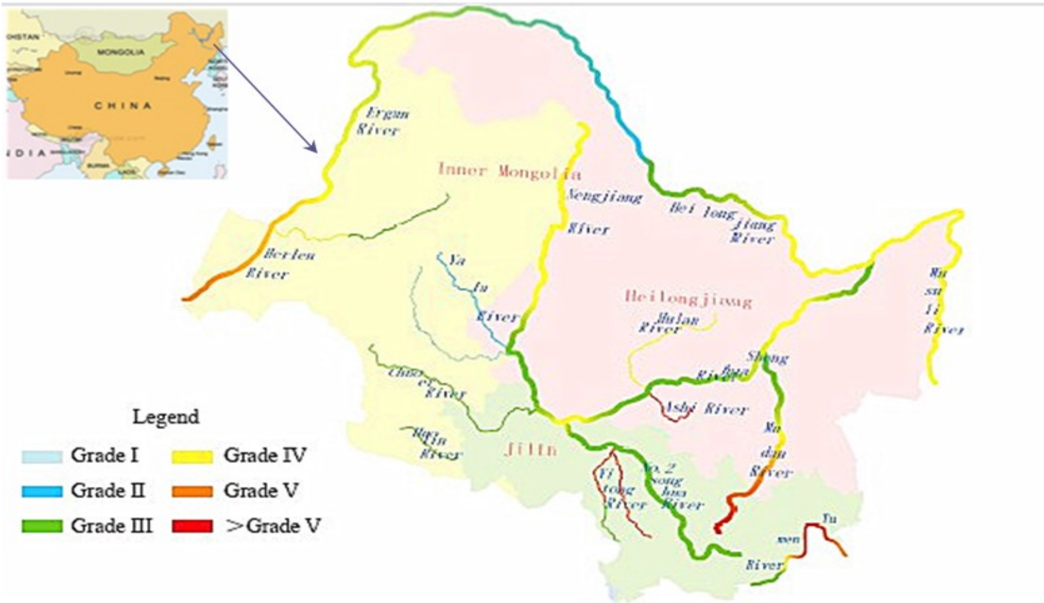

Figure 1-1 The Songhua river

Songhuajiang River Basin is a composite area of Neocathaysian system and Yinshan Tianshan zonal structural system, belonging to Haixining fold belt. The Mesozoic crustal movement formed the tectonic outline of Cathaysian system. During the Himalayan movement, the fault was flexed along the original tectonic direction based on the flattening of the eastern half, and Changbai Mountain is uplifted; The western half forms a broad depression, which is named for Songnen Plain today. The terrain in the region is high in the southeast and low in the northwest, and there are three obvious steps from Changbai Mountain in the southeast to the northwest. In the east is the middle mountain area of Changbai Mountain to the east of Weihuling Fuerling, with an altitude of 700 ~ 1000 m; The middle part is a low mountain and hilly area between Weihuling Fuerling and Daheishan, with an altitude of 400 ~ 700 m; The west is the plain area to the west of the great black mountains, with an altitude of l00 ~ 150 m.

The population density of Songhua River Basin is 166.5 persons / km^2, which is higher than the average value of the whole basin, but the distribution is uneven. The economically developed middle and lower reaches of plains and river valley terraces are the most concentrated, with a population density of more than 600 persons / km^2, while the upstream area is only 79 persons / km^2, which shows great regional differences in development degree.

The Songhua River Basin is rich in mineral resources, which mainly includes gold, nickel, iron, copper, coal, oil and limestone, diatomite and silica. The industrial sectors are relatively complete. It has become the production area of machinery, chemical industry, energy, forest industry, metallurgy, grain and local products and the industrial center of chemical industry and mechanical processing in all Provinces of the basin.

The forest resources of the upper Songhua River basin play an important role in water conservation, soil and water conservation and ecological environment protection. However, due to the past management mistakes, long-term imbalance of harvesting and breeding, the annual harvest exceeding the growth, resulting in the decline of the quantity and quality of resources, soil erosion and ecological damage.

The processing and utilization level of mineral resources in Songhua River Basin is low, comprehensive utilization is poor, and the waste is large. Most of them are discharged into the environment in form of "three wastes", resulting in water pollution. The tailings, associated ores and harmful substances in smelting wastewater in mining, and beneficiation makes the receiving water turbid, suspended solids and heavy metals seriously exceed the standard. For example, Weishahe Jiapigou gold mine, Mujihe Erdaodianzi gold mine, Yanghewangou Shenmei plant and Songshuzhen coal mine are the main pollution sources in the upper reaches of Songhua River Basin.

Songhua River Basin is an industrial area with heavy industry as the advantage, and the ratio of light industry to light industry is 1:2. The heavy industry is mainly mining industry, raw material industry and manufacturing industry, but there are obvious differences in different places in the basin. The Songhua River Basin is basically a heavy structure of raw materials. This structure consumes more raw materials, energy, water and sewage, which seriously pollutes the environment.

There are many factors affecting water pollution in Songhua River Basin, including natural factors and human factors. Geographical location and stepped geomorphic structure not only determined the development and evolution of natural factors, but also affect human life and production, industrial structure, energy structure and life behavior, as well as environmental load capacity. Human production and life, especially modern industrial production, strengthens the material and energy exchanging between human and environment, often causing a great impact on natural resources and ecological environment. A large number of industrial wastewater and urban domestic sewage are discharged into the rivers, resulting in water pollution. Water pollution and ecological damage in Songhua River Basin are related to unplanned development of natural resources, the unreasonable industrial structure and layout, which are the main factors of the formation of environmental problems in the basin.

1.2 China's Pollution Control Standards and Policies

China's State Environmental Protection Administration and the State Administration of quality supervision, inspection and Quarantine issued the environmental quality standard for surface water (GB3837-2002) in order to prevent and control water pollution, protect surface water quality, human health and maintain a good ecosystem.

The standard divides the standard projects into: basic project of surface water environmental quality standard, supplementary project of centralized surface water source of domestic and drinking water and specific project of centralized surface water source of domestic and drinking water. The basic items of surface water environmental quality standards are applicable to surface water areas with use functions such as rivers, lakes, canals, channels and reservoirs in China; Supplementary project and specific projects of centralized surface water source of domestic and drinking water are applicable to the primary and secondary protection areas of centralized surface water source of domestic and drinking water. The specific projects of surface water sources of centralized domestic and drinking water should be selected by the administrative department of environmental protection of the people's government at or above the County level according to the characteristics of surface water quality and the needs of environmental management. The supplementary projects of surface water sources of centralized domestic and drinking water and the selected special projects shall be used as the supplementary indicators of the basic projects.

According to the environmental function and protection objective of surface water area, it is divided into five categories according to the functions (Table 1.1):

Table 1-1 The water quality standards in China (mg/L)

Grade / Indicator	I	II	III	IV	V
T (^{O}C)	Rising≤1, Dropping≤2				
pH	6～9				
DO ≥	7.5	6	5	3	2
COD ≤	15	15	20	30	40
BOD_5 ≤	3	3	4	6	10
NH_3-N ≤	0.15	0.5	1.0	1.5	2.0
TP ≤	0.02 Lake 0.01	0.1 Lake 0.025	0.2 Lake 0.05	0.3 Lake 0.1	0.4 Lake 0.2
TN ≤	0.2	0.5	1.0	1.5	2.0
Cu ≤	0.01	1.0	1.0	1.0	1.0
Zn ≤	0.05	1.0	1.0	2.0	2.0
F^- ≤	1.0	1.0	1.0	1.5	1.5
Se ≤	0.01	0.01	0.01	0.02	0.02
As ≤	0.05	0.05	0.05	0.1	0.1
Hg ≤	0.00005	0.00005	0.0001	0.001	0.001
Cd ≤	0.001	0.005	0.005	0.005	0.01
Cr^{+6} ≤	0.01	0.05	0.05	0.05	0.1
Pb ≤	0.01	0.01	0.05	0.05	0.1
CN^-or-CN ≤	0.005	0.05	0.2	0.2	0.2
ArOH ≤	0.002	0.002	0.005	0.01	0.1
Oil ≤	0.05	0.05	0.05	0.5	1.0
An-ionic surfactant ≤	0.2	0.2	0.2	0.3	0.3
Sulfide≤	0.05	0.1	0.2	0.5	1.0
Escherichia coli (/L) ≤	200	2000	10000	20000	40000

Class I is mainly applicable to source water and national nature reserve;

Class II is mainly applicable to Class I protection area of surface water source of centralized domestic and drinking water, habitat of rare aquatic organisms, spawning ground of fish and shrimp, feeding ground of larvae and juveniles, etc;

Class III is mainly applicable to fishery waters and swimming areas such as centralized domestic and drinking water surface water source secondary protection area, fish and shrimp wintering ground, migration channel and aquaculture area;

Class IV is mainly applicable to general industrial water areas and entertainment water areas in which human body is not in direct contacting;

Class V is mainly applicable to agricultural water areas and general landscape requirements.

Corresponding to the above five types of water functions of surface water, the standard values of basic items of surface water environmental quality standards are divided into five categories, and the standard values of corresponding categories are implemented for different functional categories. The standard value of high water function category is stricter than that of low water function category. If the same water area has multiple use functions, the standard value corresponding to the highest function category should be implemented. The realization of the water area function and the achievement of the functional category standard have the same meaning.

1.3 Previous Studies

1.3.1 Research Progress of Global River Water Quality

Rivers are an important part of land available fresh water resources. River system is an important channel of water cycle, nutrient cycle, nitrogen cycle, carbon cycle and sediment cycle on the earth surface. It not only determines the diversity of terrestrial aquatic organisms, but also determines the function of coastal water bodies.

Every region of the world is covered with rivers, which are closest to people's living and work. It is the most easily accessible resource for people and the water body is most affected by various human activities. At present, most of the water quality monitoring, water quality management and pollution control in the world are aimed at river water quality, the same is true in China.

Early studies on river water quality focused on the relationship between the composition and origin of main solutes (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, SiO_2) and natural conditions (Clarke, 1924; alekin et al., 1964; Livingstone et al., 1963). Since the 1960s, studies on solute chemistry of major rivers on all continents have been reported, among which more famous are the studies on the Amazon River in South America (Stallard et al., 1981; Stallard et al., 1983; Stallard et al., 1987; Gaillard et al., 1997), the Orinoco River (Stallard et al., 1991; Edmond et al., 1996) and the Mackenzie River in North America (Reeder et al., 1972; Millot et al., 2003), Asian Lena River (gordeev et al., 1993; huh y et al., 1988a; huh y et al., 1988B) and Ganges Yarlung Zangbo River (sarin et al., 1989; sarin et al., 1992) In recent years, the research on water quality of global river has shifted to the impact and consequences of human activities and global changes on river water quality, and they emphasized the impact of human activities on river water quality and the effect of this impact on humans and ecosystems. Crutzen and Stoermer proposed that the current geological age be called the "Anthropocene" in 2000 (Crutzen and Stoermer., 2000). Meybeck proposed in 2003 that in the "Anthropocene", the global river system is suffering from at least eight characteristic forms, that is, the adverse consequences caused by flow control, river segmentation, sediment imbalance, flow interruption, chemical pollution, acidification, eutrophication and microbial pollution. Therefore, the composition of river water quality is not only limited to natural conditions, but also is closely related to human activities. A lot of evidence shows that human urbanization and industrialization, global change, population growth, mining, pesticide application, reservoir construction and diversion irrigation are leading to rapid changes of water quality (meybeck, 2003). A lot of monitoring work is needed to solve the water quality problems in river basins. By 2005, more than 1500 rivers and lake monitoring stations in more than 100 countries had joined the global environmental monitoring system network (global environment monitoring system, gems), which provides a foundation for building a long-term and high-quality water quality monitoring network, water quality management and pollution prevention.

1.3.2 Research Progress of Water Quality in Songhua River Basin

Compared with the international water quality monitoring, China's water quality monitoring started late, but it has developed rapidly in recent years. Since the 1980s, especially after the 1990s, more and more papers on river water chemistry in China have been published in international academic journals. For example, Hu et al. published "major ionic chemistry of Chinese rivers" in the British journal Nature in 1982, pointing out that the ionic composition of rivers in China is mainly affected by the dissolution of carbonate and evaporated salt rocks. This is the first paper published in western literature on the study of river hydrochemistry in China (Hu et al., 1982). In recent years, Chinese scholars represented by Chen Jingsheng of Peking University have published a large number of papers on the water quality changes of the Yangtze River, Yellow River and Songhua River systems in international journals (Chen et al., 2002; Chen et al., 2005). This situation reflects the great progress of river water quality research and continuous improvement of research level in China.

Researches on the main pollution characteristics of Songhua River system began the mid-1970s. At that time, Heilongjiang and Jilin Provinces carried out water pollution investigation and obtained some important research results. In 1985, the Changchun Branch of the Chinese Academy of Sciences organized the Changchun Institute of Geography and the Institute of Applied Chemistry to conduct two water quality surveys on the Songhua River system. According to the survey results, the pollution characteristics of water system were summarized and the pollution control suggestions were put forward. In 1983, He Zunshi and Cao Shuying of Changchun Institute of Applied Chemistry, Chinese Academy of Sciences determined the typical volatile organic compounds, medium volatile organic compounds and polycyclic aromatic hydrocarbons in source water system of Songhua River, and obtained more than 900 qualitative and quantitative data. In November 2005, an explosion accident occurred in the biphenyl plant of Jihua company in Jilin PetroChina, resulting in organic poisons pollution in the Songhua River. After pollution control, a large number of scientific researchers have carried out water quality monitoring and pollution evaluation in Songhua River Basin, and published some papers on the investigation and research of pollutant content and the migration and transformation of organic poisons in natural water environment (Lang Peizhen et al., 2008; Liu et al., 2013), which provided certain basic data for environmental management and pollution prevention of water bodies in Songhua River Basin. In addition, there are many papers on pollution assessment on some river sections and tributaries in Songhua River Basin (Zhao Hongmei et al., 2008; Wang Xiaomei et al., 2012).

There are many evaluation methods for river water quality in Songhua River Basin. Among them, single factor index method, comprehensive pollution index method, background value comparison method, fuzzy clustering and fuzzy correlation evaluation method are commonly used. The specific contents of these methods will be shown in Chapter III. In 1985, Wang Baoning and Wang Bingwu of Changchun Institute of Applied Chemistry, Chinese Academy of Sciences first applied fuzzy clustering and fuzzy correlation methods to evaluate the analysis and test data of 12 main indicators in wet period and freezing period of 26 sections and 44 sampling points along the river, and analyzed the pollution characteristics of Nenjiang River, Songhua River, Mudanjiang River and the downstream of Songhua River. Since then, a large number of scholars have analyzed and evaluated the water quality of the main stream and some tributaries of the Songhua River Basin, but overall pollution investigation of the whole basin system is rare.

1.3.3 Research Progress of River Sediments

Sediment is the carrier, destination and reservoir of many pollutants in water environment medium. Pollutants enter into the rivers and lakes through various ways, some of which are adsorbed by suspended solids and enter into the sediments through natural sedimentation. The sediment can be resuspended by water flow and migrated with water flow. At the same time, due to the changes of particle size, properties and hydrological conditions, the adsorbed pollutants can be released into the water body again, resulting in secondary pollution of water body. In addition, undisturbed sediments at the bottom of river often record pollution history of the water body. Combined with micro pollutants, river suspended particulate matter may be stably and permanently deposited where the flow rate is very slow. Such sediments can be used as historical archives to record the pollution levels and pollution events of these pollutants (irion, 1982). Therefore, river sediments must be focused on when the study and evaluation of river pollution is made.

Water and sediment are two different media with different density, pH and redox potential. Interaction of them forms the interface between aqueous and sedimentary facies. Although sediments are final destination of many pollutants, they pass through water sediment cycles many times before are permanently combined into sediments (brokerm, 1982). Its performance is the accumulation and pollutants release in sediments, which is not only a part of the biogeochemical cycle of pollutants in rivers, but also a stage with the most significant impact on the ecological environment of water bodies in the basin. The process is extremely complex, and the impact on the behavior of pollutants on the sediment surface is usually manifested in following situations:

(1) Effect of hydrodynamics on the behavior of pollutants in sediment surface

In rivers, the deposition rate of sediments ranges from a few millimeters to a few centimeters per year. This kind of surface sediment is easy to resuspend under the action of various exogenous forces (water flow, man-made disturbance, etc.). On the one hand, pollutants in sediments are released, resulting in secondary pollution. On the other hand, the resuspended sediments are carried into other water bodies by water flow, so that the pollutants are redistributed to the sediments in a wider range, which is also the diffusion process of pollution.

(2) Effect of sedimentary environment on the behavior of sediment surface pollutants

Organic matter, clay minerals and iron manganese oxides in sediments in natural water have adsorption capacity for pollutants. When the physical and chemical characteristics change greatly between water and sediment, due to the different forces of different pollutants combined with the sediment, some pollutants can be released again and redistributed in the sediment.

(3) Effect of biological action on the behavior of pollutants on sediment surface

There are two aspects of biological effects on sediment pollutant behavior: accumulation and release. The enrichment effect of aquatic organisms has been confirmed by many studies. The content of pollutants in aquatic organisms can indirectly reflect pollution status of water bodies. The effects of these organisms on pollutants content in sediments are as following: first, the deposition of excreta and animal residues leads to the release of pollutants; The second is the impact of biological life activities on pollutant behavior, especially benthic animals. Their feeding process can increase the rate of sediment particles entering interstitial water and overlying water, change the original properties of sediments, and make some pollutants enter interstitial water or overlying water.

1.3.4 Research Progress on Sediment Pollution Characteristics in Songhua River Basin

The investigation of sediment pollution in Songhua River Basin began in the 1980s. She Zhongsheng and others from Changchun Institute of Geography, Chinese Academy of Sciences set up 110 sampling points for each main water area of Songhua River system, including 32 Nenjiang river systems and 24 Songhua River basin systems, and the rest are distributed in Mudanjiang, Lalin River, Hulan River and Tangwang River. They measured the content of some heavy metals in sediments and studied the influence of sediment particle size on the content of heavy metals. Since the 1990s, Chinese scholars have conducted extensive and large-scale studies on heavy metals and various toxic organics in the sediments of the Songhua River Basin. Static pollutant content analysis and dynamic research are carried out, such as tracking the source and intensity of pollutants (NIE Haifeng et al., 2012; Zhang Fengying et al., 2010; Nie Haifeng et al., 2011), discussion on distribution characteristics (Lu Jilong et al., 2009; sun Xiaojing et al., 2007), ecological effects of pollutants (Lin chunye et al., 2007), etc. The long-term accumulated research data provided support for discussing the development trend of sediment pollution in Songhua River Basin.

Although many research results on sediment pollution in Songhua River Basin have been come out, it still does not meet the requirements of theory and practice for such a huge spatial scope and future development and utilization of Songhua River Basin.

1.3.5 Research Progress on Environmental Risk of Persistent Pollutants in Water Environment

Environmental risk is caused by human activities or by human activities acting on nature, which is transmitted through various environmental media. The occurrence probability and adverse consequences of events with adverse consequences such as harm, loss and even irreversible effect on the environment. The source of environmental risk can be any physical, chemical and biological factors that may lead to adverse consequences, and its object is various natural resources or ecosystems.

Toxicity of heavy metals in sediments has nothing to do with the total amount, but depends on their concentration in interstitial water, which has been confirmed by the majority of environmental workers. In anaerobic sediments, acid volatile sulfide (AVS) controls the distribution of many divalent metal ions between sediments and interstitial water (Steven et al., 2005). Simultaneous extractable metal (SEM), that is, the ratio of heavy metals (mainly Cu, Pb, Zn, Ni, CD) released simultaneously during AVS extraction to AVS, is widely used in the evaluation of sediment quality. The theory holds that when SEM / AVS < 1, heavy metals are non-toxic; When SEM / AVS > 1, heavy metals in sediments may or may not produce toxicity to benthos. The correctness of this theory has been confirmed in field and indoor experiments (DI Toro et al., 1991; Li Jincheng et al., 2004). Some scholars take TOC into account for the judgment of heavy metal toxicity (DI Toro et al., 2005).

AVS comes from the degradation of organic matter by microorganisms. It is defined as the amount of S^{2-} in the sediment extracted by 1 mol / L or 6 mol / L hcl, which is composed of complex iron sulfur compounds and heavy metal compounds. The concentration of AVS is significantly different under different environmental conditions. There is high concentration of AVS in muddy sediments with high anaerobic degree, rich organic matter and stable sediment environment; With less organic matter content, AVS content in aerobic sandy sediments will also be relatively reduced (Burton, 2007). In addition, seasonal changes in temperature, dissolved oxygen and bacterial activity can also lead to seasonal differences in AVS (Leonard et al., 1993).

Persistent organic pollutants are difficult to be biodegraded in the environment. They also have an impedance effect on chemical oxidants and adsorption. They can migrate, transform and enrich in aquatic organisms, and have a "three causing" effect. Since the late 1980s, a large number of scholars at home and abroad have been committed to study water sediment environmental quality standards, and put forward more than 10 methods to establish environmental quality standards of sediment. All research methods mainly include two categories: one is to establish the quality standard based on the experience of summarizing and analyzing the experimental results after a large number of experiments, that is, directly based on the relationship between the pollutants content in sediments and resulted biological effects; The other is the establishment method of quality standard based on theory, such as the equilibrium distribution relationship of pollutants in sediments.

The first method is represented by Long et al. They first carried out chemical analysis, toxicological test and on-site biological inspection on a large number of samples in North America and other places, established sediment environmental quality reference values (SQGs) of several types of pollutants, and established the concentration system of pollutants under different biological toxicity levels, including low biological effect (ERL), median biological effect (ERM) and threshold effect concentration (TEL) and possible effect concentration (PEL) (long, et al., 1998). The second type of method, named phase equilibrium method (Chen Yunzeng et al., 2006), indirectly considers the bioavailability of pollutants based on the thermodynamic dynamic equilibrium distribution theory and the water environmental quality standards obtained based on a large number of biological tests. It is one of the most studied methods for establishing sediment environmental quality benchmarks at present.

1.4 Research Purpose

Songhua River Basin has dense industrial layout and dense population. Its water environmental quality is closely related to the economic development and drinking water safety of the basin. This paper investigates and analyzes the environmental background value of heavy metals in Songhua River Basin, studies the process of pollution formation and mechanism of persistent pollutants in the basin, evaluates the water pollution, and analyzes the source and relative contribution of pollutants, discusses the ecological risk characteristics of persistent pollutants on aquatic organisms and the release characteristics of persistent pollutants in sediments of the basin through simulation experiments, determines the pollution formation process of Songhua River, and obtains the impact degree of the development history of industry and agriculture of the basin on the water environment quality of the basin, so as to provide reference information for the prevention and control of water pollution of Songhua River, which will provide a reference for the development planning of basin.

This paper mainly focuses on the source distribution of persistent pollutants in water and sediments of Songhua River Basin and removal of typically representative pollutants. In this paper, the whole Songhua River Basin is selected as the research object. According to the density of industrial layout and regional population density, the basin is divided into river source sub region (Changbaishan Tianchi Baishan reservoir), upstream sub region (Baishan reservoir Fengman), middle and lower sub region (Fengman Songnen intersection), which basically represents different regional environmental types of Songhua River Basin. Although there are many researches on

Songhua River Basin, a small area or some sections of the river is selected, and there are few reports on the overall research of the basin. This paper studies the overall pollution source distribution. At the same time, based on the monitoring data of water and sediment pollutants, typical pollutants are selected and pollutant removal experiments are carried out, combining with mathematical models to study the heavy metals removal and ammonia nitrogen in the water environment of Songhua River Basin. Finally, the proposed scheme and measures for total emission control of water pollutants in Songhua River Basin are put forward.

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Chapter 2

CURRENT SITUATION OF URBAN DEVELOPMENT AND POLLUTION SOURCE DISTRIUTION IN SONGHUA RIVER BASIN

CHAPTER TWO：CURRENT SITUATION OF URBAN DEVELOPMENT AND POLLUTION SOURCE DISTRIUTION IN SONGHUA RIVER BASIN

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2.1 Overview of Songhua River Basin

Songhua River is one of the seven major rivers in China and the largest tributary of Heilongjiang in China. Songhua River was called Nan River in Sui Dynasty, Nashui River in Tang Dynasty, Duck River and Huntong River in Liao and Jin Dynasties, and Huntong River and Songhua River in Qing Dynasty. Songhua River flows through Jilin and Heilongjiang Provinces; The basin covers an area of 557200 square kilometers, covering Heilongjiang, Jilin, Liaoning and Inner Mongolia; Annual runoff is 76.2 billion m^3 (Fig.2-1).

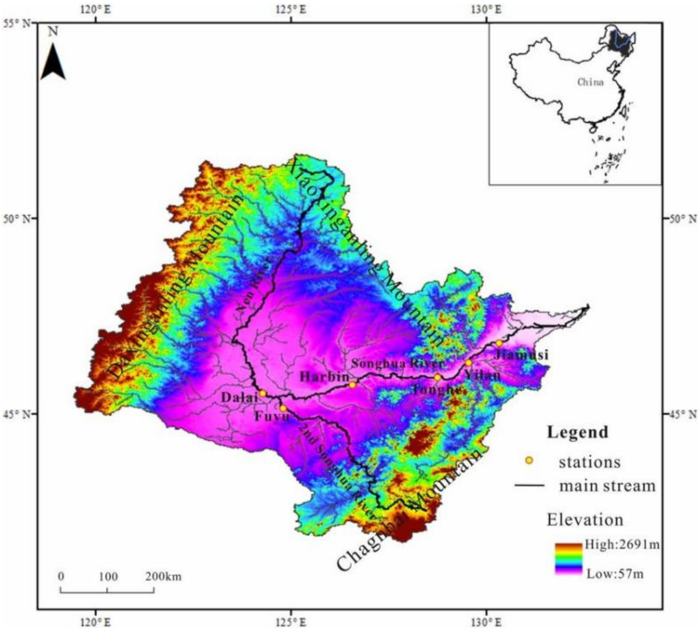

Fig.2-1 Map of Songhua river system

2.1.1 Overview of Main Stream

The Songhua River has two sources: the North source is the Nenjiang River that originates from Ilhuli Mountain, the branch of Greater Khingan Range, and the south source is the West Songhua River that originates from Tianchi, Changbai Mountain. In terms of hydrology, the positive source is the south source, and the North source is Nenjiang River, which is generally used as a tributary. From Zhengyuan (south source), the length of Songhua River is 1927 km. From North source, the length of Songhua River is 2309 km.

(1) Heyuan section

The south source of Songhua River is the Tianchi Lake of Changbai Mountain, the Northeast ridge at an altitude of 2744 meters, which is the source of Songhua River. The Songhua River flowing westward from the Tianchi Lake, whose length is 958 kilometers, with a drainage area of 73400 square kilometers, accounting for 14.33% of the total drainage area of the Songhua River. It supplies 39% of the Songhua River. In its upstream, there are two sources: South yuantoudao River and North Yuanerdao River, both of which originate from Changbai Mountain. There are five Baihe rivers arranged from west to east in the upstream of the North source Erdaojiang River, of which two Baihe rivers originate from the Tianchi Lake of Changbai Mountain and are the main source of Songhua River. The two sources began to be called Songhua River after they met at the mouth of two rivers in Jingyu County, Jilin Province. The upper and middle reaches of Songhua River have narrow river valley, large water volume, large drop and rich hydraulic resources (Fig.2-

2).

Fig.2-2 Tianchi lake of Changbai mountain

(2) Western Section of Songhua River

The main stream of Songhua River flows from the Tianchi Lake of Changbai Mountain to the northwest and flows into Nenjiang River in Songyuan City, Jilin Province. This section of Songhua River is commonly known as West Songhua River. The river has a total length of 958 km and a drainage area of 73400 square kilometers. Except that 540.8 km^2 belongs to Liaoning Province, the rest are belonging to Jilin Province, covering 26 cities and counties in Jilin Province, such as Antu, Dunhua, Jilin, Yushu and Fuyu. The main tributaries include Toudao River, Huifa River, Aolong River and Yinma River. According to the data of Songhua River Estuary Control Station from 1956 to 1979, the annual average runoff of Songhua River is 16.2 billion cubic meters, and the annual average runoff depth is 209.6 mm. The theoretical reserve of water energy in the main stream of Songhua River is 802900 kW, and the river drop is 1556 meters (Fig.2-3).

Fig.2-3 Western section of Songhua river

(3) Eastern Songhua River Section

The main stream of Songhua River flows from Nenjiang River in Songyuan City, Jilin Province to the estuary of Heilongjiang, commonly known as the eastern Songhua River. The elevation of Nenjiang River inlet is 128.22 meters. From the injection port to Tonghe County, the main stream flows to the east, below the Tonghe River and to the northeast. It flows into Heilongjiang from the right bank about 7 kilometers northeast of Tongjiang City through Zhaoyuan, Fuyu, Harbin, Bayan, Mulan, Tonghe, Yilan, Tangyuan, Jiamusi, Huachuan, Suibin, Fujin and Tongjiang. The estuary is 57.16 meters above sea level, the length of main stream is 939 kilometers, and the catchment area is 186400 square kilometers. The river network on both banks of the main stream of Songhua River is developed, with a total length of 725 km, a drop of 1007 m, an average gradient of 1.39 ‰, a steep gradient and abundant water volume. Its theoretical hydropower reserve is 516800 kW, accounting for 17.6% of the theoretical reserve of the main stream of Songhua River (Fig.2-4).

Fig.2-4 Eastern section of Songhua river

(4) Channel characteristics

According to the topography and channel characteristics of the Dongliu Songhua River, it can be divided into upper, middle and lower sections.

The upstream river section, from Sancha River (Fig.2-5) to Harbin City, which is the upper section, with a total length of 240 km and a catchment area of 30000 square kilometers. The river flows through the grassland and wetland of Songnen Plain, of which the slope from Sancha River to Xiadaiji is relatively slow, which is 0.022 ‰; The gradient of Xiadaiji and Xiejiatun River Road is 0.06 ‰; The slope from Xiejiatun to Harbin is 0.052%. There are few tributaries in this section, and there is a large tributary Lalin River on the right bank near Xiadaiji (Fig.2-6).

Fig.2-5 Sancha river

Fig.2-6 Upper reaches of Songhua river

The middle reaches of the Songhua River, from Harbin City to Jiamusi City, which is the middle section of the Dongliu Songhua River, with a river length of 432 kilometers. From Harbin City to Tonghe River, the gradient of river and road is relatively flat, ranging from 0.055 ‰ to 0.044 ‰. There is the largest tributary Hulan River on the left bank. The river road enters a length of 130 km low mountain and hilly area down 20 km. On both sides are the Piedmont transition zone of Zhang Guangcai ridge and Xiao Xing'an ridge. The river valley is narrow. On both sides are high plains and hilly areas. There are tributaries Shaoling River and Mulanda River on the left bank and Ant River on the right bank. It goes down about 70 kilometers from Tonghe County and enters the famous "three surnames" shoal area of the Songhua River in the east. The length of shoal area is about 27 kilometers, the width of water surface of the river is 1.5 ~ 2.0 kilometers, and the slope is 0.06 ‰ ~ 0.15 ‰. The depth of water is only more than 1 meter in medium and low water periods, and it drops below 1 meter in dry water, and the flow velocity is only 1 m/s. The width of shipping waterway is 500 ~ 600 m. There are many islands and sandbars, hidden reefs and many rocks raised from the water. It is a famous river section hindering navigation on the Songhua River. It crosses the Sanxing Shoal. On the right bank, there is a confluence of Mudanjiang River and Woken River, a major tributary, and Tangwang River on the left bank. The water surface of this reach is gradually widened and the depth of water is gradually increased. Near the urban area of Jiamusi City, the Songhua River is relatively straight, the wide of main channel is 800 ~ 1300 meters, the depth of water is 8 ~ 11 meters, and the river slope is 0.1 ‰ (Fig.2-7).

Fig.2-7. Middle reaches of Songhua river

The downstream river section, from Jiamusi to Tongjiang, which is the lower section of the Songhua River flowing eastward, with a total length of 267 km. It passes through the Sanjiang Plain. The two banks are alluvial plains with flat terrain and overgrown weeds. The river channel and beach are relatively open, the water channel flows vertically and horizontally, the wide of beach is 5 ~ 10 km, and there are many shoals in the river channel. Songhua River flows into Heilongjiang in the northeast of Tongjiang City. The whole lower reaches are low and flat. It has always been one of the key areas for flood control. The downstream reaches two main tributaries, Wutong River and Du Lu River (Fig.2.8).

Fig.2-8 Lower reaches of Songhua river

2.1.2 Main Tributaries

Songhua River has developed water system and numerous tributaries. There are 86 rivers with a drainage area of more than 1000 square kilometers. In the upper reaches of Songhua River, there are 3 tributaries with an area of more than 10000 square kilometers; In Nenjiang River, there are 8 tributaries with an area of more than 10000 square kilometers; In the main stream of Songhua River, there are 6 tributaries with an area of more than 10000 square kilometers. The main tributaries are introduced as following:

Nenjiang River: the largest tributary of Songhua River and one of the main rivers in Heilongjiang Province. Nenjiang River originates from the southern foot of Ilhuli Mountain in Greater Khingan Range and flows through Nenjiang River, Olunchun, Nehe, Molidawa, Fuyu, Gannan, Qiqihar, Tailai, Durbert, Da'an, Zhenlai, Zhaoyuan and other counties (cities and banners) from north to south. It joins Songhua River at Sancha estuary, with a total length of 1370 km. From Heyuan to Nenjiang County is the upstream, with narrow river valley and multi forest areas on both banks, producing larch, Mongolian Scotch pine, poplar, birch and other timber; The middle reaches from Nenjiang County to Molidawaddaur Autonomous Banner, and the lower reaches to Sancha estuary. The middle and lower reaches of the river valley are wide. At medium and high water levels, the maximum width of water surface is 450-8000 meters and the maximum water depth is 5-13 meters; At dry water level, the maximum width of water surface is 170-180 m and the maximum depth of water is 1.5-7.2 m (Fig.2-9).

Fig.2-9 Nenjiang river

Wodu River: a tributary on the East Bank of the upper reaches of Nenjiang River. It is located in the northernmost part of Nenjiang County. It originates from the north slope of the West foot of Lesser Khingan Mountains, runs from northeast to southwest, flows through the northern area of Nenjiang County, and flows into Nenjiang River in Woduhe village, Woduhe township. It has a total length of 92 kilometers, a river width of 14 meters, a water depth of 1.0 meters and a drainage area of 1488 square kilometers.

Menlu River: a tributary on the East Bank of the upper reaches of Nenjiang River. It is located in the middle of Nenjiang County. It originates from the west foot of the north section of Lesser Khingan Mountains and flows into Nenjiang River near Menlu River breeding farm. It has a total length of 142 kilometers, a width of 40 meters, a water depth of 1.1 meters and a drainage area of 5471 square kilometers (Fig.2-10).

Fig.2-10 Menlu river

Loach River: secondary tributary on the East Bank of the upper reaches of Nenjiang River. It originates from the West foot of the north section of Lesser Khingan Mountains, enters Nenjiang County from northeast to southwest, turns south, flows through the west of Heihe City and the north of Nenjiang County, and flows into Menlu River near Zuohutan township, Nenjiang County. It has a total length of 136 kilometers, a river width of 26 meters, a water depth of 0.5 meters and a drainage area of 2594 square kilometers.

Kolo River: Tributary on the East Bank of the upper reaches of Nenjiang River. It is located in the middle of Nenjiang County. It originates from the west foot of the north section of Lesser Khingan Mountains, flows through the northwest of Dedu County, crosses the south of Nenjiang County, and injects Nenjiang River near Yihege, Nenjiang County. It has a total length of 324 km, a river width of 50 m, a water depth of 1.2 m and a drainage area of 8574 km^2 (Fig.2-11).

Fig.2-11 Kolo river

Mu River: It is a secondary tributary on the east bank of Nenjiang River and is located in the east of Nenjiang County. It originates from the west side of the north section of Lesser Khingan Mountains, runs from northeast to southwest, and flows into Keluo river near Keluo village. It has a total length of 88 kilometers, a river width of 15 meters, a water depth of 0.5 meters and a drainage area of 2146 square kilometers.

Nemore River: It is a large tributary on the east bank of the middle reaches of Nenjiang River and located in the west of Heilongjiang Province. It originates in the west of Lesser Khingan Mountains, flows through Dedu, Keshan, Nehe and other counties (cities) from east to west from the source, and flows into Nenjiang River 39.6km southwest of Nehe town, Nehe City. The main tributaries include Laolai River, Yinlong River, Bai River (Shilong River), etc. It has a total length of 569 kilometers, a river width of 40-70 meters, a water depth of 1.2-3 meters, and a drainage area of 14061 square kilometers (Fig.2-12).

Fig.2-12 Nemore river

Yinlong River: It is a secondary tributary on the east bank of Nenjiang River and located in the middle of Dedu County. It originates in the west of Lesser Khingan Mountains, runs from northeast to southwest, flows through Longmen, Xianghe, Yinlong and other farms, and flows into Nemore River in the southeast of Dalian Army School Farm. It has a total length of 79 kilometers, a river width of 3-13 meters, a water depth of 0.7 meters and a drainage area of 1186 square kilometers.

Laolai River: secondary tributary on the East Bank of Nenjiang River. It originates from Dongtuomo mountain in the south of Nenjiang County, flows through Yuejin farm and Ilaha town in Nenjiang County from north to south, then enters Nehe City, flows south to Nehe town through Laolai town, and flows into Nemore River in the east. It has a total length of 115 kilometers, a river width of 10-20 meters, a water depth of 1.0 meters and a drainage area of 670 square kilometers. It is a plain river. The freezing period is from early November to early April of the next year. The basin is an agricultural area with several large state-owned farms.

Wuyuer River: It is located in the west of Heilongjiang Province and is the largest inland river in Heilongjiang Province. It originates from the west side of Lesser Khingan Mountains and flows through Beian, Kedong, Keshan, Yi'an, Fuyu and other counties (cities). The tail end gradually disappears in the large marshes in the northeast of Qiqihar City, the northwest of Lindian County and the north of Durbert Mongolian Autonomous County. It has a total length of 576 kilometers, a river width of 20-40 meters, a water depth of 0.5-2.5 meters, and a drainage area of 23110 square kilometers (Fig.2-13).

Fig.2-13 Wuyuer river

NOMIN River: a tributary on the west bank of Nenjiang River. The downstream is located in the northeast of Gannan County. In ancient times, it was called "qulishui" and "crossing the river". It originates in Inner Mongolia Autonomous Region to the east of Greater Khingan Range, flows through Molidawaddaur Autonomous Banner of Inner Mongolia Autonomous Region and Gannan County, Heilongjiang Province, and flows into Nenjiang River near Huilongtu, Gannan County. The total length is 466 kilometers, and the length of the border flow between the two Provinces is 54 kilometers. The width of river is 60-170 m and depth is 1.4-3 m. The total drainage area is 25966 square kilometers (Fig.2-14).

Fig.2-14 NOMIN river

Huanghaogou: a tributary on the west bank of Nenjiang River. Located in the north of Gannan County. It originates from Chazi mountain, Arong Banner, Inner Mongolia Autonomous Region, flows through Gushanzi and crosses the Northeast Road Boundary trench of Jin Dynasty, which enters Gannan County, flows through the north of Baoshan township, and flows into Nenjiang River in the northeast of Dongyang town through Chahayang farm. The total length is 100 km, the width of river is 4-28 m, the water depth is 0.4-2.5 m, and the drainage area is 683 square kilometers.

Allen River: tributary of the west bank of the lower reaches of Nenjiang River. It is located in the west of Heilongjiang Province. It originates from the western foot of Babao in Greater Khingan Range, flows through Arong Banner of Inner Mongolia Autonomous Region, Gannan County of Heilongjiang Province, and the northwest suburb of Qiqihar, and injects Nenjiang River near ermenqin village of Qiqihar. The total length is 318 kilometers, 57 kilometers in Heilongjiang Province. The width of river is 24-40 m and depth is 2 m. The total drainage area is 6297 square kilometers, and the drainage area in Heilongjiang Province is 1571 square kilometers.

Yinhe River: a tributary on the west bank of the lower reaches of Nenjiang River. It is located in the west of Heilongjiang Province. It was called "Yanhe" in ancient times. It originates from the east slope of Greater Khingan Range, flows through Arong Banner of Inner Mongolia Autonomous Region, Gannan County of Heilongjiang Province and the suburbs of Qiqihar, and injects Nenjiang River near Woniutu village of Qiqihar City. The total length is 215 kilometers, 55 kilometers in Heilongjiang Province. The width of river is 7-20 m and depth is 0.4-1.5 m. The total drainage area is 4778 square kilometers, and the drainage area in Heilongjiang Province is 791 square kilometers.

Yalu River: a tributary on the west bank of the lower reaches of Nenjiang River. It is located in the west of Heilongjiang Province. The old name is "Yar River". "Yalu", in Mongolian, means "border land". It originates from the east foot of Greater Khingan Range. It flows through Xiguitu banner, Zalantun City, Inner Mongolia Autonomous Region, Nianzishan District, Qiqihar City, Heilongjiang Province and Longjiang County, and injects Nenjiang River near Halatai village, Longjiang County. It has a total length of 398 kilometers and a total length of 100 kilometers in Heilongjiang Province. The width of river is 40-80 m and depth of 1.4-3 m. The total drainage area is 19640 square kilometers (Fig.2-15).

Fig.2-15 Yalu River

Jiqin River: also known as "Jiqin River". It is secondary tributary of Nenjiang River and located in the northwest of Longjiang County. It originates in the west of Huliyak at the east foot of Greater Khingan Range, runs from northwest to Southeast and flows through the east of Zalantun City, Inner Mongolia Autonomous Region, enters Longjiang County, turns northeast in the east of Laolong mountain, crosses Longxing, Yalu River, Jiqin River and other towns, and flows into Yalu River in the south of Nianzi mountain. It has a total length of 180 kilometers and a river width of about 60 meters. The flow in Longjiang County is 35 kilometers long. The total drainage area is about 2790 square kilometers.

Handahan River: also known as "Hadaikan River". It is secondary tributary of Nenjiang River and located in the south of Longjiang County. Huolong mountain, which originates in the south of Zalantun City, Inner Mongolia Autonomous Region, runs from northwest to Southeast, enters the south of Longjiang County, flows through Jingxing, Xingshan, Touzhan and other towns, and flows into Yalu River. The total length is about 162 kilometers, including 42 kilometers in Longjiang County. The total drainage area is about 4423 square kilometers (Fig.2-16).

Fig.2-16 Handahan river

Chuoer River: also known as "Chuoer River". The west bank tributary of the lower reaches of Nenjiang River. It is located in the west of Heilongjiang Province. It originates in the east foot of Greater Khingan Range, flows through Zalait banner of Inner Mongolia Autonomous Region and Longjiang and Tailai County of Heilongjiang Province, and flows into Nenjiang River in the northwest of Jiangqiao town of Tailai County. The total length is 573 kilometers, and the flow length in Heilongjiang Province is 60 kilometers. The width of river is 30-70 m and depth is 0.7-1.5 m. The total drainage area is 17435 square kilometers, and the drainage area in Heilongjiang Province is 899 square kilometers (Fig.2-17).

Fig.2-17 Chuoer river

Shuangyang River: It is a tailless river and originating in Xinsheng Township in the south of Baiquan County, it flows from south to north to Baiquan Town and then turns West. It turns southwest in Yian County and disappears in the low-lying swamp in the west of Lindian County, forming a closed flow area with Wuyuer river. The total length is 89 km, the river width is 3-15 m, the depth of water is 0.2-1.2 m, and the drainage area is 2522 square kilometers (Fig.2-18).

Fig.2-18 Shuangyang river

Hurda River: hurda, Mongolian, "bending" means. The west bank tributary of Nenjiang River. It is located in the southwest of Heilongjiang Province and originating in the territory of zalait banner of Inner Mongolia Autonomous Region, which flows from northwest to southeast through 8 towns and townships including tazicheng, Dayushu, Pingyang, Tailai and Haoxin in Tailai County, exits in the south of Haoxin Township, and injects Nenjiang River near Datun, Zhenlai County, Jilin Province. The total length is 320 km, including 110 km in Tailai County. The width of river is 46 meters and depth is 3-5 meters, with a drainage area of 1802 square kilometers, including 522 square kilometers in Tailai County.

Erlongtao River: also known as "Hulun River". It is a tailless river and originates from Erlong mountain in Solun mountain range on the east wing of Greater Khingan Range in Inner Mongolia Autonomous Region. After entering the west of Tailai County, Heilongjiang Province, it flows through tazicheng, Heping, Hongsheng and other towns in Tailai County. In 1969, the river was excavated for 8.6km and discharged into Nie laoheipaozi. The total length is 178 kilometers, and the flow length in Tailai County is 44 kilometers. The width of river is 20 m and depth is 1.0 m, with a drainage area of 2971 square kilometers (Fig.2-19).

Fig.2-19 Erlongtao river

Lalin River: also known as "Lanling River". As a large tributary on the right bank of the main stream of Songhua River, Lalin river originates from Bieshilazi mountain in the south of Zhangguangcai ridge, runs roughly from southeast to northwest, flows through Wuchang, Shulan, Yushu, Shuangcheng, Fuyu and other counties (cities), and meets the Songhua River near Duokoudian, Shuangcheng District. Most of its reaches are the boundary rivers of Heilongjiang and Jilin Provinces. The total length is 448 kilometers. The main stream is upstream above the Xilang estuary, belonging to mountainous area, with deep and narrow channel and steep gradient; The middle reaches are from Xilang estuary to Kacha estuary. The river gradient is gradually slow and the river valley is gradually open. At Wuchang hydrological station, the maximum water surface width is 750-1800 meters and the maximum depth of water is 3.2-5.6 meters at medium and high water levels; At dry water level, the maximum width of water surface is 240 m and the maximum depth of water is 0.4 m. From Kacha estuary to Songhua River Estuary, the river is downstream. The river is wide and serpentine. There is no obvious boundary between the riverbed at medium and low water levels. At Caijiagou Hydrological Station, the maximum width of water surface is 170 m and the maximum depth of water is 4.4-6.4 m at medium and high water levels; At dry water level, the maximum width of water surface is 160 m and the maximum depth of water is 2.6 m (Fig.2-20).

Fig.2-20 Lalin river

Funiu River: It is a secondary tributary on the right bank of Songhua River and located in Wuchang County in the south of Heilongjiang Province. It originates from Laobald Dingzi mountain in Zhangguangcai ridge, flows through Chong River, Longfeng Mountain, Guanghui, Weiguo, Changbao and other towns, and flows into Lalin river near Beiyinhe town. It has a total length of 240 kilometers, a river width of 10-49 meters, a water depth of 0.4-1.5 meters and a drainage area of 5289 square kilometers (Fig.2-21).

Fig.2-21 Funiu river

Chong River: It is the third-class tributary on the right bank of Songhua River and located in the south of Shangzhi City and the southeast of Wuchang County, which originates from the west foot of Zhangguangcai ridge, travels from east to west in Shangzhi City, passes through Heiyuting, enters Wuchang County, and flows into Funiu River in the south of Chonghe town. It has a total length of 70 kilometers, a river width of 27 meters and a drainage area of 950 square kilometers.

Dani River: It is a tertiary tributary on the right bank of Songhua River and located in the southwest of Shangzhi City and the east of Wuchang County. It originates in Shangzhi City on the west side of Zhangguangcai ridge. It runs from southeast to northwest to the base of Laojieji township of Shangzhi City, turns north to west, enters Zhiguang township of Wuchang County, and meets Xiaoweisha River and flows into Funiu River. It has a total length of 81 kilometers, a river width of 5-28 meters, a water depth of 0.5 meters and a drainage area of 197 square kilometers.

Grain River: It is commonly known as "Iinwushu Grain River" and also known as "Weitanggou", now also known as "Kuzha River", which is a tributary on the right bank of the main stream of Songhua River. It is located in Shuangcheng District and Harbin City in the south of Heilongjiang Province. Passive river is an artificial canal dug in the early Jin Dynasty. The grain transportation River starts from the west of Baicheng village in the west of Acheng District in the East, passes through Zhoujia town of Shuangcheng District, flows through Xinxing town of Shuangcheng District, Wujia Town and Hongqi and Yushu township of Harbin City, becomes the boundary river between Shuangcheng District and Harbin City, extends to the west, and flows into the Songhua River near the West Xiakan of Xinjiang village, Daoli District, Harbin City. The total length is 96.5 km, and the average width of riverbed is 30-50 m. The drainage area is 415 square kilometers,

Majiagou River: It is a tributary on the South Bank of the main stream of Songhua River and located in the south of Heilongjiang Province, which originates from the hilly area of Liuhaogou, Lixin Township, the west of Acheng District, flows through four areas of bungalow, power, Nangang and Taiping in Harbin, passes through two scenic spots of zoo and children's Park, and injects the Songhua River 200 m upstream of Binzhou bridge, with a total length of 44.3 km, including 34.7 km in Harbin urban area. The river channel is 30-100 meters wide and the drainage area is 240 square kilometers.

Ashi River: It is a tributary on the South Bank of the main stream of Songhua River and originates at the south foot of Daqingshan Mountain, flows from east to west near Xiquanyan River at the junction of Shangzhi and Acheng, turns to the northwest, flows through Wuchang, Acheng and Harbin, and flows into Songhua River in the eastern suburb of Harbin. The total length is 257 km. During the wet season in the middle and lower reaches, the width of water surface is 237-360 meters and the depth of water is 4-4.7 meters; In dry season, the width of water surface is 10-23.5 m and the depth of water is 0.2-0.25 m. The total drainage area is 3545 square kilometers (Fig.2-22).

Fig.2-22 Ashi river

Feiketu River: It is a tributary on the south bank of the main stream of Songhua River and located in the south of Heilongjiang Province. It is known as "Pigudun wooden water" since the Jin Dynasty, and it was named today since the Ming Dynasty. "Feiketu", in Manchu, means "gap" or "rest station". Feiketu post station was set here in the Qing Dynasty. It originates from the north slope of diaoshuihuling in Daqingshan Mountains, flows through the northwest of Binxian County and the northeast of Acheng District, and flows into Songhua River in the west of Shantun at Laoshantou of Binxian County. The total length is 100 kilometers, the width of river is 4-8 meters, the water depth is 0.4-1.2 meters, and the total drainage area is 1108 square kilometers.

Jiaban River: a tributary on the South Bank of the main stream of Songhua River. Located in Bin County, it is known as "Jiaban station River" in history. There are three tributaries at the source, namely Yuanbao River, Shidong River and Chaoyang river. They all originate from Daqingshan, the remaining vein of zhangguangcai ridge, travel from south to north, flow through Chang'an, Bin'an and other towns, and inject into Songhua River in the north of minxingtun, Xindian town. They are one of the main rivers in Bin County. It has a total length of 54 kilometers and a drainage area of 954 square kilometers.

Ma River: It is also wrote "Ant River" and a large tributary on the right bank of Songhua River. It originates from the west slope of Zhangguangcai ridge, flows through Shangzhi, Yanshou and Fangzheng counties (cities), reaches the north end of Fangzheng County, and flows into Songhua River on the other bank of Tonghe County. With a total length of 341 km, the upstream area is above one slope, which belongs to mountainous area and mostly forest area; From one slope to Yanshou County, it is the middle reaches, mostly hilly areas; The lower reaches of Yanshou County are alluvial plains. In the middle and lower reaches, the maximum width of water surface is 140-1900 meters and the maximum depth of water is 2.5-6.0 meters at medium and high water levels; At low water level, the maximum water surface is 60-145 meters and the maximum depth of water is 0.6-1.3 meters. The main tributaries include Daliangzi River and Dongliangzhu River, with a total drainage area of 10721 square kilometers (Fig.2-23).

Fig.2-23 Ma river

In 1957, the Xingfa Brigade of Hongqi Commune (now Xingfa Village, Songnan Township) was established on the right bank of the Mahe River, and the Mahe River has since obtained measured hydrological data. In 1958, the cross-section was moved to the original bridge of the Mayu River, and in 1959 to the current bridge of the Mayu River. The station name was changed to Lianhua Second Station.

Since the Mayhe River has actual measurement data, there have been two major floods. It first appeared on August 9, 1960, when the water level reached 99.86 meters above sea level, and the corresponding flow was 3890 cubic meters per second. The second appeared on August 5, 1981, when the water level reached 99.23 meters above sea level, and the corresponding flow rate was 1199 cubic meters per second. The minimum flow occurred during the freeze period in 1977, with a flow of 0.49 cubic meters per second.

In 1975, the Lianhua Hydrological Station conducted flood surveys on both banks of the Mahe River in the county. A total of 16 flood trace points were collected. The 1932 flood level at Lianhua No. 2 Station was calculated to be 114.9 meters from the base of Dalian. At the same time, it is estimated that during the flood period of 1932, the ratio from Shijiatun to Lianhua No. 1 station dropped to 1/2270, the ratio from Lianhua No. 1 station to Yongping dropped to 1/1410, and the overall ratio dropped to 1/1840. During the flood period of 1960, the cross-sectional ratio between Shijiatun and Lianhua No. 1 Station was reduced to 1/2000, and the water ratio between

Lianhua No. 1 and Yongpingtun station was 1/1430, and the overall ratio was 1/1720.

Dongliangzhu River: It is a secondary tributary on the right bank of Songhua River and located in the southeast of Heilongjiang Province. Once produced pearls, so it was named. It originates from the West foot of Zhangguangcai ridge, flows through Shangzhi, Yanshou and Fangzheng counties (cities), and flows into Mahe River in the north of Limin Village, Yanshou County. The total length is 138 kilometers, the width of river is 24-60 meters, the depth of water is 0.4-1.3 meters, and the drainage area is 2608 square kilometers.

Greater Luolemi River: It is a tributary on the South Bank of the main stream of Songhua River and is located in the east of Fangzheng County. It originates from the north slope of Zhangguangcail ridge at the junction of Fangzheng County and Hailin City, flows through Xinghuo, Wanbaoshan forest farm and daluomi town from south to north, and flows into Songhua River in the west of the town. It has a total length of 61 kilometers and a drainage area of 418 square kilometers.

Little Luolemi River: a tributary on the right bank of Songhua River. Located in the east of Fangzheng County. It originates from the north slope of Zhangguangcai ridge, flows from south to north, flows through the east of Daluomi Town, and flows into Songhua River in the west of gaoleng shipping station. It has a total length of 73 kilometers, a river width of 4-8 meters, a water depth of 0.4 meters and a drainage area of 438 square kilometers.

Mudanjiang River: It is the largest tributary on the right bank of the main stream of Songhua River and located in the southeast of Heilongjiang Province. Mudan ridge, which originates in the north of Baitou mountain in Changbai mountain range, flows through the northeast of Jilin Province and Ningan, Mudanjiang, Hailin, Linkou, Yilan and other counties (cities) in Heilongjiang Province, and flows into Songhua River in the west of Yilan County. The upstream is from Heyuan to Jingpo Lake, with a total length of 726 kilometers and 382 kilometers in Heilongjiang Province. The width of river is 100-300 m and depth is 1.0-5.0 m. The freezing period is from middle November to middle April of the next year. The main tributaries include Langlang River, Wulin River, Ushun River, Sandao River, etc. The total drainage area is 37023 square kilometers, and the drainage area in Heilongjiang Province is 28543 square kilometers (Fig.2-24).

Fig.2-24 Mudanjiang river

Xigou River of Erzhan: It is also known as "Erzhan River" and a secondary tributary of Songhua River. It is located in the west of Ning'an County, originating in the east of zhangguangcai ridge. There are two river sources, namely Nangou River of Erzhan and Beigou river of Erzhan, which are called " Erzhan River" after converging near the bus team station of Er station. From west to East, it flows into Jingpo Lake at the mouth of Er station. It has a total length of 74 kilometers, a river width of 27 meters, a water depth of 0.5 meters and a drainage area of 1010 square kilometers.

Toad River: It is a secondary tributary of Songhua River and located in the east of Ning'an County. It originates from the West foot of Laoyeling, flows from east to west to the improved seed farm in Ning'an County, turns north, flows through Wolong Township, langang town and Jiangnan Township, and flows into Mudanjiang River in Xihe village, Ning'an town. The total length is 90 km, the river width is 10-40 m, the water depth is 0.4-0.8 m, and the drainage area is 1805 square kilometers.

Wave River: It is a secondary tributary of Songhua River and located in Hailin City in the southeast of Heilongjiang Province. It originates at the east foot of Zhangguangcai ridge, flows through Changting, Jiujie, Shihe, Hainan and other towns of Hailin City, and flows into Mudanjiang River in the northeast of Longtou mountain in the suburb of Mudanjiang City. The total length is 210 kilometers, the river width is 50-125 meters, the water depth is 1-3 meters, and the total drainage area is 5225 square kilometers (Fig.2-25).

Fig.2-25 Wave river

Erdaolang River: It is the third tributary of Songhua River and located in the west of Hailin City. It originates in the east of Datudingzi, Zhangguangcai ridge, runs from west to East, flows through Erlanghe forest farm, Xinlin village management office and Badaohezi forest farm of Dahai forest and Forestry Bureau, and flows into LangHai river near Fahe forest railway station. It has a total length of 75 kilometers, a river width of 28 meters, a water depth of 0.6 meters and a drainage area of 634 square kilometers.

Shanshi River: It is the third tributary of Songhua River and located in the south central part of Hailin City. It originates from Daling and Gaolingzi on the east slope of Zhangguangcai ridge, runs from northwest to Southeast, flows through Hengdaohezi town and Shanshi Town, and flows into Langlang River in Shihe village, Shihe township. The upstream is in Hengdaohezi Town, and the flow section is also known as "Hengdaohe". The total length is 83 km, the river width is 14-25 m, the water depth is 0.4-2.0 m, and the drainage area is 726 km^2.

Toudao River: It is a secondary tributary of Songhua River and located in the middle of Hailin City. It originates from the east slope of Zhangguangcai ridge, runs from west to east, flows through the north of Hengdaohezi town and the whole territory of Chaihe Town, and flows into Mudanjiang River near Beizhan village of Chaihe town. The total length is 63 km, the river width is 25 meters in the middle reaches and 35 meters in the lower reaches. After the confluence of people in Dajiapigou, two deep puddles are formed. One water area is 1600 square meters, the water depth is 4-5 meters, and the river Dylan does not see the bottom; The other is at the foot of the mountain at the east end of the "35 forest farm", which is filled by cutting mountains and building roads. The water area is about 500 square meters and the water depth is about 2 meters. The average water depth downstream is 1.5 m. The drainage area is 859 square kilometers.

Erdao River: It is a secondary tributary of Songhua River and located in the north of Hailin City. It originates from the east slope of Zhang Guangcai's ridge, runs from west to East, crosses the whole territory of erdaohezi Town, and flows into Mudanjiang in the north of erdaohezi town. It has a total length of 67 kilometers, a river width of 30-35 meters, a water depth of 0.4-1.0 meters and a drainage area of 727 square kilometers.

Sandao River: It is a secondary tributary of Songhua River and located in the north of Hailin City. It originates from the east foot of Datudingzi, Zhangguangcai ridge, runs from west to east, flows through the whole west of Mudanjiang in sandaohezi Township, and flows into Mudanjiang in Hekou village, Sandaohezi township. It has a total length of 80 km, a river width of 22 m, a water depth of 0.3-1.0 m and a drainage area of 1370 square kilometers.

Ushhun River: It is a secondary tributary of Songhua Rive and located in Linkou County, southeast of Heilongjiang Province. It was called "Wusihun River" in the Qing Dynasty. It originates in the east of Guokui, flows from the southeast of Linkou County to the northwest, and flows into Mudanjiang on the other bank of Datun village. The total length is 141 kilometers, the river width is 30-75 meters, the water depth is 0.4-1.0 meters, and the total drainage area is 4176 square kilometers (Fig.2-26).

Fig.2-26 Ushhun river

Woken River: It is a large tributary on the right bank of Songhua River and originates from Alha mountain in Wanda Mountains, flows through Qitaihe, Boli, Huanan, Yilan and other cities and counties, and flows into Songhua River about 1km east of Yilan County. The total length is 450 kilometers. Above Taoshan mountain is a mountainous and hilly area with narrow river valley and slightly open Jinsha River. After flowing to woken Town, Boli County, it enters the open plain area. At medium and high-water levels, the maximum width of water surface is 170-290 m and the maximum depth of water is 2.2-5.2 m; At dry water level, the maximum water surface width is 10 m and the maximum water depth is 0.1 m. The freezing period is from the middle of November to the first ten days of April of the next year. The total drainage area is 11015 square kilometers (Fig.2-27).

Fig.2-27 Woken river

Qihuli River: It is a secondary tributary of Songhua River. It is located in the south of Huanan County in the east of Heilongjiang Province. It originates from Alha mountain in Wanda Mountains, turns from north to south to west, flows through Shitouhezi, Erdaogou, Yanjia, gongxinji and other towns, and flows into woken River in the northwest of Huamugang village, Gongxinji township. It has a total length of 84 kilometers, a river width of 14-20 meters and a drainage area of 1055 square kilometers.

Bahuli River: It is a secondary tributary of Songhua River. It is located in the middle of Huanan County in the east of Heilongjiang Province. In the Qing Dynasty, it was called "Bahuli River". It originates from Alha mountain in Wanda Mountains, crosses the whole territory of Huanan County from east to west, and flows into woken River in the west of Qinghe Village, Lishu township. It has a total length of 110 km, a river width of 4-20 m, a water depth of 1.4-2.0 m and a drainage area of 1260 square kilometers.

Songmu River: It is a secondary tributary of Songhua River and located in the northwest of Huanan County. It originates from caotadingzi mountain in the south of Huachuan County, flows through the northwest of Huanan County, and flows into Woken River in the west of Huanan

County. The total length is 63km, the river width is 4-25m, and the water depth is 1.2-1.5m. The drainage area is 480 square kilometers.

Lingdangmai River: It is a tributary on the right bank of Songhua River and located in the south of Huachuan County. Daqingbei mountain, which originates at the junction of Huanan and Huachuan counties, flows from south to north through hengtoushan, Changfa and simajia in the west of Huachuan County, meets yindamu River and Taiping River at Sanchakou in the southeast of Jianguo Township, and flows into Songhua River through artificial river. It has a total length of 70 kilometers, a river width of 20 meters, a water depth of 0.5 meters and a drainage area of 830 square kilometers.

Anbang River: It is a tributary on the right bank of Songhua River. It is located in the east of Heilongjiang Province. It originates from Fenshuigang, the branch of Wanda mountain, flows through Shuangyashan, Jixian and Huachuan from south to north, and flows into Songhua River in Xincheng and rural areas of Huachuan County. It has a total length of 167 km, a river width of 10-80 m, a water depth of 0.4-1.2 m, and a total drainage area of 2589 square kilometers.

Liushu River: It is a secondary tributary of Songhua River and located in the west of Jixian County. It originates from Shimenzi mountain in the north of Qixinglazi, runs from south to north, flows through Shanshan township of Jixian County, Fengle town and branch 1 and 4 of Bijiashan farm, enters Huachuan County, and flows into Anbang River through Lifeng township. It has a total length of 62 kilometers, a river width of 20-40 meters, a water depth of 1.2 meters and a drainage area of 398 square kilometers.

Hulan River: It is a large tributary on the left bank of the main stream of Songhua River. Hulan River originates from Lublowing mountain in the west of Lesser Khingan Mountains, flows through 6 counties (cities) such as Tieli, Qing’an, Suihua, Wangkui, Lanxi and Hulan, and flows into Songhua River near Zhangjiadian in the south of Hulan County. The total length is 523 kilometers (Fig.2-28).

Fig.2-28 Hulan river

Tongken River: It is also known as "Tongkeng River" and a secondary tributary on the left bank of Songhua River. It is located in the middle of Heilongjiang Province. It originates from the southwest foot of Lesser Khingan Mountains, turns from east to west and flows southward through the junction of Beian, Hailun, Baiquan, Mingshui, Qinggang and Wangkui counties (cities), and flows into Hulan River at the junction of Qinggang, Wangkui and Lanxi counties. The total length is 346 km, the width of river is 10-40 m, the depth of water is 0.4-1.0 m, and the total drainage area is 10339 km^2.

Zayin River: It is formerly known as "Zaka River", in Manchu and the third tributary of Songhua River, which is located in the north of Helen City. It originates at the junction of Hailun, Bei'an and Suiling counties (cities), crosses the north of Hailun City from northeast to southwest, and injects Tongken River near the supply and marketing village of Yonghe township. It has a total length of 105 kilometers, a river width of 12 meters, a water depth of 1.5 meters and a drainage area of 1264 square kilometers.

Hailun River: It is the third tributary of Songhua River and located in the south of Helen City, which is originated in the east of Helen City. From northeast to southwest, it crosses the south of Hailun City and injects Tongken river near Baihe Village. It has a total length of 74 kilometers, a river width of 10 meters, a water depth of 0.5 meters and a drainage area of 1141 square kilometers.

Numin River: It is also known as "Nuomin River" and a secondary tributary of Songhua River.

It is located in the middle of Heilongjiang Province. It originates from the south foot of Lesser Khingan Mountains, flows through Suiling County and Suihua City, joins the Keyin River near Sungongtun, Suihua City, and then flows into Hulan River. The total length is 265km, the width of river is 20-50 m, the depth of water is 0.5-1.0 m, and the total drainage area is 5328 square kilometers (Fig.2-29).

Fig.2-29 Numin river

Keyin River: It is the third tributary of Songhua River. It is located in the middle of Heilongjiang Province. It originates in the middle of Suiling County, with Shuangcha River upstream, starts from Jinhe village, keyinhe Township in the north, flows through the junction of Suiling, Hailun, Wangkui, Suihua and other counties (cities), and flows into Numin River at Sungongtun, Suihua City. The total length is 147 km. The width of river is 10-40 m and depth is 0.4-2.0 m, with a total drainage area of 2000 square kilometers.

Niergen River: It is formerly known as "Eyhun River" and a secondary tributary of Songhua River. It originates from Qingshui mountain at the junction of Qing'an County and Suiling County, flows from northeast to southwest, and flows into Hulan River in the southwest of luojiatun, Linhe village, Zhifu Township, Qing'an County. It is the boundary river between Qing'an County, Suiling County and Suihua City. It has a total length of 88 kilometers, a river width of 2-17 meters, a water depth of 0.7-1.0 meters and a drainage area of 523 square kilometers.

Ogen River: It is a secondary tributary of Songhua River. It is located in the middle of Heilongjiang Province. It originates in the south of Lesser Khingan Mountains, flows through the north of Qing'an County, and flows into Hulan River in the south of Zhifu township. The total length is 174km, the river width is 12-80m, the water depth is 0.4-4.0m, and the drainage area is 2002 square kilometers.

Yijimi River: It is a secondary tributary of Songhua River. It is located in the middle of Heilongjiang Province. It originates from guokuiding of Lesser Khingan Mountains, flows through the junction of Qing'an County and Tieli City, and flows into Hulan River in the east of Qingfeng Village, Qing'an County. It has a total length of 103 kilometers, a river width of 14-60 meters, a water depth of 0.5-4.0 meters, and a drainage area of 1777 square kilometers.

Anbang River: It is once known as "Angbang River", also known as "Anbai River", which is a secondary tributary of Songhua River. It is located in the middle of Heilongjiang Province. It originates from the west slope of Pingding Mountain, the branch of Lesser Khingan Mountains, runs from southeast to northwest, flows through the junction of Tieli City and Qing'an County, and flows into Hulan River in the north of Ping’an Town, Qing'an County. The total length is 102 kilometers, the river width is 6-18 meters, the water depth is 0.4-1.5 meters, and the drainage area is 904 square kilometers.

Gmuk River: It is a secondary tributary of Songhua River. It is located in the south of Qing'an County. Dadingzi Mountain, which originates at the junction of Qing'an and Mulan counties, flows down from the source to the south. After receiving shuangyinhe in gengjiatun at the north end of Xinmin Township, it turns West and flows into Hulan River in the northwest of yaowobao Tun, Yongli village, Huansheng township. It has a total length of 92 kilometers, a river width of 12 meters, a water depth of 1.3 meters and a drainage area of 803 square kilometers.

Lalinqing River: It is also known as “Lalehan River”. “Lalinqing” means "muddy lake" in Manchu. Secondary tributary of Songhua River. It is located in the southeast of Qing'an County. It originates from Guanwuye Mountain in the southeast of Qing'an County. From the source to the northwest, it is called "relying on mountains and rivers", and after merging with Liuhe River, it is called "Lalinqing River". Travel to the northwest, flow through some areas of townships such as Xinsheng, Liangli, Fengshou, Ping'an and Jiusheng, and pour into Hulan River in the northwest of Wuchangtaitun, Heping Village, Ping’an town. It has a total length of 89 kilometers, a river width of 24 meters, a water depth of 1.5 meters and a drainage area of 759 square kilometers.

Nihe River: It is a secondary tributary of Songhua River. It is located in the middle of Heilongjiang Province. It was called "Haohe" in the Qing Dynasty. It originates from Gongjiafen mountain, the branch of Lesser Khingan Mountains, flows through the junction of Bayan County and Suihua City and the junction of Lanxi and Hulan counties, and flows into Hulan River in the west of Bajia village, Hulan County. It has a total length of 240 kilometers, a river width of 14-20 meters, a water depth of 0.4-1.0 meters, and a total drainage area of 1500 square kilometers.

Shaoling River: It is a tributary on the north bank of the main stream of Songhua River. It is located in the middle of Heilongjiang Province. It is called "Shuoshui" (also known as "Shuoshui") in Jin Dynasty, and is called "Shuoro River" or "Chuole River" in Qing Dynasty. It originates from Qingfeng ridge, the remaining vein of Lesser Khingan Mountains, flows through the northwest of Mulan County and the middle of Bayan County, and flows into Songhua River near Jiangjiadian, Bayan County. It has a total length of 135 kilometers, a river width of 7-40 meters, a water depth of 0.4-1.0 meters, and a total drainage area of 2468 square kilometers (Fig.2-30).

Fig.2-30 Shaoling river

Piao River: It is a secondary tributary of Songhua River. It is located in the middle of Heilongjiang Province. The river channel bends abnormally. After the flood peak water level, the river channel often shifts, so it is called "floating river". It originates in the northwest of Bayan County, flows to Xudong village, Kangzhuang Township, Bayan County, becomes the boundary river of Hulan and Bayan counties in the west, and meets Shaoling River in the east of haojiamiao Tun, Yanglin Township, Hulan County. It has a total length of 85 kilometers, a river width of 7-10 meters, a water depth of 0.3-1.0 meters and a drainage area of 785 square kilometers.

Mulanda River: It is a north bank tributary of the main stream of Songhua River and located in Mulan County. Mulan County gets its name because of the river. Originating from the south foot of Lesser Khingan Mountains in the north of Mulan County, there are two sources, one is Moyundingzi and the other is the south foot of Qingfeng mountain. After merging, it flows from the west to the South and flows into the Songhua River near Linjiang village, Mulan County. The total length is 110 kilometers. Above Xiangmoshan reservoir is the upstream mountainous area with narrow river channel; The middle reaches are from Xiangmoshan reservoir to Jianshanzi, and the river channel gradually widens, increasing from 4-10 m to about 30 m; The downstream is below Jianshanzi, and the width of river channel is 30-50 m. The depth of water is 5.2 m in wet season and 0.2 m in dry season. The total drainage area is 1706 square kilometers.

Poplar River: It is formerly known as "Buyami River", formerly known as "Wuyegu River".

According to the records of Hulan Prefecture, "Wuye ancient river is the buyami River in Mulan County, which is locally called Poplar River." The north bank tributary of the main stream of Songhua River. It is located in the east of Mulan County. It originates from the south foot of Lanchaidingzi Mountain in the northeast of Mulan County, flows around the southwest of Yuhuangge Mountain, crosses the east of Mulan County from north to south, and flows into Songhua River near Mulan town. It has a total length of 58 kilometers, a river width of 4-15 meters, a water depth of 0.3-0.5 meters, and a drainage area of 437 square kilometers.

ChaLin River: "Sapu River" is written in Shengjing Tongzhi. It is a north bank tributary of the main stream of Songhua River and located in the west of Tonghe County, which is the largest river in Tonghe County. It originates from Mopan Mountain in the north of Tonghe County, flows from north to south, collects 28 tributaries and injects into Songhua River near Tonghe town. It has a total length of 91 kilometers, a river width of 20-70 meters, a depth of 1.0-1.2 meters, and a total drainage area of 1941 square kilometers.

Northwest River: According to the newly compiled Tonghe County annals, it was originally called "Xibo River" and "Xibo River", which was named after the residence of the survivors of Xianbei nationality. It is a tributary on the north bank of the Songhua River and located in the east of Tonghe County. It originates from Mantou Mountain in the north of Tonghe County, flows through the Northwest River irrigation area from north to Southeast, converges with Xinxing reservoir and flows into Songhua River. It has a total length of 74 kilometers, a river width of 21 meters, a water depth of 0.6 meters and a drainage area of 794 square kilometers.

Dagudong River: It is formerly known as "Dahu Teheng River" and a tributary on the north bank of the Songhua River. It is located in the east of Tonghe County. Originated from Mantou mountain in the north of Tonghe County, it is composed of eight streams. From north to Southeast, it flows into Songhua River near Qinghe town. It has a total length of 55 kilometers, a river width of 12 meters, a water depth of 0.5 meters and a drainage area of 429 square kilometers.

Xiaogudong River: It is formerly known as "xiaohutheng River" and a tributary on the north bank of the Songhua River. It is located in the east of Tonghe County, which is originated in the northeast of the County. There are two sources: one is from the human head, called the perfume river. One originates from Heixiazi ditch and Poplar Ditch. From north to Southeast, it flows into Songhua River near xiaogudong village, Qinghe town. It has a total length of 50 kilometers and a drainage area of 471 square kilometers.

Balan River: It is a tributary on the left bank of Songhua River and located in the middle of Heilongjiang Province. It originates from the north side of Wuhuadingzi, the remaining vein of Lesser Khingan Mountains, flows through the southeast of Tieli City and the northwest of Yilan County, and flows into Songhua River near Yinglan village, Yilan County. It has a total length of 108 kilometers, a river width of 20-60 meters, a water depth of 0.3-1.0 meters, and a total drainage area of 2075 square kilometers.

Tangwang River: It is the main tributary on the left bank of Songhua River and originates from the south foot of the west slope of Lesser Khingan Mountains. There are two sources of Tangwang River in the East and Tangwang River in the East. The two streams converge from north to south, flow through Yichun, Tieli and Tangyuan, and flow into Songhua River about 5 km southwest of Tangyuan County. The total length is 509 kilometers. The total drainage area is 20838 square kilometers (Fig.2-31).

Fig.2-31 Tangwang river

Xitangwang River: It is a secondary tributary of Songhua River and located in the north of Yichun City. It originates in heyushan area in the north of Yichun City, flows through Gaofeng, Erlong Mountain, Dongsheng, Shilin and other forest farms from northwest to Southeast, and joins East Tangwang River (the mainstream of Tangwang River) in the east of the central nursery. It has a total length of 64 kilometers, a river width of 9 meters, a water depth of 0.5 meters and a drainage area of 533 square kilometers.

Youhao River: It is a secondary tributary of Songhua River and located in the west of Yichun City. It originates in the east of Lesser Khingan Mountains, runs from northwest to Southeast, connects Naxi Youhao River in the north of Guangchuan forest farm, and injects Tangwang River in the east of the government of Youhao District. The total length is 83 km, the river width is 12-35 m, the water depth is 1.0-1.8 m, and the drainage area is 948 square kilometers.

Twin rivers: It is a secondary tributary of Songhua River and located in the west of Yichun City. It originates from the south slope of Lesser Khingan Mountains. There are two sources: East Kaltai River and West Kaltai river. After the two sources meet in Pingling work area, they are called "twin rivers". It flows from northwest to southeast through Shaxian village, Milin village and Xing'an village, and flows into Tangwang River near Gemini River town. It has a total length of 77 kilometers, a river width of 20-35 meters, a water depth of 1.4-2.0 meters and a drainage area of 1216 square kilometers.

Yichun River: It is a secondary tributary of Songhua River and located in the west of Yichun City, which is originating from the south slope of Lesser Khingan Mountains, it is formed by the confluence of Mohe River, Cuiluan River and Fenshi river. It turns eastward in Cuiguang village, crosses Cuiluan, Wuma River and Yichun, and injects Tangwang River near Yichun City. It has a total length of 84 kilometers, a river width of 34-60 meters, a water depth of 0.6-1.2 meters, and a total drainage area of 2466 square kilometers (Fig.2-32).

Fig.2-32 Yichun river

Wudaoku River: It is a secondary tributary of Songhua River and located in the middle of Yichun City, which originates in the south of Xiaobai Mountain. Because it flows out of Wudaoku ditch, it is named "Wudaoku River". From northeast to southwest, after receiving a tributary in the east of wudaoku business office, turn south and inject Tangwang River near Linyuan village. It has a total length of 75 km, a river width of 20-60 m, a water depth of 0.4-1.2 m and a drainage area of 1773 square kilometers.

Dafeng River: It is a secondary tributary of Songhua River and located in the east of Yichun City, which originates in the south of Laobai Mountain, runs from northeast to southwest, flows through Fengling forest farm, turns northwest to Fengmao forest farm, and flows into Tangwang River in the south of Jinshantun District. The total length is 80 km, the river width is 10-35 m, the water depth is 0.2-0.8 m, and the drainage area is 1094 square kilometers.

Southwest Chahe River: It is a secondary tributary of Songhua River and located in the south of Yichun City. It originates from the south foot of Guokuiding in Lesser Khingan Mountains, runs from northwest to southeast, turns east after "five kilometers", crosses Nancha District, and injects Tangwang River near Lvtan village. It has a total length of 85 kilometers, a river width of 7-24 meters, a water depth of 0.5 meters, and a total drainage area of 2735 square kilometers.

Gejie River: It is also known as "Gejin River" and a tributary on the left bank of the Songhua River, which is located in the middle of Tangyuan County. It originates from Gejin mountain in the northwest of Tangyuan County, so its upstream is called "Gejin River" and its downstream is called "Gejie River". Meandering from the source to the southeast, it flows into the Songhua River along the east side of the village in Xiaodong River, Shengli township. It has a total length of 57 kilometers, a river width of 8 meters, a water depth of 0.5 meters and a drainage area of 429 square kilometers.

Arlinda River: It is a tributary on the left bank of Songhua River and located in the middle of Tangyuan County. According to the newly compiled Tangyuan County Chronicle, the name of "a Lingda River" comes from "Wulinda", which is the place where the female immortal Wulinda of the Liao Dynasty lived for generations. It originates from the south side of Qingheishan Motianling in Lesser Khingan Mountains. From the source to the southeast, the river from the east of pangjiadian to the north of Heli town is the boundary river between Hegang City and Tangyuan County, and flows into Songhua River near Dexiang village, Jixiang township. The total length is 76 kilometers, the river width is 10-16 meters, the water depth is 0.7-1.5 meters, and the drainage area is 550 square kilometers.

Wutong River: It is a tributary on the left bank of the main stream of Songhua River and located in the northeast of Heilongjiang Province. It is called "main water" in Liao dynasty, and called "Wutong answer water" in Jin dynasty. It was called "Wutun River" and "Wutun River". Originating from the small white mountain of the Xingan ridge, it flows through the northern part of Hegang and Hegang, and at the junction of Luobei County and the eastern part of Tangyuan County. It is injected into the east of the Songhua River at the east part of Wutong river farm. The main tributaries are west Wutong River and Heli river. The total length is 207 km, the width of river is 30-70 m, the depth of water is 1-2 m, and the total drainage area is 4763 square kilometers (Fig.2-33).

Fig.2-33 Wutong river

Heli River: It is a secondary tributary of Songhua River and located in the south of Hegang City. It originates from Qingheishan Mountain in Lesser Khingan Mountains. The upper reaches are called "In River", the middle reaches are called "Big Heli River", and the tributaries are small Heli River, which is called "Heli River" after confluence. From northwest to Southeast, it is injected into Wutong River. It has a total length of 69 kilometers, a river width of 50 meters, a water depth of 1.0-1.5 meters and a drainage area of 879 square kilometers.

Dulu River: It is a tributary on the left bank of Songhua River and located in Luobei County in the north of Heilongjiang Province. In ancient times, it was called "Tuolun River", "Tule River" and "Tulu River". "Tulu" means "white bellied trout" in Mongolian. It originates from the east slope of Lesser Khingan Mountains, flows through the west of Luobei County from north to southeast, and flows into Songhua River at the junction of Luobei and Tangyuan counties. It has a total length of 245 kilometers, a river width of 7-20 meters, a water depth of 1.2-2.0 meters, and a total drainage area of 1798 square kilometers.

Meandering river: It is a tributary on the left bank of Songhua River and located in Suibin County, northeast of Heilongjiang Province. It originates from the swamp in the west of Suibin County, runs across the County from west to east, and flows into the Songhua River in the northeast of 290 farm area. It is named because the river is winding. The total length is 92.4 km, the width of river is 50-150 m, the depth of water is 0.4-1.5 m, and the drainage area is 1036 km^2.

2.1.3 Regional Conditions

(1) Regional location

Songhua River Basin is located in the north of Northeast China, between 41 ° 42 ′ ~ 51 ° 38 ′ N and 119 ° 52 ′ ~ 132 ° 31 ′ e. The length of Songhua River is 1927 km, its length is 920 km from east to west and width is1070 km from north to south. It spans Inner Mongolia, Jilin and Heilongjiang Provinces, with a drainage area of 556800 square kilometers, accounting for 30.2% of the total drainage area of 1.843 million square kilometers in Heilongjiang. The annual runoff is 76.2 billion cubic meters.

(2) Geomorphic elevation

The western part of Songhua River Basin is bounded by Greater Khingan Range and Erguna River, with an altitude of 700 ~ 1700 meters; The north is bounded by Lesser Khingan Mountains and Heilongjiang, with an altitude of 1000 ~ 2000 meters; The southeast is bounded by Zhangguangcai ridge, Laoye ridge, Wanda Mountains, Wusuli River, Suifen River, Tumen River and Yalu River, with an altitude of 200 ~ 2700 m; The southwest is the Songliao watershed of Songhua River and Liaohe River, with an altitude of 140 ~ 250 meters. Songnen Plain, with an altitude of 50-200 meters, is the main agricultural area in the basin. After the Songhua River flows into Heilongjiang near Tongjiang River, the famous Sanjiang Plain is formed with the vast plains in the lower reaches of Heilongjiang and Wusuli River (Fig.2-34).

Fig.2-34 Lower Songhua river plain

(3) Climate temperature

The basin is located in the north temperate monsoon climate zone, with four distinct seasons. It is warm and rainy in summer, cold and dry in winter, with large temperature difference all the year. Average temperature is between 3 ~ 5℃ for many years. The temperature in July is the highest, with a daily average of 20 ~ 25℃ and a maximum of more than 40℃; The temperature in January is the lowest, the monthly average temperature is below -20℃, and the lowest temperature near Zhalantun of Nenjiang River once reached -42.6℃ (Fig.2-35).

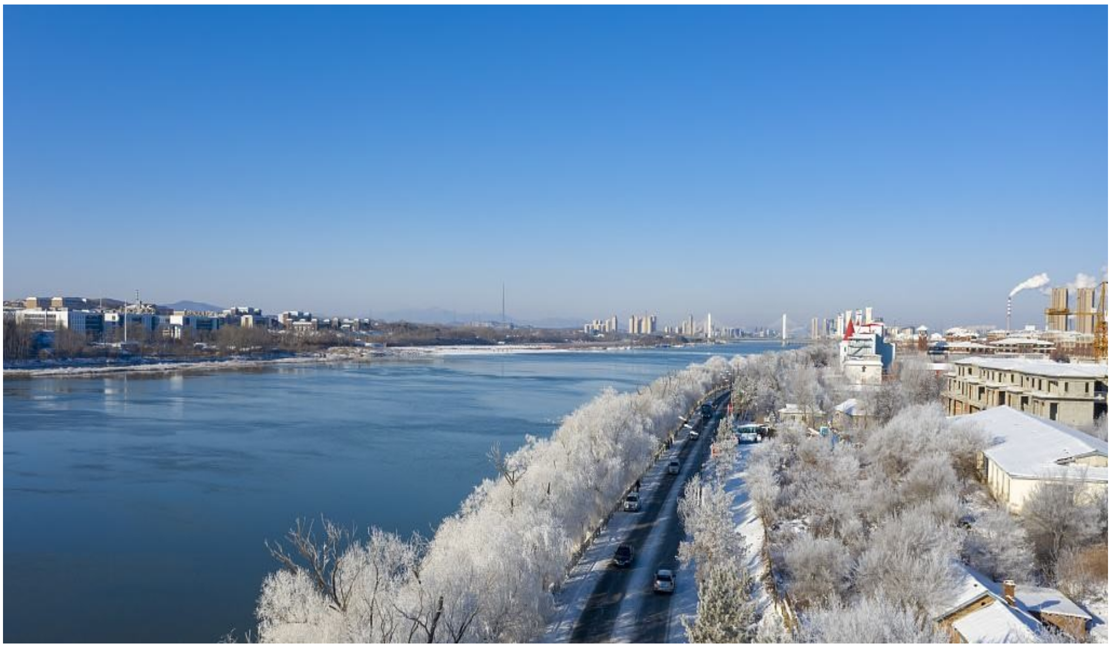

Fig.2-35 Winter in Jilin section of Songhua river

The average annual precipitation is generally about 500 mm, the precipitation in the mountainous area in the southeast can reach 700 ~ 900 mm, while in the western area of the arid basin, it is only 400 mm. The general trend is that the hilly area is large and the plain area is small; It is slightly larger in the south and middle, followed by the East, and the smallest in the west and north. The precipitation from June to September in flood season accounts for 60% ~ 80% of the whole year, and the precipitation from December to February in winter is only about 5% of the whole year.

2.1.4 Hydrological Characteristics

(1) Runoff

The average annual runoff of Songhua River reaches 76.2 billion cubic meters. Among them, the annual average runoff of Nenjiang River is 22.73 billion cubic meters; The tributary Gan River has an average annual runoff of 3.64 billion m^3, a maximum runoff of 6.564 billion m^3 (1989), a minimum runoff of 886 million m^3 (1979), and an average annual flow of 115 m^3/s; The tributary Yalu River has a dry season in February, with a flow of about 0.68 m^3/s. Flow is about 2570 m^3/s and an average flow is 718 m^3/s in a wet season in August. The multi-year average annual runoff of the Songhua River in the west is 16.2 billion cubic meters, and the multi-year average annual runoff depth is 209.6 mm.

The average annual runoff depth of Songhua River Basin is 134.3 mm for many years, equivalent to 73.3 billion m^3. The area to the south of the main stream is relatively large. The maximum value in mountainous areas can reach about 500 mm, such as Daojiang River Basin, the upper source of the second Songhua River. The second is the basin of Langlang River, a tributary of Mudanjiang River, Yijimi River, a tributary of Hulan River, and Yongcui River, a tributary of

Tangwang River, with an annual runoff depth of more than 400 mm. The annual runoff depth of Songnen Plain is only 20 ~ 30 mm. The regional distribution trend of annual runoff and annual precipitation is basically the same. The water in Songhua River Basin is mainly supplied by atmospheric precipitation and supplemented by melt water. Therefore, the annual distribution of runoff also has the characteristics of obvious seasonal variation. More than 90% of the inflow of each river is concentrated in the smooth flow period from April to October, of which the runoff from June to September accounts for about 55 ~ 80% of the whole year. The flood is mostly concentrated from July to August, and the main stream can be extended to early September. The flood lasts for about 60 days. Due to the large drainage area, propagation time of flood is long. The flood in Songhua River Basin is mainly caused by rainstorm, followed by the flood peak caused by the simultaneous rise of several tributaries. Seasonal melt water supply in spring generally forms spring flood with different degrees. The runoff from April to May accounts for about 15 ~ 30% of the whole year, while the runoff in winter is the smallest, forming the obvious characteristics of abundant water in summer and low water in winter. The interannual variation of runoff is large, and it shows obvious periodic variation of continuous abundant and continuous dry and alternating abundant and dry, but the cycle length is different. The annual runoff rheological difference in the basin, CV value is generally 0.4 ~ 1.0, and the upper reaches of the second Songhua River is small, only 0.2 ~ 0.5; Western region is the largest, which is up to 0.9 ~ 1.0 in areas with little water flow such as Wuyuer River, Shuangyang River and Taoer River. The difference of runoff in wet and dry seasons is several times to dozens of times. For example, Shuangyang station of Shuangyang River has a catchment area of 1861 square kilometers. The water volume in wet season in 1969 was 236 million cubic meters, and that in dry year in 1968 was only 0.0419 million cubic meters. The ratio of water volume in wet and dry years was 56.3.

(2) Flood characteristics

After the flood season in 1998, the precipitation in Nenjiang River Basin in the upper reaches of Songhua River was obviously excessive, and three major floods occurred successively. The first flood occurred from the end of June to the beginning of July, the second flood occurred from the end of July to the beginning of August, and the third flood occurred in the first and middle of August, which is a large flood in the whole Nenjiang River Basin. Affected by the water from various tributaries, the water level in the main stream of Nenjiang river rises rapidly, and the highest water levels of Lianmeng, Qiqihar, Jiangqiao and Dalai hydrological stations exceed the historical measured highest water levels by 0.25, 0.69, 1.61 and 1.27 meters respectively. In the case of six overtopping breaches of Nenjiang River embankment, the peak discharge of Qiqihar, Jiangqiao and Dalai stations exceeded that of 1932.

The highest water level in Harbin, the main stream of Songhua River, was 120.89 m on August 22, 0.84M higher than the historical measured highest water level, and the flow was 16600 m^3/s, which was the first major flood in the 20th century. There are two kinds of floods in Songhua

River Basin: one is caused by heavy rain covering a large area in flood season; The second is the continuous rainy weather in a certain area of the basin in the flood season, which can last for one month or more. The rainstorm in this continuous rainy day forms a flood.

The flood in Songhua River basin includes spring flood and summer flood. The time of spring flood is basically the same as that of ice flood when the river opens in early spring. It occurs from April to May every year, and ice dams often appear in ice flood. According to the statistics of Yilan station, in the 21 years from 1956 to 1976, ice dams occurred in 13 years. The height of ice dams is generally 4 ~ 6 m, up to 15 m, and the length of ice dams is 5 ~ 10 km. The summer and autumn flood occurs from June to August, sometimes postpones to September (Fig.2-36).

Fig.2-36 Flooded Songhua river

(3) Hydraulic resources

The total amount of water resources in the whole basin is 88.028 billion cubic meters, of which the total amount of surface water resources and exploitable groundwater is 85.15 billion cubic meters. The total amount of surface water resources is 73.47 billion cubic meters, of which Nenjiang River is 22.73 billion cubic meters, accounting for 30.9%; The positive source of Songhua River is 17.2 billion cubic meters, accounting for 23.5%; The main stream of Songhua River is 33.48 billion cubic meters, accounting for 45.6%.

Songhua River Basin is rich in hydropower resources, and the main stream of Songhua River, Nenjiang River and Mudanjiang River are concentrated in the west. There are 71 main and tributary rivers with a theoretical water energy reserve of more than 10000 kW in the basin, with a total theoretical reserve of 6.5985 million kW, of which the main and tributary of the Songhua River in the west is 1.3982 million kW, accounting for 21.2% of the whole basin; The trunk and tributaries of Nenjiang River are 2.2712 million kW, accounting for 34.4%; The main stream of Songhua River and its tributaries are 2.9291 million kW, accounting for 44.4%.

2.1.5 Natural Resources

(1) Mineral resources

The Songhua River Basin is covered with overlapping mountains and covered with virgin forests. The timber accumulated on the Changbai Mountain, Greater Khingan Range, Lesser Khingan Mountains and other mountains, with a total of 1 billion cubic meters, is the largest forest area in China. Mineral reserves are also very rich. In addition to the main coal, there are gold, copper, iron and so on.

(2) Animal and plant resources

The Songhua River Basin is fertile and rich in soybeans, corn, sorghum and wheat. In addition, flax, cotton, tobacco, apples and sugar beets are also of good quality. Songhua River is also a large freshwater fish farm in Northeast China. It is rich in fish resources. Valuable species such as "three flowers and five Luo", big white fish and mandarin fish have long been famous in the world. There are 77 species of fish in the whole basin. It is an important place of origin for freshwater fish in northern China. It is rich in carp, grass carp and catfish. The annual supply of carp, Qing, Yu and Zheluo fish is more than 40 million kg (Fig.2-37).

Fig.2-37 Winter fishing in Songhua river

2.1.6 Development and Utilization

(1) Hydropower project

Songhua River Basin is rich in hydropower resources. It is planned to build 21 hydropower stations with a total installed capacity of 4.1504 million kW and an average annual power generation of 9.155 billion kwh. Eight hydropower stations above 10000 kW have been built, with a total installed capacity of 3.3881 million kW and an annual power generation of 56.69 kwh. The development tasks of each river section are different: ① in the upper reaches of Nenjiang River, four hydropower stations of Wodu River, Woli River, Gugu River and kumotun are planned and arranged, with a total utilization head of 125 m, a total storage capacity of 13.7 billion m^3 and a total installed capacity of 358400 kW; ② Nierji (Fig.2-38) and Dalai water control projects are planned to be set in the middle and lower reaches of Nenjiang River. The total storage capacity of Nierji hydroproject is 8.22 billion m^3, of which the flood control storage capacity is 2.464 billion m^3, which can increase the flood control standard of Qiqihar from once in 50 years to once in 100 years; ③ The development task of the section above Fengman Hydropower Station on Songhua River is mainly to make power generation, taking into account flood control.

Fig.2-38 Nierji water control

The most upstream Songshan junction is a water diversion junction, which regulates the water flow of the source of Songhua River through the reservoir and leads it to the tributary Songjiang River with a 12.6 km long diversion tunnel. It gathers the water of the two rivers and generates power by the three-stage hydropower stations built in Shangxiaoshan, Shuanggou and Shilong of Songhua River, with a total installed capacity of 510000 kW.

The tributary Songjiang River flows into the main stream at the upstream of Baishan hydropower station. Through the regulation of Baishan and Fengman reservoirs, the flood with a return period of less than 100 years can be controlled and discharged to 5500 m^3/s; ④ The HA Da Shan hydro junction is planned and arranged below the Fengman river. The total storage capacity is 4 billion 220 million cubic meters, of which 3 billion 350 million cubic meters are regulated. Through its regulation, it can provide an additional water volume of 8.1 billion m3 / year; ⑤ The development task of the main stream of Songhua River is to channel the river to meet the navigation requirements, and a 6-level shipping hub is set up.

By 2014, 6551 large, medium and small reservoirs have been built in Songhua River Basin, with a total storage capacity of 25.728 billion cubic meters, including 22 large reservoirs, with a total storage capacity of 24.047 billion cubic meters and a flood control storage capacity of 6.416 billion cubic meters. Among the total storage capacity of large reservoirs, Fengman and Baishan reservoirs on the main stream of Songhua River have a storage capacity of 15.563 billion cubic meters, accounting for 64.7% of the total storage capacity of large reservoirs in the basin, while the flood control storage capacity of reservoirs is 2.652 billion cubic meters, accounting for 41.3% of the total flood control storage capacity of large reservoirs.

22 large reservoirs control a drainage area of 104100 square kilometers, accounting for 18.7% of the total drainage area. There are 103 medium-sized reservoirs with a total storage capacity of 2.76 billion cubic meters, but the flood control storage capacity is small, and most of them are

built for farmland irrigation. The long-distance water diversion project from Songhua River to Changchun was started in September 1994 and officially opened in November 1998. The water diversion project diverts water from Shitoumen reservoir of Songhua River in Jilin Province to Changchun, with a length of 63 km, which can delay the water shortage in Changchun.

Fengman Hydropower Station (Fig.2-39)

Fig.2-39 Fengman hydropower station

Fengman Hydropower Station was built on the Songhua River and located in Jilin City, Jilin Province. It is the first large-scale hydropower station in China. It is known as the "mother of hydropower in China". It was built in 1937. The first unit began to generate electricity in 1943. At that time, the power generation scale was small, and it was damaged on the eve of liberation. After the founding of the people's Republic of China, it has been vigorously repaired and reconstructed by the government and has become the main power plant of the Northeast power grid. In 1988, a total of 10 units were installed with a total installed capacity of 720000 kW after the second phase expansion project was launched. The total installed capacity reached 1.025 million kW after the third phase expansion project was completed.

Fengman Hydropower Station has a dam height of 91.7 m and a dam length of 1080 m, which makes the lake water form a drop of 67 m. It flows straight down, such as Bai Lian hanging, spraying beads and splashing jade, which is very spectacular. Songhua Lake on the dam is a water control hub for comprehensive utilization of power generation, flood control, irrigation, shipping, aquaculture, urban water use, tourism scenic spots and so on.

Baishan hydropower station (Fig.2-40)

Fig.2-40 Baishan hydropower station

Baishan hydropower station is the largest hydropower station in Northeast China. It is located in Baishan Town, Huadian City, Jilin Province, upstream of Songhua River. It was officially built in November 1981. The main power house is 54 meters high and accommodates five vertical shaft Francis turbine generator units with a single unit capacity of about 300000 kW. The total installed capacity is 1.7 million KW and the annual power generation is 2.037 billion kwh, which is sent to the Northeast power grid through 220 kV transmission line.

The dam of Baishan hydropower station is a three-core circular concrete gravity arch dam, with a maximum dam height of 149.5 m, a crest arc length of 676.5 m, and a maximum water storage capacity of 6.4 billion cubic meters of Baishan reservoir.

Baishan hydropower station is a large-scale backbone power station focusing on power generation, with comprehensive benefits such as flood control, ice cream prevention and aquaculture.

Hongshi Hydropower Station (Fig.2-41)

Fig.2-41 Hongshi hydropower station

Hongshi hydropower station is also located in Huadian City, Jilin Province, in the upper reaches of Songhua River, under the jurisdiction of Baishan power plant. Hongshi hydropower station is equipped with four 50000 kW axial-flow fixed propeller turbine generator units. At the end of 1985, the first unit generated power, with a designed power generation capacity of 440 million kwh, and supplied power to Jilin through 66 kV transmission line.

The dam of Hongshi hydropower station is a concrete gravity dam with a maximum dam height of 46 m and a dam length of 438 m. The maximum storage capacity of Hongshi reservoir is 284 million cubic meters.

(2) Shipping

The navigation mileage of Songhua River is 1447 kilometers. Navigable steam turbines below Jilin and Qiqihar; 1000-ton river ships below Harbin; Mudanjiang River, Tongken River and Nenjiang river section from Qiqihar City to Nenjiang County can be navigable by wooden boats. The navigation period is from middle of April to early November.

The abundant products and developed industrial and agricultural production in the Songhua River Basin have promoted the development of water transportation in the Songhua River. The transportation business is very busy, especially in the main stream of the Songhua River. It is the main water transportation trunk line in Northeast China, and the freight volume accounts for about 95% of Heilongjiang water system. The main materials transported are wood, grain, building materials, coal, steel and its products, daily necessities, etc.

The main ports of Songhua River include Harbin, Jiamusi, Qiqihar, Mudanjiang and Jilin. Among them, Harbin and Jiamusi are the most important, with night navigation and mechanized loading and unloading equipment. Harbin (Fig.2-42) is a transit port for railway and water transportation. The port conditions are good, and ships can still enter the port with full load in dry season. Due to the influence of river distribution, the role of Harbin port is mainly limited to the northeast.

Fig.2-42 Shipping in Harbin section of Songhua river

2.2 Urban Development

Songhua River basin administrative region involves 25 prefectures (cities, prefectures and leagues) and 105 counties (banners, districts and cities) in Heilongjiang, Jilin and Inner Mongolia. Important cities include Harbin, Qiqihar, Jilin, Changchun, Jiamusi, Mudanjiang, Hegang, Daqing, Songyuan and Ulanhot. The study area does not involve Inner Mongolia, mainly including the areas covered by Heilongjiang and Jilin Province.

The Nenjiang River Basin mainly flows through Hulunbuir City, Qiqihar City, Heihe City, Suihua City, Xing'an League, Daqing City, Baicheng City, Tongliao City, Songyuan City, etc; The second Songhua River mainly flows through Fushun City, Tonghua City, Liaoyuan City, Jilin City, Siping City, Changchun City, Harbin City, etc; The main stream of Songhua River mainly flows through Harbin, Qiqihar, Yichun, Heihe, Suihua, Jilin, Changchun, Songyuan, Jiamusi, Qitaihe, Hegang, Yanbian Korean Autonomous Prefecture, Mudanjiang, etc., including Harbin, the capital of Heilongjiang Province, Changchun, the capital of Jilin Province, Jilin, Qiqihar and Daqing, Jiamusi and other cities are important cities in Three Northeastern Provinces. In 2017, the total population in the Songhua River Basin was about 90.8 million, accounting for about 4.1% of the total population in China. Average population density is about 101 persons / km^2, which is lower than national average population density (142.76 / km^2). A densely populated Songnen Plain centered on Harbin and Changchun has been formed. The spatial distribution of population is most concentrated in the central and eastern plains and hilly transition areas of the basin, and the mountainous areas at the edge of the basin are sparsely populated. The urbanization rate reached 49.8%. The total GDP is about 1.8 trillion yuan, and the per capita GDP is 28000 yuan, which is slightly lower than the national average. On the whole, it is at the medium level in China.

CHAPTER 2: CURRENT SITUATION OF URBAN DEVELOPMENT AND POLLUTION SOURCE DISTRIUTION IN SONGHUA RIVER BASIN

For social and economic conditions of Jilin Province in 2017, a regional GDP of 1528.894 billion yuan is achieved, and an increase of 5.3% over the previous year at comparable prices is made. Among them, the added value of the primary industry was 142.921 billion yuan, an increase of 3.3%; The added value of the secondary industry was 701.285 billion yuan, an increase of 3.9%; The added value of the tertiary industry was 644.688 billion yuan, an increase of 7.5%. According to the resident population, the per capita regional GDP of the whole Province reached 56102 yuan, an increase of 6.0% over the previous year. The structure ratio of the three industries is 9.3:45.9:44.8, and the contribution rates to economic growth are 6.9%, 36.9% and 56.2% respectively.

For social and economic conditions of Heilongjiang Province in 2017, a regional gross domestic product (GDP) of 1619.999 billion yuan is achieved, and an increase of 6.4% over the previous year in terms of comparable value is made. Among them, the added value of the first GDP was 296.88 billion yuan, an increase of 5.4%; The added value of the secondary industry was 428.97 billion yuan, an increase of 2.9%; The added value of the tertiary industry was 894.14 billion yuan, an increase of 8.7%. The tertiary industrial structure is 18.3:26.5:55.2. Per capita GDP reached 42699 yuan, and an increase of 6.7% over the previous year is made. The added value of the non-public economy was 863.46 billion yuan, an increase of 7.8% over the previous year, accounting for 53.3% of the provincial GDP. There are 235000 non-public economic enterprises in the province, with 3158000 employees, 779.86 billion yuan of fixed asset investment, 10.22 billion US dollars of total import and export value and 103.9 billion yuan of tax revenue.

The key factories in the Songhua River Basin mainly come from Heilongjiang and Jilin Provinces. The number of enterprises in the two Provinces accounts for 84% of the whole basin, and they are mainly located in 13 prefecture level cities, accounting for more than 80%. They are the main control areas (Fig. 2-43). The key industries are agricultural and sideline processing, papermaking, beverage manufacturing and petrochemical industry; Petrochemical (petrochemical, chemical, coal chemical) and pharmaceutical industries are the main contributors of heavy metals and toxic organics in the Songhua River, with a high proportion of high-risk pollution sources; The industrial layout of key industries and the rapid development of regional economy will still exert great pressure on the restoration of water ecological integrity in Songhua River Basin.

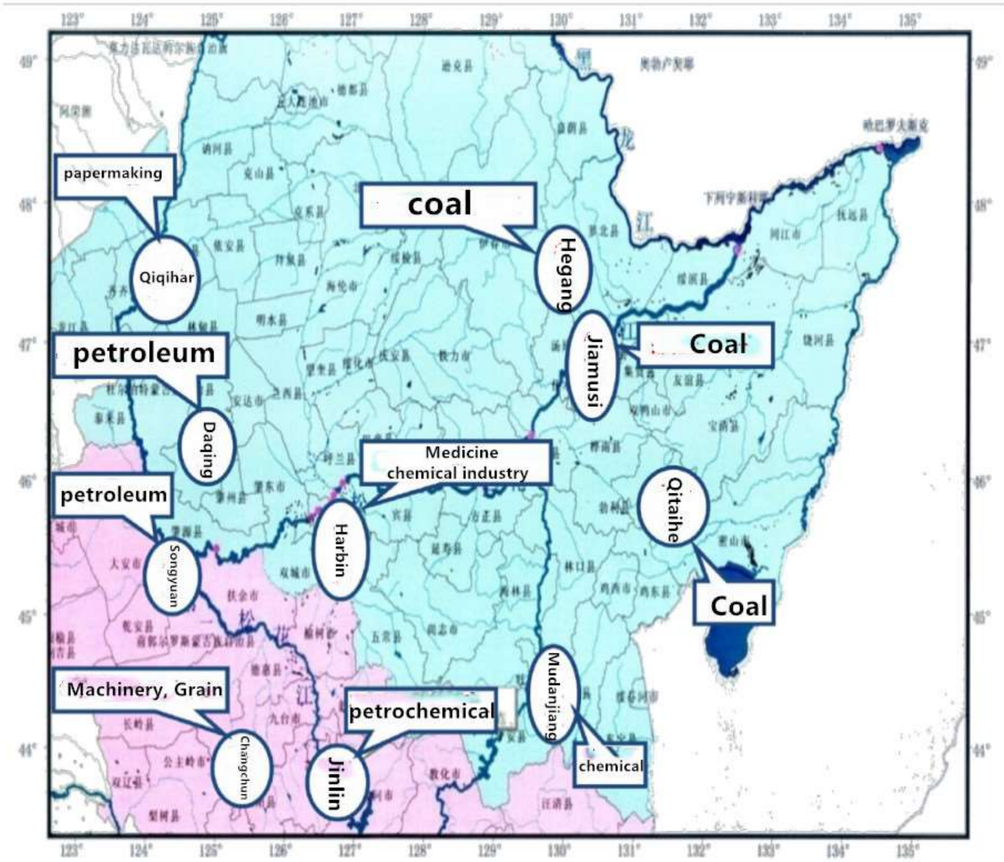

Fig. 2-43 Distribution characteristics of key industries in Songhua river

2.3.Distribution of Pollution Sources

2.3.1.Division of Pollution Sources

Water pollution sources can be divided into point sources, non-point sources, also known as non-point sources, and endogenous sources. The point source mainly comes from the centralized discharge of industrial and domestic sewage, and the non-point source pollution comes from a wide range of sources, mainly from rural domestic sewage, dissolved solid waste, chemical fertilizers and pesticides, decentralized livestock and poultry breeding, water and soil loss, etc. the endogenous mainly refers to the release of stream sediments.

2.3.2.Investigation of Pollution Sources

(1) Domestic sewage survey

The urban domestic sewage in Songhua River Basin is discharged into the sewage treatment plant. Rural domestic sewage pipelines have not been completed. Rural domestic sewage is mainly splashed on the ground or poured on small rivers and ditches. A large amount of domestic sewage discharged for a long time in some places leads to black and smelly inflow, which is washed by rainfall. With the rainwater flowing into rivers, lakes and reservoirs, resulting in serious pollution of the water environment. The main pollutants of domestic sewage are nitrogen, phosphorus, etc.

(2) Industrial wastewater survey

The industries in Songhua River Basin are mainly heavy industry and chemical industry, the main pollutants of heavy industry pollution sources are heavy metals, and the main pollutants of chemical industry are organic substances.

(3) Investigation of solid waste pollution

As the rural population is scattered, and most rural areas do not have designated waste stacking sites and special waste collection, transportation, landfill and treatment systems. In addition, some villagers in rural areas have poor awareness of environmental protection, and many solid wastes that are difficult to recycle, such as crop straw, old clothes, disposable plastic products, waste batteries, light tubes, light bulbs, etc., are dumped at random in the fields, roadsides, at the foot of mountains and streams. Because these wastes are difficult to decompose, there are more and more exposed garbage in rural areas, which has seriously affected the living environment in rural areas. With the passage of time, the mixed garbage rots, stinks, ferments and even reacts. It will not only release gases harmful to human health, but also the leachate of garbage will pollute the water body.

(4) Investigation on chemical fertilizer and pesticide pollution

Songhua River Basin is an important commercial grain base in China. The application of chemical fertilizers and pesticides has become an important way to improve the level of land output. This modern agricultural production is also the most important source of non-point source pollution. In agricultural production activities, the unreasonable application of chemical fertilizer leads to nitrogen, phosphorus and other nutrients, pesticide residues and other organic or inorganic pollutants entering the water body through farmland surface runoff and farmland leakage. Cause serious pollution of water environment.

(5) Investigation on pollutant emission from decentralized livestock and poultry breeding

We didn't pay much attention to livestock and poultry breeding in the past, but its pollution to the environment is also quite serious. For example, the pollutant emission of a pig is equivalent to that of 7 people, and the emission of a horse is equivalent to that of 20 people. Therefore, the impact of livestock and poultry breeding pollution on water environment can not be ignored.

(6) Soil and water loss pollution survey

Songhua River Basin belongs to monsoon climate, with concentrated precipitation. The precipitation in rainy season often reaches 60% - 80% of the annual precipitation, and there are many rainstorms. In addition, food production is unilaterally emphasized, the comprehensive development of agriculture, forestry and animal husbandry is ignored according to local conditions. Forests are indiscriminately cuts down, and even tree roots and lawns are dug. The sharp reduction of trees and the exposure of the earth’s surface have exacerbated soil erosion. Soil erosion mainly brings nitrogen and phosphorus enrichment and sedimentary pollution.

According to the above investigation methods, the COD, ammonia nitrogen, total nitrogen and total phosphorus of river inflow in non-point source pollution sources and their contribution rate in

Songhua River Basin are preliminarily obtained. It is shown in Table 2-1 for details. Compared with the point source survey results of Songhua River Basin, the overall situation of pollution sources in Songhua River Basin is obtained, which is shown in Table 2-2.

Table 2-1 Survey results of non-point source contribution rate in Songhua river basin

Investigation item	COD		Ammonia nitrogen		Total nitrogen		Total phosphorus	
	t/a	%	t/a	%	t/a	%	t/a	%
Domestic sewage	40577.3	12.0	2590.9	8.5	5181.7	2.0	1052.5	1.5
Solid waste			118.6	0.4	1185.8	0.5	1242.4	1.7
Fertilizers and pesticides			12511.1	40.8	125111.8	48.9	32801.4	45.3
Livestock and poultry	297986.8	88.0	7379.6	24.1	44085.0	17.2	16887.7	23.3
Soil erosion			8046.6	26.3	80466.3	31.4	20400.0	28.2
Songhua River Basin	338564.1	100.0	30646.8	100.0	256030.6	100.0	72384.0	100.0

Table 2-2 Comparison of point + non-point source contribution rate in Songhua river basin

Investigation item	COD		Ammonia nitrogen		Total nitrogen		Total phosphorus	
	t/a	%	t/a	%	t/a	%	t/a	%
Amount of non-point source entering the river	338564.1	42.6	30646.8	45.4	256030.6	77.8	72384.0	86.7
Amount of point source entering the river	455309.0	57.4	40561.7	54.6	70657.0	22.2	12353.6	13.3
Total amount of pollutants entering the river	793873.1	100.0	71208.5	100.0	326687.6	100.0	84737.6	100.0

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Chapter 3

METHOD OF DATA COLLECTING, EXPERIMENT AND ANALYSIS

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3.1 Research Route

Based on the data of pH, DO, COD, heavy metals, NH_3-N and other water quality monitoring indicators of 11 sections, which is in Songhua River Basin from 2016 to 2019, the trend, periodicity and fluctuation of water quality monitoring indicators and the contribution of water quality indicators to water quality categories are analyzed.

The main pollutants in Songhua River Basin are obtained through the analysis of monitoring data. At the same time, effective removal methods of main pollutants are studied through the experiments.

Through the total amount control of pollution sources, the variation law of water quality in typical sections of Songhua River Basin is studied, and some suggestions on water environment protection are put forward.

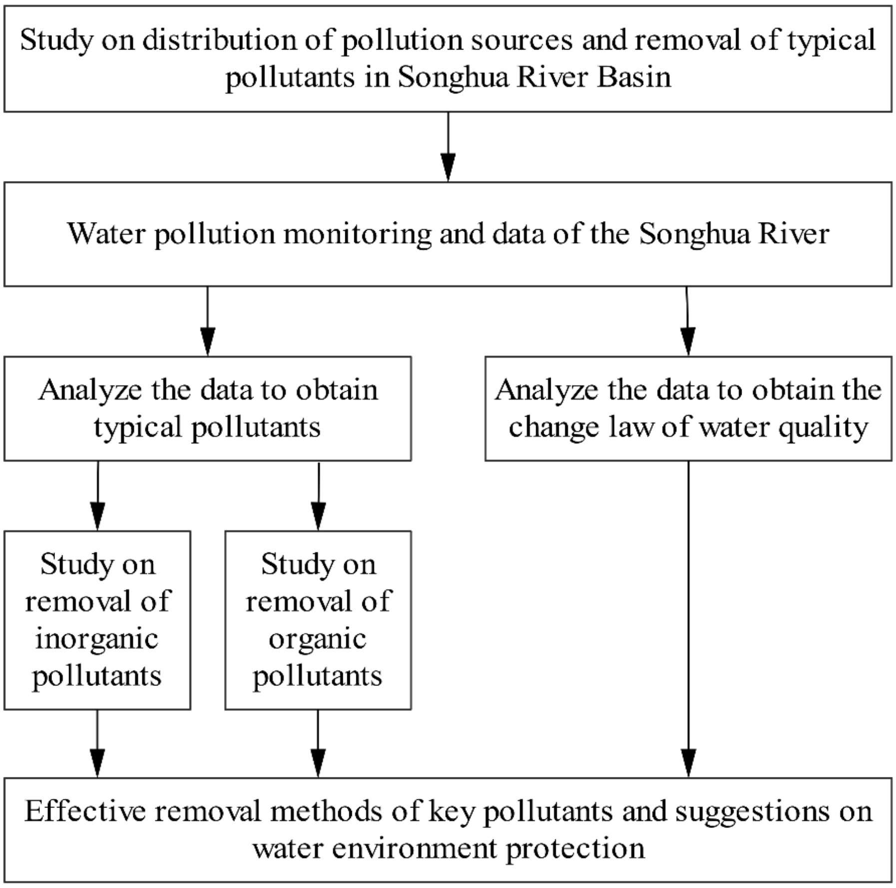

Fig. 3-1 Research roadmap

3.2 Data Collecting

3.2.1 Selection Of Section

Based on the data of pH, DO, COD, heavy metals, NH_3-N and other water quality monitoring indicators of 11 sections in Songhua River Basin from 2016 to 2019, the trend, periodicity and fluctuation of water quality monitoring indicators and the contribution of water quality indicators to water quality categories are analyzed.

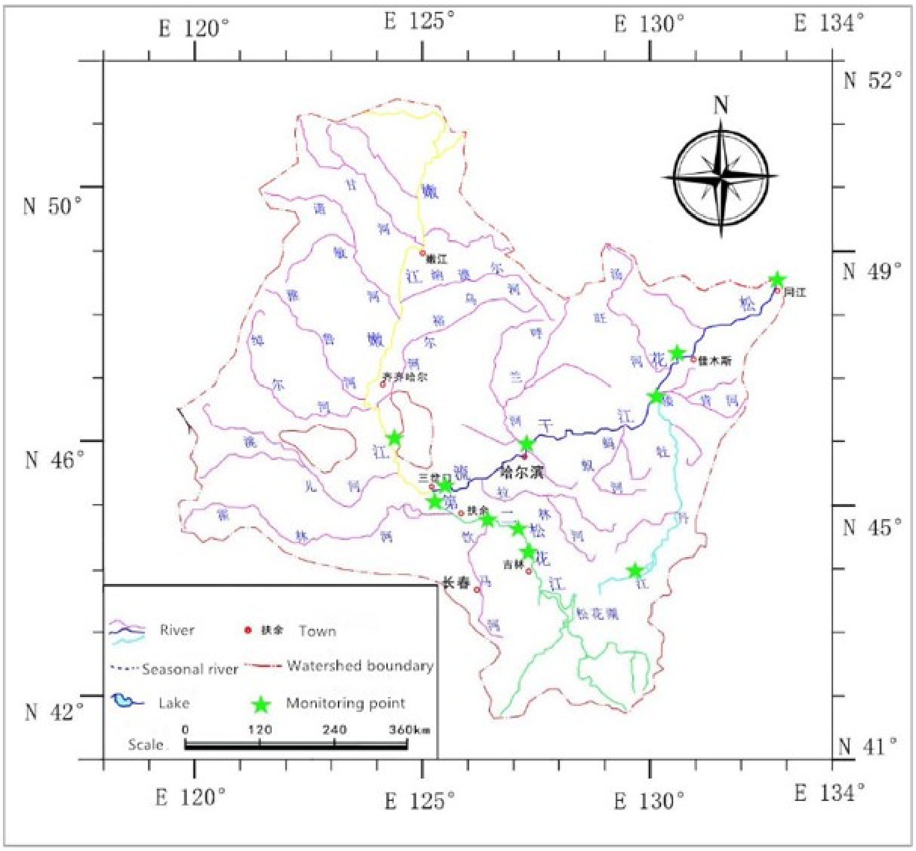

Fig 3-2 Distribution of water quality monitoring sections

Table 3-1 Summary table of basic conditions of water quality monitoring sections

Name of monitoring section	Coordinate	Position	Primary function area	Water functional area	Secondary function area	Water functional area	Control target
Jinlin Xilangkou	N44°18′11″ E126°29′37″	The second Songhua River	Jilin、Changchun Development Zone	Majia-Wujintun Bridge	Jilin、Changchun Agricultural Development Zone	Tongqi River-Songmu	III
Changchun Songhuajiang Village	N44°46′8″ E125°55′37″	The second Songhua River	Fuyu Protection Zone	Wujintun Bridge-Halamaodu	——	——	III
Songyuan Songlin	N45°12′28″ E124°43′33″	The second Songhua River	Jinlin and Heilongjiang Buffer Area	Shiqiao-Sancha River	——	——	III

Name of monitoring section	Coordinate	Position	Primary function area	Water functional area	Secondary function area	Water functional area	Control target
Zhaoyuan	N45°28′15″ E124°59′20″	Main stream of Songhua River	Jinlin and Heilongjiang Buffer Area	Sancha River-Linjiang Village	——	——	III
Tongxin Island in Jiamusi	N46°50′41″ E130°21′19″	Main stream of Songhua River	Jiamusi Development Zone	Tangwang River inlet-Fuhe Village	Jiamusi agricultural and industrial zone	Tangwang River inlet-Jiamusi	IV
Tongjiang	N47°41′15″ E132°29′3″	Before remitting to Heilong River	Sanjiangkou Fish reserve	Tong jiang-Heilong River	——	——	III
Baishatan in Baicheng	N46°14′15″ E124°57′20″	Nen River	Tailai County Development Zone	Jiangqiao Village-Guangrong Village	Tailai County fishery area	Jiangqiao Village-Guangrong Village	III
XIndian in Dunhua	N43°44′16″ E126°41′49″	Jilin and Heilongjiang junction	Jinlin and Heilongjiang Buffer Area	Dashanzui-Jingbo Lake	——	——	III
Yilan in Mudan River	N46°18′52″ E129°33′1″	Mudan River Estuary	Yilan County reserve	Lianhua Lake-Songhua River	——	——	III
Yinma River Estuary	N44°52′14″ E125°45′48″	Before Yinma River flows into Songhua River	Nongan and Dehui Buffer Area	Yitong River-The Second Songhua River	——	——	III
Hulan River Estuary	N46°56′40″ E125°41′49″	Before Hulan River flows into Songhua River	Hulan Development Zone	Shenshu Village-Songhua River	Hulan River Transition Zone	Hulan River Railway Bridge-Songhua River	IV

3.2.2 Study Period

The water quality index monitoring data used in this paper belongs to the period from 2008 to 2018. The trend, periodicity, fluctuation (randomness) of water quality monitoring index value, the contribution of water quality index to the change of water quality category and the sensitivity of water quality category to water quality index are studied from 2008 to 2018. Research period of water quality target accessibility analysis is fixed from 2019 to 2025.

The data used in this paper mainly come from the following units and platforms: the river section water quality index monitoring data comes from China environmental monitoring station (http://www.cnemc.cn/sssj/szzdjczb/index.shtml). The weekly report of automatic water quality monitoring can be downloaded from the website. In the downloaded weekly report, the weekly pH, dissolved oxygen, permanganate index, ammonia nitrogen, water quality grade and other relevant data of national key water quality monitoring sections can be found. The statistical data used for the analysis of change law of water quality indicators are mainly from the "national data" platform of the National Bureau of statistics of the People’s Republic of China (https://data.stats.gov.cn/index.htm), the statistical data of data platform can be used to obtain the target data after screening under different conditions. The cartographic data comes from "China Center" (https://www.osgeo.cn/) and refer to the data service platform of the Ministry of natural resources of the People’s Republic of China (http://www.mnr.gov.cn/sj/sjfw/). The mapping of OSGeo China Center can be obtained by following the official account of WeChat's open-source collection. The service platform of the Ministry of natural resources needs to apply to the platform after registration, and can be used after approval. Some materials need to be purchased and used for payment.

3.3 Experiment Design

3.3.1 Determination Method of Heavy Metals

The drugs and instruments required for collection of sediment samples, the determination of basic physical and chemical indexes and determination of heavy metals in this experiment are shown in Table 3-2 and Table 3-3.

Table 3-2 Instruments and equipment

No.	Equipment name	Models	Manufacturer
1	Electronic balance	AEL-200	Xiangxi Balance Factory
2	Microwave Digestion Apparatus	CEM-Mars Xpress	American Peian Technology Co., Ltd.
3	Heating plate	EG20A plus	Henan Bojin Instrument Co., Ltd.
4	Constant temperature oven	DH-101-3	Dongguan Hualubao Machinery Equipment Co., Ltd.
5	TOC meter	SSM-5000A	Shimadzu Corporation (Japan)
6	Vacuum Freeze Dryer	Drying device	Guangzhou Gangran Electromechanical Equipment Co., Ltd.
7	Particle size analyzer	Hydro 2000Mu	Malvern Instruments, UK
8	ICP-MS	7500 series	Agilent Technologies, Inc.
9	CNC ultrasonic cleaner	Scientz-5000TQC	Deka Precision Measuring Instrument Co., Ltd.
10	Constant temperature water bath	HH-WO	Haiyikai Instrument Equipment Co., Ltd.
11	Constant temperature oscillator	HY-5	Changzhou Aohua Instrument Co., Ltd.
12	Centrifuge	TD5A	Changzhou Wanhe Instrument Manufacturing Co., Ltd.

Table 3-3 Reagents used in experiments

No.	Reagent	Model	Manufactor
1	Hydrofluoric Acid	Guaranteed Reagent	Beijing Hongtu Chemical Co., Ltd
2	Nitric Acid	Analytical purity	Beijing Hongtu Chemical Co., Ltd
3	Hydrogen Peroxide	Analytical purity	Beijing Hongtu Chemical Co., Ltd
4	Hydrocarbon Amine Hydrochloride	Analytical purity	Beijing Hongtu Chemical Co., Ltd
5	Glacial Acetic Acid	Analytical purity	Beijing Hongtu Chemical Co., Ltd
6	Sodium Hydroxide	Analytical purity	Beijing Hongtu Chemical Co., Ltd

The determination of heavy metals in surface sediment samples includes the determination of total amount and occurrence form content of heavy metals, which mainly includes 11 kinds of heavy metals such as Cr, Ni, Zn, Cu, as, CD, Pb, V, Co, Sn and Sb.

Prepare the reagents and instruments required for the experiment. Prepare 2% nitric acid solution and make it into an acid cylinder. In order to reduce the experimental error, all experimental instruments shall be soaked in the acid cylinder for more than 24 h before the experiment. Weigh 0.100 g of freeze-dried and 100 mesh sieved sediment sample and put it into the digestion tube, add 5 ml of concentrated HNO_3, 2 ml H_2O_2 and 3 ml HF, close the cover, put the digestion tube in the microwave digestion instrument for digestion, cool to room temperature after digestion, remove the cover of the digestion tube, put the digestion tube in a water bath pot, and keep the constant temperature (85°C) for 30 minutes until there is no red substance, Then pour the digestion solution into the crucible and put it on the heating plate to drive out the acid. After driving out the acid, transfer the digestion solution to a 50ml colorimetric tube, dilute it to the scale with ultrapure water, shake it well, and the solution passes 0.45 μm mixed fiber membrane, stored at 4°C, and the total content of heavy metals was determined by ICP-MS.

In this experiment, the occurrence forms of heavy metals were studied by BCR fractional extraction. Preparation of solution: ultrapure water is used as experimental water, superior pure hydrofluoric acid is used, and analytical pure is used for other reagents.

(1) Acetic acid 0.11 mol/l: In the fume hood, 25 ± 0.2 ml glacial acetic acid is added to about 0.5 L (500 ml) distilled water (1L polypropylene or polyethylene bottle), it is continued to dilute to 1 L with distilled water, 250 ml (0.43 mol/l) of this solution is taken, and then is diluted to 1L.

(2) Hydroxylamine hydrochloride $NH_2OH \cdot HCl$, 0.5 mol/1: 34.75 g $NH_2OH \cdot HCl$ is dissolved in 400 ml distilled water, the solution is transferred to a 1L long neck volumetric flask, 2 mol / l HNO_3 of 25 ml is transferred into the solution with a pipette, and the volume is fixed to 1L with distilled water.

(3) Hydrogen peroxide H_2O_2 8.8 mol/1: Hydrogen peroxide provided by the manufacturer is used as the supplied sample, and pH is controlled to be stable between 2 – 3 (preferably pH = 1.5).

(4) 1 mol/L ammonium acetate solution: 77.083 g ammonium acetate (CH_3COONH_4) is weighed, one liter is prepared, and pH is adjusted to 2.0 with concentrated nitric acid. Experimental steps of BCR fractional extraction are followed:

Exchangeable state: the sample is dried by natural air and sieved by 100 mesh. 0.5000 g of sample is weighed into a 100 ml polypropylene centrifuge tube, 40 ml of 0.11 mol/L HAC extract is added and shaken at room temperature for 16 h (250 R/min) to ensure that the mixture in the tube is in suspension, and then is centrifuged (4000 R/min, 20 min), the supernatant in a polyethylene bottle is poured out, it is stored in a 4℃ refrigerator, and the exchangeable content of heavy metals is determined by ICP-MS. 20 ml high-purity water is added to clean the residue, shaken for 20 min, is centrifuged and the cleaning solution is discarded.

Reducible state: 0.5 mol/L $NH_2OH \cdot HCl$ is added to the residue extracted in the first step, 40 ml is extracted, shaken for 16 h, and centrifuged. The other operations are the same as in the first step.

Oxidizable state: 10 ml of 8.8 mol/l H_2O_2 is slowly added to the residue extracted in the second step, the centrifuge tube is covered, oscillated occasionally, digested at room temperature for 1h, then heated in a water bath to 85℃ for 1h, the cover for digestion for the first 0.5 h is removed, shaken by hand, it is heated up until the solution is nearly dry (reduced to 1-2 ml), 10 ml H_2O_2 is added and the above process is repeated. After cooling, 50 ml of 1 mol/l $1NH_4OAC$ extract is added and shaken at room temperature for 16 h. The rest operations are the same as the first step.

Residue state: The remaining residue in the centrifuge tube in the oven is dried, about 0.2 g sediment is weighed and put into the digestion tube, 5 ml concentrated HNO_3, 2ml H_2O_2 and 3 ml HF are added, the cover is closed, the digestion tube in the microwave digestion instrument is put for digestion, cooled to room temperature after digestion, the cover of the digestion tube is removed, the digestion tube in the water bath pot is put and kept for the constant temperature (85℃) for 30 min. Until there is no red substance, then the digestion solution is poured into the crucible and put on the heating plate to drive out the acid. After driving out the acid, the digestion solution is transferred to a 50 ml colorimetric tube, diluted to the scale with ultrapure water, shaken well, and the solution passes 0.45 μm mixed fiber membrane, stored at 4℃, and the content of heavy metal residue was determined by ICP-MS.

3.3.2 Experimental Method

In addition to the data directly obtained from the monitoring points, other physical and chemical indexes are determined by international standard methods.

COD adopts potassium dichromate method.

Ammonia nitrogen is determined by Nessler reagent spectrophotometry.

3.4 Analysis method

3.4.1 Correlation Analysis and Principal Component Analysis

The pollution sources of heavy metals in sediments are generally divided into natural sources and human activities, and there is a certain correlation between heavy metals from the same source. The correlation analysis between heavy metals in this study is expressed by Pearson correlation coefficient.

Principal component analysis is a very important method in multivariate statistical analysis. They are combined into fewer factors through the correlation coefficient between variables through dimensionality reduction processing and analysis of the original data, and the pollution source of heavy metals in sediments is determined through the correlation between factors. This method can reduce the dimension and maintain effectiveness of the data. Generally, the factor with characteristic value greater than 1 is extracted as the main component. Through the load degree of heavy metals between different factors, the pollution source of heavy metals in Songhua River Sediments in different water periods is further judged according to local natural conditions and human activities.

3.4.2 Mathematical Model of Seasonal Kendall Test

In this paper, the seasonal Kendall test mathematical model combined with Sen slope estimation formula is used to estimate the pH of water quality monitoring indicators at typical sections of Songhua River Basin from 2008 to 2018 Dissolved oxygen (DO), permanganate index (COD_{Mn}), ammonia nitrogen (NH_3-N). The seasonal Kendall test mathematical model is widely used in the current research on the change trend of water quality. The research method of model is to compare the water quality index values in the same season within a cycle, which can greatly reduce the impact of the periodic change of flow, researching on the change trend of water quality; and during the research process, only the data is considered according to the relative size in the development direction of time series, the influence of missing measured values and disaster data on the change trend of water quality can be reduced to a certain extent. Therefore, this method is an ideal model method of studying the change trend of water quality and the interannual change law of water quality indicators.

(1) Model principle:

The seasonal Kendall test mathematical model belongs to the nonparametric test method. Zero assumes that H0 is a random variable (measured value of water quality index) independent of time. It is assumed that the water quality data of 52 seasons (52 weeks in a year) in a cycle have the same probability distribution.

The observation sequence x of water quality data for N years and P weeks is expressed as following:

$$X=\begin{bmatrix} x_{11'} & x_{12'} & \cdots & x_{1P} \\ x_{21'} & x_{22'} & \cdots & x_{2p} \\ \cdots & \cdots & \cdots & \cdots \\ x_{n1} & x_{2p} & \cdots & x_{np} \end{bmatrix} \quad (3\text{-}1)$$

Where xnp is the measured value of water quality index in the p-th season of the n-th cycle.

a). For the ith season (where I ≤ P) of P seasons, the following calculation is performed:

definition:

$$G(x_{ij}-x_{ik})=\begin{cases} 1, 当(x_{ij}-x_{ik})>0 \\ 0, 当(x_{ij}-x_{ik})=0 \\ -1, 当(x_{ij}-x_{ik})<0 \end{cases} \quad (3\text{-}2)$$

Compared with the water quality monitoring data in season I, if the later water quality data index value is greater than the index value of the previous water quality data index, it is marked for "1"; If the later water quality data index value is less than the previous water quality data index value, it is marked for "- 1"; it is marked for "0" if they are equal.

$$S_i=\sum_{k=1}^{n-1}\sum_{j=k+1}^{n}G(x_{ij}-x_{ik}) \quad (i \leqslant k < j \leqslant n) \quad (3\text{-}3)$$

In the above formula, Si is the sum of signs in season I.

If Ni is the number of non-missing measured values in season I, then the number of difference data pairs that can be used as comparison in this season, which is Mi, then:

$$m_i=\sum_{k=1}^{n-1}\sum_{j=k+1}^{n}\left|G(x_{ij}-x_{ik})\right|=\frac{n_i(n_i-1)}{2} \quad (3\text{-}4)$$

Under the null hypothesis, the random sequence Si (I = 1,2..., P) approximately obeys the normal distribution, and the mean e (SI) and variance of Si are calculated. Since Si approximately conforms to the normal distribution, there are:

$$E(S_i)=0 \quad (3\text{-}5)$$

$$\sigma_i^2=Var(S_i)=\frac{n_i(n_i-1)(2n_i+5)}{18} \quad (3\text{-}6)$$

When Ni is a non-missed measurement value, the values of Ti water quality indicators are the same:

$$\sigma_i^2=Var(S_i)=\frac{n_i(n_i-1)(2n_i+5)}{18}-\frac{\sum_t t_i(t_i-1)(2t_i+5)}{18} \quad (3\text{-}7)$$

b). Study on the overall situation of P seasons

Order:

$$S = \sum_{i=1}^{p} S_i \qquad (3\text{-}8)$$

$$m = \sum_{i=1}^{p} m_i \qquad (3\text{-}9)$$

Under the null hypothesis, the mean and variance of P season are calculated as following:

$$E(S) = \sum_{i=1}^{p} E(S_i) = 0 \qquad (3\text{-}10)$$

$$\begin{aligned} \sigma^2 = Var(S\ ) &= \sum_{i=1}^{p} \sigma_i^2 + \sum_{ih} \sigma_{ih} \\ &= \sum_{i=1}^{p} Var(S_i) + \sum_{i=1}^{p} \sum_{i=h}^{p} Cov(S_i, S_h) \\ &= \sum_{i=1}^{p} \frac{n_i(n_i-1)(2n_i+5)}{18} \end{aligned} \qquad (3\text{-}11)$$

When the number of Ti (I = 1,2..., P) in the water quality index series in N years is the same, there are:

$$\sigma^2 = Var(S) = \sum_{i=1}^{p} \frac{n_i(n_i-1)(2n_i+5)}{18} - \frac{\sum_t t_i(t_i-1)(2t_i+5)}{18} \qquad (3\text{-}12)$$

Kendal study found that when n ≥ 10, s also obeys the normal distribution, and the standard deviation Z is:

$$Z = \begin{cases} \dfrac{S-1}{\left[\sigma^2\right]^{1/2}}, S > 0 \\ 0, S = 0 \\ \dfrac{S+1}{\left[\sigma^2\right]^{1/2}}, S < 0 \end{cases} \qquad (3\text{-}13)$$

c). Trend test

Define inspection measurement as τ= S / m, the original hypothesis is $|Z| \le Z_{\alpha/2}$ accepted in the two tailed trend test. Z here is: $FN(Z_{\alpha/2}) = \alpha/2$, FN is the standard normal distribution function, that is:

$$FN = \frac{1}{\sqrt{2\pi}} \int_{|z|}^{\infty} e^{-\frac{t^2}{2}} dt \qquad (3\text{-}14)$$

$$\alpha = \frac{2}{\sqrt{2\pi}} \int_{|z|}^{\infty} e^{-\frac{t^2}{2}} dt = (1 + erf \frac{t}{\sqrt{2}})\Big|_{|z|}^{\infty} \qquad (3\text{-}15)$$

$$\alpha = 1 - erf \frac{|z|}{\sqrt{2}} \qquad (3\text{-}16)$$

When taking the significant level α 0.1 and 0.01, when α< 1.0 indicates that the inspection is significant; When α< 0.1, it indicates that the inspection is highly significant; When α> 1.0, it indicates that the inspection effect is not significant. When τ< 0, it indicates that the index value shows a downward trend. When τ> 0, it indicates that the water quality index value shows an upward trend.

(2) Trend slope estimation combined with Sen slope estimation formula

The seasonal Kendall test mathematical model can be used to analyze the change trend of water quality indicators with time series, but the size of the change trend cannot be given quantitatively. The Sen slope estimation formula can be used to calculate the size of the trend, and the slope estimation formula can greatly reduce the impact of disaster value on the trend slope estimation value. The relevant calculation process is as following:

Let the slope estimate be B. for all slopes x_{ij}, x_{ik} ($i = 1,2,...,p; j = 1,2,...,n$) of any two water quality index values in the b_{ijk} seasonal time series, the following formula holds:

The overall situation of *P* seasons is as follows:

$$b_{ijk} = \frac{x_{ik} - x_{ij}}{k - j} \qquad (1 \le j < k \le n_i) \qquad (3\text{-}17)$$

$$b = \sum_{i=1}^{p} b_{ijk} \qquad (3\text{-}18)$$

The slope estimate *B* takes the median of all b_{ijk}.

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Chapter 4

ANALYSIS AND REMOVAL OF MAJOR POLLUTANTS HEAVY METAL

CHAPTER FOUR：ANALYSIS AND REMOVAL OF MAJOR POLLUTANTS HEAVY METAL

4.1 Analysis of Heavy Metal Pollutants

Heavy metals generally refer to metals with a density of more than 4.5 g/cm^3, including more than 40 kinds of heavy metals such as Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and Sb. Whether the air, soil, rivers or even food contain heavy metals, most heavy metals contain certain hazards. With the passage of time and the changes in environmental conditions, different types of heavy metals produced varying hazards. The water environment of basin mainly includes rivers, lakes, reservoirs, marine and industrial water, domestic sewage and other water bodies. Heavy metal pollution in water environment mainly refers to that the heavy metals discharged into the water body exceed the self-purification capacity of the water body, resulting in a series of changes in the water body, so the water quality is worsened and certain harm is caused to human health and organisms in the water. At home and abroad, with the rapid development of economy and the continuous expansion of various industries, the heavy metal pollution of river basin water environment is becoming more and more serious.

4.1.1 Content and Spatial Distribution of Heavy Metals in Sediments of Songhua River During Normal Water Period

4.1.1.1 Total Content and Spatial Distribution of Heavy Metals in Sediments of Songhua River in Normal Water Period

The total content of 11 heavy metals in surface sediments of Songhua River Basin in normal water period is shown in Table 4-1. The total content ranges of Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and Sb are 11.34 ~ 88.83, 5.21 ~ 66.54, 4.58 ~ 87.61, 7.34 ~ 46.02, 5.21 ~ 26.22, 0.08 ~ 2.09, 14.49 ~ 42.30, 16.00 ~ 187.12, 3.05 ~ 24.64, 6.18 ~ 16.64 and 0.53 ~ 2.21mg/kg respectively. The order of total content of 11 heavy metals is V > Zn > Cr > Cu > Ni > Pb > Sn > As > Co > Cd > Sb. Among them, the concentration of V is the largest, and its average value is 78.18 mg/kg; The concentration of sb was the lowest, with an average of 1.12 mg/kg; The second is Cd, with an average concentration of 1.14 mg/kg; The average concentration range of Co, As, Sn, Pb, Ni, Cu, Cr and Zn is 12.01 ~ 55.18 mg/kg. The average concentrations of Cr, Ni, Zn, Cu, V and Co are lower than the background value of surface sediments, showing no pollution or low pollution level, while the concentrations of As, Cd, Pb, Sn and Sb are higher than the background value, indicating that these heavy metals have certain pollution. The pollution of as and Sb is the most serious, and the concentration of heavy metals is 7 times of the background value; The contents of Cd and Sn were 3 times of the background value; The content of Pb is slightly higher than the background value. From the relationship with the background value, the pollution degree of 11 heavy metals is Sb > As > Sn > Cd > Pb > V > Cr > Cu > Zn > Ni > Co. The maximum coefficients of variation of Ni and Cd are 49.57% and 49.12% respectively, indicating that their spatial variability is large.

Table 4-1 Heavy metal concentration of sediments in Songhua River in September

	Average value	Maximum	Minimum	Coefficient of variation	Background value
Cr	51.38	88.83	11.34	36.92	63
Ni	24.87	66.54	5.21	49.57	57
Zn	55.18	87.61	4.58	33.78	86
Cu	28.12	46.02	7.34	31.11	38
As	13.76	26.22	5.21	34.52	1.9
Cd	1.14	2.09	0.08	49.12	0.35
Pb	24.49	42.30	14.49	19.11	15
V	78.18	187.12	16.00	43.56	99
Co	12.01	24.64	3.05	43.38	32
Sn	13.90	16.64	6.18	13.67	4.1
Sb	1.12	2.21	0.53	30.35	0.15

In September 2017, the content of heavy metals in 27 surface sediments of Songhua River Basin during normal water period ranged from 101.16 to 486.03 mg/kg, The average content is 313.54 mg/kg (Fig.4-1). The maximum concentration of heavy metals occurs at point DH6 (Huayuankou) of the second Songhua River section, with a concentration of 486.03 mg/kg, and the minimum value occurs at point SH13 of the main stream section of the Songhua River (Wenchun bridge), the concentration is 101.16 mg/kg. The average concentration of heavy metals in the second Songhua River section is 372.33 mg/kg, and the average concentration of heavy metals in the main flow section of the Songhua River is 292.54 mg/kg. Generally speaking, the concentration of heavy metals in the surface sediments of the second Songhua River section of the Songhua River in peacetime is higher than that in the main flow section of the Songhua River.

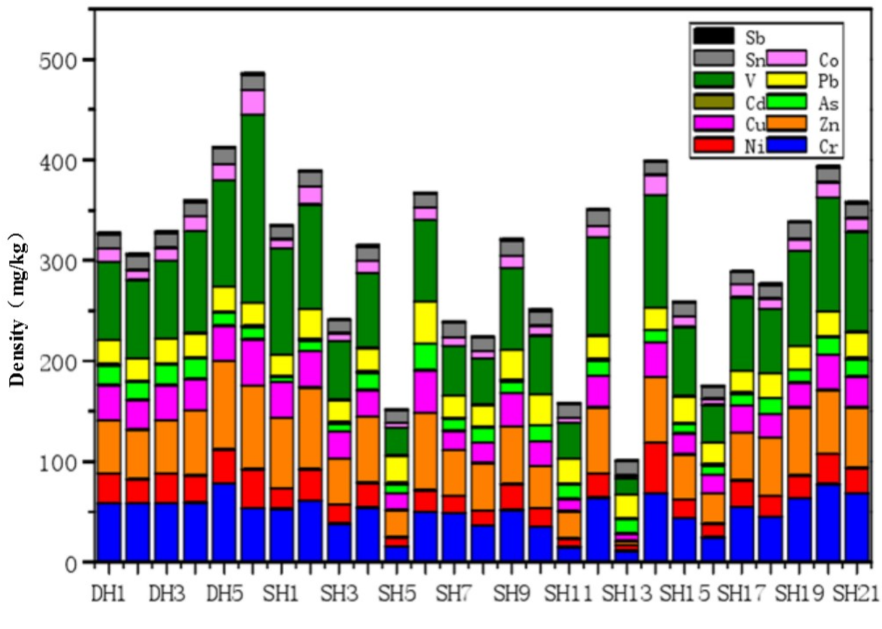
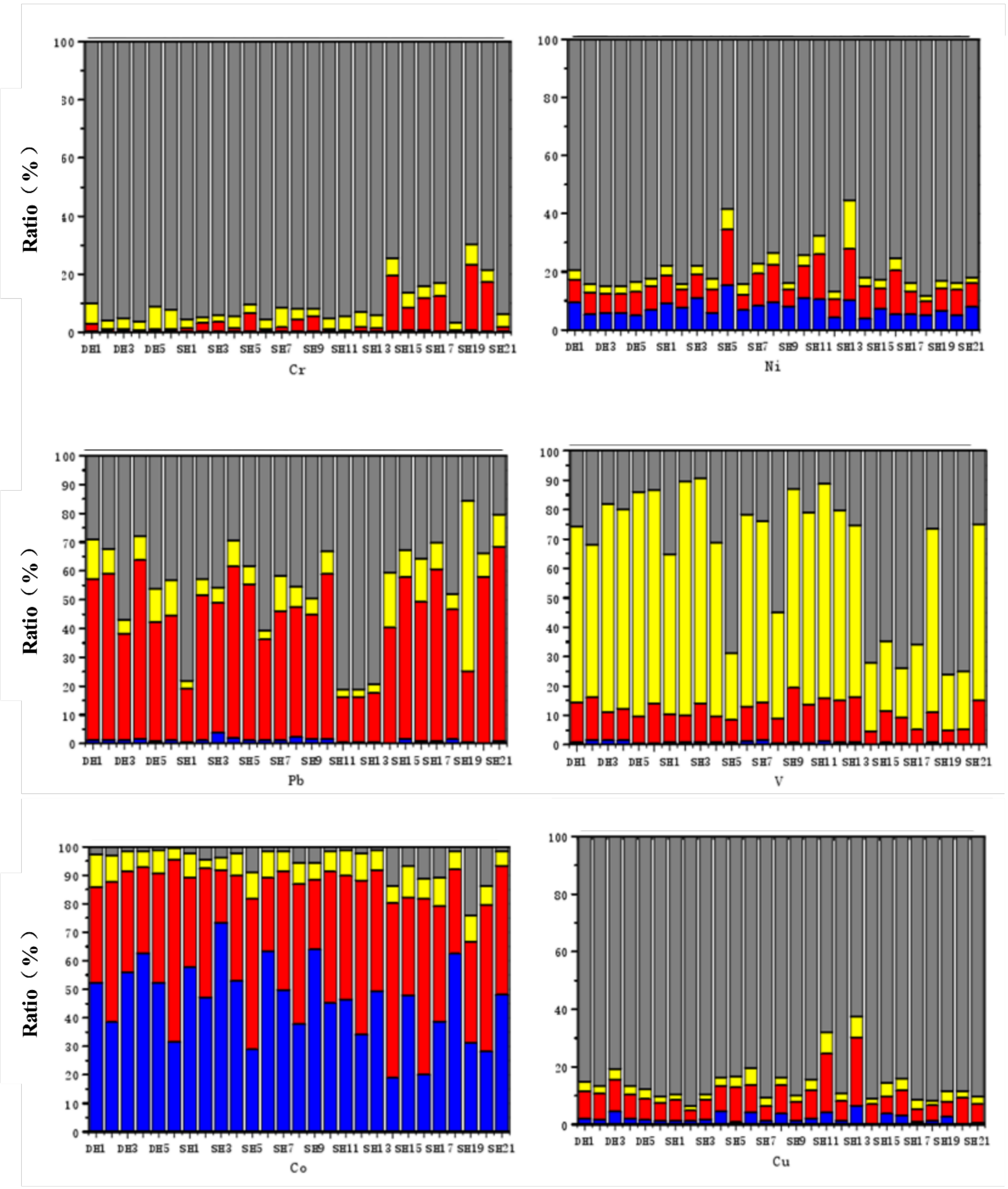


Fig. 4-1 Heavy metal concentration of sediments in Songhua river in September

In September 2017, the proportion of Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and Sb in the sediment of Songhua River in the normal water period is shown in Figure 4-2. The chemical forms of Cr, Ni, Cu, Cd, Sn and Sb are mainly in residue state, accounting for 56.89 ~ 96.79%, 55.33 ~ 88.41%, 62.55 ~ 91.67%, 89.33 ~ 98.34%, 97.35 ~ 98.89% and 94.38 ~ 98.67% respectively. The proportion of acid extracted state, reducible state and oxidizable state is very low, indicating that the migration and transformation ability of these heavy metals between different forms is low, and it has relatively stable chemical properties and low ecological risk, which is difficult to cause secondary pollution to the environment. Zn and Co are mainly in weak acid extraction state and reducible state. The proportion of weak acid extraction state is 11.65 ~ 75.57% and 20.02 ~ 63.97% respectively, and the proportion of reducible state is 8.14 ~ 42.33% and 18.48 ~ 64.02% respectively, indicating that the chemical properties of Zn and Co are unstable and the bioavailability is high. When the external condition changes, migration and transformation are present, secondary pollution to the environment is easy to cause, and attention must be paid to it. The proportion of the four forms of as is relatively uniform, accounting for 1.07 ~ 52.72%, 3.88 ~ 22.76%, 26.33 ~ 55.87% and 9.46 ~ 54.26% respectively. Pb is mainly reducible and residual, accounting for 15.9 ~ 62.08% and 20.38 ~ 81.25% respectively. V is mainly in oxidizable state and residual state, accounting for 18.98 ~ 79.32% and 9.48 ~ 76.05% respectively. It shows that As, Pb and V have certain chemical activity and bioavailability, and there are potential hazards.

Acid extraction state of heavy metals Reducible state and oxidizable state (F1 + F2 + F3) are called bioavailable forms. The higher the content of bioavailable forms, the easier it is to migrate and transform, resulting in secondary pollution. Therefore, bioavailable states (F1 + F2 + F3) should be considered in studying chemical forms of heavy metals. The order of proportion of bioavailable forms of heavy metals in sediments of Songhua River Basin in peacetime is Co (94.21%) > Zn (81.73%) > V (65.21%) > As (65.08%) > Pb (55.06%)> Ni (20.48%) > Cu (14.05%) > Cr (10.65%) > Cd (4.68%) > Sb (2.62%) > Sn (1.87%). The highest bioavailable forms of Co appear in DH6 (99.47%) of the second Songhua River section; the highest bioavailable forms of Zn, As, V and Pb appear in SH6 (98.54%), SH5 (90.54%), SH3 (90.52%) and SH19 (84.2%) of the main stream section of the Songhua River respectively, indicating that heavy metals are easy to cause secondary pollution at these points, which may have high ecological risk.


Ratio（%）
Cr
Ni
Ratio（%）
Pb
V
Ratio（%）
Co
Cu
DH1 DH3 DH5 SH1 SH3 SH5 SH7 SH9 SH11 SH13 SH15 SH17 SH19 SH21

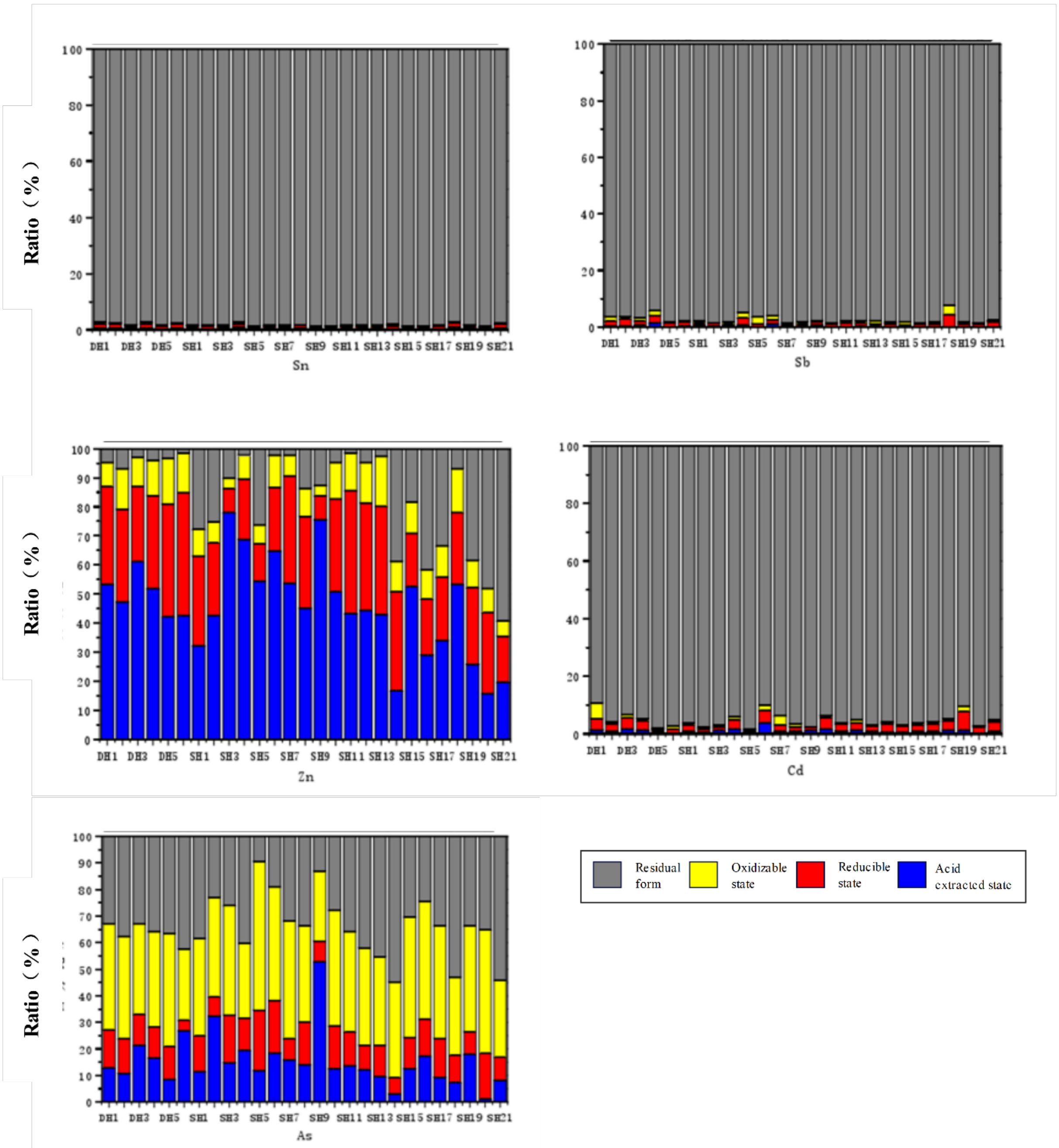


Fig.4-2 Characteristics of heavy metal forms in sediments of the Songhua river in September

4.1.1.2 Correlation Analysis of Heavy Metals in Surface Sediments in Normal Water Period

The correlation matrix of Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and sb11 heavy metals in Songhua River Sediments in normal water period is shown in Table 4-2. According to the correlation coefficient, among the 11 heavy metals, Cr, Ni, Zn, Cu, As, V and Co show a high positive correlation, with a significant correlation at the level of 0.01. Among them, the correlation coefficient between Ni and Co is the highest, 0.912, 0.861, and 0.814. It shows that these seven heavy metals have common pollution sources. Sn has negative correlation with Ni and Co, and the correlation coefficients are -0.415 and -0.175 respectively, indicating that the sources of Sn, Ni and Co are greatly different and non-interference with each other. Sn has a positive correlation with As and Pb, which is significantly correlated at the level of 0.05. The correlation coefficients are 0.438 and 0.398 respectively, indicating that Sn has similar pollution sources with As and Pb. There is a high positive correlation between Sb, As and Pb, which is significantly correlated at the level of 0.01. The correlation coefficients are 0.708, 0.501 and 0.566 respectively, indicating that the three heavy metals have a common pollution source. The correlation between Cd and all other heavy metals is very low, indicating that pollution sources of Cd have significantly different sources.

Table 4-2 Correlation analysis of heavy metals in sediments of Songhua river

	Cr	Ni	Zn	Cu	As	Cd	Pb	V	Co	Sn	Sb
Cr	1										
Ni	0.814**	1									
Zn	0.779**	0.595*	1								
Cu	0.707**	0.622*	0.861**	1							
As	0.064**	-0.148	0.142	0.245	1						
Cd	0.080	-0.065	-0.001	0.117	-0.205	1					
Pb	-0.181	-0.037	0.166	0.247	0.566"	-0.179	1				
V	0.643**	0.537*	0.832**	0.850**	0.088	0.116	0.036	1			
Co	0.789**	0.912	0.752	0.760**	-0.023	-0.056	-0.112	0.770**	1		
Sn	-0.037	-0.415	0.216	0.150	0.438	0.057	0.398	0.326	-0.175	1	
Sb	0.035	-0.093	0.194	0.349	0.708**	0.225	0.501**	0.197	0.050	0.330	1

4.1.1.3 Principal Component Analysis of Heavy Metals in Surface Sediments in Normal Water Period

The correlation matrix of Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and Sb and 11 kinds of heavy metals in Songhua River Sediments in normal water period is shown in Table 4-3. Three main components are extracted through analysis. The eigenvalue of first component is 4.789, the variance contribution rate is 43.53%, the eigenvalue of second component is 2.775, the variance contribution rate is 25.23%, the third eigenvalue is 1.213, the variance contribution rate is 11.03%, and the cumulative variance contribution rate of the three principal components is 79.79%. Cr, Ni, Zn, Cu, V and Co have the largest load on the first component, which are 0.877, 0.807, 0.913, 0.920, 0.878 and 0.919 respectively, indicating that the first component is main pollution source of these six heavy metals. These six total metals also show high correlation according to the correlation analysis. According to the concentration distribution, the average concentrations of the six heavy metals that Cr, Ni, Zn, Cu, V and Co are lower than the background value of surface sediments, showing no pollution or low pollution, which indicates that their pollution is less disturbed by human beings. It can be inferred that the first principal component mainly comes from natural sources. As, Pb, Sn and Sb have the largest load on the second component, which are 0.816, 0.796, 0.713 and 0.763 respectively, indicating that the second component is the main pollution source of these four heavy metals. According to the concentration distribution, they all have a certain degree of pollution and are seriously disturbed by human beings. As we all know, Pb pollution mainly comes from exhaust emission of motor vehicle and emission of industrial lead, as Sn and Sb mainly come from the sewage discharge of some heavy industries, enterprises and manufacturing industries. Therefore, it can be inferred that the second component is mainly composed of traffic sources and industrial sources. The load of Cd element on the third component is the largest, which is 0.946, indicating that the third component is the main pollution source of Cd, and pesticides, chemical fertilizers, phosphate fertilizers and pesticides are generally the main sources of Cd pollution. It indicates that the Cd pollution of Songhua River Sediments in peacetime is mainly caused by human extensive use of pesticides and chemical fertilizers, so it is inferred that the third component is main agricultural source.

Table 4-3 Principal component analysis of metals in sediment Songhua river in September

Element	Factor		
	1	2	3
Cr	0.877	-0.189	0.009
Ni	0.807	-0.468	-0.185
Zn	0.913	0.128	-0.002
Cu	0.920	0.211	0.060
As	0.141	0.816	-0.274
Cd	0.051	-0.017	0.946
Pb	0.028	0.796	-0.261
V	0.878	0.119	0.182
Co	0.919	-0.237	-0.136
Sn	0.063	0.713	0.243
Sb	0.216	0.763	0.163
Eigen value	4.789	2.775	1.213
Total variance%	43.53	25.23	11.03
Cumulative%	43.53	68.76	79.79

4.1.1.4 Summary

This chapter takes 27 surface sediments in Songhua River Basin during the normal water period in September as the object, studies the spatial distribution and occurrence characteristics of heavy metals, and analyzes their pollution sources by correlation analysis and principal component analysis. The main conclusions are as following:

(1) In September 2017, the content of heavy metals in 27 surface sediments of Songhua River Basin during the normal water period ranged from 101.16 to 486.03 mg/kg, with an average content of 313.54 mg/kg. The total concentration of 11 kinds of heavy metals was V > Zn > Cr > Cu > Ni > Pb > Sn > As > Co > Cd > Sb.

(2) The chemical forms of Cr, Ni, Cu, Cd, Sn and Sb are mainly residual, Zn and Co are mainly weak acid extraction and reducible, Pb is mainly reducible and residual, V is mainly oxidizable and residual, and proportion of the four forms of As is relatively uniform.

(3) According to the correlation coefficient, among the 11 heavy metals, Cr, Ni, Zn, Cu, As, V and Co show a high positive correlation, indicating that these seven heavy metals have a common pollution source; Sn shows a negative correlation with Ni and Co, indicating that the sources of Sn, Ni and Co are greatly

different and do not interfere with each other; Cd and all other heavy metals The correlation of heavy metals is very low, indicating that Cd pollution sources have significantly different sources. Through principal component analysis, three main components were extracted, and the contribution rate of the first component was 43.53%. It was inferred that the first principal component mainly came from natural sources, including Cr, Ni, Zn, Cu, V and Co; The contribution rate of the second component is 25.23%. It is inferred that the second component is mainly composed of traffic sources and industrial sources, including as, Pb, Sn and Sb; The contribution rate of the third component is 11.03%. It is inferred that the third component is mainly agricultural source, including Cd.

4.1.2 Heavy Metal Content and Spatial Distribution in Sediments of Songhua River in High Water Period

4.1.2.1 Total Content and Spatial Distribution of Heavy Metals in Sediments of Songhua River in Wet Season

The contents of 11 heavy metals in surface sediments of Songhua River Basin in wet season are shown in Table 4-4. The total concentrations of Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and Sb are 14.56 ~ 51.18, 3.73 ~ 21.19, 6.70 ~ 58.89, 9.60 ~ 50.78, 3.27 ~ 11.31, 0.69 ~ 1.97, 19.14 ~ 42.38, 10.91 ~ 72.16, 2.15 ~ 10.80, 8.42 ~ 14.81 and 0.61 ~ 1.94 mg/kg respectively. The total concentrations of 11 heavy metals were V > Zn > Cu > Cr > Pb > Ni > Sn > Co > As > Cd > Sb. Among them, the concentration of Sb is the lowest, with an average of 1.13 mg/kg; The second is Cd, with an average concentration of 1.26 mg/kg; The average concentrations of as, Co, Sn, Ni, Pb, Cr, Cu and Zn ranged from 6.17 to 34.26 mg/kg; The concentration of V is the largest, with an average of 47.03 mg/kg. The average concentrations of Cr, Ni, Zn, Cu, V and Co are lower than the background value of surface sediments, showing no pollution or low pollution, while the concentrations of As, Cd, Pb, Sn and Sb are higher than the background value, indicating that these heavy metals have certain pollution. The pollution of Sb is the most serious, and the concentration of heavy metals is 7.5 times of the background value; The contents of Cd, As and Sn are 3 times as high as the background value; The content of Pb is twice the background value. From the ratio with background value, the pollution degree of 11 heavy metals is Sb > Cd > As > Sn > Pb > V > Cr > Cu > Zn > Ni > Co. The maximum coefficients of variation of Ni and as are 37.83% and 37.76% respectively, indicating that their spatial variability is large.

Table 4-4 Heavy metal concentration of sediments in Songhua river in June

	Average value	Maximum	Minimum	Coefficient of variation	Background value
Cr	30.67	51.18	14.56	32.14	63
Ni	12.74	21.19	3.73	37.83	57
Zn	34.26	58.89	6.70	33.80	86
Cu	31.24	50.78	9.60	30.63	38
As	6.17	11.31	3.27	37.76	1.9
Cd	1.26	1.97	0.69	35.71	0.35
Pb	28.89	42.38	19.14	22.22	15
V	47.03	72.16	10.91	36.44	99
Co	6.63	10.80	2.15	34.38	32
Sn	12.44	14.81	8.42	16.80	4.1
Sb	1.13	1.94	0.61	26.54	0.15

It can be seen from Figure 4-3 that the content of heavy metals in 14 surface sediments of Songhua River Basin in June 2017 was 141.2-291.33 mg/kg, with an average content of 222.61 mg/kg. The maximum concentration of heavy metals is 291.33 mg/kg at SS11 point (Shaling Village) in the main stream section of the Songhua River, and the minimum concentration is 141.2 mg/kg at SS13 point (Xinhe Village) in the main stream section of the Songhua River. Only one-point DS1 is collected in the second Songhua River section, with a heavy metal concentration of 191.1mg/kg, and the average heavy metal concentration in the main stream section of the Songhua River is 214.09 mg/kg.

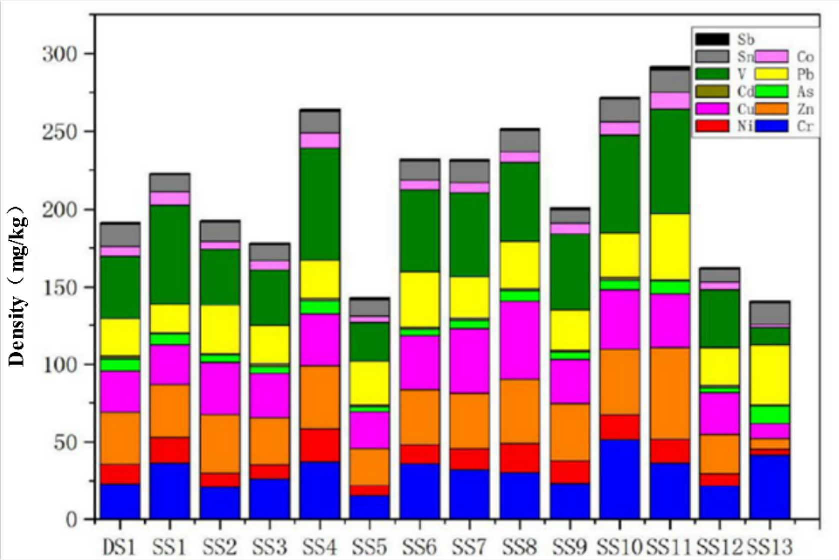
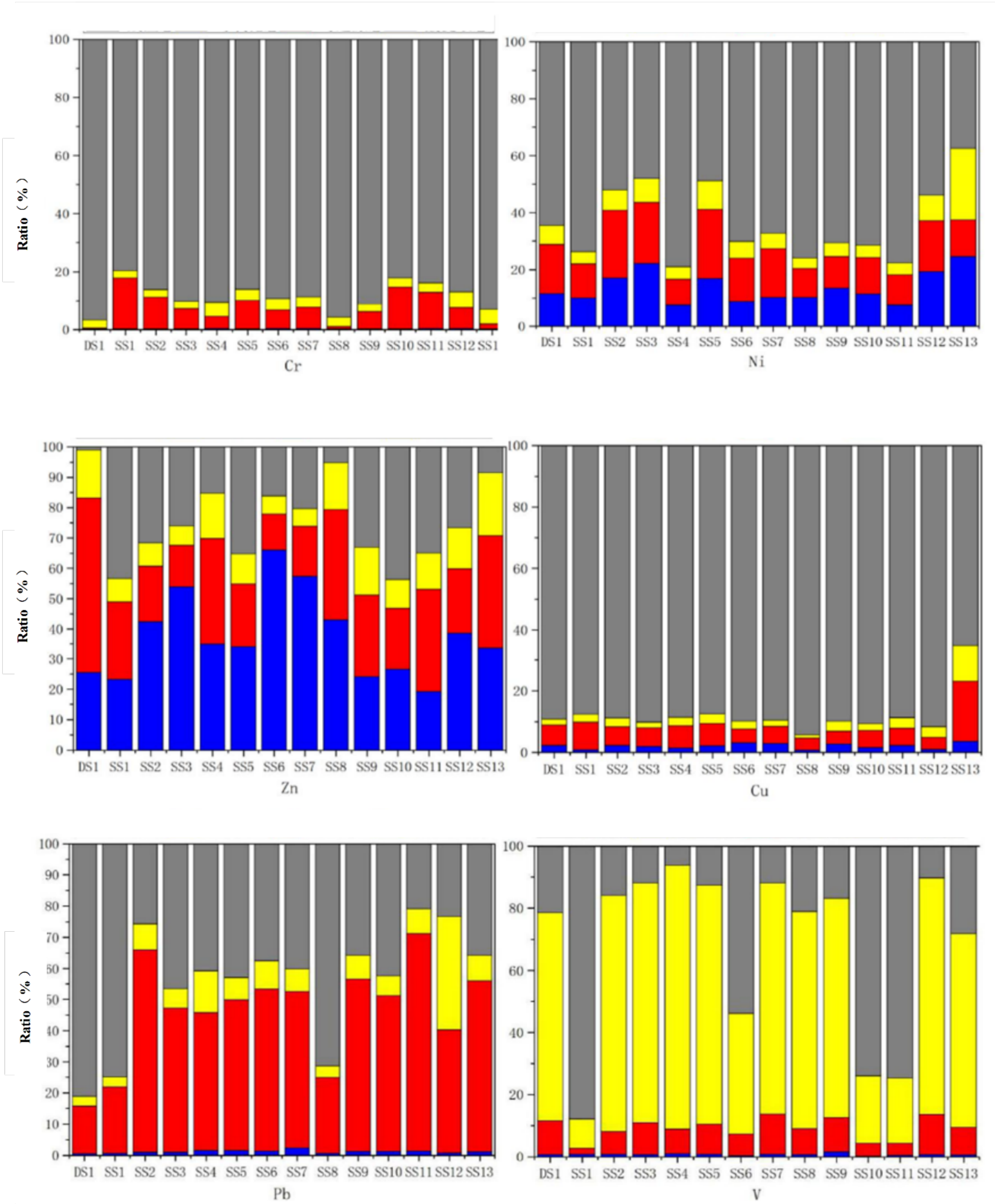


Fig. 4-3 Heavy metal concentration of sediments in Songhua river in June

Figure 4-4 shows the proportion of 11 heavy metals (Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and Sb) in Songhua River sediments during wet season in June 2017. The chemical forms of Cr, Ni, Cu, Cd, Sn and Sb are mainly residual, accounting for 79.62 ~ 96.80%, 37.34 ~ 79.07%, 65.23 ~ 94.31%, 71.34 ~ 98.15%, 83.82 ~ 98.75% and 66.02 ~ 99.06%, respectively. The proportion of acid extracted state, reducible state and oxidizable state is very low, indicating that the migration and transformation ability between different forms of these heavy metals is low, it has relatively stable chemical properties and low ecological risk, and is not easy to cause secondary pollution to the environment. Zn and Co are mainly in weak acid extraction state and reducible state. The proportion of weak acid extraction state is 19.19 ~ 66.01% and 26.73 ~ 58.15% respectively, and the proportion of reducible state is 11.92 ~ 57.71% and 20.49 ~ 50.59% respectively, indicating that the chemical properties of Zn and Co are unstable and the bioavailability is high. Migration and transformation will occur when the external conditions change, it is easy to cause secondary pollution to the environment and should be paid attention to. The proportion of the four forms of as is relatively uniform, accounting for 6.1 ~ 23.02%, 7.02 ~ 16.76%, 26.1 ~ 54.29% and 12.48 ~ 50.62%. Pb is mainly reducible and residual, accounting for 15.19 ~ 69.8% and 20.91 ~ 81.14% respectively. V is mainly in oxidizable state and residual state, accounting for 9.5 ~ 85.09% and 6.12 ~ 87.88% respectively. It shows that as, Pb and V have certain chemical activity and bioavailability, and there are potential hazards.

The proportion of bioavailable forms of heavy metals in sediments of Songhua River Basin in wet season is Co (88.35%) > Zn (75.63%) > As (70.14%) > V (68.09%) > Pb (55.80%) > Ni (36.39%) > Cu

(11.95%) > Cr (11.35%) > Cd (6.38%) > Sb (4.70%) > Sn (2.80%). The highest bioavailable forms of Co and Zn appeared in DS1 of the second Songhua River section, accounting for 98.53% and 98.85% respectively; The highest bioavailable forms of as and V appeared in SS4 in the main stream of Songhua River, accounting for 87.52% and 93.88% respectively. The highest bioavailable forms of Pb appeared in SS11 (79.08%), indicating that heavy metals at these points are easy to cause secondary pollution and have higher ecological risk. The bioavailable forms of Ni, Cu, Cr, Cd, Sb and Sn are relatively low, the chemical structure is relatively stable, and it is not easy to cause secondary pollution.



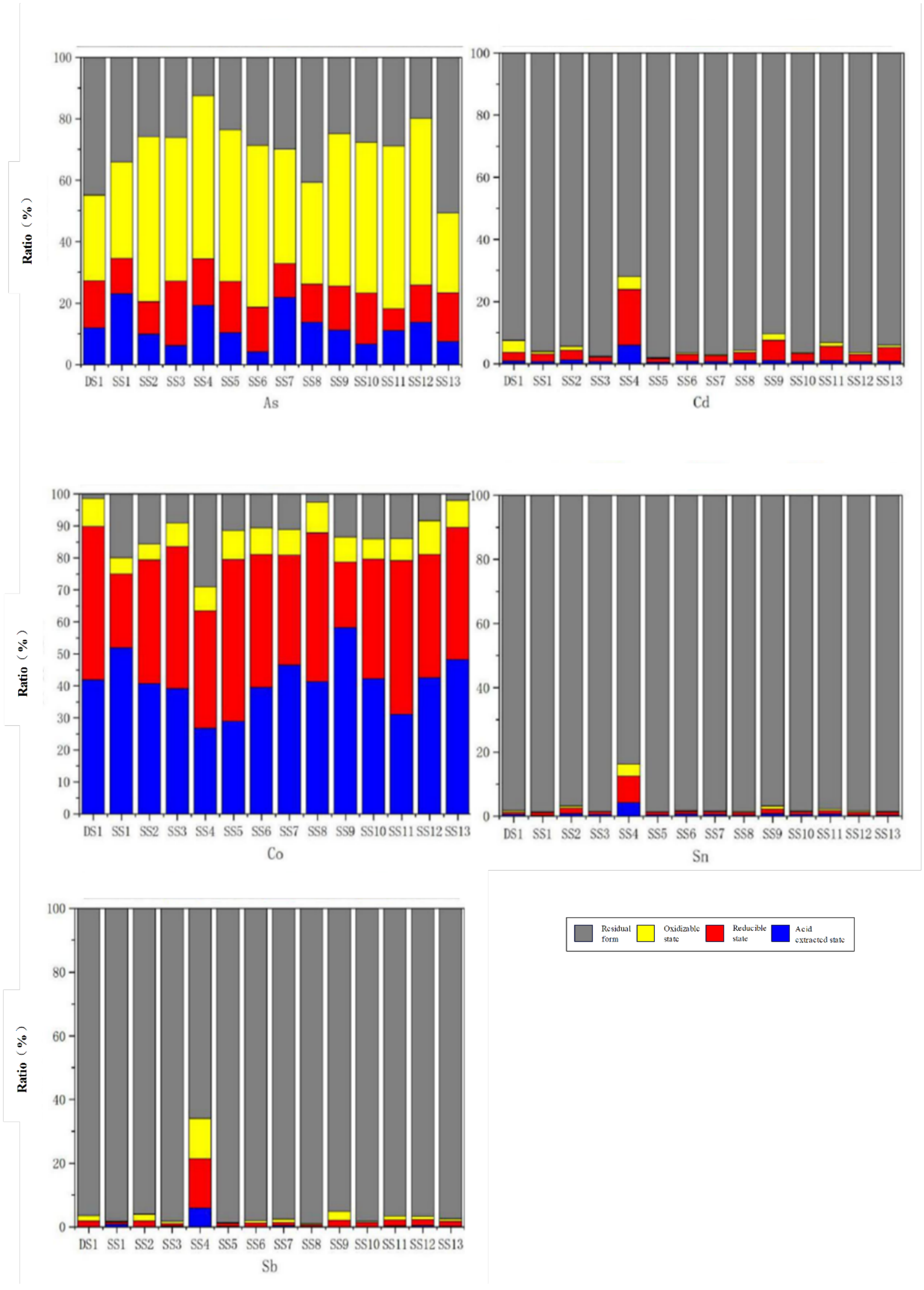


Fig.4-4 Characteristics of heavy metal forms in sediments of the Songhua river in June

4.1.2.2 Correlation Analysis of Heavy Metals in Surface Sediments in Wet Season

The correlation matrix of Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and Sb in Songhua River sediments during wet season is shown in Table 4-5. According to the correlation coefficient, Cr, As and Sn showed positive correlation at the level of 0.05, and the correlation coefficients are 0.561 and 0.594 respectively, indicating that there are similar pollution sources between them; The five heavy metals Ni, Cu, V, Co and Zn have high correlation, which is significantly correlated at the level of 0.01. The correlation coefficient of

Co and V is the highest, 0.968, Ni and V is 0.909, Co and V is 0.968, Zn and Co is 0.884, and CO and Ni is 0.862, It shows that these five heavy metals have common pollution sources. As has negative correlation with Cu, Zn, Co and Cd, and the correlation coefficients are -0.246, -0.059, -0.023 and -0.279 respectively, indicating that these metal pollution sources have great differences and do not affect each other. PB has a positive correlation with sb and as, which is significantly correlated at the level of 0.01. The correlation coefficients are 0.683 and 0.566 respectively, indicating that there are similar pollution sources between them. The correlation between Cd and all other heavy metals is very low, indicating that Cd pollution sources have significantly different sources.

Table 4-5 Correlation analysis of heavy metals in sediments of Songhua river in June

	Cr	Ni	Zn	Cu	As	Cd	Pb	V	Co	Sn	Sb
Cr	1										
Ni	0.369	1									
Zn	0.178	0.737**	1								
Cu	0.125	0.681**	0.730*	1							
As	0.561*	0.203	-0.059	-0.246	1						
Cd	0.053	0.061	0.060	0.228	-0.279	1					
Pb	0.288	-0.254	0.136	-0.015	0.566**	-0.385	1				
V	0.466	0.909*	0.827**	0.627**	0.088	0.118	-0.156	1			
Co	0.431	0.862**	0.884**	0.563	-0.023	9900	-0.050	0.968	1		
Sn	0.594*	0.270	0.228	0.201	0.438*	0.088	0.466*	0.193	0.229	1	
Sb	0.099	0.021	0.381	-0.089	0.708**	-0.342	0.683**	0.093	0.260	0.466	1

4.1.2.3 Principal Component Analysis of Heavy Metals in Surface Sediments in Wet Season

The correlation matrix of Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and Sb and 11 heavy metals in Songhua River Sediments in wet season is shown in Table 4-6. Through analysis, three main components are extracted. The eigenvalue of the first component is 4.509, the variance contribution rate is 40.98%, the eigenvalue of the second component is 2.772, the variance contribution rate is 25.20%, the third eigenvalue is 1.418, the variance contribution rate is 12.89%, and the cumulative variance contribution rate of the three principal components is 79.08%. Cr, Ni, Zn, Cu, V and Co have the largest load on the first component, which are 0.536, 0.899, 0.882, 0.702, 0.932 and 0.942 respectively, indicating that the first component is the main pollution source of the six heavy metals. According to the correlation analysis, the six total metals also show a high correlation. According to the concentration distribution, Cr, Ni, Zn, Cu, V and Co, the average concentrations of the six heavy metals are lower than the background value of surface sediments, showing no pollution or low pollution, indicating that their pollution is less disturbed by human beings. It can be inferred that the first principal component mainly comes from natural sources. As, Pb, Sn and Sb have the largest load on the second component, which are 0.744, 0.787, 0.656 and 0.693 respectively, indicating that the second component is the main pollution source of these four heavy metals. According to the concentration distribution, they all have a certain degree of pollution and are seriously disturbed by human beings. As we all know, Pb pollution mainly comes from motor vehicle exhaust emission and industrial lead emission, as Sn and Sb mainly come from the sewage discharge of some heavy industries, enterprises and manufacturing industries. Therefore, it can be inferred that the second component is mainly composed of traffic sources and industrial sources. The load of Cd element on the third component is the largest, which is 0.481, indicating that the third component is the main pollution source of Cd, and pesticides, chemical fertilizers, phosphate fertilizers and pesticides are generally the main sources of Cd pollution. It indicates that the Cd pollution of Songhua River Sediment in wet season is mainly caused by human extensive use of pesticides and chemical fertilizers, so it is inferred that the third component is mainly agricultural source.

Table 4-6 Principal component analysis of metals in sediment form Songhua river in June

Element	Factor		
	1	2	3
Cr	0.536	0.424	0.046
Ni	0.899	-0.240	0.103
Zn	0.882	-0.140	-0.391
Cu	0.702	-0.377	-0.151
As	0.255	0.744	0.429
Cd	0.087	-0.459	0.481
Pb	0.087	0.787	-0.379
V	0.932	-0.248	0.011
Co	0.942	-0.130	-0.082
Sn	0.472	0.656	0.339
Sb	0.290	0.693	-0.503
Eigen value	4.509	2.772	1.418
Total variance%	40.98	25.20	12.89
Cumulative%	40.98	66.19	79.08

4.1.2.4 Summary

This chapter takes 27 surface sediments in Songhua River Basin during the wet season in June as the object, studies the spatial distribution and occurrence characteristics of heavy metals, and analyzes their pollution sources by correlation analysis and principal component analysis. The main conclusions are as follows:

(1) In June 2017, during the wet season, the content of heavy metals in 14 surface sediments of Songhua River Basin ranged from 141.2 to 291.33 mg/kg, with an average content of 222.61 mg/kg. The maximum concentration of heavy metals occurred in the main stream of Songhua River. SS11 point (Shaling Village). The total concentration of 11 heavy metals is V > Zn > Cu > Cr > Pb > Ni > Sn > Co > As > Cd > Sb. From the ratio with the background value, the pollution degree of 11 heavy metals is Sb > Cd > As > Sn > Pb > V > Cr > Cu > Zn > Ni > Co.

(2) The chemical forms of Cr, Ni, Cu, Cd, Sn and Sb are mainly in residual state, Zn and Co are mainly in weak acid extraction state and reducible state, Pb is mainly in reducible state and residual state, V is

mainly in oxidizable state and residual state, and the proportion of the four forms of As is relatively uniform. The bioavailability forms of heavy metals in sediments of Songhua River Basin in wet season, the proportion of (F1 + F2 + F3) is Co (88.35%) > Zn (75.63%) > As (70.14%) > V (68.09%) > Pb (55.80%) > Ni (36.39%) > Cu (11.95%) > Cr (11.35%) > Cd (6.38%) > Sb (4.70%) > Sn (2.80%).

(3) According to the correlation coefficient, there is a high correlation between 11 heavy metals, Ni, Cu, V, Co and Zn, and five heavy metals, indicating that these five heavy metals have a common pollution source; as has a negative correlation with Cu, Zn, Co and Cd, indicating that their sources are quite different and do not interfere with each other; Cd has a high correlation with all other heavy metals, indicating that Cd pollution sources have significantly different sources. Through principal component analysis, three main components are extracted. It is inferred that the first principal component mainly comes from natural sources, including Cr, Ni, Zn, Cu, V and Co; It is inferred that the second component is mainly composed of traffic sources and industrial sources, including as, Pb, Sn and Sb; The third component is mainly agricultural source, including Cd.

4.1.3 Content and Spatial Distribution of Heavy Metals in Sediments of Songhua River in Dry Season

4.1.3.1 Total Content and Spatial Distribution of Heavy Metals in Sediments of Songhua River in Dry Season

The contents of 11 heavy metals in surface sediments of Songhua River Basin during the dry season in March are shown in table 5.7. The total concentrations of Cr, Ni, Zn, Cu, as, CD, Pb, V, Co, Sn and Sb were 11.64 ~ 87.45, 2.87 ~ 20.94, 15.31 ~ 41.73, 8.08 ~ 39.73, 1.69 ~ 5.23, 0.30 ~ 2.17, 24.33 ~ 42.60, 5.63 ~ 65.39, 1.36 ~ 8.19, 8.20 ~ 15.78 and 0.29 ~ 1.55mg/kg respectively. The total concentrations of 11 heavy metals were V > CR > Pb > Zn > Cu > Sn > Ni > co > as > CD > sb. Among them, the concentration of sb is the lowest, with an average of 1.01mg/kg; The second is CD, with an average concentration of 1.56mg/kg; The average concentrations of as, Co, Sn, Pb, Ni, Cu, Zn and Cr ranged from 3.43 to 32.97 mg / kg; The concentration of V is the largest, with an average of 35.62 mg/kg. The average concentrations of Cr, Ni, Zn, Cu, V and Co are lower than the background value of surface sediments, showing no pollution or low pollution, while the concentrations of As, Cd, Pb, Sn and Sb are higher than the background value, indicating that these heavy metals have certain pollution. The pollution of sb is the most serious, and the concentration of heavy metals is 6.7 times of the background value; The second is Cd, and the concentration of heavy metals is 4.5 times of the background value; The content of Sn is 2.8 times of the background value, and the content of as and Pb is 2 times of the background value. From the ratio with background value, the pollution degree of 11 heavy metals is Sb > Cd > Sn > Pb > As > Cu > Cr > V > Zn > Ni > Co. The maximum coefficients of variation of Cr and V were 60.08% and 54.77% respectively, indicating that their spatial variability was large.

Table 4-7 Heavy metal concentration of sediments in Songhua river in March

	Average value	Maximum	Minimum	Coefficient of variation	Background value
Cr	32.97	87.45	11.64	60.08	63
Ni	9.99	20.94	2.87	48.54	57
Zn	28.79	41.73	15.31	31.64	86
Cu	25.98	39.73	8.08	38.14	38
As	3.43	5.23	1.69	26.53	1.9
Cd	1.56	2.17	0.30	27.56	0.35
Pb	30.22	42.60	24.33	16.21	15
V	35.62	65.39	5.63	54.77	99
Co	4.59	8.19	1.36	44.22	32
Sn	11.79	15.78	8.20	21.63	4.1
Sb	1.01	1.55	0.29	31.68	0.15

It can be seen from Figure 4-5 that the content of heavy metals in 17 surface sediments of Songhua River Basin during the dry season in March 2017 ranged from 132.21 to 253.57 mg/kg, with an average content of 185.26mg/kg. The maximum concentration of heavy metals occurs at point SD7 in the main stream section of Songhua River, and the concentration is 253.57 mg/kg, The minimum value appears at ND4 point of Nenjiang section (Jiangqiao), the concentration of heavy metals is 132.21 mg/kg. The average concentration of heavy metals in Nenjiang River Basin is 205.99 mg/kg, the average concentration of heavy metals in the second Songhua River section is 174.03 mg/kg, and the average concentration of heavy metals in the main stream section of Songhua River is 180.33 mg/kg. Generally speaking, the concentration of heavy metals in surface sediments of Songhua River in dry season in Nenjiang River Basin is higher than that in the second Songhua River section and higher than that in the main stream section of Songhua River.

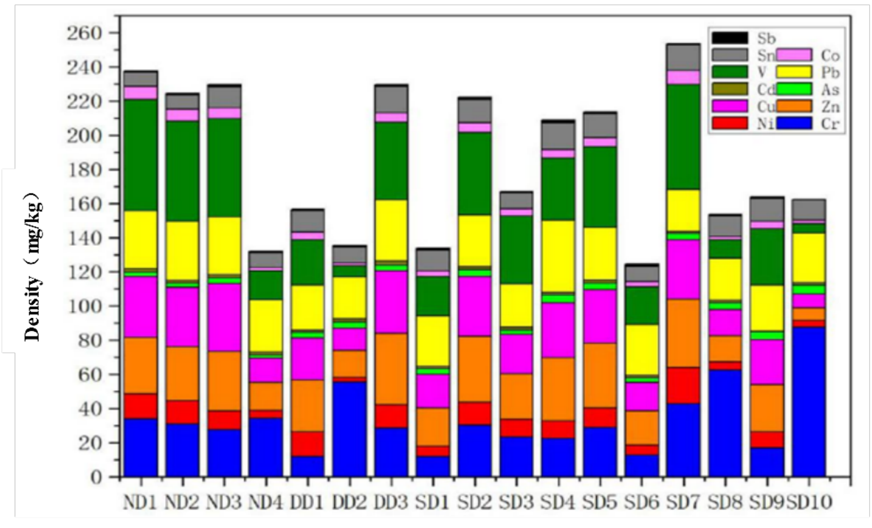
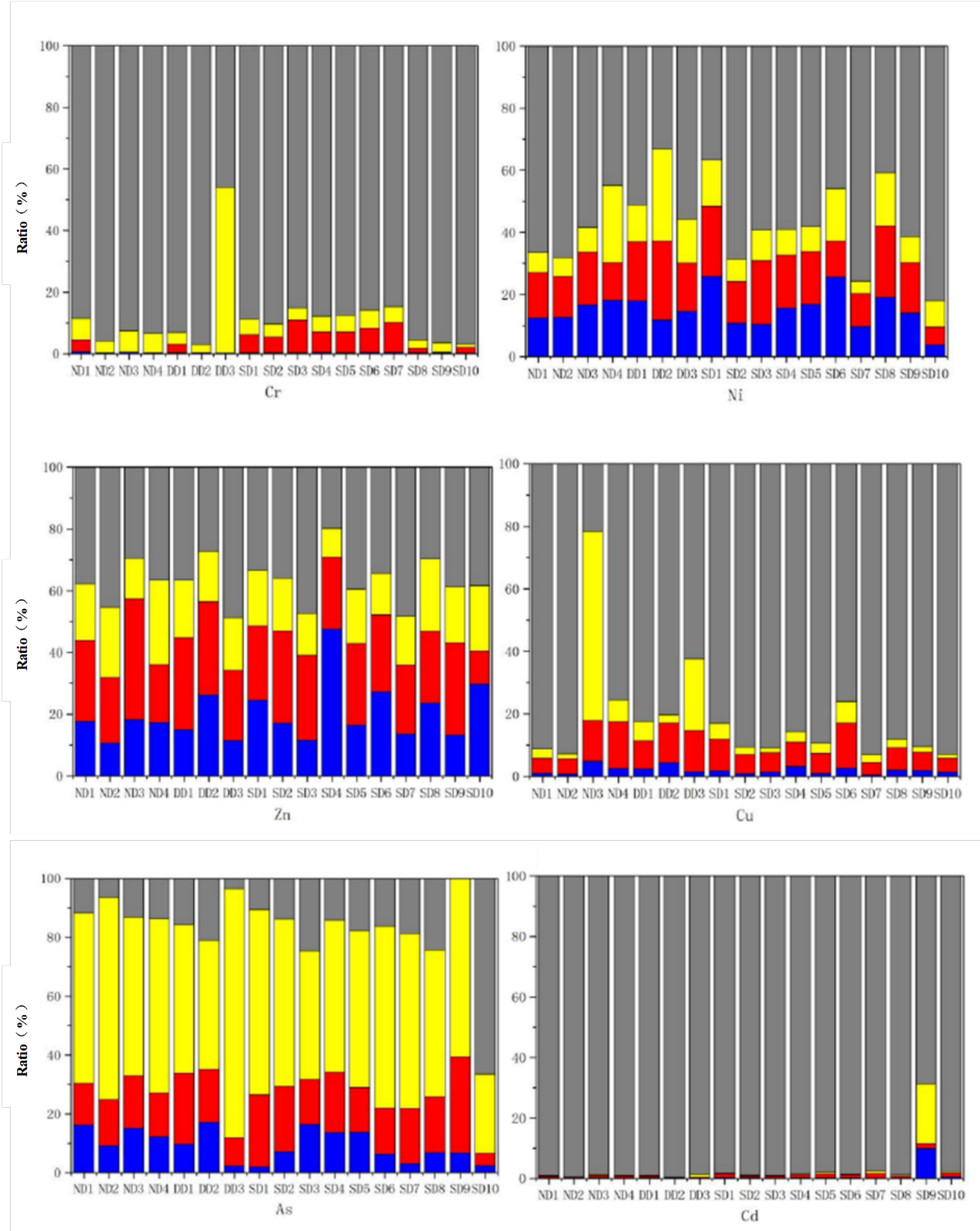


Fig. 4-5 Heavy metal concentration of sediments in Songhua river in March

It can be seen from Figure 4-6 that in March 2017, the proportion of Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and Sb in 11 heavy metals in Songhua River sediments during the dry season. The chemical forms of Cr, Ni, Cu, Cd, Sn and Sb are mainly residual, accounting for 46.26-96.79%, 33.23-82.06%, 21.65-93.05%, 68.66-99.57%, 74.00-97.99% and 82.23-98.27% respectively, of which the oxidizable state of Cr at DD3 point accounts for 53.82%, the oxidizable state of Cu at Nd3 point accounts for 60.5%, and the acid extracted state of other points. The proportion of reducible state and oxidizable state is very low, indicating that these heavy metals have low migration and transformation ability between different forms, relatively stable chemical properties and low ecological risk, and are not easy to cause secondary pollution to the environment. Co is mainly in weak acid extraction state and reducible state. The proportion of weak acid extraction state is 24.00-62.90%, and the proportion of reducible state is 24.97-55.50%, indicating that the chemical properties of Co are unstable and the bioavailability is high. When the external conditions change, migration and transformation will occur, which is easy to cause secondary pollution to the environment, which should be paid attention to. The proportion of the four forms of Zn is relatively uniform, accounting for 10.48-47.56%, 10.92-39.29%, 9.41-27.31% and 27.17-48.85%, respectively. As and V are mainly in oxidizable state, accounting for 27.00-84.48% and 77.20-89.1%, respectively. Pb is mainly reducible and residual, accounting for 10.35-59.04% and 24.74-85.88%, respectively. It shows that As, Pb and V have certain chemical activity and bioavailability, and there are potential hazards.

The proportion of bioavailable forms of heavy metals in sediments of Songhua River Basin in dry season is V (94.62%) > Co (93.82%) > As (82.82%) > Zn (63.09%) > Pb (54.43%) > Ni (43.17%) > Cu (18.33%) > Cr (11.27%) > Sn (5.14%) > sb (3.93%) > Cd (3.01%). The highest bioavailable forms of V and Co appeared in ND2 (99.97% and 99.98%) in Nenjiang River Basin, and the highest bioavailable forms of Pb appeared in DD3 (75.25%) in the second Songhua River; The highest bioavailable forms of As and Zn appear in SD9 (99.99%) and SD4 (80.28%) in the main stream of Songhua River, indicating that heavy metals are easy to cause secondary pollution and have higher ecological risk.


Ratio（%）
0
20
40
60
80
100
ND1 ND2 ND3 ND4 DD1 DD2 DD3 SD1 SD2 SD3 SD4 SD5 SD6 SD7 SD8 SD9 SD10
Cr
Ni
Zn
Cu
As
Cd

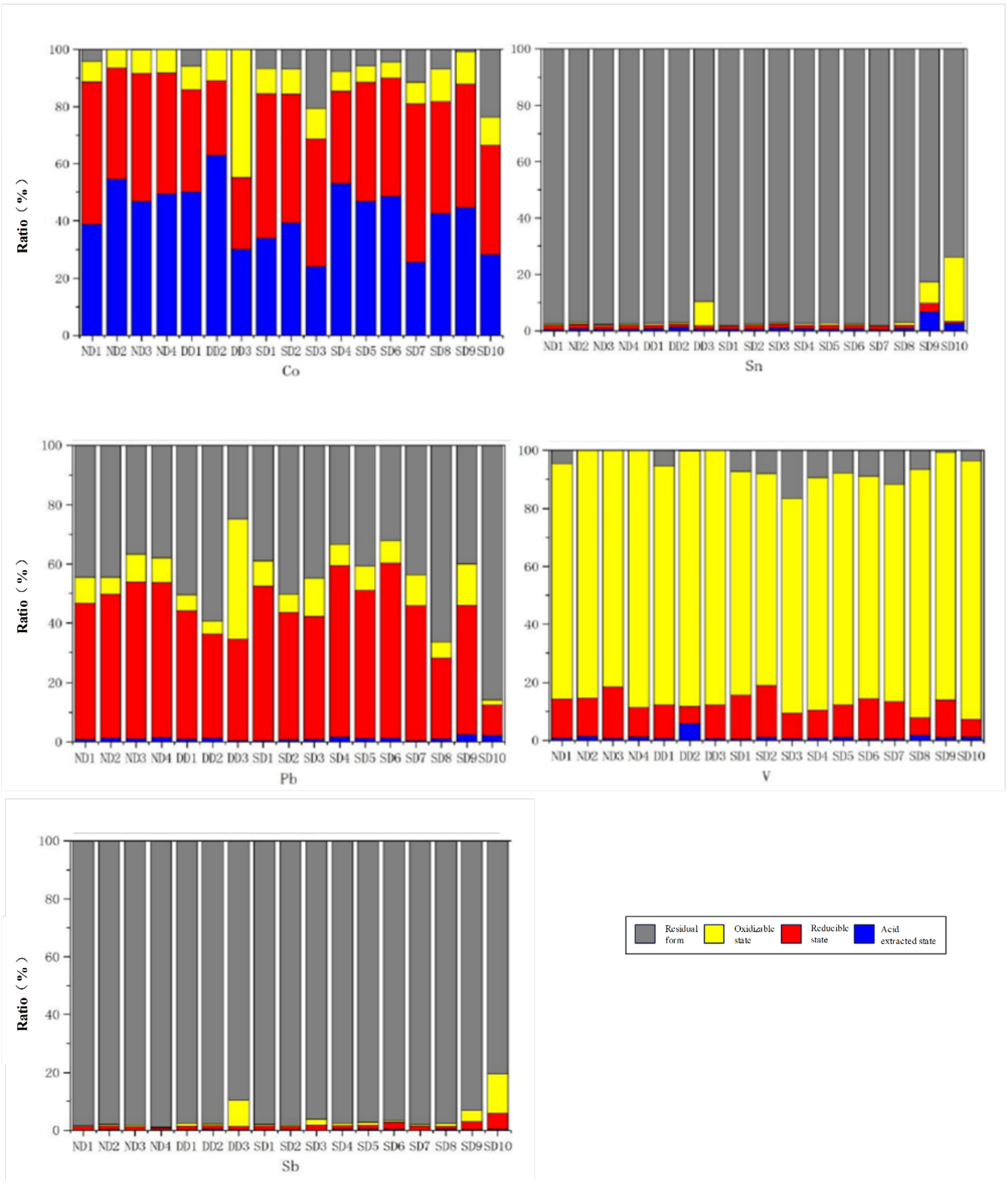


Fig. 4-6 Characteristics of heavy metal forms in sediments of the Songhua river in March

4.1.3.2 Correlation Analysis of Heavy Metals in Surface Sediments in Dry Season

The correlation matrix of Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and Sb in the sediments of Songhua River in dry season is shown in Table 4-8. According to the correlation coefficient, Ni and Cr, Zn, Cu, V and Co show positive correlation at the level of 0.01. The correlation coefficients are 0.620, 0.858, 0.828, 0.854 and 0.915, respectively. The correlation coefficient is high, indicating that they have common pollution sources; Pb has a certain correlation with Zn, Cu and Sb, which is significantly correlated at the level of 0.05. The correlation coefficients are 0.491, 0.506 and 0.527, indicating that there are similar pollution sources between them; The correlation coefficient of as and Sn is 0.700, which shows a positive correlation, and the correlation with other heavy metals is very low, indicating that the pollution sources of As and Sn are the same. The correlation between Cd and all other heavy metals is very low, indicating that Cd pollution sources have significantly different sources.

Table 4-8 Correlation analysis of heavy metals in sediments of Songhua river in March

	Cr	Ni	Zn	Cu	As	Cd	Pb	V	Co	Sn	Sb
Cr	1										
Ni	0.620**	1									
Zn	0.355	0.858**	1								
Cu	0.435	0.828*	0.919*	1							
As	0.406	-0.085	0.148	-0.067	1						
Cd	0.263	-0.084	0.059	0.083	-0.337	1					
Pb	-0.262	0.173	0.491*	0.506	0.054	0.257	1				
V	-0.373	0.854*	0.841*	0.938**	-0.232	0.113	0.394	1			
Co	-0.348	0.915*	0.836**	0.911**	-0.161	-0.021	.0356	0.971*	1		
Sn	-0.051	0.366	0.598*	0.374	0.700**	-0.262	0.220	0.148	0.202	1	
Sb	-0.620	0.082	0.361	0.431	-0.137	0.150	0.527*	0.234	0.168	0.284	1

4.1.3.3 Principal Component Analysis of Heavy Metals in Surface Sediments in Dry Season

The correlation matrix of Cr, Ni, Zn, Cu, As, Cd, Pb, V, Co, Sn and Sb 11 heavy metals in Songhua River Sediments in dry season is shown in Table 4-9. Through analysis, three main components are extracted. The eigenvalue of the first component is 5.258, the variance contribution rate is 47.80%, the eigenvalue of the second component is 2.020, the variance contribution rate is 18.36%, the third eigenvalue is 1.537, the variance contribution rate is 13.97%, and the cumulative variance contribution rate of the three principal components is 80.01%. Cr, Ni, Zn, Cu, Pb, V and Co have the largest load on the first component, which are 0.511, 0.871, 0.950, 0.976, 0.534, 0.926 and 0.921 respectively, indicating that the first component is the main pollution source of the seven heavy metals. According to the correlation analysis, the six total metals also show a high correlation. According to the concentration distribution, Cr, Ni, Zn, Cu, Pb, V and Co. The average concentrations of the six heavy metals are lower than the background value of surface sediments, showing no pollution or low pollution, indicating that their pollution is less disturbed by human beings. It can be inferred that the first principal component mainly comes from natural sources. As, Sn and sb have the largest load on the second component, which are 0.945, 0.806 and 0.801 respectively, indicating that the second component is the main pollution source of these three heavy metals. According to the concentration distribution, they all have a certain degree of pollution and are seriously disturbed by human beings. It is well known that As, Sn and Sb mainly come from the sewage discharge of some heavy industries, enterprises and manufacturing industries, Therefore, it can be inferred that the second component is mainly composed of industrial sources. The load of Cd element on the third component is the largest, which is 0.802, indicating that the third component is the main source of Cd pollution, and pesticides, chemical fertilizers, phosphate fertilizers and pesticides are generally the main sources of Cd pollution. It indicates that the Cd pollution of Songhua River Sediment in wet season is mainly caused by human extensive use of pesticide and chemical fertilizers. Therefore, it is inferred that the third component is mainly agricultural source.

Table 4-9 Principal component analysis of metals in sediment form Songhua river in March

Element	Factor 1	Factor 2	Factor 3
Cr	0.511	0.330	-0.038
Ni	0.871	0.080	-0.086
Zn	0.950	0.220	0.123
Cu	0.976	-0.018	0.067
As	-0.075	0.945	0.170
Cd	0.032	-0.490	0.802
Pb	0.534	-0.061	0.370
V	0.926	-0.175	0.065
Co	0.921	-0.073	-0.011
Sn	0.420	0.806	0.018
Sb	0.455	0.801	-0.095
Eigen value	5.258	2.020	1.537
Total variance%	47.80	18.36	13.97
Cumulative%	47.80	66.16	80.13

4.1.3.4 Summary

Taking 27 surface sediments in Songhua River Basin during the dry season in March as the object, this chapter studies the spatial distribution and occurrence characteristics of heavy metals, and analyzes their pollution sources by correlation analysis and principal component analysis. The main conclusions are as following:

(1) In March 2017, the content of heavy metals in 17 surface sediments of Songhua River Basin during the dry season ranged from 132.21 to 253.57 mg/kg, with an average content of 185.26 mg/kg. The total concentration of 11 kinds of heavy metals was V > Cr > Pb > Zn > Cu > Sn > Ni > Co > As > Cd > Sb. From the ratio with the background value, the pollution degree of 11 kinds of heavy metals was Sb > Cd > Sn > Pb > As > Cu > Cr > V > Zn > Ni > Co. Generally speaking, the concentration of heavy metals in surface sediments of Songhua River in dry season in Nenjiang River Basin is higher than that in the second Songhua River section and higher than that in the main stream section of Songhua River.

(2) The chemical forms of Cr, Ni, Cu, Cd, Sn and Sb are mainly residual, Co is mainly weak acid extraction and reducible, the proportion of the four forms of Zn is relatively uniform, As and V are mainly oxidizable, Pb is mainly reducible and residual. The bioavailability forms of heavy metals in sediments of Songhua River Basin in dry season, the order of (F1 + F2 + F3) proportion is V (94.62%) > Co (93.82%) > As (82.82%) > Zn (63.09%) > Pb (54.43%) > Ni (43.17%) > Cu (18.33%) > Cr (11.27%) > Sn (5.14%) > Sb (3.93%) > Cd (3.01%).

(3) According to the correlation coefficient, among the 11 heavy metals, Ni and Cr, Zn, Cu, V and Co show positive correlation, indicating that the five heavy metals have common pollution sources; Pb and Zn, Cu and Sb have certain correlation, indicating that they have similar pollution sources; the correlation between Cd and other heavy metals is very low, indicating that the pollution sources of Cd are significantly different Same source. Through principal component analysis, three main components are extracted. It is inferred that the first principal component mainly comes from natural sources, including Cr, Ni, Zn, Cu, Pb,

V and Co; It is inferred that the second component is mainly composed of common sources, including As, Sn and sb; It is inferred that the third component is mainly agricultural source, including Cd.

4.1.4 Comparison of heavy metal content and pollution degree in sediments at different water periods

This chapter mainly compares the content and occurrence characteristics of 11 kinds of heavy metals in different water periods in Songhua River Basin, and the changes of heavy metal content in sediments in dry season, normal season and wet season are studied, so as to provide a theoretical basis for water ecological protection and ecological restoration in Songhua River Basin.

4.1.4.1 Time Distribution Characteristics of Total Heavy Metals in Sediments

As the sampling points in Songhua River Basin are different in dry season, normal season and wet season, and the tributaries are also different, the whole basin is divided into upstream, middle and downstream to study and compare the content and pollution degree of heavy metals in sediments (Table 4-10).

Table 4-10 Basic information on sampling points of surface sediments in Songhua river

Location	Section name	Number of March	Number of June	Number of September
	Kolo River Bridge	ND1	-	-
	Middle Uyur River	ND2	-	-
	Boho head	ND3	-	-
	Jiangqiao	ND4	-	-
	Middle Reaches of Liuhe River	DD1	-	-
	Wanjin Pagoda	DD2	-	-
	Pine forest	DD3	-	-
	Songhua River Village	-	DS1	DH1
	xinqiaotun	-	-	DH2
	Changyi	-	-	DH3
Upstream	Sanjiazi	-	-	DH4
	Lengchang Village	-	-	DHS
	Huayuankou	-	-	DH6
	Zhaoyuan		SS1	IHS
	Dadingzi Mountain		SS2	SH2
	Yu Guangtun		SS3	
	Zhangjiatun		SSS	
	Lao Fumin		SS6	
	Court Hill Village		SS7	
	iron force		SS9	
	middle larin river	DS1	-	-
	Middle Ash River	DS2	-	-
	fruit tree farm	DS3	-	-
	Chaihe Bridge	DS4	SS4	SH4
	Inside the Mudanjiang Estuary	DS5	-	-
	Middle Reaches of Hulan River		SS10	SH10
	Xiajiawazi			SH3
	Zhengfu Village			SH5
	dongchuantun			SH6
	Nanguan Village			SH9
Midstream	reed river			SH11
	Qingyang			SH12
	Wenchun Bridge			SH13
	Dongchengzi Village			SH14
	under the boulder			SH15
	Shahe section			SH16
	III			SH17
	Middle Reaches of the Waken River	DS6	-	-
	Juyuan Forest Farm	DS7		SH7
	on Jiamusi	DS8	SS8	SH8
	Xilin	DS9		

Location	Section name	Number of March	Number of June	Number of September
Midstream	Tongjiang	DS10		
	Sand Ridge Village		SS11	
Downstream	Tanglin Forest Farm		SS12	
	Xinhe Village		SS13	
	Lake Village			SH18
	Birch Youth Point			SH19
	Anxing Village			SH20
	Sands			SH21
	Sand peony import			SH22

The content range of heavy metals in different periods of different river sections in dry season, normal season and wet season in Songhua River sediments is shown in Table 4-11. The total concentration range of heavy metals in the dry season in March in the whole Songhua River Basin is 124.64 ~ 253.57 mg/kg, with an average value of 185.26 mg/kg, of which the content of heavy metals in the upper reaches of Songhua River is 132.21 ~ 237.64 mg/kg, with an average value of 192.29 mg/kg, and the concentration of heavy metals in the middle reaches of Songhua River is 133.86 ~ 222.03 mg/kg, with an average value of 189.05 mg/kg, The concentration of heavy metals in the lower reaches of Songhua River is 124.64 ~ 253.57 mg/kg, with an average of 171.61 mg/kg. During the wet season in June, the total concentration of heavy metals in the whole basin of Songhua River ranges from 141.20 to 291.33 mg/kg, with an average value of 222.61 mg/kg, of which the content of heavy metals in the upper reaches of Songhua River ranges from 143.30 to 232.03 mg/kg, with an average value of 199.07 mg/kg, the concentration of heavy metals in the middle reaches of Songhua River ranges from 263.93 to 271.81 mg/kg, with an average value of 267.87 mg/kg, and the concentration of heavy metals in the lower reaches of Songhua River ranges from 141.22 to 291.33 mg/kg, The average value was 211.50 mg/kg. During the normal water period in September, the total concentration of heavy metals in the whole basin of Songhua River ranges from 101.16 to 486.03 mg/kg, with an average value of 313.54 mg/kg, of which the content of heavy metals in the upper reaches of Songhua River ranges from 306.73 to 486.03 mg/kg, with an average value of 368.43 mg/kg, the concentration of heavy metals in the middle reaches of Songhua River ranges from 101.16 to 399.29 mg/kg, with an average value of 260.28 mg/kg, and the concentration of heavy metals in the lower reaches of Songhua River ranges from 224.49 to 393.92 mg/kg, the average value is 312.34 mg/kg.

Table 4-11 Comparison of heavy metal content ranges in different river section of Songhua river in different periods

Place	Period	Total concentration range of heavy metals (mg/kg)
whole basin	dry season in March	124.64~253.57
Upper Songhua River	dry season in March	132.21~237.64
Middle Reaches of Songhua River	dry season in March	133.86~222.03
Lower Songhua River	dry season in March	124.64~253.57
whole basin	June wet season	141.20~291.33
Upper Songhua River	June wet season	143.30~232.03
Middle Reaches of Songhua River	June wet season	263.93~271.81
Lower Songhua River	June wet season	141.22~291.33
whole basin	Flat water period in September	101.16~486.03
Upper Songhua River	Flat water period in September	306.73~486.03
Middle Reaches of Songhua River	Flat water period in September	101.16~399.29
Lower Songhua River	Flat water period in September	224.49~393.92

It can be seen from Figure 4-7 that the distribution law of heavy metal concentration in sediments during the dry season in March is: upper reaches of Songhua River > middle reaches of Songhua River > lower reaches of Songhua River. In the wet season in June, the distribution law of heavy metal concentration in sediments is: the middle reaches of Songhua River > the lower reaches of Songhua River > the upper reaches of Songhua River. The distribution law of heavy metal concentration in sediments during the normal water period in September is as following: the upper reaches of Songhua River > the lower reaches of Songhua River > the middle reaches of Songhua River. In general, the content of heavy metals in the sediments in the upper reaches of the Songhua River is high, and the content of heavy metals in the lower reaches is the lowest, which reflects that the non-point source pollution in the upper reaches of the Songhua River is the most serious, possibly because a large number of petrochemical and other industrial enterprises were concentrated in the upper reaches of the Songhua River Basin, and the industrial pollution of these petrochemical enterprises may be one of the main sources of heavy metal pollution, Therefore, the total content of heavy metals in the upper reaches of Songhua River is relatively high. It is suggested that the number of petrochemical enterprises around the basin should be controlled in the future, and the control of toxic and harmful substances such as heavy metals in the above enterprises should be strengthened to reduce the emission of heavy metals from the source. The temporal variation law of total heavy metals in sediments of the whole Songhua River Basin is normal water period > high water period > low water period. In the normal water period, the content of heavy metals in the upper reaches of the Songhua River is much higher than that in the dry and high-water periods. The temporal variation law of heavy metals in the middle reaches of the Songhua River is high water period > normal water period > low water period, The temporal variation law of heavy metal content in the lower reaches of Songhua River is normal water period > high water period > low water period. The content of heavy metals in the surface sediments of each section of Songhua River in the normal water period in September is higher than that in the dry season in March and the wet season in June, which is related to the relatively heavy non-point source and soil erosion near the rain period in July and August, and more heavy metals entering the river. The temporal and spatial distribution of heavy metals in surface sediments in the study area is consistent with the research results of Liu Baolin and others.

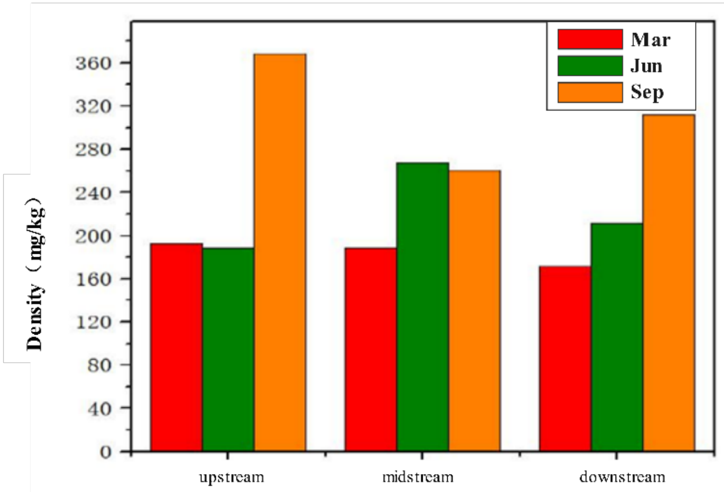


Fig. 4-7 Average concentration of heavy metals in various river sections of Songhua river

4.1.4.2 Summary

This chapter mainly compares and studies the content and pollution degree of heavy metals in surface sediments of Songhua River Basin in different periods (dry season, wet season and flat season). The main conclusions are as following:

Through comparison, it is found that the time variation law of the total amount of heavy metals in the sediments of the whole Songhua River Basin is normal water period > high water period > low water period. In the normal water period, the content of heavy metals in the upper reaches of the Songhua River is much higher than that in the dry and high-water periods. The time variation law of heavy metals in the middle reaches of the Songhua River is high water period > normal water period > low water period, The temporal variation law of heavy metal content in the lower reaches of Songhua River is normal water period > high water period > low water period.

4.2 Removal of Heavy Metal Pollutants

In this study, the pollution status of heavy metals (Zn, Pb, Ni and Cr) in the sediments of the Songhua River in an urban area with petrochemical industries were assessed. Effect of temperature, reaction time, pH and nano zero valent iron dosage on Pb, Cr and Ni removal are studied.

4.2.1 Experimental Study and Conclusion

Especially those rivers flowing through urban central areas and industrial areas of Songhua River, due to the receipt of a large amount of domestic sewage, industrial wastewater and other pollutants carried by surface runoff, the pollutant content of these rivers is often high, especially heavy metal pollution. Heavy metals in chemistry generally refer to metals having a relative density greater than or equal to 5.0 g/cm^3, including Hg, Cd, Cu, Pb, Zn, Cr, and the like. Heavy metals are considered to be a class of highly hazardous and difficult to treat environmental pollutants because of their ease of accumulation in living organisms, their concealment and endurance in the environment, and their ability to migrate over long distances. Heavy metals not only have safety hazards in food, but also pose a serious threat to the normal growth and development of animals and plants and the virtuous cycle of the ecological environment.

The heavy metal pollutants in the water body are gradually enriched and accumulated in the sediment through adsorption, coordination, precipitation, etc., and the concentration in the sediment is usually several times higher than that in the overlying water. The change of external environmental conditions can easily break the dynamic balance of adsorption and desorption of heavy metal pollutants between sediment and overlying water. At this time, heavy metal contaminated sediments become pollution sources and release heavy metals into water bodies, resulting in secondary pollution of water bodies. As a result of the deterioration of the water quality environment, the ecosystem will be in danger due to the pollution of the water body on which it depends. Therefore, the research and treatment of heavy metal pollution in sediments in the water environment is one of the important ways to solve the problem of water pollution.

Nanomaterials have high reactivity due to its unique surface properties, quantum size effects and macroscopic quantum tunneling effects, which play an important role in environmental fields such as catalysis, adsorption and degradation of pollutants. Nanomaterials are widely used in industrial and domestic sewage treatment, polluted soil and sediment treatment, air pollution control and other pollution remediation processes. Metal and its oxide nanomaterials, dendritic polymers, carbon nanomaterials and polymer nanocomposites are widely used as environmental remediation nanomaterials. They can remove pollutants through chemical degradation (photocatalysis), reduction, adsorption and precipitation . Nano zero valence iron (nZVI), as an environmentally friendly material, is an effective material for groundwater remediation. nZVI has a low redox potential of −0.44 V, which is lower than that of common heavy metals (Pb, Cd, Ni, Cr) and organic pollutants (chlorinated hydrocarbons), so nZVI is usually used as an electron donor during the remediation process. Tuček et al. studied the mechanism of reduction of arsenic by nZVI with iron oxide shell. nZVI could reduce As(V) to As(III) or As(0) under anoxic conditions, and the reduced products were fixed between iron oxide shell and nZVI core to reduce the migration of As. FeOOH is widely used as sorbents and Fenton-like catalyst to remove contaminants from aqueous solutions. Due to the formation of ternary surface complexes (≡$FePO_4UO_2$), the maximum adsorption capacity of U(VI) by three-dimensional flower-like goethite was 112.36 mg/g after being modified by NaH_2PO_4 [14]. FeOOH can also reduce certain heavy metal ions. Yang et al. showed that β-FeOOH supported activated carbon reduced Cr(VI) to Cr(III) in aqueous solutions.

Nano zero-valent iron (NZVI) form for the treatment of halogenated organic molecules, nitrates, dyes, nitroaromatic compounds, pesticides and heavy metals [19]. Outstanding benefits like high surface area, fast kinetics, high reactivity and small particle size.

In this study, the pollution status of heavy metals (Zn, Pb, Ni and Cr) in the sediments of the Songhua River in an urban area with petrochemical industries were assessed. Effect of temperature, reaction time, pH and nano zero valent iron dosage on Pb, Cr and Ni removal are studied.

4.2.2 Materials and Methods

Study area and Sampling. The study area is the Songhua River in Harbin City. The river is the major domestic water source for local residentials. Harbin City is an industrial City where the Harbin Petrochemical Company, PetroChina Co. Ltd, the largest petrochemical industry in Heilongjiang Province, is located. Harbin City is located in the north temperature zone, with a continental monsoon climate.

Chemical Analysis. Two grams of sediment samples were digested using the $HClO_4$-HNO_3-HF method, and the concentrations of Pb, Ni, and Cr in the extracts were determined by inductively coupled plasma atomic emission spectrometry, ICP/AES (ICPS-7500, Shimadzu, Japan).

4.2.3 Results and Discussion

Effect of pH and reaction time on Cr removal is shown in Fig.4-8 and Fig.4-9. Cr removal increased when the pH in the water increased from 7.7 to 8.7. Cr removal decreased while the pH in the water increased from 8.7 to 9.7. Cr removal is 94.56% when pH is 9.7.

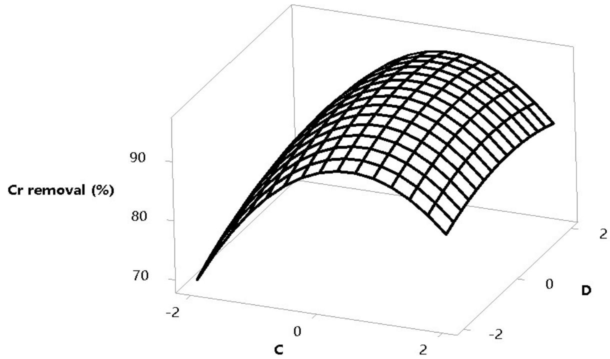


Fig. 4-8 Surface plot of Cr removal (%) vs D, C

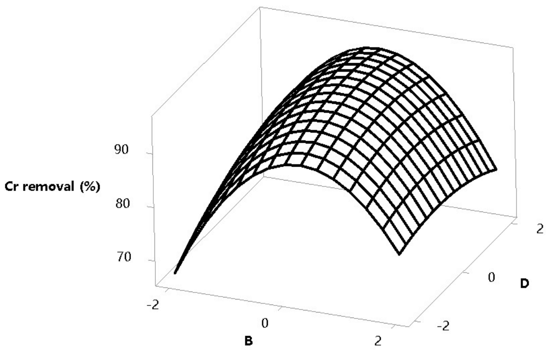


Fig. 4-9 Surface plot of Cr removal (%) vs D, B

Cr removal increased when the reaction time increased from 5 to 10 min. Cr removal is 94.56% when reaction time is 10 min. pH and reaction time have a strong interaction.

Effect of nano zero valent iron dosage on Cr removal is shown in Fig.4-10 and 4-11, 4-12. Cr removal increased when the nano zero valent iron dosage from 5.0 g/L to 10.0 g/L. Cr removal is 94.56% when nano zero valent iron dosage is 10.0 g/L.

Based on the selected range for this study, the presence of nano zero valent iron increased the production rate of OH•. Other less oxidation potential radicals may be produced and ultimately when the concentration of OH• radicals are too high. Thus these cumulative effects increased the removal.

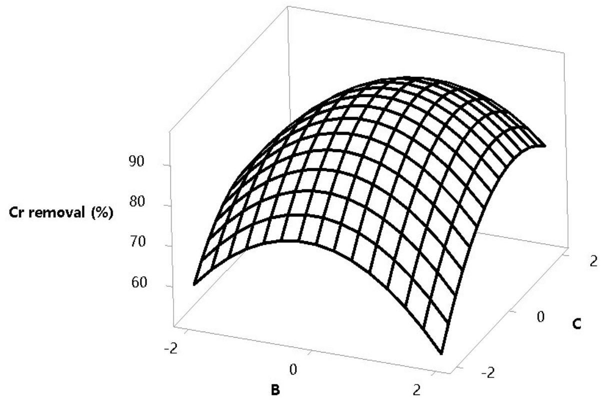


Fig. 4-10 Surface plot of Cr removal (%) vs C, B

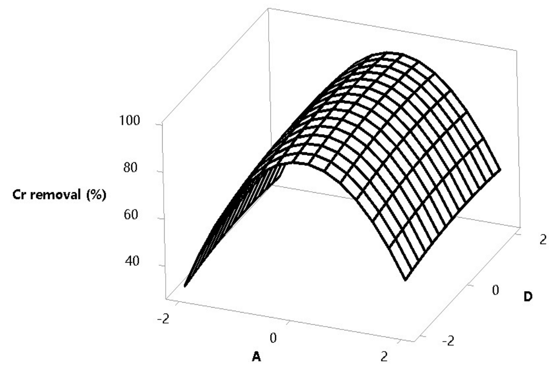


Fig. 4-11 Surface plot of Cr removal (%) vs D, A

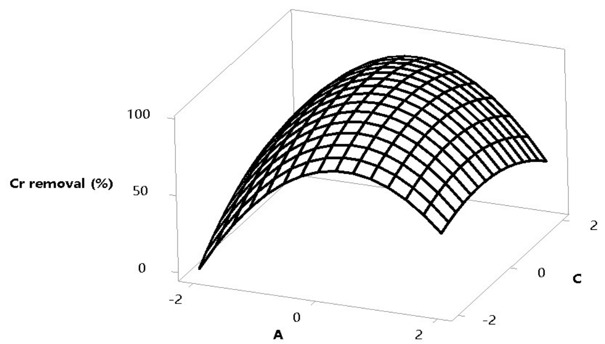


Fig. 4-12 Surface plot of Cr removal (%) vs C, A

For Fig.4-13, at a pH of the reaction solution is 7.7, the nano zero valent iron dosage is 10 g/L, when the temperature increases, the Cr removal rate increased significantly, especially when the temperature from 20 to 40°C, Cr removal increased from 57.26%, 61.02% to 67.4%, 95.5%, Cr removal efficiency increased by 10.14%, 34.48%.

Effect of temperature on the Cr removal are mainly present based on two points, the first temperature rises will reduce the activation energy of the reaction, so that the reaction can not occur previously occurred in the reaction temperature is raised or the original reaction can occur more efficient, and the second is that, as the temperature increases, the solubility of the gas decreases, Cr removal increases.

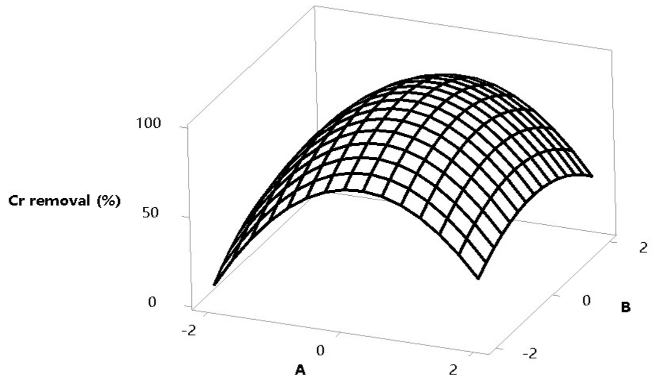


Fig. 4-13 Surface plot of Cr removal (%) vs B, A

Table 4-12 Effect of temperature on Pb and Ni removal

Temperature (°C)	Reaction time (s)	Pb removal with 10 g/L nano zero valent iron (%)	Ni removal with 10 g/L nano zero valent iron (%)
20	60	70.66	70.97
	180	71.43	73.54
	300	75.23	79.55
	540	78.89	81.63
30	60	75.24	76.41
	180	80.16	84.65
	300	82.56	85.96
	540	82.89	86.52
40	60	80.57	83.88
	180	81.35	88.66
	300	84.64	91.63
	540	89.63	96.64

Table 4-12 shows the Pb and Ni removal in relation to the effect of temperature from 20 to 40°C without nano zero valent iron, or with nano zero valent iron. Experimental results show that the Pb and Ni removal increased with the increasing reaction temperature.

The results show that adding a small amount of nano zero valent iron can raise the Pb and Ni removal. The highest Pb and Ni removal is 89.63%, 96.64% when temperature is 40°C, reaction time is 540 s, and nano zero valent iron is 10 g/L.

4.2.4 Conclusions

Information is presented regarding the concentration levels in the sediment of the Songhua River in a petrochemical industrial area. To consider nano zero valent iron as a treatment method to Pb, Cr and Ni, knowledge of the impact of the operating conditions such as temperature, reaction time, pH and nano zero valent iron dosage is required. Experimental results indicated that adding the nano zero valent iron accelerates the Pb, Cr and Ni removal. The best removal efficiency of Cr reached 95.5%. The highest Pb and Ni removal is 89.63%, 96.64% when temperature is 40°C, reaction time is 540 s, and nano zero valent iron is 10 g/L.

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Chapter 5

ANALYSIS AND REMOVAL OF MAIN POLLUTANT AMMONIA NITROGEN

CHAPTER FIVE：ANALYSIS AND REMOVAL OF MAIN POLLUTANT AMMONIA NITROGEN

Non metallic pollutants mainly include COD, ammonia nitrogen and petroleum organic pollutants. This chapter takes Songyuan City, a major City in Songhua River Basin, as an example to investigate and analyze the main sources and removal methods of non-metallic pollutants.

5.1 Investigation and Analysis of Non-metallic Pollutants

5.1.1 Investigation of Non-metallic Pollution Sources

5.1.1.1 Investigation on Pollution Sources of Key Industries

There are 13 major industrial pollution sources in Songyuan. In 2017, the discharge of industrial wastewater from key industrial pollution sources was 12.26 million tons, and the discharge of main pollutants COD and ammonia nitrogen were 2257 tons and 993 tons, respectively. Among the key industrial pollution sources, 6 have reached the standard, accounting for 46% of the total. The industrial pollution sources exceeding the standard are mainly concentrated in chemical industry, grain deep processing and other industries. It is shown in Table 5-1 for details.

Table 5-1 Pollutant discharge from key industrial pollution sources in Songyuan city

List of companies	Wastewater discharge (10,000 tons/year)	Compliance	COD emissions (ton/year)	Ammonia nitrogen emissions (ton/year)
Qianguo Petrochemical Company	270	up to standard	248.4	48.6
Songwon Refinery	29	not to standard	9	6
Jilin Fuji Protein Company	35	up to standard	112.35	11.38
Jilin Fuji Protein Company	48	not to standard	249.6	19.44
(Qianguo Factory)	95	up to standard	131.1	47.5
Celeste	120	not to standard	744	54
Ji'an Biochemical Songyuan Company	24	up to standard	48.24	8.23
dacheng biochemical co., ltd.	132	up to standard	300	20
Ji'an Biochemical Qian'an Alcohol Company	99	not to standard	90	10
kanan linen mill	66	not to standard	60	19
Fuyu Chemical Co., Ltd.	4	not to standard	6	1
Fuyu Mitsuizi Furfural Factory	264	not to standard	223	745
Changshan Fertilizer Factory	40	up to standard	35	3

The pollution of Songhua River in Songyuan City is mainly concentrated in the urban area. The sewage of six enterprises in the city is directly or indirectly discharged into Songhua River. It is shown in Table 5-2 for details.

Table 5-2 Details of enterprises discharging sewage into Songhua river

Sewage unit	industry	SS (mg/l)	Ar-OH (mg/1)	COD (mg/1)	BOD: (mg/1)	Oil (mg/1)	pH	As (mg/1)	NH_3-N (mg/1)	Displacement (t/d)
Qianguo Petrochemical Company	petroleum	90	0.024	92	56	6.74	7.8		18	7500
Jilin Fuji Protein Company	food processing	146		321	192		6.9		32.52	700
Jilin Fuji Protein Company	food processing	340		520	290		8		40.5	500
(Qianguo Factory)	food processing	810		620	300		6		45	
Ji'an Biochemical Songyuan Company	food processing	204		138	60		7.5		50	2300
Celeste	food processing	97		201	90		8.6		34.31	800

5.1.1.2 Domestic Sewage Investigation

Songyuan has a total population of 2.79 million along the river and 460000 non-agricultural people in the urban area. There are 13 sewage outlets along the urban area, including 6 along the north of the river and 7 along the south of the Yangtze River. After the establishment of the south of the Yangtze River sewage treatment plant in 2006, four sewage outlets were banned, so there are now 6 sewage outlets in the north of the river. There are three sewage outlets in Jiangnan. The sewage from the sewage treatment plant mainly comes from domestic sewage and some industrial wastewater in Jiangnan urban area. The COD 400-600 mg / L of domestic sewage is required to be treated less than 500 mg / L of industrial water, and the daily treatment capacity is 35000 tons / day. In terms of the total discharge, the proportion of total domestic sewage is high, and urban domestic pollution is an important pollution source of Songhua River. The specific calculation is shown in the following public test:

Municipal domestic sewage discharge coefficient = per capita domestic water consumption × Drainage conversion coefficient

For Songyuan City, 125 L / person / day × 0.8 = 100 L / person / day

Urban domestic sewage discharge = urban domestic sewage discharge coefficient × Number of non-agricultural population in cities and towns × 365 =100 × four hundred and sixty thousand × 365 = 167900000000 L = 1679000000 tons

Cod production of urban domestic sewage = cod production coefficient of urban domestic sewage × Number of non-agricultural population in cities and towns × 365 = 60g / person day × four hundred and sixty thousand × 365 = 10074000000 g = 10074t

Ammonia nitrogen production in urban domestic sewage = ammonia nitrogen production coefficient in urban domestic sewage × Number of non-agricultural population in cities and towns × 365 = 7g / person day × four hundred and sixty thousand × 365 = 1175300000 g = 1175.3 t

5.1.1.3 Investigation on Pollution Sources of Livestock and Poultry Breeding

In 2016, there were 28 large-scale livestock and poultry farms in Songyuan area, the breeding quantity was converted into 21125 pigs, the daily water consumption was 340.54 tons, the annual COD emission was 116.54 tons, and the ammonia nitrogen emission was 38.46 tons. The main pollutants are used locally or discharged disorderly, and do not enter the Songhua River (Table 5-3). Therefore, according to the survey results, the pollutants of large-scale livestock and poultry farms in Songyuan City are not discharged into the river.

Table 5-3 Farm scale and emission mode in Songyuan area

Area name	Number of large-scale livestock and poultry farms (pieces)	The number of breeding is converted into pigs (head)	Water consumption (t/d)	Way of discharge	COD emissions (t)	Ammonia nitrogen emission (t)
Songyuan City	1	100	8.5	In-place utilization	0	0
Ningjiang District	4	2167	185	after rinsing	35.54	12.24
Qianguo County	12	7183	30.29	emission	131	26.22
Changling County	11	11675	116.75	Disorderly discharge	0	0

5.1.1.4 Agricultural Non-point Source Pollution Survey

The so-called non-point source pollution is defined by the American Clean Water Act Amendment (1997) as "pollutants enter the surface and groundwater in the form of wide area, dispersion and trace". It is reported that in agriculture, 20% ~ 30% of cultivated land in China has excessive nitrogen nutrients, the utilization rate of nitrogen fertilizer in agricultural production is 30% ~ 50%, the underground leakage loss of nitrogen fertilizer is 10%, and the loss of farmland drainage and storm runoff is 15%; The utilization rate of phosphate fertilizer is 10% ~ 25%. A large number of nitrogen and phosphorus nutrients enter the river with farmland drainage or rainwater, resulting in pollution of surface water and groundwater and eutrophication of the lake. In addition, because the utilization rate of pesticides is less than 30%, more than 70% of pesticides are lost in the environment, which seriously affects the agricultural ecological environment. In particular, pesticides in soil are washed into rivers, lakes and seas by irrigation water and rainwater, polluting water sources. The degree of pesticide pollution in different water bodies is as follows: farmland water > gutter water > runoff > pond water > shallow groundwater > river water > tap water > deep groundwater > seawater.

Songyuan City has 715678 hectares of dry fields and 46506 hectares of paddy fields. The fertilization situation of paddy fields is close to that of dry fields. Each hectare of dry fields uses 1 ton of urea, 1 ton of ammonia sulfate and 5000 ml of herbicides. However, due to the lack of investigation data on agricultural chemical fertilizers and pesticides by relevant departments, this paper only lists the use of chemical fertilizers and pesticides in Ningjiang District of Songyuan City in Table 5-4 and Table 5-5.

Table 5-4 Use of chemical fertilizer in Ningjiang district, Songyuan city in 2016

cultivated area	main crops	Main fertilizer usage				
		nitrogen	phosphorus	Potassium	Average usage	Total
497	corn	18000 t	12000 t	6000 t	48 kg/mu	36000 t

Table 5-5 Pesticide use in Ningjiang district of Songyuan city in 2016

cultivated area	main crops	Pesticide name and dosage							
		name	dosage	name	dosage	name	dosage	name	dosage
497	corn	Acetochlor	111,800 kg	atrazine	149,100 kilograms	Yu Nong Le	74,500 kilograms	0.45 kg/mu	335,400 kilograms

5.1.1.5 Investigation on Pollution Sources of Oilfield Exploitation

PetroChina Jilin Oilfield Company has 11000 oil wells, 351 oil wells along the second Songhua River and on the island, including 181 single well tanks and 170 gathering and transmission.

The pollution source of oilfield development project is mainly centered on the oil well, which consists of various process processes such as drilling, downhole operation, oil production, oil and gas gathering and transportation, storage and transportation, etc, As well as the regional pollution sources composed of metering station (oil gathering and water distribution room), transfer station, combined station, oil and gas pipeline network and other facilities. According to the field investigation and analysis, it is determined that the pollution to the second Songhua River in the process of oilfield exploitation is mainly drilling wastewater, workover and well washing wastewater in downhole operation, oily wastewater and landing oil and other solid wastes.

(1) Wastewater pollutant discharge

Wastewater during construction

Drilling wastewater. Wastewater discharged from flushing drilling equipment and maintenance during oil well drilling in the early stage of oilfield development.

According to the survey, 0.29 m^3 of wastewater will be produced per 1 m of drilling depth. According to the calculation of about 500 m deep wells along both banks of the river, each well produces 145 m^3 of wastewater.

Domestic sewage. There are 200-500 persons on the construction site every day, and each person discharges 50 L / D sewage. Because the construction site is scattered, it can be ignored.

Wastewater in production period

Workover wastewater. Generally, once a year, each workover generates 20-80 m^3 of wastewater for each well. The existing oil wells along the river produce a total of 7020-28080 m^3.

Well washing wastewater. One cycle is 90 days. The well is washed to remove the dirt at the bottom of the well. The well washing wastewater mainly contains petroleum, surfactant, acid-base and other chemicals, 720 m^3 wastewater. Table 5-6 shows the types and concentrations of pollutants in well washing wastewater.

Table 5-6 Concentration of pollutants in underground operation wastewater (mg/l)

Pollutants	COD	Petroleum	Volatile phenol	Sulfide
concentration	60-100	1000-3000	3-5	1-5

Oil production wastewater.

Oil production wastewater is mainly the edge water, bottom water contained in the oil layer itself and a large amount of water injected during oil displacement. The water content can reach 10% - 85%, and the water content increases with the increase of oil production time. When oil is stored in single well tanks, it is transported by tanker. After the upper oil is transported away, the oily wastewater is usually discharged into the seepage pit of the well pad.

Domestic sewage is ignored. Generally, there are fewer workers in the oil production area after completion.

(2) Solid waste

Construction period: landing crude oil during oil test. Oil test shall be conducted before putting into production. The crude oil shall be discharged into the land or oil pool through the nozzles at different ports at the wellhead to calculate the oil production. Therefore, during oil testing, some crude oil is scattered in the well pad and becomes landing oil. 1-1.5 t/a for each well. Oil test shall be carried out before production, and the recovery rate through nozzles at different positions at the oil well outlet shall be more than 90%. The landing oil is 0.1-0.15 tons.

Production period: the production period is mainly one workover per year. Each well produces 0.4-1.0t of landing oil each time, and the oil wells along the river produce 175.4-351t in total, which is generally recovered by 90%. If the well pad is paved with thick plastic cloth, it can reach 100%.

5.1.2 Investigation and Analysis

Sulfide, cyanide, benzene, toluene and xylene are not detected; pH, BOD_5, COD_{Mn}, ammonia nitrogen and volatile phenol all meet the requirements of the evaluation standard in wet, normal and dry seasons, and petroleum exceeds the standard.

Dry season: in each year, the standard indexes of pollutants in the sections of livestock farm, Xidazuzi and swill tank are less than 1, and all pollutants do not exceed the standard.

Normal water period: the standard index of pollutants at each monitoring section is less than 1, and all pollutants do not exceed the standard. In 2016, the oil at the swill tank section exceeded the standard by 0.12 times, and in 2017, the oil at the swill tank section exceeded the standard by 0.09 times.

Wet season: the standard index of each pollutant at each monitoring section is less than 1, and each pollutant does not exceed the standard; In 2016, the oil in swill tank section exceeded the standard by 0.16 times, and in 2017, the oil in swill tank section exceeded the standard by 0.12 times.

To sum up, the water quality of the Songyuan section of the second Songhua River has been polluted to a certain extent. Although the West Dazuizi section has not evaluated the exceeding standard factor, it can not meet the requirements of "Class III" water area in the environmental quality standard for surface water (GB3837-2002). In this evaluation, "Class IV" water area is used for evaluation.

Table 5-7 List of comprehensive evaluation results of pollution factors（2015-2019）

Project	Water quality factor						
	pH	BOD_5	COD_{Mn}	NH_3-N	Volatile phenol	Petroleum	∑Kj
Comprehensive labeling index	2.27	2.66	6.56	6.17	4.2	5.77	27.63
Ki	8.22%	9.63%	23.74%	22.33%	15.20%	20.88%	100%
Sort	6	5	1	2	4	3	-

Project	Water quality factor						
	pH	BOD_5	CODMn	NH_3-N	Volatile phenol	Petroleum	∑Kj
Comprehensive labeling index	2.33	3.11	6.78	6.2	5.2	5.48	29.1
Ki	8.01%	10.69%	23.30%	21.31%	17.87%	18.83%	100%
Sort	6	5	1	2	4	3	-

Project	Water quality factor						
	pH	BOD_5	COD_{Mn}	NH_3-N	Volatile phenol	Petroleum	∑Kj
Comprehensive labeling index	2.03	3.34	6.93	7.34	5.9	6.09	31.63
Ki	6.42%	10.56%	21.91%	23.21%	18.65%	19.25%	100%
Sort	6	5	2	1	4	3	-

Project	Water quality factor						
	pH	BOD_5	COD_{Mn}	NH_3-N	Volatile phenol	Petroleum	∑Kj
Comprehensive labeling index	2.18	3.22	6.99	7.44	5.9	6	31.73
Ki	6.87%	10.15%	22.03%	23.45%	18.59%	18.91%	100%
Sort	6	5	2	1	4	3	-

It can be seen from Table 5-7 that the comprehensive ranking of the evaluation factors of the Songyuan section of the second Songhua River in each year shows that COD and ammonia nitrogen are always in the top two in the five years of evaluation, petroleum is in the third, and volatile phenol, BOD_5 and pH are in the fourth, fifth and sixth every year.

It can be seen that the main pollutants in the Songyuan section of the second Songhua River are COD, petroleum and ammonia nitrogen, which are classified into oxygen consuming organic matter and petroleum according to the hazard characteristics of pollutants. Among them, the pollution of petroleum is mainly caused by industrial wastewater. The pollution of ammonia nitrogen and COD is not only directly related to industrial wastewater, but also related to domestic sewage.

Among the three conventional monitoring sections in the Songyuan section of the second Songhua River, the water quality of the livestock farm section is the best, followed by the swill tank section, and the Xidazuzi section is the most polluted. The reason is that the river section from the livestock farm section to the Xidazuizi section receives the industrial wastewater and urban domestic sewage from Songyuan City. After a period of time and distance of water degradation, the pollutant concentration in the river is reduced through self-purification, and the pollution degree is alleviated in the swill tank section.

5.1.3 Investigation Conclusion

According to the evaluation results of water quality in Songyuan section of the second Songhua River, sulfide, cyanide, benzene, toluene, xylene, pH, BOD_5, COD_{Mn}, SS and ammonia nitrogen meet the requirements of the evaluation standard, and petroleum exceeds the standard, indicating that the water quality in Songyuan section of the second Songhua River has been polluted to a certain extent, The section from livestock farm to Xidazuzi section can no longer meet the requirements of "Class III" water area in the environmental quality standard for surface water (GB3837-2002).

According to the comprehensive evaluation results of monitoring sections, among the three conventional monitoring sections in Songyuan river section, the water quality of livestock farm section is the best, followed by swill tank section, and Xidazuzi section is the most polluted. The main reason is that the industrial wastewater and urban domestic sewage from Songyuan City are accepted in the section of livestock farm section - Xidazuizi section. After a period of time and distance of water degradation, the pollutants in the river are reduced through self-purification, and the pollution degree is alleviated in the section of swill tank.

Ammonia nitrogen increased year by year, but decreased slightly by 2017, and COD_{Mn} increased year by year, indicating that the amount of industrial and domestic sewage discharged into the second Songhua River increased. Oil increased year by year from 2016 to 2018 and began to decline in 2019, indicating that the oil content in the river decreased in recent years due to the prevention and control measures taken in early 2019.

5.2 Cause Analysis of Water Environment Pollution in Songyuan Section of the Second Songhua River

According to the comprehensive evaluation results of pollution factors, the main pollution factors in Songyuan river section are COD_{Mn}, petroleum and ammonia nitrogen; Among them, oil pollution is mainly caused by industrial wastewater; The pollution of ammonia nitrogen and COD is not only directly related to industrial wastewater, but also related to domestic sewage.

COD_{Mn} and ammonia nitrogen

COD_{Mn} increased year by year, and ammonia nitrogen increased year by year, but decreased slightly by 2017. From the aspect of domestic sewage, the increase year by year is mainly due to: firstly, the non-agricultural population in Songyuan City is increasing, resulting in the increase of domestic sewage; Secondly, a large amount of domestic sewage is directly discharged into the river without treatment; Third, ammonia nitrogen decreased in 2017 because the expansion of Songyuan Jiangnan sewage treatment plant began trial operation in August 2017, increasing the sewage treatment capacity.

From the perspective of industry, Songyuan's industry has developed rapidly in recent years without taking good treatment measures. First, the original enterprise sewage treatment facilities are not complete and the production process is backward; Secondly, new enterprises do not fully abide by the principle of "three Simultaneities" when investing and constructing; Third, the regulatory capacity of relevant law enforcement departments is insufficient, and the phenomenon of sewage secretly discharged and missed discharged by enterprises is still common.

From the aspect of livestock and poultry breeding: according to the previous pollution source investigation, the pollutants produced by livestock and poultry farms in Songyuan City are not discharged into Songhua River.

From the aspect of Agriculture: for the vast areas of China, the pollution caused by pesticides and chemical fertilizers to river water quality should be paid enough attention. Moreover, the harm of non-point source pollution is almost the same as or more serious than that of point source in other watersheds. However, the situation of Songyuan section of Songhua River should be analyzed in detail: the soil in Songhua River Basin is fertile, and the use of chemical fertilizer per unit area is far less than that in other parts of China. Moreover, there are dams on both sides of the river from the storage pasture to the swill tank. There are marshes and grasslands outside the dam, and there is no cultivated land in the flood discharge area, so there is little non-point source pollution. Compared with the point source pollution harm caused by industrial wastewater discharge, the non-point source pollution of Songhua River can be ignored. This feature is very important for mastering the pollution control of Songhua River.

In addition, the surface runoff of Songhua River is small, which is mainly replenished by rainfall. When there is little rainfall, the discharged sewage can not be diluted, resulting in high pollutant concentration.

5.3 Ammonia Nitrogen Removal

Through the investigation and analysis of pollution sources in agriculture and aquaculture, ammonia nitrogen has become the first organic pollutant in the total content of water.

The main source of ammonia nitrogen is the excreta of animal husbandry.

Next, horse manure is taken as an example to study the treatment of animal excreta.

5.3.1 Introduction

The continuous increase in global population, has led to excessive demand for water, energy, and high rate of solid waste generation (Owamah et al. 2020). This excessive demand for energy has in turn put great pressure on conventional energy resources such as fossil fuels. Dairy production has also become an important industry in Nigeria and world-over and contributes about 7% of the aggregate agricultural production worth. The expansion in livestock production has resulted in the generation of huge quantity of livestock manure, which is of great environmental concern in areas such as release of greenhouse gas (GHG), contamination of surface water, etc. Furthermore, much of this livestock manure comes from cattle. The demand to decrease the carbon footprint of ruminants, as they contribute the hugest amount (61%) to livestock-related GHG emissions has become commonplace. During anaerobic digestion, while biogas for heat and power generation is produced, biofertilizer for agriculture is also obtained as the digestate (Menardo and Balsari 2012). Generation of biogas takes place as microorganisms degrade organic matters into methane and carbon (IV) oxide.

Amongst all the treatment options, anaerobic digestion (AD) is a technology that is widely used. However, horse dung AD regularly presents low efficiencies due to the high concentration of ammonia and its low hydrolysis rate (Bonmatí et al. 2001; Hansen et al. 1998). Incineration is a valuable means of waste disposal with the advantage of being highly effective in reducing the volume of waste. Unfortunately, incinerators generate large volumes of off-gases. Furthermore, the auxiliary fuel must be added to the incinerator to keep the incineration temperature constant (Danielle et al. 2014). Biogas treatment is a cheap treatment method for horse dung. However, it is occupied with a large space and the slag treatment is difficult (Cheng et al. 2013). Fermentation can effectively reduce the volume of waste. Unfortunately, fermentation period is too long and it is occupied with a large space (López-Garzón and Straathof, 2014). As mentioned above, no technology currently has reached a satisfactory solution from the environmental and highly effective point of view. Consequently, there is a need for environmentally benign technologies capable to effectively neutralize horse dung and reduce its adverse impacts on the environment.

Supercritical water gasification (SCWG) is a promising technology since it can produce hydrogen by complete gasification of organic matters in water without drying procedure which is an energy-intensive process and required as a pretreatment of aqueous feedstocks in conventional gasification processes. Furthermore supercritical water has an extraordinary ability to suppress char formation during the decomposition of organic compounds (Lee 2011). Char is known to be a refractory byproduct formed in a significant amount during steam gasification of biomass at atmosphere (Herguido et al. 1992), or hydrothermal treatments of glucose (Fang et al. 2008) and cellulose (Fang et al. 2008; Minowa and Fang, 1998) in hot liquid water at temperatures up to 350°C (subcritical water conditions) unless appropriate catalysts are used. These impressive abilities of supercritical water to treat organic materials are based on its unique thermophysical properties (Shaw et al. 1991; Wofford and Gloyna, 1995). Under SCWG conditions, water is not only a solvent, but also an active reactant contributing to gasification chemistry (Antal et al. 2000).

Several kinds of catalysts were studied in biomass SCWG in the decades of development (Azadi and Farnood, 2011; Savage 2009), such as metals, metal oxide, activated carbons and alkalis. Generally speaking, the catalysts can be grouped into two categories: heterogeneous and homogeneous catalysts. Alkali is the most frequently used homogeneous catalyst in SCWG, which attracted many researchers' attention because it can be mixed with the feedstock uniformly other than the heterogeneous catalysts (Kruse et al. 2000; Sınağ et al. 2010; Sınağ et al. 2004; Sınağ et al. 2003; Williams et al. 2010; Williams et al. 2010; Williams et al. 2010; Yanik et al. 2008). Some organic wastes, such as the alkaline black liquor contain alkali, of which can be taken advantage to catalyze the biomass SCWG (Cao et al. 2011; Sricharoenchaikul 2009; Rönnlund et al. 2011). Several researchers found that the presence of alkali can promote water-gas shift reaction (WGS) in SCWG, which consumes CO and H_2O and generates H_2 and CO_2 (Kruse et al. 2000; Sınağ et al. 2010; Sınağ et al. 2004; Sınağ et al. 2003; Williams et al. 2010; Williams et al. 2010; Williams et al. 2010; Yanik et al. 2008). The lower CO fraction in the gas product is advantageous because fewer subsequent purification processes are needed for the terminal application of the gas product. Besides, active hydrogen can be generated in catalyzing WGS reaction in SCWG with the presence of alkali, which can inhibit the char/coke formation and improve the gas yield.

In this study, the influence of LiOH in SCWG of horse dung was investigated. Firstly, the gasification performance of horse dung with and without LiOH in supercritical water was compared. Then the influence of the accumulated alkali in the reactor on the subsequent gasification of horse dung without alkali was studied with a longer reaction time.

5.3.2 Experiments

5.3.2.1 Apparatus and Method

The experiments were conducted in a laboratory-scale, continuous reactor with a volume capacity of 600 mL designed to a maximum temperature and pressure of 650°C and 40 MPa. The flow diagram of the experimental setup is shown in Fig. 5-1. All wetted parts, from the pumps to the condenser, were made of stainless steel (1Cr18Ni9Ti). The stirrer was used to keep from the formation of char resulting from thermal cracking of horse dung (Table 5-8 shows the characteristics of horse dung used in this study) at the walls of the reactor. The electric furnace was used as heater. The heating wires of electric furnace were placed below and around the reactor. The reaction temperature was monitored directly using thermocouple (inserted inside the reactor) and controlled within 1°C by a temperature controller (Shandong Huayi Instrumentation Co., N-9000 Digital Controller). Before the experiment, the reactor was loaded with horse dung and deionized water to bring the total volume of liquid to 90–125 mL, and concentration of horse dung is approximately corresponding to initial COD of 1000–2000 mg/L. Then, nitrogen gas was used to purge the reactor for 15 min. After purging, the reactor was heated for about 60 min. Upon reaching the reaction condition of reaction temperature 560°C and pressure 25 MPa, reaction temperature remained stable within 1°C, then the specified amount of LiOH was fed into the reactor at room temperature. The reaction was conducted for a given reaction time from 15 to 65 min. After the reaction, the sample valve of reactor was opened and the effluent was cooled rapidly in a shell and tube heat exchanger and then depressurized to ambient condition. The product stream was then separated into liquid and vapor phases. The liquid products were collected in a graduated cylinder. Gaseous samples were collected with sample tubes.

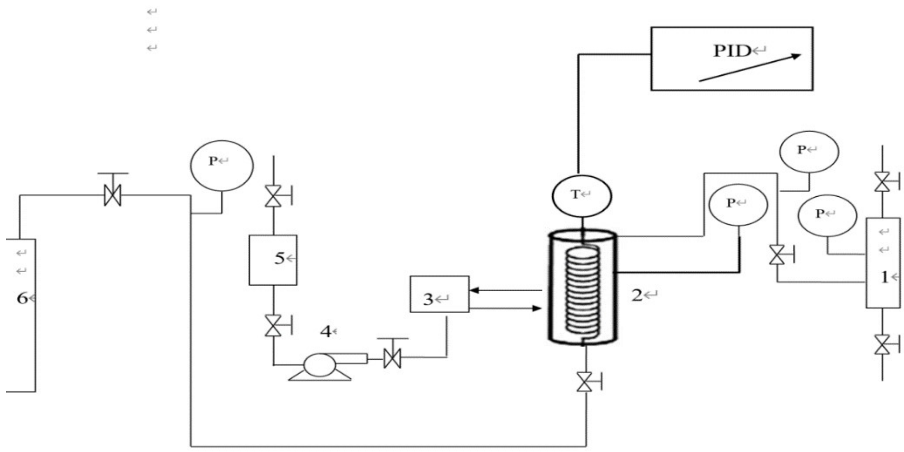

Fig 5-1 Schematic diagram of experimental setup

1. Gas-liquid separator 2. High-pressure Autoclave 3. Heater 4. High pressure pump 5. Oxidant container 6. Nitrogen container

Table 5-8 Characteristics of horse dung

Characteristics	Concentration(mg/L)
Total oxygen demand (TCOD)	57860
Total suspended solids (TSS)	25070
Soluble oxygen demand (SCOD)	28570
Volatile fatty acids (VFAs)	12680
Volatile suspended solids (VSS)	17990

5.3.2.2 Chemical Analysis

The gas yield was measured by a wet type flow meter. The composition of the gas product was analyzed by a gas chromatography (Perkinelmer Clarus 680) with a thermal conductivity detector (TCD). The high-purity helium is used as the carrier gas (purity > 99.999%). A carbon molecular sieve column (TDX-01) purchased from Beijing Beifenruili Analytic Instrument Co., Ltd. in China is used operating at 70 °C for 2 min, heating at 50°C /min ramp to 140°C and hold for 10 min. The determination of the sodium content in the aqueous sample was conducted in inductively coupled plasma-atomic emission spectrometry.

5.3.3 Results and Discussion

5.3.3.1 SCWG of Horse Dung without LiOH

Horse dung was gasified without catalyst addition at 560°C and 25 MPa in the continuous reactor for a long reaction time. H_2, CH_4, CO and CO_2 are main compositions of the gas product. The results changed with changing reaction time (Fig. 5-2). It can be seen that CO fraction increased with the reaction time and the H_2 fraction decreased. This may be because the reactant concentration in the reactor increased with more horse dung fed into the reactor in a longer reaction time. The previous literatures (Jin et al. 2010; Lu et al. 2008) indicated that high concentration of biomass is hard to decompose and gasify. More CO, lower gasification rate and less H_2 were generated in the process of SCWG of biomass with higher concentration, and they are consistent with the variation trend of gasification results at earlier stage. Moreover, during the process of SCWG, reaction environment in the reactor is changed by horse dung decomposition. The generated intermediates from decomposition of horse dung may have negative effects on WGS reaction, which led to higher CO fraction and lower H_2 fraction. After 20 min of reaction, the gas product reached the stable state and remained constant. The gas product under the stable state contained about 26% CO, 35% CO_2, 10% CH_4, 29% H_2 and the gas yield was 15 mol/kg.

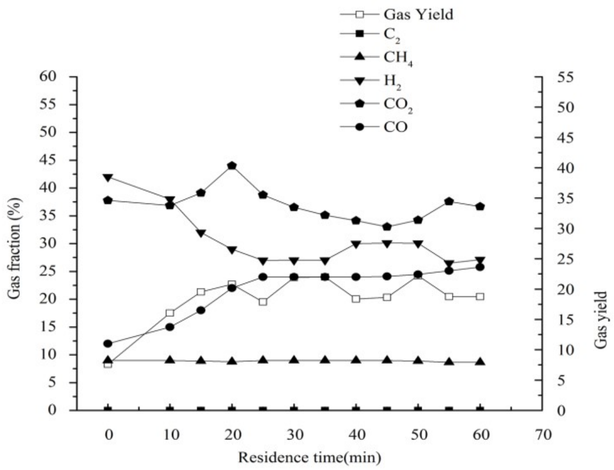

Fig 5-2 The composition and total yield of the gas product from SCWG of horse dung (560°C, 25MPa)

5.3.3.2 SCWG of Horse dung with 100 mg/L LiOH

When catalyst (100 mg/L LiOH) was added to the reactor for SCWG of horse dung at 25 MPa and 560°C, the composition and yield of gas product was shown in Fig. 5-3. The variation was different from non-catalytic gasification. After reaction of 35 min, the composition of gas was stable. The composition of gas product is mainly about 3% CO, 43.5% CO_2, 47% H_2 and 6.5% CH_4 under the stable state. Less CO and more H_2 were generated comparing with the gas product obtained from non-catalytic gasification as described above. This difference was reported in several literatures that are attributed to the acceleration of WGS reaction by alkali (Penninger et al. 2002; Kruse and Faquir, 2007; Tester et al. 1998; Matsumura and Minowa, 2004; Zhao et al. 2013; Molino et al. 2014). In addition, the gas yield increased owning to the presence of LiOH. The total gas yield reached about 20 mol/kg when reaction time was 45 min that was higher than noncatalytic gasification of horse dung (about 15 mol/kg).

For SCWG of horse dung without adding LiOH, another difference was that the gasification results with adding 100 mg/L LiOH took longer time to reach the stable state. The composition of gas took about 35 min to reach the stable state with adding 100mg/L LiOH as the catalyst. For the gas yield, longer time was taken (about 45 min). Both of them were longer than SCWG of horse dung without adding catalyst (20 min, Fig. 5-3).

As it is described above, at the earlier stage, the increasing concentration and the generated intermediates played a negative role in the gasification, which increased the CO fraction and decreased total gas yield, the H2 fraction. However, variation tendency of the catalytic gasification results with 100 mg/L LiOH was opposite to non-catalytic gasification of horse dung. At the earlier stage, CO fraction was continuous to decrease, while H_2 fraction and gas yield were continuous to increase. The opposite variation tendency was determined by the precipitation of alkalis in the reactor. As it is described above, because the inorganic matters kept low solubility in supercritical water and they can precipitate in the reactor. The precipitation of the alkali can lead to the accumulation of the alkali in the reactor within a longer reaction time. It is known that from Le Chatelier's principle, when concentration of alkali increased, the reaction equilibrium is shifted to the positive direction. That is conducive to WGS reaction. In addition, concentration of alkali increased and it led the percentage of activated molecular in unit volume increased. It is known that from collision theory, increasing the percentage of activated molecular in unit volume will lead higher effective collision and more reaction probability of particles. As a result, the different variation tendency was obtained from that without catalyst, where the H_2 fraction and gas yield increased and the CO fraction decreased with the reaction time in the earlier stage. This may also be the reason for the longer unstable time in LiOH-catalyzed SCWG of horse dung than non-catalytic gasification.

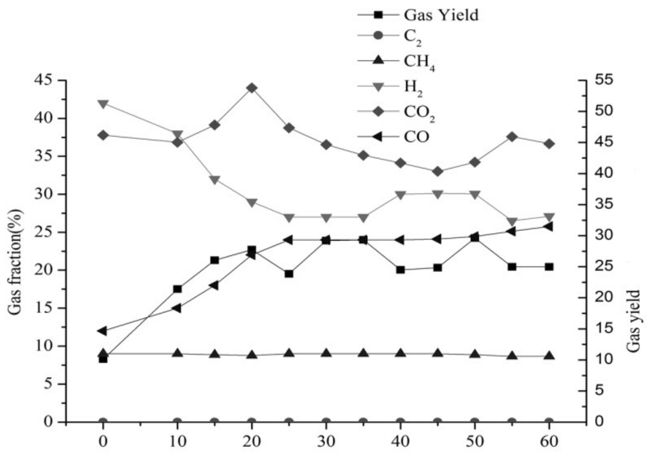

Fig 5-3 The composition and total yield of the gas product from SCWG of horse dung with 100 mg/L LiOH as the catalyst (560°C, 25MPa)

It needs to be mentioned that the alkali accumulated in the reactor may not only contain LiOH fed with the feedstock, but also contain other Li+ salts. For example, LiOH can be transformed into Li_2CO_3 and $LiHCO_3$ through reacting with CO_2 generated in the gasification (Equations (1) & (2)). However, these salts are reported to be also effective in catalyzing WGS reaction and increasing gas yield in SCWG (Williams et al. 2010; Kruse et al. 2009). As a result, the catalytic activity was further improved with more Li+ salts accumulated in the reactor, which resulted in the decrease of CO fraction and increase of the H2 fraction and gas yield at the earlier stage.

$$2LiOH + CO_2 \rightarrow Li_2CO_3 + H_2O \qquad (5\text{-}1)$$

$$Li_2CO_3 + H_2O + CO_2 \rightarrow 2LiHCO_3 \qquad (5\text{-}2)$$

5.3.3.3 SCWG of Horse dung with 150 mg/L LiOH

Horse dung treatment was conducted via SCWG with 150 mg/L LiOH as the catalyst at 25 MPa and 560°C. The results also varied with the reaction time at the earlier stage because of LiOH (Fig.5-4). The composition of gas and yield from this experiment took less time to reach the stable state comparing with SCWG of horse dung with 100mg/L LiOH. The composition of gas took about 20 min to reach the stable state (Fig. 5-4) and it is almost a half of that with 100 mg/L LiOH. As described above, concentration of alkali in the reactor and their catalytic effect can improve owning to the precipitation and accumulation of Li+ salts. This caused H_2 fraction increasing and CO fraction decreasing. While enough alkali for SCWG of horse dung is accumulated in the reactor after a certain time, the results reached stable state. The composition of gas from SCWG of horse dung with 150 mg/L LiOH took less time to reach stable state. The reason may be that the concentration of Li+ salts provided with 150 mg/L LiOH in this experiment was more than that with 100 mg/L LiOH. Reaction speed for SCWG of horse dung with 150 mg/L LiOH is faster than that with 100 mg/L LiOH. Therefore, it reached the saturated state more quickly than that with 100 mg/L LiOH.

It is also worth noting that similar gasification results were gained from horse dung with different concentration of LiOH at the stable state. After about reaction of 20 min, the composition of gas product from horse dung with 150mg/L LiOH reached stable state (Fig. 5-4). The composition of gas is mainly about 47% H_2, 44% CO_2, 2% CO and 4.5% CH_4. This was very similar to the gas product from horse dung with 150 mg/L LiOH in the stable state under the same reaction condition. The gas yield from SCWG of horse dung with 150mg/L LiOH is about 21 mol/kg, which is also close to that with 100 mg/L LiOH as the catalyst (about 20.6 mol/kg). These results may be related to the accumulation of alkali in the reactor.

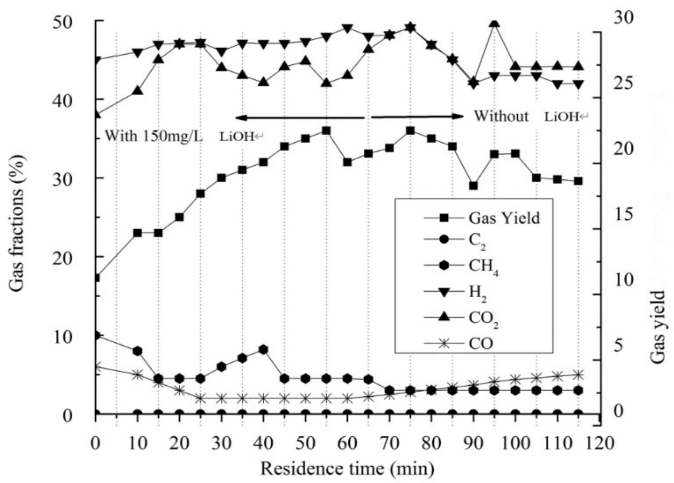

Fig 5-4 The composition and total yield of the gas product from SCWG of horse dung with 150 mg/L LiOH and without LiOH (560°C, 25MPa)

After about 60 min of horse dung gasification with 150 mg/L LiOH, the feedstock to horse dung was switched and the temperature and pressure were not changed. Gasification of horse dung was continued and the results were almost unchanged at earlier stage after the feedstock was switched. The results changed slightly with time after longer reaction time (Fig. 5-4). After about 65 min, the H_2 fraction decreased to 43%, the CO fraction increased to 9% and the gas yield decreased from 20.6 to 19.1 mol/kg. These results demonstrated that the catalytic effect reduced slightly after longer reaction time. Two reasons may be interpreted. Firstly, catalytic activity of LiOH is different from Li_2CO_3 and $LiHCO_3$. It is reported that LiOH cannot only accelerate the WGS reaction through the formation of HCOOLi just like Li_2CO_3 and $LiHCO_3$, but can also capture CO_2 in the gas product and shift the WGS reaction equilibrium in the forward direction. Therefore, LiOH exhibited higher catalytic activity than Li_2CO_3 and $LiHCO_3$. More LiOH were converted into Li_2CO_3 or $LiHCO_3$ in the reactor with horse dung gasification proceeding, and no more fresh LiOH was supplied. This reduced the ratio of LiOH to Li_2CO_3 and $LiHCO_3$ in the reactor and the catalytic effect of the accumulated alkalis in the reactor. Secondly, some alkali may be entrained away by water, which may reduce the Li+ salts in the reactor and its catalytic activity.

Comparing with the gasification of horse dung without any catalysts, the accumulative Li+ salt still showed high catalytic activity on subsequent SCWG of horse dung, even after 65 min. The H_2 fraction

(43%) was still much higher and the CO fraction (9%) was lower compared with that from noncatalytic SCWG (29% and 26% respectively). The gas yield was 19.1mol/kg after 65 min of reaction, which was still higher than that of SCWG of horse dung without catalyst (15 mol/kg).

These results may be useful in the future development of the SCWG process. Based on this result, the alkali catalyst needs not to be added in the whole gasification process. That is, we can gasify the biomass with alkali for a while in the first stage. When adequate alkali was accumulated in the reactor, the subsequent fed biomass without catalyst can take advantage of the catalytic activity of the accumulative alkalis in the reactor. The supplement of catalyst may be needed when the catalytic activity was reduced or the alkali was entrained away. Two benefits can be achieved from this method. Firstly, the plugging problem owing to the precipitated alkali can be avoided with less alkali fed in. Secondly, this can also reduce the input of the alkali catalyst, which can reduce the cost of the gasification process.

5.3.3.4 Analysis of Reaction Kinetics

The reaction order assigned to the four lumps based on the oxidative abilities of different lump pseudo species. Since CO, CH_4 and CO_2 are simple compounds, it was argued that a first order should be given to CO, CH_4 and CO_2. However, since feedstock lump contains a mixture of several thousand compounds of widely different properties, it was suggested that a n order should be assigned to the feedstock lump (Reaction net can be represented in Fig. 5-5.

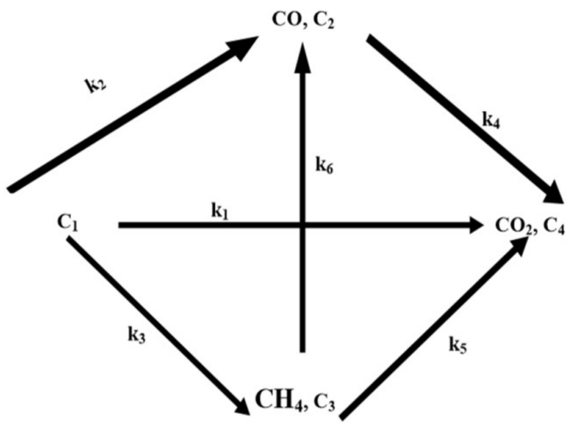

Fig. 5-5 Reaction net of four lumped kinetics model

Based on these assumptions, the following equations can be considered:

Horse dung consumption rate

Horse dung consumption rate

$$\frac{dC_1}{dt} = -(k_1 + k_2 + k_3)C_1^n \quad (5\text{-}3)$$

CO formation rate

$$\frac{dC_2}{dt} = k_2 C_1^n + k_6 C_3 - k_4 C_2 \quad (5\text{-}4)$$

CH_4 formation rate

$$\frac{dC_3}{dt} = k_3 C_1^n - k_5 C_3 - k_6 C_3 \tag{5-5}$$

CO_2 formation rate

$$\frac{dC_4}{dt} = k_1 C_1^n + k_4 C_2 + k_5 C_3 \tag{5-6}$$

where k_i (i=1, 2, ..., 6) the reaction rate coefficient assuming an Arrhenius law:

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \tag{5-7}$$

The kinetic parameters to be determined are reaction order and vector k = [k_1, k_2, k_3, k_4, k_5, k_6]. Parameter identification rests on solving the nonlinear least-squares problem U by minimizing the sum of squared errors (SSE):

$$U \begin{cases} SSE(\underline{k}, n) = \sum_{i=1}^{n} \sum_{j=1}^{m} (\overline{Y_{ij}} - Y_{ij})^2 \\ k_1, k_2, k_3, k_4, k_5, k_6 \geq 0 \end{cases} \tag{5-8}$$

Where Yij is the jth state variable from the ith experimental run in the kinetic data set P ={Pi; i=1, n; Pi ∋ Rn}.The bar stands for the model-predicted quantities. The reaction rate constants were estimated by a multi variable non-linear least squares, combining a Runge–Kutta integration algorithm with nonlinear least-squares provided in optimization toolbox of MATLAB. The identification results showed that the reaction order of feedstock lump is 1.5. Arrhenius parameters (pre-exponential factor and activation energy) have been estimated by linear regression of ln(ki) versus 1/T from the slopes and intercept of Arrhenius plots in Fig. 5-6.

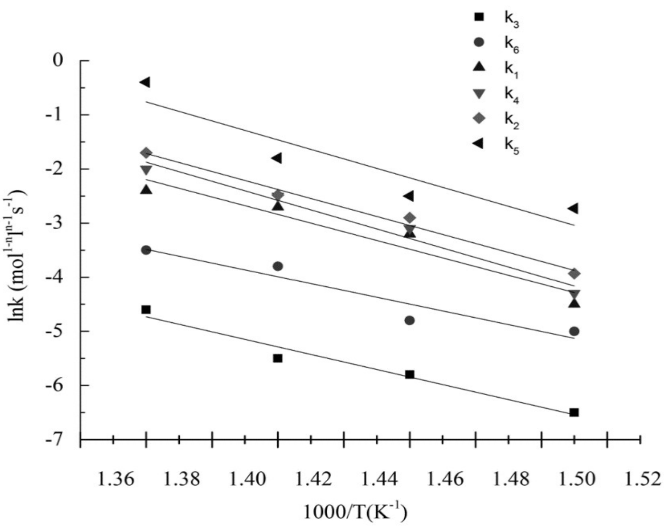

Fig. 5-6 Arrhenius plots for SCWG of horse dung

The results showed that a linear relationship of ln(ki) versus 1/T was obtained and correlation coefficients are between 0.9631 and 0.9937. The kinetic parameters obtained listed in Table 5-9.

Table 5-9 Parameters of the four lumped kinetics model

Parameters	Reaction rate constant $[(mol/L)^{1-n}\ s^{-1}]^a$				Ea (kJ/mol)	Pre-exponential factor $[(mol/L)^{1-n}\ s^{-1}]^a$	Correlation coefficient
k_1	0.0194	0.0388	0.0579	0.088	98.5	1.19×10^6	0.9866
k_2	0.0482	0.0703	0.137	0.191	94.6	1.38×10^6	0.9851
k_3	0.00194	0.00336	0.00448	0.00965	102	1.78×10^5	0.9631
k_4	0.0105	0.0314	0.0726	0.127	166	1.56×10^{11}	0.9866
k_5	0.00821	0.0334	0.0767	0.247	220	1.69×10^{15}	0.9937
k_6	0.0052	0.0077	0.0133	0.0303	115	5.88×10^6	0.9689

[a] For k_1, k_2 and k_3, n = 1.5, for k_4, k_5 and k_6, n=1.

5.3.4 Conclusions

The gas product was mainly composed of H_2, CO, CH_4 and CO_2 in SCWG of horse dung at 25 MPa and 560°C. The presence of LiOH increased H_2 fraction and decreased CO fraction in the gas product via promoting WGS reaction, and it also increased the gas yield. The precipitated alkali in the reactor still showed high catalytic effect on the subsequent gasification of horse dung without further adding the alkali. The catalytic activity was slightly reduced owning to the transformation of LiOH to Li_2CO_3 and $LiHCO_3$. A novel 4-lump kinetic model for horse dung in SCWG including feedstock, CH_4, CO, and CO_2 lumps is proposed. The kinetic parameters are estimated for each involved reaction. The identification results showed that the reaction order of feedstock lump is 1.5.

5.3.5 Experimental Study and Conclusion

In this chapter, horse manure is selected as the main pollution source of ammonia nitrogen, The influence of alkali on the gasification of horse dung at 560°C, 25 MPa was investigated. The results show that LiOH addition increased H_2 fraction and the gas yield. The precipitated alkali in the reactor still showed high catalytic effect on the subsequent gasification of horse dung without further adding the alkali. A novel 4-lump kinetic model for horse dung in SCWG including feedstock, CH_4, CO, and CO_2 lumps is proposed.

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Chapter 6

STUDY ON THE CHANGE LAW OF WATER QUALITY IN SONGHUA RIVER BASIN

CHAPTER SIX：STUDY ON THE CHANGE LAW OF WATER QUALITY IN SONGHUA RIVER BASIN

6.1 Study on Trend Change Law of Water Quality Monitoring Index Value

6.1.1 Research Methods

In this paper, the seasonal Kendall test mathematical model combined with Sen slope estimation formula is used, and is to estimate the pH of water quality monitoring indicators at typical sections of Songhua River Basin from 2008 to 2018. Dissolved oxygen (DO), permanganate index (COD_{Mn}), ammonia nitrogen (NH_3-N) is selected. The seasonal Kendall test mathematical model is widely used in the current research on the change trend of water quality. The research method of the model is to compare the water quality index values in the same season in a cycle, which can greatly reduce the impact of the periodic change of flow on the research on the change trend of water quality; and in the research process, only the data is considered According to the relative size in the development direction of time series, the influence of missing measured values and disaster data on the change trend of water quality can be reduced to a certain extent. Therefore, this method is an ideal model method to study the change trend of water quality and the interannual change law of water quality indicators.

6.1.2 Research Process and Results of Trend Change Law of Water Quality Indicators

The research data on the trend change law of water quality indicators mainly include the water quality monitoring index data of 10 sections such as Songhuajiang village, Zhaoyuan, Tongjiang and Baicheng white beach in Changchun from 2008 to 2018. According to the basic data conditions in this paper and the change law of river water quality, each calendar year is set as a cycle, and each week (week) is set as a season, so each cycle (year) has 52 ~ 53 seasons. In order to facilitate unified comparison, analysis and research, each cycle is set as 52 seasons in this paper.

Table 6-1 Calculation results table of trend change law of water quality index values of some monitoring sections in Songhua River Basin

Serial	The Name of the Section	Testing Time	Monitoring Index	Kendall Test Statistics τ (S/m)	Variation Trend	α	Level of Significance	Annual Variation of Index Value
1	Jilin Stream Langkou（A01）	2012-2018	Dissolved Oxygen	0.257463	↑	0	Highly Significant	0.275
2			Permanganate Index	0.259328	↑	0	Highly Significant	0.15
3			Ammonia Nitrogen	0.188433	↑	0.000002	Highly Significant	0.015
4			PH Value	0.453358	↑	0	Highly Significant	0.1113
5	Songhuajiang Village, Changchun（A02）	2007-2018	Dissolved Oxygen	0.424103	↑	0	Highly Significant	0.1837
6			Permanganate Index	0.329029	↑	0	Highly Significant	0.105
7			Ammonia Nitrogen	-0.335385	↓	0	Highly Significant	-0.02
8			PH Value	0.070256	↑	0.006884	Highly Significant	0.01

Serial	The Name of the Section	Testing Time	Monitoring Index	Kendall Test Statistics τ (S/m)	Variation Trend	α	Level of Significance	Annual Variation of Index Value
9	Songyuan Pine Forest（A03）	2012-2018	Dissolved Oxygen	0.114943	↑	0.00511	Highly Significant	0.15
10			Permanganate Index	-0.397206	↓	0	Highly Significant	-0.4
11			Ammonia Nitrogen	0.086705	↑	0.035518	Significant	0.015
12			PH Value	0.031311	↑	0.471511	Non-Significant	0.008
13	Zhaoyuan（A04）	2007-2018	Dissolved Oxygen	0.07797	↑	0.005161	Highly Significant	0.0594
14			Permanganate Index	0.207339	↑	0	Highly Significant	0.1667
15			Ammonia Nitrogen	-0.364463	↓	0	Highly Significant	-0.0575
16			PH Value	-0.075776	↓	0.005698	Highly Significant	-0.0127
17	Jiamusi, Tongxin Island（A05）	2014-2018	Dissolved Oxygen	0.527027	↑	0	Highly Significant	1.01
18			Permanganate Index	-0.273333	↓	0.000025	Highly Significant	-0.35
19			Ammonia Nitrogen	-0.296774	↓	0.000004	Highly Significant	-0.0575
20			PH Value	0.093333	↑	0.190992	Non-Significant	0.0725
21	Tongjiang（A06）	2007-2018	Dissolved Oxygen	0.415287	↑	0	Highly Significant	0.36
22			Permanganate Index	-0.096815	↓	0.00029	Non-Significant	-0.0333
23			Ammonia Nitrogen	0.083439	↑	0.002501	Highly Significant	0.0068
24			PH Value	0.250955	↑	0	Highly Significant	0.056
25	Baicheng White Sand Beach （B01）	2007-2018	Dissolved Oxygen	-0.144535	↓	0	Highly Significant	-0.1032
26			Permanganate Index	0.207339	↑	0	Highly Significant	0.1667
27			Ammonia Nitrogen	-0.517365	↓	0	Highly Significant	-0.055
28			PH Value	0.206186	↑	0	Highly Significant	0.03

Serial	The Name of the Section	Testing Time	Monitoring Index	Kendall Test Statistics τ (S/m)	Variation Trend	α	Level of Significance	Annual Variation of Index Value
29	Dunhua Xindian, Jilin（C01）	2012-2018	Dissolved Oxygen	-0.286792	↓	0	Highly Significant	-0.26
30			Permanganate Index	-0.081132	↓	0.035378	Significant	-0.0833
31			Ammonia Nitrogen	0.396226	↑	0	Highly Significant	0.0225
32			PH Value	0.258491	↑	0	Highly Significant	0.0583
33	Yilanmudan Rive Estuary（C02）	2014-2018	Dissolved Oxygen	0.050847	↑	0.567128	Non-Significant	0.0733
34			Permanganate Index	-0.194915	↓	0.005221	Highly Significant	-0.1875
35			Ammonia Nitrogen	0.101695	↑	0.200487	Non-Significant	0.0042
36			PH Value	0.305085	↑	0.000062	Highly Significant	0.1175
37	Yinma Rive Estuary（D01）	2014-2018	Dissolved Oxygen	0.317919	↑	0	Highly Significant	0.68
38			Permanganate Index	-0.381503	↓	0	Highly Significant	-0.975
39			Ammonia Nitrogen	-0.595376	↓	0	Highly Significant	-2.1533
40			PH Value	-0.028902	↓	0.573588	Non-Significant	-0.005

6.1.3 Summary and Analysis

In this paper, the trend of water quality index is studied, Kendall seasonal test method and Sen slope estimation are used to estimate 10 sections and 4 indicators in Songhua River Basin from 2008 to 2018 (pH, dissolved oxygen, permanganate index and ammonia nitrogen) were cross combined to form 40 index value sequences arranged in time. Through the research, it was found that among the 40 index value sequences arranged in time, there were 33 significant, 2 significant and 5 non-significant sequences respectively. Among the 35 highly significant and significant sequences, the pH increased by 7, the sum of the interannual increment of pH of the corresponding 7 sections is 0.3831, the decrease is 1, and the sum of the interannual decrement of pH of the corresponding 1 section is 0.0127; Dissolved oxygen index values increased in 7 sections, the sum of interannual increment of dissolved oxygen index values of corresponding 7 sections was 2.7180, decreased in 2 sections, and the sum of interannual decrease of dissolved oxygen index values of corresponding 2 sections was 0.3632; 4 permanganate index values increased, the sum of annual increment of permanganate index values of corresponding 4 sections was 0.5883, 6 decreased, and the sum of annual decrease of permanganate index values of corresponding 6 sections was 2.0292; Four ammonia nitrogen index values increased, the sum of annual increment of ammonia nitrogen index values of the corresponding four sections was 0.0593, four decreased, and the sum of annual decrease of ammonia nitrogen index values of the corresponding four sections was 2.3433.

Among the four indexes, pH has no direct relationship with water quality category; The higher the index value of dissolved oxygen, the better the water quality; Permanganate index and ammonia nitrogen index are both indicators. The lower the index value, the better the water quality. According to the change of each index calculated and analyzed in the corresponding section from 2008 to 2018, it can be found that whether from the perspective that the number of sections with good water quality conditions is greater than the number of sections with poor water quality conditions, or from the perspective that the sum of the positive changes of similar index values is greater than the sum of the negative changes, All proved that the water quality of Songhua River Basin showed a good development trend from 2008 to 2018.

6.2 Study on Periodic Change Law of Water Quality Monitoring Index Value

6.2.1 Research Methods

The value of river water quality monitoring index will fluctuate randomly due to the influence of many factors such as temperature change, flow change and pollutant discharge change. The random fluctuation will have a great impact on the periodic research of water quality detection index value because of its uncontrollable contingency. In order to reduce the adverse impact of the fluctuation of water quality monitoring index value affected by accidental factors on its periodic research, the multi-year average value of the index value is calculated in this study, and the random fluctuation of river water quality index value is filtered for the first time. The time interval expansion method is to expand the time unit and sum up the data elements in the newly determined time unit to obtain a new time series, so as to reduce the influence of accidental factors in the time interval unit. If the time series Xi (I = 1,2,3,... N) with time interval T is known, and its time interval is expanded to 3T, the following transformation is required:

Order:

$$S_i = \begin{cases} x_n + x_1 + x_2 (i = 1) \\ x_{i-1} + x_i + x_{i+1} (i \neq 1, n) \\ x_{n-1} + x_n + x_1 (i = n) \end{cases} \qquad (6\text{-}1)$$

$$x_i^{'} = \frac{S_i}{3} \quad (i=1,2,3...n) \qquad (6\text{-}2)$$

Then 'IX is the new time series with a time interval of 3T. The larger the time interval expansion, the smoother the change curve drawn by the new time series, and the more serious the loss of the characteristics of the original data. Therefore, when using the time interval expansion method to process time series data, we should pay attention to the selection of appropriate time interval expansion. In this paper, the time interval expansion method with time interval expansion multiple of 5 times is used to filter out the random fluctuation of multi-year average time series data of water quality monitoring data for the second time. Finally, the data processed twice are drawn into the periodic change curve of river water quality monitoring indicators according to the time series, and then the periodic change law of water quality indicators of the section is studied and analyzed.

6.2.2 Analysis and Research on Periodic Change Law of Water Quality Index

In this paper, the research on the periodic change law of water quality indicators is carried out on the premise that each cycle corresponds to a calendar year. In order to compare the change rules between different sections, the river water quality monitoring sections are divided into five groups in this study, as shown in Table 6-2:

Table 6-2 Grouping table of research sections on periodic changes of water quality monitoring indicators

Serial Num ber	The Dr awing Numbe r	Name of Mo nitoring Secti on	Monitoring Secti on Number	The Section Position	Setting the Group Destina tion
1	3-1a、3-2a、3-3a、3-4a	Jilin Stream Langkou	A01	Located in the second Songhua River	All of them are located in th e second Songhua River fro m Jilin City to Sanchaokou River section. The periodic change rule of the Second Songhua River water qualit y monitoring index is anal yzed and studied
2		Songhuajiang Village, Chan gchun	A02	Located in the second Songhua River	
3		Songyuan Pin e Forest	A03	The second Songhua River, bef ore the second Songhua River joins the Nen River	
4	3-1b、3-2b、3-3b、3-4b	Zhaoyuan	A04	Upper reaches of Songhua River trunk stream	All of them are located in th e main stream of Songhua River. The periodic variatio n of water quality monitori ng indexes in the main stre am of Songhua River is ana lyzed
5		Jiamusi, Tong xin Island	A05	Middle reaches of Songhua River	
6		Tongjiang	A06	Before the Songhua River flows into Heilongjiang	
7	3-1c、3-2c、3-3c、3-4c	Songyuan Pin e Forest	A03	The second Songhua River and Nen River confluence	It is located in the main stre am of Nenjiang River, the Second Songhua River and the Songhua River respectiv ely. The periodic changes of water quality monitoring in dexes before and after the N en River and the second So nghua River merge into the Songhua River are analyzed
8		Zhaoyuan	A04	Located in the Second Songhua River trunk stream, the Second Songhua River and N en River confluence	
9		Baicheng Whi te Sand Beach	B01	Nen River as before the Songhua River	
10	3-1d、3-2d、3-3d、3-4d	Jiamusi, Tong xin Island	A05	Located in Songhua River main stream, in the Mudan River into the downstream point	Study on periodic changes of water quality monitoring indexes in Mudan River, a main tributary of Songhua River
11		Dunhua Xindi an, Jilin	C01	Located in the upper reaches of Mudan River, Mudan River Jilin and Heilongjiang junction	
12					
13		Yilanmudan R ive Estuary	C02	It is located at the mouth of Mudan River,before Mudan River enters Songhua River	
14	3-1e、3-2e、3-3e、3-4e	Banlou, Chan gchun	D01	Located at the mouth of Yinma River, Yinma River enters the Second Songhua River	Analysis and research on periodic variation law of water quality in Mudan River, Yinma River and Hulan River, the main tributaries of Songhua River
15		The Hulan Ri ver Estuary	E01	Located at the mouth of Hulan River, Hulan River flows into Songhua River	

(1) According to the grouping, Figure 3-1 periodic change curve of pH in typical sections of Songhua River Basin is drawn respectively, which includes five curves of pH changing with time in a year. Through these five curves, the annual (periodic) change law of water quality monitoring index pH in typical sections of Songhua River Basin is analyzed and studied.

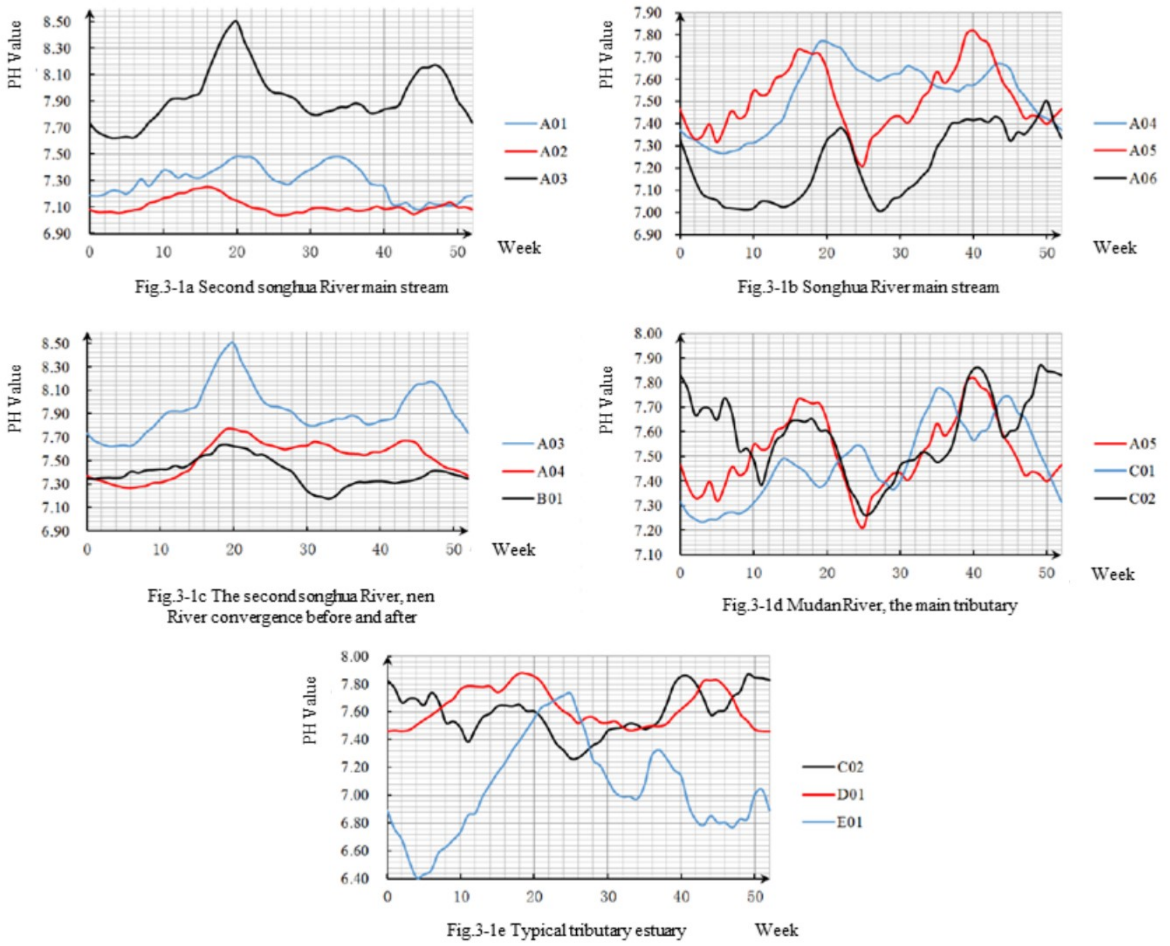

Figure 6-1 Periodic change curve of pH in typical sections of Songhua River basin

The three curves in figure 6-1a are obtained from the processing of pH monitoring data of three sections of Jilin xilangkou (A01), Changchun Songhuajiang Village (A02) and Songyuan pine forest (A03) on the second Songhua River. The pHs of Xilangkou section in Jilin and Songhuajiang Village section in Changchun are relatively stable, and the annual periodic change is not obvious enough. The periodic change of A01 curve can be divided into two periods. The curve from week 5 to week 41 shows an insignificant "three peak type", and the curve from week 42 to week 5 of the next year shows a horizontal curve with slight fluctuation; The annual periodic change of A02 curve can also be divided into two periods. The curve section from week 5 to week 25 presents a single peak curve, and the curve section from week 26 to week 4 of the next year presents an overall level with slight fluctuations; The pH of section of Songyuan pine forest changes violently and the periodicity is very obvious. The A03 curve shows an obvious double peak type. The first peak starts from the 4th week to the 31st week, and the second peak starts from the 32nd week to the 4th week of the next year. Considering the three sections, from the perspective of waveform, the similarity of curve waveform of the three sections is not high, indicating that there are many interference factors between the three sections, which affect the pH; In the whole cycle, the pH index monitoring value of the section of Songyuan pine forest in the downstream is significantly higher than that of xilangkou in Jilin and Songhuajiang village in Changchun; In the same monitoring period, the pH index monitoring value of xilangkou section in Jilin is slightly higher than that of Songhuajiang Village section in Changchun, which can be regarded as a high probability event.

The three sections of Zhaoyuan (A04), Jiamusi Tongxin Island (A05) and Tongjiang (A06) in figure 6-1b are located in the main stream of Songhua River. A04 and A06 in the three curves are "three peaks", in which the two troughs adjacent to the second peak of A04 curve have little difference from the pH at the peak; The adjacent trough after the second peak of A06 curve also has little difference from the pH at the peak; A05 curve is "bimodal". The first peak appears from the 5th week to the 25th week, with a peak in 16 to 19 weeks, and the second peak appears from the 26th week to the 4th week of the next year, with a peak in 39 to 41 weeks. According to the comprehensive analysis, the following four points can be seen: A04 and A05 curves cross each other. In the period of 20 weeks to 30 weeks, A04 curve is significantly higher than A05 curve, A05 curve is significantly higher than A04 curve in the 38th to 42nd weeks, and the trend and height of the two curves in other periods are roughly the same; At the same time, the pH represented by A04 and A05 curves is significantly higher than that of A06 curves. There are two possible reasons. On the one hand, there may be acidic substances discharged into the river water in Jiamusi Tongjiang section, on the other hand, the high latitude and low water temperature of A06 Tongjiang section affect the ionization of alkaline substances in the water, Therefore, the pH is lower than A04 Zhaoyuan section and A05 Jiamusi Tongxin Island section; The first fluctuation of A04 and A06 curves is obvious. Taking the second and third fluctuations as a fluctuation, it can be found that A05 curve and A06 curve have high similarity, but compared with A05 curve, the peak of A06 curve has a certain lag; The two curves A04 and A06 are also similar. At the same time, the time points of the three peaks of A06 curve also lag behind the time points of the three peaks of A04 curve.

Baicheng White Beach (B01) involved in Figure 6-1c Songlin Songyuan (A03) and Zhaoyuan (A04) the three sections are respectively located at the intersection of Nenjiang River and the second Songhua River converging into the main stream of Songhua River - Nenjiang River at the upstream of Sanchakou, the second Songhua River and the main stream of Songhua River at the downstream. The A03 and A04 curve lines in figure 6-1c have been described and will not be repeated here. The B01 curve of Baicheng white beach section can be regarded as a bimodal curve, and the first fluctuation period is from week 1 to week 33 , the wave peak appears between the 17th and 20th weeks, the second wave period is from the 34th to 52nd weeks, and the wave peak is between the 46th and 50th weeks. Through comprehensive analysis of the three curves, the waveforms of the three curves are similar, showing that there is a fluctuation with large amplitude at both ends and an insignificant fluctuation with small amplitude in the middle; The fluctuation ranges of pHs of the three are different, showing that A03 is the largest, A04 is the middle and

B01 is the smallest; In terms of pH range, A03 is the highest, A04 is the middle and B01 is the lowest; The characteristic "inheritance" of A04 curve to A03 curve and B01 curve is obvious, which is consistent with the main stream of Songhua River formed by the confluence of Nenjiang River and the second Songhua River. There are two possible reasons: first, the pH index value of Zhaoyuan section is greatly affected by the water from Nenjiang River and the second Songhua River, and second, the influencing factors affecting the pHs of the three sections are similar, Resulting in similar waveforms.

Figure 6-1d relates to Mudanjiang, Jilin Dunhua Xindian (C01) The three sections of Yilan estuary (C02) of Mudanjiang River and Tongxin Island (A05) of Jiamusi, the main stream of Songhua River, are mainly used to analyze the periodic relationship between pHs of Mudanjiang River, the main tributary of Songhua River, and the main stream of Songhua River. C01 is "multi peak type" In the fluctuation curve, there are two low-level fluctuations with relatively small fluctuation range from week 3 to 29, and two high-level fluctuations with relatively small fluctuation range from week 30 to week 2 of the next year; The C02 curve presents a "three peak type", the first complete fluctuation in the 11th-25th week, the second complete fluctuation in the 26th-44th week, and the third fluctuation with uneven waveform curve from the 45th week to the 10th week of the next year. Based on the three curves, A05 curve and C02 curve have the same trend, similar fluctuation range and pH fluctuation range between weeks 12-44, which show excellent fitting. At the same time, the fluctuation of A05 curve does not lag behind C02, so it can be concluded that there is little causal relationship between them, However, the factors affecting the pH index value of the two sections should have similar changes during this period. This conclusion will help to distinguish what factors affect the change of pH of the two sections; From the pH fluctuation of C01 and C02 sections, it can be seen that the pH of Mudanjiang fluctuates and does not show similar regularity.

Figure 6-1e relates to Yilan estuary of Mudanjiang River (C02) Yinma River Estuary (D02) and Hulan River Estuary (E05) are three sections. Yinma River, Mudanjiang River and Hulan River are three typical tributaries of Songhua River, which flow into the middle and lower reaches of the second Songhua River, the upper reaches of the main stream of Songhua River and the middle reaches of Songhua River respectively. D01 curve shows "three peaks" , the dividing points of the three waveforms are the first week, the 15th week and the 33rd week, the three peaks appear in the 10th-14th week, the 17th-19th week and the 43rd-45th week respectively, and show an overall level curve segment with slight fluctuation in the 28th-36th week; Since the monitoring data of Hulan River Estuary section is only one year, the curve drawn fluctuates violently, so the research value is not very obvious. This monitoring section is the only section in which the river is weakly acidic in a long continuous period.

Through the analysis of the five curves in Figure 6-1, it can be found that the annual periodic change curve of pH in the study section is mainly "double peak type" and "three peak type". The pH of most sections is higher in the two time fixed periods before and after the freezing period, and the pH of river water is lower in the freezing period and summer.

(2) According to the grouping situation, five curves of Fig. 6-2a, Fig. 6-2b, Fig. 6-2c, Fig. 6-2d and Fig. 6-2e are drawn respectively. Next, the annual periodic change law of dissolved oxygen in the water quality monitoring index of typical sections of Songhua River Basin is analyzed.

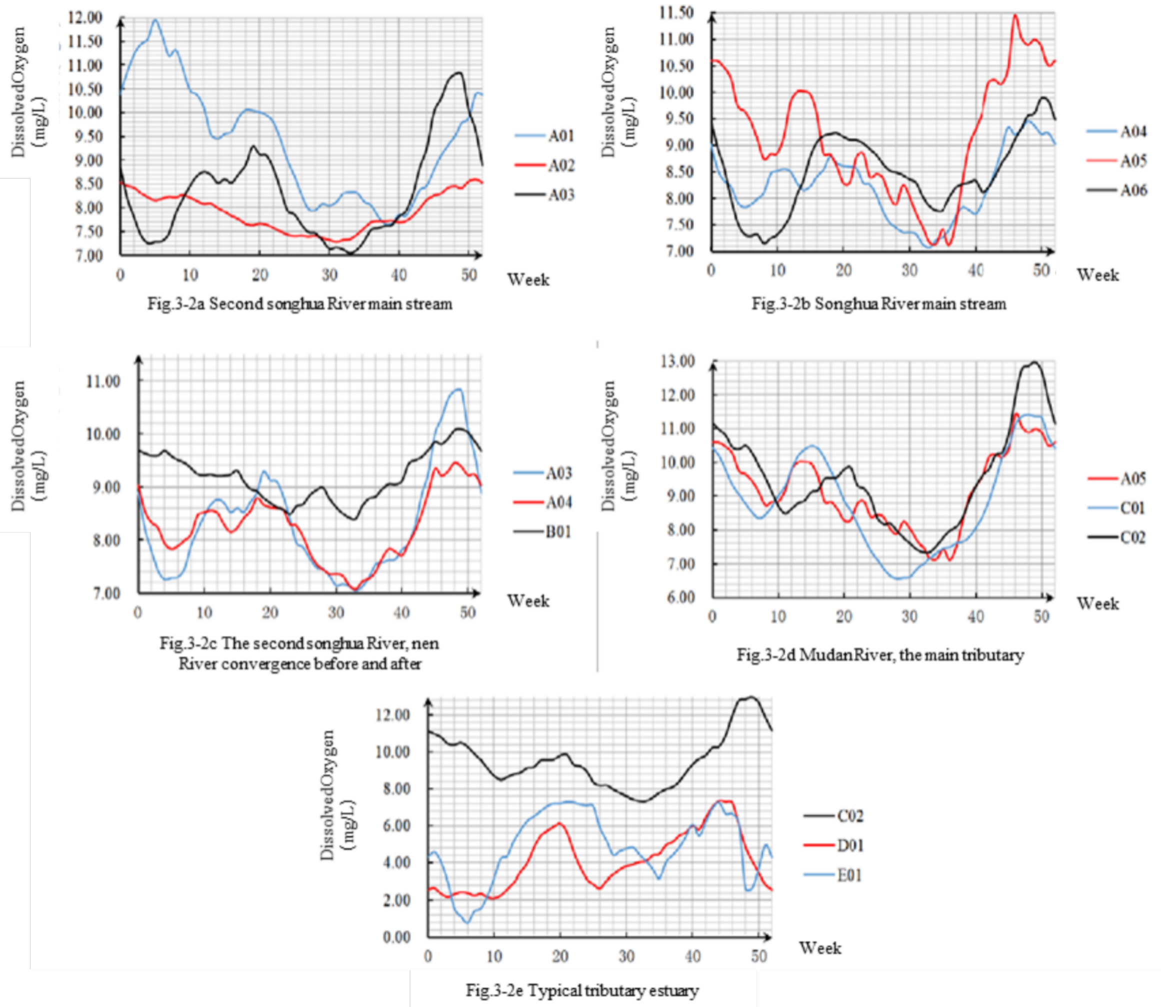

Figure 6-2 Periodic variation curve of dissolved oxygen in typical sections of Songhua River Basin

Considering that Songhua River Basin is located in the middle and high latitudes and has the seasonal characteristics of "long winter and short summer", the number of weeks occupied by each season is divided as follows: the 9th-22nd week in spring; Summer is the 23rd-34th week; 34-47 weeks in autumn; Winter is the 48th week to the 8th week of the next year. According to the above four seasons division method, through the analysis of the monitoring value of dissolved oxygen index of the section of Songhua River Basin, it can be seen that the dissolved oxygen concentration in the river is winter, spring, autumn and summer from high to low.

Dissolved oxygen in river water is jointly affected by physical and biochemical factors. Physical factors such as river flow pattern and air pressure affect the transmission, distribution and saturation of dissolved oxygen in water, while photosynthesis, atmospheric reoxygenation, organic matter oxidation reaction, ammonia nitrogen nitrification Biochemical processes such as phytoplankton respiration and sediment oxygen consumption affect the production and consumption of dissolved oxygen. These physical and biochemical factors are almost affected by the change of water temperature. Therefore, around the periodic change of water temperature in a year, a reasonable explanation for the periodic change of dissolved oxygen concentration in river water can be found.

By observing Fig. 6-2, it can be found that the periodic change law curve of dissolved oxygen index in most sections of Songhua River Basin presents an obvious "W" type. The first trough of the "W" curve appears because the rivers in the Songhua River basin generally have an ice cover period. Firstly, after the river surface is frozen, the dissolved oxygen in the water is consumed by the life activities of aerobic aquatic organisms; Secondly, the ice layer on the river hinders the transformation of O2 into dissolved oxygen in the air; Finally, due to low temperature and poor light transmittance of water surface after freezing, aquatic plants can not carry out photosynthesis smoothly during freezing period. The above three aspects lead to the gradual decrease of dissolved oxygen concentration in the river ice cover; Before and after the Spring Festival, the water temperature in the Songhua River Basin began to rise gradually, the river surface also began to unseal gradually, the dissolved oxygen in the water was gradually supplemented, the dissolved oxygen concentration began to rise, and the first trough began to hit the bottom and rebound.

Relevant studies show that the saturation of dissolved oxygen in water is negatively correlated with the water temperature. Within a certain temperature variation range, the dissolved oxygen concentration in river water is negatively correlated with the water temperature. The second "trough" is closely related to this objective law. As the water temperature continues to rise gradually, the dissolved oxygen concentration in the river gradually reaches the dissolved oxygen saturation, the curve appears an inflection point, and then the second trough begins to appear. Then the dissolved oxygen concentration in the water begins to decrease. With the seasonal change, the water temperature rises to a certain extent and then begins to decrease. At this time, the dissolved oxygen concentration in the river begins to rise under the influence of the water temperature, and the dissolved oxygen concentration in the water reaches the lowest point. The inflection point of the second trough of the "W" curve appears, and the dissolved oxygen concentration in the water begins to rise again until the river reaches the freezing period, After the dissolved oxygen concentration reaches the peak, the dissolved oxygen concentration in the water begins to decline again, and the "W" curve in the next cycle begins to appear again.

(3) According to the grouping of sections, five curves are drawn in Figure 6-3a, Figure 6-3b, Figure 6-3c, Figure 6-3d and Figure 6-3e to analyze the annual (periodic) change law of permanganate index, a water quality monitoring index of typical sections in Songhua River Basin.

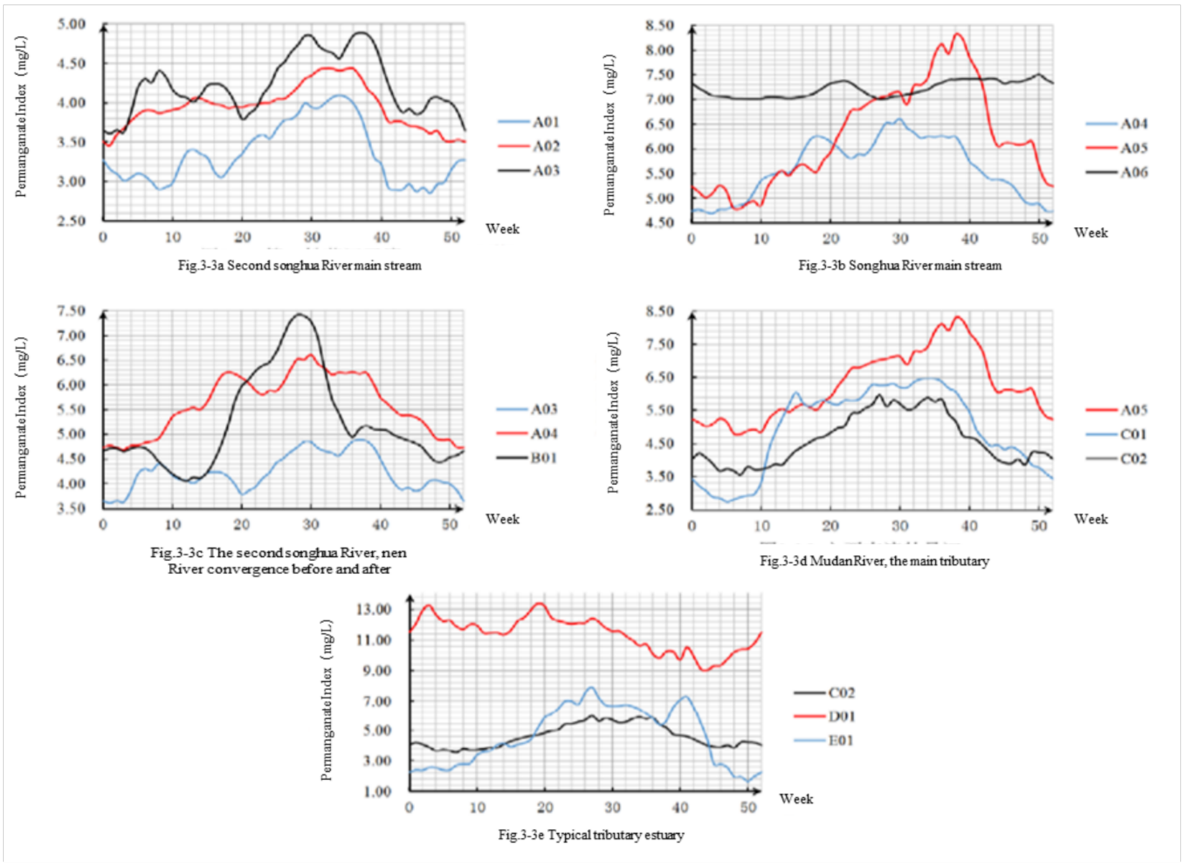

Figure 6-3 Periodic variation curve of permanganate index in typical sections in Songhua River basin

It can be seen from Figure 6-3, in the study section, except Yinmahe estuary (D01) section, which did not show the same periodic fluctuation as other sections because of the extremely poor water quality during the study period, the other 10 sections showed a "single peak" with high similarity Periodic fluctuation form. There are two reasons why the permanganate index of Songhua River Basin is significantly higher than that of normal and dry seasons. First, in the wet season, the rainfall intensity is high, and the reductive humus on the surface of the basin is entrained by rainfall. With the runoff entering rivers and other water bodies, the permanganate index of river water bodies increases; Secondly, Songhua River Basin is located in Songnen Plain and is the main commercial grain production base in China. Taking Heilongjiang Province as an example, relevant literature shows that the chemical oxygen demand emissions of agricultural sources and domestic sources in Heilongjiang Province account for 64.67% and 32.08% of the total emissions respectively. The wet season of Songhua River Basin is in summer and autumn. Compared with the normal and dry seasons, the Songhua River Basin has high temperature, abundant rain, lush growth of various surface plants, the fastest metabolism, and will produce more rotten branches and leaves. Due to the high rainfall intensity, this humus is easy to enter the river channel due to surface runoff, resulting in the increase of organic matter concentration in the river.

Through the analysis of the monitored value of permanganate index in each section of Songhua River Basin, it can be concluded that in the four seasons, the permanganate index is the highest in summer, the second in autumn, the third in spring and the lowest in winter.

According to the grouping of sections, five curves of Fig. 6-4a, Fig. 6-4b, Fig. 6-4c, Fig. 6-4d and Fig. 6-4e are drawn respectively to analyze and study the annual (periodic) change law of ammonia nitrogen, a water quality monitoring index in typical sections of Songhua River Basin.

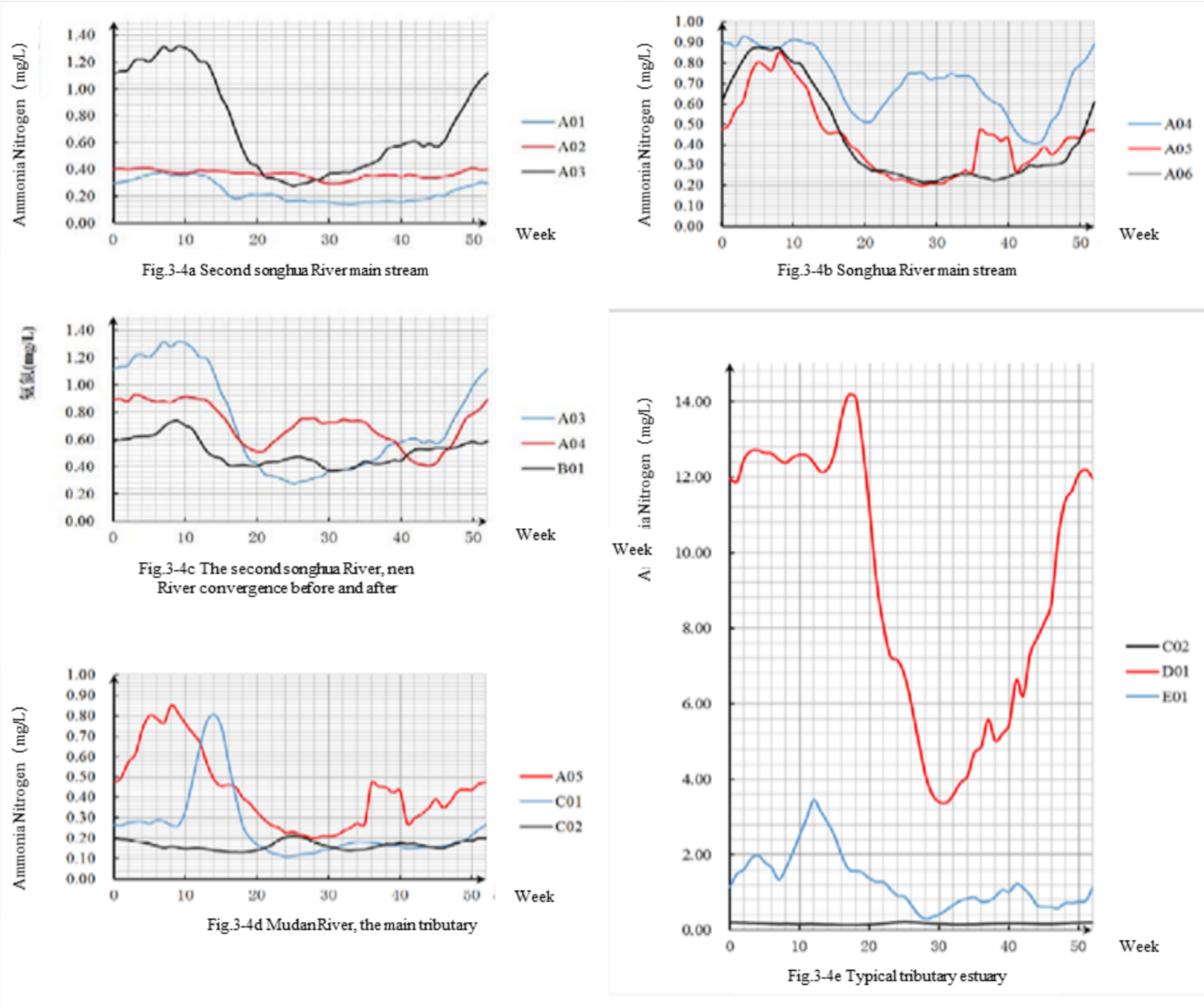

Figure 6-4 Ammonia nitrogen periodic change curve of typical sections in Songhua River basin

According to the observation and analysis in Figure 6-4 below, through the sorting and analysis of the ammonia nitrogen index monitoring values of 11 research sections, it is found that in the four seasons of the whole basin, the ammonia nitrogen index values show the statistical law of winter > spring > autumn > summer. Among the 11 study sections, the ammonia nitrogen index values of Songhuajiang Village (A02) in Changchun and Mudanjiang estuary (C02) in Yilan are relatively stable, and the periodic fluctuation characteristics in the year are not obvious.

Jilin xilangkou (A01) and Tongjiang (A06) show similar periodic fluctuation laws, and the fluctuation curve shows "U" The ammonia nitrogen index value reaches the peak at the end of January every year, and then after a 30-40 day stable period of index value, the index value begins to decline. The next turning point occurs when the river is unsealed. At this time, the ammonia nitrogen index value shows a relatively stable low value until the river is frozen. When the river is frozen, the ammonia nitrogen index value begins to rise again, It will reach the peak again at the end of January of the next year, and one cycle will be completed. From the time node of the periodic fluctuation, it can be seen that the existence of the river freezing period in the Songhua River Basin is the main driving factor for the formation of the periodic fluctuation of the two sections.

The periodic change law curves of Xindian (C01), Hulan River Estuary (E01), Zhaoyuan (A04), Tongxin Island (A05) and Songlin Songyuan (A03) in Dunhua, Jilin Province show a "W" shape. Compared with the Langkou section and Tongjiang section of Jilin River, there is an increase and decrease fluctuation process in spring and summer. Take Heilongjiang Province as an example to analyze "W" The second national survey of pollution sources shows that ammonia nitrogen emissions in Heilongjiang Province mainly come from domestic sources and agricultural sources, and the sum of the two exceeds 95% of the total emissions. Domestic sources mainly come from domestic sewage discharge and livestock breeding, and agricultural sources mainly come from the use of chemical fertilizer and wastewater discharge from agricultural product processing industry, The highest intensity of agricultural production, living and other daily production and operation activities in the Songhua River Basin is in summer, which is the peak period of the use of chemical fertilizers and pesticides. The unused pesticides and fertilizers enter the water body with the process of farmland drainage and surface runoff, This leads to a complete wave peak in some sections greatly affected by daily production activities and agricultural production activities in summer. Whether the fluctuation is severe depends on the degree of impact on the section. As for the formation of another wave peak in the cycle, it is also caused by the freezing period of rivers in the basin.

6.3 Study on Fluctuation (Randomness) of Water Quality Monitoring Index Value

6.3.1 Research Methods

After arranging the "time index value" curve of multiple water quality monitoring index values in the same section according to the time sequence, it will be found that the index values appear to fluctuate "irregularly" in the time series. Similar to hydrological cycle process, the influencing factors of water quality monitoring index value mainly include natural conditions and human activities. The result of water quality index value is the unity of necessity and contingency, in which certainty and uncertainty coexist. The research on the fluctuation (randomness) of water quality index is to study the inevitability and contingency change law of section water quality data. It is to analyze the possible probability of different monitoring index values within a certain value range, and to measure the possibility of extreme situations of the index.

In this paper, the fluctuation of water quality monitoring index value is studied. Firstly, the 52 weeks (weeks) of the whole year are divided into four periods: 1-13 weeks, 14-26 weeks, 26-39 weeks and 40-52 weeks. Then, the ratio of the intermediate parameter - "water quality index monitoring value" to its "multi-year average value of monitoring values in the same monitoring period" is calculated (expressed in the text); then calculate the main parameter for Volatility Analysis and Research - "the number of monitoring values in the specified interval in the same period in all years" as a percentage of "the total number of monitoring values in the same period in all years" (expressed in P in the text).

$$K_i^n = \frac{x_i^n}{\overline{x^n}} \qquad (6\text{-}3)$$

$$\overline{x^n} = \frac{x_1^n + x_2^n + x_3^n + \cdots + x_i^n + \cdots + x_{m-1}^n + x_m^n}{m} \qquad (6\text{-}4)$$

$$\begin{aligned} P &= \frac{l_1^{'} + l_2^{'} + l_3^{'} + \cdots + l_i^{'} + \cdots + l_{m-1}^{'} + l_m^{'}}{L} \times 100\% \\ &= \frac{L_m^{'}}{L} \times 100\% \end{aligned} \qquad (6\text{-}5)$$

6.3.2 Research Process and Results

In the research process of this paper, firstly, according to the research methods in the previous section, Table 6-3 shows research parameters on the fluctuation of water quality monitoring index values of Xilangkou section in Jilin Province".

Table 6-3 Statistical table of research parameters for the volatility of index values of Xilangkou section in Jilin province

No.	Time	K_i^n Section	NH_3-N		pH		DO		COD_{Mn}	
			L_i'	P	L_i'	P	L_i'	P	L_i'	P
1	1-13 weeks	(0,0.5]	16	23.88%	0	0.00%	0	0.00%	0	1.00%
2		(0.5,0.8]	14	20.90%	0	0.00%	8	11.94%	7	10.54%
3		(0.8,0.9]	6	8.96%	0	0.00%	12	17.91%	13	19.40%
4		(0.9,1.1]	4	5.97%	62	92.54%	30	44.78%	30	44.78%
5		(1.1,1.2]	4	5.97%	5	7.46%	11	16.42%	9	13.43%
6		(1.2,1.5]	8	11.94%	0	0.00%	6	8.96%	8	11.94%
7		(1.5,2]	13	19.40%	0	0.00%	0	0.00%	0	0.00%
8		(2,+∞)	2	2.99%	0	0.00%	0	0.00%	0	0.00%
9	14-26 weeks	(0,0.5]	14	21.88%	0	0.00%	0	0.00%	0	0.00%
10		(0.5,0.8]	17	26.56%	0	0.00%	8	12.50%	9	14.06%
11		(0.8,0.9]	4	6.25%	0	0.00%	6	9.38%	10	15.63%
12		(0.9,1.1]	6	9.38%	64	100.00%	36	56.25%	26	40.63%
13		(1.1,1.2]	0	0.00%	0	0.00%	10	15.63%	10	15.63%
14		(1.2,1.5]	9	14.06%	0	0.00%	4	6.25%	9	14.06%
15		(1.5,2]	12	18.75%	0	0.00%	0	0.00%	0	0.00%
16		(2,+∞)	2	3.13%	0	0.00%	0	0.00%	0	0.00%
17	26-39 weeks	(0,0.5]	8	12.70%	0	0.00%	0	0.00%	0	0.00%
18		(0.5,0.8]	12	19.05%	0	0.00%	3	4.76%	6	9.52%
19		(0.8,0.9]	8	12.70%	1	1.59%	14	22.22%	10	15.87%
20		(0.9,1.1]	11	17.46%	62	98.41%	29	46.03%	32	50.79%
21		(1.1,1.2]	12	19.05%	0	0.00%	12	19.05%	8	12.70%
22		(1.2,1.5]	3	4.76%	0	0.00%	5	7.94%	6	9.52%
23		(1.5,2]	6	9.52%	0	0.00%	0	0.00%	1	1.59%
24		(2,+∞)	3	4.76%	0	0.00%	0	0.00%	0	0.00%
25	40-52 weeks	(0,0.5]	12	18.46%	0	0.00%	0	0.00%	4	6.15%
26		(0.5,0.8]	14	21.54%	0	0.00%	7	10.77%	11	16.92%
27		(0.8,0.9]	5	7.69%	2	3.08%	9	13.85%	10	15.38%
28		(0.9,1.1]	10	15.38%	59	90.77%	33	50.77%	18	27.69%
29		(1.1,1.2]	2	3.08%	3	4.62%	7	10.77%	6	9.23%
30		(1.2,1.5]	10	15.38%	1	1.54%	9	13.58%	10	15.38%
31		(1.5,2]	10	15.38%	0	0.00%	0	0.00%	6	9.23%
32		(2,+∞)	2	3.08%	0	0.00%	0	0.00%	0	0.00%
33	All Year	(0,0.5]	50	19.31%	0	0.00%	0	0.00%	4	1.54%
34		(0.5,0.8]	57	22.01%	0	0.00%	26	10.04%	33	12.74%
35		(0.8,0.9]	23	8.88%	3	1.16%	41	15.83%	43	16.60%
36		(0.9,1.1]	31	11.97%	247	95.37%	128	49.42%	106	40.93%
37		(1.1,1.2]	18	6.59%	8	3.09%	40	15.44%	33	12.74%
38		(1.2,1.5]	30	11.58%	1	0.39%	24	9.27%	33	12.74%
39		(1.5,2]	41	15.83%	0	0.00%	0	0.00%	7	2.70%
40		(2,+∞)	9	3.47%	0	0.00%	0	0.00%	0	0.00%

Using the same method, the corresponding section index value fluctuation research parameters of the other 9 sections except the Hulan River Estuary section are counted (considering the limited space of the article, the paper only lists the statistical table of research parameters on the fluctuation of water quality monitoring index values of Xilangkou section in Jilin Province). According to the statistical table of parameters of each section and the whole basin of Songhua River Basin, through further calculation and sorting, the probability distribution table of water quality monitoring index values of each research section and the whole basin of Songhua River Basin is prepared as follows:

Table 6-4 Probability distribution of water quality monitoring index values at Xilangkou section of Jilin province

serial number	Period (indicator name)	Range of K_i^n value	Number of samples	probability	serial number	Period (indicator name)	Range of K_i^n value	Number of samples	probability
1	1-13 week (Ammonia nitrogen)	(0.9,1.1]	67	0.0597	30	1-13 week (DO)	(0.5,1.5]	67	1
2		(0.8,1.2]		0.209	31	14-26 week (DO)	(0.9,1.1]	64	0.5625
3		(0.5,1.5]		0.5373	32		(0.8,1.2]		0.8125
4		(0.5,2.0]		0.7313	33		(0.5,1.5]		1
5	14-26 week (Ammonia nitrogen)	(0.9,1.1]	64	0.0938	34	26-39 week (DO)	(0.9,1.1]	63	0.4603
6		(0.8,1.2]		0.1563	35		(0.8,1.2]		0.873
7		(0.5,1.5]		0.5625	36		(0.5,1.5]		1
8		(0.5,2.0]		0.75	37	40-52 week (DO)	(0.9,1.1]	65	0.5077
9	26-39 week (Ammonia nitrogen)	(0.9,1.1]	63	0.1746	38		(0.8,1.2]		0.7538
10		(0.8,1.2]		0.4921	39		(0.5,1.5]		1
11		(0.5,1.5]		0.7302	40	a year (DO)	(0.9,1.1]	259	0.4942
12		(0.0,2.0]		0.9524	41		(0.8,1.2]		0.8069
13	40-52 week (Ammonia nitrogen)	(0.9,1.1]	65	0.1538	42		(0.5,1.5]		1
14		(0.8,1.2]		0.2615	43	1-13 week (COD_{Mn})	(0.9,1.1]	67	0.4478
15		(1.2,0.8]		0.7516	44		(0.8,1.2]		0.791
16		(0.5,2.0]		0.7846	45		(0.5,1.5]		1

Table 6-5 Probability distribution of water quality monitoring index values of Songhuajiang village section in Changchun city

serial number	Period (indicator name)	Range of Kin value	Number of samples	probability	serial number	Period (indicator name)	Range of Kin value	Number of samples	probability
1	1-13 week (Ammonia nitrogen)	(0.9,1.1]	128	0.25	27	1-13 week	(0.9,1.1]	128	0.5703
2		(0.8,1.2]		0.5078	28	-	(0.8,1.2]		0.9063
3		(0.5,1.5]		0.8906	29	(DO)	(1.2,0.81		0.0625
4		(0.5,2.0]		0.9609	30	14-26 week	(0.9,1.1]		0.7419
5	14-26 week (Ammonia nitrogen)	(0.9,1.1]	124	0.2823	31	(DO)	(0.8,1.2]	124	0.9516
6		(0.8,1.2]		0.5645	32	26-39 week	(0.8,1.5]		1
7		(0.5,1.5]		0.879	33	(DO)	(0.9,1.1]		0.7818
8		(0.5,2.0]		0.9435	34		(0.8,1.2]	110	0.9636
9	26-39 week (Ammonia nitrogen)	(0.9,1.1]	110	0.2182	35		(0.5,1.5]		1
10		(0.8,1.2]		0.3909	36	40-52 week	(0.9,1.1]		90
11		(0.5,1.5]		0.8	37	(DO)	(0.8,1.2]	110	0.9364
12		(0.0,1.5]		0.9364	38		(0.8,1.5]		0.9818
13		(0.0,2.0]		1	39	a year	(0.9,1.1]	472	0.6716
14		(0.9,1.1]		0.1909	40	(DO)	(0.8,1.2]		0.9386
15		(0.8,1.2]		0.3545	41		(0.9,1.1]		0.5703
16	40-52 week (Ammonia nitrogen)	(0.5,1.5]	110	0.8091	42	1-13 week (CODMn)	(0.8,1.2]	128	0.9063
17		(0.0,1.5]		0.9182	43		(0.8,1.5]		0.9688
18		(0.0,2.0]		1	44		(0.9,1.1]		0.7419
19		(0.9,1.1]		0.2373	45	14-26 week (CODMn)	(0.8,1.2]	124	0.9516
20	a year (Ammonia nitrogen)	(0.8,1.2]	472	0.4597	46		(0.8,1.5]		1
21		(0.5,1.5]		0.8475	47		(0.9,1.1]	110	0.7818
22	1-13 week pH	(0.9,1.1]	128	1	48	26-39 week (CODMn)	(0.8,1.2]		0.9636
23	14-26 week pH	(0.9,1.1]	124	1	49		(0.9,1.1]		0.6
24	26-39 week pH	(0.9,1.1]	110	0.9909	50	40-52 week (CODMn)	(0.8,1.2]	110	0.9364
25	40-52 week pH	(0.9,1.1]	110	1	51	a year	(0.9,1.1]	470	0.4149
26	a year (pH)	(0.9,1.1]	472	0.9979	52	(CODMn)	(0.8,1.2]		0.7447
					53		(0.5,1.5]		0.9894

Table 6-6 Probability distribution of water quality monitoring index values of SongYuan SongLin section

No.	Time (Index)	K_i^n Section	Number of samples	Probability	No.	Time (Index)	K_i^n Section	Number of samples	Probability
1	1-13week（NH3-N）	（0.9,1.1]	66	0.0909	29	14-26week（DO）	（0.9,1.1]	64	0.5469
2		（0.8,1.2]		0.2121	30		（0.8,1.2]		0.7813
3		（0.5,1.5]		0.6818	31		（0.5,1.5]		1.0000
4		（0.0,2.0]		1.0000	32	26-39week（DO）	（0.9,1.1]	61	0.6557
5	14-26week（NH3-N）	（0.9,1.1]	64	0.1875	33		（0.8,1.2]		0.9016
6		（0.8,1.2]		0.3594	34		（0.5,1.5]		1.0000
7		（0.5,1.5]		0.7656	35	40-52week（DO）	（0.9,1.1]	65	0.3692
8		（0.0,2.0]		0.9688	36		（0.8,1.2]		0.6615
9	26-39week（NH3-N）	（0.9,1.1]	60	0.3167	37		（0.5,1.5]		1.0000
10		（0.8,1.2]		0.5500	38	all year（DO）	（0.9,1.1]	256	0.5117
11		（0.5,1.5]		0.9000	39		（0.8,1.2]		0.7422
12		（0.0,2.0]		1.0000	40		（0.5,1.5]		0.9961
13	40-52week（NH3-N）	（0.9,1.1]	65	0.2462	41	1-13week（COD_{Mn}）	（0.9,1.1]	63	0.1429
14		（0.8,1.2]		0.4462	42		（0.8,1.2]		0.3651
15		（0.5,1.5]		0.9077	43		（0.5,1.5]		0.9048
16		（0.5,2.0]		0.9846	44	14-26week（COD_{Mn}）	（0.9,1.1]	63	0.2540
17	all year（NH3-N）	（0.9,1.1]	255	0.2078	45		（0.8,1.2]		0.4286
18		（0.8,1.2]		0.3882	46		（0.5,1.5]		0.9206
19		（0.5,1.5]		0.8118	47	26-39week（COD_{Mn}）	（0.9,1.1]	60	0.3000
20		（0.0,2.0]		0.9922	48		（0.8,1.2]		0.7833
21	1-13week（pH）	（0.9,1.1]	66	1.0000	49		（0.5,1.5]		0.9667
22	14-26week（pH）	（0.9,1.1]	62	1.0000	50	40-52week（COD_{Mn}）	（0.9,1.1]	65	0.2923
23	26-39week（pH）	（0.9,1.1]	60	1.0000	51		（0.8,1.2]		0.4923
24	40-52week（pH）	（0.9,1.1]	65	0.9846	52		（0.5,1.5]		0.8923
25	all year（pH）	（0.9,1.1]	253	0.9960	53		（0.0,1.5]		0.9846
26	1-13week（DO）	（0.9,1.1]	66	0.4848	54	all year（COD_{Mn}）	（0.9,1.1]	251	0.2470
27		（0.8,1.2]		0.6364	55		（0.8,1.2]		0.5139
28		（0.5,1.5]		0.9848	56		（0.5,1.5]		0.9203
					57		（0.0,1.5]		0.9721

Table 6-7 Probability distribution of water quality monitoring index values of Zhaoyuan section

No.	Time (Index)	K_i^n Section	Number of samples	Probability	No.	Time (Index)	K_i^n Section	Number of samples	Probability
1	1-13week（NH3-N）	（0.9,1.1]	111	0.1712		14-26week（DO）	（0.9,1.1]	117	0.4615
2		（0.8,1.2]		0.3784			（0.8,1.2]		0.7778
3		（0.5,1.5]		0.7027			（0.5,1.5]		1.0000
4		（0.0,2.0]		0.9910		26-39week（DO）	（0.9,1.1]	109	0.5046
5	14-26week（NH3-N）	（0.9,1.1]	118	0.1695			（0.8,1.2]		0.8073
6		（0.8,1.2]		0.2881	33		（0.5,1.5]		1.0000
7		（0.5,1.5]		0.6017	34	40-52week（DO）	（0.9,1.1]	92	0.2391
8		（0.0,2.0]		0.9576	35		（0.8,1.2]		0.5109
9	26-39week（NH3-N）	（0.9,1.1]	109	0.1101	36		（0.5,1.5]		0.9891
10		（0.8,1.2]		0.2018	37	all year（DO）	（0.9,1.1]	429	0.3893
11		（0.5,1.5]		0.4862	38		（0.8,1.2]		0.6807
12		（0.0,2.0]		0.9541	39		（0.5,1.5]		0.9907
13	40-52week（NH3-N）	（0.9,1.1]	92	0.0652	40	1-13week（COD_{Mn}）	（0.9,1.1]	111	0.2883
14		（0.8,1.2]		0.1848	41		（0.8,1.5]		0.6757
15		（0.5,1.5]		0.4674	42		（0.5,2.0]		1.0000
16		（0.0,2.0]		0.9565	43	14-26week（COD_{Mn}）	（0.9,1.1]	118	0.1864
17	all year（NH3-N）	（0.9,1.1]	430	0.1326	44		（0.8,1.2]		0.4661
18		（0.8,1.2]		0.2674	45		（0.5,1.5]		0.9237
19		（0.5,1.5]		0.5698	46		（0.0,2.0]		1.0000
20		（0.0,2.0]		0.9651	47	26-39week（COD_{Mn}）	（0.9,1.1]	109	0.2752
21	1-13week（pH）	（0.9,1.1]	111	1.0000	48		（0.8,1.2]		0.5780
22	14-26week（pH）	（0.9,1.1]	118	0.9492	49		（0.5,1.5]		0.9266
23		（0.8,1.2]		1.0000	50		（0.0,2.0]		0.9908
24	26-39week（pH）	（0.9,1.1]	109	0.9817	51	40-52week（COD_{Mn}）	（0.9,1.1]	92	0.2935
25		（0.8,1.2]		1.0000	52		（0.8,1.2]		0.5326
26	40-52week（pH）	（0.9,1.1]	92	0.9565	53		（0.5,1.5]		0.9783
27		（0.8,1.2]		1.0000	54		（0.0,2.0]		1.0000
28	all year（pH）	（0.9,1.1]	430	0.9721	55	all year（COD_{Mn}）	（0.9,1.1]	430	0.2581
29		（0.8,1.2]		1.0000	56		（0.8,1.2]		0.5093
30	1-13week（DO）	（0.9,1.1]	111	0.3243	57		（0.5,1.5]		0.9419
31		（0.8,1.2]		0.5946	58		（0.0,2.0]		0.9977
32		（0.5,1.5]		0.9730					

Table 6-8 Probability distribution of water quality monitoring index values of Tongxin island section in Jiamusi city

No.	Time (Index)	K_i^n Section	Number of samples	Probability	No.	Time (Index)	K_i^n Section	Number of samples	Probability
1	1-13week（NH3-N）	（0.9,1.1]	37	0.2162	32	1-13week（DO）	（0.5,1.5]	37	1.0000
2		（0.8,1.2]		0.3514	33	14-26week（DO）	（0.9,1.1]	31	0.3548
3		（0.5,1.5]		0.7297	34		（0.8,1.2]		0.5484
4		（0.0,2.0]		1.0000	35		（0.5,1.5]		0.9677
5	14-26week（NH3-N）	（0.9,1.1]	31	0.0323	36		（0.5,2.0]		1.0000
6		（0.8,1.2]		0.2258	37	26-39week（DO）	（0.9,1.1]	35	0.1429
7		（0.5,1.5]		0.8387	38		（0.8,1.2]		0.3143
8		（0.0,2.0]		1.0000	39		（0.5,1.5]		0.9429
9	26-39week（NH3-N）	（0.9,1.1]	36	0.1111	40	40-52week（DO）	（0.9,1.1]	40	0.2250
10		（0.8,1.2]		0.3611	41		（0.8,1.2]		0.5750
11		（0.5,1.5]		0.8611	42		（0.5,1.5]		1.0000
12		（0.0,2.0]		0.9722	43	all year（DO）	（0.9,1.1]	143	0.2797
13	40-52week（NH3-N）	（0.9,1.1]	40	0.2500	44		（0.8,1.2]		0.5245
14		（0.8,1.2]		0.3500	45		（0.5,1.5]		0.9790
15		（0.5,1.5]		0.9000	46	1-13week（COD_{Mn}）	（0.9,1.1]	37	0.1892
16		（0.0,2.0]		1.0000	47		（0.8,1.2]		0.5135
17	all year（NH3-N）	（0.9,1.1]	144	0.1597	48		（0.5,1.5]		1.0000
18		（0.8,1.2]		0.3264	49	14-26week（COD_{Mn}）	（0.9,1.1]	31	0.3871
19		（0.5,1.5]		0.8333	50		（0.8,1.2]		0.6129
20		（0.0,2.0]		0.9931	51		（0.5,1.5]		1.0000
21	1-13week（pH）	（0.9,1.1]	37	0.9189	52	26-39week（COD_{Mn}）	（0.9,1.1]	36	0.4444
22		（0.8,1.2]		1.0000	53		（0.8,1.2]		0.8333
23	14-26week（pH）	（0.9,1.1]	31	1.0000	54		（0.5,1.5]		0.9722
24	26-39week（pH）	（0.9,1.1]	36	1.0000	55		（0.5,2.0]		1.0000
25	40-52week（pH）	（0.9,1.1]	40	0.9250	56	40-52week（COD_{Mn}）	（0.9,1.1]	40	0.4250
26		（0.9,1.2]		1.0000	57		（0.8,1.2]		0.8000
27	all year（pH）	（0.9,1.1]	144	0.9583	58		（0.5,1.5]		1.0000
28		（0.8,1.2]		1.0000	59	all year（COD_{Mn}）	（0.9,1.1]	144	0.3611
29		（0.9,1.2]		0.9931	60		（0.8,1.2]		0.6944
30	1-13week（DO）	（0.9,1.1]	37	0.4054	61		（0.5,1.5]		0.9931
31		（0.8,1.2]		0.6486					

Table 6-9 Probability distribution of water quality monitoring index values of Tongjing section

No.	Time (Index)	K_i^n Section	Number of samples	Probability	No.	Time (Index)	K_i^n Section	Number of samples	Probability
1	1-13week（NH3-N）	（0.9,1.1]	102	0.2549	35	1-13week（DO）	（0.5,1.5]	102	0.9314
2		（0.8,1.2]		0.5000	36		（0.5,2.0]		1.0000
3		（0.5,1.5]		0.9118	37	14-26week（DO）	（0.9,1.1]	118	0.4322
4		（0.0,2.0]		1.0000	38		（0.8,1.2]		0.6949
5	14-26week（NH3-N）	（0.9,1.1]	118	0.2034	39		（0.5,1.5]		0.9831
6		（0.8,1.2]		0.3220	40		（0.5,2.0]		1.0000
7		（0.5,1.5]		0.7034	41	26-39week（DO）	（0.9,1.1]	106	0.5377
8		（0.0,2.0]		0.9068	42		（0.8,1.2]		0.7830
9	26-39week（NH3-N）	（0.9,1.1]	106	0.0943	43		（0.5,1.5]		0.9623
10		（0.8,1.2]		0.2547	44		（0.5,2.0]		1.0000
11		（0.5,1.5]		0.7547	45	40-52week（DO）	（0.9,1.1]	98	0.3571
12		（0.0,2.0]		0.9717	46		（0.8,1.2]		0.6735
13	40-52week（NH3-N）	（0.9,1.1]	98	0.1939	47		（0.5,1.5]		1.0000
14		（0.8,1.2]		0.3469	48	all year（DO）	（0.9,1.1]	424	0.4057
15		（0.5,1.5]		0.8878	49		（0.8,1.2]		0.6509
16		（0.0,2.0]		0.9898	50		（0.5,1.5]		0.9693
17	all year（NH3-N）	（0.9,1.1]	424	0.1863	51		（0.5,2.0]		1.0000
18		（0.8,1.2]		0.3538	52	1-13week（COD_{Mn}）	（0.9,1.1]	102	0.4118
19		（0.5,1.5]		0.8090	53		（0.8,1.2]		0.7157
20		（0.0,2.0]		0.9646	54		（0.5,1.5]		0.9216
21	1-13week（pH）	（0.9,1.1]	102	0.9412	55		（0.0,2.0]		0.9510
22		（0.8,1.1]		1.0000	56	14-26week（COD_{Mn}）	（0.9,1.1]	118	0.5678
23	14-26week（pH）	（0.9,1.1]	118	0.7881	57		（0.8,1.2]		0.7881
24		（0.8,1.2]		0.9746	58		（0.5,1.5]		1.0000
25	26-39week（pH）	（0.8,1.5]	106	1.0000	59	26-39week（COD_{Mn}）	（0.9,1.1]	106	0.6509
26		（0.9,1.1]		0.8774	60		（0.8,1.2]		0.8396
27		（0.9,1.2]		0.9811	61		（0.5,1.5]		0.9906
28		（0.8,1.5]		1.0000	62	40-52week（COD_{Mn}）	（0.9,1.1]	98	0.6735
29	40-52week（pH）	（0.9,1.1]	98	0.8980	63		（0.8,1.2]		0.9286
30		（0.8,1.2]		1.0000	64		（0.5,1.5]		1.0000
31	all year（pH）	（0.9,1.1]	424	0.8726	65	all year（COD_{Mn}）	（0.9,1.1]	424	0.5755
32		（0.8,1.2]		0.9906	66		（0.8,1.2]		0.8160
33	1-13week（DO）	（0.9,1.1]	102	0.2843	67		（0.5,1.5]		0.9788
34		（0.8,1.2]		0.4412	68		（0.0,2.0]		0.9882

Table 6-10 Probability distribution of water quality monitoring index values of white Beach section in Baicheng city

No.	Time (Index)	K_i^n Section	Number of samples	Probability	No.	Time (Index)	K_i^n Section	Number of samples	Probability
1	1-13week（NH3-N）	（0.9,1.1]	127	0.1181	35	14-26week（DO）	（0.9,1.1]	123	0.4309
2		（0.8,1.2]		0.2520	36		（0.8,1.5]		0.9187
3		（0.5,1.5]		0.7717	37		（0.5,1.5]		1.0000
4		（0.0,2.0]		0.9134	38	26-39week（DO）	（0.9,1.1]	111	0.4414
5	14-26week（NH3-N）	（0.9,1.1]	123	0.0976	39		（0.8,1.5]		0.9189
6		（0.8,1.2]		0.2195	40		（0.5,1.5]		1.0000
7		（0.5,1.5]		0.5610	41	40-52week（DO）	（0.9,1.1]	110	0.4455
8		（0.0,2.0]		0.9593	42		（0.8,1.2]		0.7273
9	26-39week（NH3-N）	（0.9,1.1]	111	0.0180	43		（0.5,1.5]		1.0000
10		（0.8,1.2]		0.1081	44	all year（DO）	（0.9,1.1]	471	0.4628
11		（0.5,1.5]		0.4955	45		（0.8,1.2]		0.7983
12		（0.0,2.0]		0.8829	46		（0.5,1.5]		0.9958
13	40-52week（NH3-N）	（0.9,1.1]	110	0.0727	47		（0.0,2.0]		1.0000
14		（0.8,1.2]		0.1909	48	1-13week（COD_{Mn}）	（0.9,1.1]	127	0.3307
15		（0.5,1.5]		0.5545	49		（0.8,1.2]		0.5512
16		（0.0,2.0]		0.9091	50		（0.5,1.5]		0.9685
17	all year（NH3-N）	（0.9,1.1]	471	0.0786	51		（0.0,2.0]		1.0000
18		（0.8,1.2]		0.1953	52	14-26week（COD_{Mn}）	（0.9,1.1]	123	0.3496
19		（0.5,1.5]		0.6008	53		（0.8,1.2]		0.6016
20		（0.0,2.0]		0.9172	54		（0.5,1.5]		0.9512
21	1-13week（pH）	（0.9,1.1]	127	0.9921	55		（0.0,2.0]		1.0000
22		（0.8,1.1]		1.0000	56	26-39week（COD_{Mn}）	（0.9,1.1]	111	0.3153
23	14-26week（pH）	（0.9,1.1]	123	0.9187	57		（0.8,1.2]		0.5856
24		（0.8,1.2]		1.0000	58		（0.5,1.5]		0.9009
25	26-39week（pH）	（0.9,1.1]	111	0.9189	59		（0.0,2.0]		0.9910
26		（0.8,0.9]		0.0270	60	40-52week（COD_{Mn}）	（0.9,1.1]	110	0.4545
27	40-52week（pH）	（0.9,1.1]	110	0.9818	61		（0.8,1.2]		0.7545
28	40-52week（pH）	（0.8,1.2]		1.0000	62		（0.5,1.5]		0.9909
29	all year	（0.9,1.1]	471	0.9533	63		（0.0,1.5]		1.0000
30		（0.8,1.2]		1.0000	64	all year（COD_{Mn}）	（0.9,1.1]	471	0.3609
31	1-13week（DO）	（0.9,1.1]	127	0.5276	65		（0.8,1.2]		0.6200
32		（0.8,1.2]		0.8268	66		（0.5,1.5]		0.9533
33		（0.5,1.5]		0.9843	67		（0.0,2.0]		0.9979
34		（0.0,2.0]		1.0000					

Table 6-11 Probability distribution of water quality monitoring index values of Xindian section in Dunhua City, Jilin province

No.	Time (Index)	K_i^n Section	Number of samples	Probability	No.	Time (Index)	K_i^n Section	Number of samples	Probability
1	1-13week（NH_3-N）	（0.9,1.1]		0.2090	32	14-26week（DO）	（0.5,1.5]	64	1.0000
2		（0.8,1.2]	67	0.3284	33	26-39week（DO）	（0.9,1.1]		0.5323
3		（0.5,1.5]		0.8358	34		（0.8,1.2]	62	0.8226
4		（0.0,2.0]		1.0000	35		（0.5,1.5]		1.0000
5	14-26week（NH3-N）	（0.9,1.1]		0.1719	36	40-52week（DO）	（0.9,1.1]		0.7077
6		（0.8,1.2]	64	0.2969	37		（0.8,1.2]	65	0.9538
7		（0.5,1.5]		0.7344	38		（0.5,1.5]		1.0000
8		（0.0,1.5]		0.8906	39	all year（DO）	（0.9,1.1]		0.5659
9		（0.0,2.0]		0.9375	40		（0.8,1.2]	258	0.8643
10	26-39week（NH3-N）	（0.9,1.1]		0.2742	41		（0.5,1.5]		1.0000
11		（0.8,1.2]		0.4355	42	1-13week（COD_{Mn}）	（0.9,1.1]		0.3134
12		（0.5,1.5]	62	0.8387	43		（0.8,1.2]	67	0.4925
13		（0.0,2.0]		0.9516	44		（0.5,1.5]		0.9403
14	40-52week（NH3-N）	（0.9,1.1]		0.1538	45		（0.0,2.0]	67	0.9851
15		（0.8,1.2]		0.4000	46	14-26week（COD_{Mn}）	（0.9,1.1]		0.4844
16		（0.5,1.5]	65	0.8000	47		（0.8,1.2]		0.7500
17		（0.0,2.0]		0.9538	48		（0.5,1.5]	64	0.9844
18	all year（NH3-N）	（0.9,1.1]		0.2016	49		（0.5,1.5]		0.9844
19		（0.8,1.2]		0.3643	50		（0.5,2.0]		1.0000
20		（0.5,1.5]	258	0.8023	51	26-39week（COD_{Mn}）	（0.9,1.1]		0.2419
21		（0.0,2.0]		0.9612	52		（0.8,1.2]		0.6290
22	1-13week（pH）	（0.9,1.1]	67	1.0000	53		（0.5,1.5]	62	0.9355
23	14-26week（pH）	（0.9,1.1]	64	1.0000	54		（0.5,2.0]		1.0000
24	26-39week（pH）	（0.9,1.1]	62	1.0000	55	40-52week（COD_{Mn}）	（0.9,1.1]		0.4462
25	40-52week（pH）	（0.9,1.1]	65	1.0000	56		（0.8,1.2]	65	0.7231
26	all year（pH）	（0.9,1.1]	258	1.0000	57		（0.5,1.5]		0.9692
27	1-13week（DO）	（0.9,1.1]		0.4776	58		（0.0,1.5]		1.0000
28		（0.8,1.2]	67	0.7463	59	all year（COD_{Mn}）	（0.9,1.1]		0.3721
29		（0.5,1.5]		1.0000	60		（0.8,1.2]	258	0.6473
30	14-26week（DO）	（0.9,1.1]	64	0.5469	61		（0.5,1.5]		0.9574
31		（0.8,1.2]		0.9375	62		（0.0,2.0]		0.9961

Table 6-12 Probability distribution of water quality monitoring index values of Mudanjiang Estuary section in Yilan county

No.	Time (Index)	K_i^n Section	Number of samples	Probability	No.	Time (Index)	K_i^n Section	Number of samples	Probability
1	1-13week（NH3-N）	（0.9,1.1]	28	0.2143	31	14-26week（DO）	（0.8,1.5]	30	1.0000
2		（0.8,1.2]		0.4643	32	26-39week（DO）	（0.9,1.1]	37	0.4865
3		（0.5,1.5]		0.9286	33		（0.8,1.2]		1.0000
4		（0.0,2.0]		1.0000	34	40-52week（DO）	（0.9,1.1]	35	0.2857
5	14-26week（NH3-N）	（0.9,1.1]	30	0.5000	35		（0.8,1.2]		0.5429
6		（0.8,1.2]		0.8333	36		（0.5,1.5]		0.9714
7		（0.5,1.5]		1.0000	37		（0.5,2.0]		1.0000
8	26-39week（NH3-N）	（0.9,1.1]	37	0.2973	38	all year（DO）	（0.9,1.1]	130	0.5462
9		（0.8,1.2]		0.7027	39		（0.8,1.2]		0.8692
10		（0.5,1.5]		1.0000	40		（0.5,1.5]		0.9923
11	40-52week（NH3-N）	（0.9,1.1]	35	0.1429	41		（0.5,2.0]		1.0000
12		（0.8,1.2]		0.3714	42	1-13week（COD_{Mn}）	（0.9,1.1]	28	0.5000
13		（0.5,1.5]		0.8571	43		（0.8,1.2]		0.8241
14		（0.0,2.0]		1.0000	44		（0.5,1.5]		0.9643
15	all year（NH3-N）	（0.9,1.1]	130	0.2846	45		（0.0,1.5]		1.0000
16		（0.8,1.2]		0.5923	46	14-26week（COD_{Mn}）	（0.9,1.1]	30	0.5000
17		（0.5,1.5]		0.9462	47		（0.8,1.2]		0.8000
18		（0.0,2.0]		1.0000	48		（0.5,1.5]		1.0000
19	1-13week（pH）	（0.9,1.1]	28	0.9643	49	26-39week（CODMn）	（0.9,1.1]	37	0.4054
20		（0.8,1.1]		1.0000	50		（0.8,1.2]		0.7838
21	14-26week（pH）	（0.9,1.1]	30	1.0000	51		（0.5,1.5]		1.0000
22	26-39week（pH）	（0.9,1.1]	37	1.0000	52	40-52week（COD_{Mn}）	（0.9,1.1]	35	0.4857
23	40-52week（pH）	（0.9,1.1]	35	0.9143	53		（0.8,1.2]		0.6571
24		（0.8,1.2]		1.0000	54		（0.5,1.5]		0.9714
25	all year（pH）	（0.9,1.1]	130	0.9692	55		（0.0,1.5]		1.0000
26		（0.8,1.2]		1.0000	56	all year（COD_{Mn}）	（0.9,1.1]	130	0.4692
27	1-13week（DO）	（0.9,1.1]	28	0.7857	57		（0.8,1.2]		0.7615
28		（0.8,1.2]		1.0000	58		（0.5,1.5]		0.9846
29	14-26week（DO）	（0.9,1.1]	30	0.7000	59		（0.0,1.5]		1.0000
30		（0.8,1.2]		0.9667					

Table 6-13 Probability distribution of water quality monitoring index values at the mouth section of Yinma river

No.	Time (Index)	K_i^n Section	Number of samples	Probability	No.	Time (Index)	K_i^n Section	Number of samples	Probability
1	1-13week（NH_3-N）	（0.9,1.1]	41	0.2195	33	14-26week（DO）	（0.0,2.0]	38	1.0000
2		（0.8,1.2]		0.4634	34		（0.9,1.1]		0.3889
3		（0.5,1.5]		1.0000	35	26-39week（DO）	（0.8,1.2]	36	0.4722
4	14-26week（NH_3-N）	（0.9,1.1]	38	0.1579	36		（0.5,1.5]		0.9167
5		（0.8,1.2]		0.3684	37		（0.5,2.0]		1.0000
6		（0.5,1.5]		0.7895	38	40-52week（DO）	（0.9,1.1]	41	0.1951
7		（0.0,2.0]		1.0000	39		（0.8,1.2]		0.4634
8	26-39week（NH_3-N）	（0.9,1.1]	36	0.0833	40		（0.5,1.5]		0.8293
9				0.0833	41		（0.0,2.0]		0.9512
10		（0.5,1.5]		0.6111	42	all year（DO）	（0.9,1.1]	156	0.2244
11		（0.0,2.0]		0.9444	43		（0.8,1.2]		0.3846
12	40-52week（NH_3-N）	（0.9,1.1]	41	0.2195	44		（0.5,1.5]		0.7885
13		（0.8,1.2]		0.3171	45		（0.0,2.0]		0.9808
14		（0.5,1.5]		0.6098	46	1-13week（COD_{Mn}）	（0.9,1.1]	41	0.2927
15		（0.0,2.0]		0.9512	47		（0.8,1.2]		0.6585
16	all year（NH_3-N）	（0.9,1.1]	156	0.1731	48		（0.5,1.5]		1.0000
17		（0.8,1.2]		0.3141	49	14-26week（COD_{Mn}）	（0.9,1.1]	38	0.3421
18		（0.5,1.5]		0.7564	50		（0.8,1.2]		0.5526
19		（0.0,2.0]		0.9744	51		（0.5,1.5]		1.0000
20	1-13week（pH）	（0.9,1.1]	41	1.0000	52	26-39week（COD_{Mn}）	（0.9,1.1]	36	0.4722
21	14-26week（pH）	（0.9,1.1]	38	1.0000	53		（0.8,1.2]		0.8056
22	26-39week（pH）	（0.9,1.1]	36	1.0000	54		（0.5,1.5]		0.9722
23	40-52week（pH）	（0.9,1.1]	41	1.0000	55		（0.5,2.0]		1.0000
24	all year（pH）	（0.9,1.1]	156	1.0000	56	40-52week（COD_{Mn}）	（0.9,1.1]	41	0.3902
25	1-13week（DO）	（0.9,1.1]	41	0.0976	57		（0.8,1.2]		0.5854
26		（0.9,1.2]		0.1707	58		（0.5,1.5]		0.9756
27		（0.5,1.2]		0.4146	59		（0.5,2.0]		1.0000
28		（0.5,1.5]		0.5854	60	all year（COD_{Mn}）	（0.9,1.1]	156	0.3718
29		（0.0,2.0]		0.9756	61		（0.8,1.2]		0.6474
30	14-26week（DO）	（0.9,1.1]	38	0.2368	62		（0.5,1.5]		0.9872
31		（0.8,1.2]		0.4474	63		（0.5,2.0]		1.0000
32		（0.5,1.5]		0.8421					

Table 6-14 Probability distribution of water quality monitoring index values in Songhua river basin

No.	Time (Index)	K_i^n Section	Number of samples	Probability	No.	Time (Index)	K_i^n Section	Number of samples	Probability
1	1-13week（NH3-N）	（0.9,1.1]	774	0.1796	39	14-26week（DO）	（0.9,1.1]	773	0.5136
2		（0.8,1.2]		0.3682	40		（0.8,1.2]		0.7943
3		（0.5,1.5]		0.7933	41		（0.5,1.5]		0.9884
4		（0.0,2.0]		0.9819	42		（0.0,2.0]		1.0000
5	14-26week（NH3-N）	（0.9,1.1]	774	0.1835	43	26-39week（DO）	（0.9,1.1]	730	0.5288
6		（0.8,1.2]		0.3450	44		（0.8,1.2]		0.8164
7		（0.5,1.5]		0.7106	45		（0.5,1.5]		0.9877
8		（0.0,2.0]		0.9625	46		（0.5,2.0]		0.9986
9	26-39week（NH3-N）	（0.9,1.1]	730	0.1548	47		（0.0,2.0]		1.0000
10		（0.8,1.2]		0.3247	48	40-52week（DO）	（0.9,1.1]	721	0.4189
11		（0.5,1.5]		0.7096	49		（0.8,1.2]		0.7087
12		（0.0,2.0]		0.9589	50		（0.5,1.5]		0.9875
13	40-52week（NH3-N）	（0.9,1.1]	721	0.1581	51		（0.0,2.0]		0.9972
14		（0.8,1.2]		0.3093	52	all year（DO）	（0.9,1.1]	2998	0.4753
15		（0.5,1.5]		0.7254	53		（0.8,1.2]		0.7528
16		（0.0,2.0]		0.9695	54		（0.5,1.5]		0.9810
17	all year（NH3-N）	（0.9,1.1]	2999	0.1694	55		（0.0,2.0]		0.9990
18		（0.8,1.2]		0.3374	56	1-13week（COD_{Mn}）	（0.9,1.1]	771	0.3658
19		（0.5,1.5]		0.7352	57		（0.8,1.2]		0.6342
20		（0.0,2.0]		0.9683	58		（0.5,1.5]		0.9624
21	1-13week（pH）	（0.9,1.1]	774	0.9793	59		（0.0,2.0]		0.9922
22		（0.8,1.2]		1.0000	60	14-26week（COD_{Mn}）	（0.9,1.1]	773	0.4489
23	14-26week（pH）	（0.9,1.1]	772	0.9469	61		（0.8,1.2]		0.6869
24		（0.8,1.2]		0.9961	62		（0.5,1.5]		0.9728
25		（0.8,1.5]		1.0000	63		（0.0,2.0]		1.0000
26	26-39week（pH）	（0.9,1.1]	730	0.9644	64	26-39week（COD_{Mn}）	（0.9,1.1]	730	0.4521
27		（0.8,1.2]		0.9986	65		（0.8,1.2]		0.7562
28		（0.8,1.5]		1.0000	66		（0.5,1.5]		0.9616
29	40-52week（pH）	（0.9,1.1]	721	0.9598	67		（0.0,2.0]		0.9973
30		（0.8,1.2]		0.9986	68	40-52week（COD_{Mn}）	（0.9,1.1]	721	0.4716
31		（0.8,1.5]		1.0000	69		（0.8,1.2]		0.7393
32	all year（pH）	（0.9,1.1]	2997	0.9626	70		（0.5,1.5]		0.9806
33		（0.8,1.2]		0.9983	71		（0.0,2.0]		1.0000
34		（0.8,1.5]		1.0000	72	all year（COD_{Mn}）	（0.9,1.1]	2993	0.3859
35	1-13week（DO）	（0.9,1.1]	774	0.4393	73		（0.8,1.2]		0.6632
36		（0.8,1.2]		0.6925	74		（0.5,1.5]		0.9639
37		（0.5,1.5]		0.9612	75		（0.0,2.0]		0.9973
38		（0.0,2.0]		0.9987					

By analyzing the probability distribution table of all the above water quality monitoring index values, the following conclusions can be drawn:

(1) In general, among the four indexes of ammonia nitrogen, pH, dissolved oxygen and permanganate

index, the index with the smallest fluctuation range around its multi-year same mean value in the same period is pH, the index with the largest fluctuation is ammonia nitrogen, and the other two indexes of dissolved oxygen and permanganate index are in the middle.

(2) Ammonia nitrogen (NH_3-N) index: the section with the smallest fluctuation range of ammonia nitrogen index value around its multi-year same mean value in the same period is Mudanjiang River Estuary section, followed by Changchun Songhuajiang Village section. The sections with large fluctuation range are Jilin xilangkou section, Zhaoyuan section and Yinmahe River Estuary section; in the time period, the ammonia nitrogen index shows great differences in different sections and fails to show a unified law.

(3) pH: Among all sections in Songhua River Basin, the sections with small fluctuation range of pH index around its multi-year same mean value in the same period are Jilin Dunhua Xindian section and Yinmahe estuary section. The values of all pH monitoring values at any time of the two sections are (0.9, 1.1)], the probability is 100%, and the section with the largest fluctuation range is Tongjiang section; in terms of time period, the period with the largest fluctuation range is the river freezing and unsealing period of 14-26 weeks, and the period with the smallest fluctuation range is the freezing and unsealing period of 1-13 weeks.

(4) Dissolved oxygen (DO) index: among all sections of Songhua River Basin, the section with the smallest fluctuation range around its multi-year same mean value in the same period is Changchun Songhua River Village, followed by Jilin Dunhua Xindian section. The section with the largest fluctuation range is Yinmahe River Estuary, followed by Tongjiang section; the period with the smallest fluctuation range is 26-39 weeks, and the maximum period is 40-52 weeks.

(5) Permanganate index (COD_{Mn}) index: among all sections of Songhua River Basin, the section with the smallest fluctuation range of permanganate index around its multi-year same mean value in the same period is Changchun Songhuajiang village, followed by Tongjiang section and Jilin Xilangkou section, and the sections with the largest fluctuation range are Songyuan pine forest section and Zhaoyuan section; the period with the smallest fluctuation range is 14-26 weeks, and the larger period is 1-13 and 26-39 weeks.

6.3.3 Application of Probability Distribution Table of Water Quality Monitoring Index Value

In daily water environment management, it is often necessary to estimate or predict the water quality index value in a certain period. Due to the trend, gradual change and periodic fluctuation of the water quality monitoring index value, When the annual average value and annual probability distribution table (or function) of indicators are directly used to estimate the value or range of water quality monitoring indicators in a certain period, there is often a large deviation. The "probability distribution table of water quality monitoring indicator value" and the corresponding "multi-year average value of water quality monitoring indicators" will be obtained. The combined use can greatly improve the accuracy of water quality monitoring index value estimation and narrow the scope of index estimation. There are three main reasons:

(1) By observing the probability distribution table of water quality monitoring index values obtained in this paper (hereinafter referred to as the probability distribution table), it can be found that different

sections will lead to differences in the probability distribution of index values;

(2) The periodic fluctuation of the index value leads to seasonal differences in the value range in different periods. The probability distribution table lists the probability distribution of the index value in different periods, making the probability value more accurate in time;

(3) In the index value estimation and prediction method in this paper, taking all the index monitoring values in the sample year as the unit of week, the average value of the monitoring values obtained from the weeks with the same order in different years can be obtained. In the process of index value prediction, the error caused by seasonal differences can be reduced.

6.4 Summary of this Chapter

Based on the trend of water quality monitoring index values, it is found that the water quality of Songhua River Basin shows a good development trend as a whole during the study period; Through the periodic study of water quality monitoring index values, the periodic changes of pH, dissolved oxygen, permanganate index and ammonia nitrogen in a calendar year in Songhua River Basin are studied and expounded; Through the study on the fluctuation (randomness) of water quality monitoring index values, the probability distribution of four indexes in different periods is calculated, which can provide reference for the estimation and prediction of index values.

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Chapter 7

STUDY ON THE RELATIONSHIP BETWEEN WATER QUALITY CATEGOY AND WATER QUALITY INDEX VALUE AND TOTAL AMOUNT CONTROL OF POLLUTION SOURCES

CHAPTER SEVEN: STUDY ON THE RELATIONSHIP BETWEEN WATER QUALITY CATEGOY AND WATER QUALITY INDEX VALUE AND TOTAL AMOUNT CONTROL OF POLLUTION SOURCES

CHAPTER 7: STUDY ON THE RELATIONSHIP BETWEEN WATER QUALITY CATEGOY AND WATER QUALITY INDEX VALUE AND TOTAL AMOUNT CONTROL OF POLLUTION SOUR CES

7.1 Analysis of Contribution of Water Quality Indicators to Changes in Water Quality Categories

7.1.1 Calculation Method of Contribution

The contribution of water quality monitoring indicators to the change of water quality category is used to measure the effect of the change of a water quality monitoring indicator on the change of water quality category in a period of time. Through the analysis of the contribution of the change of monitoring index value to the change of water quality category, the water quality monitoring indicators causing the change of water quality category in this period can be sorted, so as to determine the main driving factors causing the change of water quality category. In addition, the sustainability of the change trend of water quality category can be judged by combining the contribution of monitoring index with the current water quality situation. The contribution of water quality monitoring indicators to changes in water quality categories (hereinafter referred to as "contribution") is the sum of "changes in water quality categories caused by changes in water quality monitoring indicators" and "changes in water quality categories" during the study period It is mainly affected by the water quality status at the beginning of the period, the types of water quality monitoring indicators, the change of water quality monitoring indicator value and the change of water quality category. The calculation formula is as follows:

$$f(z) = \frac{dy}{dz} \qquad (7\text{-}1)$$

Where:

f(*z*) - contribution of water quality monitoring indicators to changes in water quality categories;

dy -- sum of changes in water quality categories caused by changes in water quality monitoring index values in previous monitoring results during the study period;

dz - sum of changes in water quality categories in previous monitoring results during the study period;

The following points should be pointed out:

①The calculated F (z) value can be divided into positive and negative. A positive value represents that the development direction of the water quality condition caused by the index value is the same as that of the actual water quality condition during the period, while a negative value represents the opposite direction;

② Only on the basis of one of the two preconditions of "simultaneous section, same section and different indicators" or "different period, same section and same indicator", can the calculated F (z) values be compared with each other, and its size has practical significance. The greater the absolute value of the contribution f (z) value of the indicator, the greater the influence of the water quality indicator on the water quality category;

③ The special "f (z) = 1" does not represent that 100% of the change of water quality category is caused by this index, but "f (z) = 0" can represent that the index value has no direct impact on the change of water quality category;

④ The sum of the contribution values of all indicators is not necessarily equal to "1", because under some specific conditions, the effects of different indicators will be repeated or offset.

7.1.2 Calculation of Section Contribution

It can be seen from the introduction of the contribution calculation method in the previous section that there are two different comparison dimensions for the comparison of contribution degrees. One is the comparison of contribution degrees between different monitoring indicators with the same period, the same section. In this case, comparing the contribution degree f (z) value can determine the main driving factors leading to the change of water quality category; Another situation is that the time periods are different, the sections are the same, and the monitoring indicators are the same. In this case, by comparing the contribution f (z) value, we can get the change trend of the influence of the monitoring indicator on the change of water quality category in different time periods. Combined with the actual conditions of relevant standards and sections, we can judge whether the relevant trend is sustainable, Judge the safety and importance of indicators. Table 7-1 and Table 7-2 respectively show the contribution of some research sections calculated under two different dimensions: according to the water quality monitoring index value data of six sections in Jilin xilangkou, Changchun Songhuajiang village and Songlin Songyuan from 2015 to 2016, the index contribution of these six sections is calculated and calculated, and the following Table 7-1 is obtained:

Table 7-1 Statistical table of Iindex contributions of some monitoring sections in the Songhua river basin at the same time (2014-2016)

No.	Section	Index	*dz*	*dy*	Contribution degree *f(y)*
1	Jilin Xilangkou	DO	-12	1	-0.083
2		Permanganate index	-12	7	-0.583
3		NH_3-N	-12	-7	0.583
4	Changchun Songhuajiang Village	DO	1	0	0.000
5		Permanganate index	1	8	8.000
6		NH_3-N	1	-8	-8.000
7	Songyuan Songlin	DO	22	0	0.045
8		Permanganate index	22	1	0.000
9		NH_3-N	22	-15	-0.682
10	Jiamusi Tongxin Island	DO	5	0	0.000
11		Permanganate index	5	-4	-0.800
12		NH_3-N	5	3	0.600
13	Baicheng Baishatan	DO	-6	0	0.000
14		Permanganate index	-6	-6	1.000
15		NH_3-N	-6	0	0.000
16	Yinma River Estuary	DO	-3	0	0.000
17		Permanganate index	-3	-1	0.333
18		NH_3-N	-3	-2	0.667

The contribution degree f (y) of some sections in Table 7-1 is interpreted below:

Firstly, the contribution degree of xilangkou section in Jilin Province is interpreted. During the study period, the section "DZ < 0", indicating that the water quality of the section is better as a whole; The contribution degree f (y) of dissolved oxygen index and permanganate index is less than 0, indicating that the influence direction of the two indexes on water quality category is opposite to the actual development direction of water quality category, which is a negative driving index. If the contribution degree f (y) of permanganate index is less than 0, its influence direction is the same as the development direction of water quality category, which is a positive driving index; The absolute values of the contribution of dissolved oxygen, permanganate index and ammonia nitrogen are 0.083, 0.583 and 0.583 respectively. Permanganate index = ammonia nitrogen > dissolved oxygen, indicating that the influence of the three indicators on water quality categories is equal to that of ammonia nitrogen, and both are higher than that of dissolved oxygen.

Then, the contribution calculation results of Baicheng white beach section are interpreted. The contribution f (y) values of dissolved oxygen, permanganate index and ammonia nitrogen are 0, 1 and 0 respectively, which shows that the two indexes of dissolved oxygen and ammonia nitrogen have no influence on the change of water quality category of the section during the study period; The contribution of permanganate index F (y) = 1, but it does not indicate that the change of water quality category is completely caused by the change of this index.

Finally, the calculation results of the contribution degree of the Yinma River Estuary section are interpreted. In this section, the absolute value of the contribution degree of the three indicators is sorted from large to small: ammonia nitrogen > permanganate index > dissolved oxygen, that is, the influence of the three indicators on the change of water quality category is sorted from large to small: ammonia nitrogen > permanganate index > dissolved oxygen, indicating that in ammonia nitrogen Among the three indexes of permanganate index and dissolved oxygen, the main driving force index of water quality category change is ammonia nitrogen.

The interpretation of the index contribution of the other sections can be easily completed with reference to the above three sections, which will not be repeated here.

According to the water quality monitoring index value data of Baicheng white beach section from 2010 to 2016, the following Table 7-2 is obtained through contribution calculation, and the corresponding histogram 7-1 is drawn according to the data in the table:

Table 7-2 Statistical table of index contributions of Baicheng Baishatan section in different time periods

No.	Time	Index	*dz*	*dy*	Contribution degree *f(y)*
1		DO	6	0	0.000
2	2010-2011	Permanganate index	6	6	1.000
3		NH_3-N	6	1	-0.167
4		DO	-19	0	0.000
5	2011-2012	Permanganate index	-19	-3	0.158
6		NH_3-N	-19	-7	0.368
7		DO	5	2	4.000
8	2012-2013	Permanganate index	5	17	3.400
9		NH_3-N	5	-7	-1.400
10		DO	4	0	0.000
11	2013-2014	Permanganate index	4	4	1.000
12		NH_3-N	4	3	0.750
13		DO	9	0	0.000
14	2014-2015	Permanganate index	9	9	1.000
15		NH_3-N	9	0	0.000
16		DO	-6	0	0.000
17	2014-2016	Permanganate index	-6	-6	1.000
18		NH_3-N	-6	0	0.000

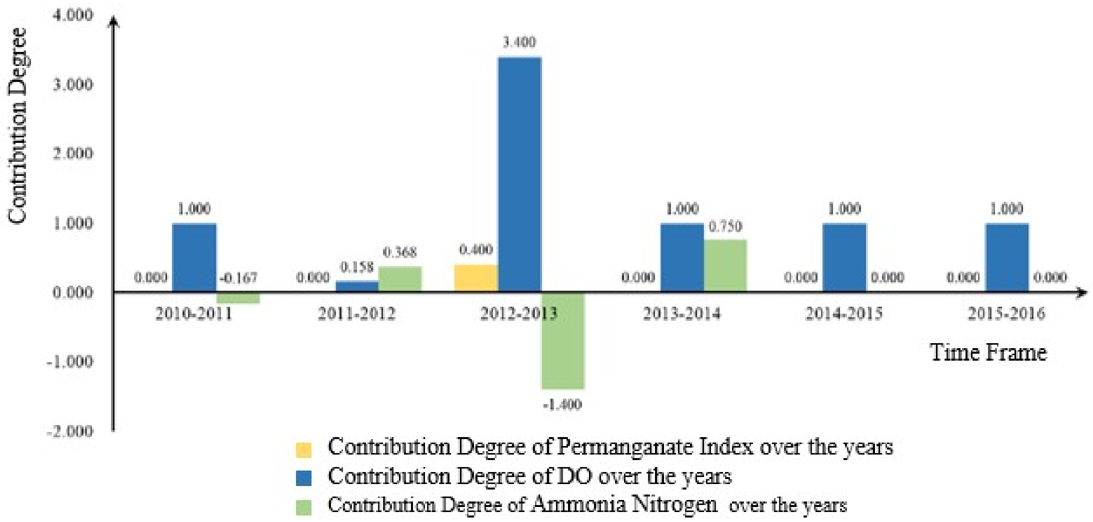

Figure 7-1 Histogram of the index contribution of Baicheng Baisha Beach section from 2010 to 2016

Table 7-2 is explained below. From Figure 7-1, we can more intuitively find the size, positive and negative and changes of the contribution of dissolved oxygen, permanganate index and ammonia nitrogen of Baicheng white beach section from 2010 to 2016. We can mainly draw the following conclusions:

① the main driving factor for the change of water quality category of Baicheng white beach from 2010 to 2016 is permanganate index, And the driving direction is consistent with the development direction of water quality change;

② The dissolved oxygen index has the least influence on the change of water quality category. In the calculation and comparison of contribution degree for 6 consecutive times, 5 times have no influence, and only one time shows the influence consistent with the change direction of water quality category, but the influence is the lowest in the three indexes;

③ Ammonia nitrogen index showed influence in 2010-2014, but did not show influence on the change of water quality category in 2014-2016.

7.2 Sensitivity Analysis of Water Quality Category to Water Quality Monitoring sStandard Indicators

7.2.1 Analysis and Calculation Method of Sensitivity of Water Quality Category to Water Quality Monitoring Indicators

The sensitivity of water quality category to water quality monitoring indicators refers to whether the water quality category changes and the degree of change if the water quality monitoring indicators change to a certain extent under a certain water quality condition. Under a certain water quality condition, when the change amount of water quality detection index is constant, the greater the change degree of water quality category, indicating that the water quality category is more sensitive to the change of water quality index value. Through the research and Analysis on the change sensitivity of water quality category, we can determine what kind of water quality index will change and what degree of change will change the water quality category. Obviously, the sum of human, material and financial costs to adjust the water quality index value to this degree is the cost to adjust the target change of water quality category.

The most widely used methods of sensitivity analysis include impulse response, range analysis and elastic analysis. In this paper, the elastic analysis method is used to analyze the sensitivity of water quality categories to water quality monitoring values. In this paper, the elasticity analysis method of balance of payments adjustment is used for reference in the process of index sensitivity analysis (this method was founded by Joan Robinson, an economist at the University of Cambridge, UK, based on Marshall microeconomics and local equilibrium analysis method in the era of Microeconomics). The sensitivity analysis of water quality categories to water quality monitoring indicators takes the water quality status of the river at a certain time node as the initial data to analyze the single index value or multiple index values of water quality monitoring indicators Conduct different degrees of simulation adjustment, and judge the water quality grade after the index value adjustment according to the new water quality monitoring index value. According to the ratio between the adjustment amount of monitoring index value and the change of water quality grade, the sensitivity of water quality grade to the change of each water quality monitoring index value can be judged.

In this paper, the sensitivity of the change of water quality monitoring index value to the change of water quality category can be divided into real value and treatment value. The real value of sensitivity is expressed by the ratio of "the sum of the change of water quality category" to "the sum of the change of water quality monitoring index value" in the period, and its size is mainly affected by the water quality condition, the type of water quality monitoring index The change of water quality monitoring index value and water quality category are affected by four factors. The calculation formula is as follows:

$$g(x) = \frac{dz}{\Delta x} \qquad (7\text{-}2)$$

Where:

$g(x)$ - real value of sensitivity of water quality monitoring index value change to water quality category change;

dz - sum of changes in water quality categories during the study period;

Δx- sum of changes in water quality monitoring index values during the study period;

Using formula (7-2) when analyzing and studying the real value of sensitivity of water quality indicators, on the premise of controlling variables, it is of practical significance to compare the real value of sensitivity of a single water quality monitoring indicator value in different periods. However, if the real value of sensitivity of different indicators in the same period is compared, there is no practical significance, because in different periods The relationship between "the sum of changes in water quality categories" and "the sum of changes in water quality monitoring index values" is artificially given by us. This relationship is the standard table of quasi basic items of surface water environmental quality table. Therefore, in order to facilitate the comparison of the contribution of different monitoring indicators, the real value of sensitivity needs to be further processed. This paper multiplies the real value of sensitivity by the sensitivity coefficient of water quality monitoring index to weaken the influence of the artificial regulation of "water quality monitoring index type" on the sensitivity calculation results. The calculated result is called the sensitivity treatment value, and the calculation formula is as follows (7-3):

$$h(x) = g(x) \times n \qquad (7\text{-}3)$$

Where

$h(x)$ - sensitivity treatment value of water quality monitoring index value change to water quality category change;

n - sensitivity coefficient of water quality monitoring index, which is the difference between class II water standard limit and class IV water standard limit in GB 3837-2002 environmental quality standard for surface water. The coefficients n corresponding to the three indexes studied in this paper are - 3, 6 and 1 respectively.

7.2.2 Calculation and Analysis of Sensitivity of Water Quality Category to Water Quality Index

In the calculation of the sensitivity of water quality categories to water quality indicators in this part, four sections of Songhuajiang village, Zhaoyuan, Tongjiang and Baicheng white beach in Changchun are selected as the research sections, based on the water quality index monitoring data of the above four sections in 2018, Δ The value of X is selected from 3.1 The absolute value of interannual variation B of each index value calculated in Section 2 is an integral multiple.

Table 7-3 Sensitivity analysis parameters of some sections in the Songhua river basin

Number	Section name	Index	Interannual variation	Index value adjustment multiple
1	Changchun Songhuajiang Village	DO	0.1837	All integers 【-10,10】
2		Permanganate index	0.1050	
3		NH_3-N	0.0200	
4	Zhaoyuan	DO	0.0594	
5		Permanganate index	0.1667	
6		NH_3-N	0.0575	
7	Tongjiang	DO	0.3600	
8		Permanganate index	0.0333	
9		NH_3-N	0.0068	
10	Baicheng Baishatan	DO	0.1032	
11		Permanganate index	0.1667	
12		NH_3-N	0.0550	

According to the above contents in this section, draw broken line diagrams 7-2, 7-3, 7-4 and 7-5 of sensitivity treatment values of four sections respectively, and interpret the key information shown in the four diagrams.

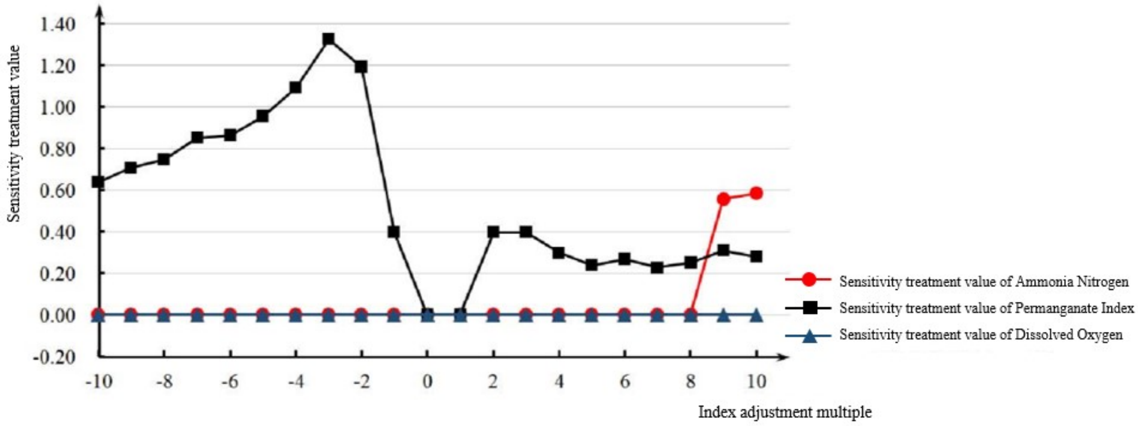

Figure 7-2 Broken line diagram of water quality category sensitivity treatment value of Changchun Songhuajiang Village section in 2018

By observing Figure 7-2, it can be found that based on the water quality status of the section in Songjiang village, Changchun in 2018, the water quality category of the section shows long-term and continuous high sensitivity to the permanganate index, indicating that the safety of the permanganate index is low. Therefore, great attention should be paid to the permanganate index value in the water environment treatment, restoration and protection, At the same time, the production and operation activities and natural development process closely related to permanganate index should be important treatment objects; The sensitivity to dissolved oxygen index remains zero, indicating that the safety of dissolved oxygen index is very high. According to the current development trend, there is no need to invest too much resources to pay attention; The sensitivity to ammonia nitrogen index is zero at - 10 ~ 8 times the adjustment amount of B, and directly jumps above the permanganate index at 9 and 10 times, indicating that the ammonia nitrogen index has a certain degree of safety and does not need to invest too much energy and resources to pay attention in a short time, but it is necessary to be vigilant that when the index continues this trend for a long time, the sensitivity of water quality category to it will suddenly increase, This moment should be avoided.

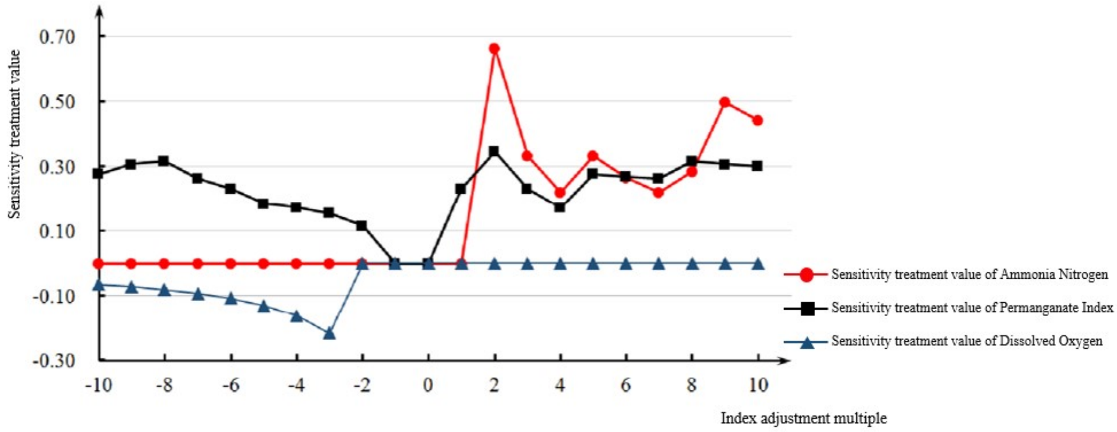

Figure 7-3 Broken line diagram of water quality category sensitivity treatment values at Zhaoyuan section in 2018

By observing Fig. 7-3, it can be found that the water quality category of Zhaoyuan section also shows long-term and continuous high sensitivity to permanganate index, which has the same meaning as the above paragraph and will not be repeated here; As we all know, the dissolved oxygen index is the only index with higher index value and lower water quality category. Therefore, when the dissolved oxygen index value decreases, the water quality will deteriorate. It can be seen from the figure that once the dissolved oxygen value decreases to 3b, the water quality category will suddenly deteriorate greatly, while when the dissolved oxygen value gradually increases within the range of 0 ~ 10B, the water quality category will not improve, It indicates that the dissolved oxygen index is near the minimum limit line of safety value, and corresponding water environmental protection measures should be taken to improve the dissolved oxygen index value of water body; Compared with dissolved oxygen index, the sensitivity of water quality category to ammonia nitrogen index changes more violently and will show more quickly, indicating that it is urgent to take corresponding control measures for production and operation activities that cause the rise of ammonia nitrogen index.

The following conclusions can be drawn by observing Figure 7-4. In Tongjiang section, the sensitivity of water quality category to dissolved oxygen, permanganate index and ammonia nitrogen index is relatively low in a short period of time. According to the current development trend, permanganate index will take the lead in becoming the index causing water quality change after a period of time; If we want to improve the water environment quality, we can start from the relevant factors affecting permanganate index and dissolved oxygen, and the treatment effect will appear after a long time.

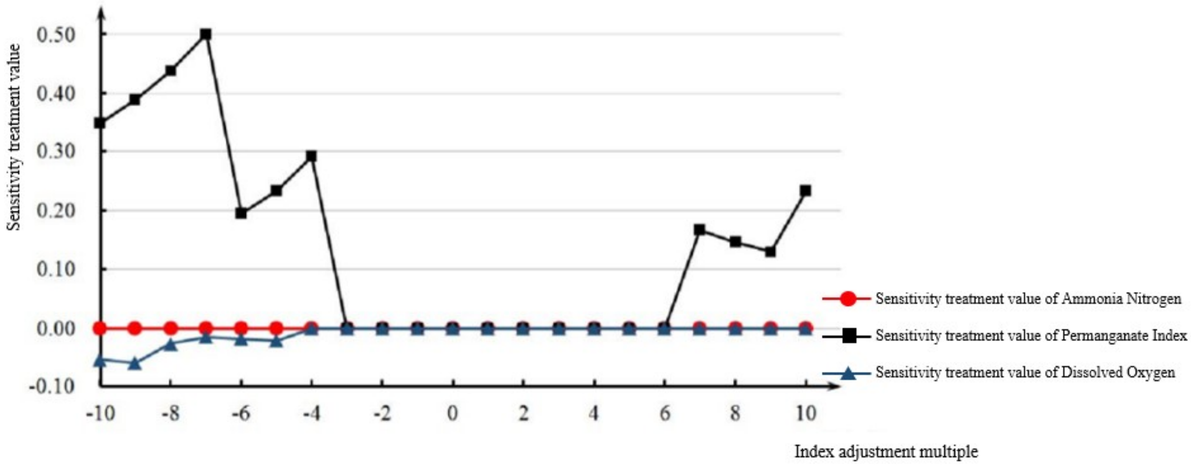

Figure 7-4 Broken line graph of water quality category sensitivity treatment value of Tongjiang section in 2018

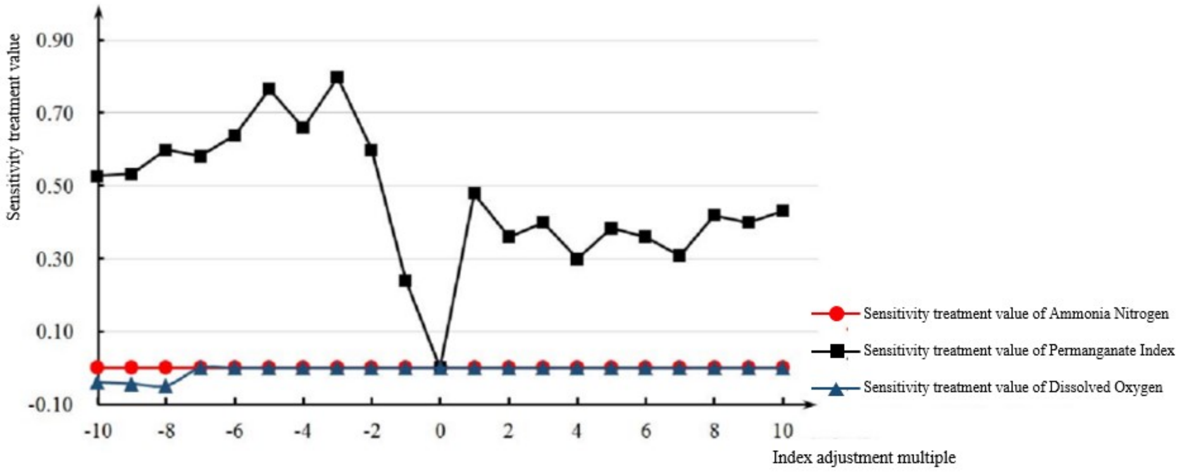

Figure 7-5 Broken line graph of water quality category sensitivity treatment value of Baicheng Baisha Beach section in 2018

It can be seen from Figure 7-5 that the water quality category of Baicheng white beach section also maintains long-term and continuous high sensitivity to permanganate index, and its representative meaning will not be repeated here; The ammonia nitrogen index is not shown in the range of - 10 ~ 10B index value adjustment; It shows low sensitivity to dissolved oxygen only in the range of - 10 ~ - 7b index adjustment, so there is no need to pay too much attention at present.

Based on the four broken line diagrams in Figure 7-2, Figure 7-3, Figure 7-4 and Figure 7-5 and the interpretation of the four diagrams above, it can be found that several sections need to focus on permanganate index indicators for a long time, and some sections need to invest corresponding resources and energy on dissolved oxygen or ammonia nitrogen indicators. From part to whole, the water environment management of most sections of Songhua River Basin should pay most attention to the emission of chemical oxygen demand, and actively take measures to reduce the emission of ammonia nitrogen pollutants from domestic and agricultural sources.

7.3 Sensitivity Analysis Conclusion

The research and analysis of contribution and sensitivity plays a very important guiding role in determining the key work of inland river water environmental management in the next period. Through the study on the contribution degree of some sections in Songhua River Basin, it is found that from 2015 to 2016, the influence of Jilin xilangkou section on water quality category is equal to permanganate index and ammonia nitrogen, and both are higher than dissolved oxygen index. The contribution degree of Yinma River Estuary section index to the change of water quality category is ammonia nitrogen, permanganate index and dissolved oxygen from large to small; From 2010 to 2016, the change of permanganate index value of Baicheng white beach section is the main driving factor for the change of water quality category of the section from 2010 to 2016. Through the calculation and analysis of the sensitivity of some sections in Songhua River Basin, it is found that the key indicators of the four sections are permanganate indicators, and the most important resource for water environment management is the emission of chemical oxygen demand.

By carrying out sensitivity analysis and combining with the research results of the change trend of water quality monitoring index value, the water quality monitoring index can be divided into risk index and safety index; Combined with the requirements of water environment treatment, which water environment treatment route is the best to achieve and water environment treatment objectives can be gained, and the direction for river water environment treatment is pointed out. Through the analysis of the contribution of the change of monitoring index value to the change of water quality category, the water quality monitoring indicators causing the change of water quality category in this period can be sorted, so as to determine the main driving factors causing the change of water quality category. In addition, the sustainability of the change of water quality category can be judged by combining the contribution of monitoring index with the current water quality situation.

7.4 Accessibility Analysis of Water Quality Objectives

7.4.1 Determination of Water Quality Objectives

On March 12, 2021, item 17 of the main indicators of economic and social development during the 14th Five Year Plan period in column 1 of the outline shows that the proportion (%) of surface water reaching or better than Class III water body in China will be 83.4% in 2020, and the outline requires that this proportion should reach 85% by 2025.

To determine the water quality target, we must consider the status of water function zoning and the water quality target of water function zone. In 1999, the Ministry of water resources began to organize the national water function zoning; In 2011, the State Council officially approved the water function zoning of national important rivers and lakes (2011-2030); in 2013, the water resources department of the Ministry of water resources and the General Institute of water resources and hydropower planning and design of the Ministry of Water Resources prepared the manual of water function zoning of national important rivers and lakes (hereinafter referred to as the manual). The nine sections studied in this subsection are listed in the manual The section water quality control objectives specified in have been described in Chapter II of this paper and will not be repeated here.

Based on the contents of the outline and the manual, it is set that the water quality target of Songhua River Basin in 2025 is that the proportion of class III water quality section reaches or exceeds 85%, and shall meet the water quality control target of water functional area required in the manual.

7.4.2 Water Quality Target Accessibility Calculation

Based on the trend study of water quality monitoring index value with time and the existing water quality monitoring data of corresponding sections, the accessibility analysis of water quality objectives in this paper predicts the dissolved oxygen index, permanganate index and ammonia nitrogen index values of each section in 2025. The index value prediction is carried out according to formula 7-4.

$$R = R_0 + b \times \Delta t \quad (7\text{-}4)$$

Where:

R -- predicted value of water quality monitoring index at the end of the period;

R_0 -- monitoring value of water quality monitoring index at the beginning of the period;

Δt - length of time period, in this paper, "year" is taken as the unit;

B - change rate of monitoring value of water quality index during the period. In this paper, the interannual change B of index value corresponding to each index is taken;

According to the research results on the change trend of water quality indicators of each section of Songhua River Basin from 2008 to 2018, after predicting the water quality indicators of some sections in the basin in 2025, take the prediction results as the evaluation data, make an "optimistic" judgment on the water quality category of each section, and then summarize the water quality status of some sections in Songhua River Basin in 2025 to get Table 7-4.

Table 7-4 Summary table of water quality prediction status of some monitoring sections in Songhua river basin in 2025

Seria Number	The Name of the Section	The annual water frequency reaches or is better than class III	Water quality target of water functional area of section	The mean value of the index was used to distinguish the water quality of the section
1	Jilin Stream Langkou	88.46%	III	III
2	Songhuajiang Village, Changchun	90.38%	III	III
3	Songyuan Pine Forest	75.00%	III	III
4	Zhaoyuan	23.08%	III	IV
5	Jiamusi, Tongxin Island	92.31%	IV	II
6	Tongjiang	86.54%	III	III
7	Baicheng White Sand Beach	32.69%	III	IV
8	Dunhua Xindian, Jilin	65.38%	III	III
9	Yinma Rive Estuary	88.46%	III	II

According to the contents listed in Table 7-4, According to the measures for environmental quality assessment of surface water (for Trial Implementation), after judging the water quality category of sections by the arithmetic mean value of monitoring indicators within the year, it can be seen that 7 of the 9 sections are better than or reach class III water, with a compliance rate of 77.78%, which does not meet the requirements of the outline Binding index requirements mentioned; According to the annual standard of water functional area with compliance rate not less than 80%, it can be found that 5 of the 9 sections meet the standard, and the compliance rate is 55.56%, which also fails to meet the corresponding objectives and requirements in the manual.

7.4.3 Analysis Conclusion of Water Quality Target Accessibility

According to the above analysis and calculation results in this section, it can be concluded that when the development trend of water quality in Songhua River Basin from 2008 to 2018 continues to develop to 2025, the water quality objectives in the outline and manual will not be achieved, and the water quality objectives are not reachable. In order to achieve the corresponding water quality objectives, positive changes should be made in the water environment management and protection of the basin.

7.5 Analysis on Key Points of Water Environment Protection

7.5.1 Permanganate Index

The Songhua River Basin should focus on organic pollutants and nitrogen-containing pollutants. The

Songhua River Basin should focus on permanganate index and ammonia nitrogen index. Among the four indexes studied in this paper, pH, dissolved oxygen, permanganate index and ammonia nitrogen, the water quality category has the highest sensitivity to permanganate index, indicating that the influencing factors of permanganate index index have the greatest impact on the change of water quality category. Through various water environment protection measures, Adjusting the influencing factors of permanganate index will have the most obvious effect on water environment protection. According to the second national census of pollution sources, the percentages of chemical oxygen demand emissions from agricultural sources, domestic sources and industrial sources in the total annual emissions in 2017 were 49.77%, 45.86% and 4.24% respectively.

7.5.2 Ammonia Nitrogen Index:

Among the four indicators, the fluctuation range of ammonia nitrogen index value is the largest, which shows that the influencing factors of ammonia nitrogen index are the most likely to cause sudden major environmental safety problems. It is necessary to invest enough resources and energy to pay attention to and intervene the influencing factors of ammonia nitrogen index. In China, ammonia nitrogen emissions mainly come from domestic sources and agricultural sources.

7.5.3 Dissolved Oxygen Index and pH Index:

The safety of dissolved oxygen index is high. The dissolved oxygen index of most sections is maintained at class I and II water quality standards, and the index of most sections is developing well, which does not need much attention; The fluctuation of pH index is small, the change trend is not obvious, and there is no need to pay too much attention.

7.5.4 Analysis of Main Pollution Sources

The discharge of pollutants from domestic sources mainly comes from the domestic sewage discharge of residents. The Songhua River Basin is vast and sparsely populated. Residents other than cities and towns mainly live in the form of villages and farms. Therefore, the domestic sources can be regarded as point source pollution, mainly in the form of random disposal of solid wastes, domestic sewage and solid-liquid feces of toilets from kitchen and daily cleaning activities.

Agricultural sources are mainly planting, livestock breeding and aquaculture, in the form of non-point source pollution. Some studies have shown that when the proportion of farmland in the watershed area exceeds a certain limit value, the N concentration in the watershed water body will rise sharply, which reflects the important impact of planting industry on the ammonia nitrogen concentration in the water body from one side. In Songhua River area, the planting industry is developed, making it the main source of ammonia nitrogen. The main discharge mode is that in the process of agricultural planting, chemical fertilizers and pesticides are overused, crops are not fully absorbed and utilized, and the underutilized chemical fertilizers and pesticides become nitrogen-containing organic pollutants. When heavy rainfall or farmland irrigation retreat, they enter rivers and water bodies in surface runoff. Studies have shown that the nitrogen source pollution caused by livestock breeding industry mainly enters the external environment in the form of livestock manure and feed, and the proportion of feed has been roughly equivalent to the chemical fertilizer emission of planting industry; The causes of nitrogen source pollution in aquaculture mainly include excessive feeding of aquaculture feed, incomplete discharge of tail water treatment in aquaculture pond, unreasonable sediment treatment in aquaculture area, etc.

7.5. 5 Suggestions

In general, according to different action principles, river water pollution control can be divided into four categories, including physics, chemistry, biology and management policy guidance; According to the different links of water pollution control measures, it can be divided into three categories: source control, discharge process control and end treatment. Based on the water environment situation of Songhua River Basin and the previous research experience, this paper puts forward some suggestions on water environment treatment of Songhua River basin with the guiding ideology of "reduction of pollution source, interception and treatment of emission process, end consumption and efficiency improvement, and recycling of by-product resources".

(1) Pollution source reduction:

The emission reduction of industrial source pollution is of great significance to improve the quality of water environment, which can be realized around industrial technology innovation, production process upgrading, industrial structure transformation and upgrading and industrial layout optimization. In the specific operation, strengthen the supervision and management of small and scattered sewage enterprises, eliminate direct and illegal discharge, and strictly implement the emission standards and relevant industrial elimination policies; Strengthen pollution control and environmental supervision over major pollutant discharge industries to achieve comprehensive and stable discharge up to standard; Raise the entry threshold for enterprises, strengthen the cleaner production review of enterprises, and vigorously develop the circular economy.

With dense population, nitrogen pollution of surface water caused by large-scale agricultural production and livestock breeding has become a world problem. In terms of agricultural source emission reduction, corresponding suggestions are put forward in three aspects:

In terms of fertilizer reduction in planting industry: we can control the use of fertilizer in agricultural planting by improving and popularizing environmental protection fertilization technology, vigorously promoting large-scale agricultural operation, legal supervision and price regulation, best management practice (BMPs) and other means and policies to reduce the emission of fertilizer at the source of planting industry;

For the reduction of pollution sources in livestock and poultry breeding industry, technologies such as feed nutrition regulation and emission reduction, greenhouse management and emission reduction, fertilizer utilization of fecal sewage and production of animal protein from breeding fecal sewage can be used preferentially;

Attention should also be paid to establishing a classified policy system, bringing small and medium-sized livestock and poultry farmers into the supervision system, and guiding local organic fertilizer projects to gradually become standardized and industrialized; Promote the full resource utilization of livestock and poultry breeding waste, gradually build a regional livestock and poultry breeding industry waste resource market trading system, and deepen the whole industrial chain of livestock and poultry breeding waste resource utilization.

In terms of pollution source reduction technology of aquaculture industry, three-dimensional aquaculture of water body, zoning aquaculture of water area and in-situ purification of water quality can be adopted; In the construction of laws and regulations, we should improve the legal responsibility system and refine the relevant norms of comprehensive prevention and control. At the same time, we should strengthen law enforcement supervision and enforce the law strictly.

Reduction control of living source: the available means are relatively limited. Reducing sewage discharge through water-saving means not only reduces the expenditure on sewage treatment capacity, but also saves precious water resources, which is a method of killing two birds with one stone.

(2) Interception treatment during discharge:

The main measures can be taken to popularize the rainwater and sewage diversion technology; Construction of constructed wetlands, ecological ditches, and vegetation buffer zones; The purpose of pollutant interception and reduction is realized by means of on-site interception and treatment of surface runoff;

(3) End absorption and efficiency improvement:

In view of the sparsely populated Songhua River Basin and good engineering conditions, the pre storage technology is an engineering pollution reduction measure worthy of consideration and application. The pre storage technology can effectively reduce the pollutant bearing pressure of surface water body and the concentration of N and P in water body; By adjusting the intensity of pollutants discharged into the end water body, the environmental absorption capacity can be brought into full play on the basis of not exceeding the environmental carrying capacity; Finally, we should regularly clean and dredge the sediment of key rivers in a planned way to solve the situation that the river treatment effect is not ideal due to the slow release of organic pollutants deposited in the river sediment for many years.

(4) Recycling of by-product resources:

In terms of domestic sources and aquaculture, the use of domestic sewage ecological treatment and resource utilization technology, sludge (pond and river sediment) resource utilization technology will be explored. In terms of livestock breeding, the combined application technology of livestock manure and aquaculture area sediment and chemical fertilizer is explored. Treatment of straw and other planting by-products is particularly important for Songhua River Basin, which is an important commercial grain base. Straw and packaging recycling and resource utilization technology can be adopted, for example, township governments, farmers and enterprises can be jointed to carry out the multi subject collaborative treatment mode of agricultural waste pollution, which not only solves the pollution problem of agricultural waste, but also realizes the resource utilization technology such as straw.

It should be noted that the Songhua River Basin is located in Northeast China with special natural conditions. It is very important to determine the technology and policy of "adjusting measures to local conditions". For example, "straw returning to the field" has a great effect on environmental protection and material circulation. However, the ground temperature in Songhua River Basin in winter is very low, and microorganisms in soil cannot effectively decompose the straw and returned to the field. The residual straw in the farmland will bring trouble to the sowing in the coming year.

7.5.6 Technical Method of Total Amount Control

7.5.6.1 Basic Types and Essence of Total Amount Control

According to different technical routes, total amount control can be divided into three modes: capacity total amount control, target total amount control and industry total amount control. Its essence is to establish the input response relationship between pollution sources and environmental quality between pollution sources and environmental objectives. In order to achieve environmental objectives, optimize the decision-making scheme under limited time, investment and technical conditions, and seek the best combination point between environmental quality requirements and technical and economic conditions through these two quantitative relationships.

7.5.6.2 Technical Route of Total Amount Control

The implementation of total amount control shall be based on the guiding principles of comprehensiveness, scientifiCity, regionality, decomposition and operability, connect pollution sources with environmental objectives, and distribute around the objectives of total amount control. Finally reflected in the pollutant discharge permit. The technical route of total amount control is shown in Figure 7-6.

The selection of total amount control technical route shall comprehensively consider the regional economic development level, the division of environmental functional areas, the current situation of environmental quality, pollution sources, natural environment characteristics and national and local environmental protection policies.

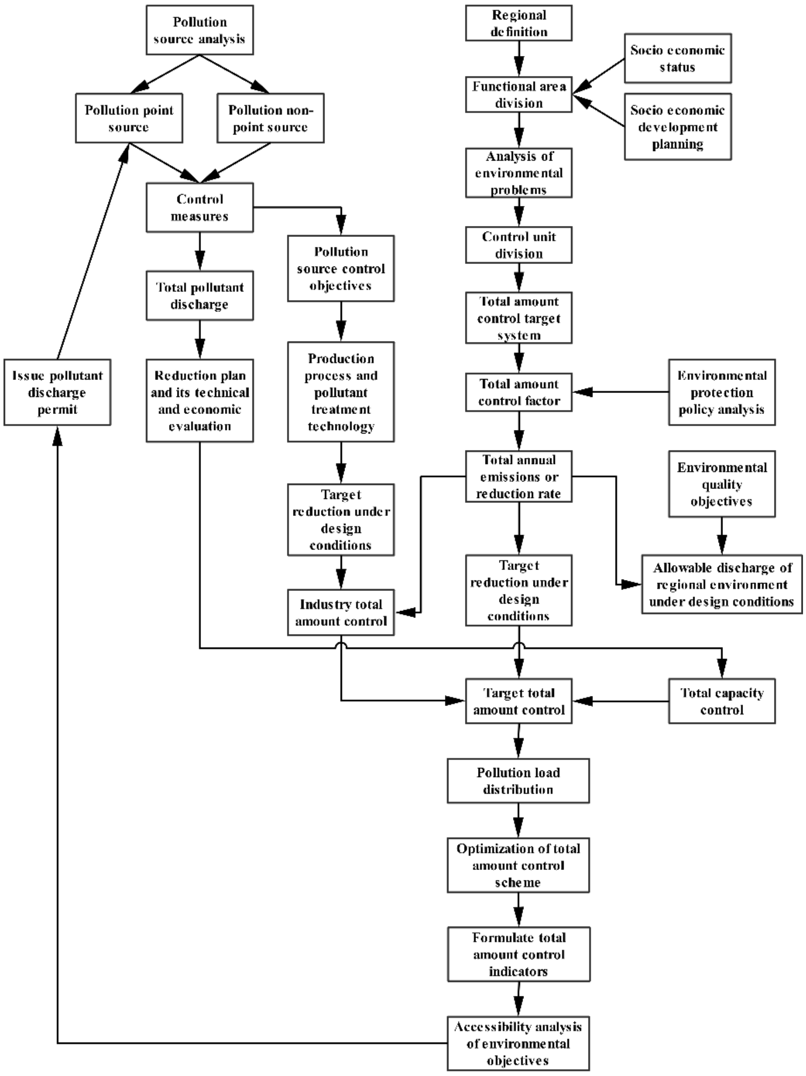

Fig. 7-6 The technique chart for total quantity control of pollutants emission

7.5.6.3 Technical Methods of Total Amount Control

(1) Methods for establishing total amount control objectives

Corresponding to different technical routes, the objectives include industry total amount control objectives, target total amount control objectives and capacity total amount control objectives.

Establishment of industry total amount control target

Firstly, analyze the environmental problems, industrial structure and pollution sources, and determine the main controlled pollutants, key controlled industries and main controlled pollution sources; Then the total amount control target is determined by comprehensively considering the economic and technological level.

Establishment of target total amount control target

This goal includes target value and index system.

① The target value is determined according to the following conditions: A. take the pollutant emission level in a certain period or the pollutant reduction determined based on this as the basic target; b. The target total amount determined to maintain the environmental quality of a certain period or a certain standard; c.

The target total amount constrained by economic investment; d. Cooperate with the target total amount determined by the government administration.

② The index system reflects the requirements of total amount control and is a reflection of constraints. The target total amount control index system of water pollutants includes: A. industrial water consumption, industrial water reuse rate and fresh water consumption; b. Total discharge of industrial wastewater and domestic sewage; c. Industrial wastewater treatment capacity, treatment rate, treatment standard rate, reuse amount and reuse rate; d. Industrial wastewater discharge with output value of 10000 yuan; e. Types of pollutants in wastewater and their respective production, discharge and removal.

Establishment of total capacity control objectives

The total capacity control target is based on the regional distributable environmental capacity, or the pollutant emission is controlled within the limit of regional environmental capacity, and the excess part is taken as the reduction target; Then the allocable environmental capacity or pollutant reduction is allocated to the pollution source as the capacity control target. Therefore, the goal of total capacity control is to calculate the distributable environmental capacity or pollutant reduction goal on the basis of determining the impact coefficient.

(2) Formulation method of total amount control scheme

The formulation of the total amount control plan should follow two principles: first, it does not consider whether the emission concentration meets the standard, does not require the average reduction of all pollution sources, and the maximum reduction of pollutants is preferred; Second, protect key functional areas and do not require each environmental functional area to implement the same environmental standard.

When formulating the total amount control scheme, appropriate sewage outlet, feasible pollution control measures, regional control or centralized treatment scheme shall be selected.

(3) Total amount control target allocation method

Selecting appropriate methods and formulating scientific, reasonable and feasible target distribution scheme of total amount control is the key to the implementation of total amount control. The distribution of total amount control objectives should fully reflect the principles of fairness and efficiency, and a series of distribution methods have been formed based on these two principles:

Distribution method based on the principle of Equity:

① Equal proportion distribution method;

② Weighted distribution method;

③ Paid distribution method of pollutant discharge index;

④ Equal pollution contribution distribution method;

⑤ Administrative coordination and distribution law.

The allocation method based on the efficiency principle: the allocation of total amount control objectives is required to minimize the cost of regional pollution control on the premise of achieving certain environmental objectives. The commonly used methods are finite programming, nonlinear programming, integer programming, dynamic programming, discrete programming, grey programming and fuzzy mathematical programming.

(4) Technical methods of emission trading

The basic content of Emission Trading: the government issues or sells emission permits to emission units; The pollutant discharge unit shall discharge pollutants according to the provisions of the pollutant discharge permit; Emission permits and the emission rights they represent can be traded according to certain norms without affecting the established environmental objectives. The advantage of emission trading is to make full use of the market regulation mechanism to minimize the cost of regional pollution control on the premise of realizing the environmental goal.

7.5.7 Total Amount Control of Water Pollutants in Songhua River Basin

7.5.7.1 Analysis of Main Environmental Problems in Songhua River Basin

Pollution source analysis

In 1995, the Songhua River Basin received a total of 41808.52 tons of wastewater from Jilin Province × 104t。 The pollution sources are mainly concentrated in Jilin, Changchun and Songyuan, accounting for 83% of the whole basin; The emission accounts for 80%, and the equivalent pollution load accounts for 90%; The main polluted waters are the Jilin section of Songhua River and the Changchun section of Yitong River; The main polluting industries are chemical industry, papermaking, chemical fiber, food processing, non-ferrous metal mining and beneficiation, coal chemical industry, etc; The main pollutants are chemical oxygen demand, volatile phenol and petroleum.

Selection of control factors

According to the national total amount control requirements and the pollutant characteristics of Songhua River Basin in Jilin Province, the following 9 pollutants are determined as the total amount control factors of Songhua River Basin; Chemical oxygen demand (COD_{Cr}), petroleum, cyanide, arsenic, mercury, lead, cadmium, hexavalent chromium and volatile phenol (volatile phenol is the characteristic pollutant of the river basin, and the other 8 are the national controlled pollutants). Among them, chemical oxygen demand and volatile phenol are the key control objects.

7.5.7.2 Division of Control Unit

According to the natural conditions, types and spatial distribution of water pollutants in the Songhua River Basin, and in combination with the division of functional areas and administrative divisions, the Songhua River Basin is divided into two control units:

Control unit in the middle and lower reaches of Songhua River: 207km from Longtanshan bridge to swill tank section. Most of the main pollution sources in Songhua River Basin are distributed here. The control unit is further divided into three sub control units; Jilin City section, Changchun City section and Songyuan City section.

Songhua River control unit: including the upstream of Songhua River and all tributaries flowing into Songhua Lake. The control unit can be divided into 4 sub control units in the upper reaches of Huifa River, LAFA River, Piao River and Songhua River.

The following takes Jilin sub control unit as an example to illustrate the determination and distribution of CODCr total amount control objectives.

7.5.7.3 Formulation of Total Amount Control Scheme for Control Units in the Middle and Lower Reaches of Songhua River

(1) Determination of influence coefficient

Taking the swill tank as the control section of the control unit in the middle and lower reaches of the main stream of Songhua River, all pollution sources in Jilin and Changchun are generalized into one point, and the pollutant attenuation from Hadawan and Nanguan bridge to the swill tank section is calculated respectively; At the same time, swill tank is also the control section of Songyuan City. One dimensional water quality model was used in the study. The water volume of each node and the input and output of pollutants are obtained by recursive balance according to the increase and decrease of the river section according to the principle of material balance and water balance; The self-purification coefficient of COD_{Cr} is obtained by water mass tracking experiment and indoor simulation experiment; The design conditions are also obtained after treatment according to the corresponding technology. After calculation, the influence coefficients of Jilin, Changchun and Songyuan on the section of swill tank are 0.479, 0.646 and 0.973 respectively.

(2) Calculation of environmental capacity:

At 90% guarantee rate, the water quality target of swill tank section is calculated as class III surface water (GB3837-88) environmental capacity of coder in standard time. The diluted environmental capacity of the river section of Jilin City is calculated with the sentry as the control section; the self purification environmental capacity is calculated with the functional sections of Longtan bridge, sentry, Songhuajiang village, livestock farm and swill tank as the control section; the transportation environmental capacity is calculated according to the water intake of industrial and agricultural production and domestic water in this river section Accounting. The environmental capacity of uncontrollable load is estimated according to the perennial monitoring data of Fengman dam, and then the distributable environmental capacity of the whole river section is calculated. The distributable environmental capacity of other river sections or river sections is also calculated according to their respective conditions. The calculation results are shown in Table 7-5.

Table 7-5 The calculated results of distributed environmental capacity in each zone under the guaranteed ratio of 90%

River section	Sewage City	Environmental Capacity（t/a）				Actual emissions
		Dilution capacity	Self purification capacity	Transfer capacity	Total	
Fengman-Songhuajiang Village	Jilin	41026	16826	10001	67853.5	92700
Songhuajiang Village-Livestock farm	Changchun	8752.7	9811.2	0	18563.9	97300
Livestock farm-Ganshuigang	Songyuan	1470	2765	0	4235	19300

(3) Total amount control scheme:

According to the distributable environmental capacity of the river section where Jilin, Changchun and Songyuan are located, combined with the total pollutant discharge of the three cities in 1995 and their influence coefficients on the swill tank section, through optimization decision-making and feasibility analysis, the following optimal scheme is put forward: while controlling the pollution source of the main stream of Songhua River, step up the treatment of Yitong River, and the COD_{Cr} reduction rate of Jilin and Changchun is 45%, 60% in Songyuan City.

7.5.7.4 Formulation of Total Amount Control Scheme for Sub Control Units in Jilin City

(1) The total amount control target is determined according to the total amount control scheme of the control unit in the middle and lower reaches of the main stream of Songhua River. The COD_{cr} of Jilin City is reduced by 45% on the current basis, that is, the reduction of COD_{Cr} is 41715 t/a and the emission is 50985 t / a.

(2) According to the investigation of pollution sources and existing pollution treatment facilities, after repeated consultation with pollutant discharge units and Environmental Protection Bureau, and combined with the investment benefit analysis of each scheme, the total amount control scheme uses the discrete programming method to determine the pollutant treatment cost of Jilin City as the objective function, and the constraint condition is that the total reduction is not lower than the total control target reduction, i.e. 41715 t / a.

Finally, the optimal scheme is determined: build an urban sewage treatment plant, which can reduce codcr26000t / A in domestic sewage, and accept the industrial wastewater treated by 9 enterprises such as Jilin Ferroalloy Plant, which can reduce COD_{Cr} by 3856 t/a. Expanding the pollution load capacity of Jihua sewage treatment plant and increasing the acceptance of industrial wastewater treated by 7 enterprises in the dye plant of Jihua company can reduce COD_{Cr} by 5680 t/a. Three enterprises such as Jilin Paper Co., Ltd. can reduce codcr10211.5% after transformation of production process and secondary biochemical treatment 2 t/a. Six enterprises such as Jilin thermal power plant can also increase COD_{Cr} reduction by 267.0 t/a by strengthening management without increasing investment and operation costs. A total investment of 164 million yuan is required for this scheme. When the average annual cost of pollution treatment facilities increases by 22.67 million yuan, the total COD_{Cr} emission can be reduced by 42543.9 t/a. The total amount control target of Jilin City can be achieved, and the water quality of Senkou and Songhuajiang village sections can meet the requirements of class IV and class III water bodies of surface water respectively.

7.5.7.5 Control Measures for Total Discharge of Water Pollutants in Songhua River Basin

The key to the smooth implementation of total amount control lies in three links: controlling new pollution sources, reducing existing pollution sources and comprehensive environmental improvement.

(1) Existing pollution source reduction measures

① According to the characteristics of the basin and industry, take treatment measures within a time limit for units that exceed the standard;

② Units included in the total amount control plan must adhere to the principles of "replacing the old with the new" and "increasing production without increasing pollution" when expanding or technological transformation;

③ Promote the best practical environmental control technology to ensure the high technical content of pollution prevention and control;

④ Promote cleaner production technology, accelerate economic development and the transformation of production mode from extensive to intensive.

(2) New pollution source control measures

① The new project meets the total amount control requirements of the basin and the national and local pollutant discharge standards;

② Clean production audit must be conducted for new projects, and their production technology and pollution control must reach the advanced level of the same industry in China; The imported projects are required to reach the international advanced level;

③ The environmental impact assessment shall be approved according to the regional environmental capacity and the approved indicators of total amount control.

(3) Comprehensive environmental improvement measures

Including construction of urban sewage treatment facilities, potential development of existing sewage treatment facilities and wastewater recycling:

① There are nearly 10 urban sewage treatment plants under construction or planning in the Songhua River Basin, including 3 in Changchun. One in Jilin City and one in Songyuan City, and the rest are distributed in other cities and towns in the basin;

② At present, the existing sewage treatment facilities do not require the inlet and outlet concentration of pollutants to meet the standard, but only pay attention to the maximum reduction of pollution load; At the same time, strengthen management and seek benefits from management;

③ After secondary treatment, the sewage can be used for farmland irrigation and urban greening, which not only further reduces the pollutant load of Songhua River system, but also alleviates the contradiction of water shortage.

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Chapter 8

CONCLUSION AND PROSPECT

CHAPTER EIGHT: CONCLUSION AND PROSPECT

8.1 Heavy Metal Pollutants

Based on the analysis method of heavy metals and occurrence forms in sediments, taking Songhua River Basin as the research object, this paper studies the content distribution characteristics, occurrence form characteristics and ecological risk assessment of heavy metals in surface sediments in dry season, wet season and flat season respectively; The spatial and temporal distribution characteristics of heavy metal content and pollution degree in sediments were studied. At the same time, the source of heavy metals in the study area was analyzed by Pearson correlation coefficient and principal component analysis. In addition, an experimental method is proposed to improve the removal efficiency of heavy metal pollutants. The main conclusions are as follows:

(1) In September 2017, the content of heavy metals in 27 surface sediments of Songhua River Basin in the normal water period ranged from 101.16 to 486.03 mg/kg, with an average content of 313.54 mg/kg. The total concentration of 11 kinds of heavy metals was V > Zn > Cr > Cu > Ni > Pb > Sn > As > Co > Cd > Sb. In June 2017, the content of heavy metals in 14 surface sediments of Songhua River Basin in the wet water period ranged from 141.2 to 291.33 mg/kg, with an average content of 222.61 mg/kg. The total concentrations of 11 heavy metals were V > Zn > Cu > Cr > Pb > Ni > Sn > Co > As > Cd > Sb. In March 2018, the content of heavy metals in 17 surface sediments of Songhua River Basin during the dry season ranged from 132.21 to 253.57 mg/kg, with an average content of 185.26 mg/kg. The total concentrations of 11 heavy metals were V > Cr > Pb > Zn > Cu > Sn > Ni > Co > As > Cd > Sb.

(2) In September 2017, the chemical forms of Cr, Ni, Cu, Cd, Sn and Sb in Songhua River sediments during the normal water period were mainly residual, Zn and Co were mainly weak acid extraction and reducible, the proportion of the four forms of as was relatively uniform, Pb was mainly reducible and residual, V was mainly oxidizable and residual, and the proportion of bioavailable forms was The order of specific size was Co (94.21%) > Zn (81.73%) > V (65.21%) > as (65.08%) > Pb (55.06%) > Ni (20.48%) > Cu (14.05%) > Cr (10.65%) > Cd (4.68%) > Sb (2.62%) > Sn (1.87%). During the wet season in June 2017, the chemical forms of Cr, Ni, Cu, Cd, Sn and Sb in Songhua River sediments are mainly residual, Zn and Co are mainly weak acid extraction and reducible, the proportion of the four forms of as is relatively uniform, Pb is mainly reducible and residual, and V is mainly oxidizable and residual. The proportion of bioavailable forms of heavy metals in sediments of Songhua River Basin in wet season is Co (88.35%) > Zn (75.63%) > As (70.14%) > V (68.09%) > Pb (55.80%) > Ni (36.39%) > Cu (11.95%) > Cr (11.35%) > Cd (6.38%) > Sb (4.70%) > Sn (2.80%). Cr, Ni, Cu, Cd, Sn and Sb in dry season in March 2017.

The chemical form is mainly residue state, Co is mainly weak acid extraction state and reducible state, and the four forms of Zn are different.

The proportion is relatively uniform. As and V are mainly in oxidizable state, and Pb is mainly in reducible state and residual state. pine

The proportion of bioavailable forms of heavy metals (F1 + F2 + F3) in sediments of Huajiang River Basin in dry season is V (94.62%)> Co (93.82%) >As (82.82%) > Zn (63.09%) > Pb (54.43%) > Ni (43.17%) > Cu (18.33%) > Cr (11.27%) > Sn (5.14%) > Sb (3.93%) > Cd (3.01%).

(3) During the normal water period in September 2017 and the wet water period in June 2017, three main components were extracted by principal component analysis. It is inferred that the first principal component mainly comes from natural sources, including Cr, Ni, Zn, Cu, V and Co; it is inferred that the second component mainly consists of traffic sources and industrial sources, including As, Pb, Sn and Sb; it is inferred that the third component is mainly agricultural sources, including Cd. During the dry season in March 2017, three main components were extracted through principal component analysis. It was inferred that the first principal component mainly came from natural sources, including Cr, Ni, Zn, Cu, Pb, V and Co; It is inferred that the second component is mainly composed of common sources, including As, Sn and Sb; It is inferred that the third component is mainly agricultural source, including Cd.

(4) In the normal water period in September 2017, according to the evaluation results of the local cumulative index method, the Igeo pollution index is as follows: Sb > As > Sn > Cd > Pb > V > Cr > Cu > Zn > Co > Ni. The heavy metal ire pollution index is as follows: Cd > As > Pb > Cu > Ni > Co > Cr > V > Zn. According to the risk assessment index method (RAC) according to the assessment results, the average risk assessment index of sediments is Co > Zn > Cd > As > Ni > Cu > Pb > V > Sn > Cr > Sb in order from large to small. In the wet season in June 2017, according to the assessment results of local accumulation index method, the Igeo pollution index is: Sb > Cd > As > Sn > Pb > Cu > V > Cr > Zn > Ni > Co. according to the potential ecological risk assessment results, the ire pollution index of heavy metals is in order Cd > As > Pb > Cu > Ni > Co > Cr > V > Zn. According to the risk assessment index method (RAC) according to the assessment results, the average risk assessment index of sediments is Co > Zn > Ni > As > Cd > Cu > Pb > V > Sn > Cr > Sb from large to small. During the dry season in March 2017, according to the assessment results of local accumulation index method, the Igeo pollution index is: Sb > Cd > Sn > As > Pb > Cu > Cr > V > Zn > Ni > Co. according to the potential ecological risk assessment results, the ire pollution index of heavy metals is Cd > As > Pb > Cu > Zn > Co >Cr>V>Ni. According to the evaluation results of risk assessment index method (RAC), the average risk assessment index of sediment is Co > Ni > Zn > As > Cd > V > Cu > Pb > Cr > Sn > Sb from large to small.

(5) Through comparison, it is found that the time variation law of the total amount of heavy metals in the sediments of the whole Songhua River Basin is normal water period > high water period > low water period. In the normal water period, the content of heavy metals in the upper reaches of the Songhua River is much higher than that in the dry and high water periods. The time variation law of heavy metals in the middle reaches of the Songhua River is high water period > normal water period > low water period, and the content of heavy metals in the lower reaches of the Songhua River The law of variation among is normal water period > high water period > low water period. Through the comparison of geoaccumulation index method, it is found that the order of heavy metal pollution degree in Songhua River Sediments in wet season in June and flat season in September is: upstream > midstream > downstream.

(6) To consider nano zero valent iron as a treatment method to Pb, Cr and Ni, knowledge of the impact of the operating conditions such as temperature, reaction time, pH and nano zero valent iron dosage is required. Experimental results indicated that adding the nano zero valent iron accelerates the Pb, Cr and Ni

removal. The best removal efficiency of Cr reached 95.5%. The highest Pb and Ni removal is 89.63%, 96.64% when temperature is 40°C, reaction time is 540 s, and nano zero valent iron is 10 g/L.

8.2 Ammonia Nitrogen Pollutants

(1) The ammonia nitrogen concentration in urban river section and non urban river section increases and decreases in varying degrees respectively. Cities distributed along the way have an important impact on the increase of ammonia nitrogen concentration; in non urban river section, nitrification plays an important role in the attenuation of ammonia nitrogen concentration, and temperature is the main environmental factor controlling its occurrence. According to the change of water quality, Songhua River can be divided into two parts, it is divided into fm-shjc, shjc-sl, zy-hlhx and jmss-tj. Cities distributed along the river are important control nodes, especially the contribution rate of ammonia nitrogen pollution of urban domestic sewage is large. It is suggested to further strengthen the sewage treatment in this river section and reduce the discharge of ammonia nitrogen.

(2) The Songhua River is characterized by a long ice cover period. During the ice cover period, the water flow and temperature reduced, the self-purification capacity of the water body is weakened, and the ammonia nitrogen concentration in the water body reaches the peak from the end of the ice cover period to the snowmelt period in spring. The ice cover period is mainly affected by point source pollution, and the snowmelt period is jointly affected by point source and non-point source pollution. Therefore, the point source pollution load and snowmelt period in the ice cover period are controlled non-point source pollution is an important means to ensure that ammonia nitrogen in Songhua River reaches the standard. In order to coordinate the contradiction between economic development and environmental protection, it is very necessary to formulate corresponding discharge standards according to the water period.

(3) Through seasonal Kendal inspection, it is found that on the whole, the water quality of Songhua River is gradually getting better, and the "recuperation" in Songhua River Basin has achieved initial results, so the "recuperation" in Songhua River Basin should be further strengthened.

(4) In this chapter, horse manure is selected as the main pollution source of ammonia nitrogen, The influence of alkali on the gasification of horse dung at 560°C, 25 MPa was investigated. The results show that LiOH addition increased H_2 fraction and the gas yield. The precipitated alkali in the reactor still showed high catalytic effect on the subsequent gasification of horse dung without further adding the alkali. A novel 4-lump kinetic model for horse dung in SCWG including feedstock, CH_4, CO, and CO_2 lumps is proposed.

8.3 Change Law of Water Quality

pH, dissolved oxygen, permanganate index and ammonia nitrogen of 11 sections of Songhua River Basin from 2008 to 2018 is used as the research object, this paper explores the water quality change law of some sections of Songhua River Basin. Through the calculation, analysis and sorting of this paper, the following research conclusions are obtained:

(1) In the research on the trend change law of water quality index values, this paper studies the change trend of 10 sections and 4 indexes in Songhua River Basin from 2008 to 2018 by using seasonal Kendall

mathematical test model and Sen slope estimation. Through the research, it is found that there is a double tailed trend of the change trend of 35 index value series in different sections from 2008 to 2018 The test significance level is highly significant or significant. Based on the 35 index value series, one-step calculation and analysis can find that whether from the perspective that the number of sections with good water quality conditions is greater than the number of sections with poor water quality conditions, or from the perspective that the positive change of similar index values is greater than the negative change, it proves that the overall water quality situation of Songhua River has shown a good development trend from 2008 to 2018.

(2) In the study on the periodic change law of water quality index values, it is found that the periodicity of four indexes in 11 sections of Songhua River Basin from 2008 to 2018 is as following: the periodic change curve of pH mostly presents "double peak type" or "three peak type" , the pH of most sections is higher in the two time periods before and after the freezing period, and the pH of river water is lower in the freezing period and summer; The periodic change curve of dissolved oxygen index value in most sections shows an obvious "W" type. The dissolved oxygen concentration in the river is winter, spring, autumn and summer from high to low; The periodic change curve of permanganate index shows a "single peak", and the average value of the index is summer, autumn, spring and winter from high to low; The periodic change curve of ammonia nitrogen index value presents "U" type or "W" type, and the average value of the index is arranged from large to small as winter, spring, autumn and summer.

(3) In terms of the fluctuation of water quality index values, this paper mainly studies the section values of Songhua River Basin from 2008 to 2018 ("water quality index monitoring values" and "multi-year average values of monitoring values in the same monitoring period" Probability distribution of. It is found that the index value fluctuates around its average value over the same period of many years, the index with the smallest fluctuation is pH, the index with the largest fluctuation is ammonia nitrogen, and the other two indexes, dissolved oxygen and permanganate index, are in the middle.

8.4 Water Quality Indicators

(1) In terms of the contribution of water quality indicators to the change of water quality categories, this paper found that from 2015 to 2016, permanganate index and ammonia nitrogen had the same influence on the water quality categories of Xilangkou section in Jilin Province, and were higher than dissolved oxygen index. The contribution of Yinma River Estuary section indicators to the change of water quality categories from large to small was ammonia nitrogen and permanganate index. dissolved oxygen; From 2010 to 2016, the change of permanganate index value of Baicheng white beach section is the main driving factor for the change of water quality category of the section from 2010 to 2016.

(2) In the research on the sensitivity of water quality categories to water quality indicators, this paper studies the water quality monitoring data of four sections in Changchun Songhuajiang village, Zhaoyuan, Tongjiang and Baicheng white beach in 2018. It is found that the key indicators of the four sections are permanganate index, and the most important resource for water environment management is the discharge of chemical oxygen demand.

(3) In terms of the accessibility analysis of water quality objectives in Songhua River Basin, this paper takes the outline of China's 14th five-year plan and the manual of water function zoning of national important rivers and lakes as an example The water quality target of Songhua River Basin in 2025 is determined. Through calculation and analysis, it is found that when the development trend of water quality in Songhua River Basin from 2008 to 2018 continues to develop to 2025, the set water quality objectives will not be achieved. In order to achieve the corresponding water quality objectives, positive changes should be made in the water environment management and protection of the basin.

8.5 Total Amount Control

The key to the smooth implementation of total amount control lies in three links: controlling new pollution sources, reducing existing pollution sources and comprehensive environmental improvement.

(1) Existing pollution source reduction measures

① According to the characteristics of the basin and industry, take treatment measures within a time limit for units that exceed the standard;

② Units included in the total amount control plan must adhere to the principles of "replacing the old with the new" and "increasing production without increasing pollution" when expanding or technological transformation;

③ Promote the best practical environmental control technology to ensure the high technical content of pollution prevention and control;

④ Promote cleaner production technology, accelerate economic development and the transformation of production mode from extensive to intensive.

(2) New pollution source control measures

① The new project meets the total amount control requirements of the basin and the national and local pollutant discharge standards;

② Clean production audit must be conducted for new projects, and their production technology and pollution control must reach the advanced level of the same industry in China; The imported projects are required to reach the international advanced level;

③ The environmental impact assessment shall be approved according to the regional environmental capacity and the approved indicators of total amount control.

(3) Comprehensive environmental improvement measures

Including construction of urban sewage treatment facilities, potential development of existing sewage treatment facilities and wastewater recycling:

① There are nearly 10 urban sewage treatment plants under construction or planning in the Songhua River Basin, including 3 in Changchun. One in Jilin City and one in Songyuan City, and the rest are distributed in other cities and towns in the basin;

② At present, the existing sewage treatment facilities do not require the inlet and outlet concentration of pollutants to meet the standard, but only pay attention to the maximum reduction of pollution load; At the same time, strengthen management and seek benefits from management;

③ After secondary treatment, the sewage can be used for farmland irrigation and urban greening, which not only further reduces the pollutant load of Songhua River system, but also alleviates the contradiction of water shortage.

8.6 Main Innovations

In this paper, two efficient removal methods of main pollutants are proposed, which are not only limited to the Songhua River Basin, but also applicable to the pollution control of other waters.

(1) Effect of temperature, reaction time, pH and nano zero valent iron dosage on Pb, Cr and Ni removal are studied. Experimental results indicated that adding the nano zero valent iron accelerates the Pb, Cr and Ni removal.

(2) A novel 4-lump kinetic model for horse dung in SCWG including feedstock, CH_4, CO, and CO_2 lumps is proposed. The kinetic parameters are estimated for each involved reaction. The identification results showed that the reaction order of feedstock lump is 1.5.

8.7 Suggestions and Future Work Direction

(1) The research on the content and pollution degree of heavy metals in sediment columnar samples in Songhua River Basin should be strengthened, and the ecological risk assessment of the occurrence forms of heavy metals in sediments should be further studied. Combined with the heavy metal pollution and industrial development in Songhua River Basin, the ecological risk source should be determined and corresponding treatment measures should be taken, which has important significance for the treatment and source control of heavy metals in the basin Practical significance.

(2) The in-depth removal test of persistent pollutants in Songhua River Basin and the enrichment test of benthos on persistent pollutants are carried out, so as to more intuitively analyze the biological toxicity of persistent pollutants in Songhua River Basin and its impact on the basin ecosystem.

(3) Based on the monitoring data of water and sediment in different water periods and years, the distribution law and distribution characteristics of persistent pollutants in the water and sediment of Songhua River basin can be studied. Combined with the data of pollution discharge from coastal pollution sources and the data of economic development, the relationship between water pollution, pollution source discharge and coastal economic development level in Songhua River basin can be analyzed quantitatively by mathematical model. In-depth and reasonable suggestions for watershed development planning are provided.