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# Water Quality Impacts from Agricultural Land-Use in the Karst Groundwater Basin of Qingmuguan, Chongqing, China

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**WATER QUALITY IMPACTS FROM AGRICULTURAL LAND-USE IN THE  
KARST GROUNDWATER BASIN OF QINGMUGUAN, CHONGQING,  
CHINA**

Date Recommended

11/17/08



Director of Thesis



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WATER QUALITY IMPACTS FROM AGRICULTURAL LAND-USE IN THE  
KARST GROUNDWATER BASIN OF QINGMUGUAN, CHONGQING, CHINA

A Thesis  
Presented to  
The Faculty of the Department of Geography and Geology  
Western Kentucky University  
Bowling Green, Kentucky

In Partial Fulfillment  
Of the Requirements for the Degree  
Master of Geosciences

By  
Ted W. Baker

December 2008

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# WATER QUALITY IMPACTS FROM AGRICULTURAL LAND-USE IN THE KARST GROUNDWATER BASIN OF QINGMUGUAN, CHONGQING, CHINA

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Karst regions are composed of soluble rock, often limestone, which leads to the formation of fissures, sinkholes and water flow conduits such as caves. Pollutants in karst waters tend to be quickly directed and concentrated into these subsurface conduits. As a result of this and other factors, water resources are especially sensitive to contamination and pollution in karst areas. Pollutant concentrations going into fluvial systems travelling through the subsurface in karst areas are often very similar to the concentrations arriving at outlets such as springs. Areas connected by karst conduit flows must be distinctly determined and special attention should be given to water quality impacts from land-use practices near conduit inputs. The climate which affects a certain karst area can also have different impacts on water resources considerations. For example, in the temperate climate of Kentucky precipitation is essentially even in distribution throughout the year. In contrast, southwest China is affected by a monsoon climate with high precipitation in the spring to summer and drier conditions in other seasons. In the wet season large storm pulses can effectively transport contaminants to water sources resulting in loads that can be unhealthy for frequent human consumption in drinking water. The dry seasons can be particularly severe in karst areas as water quickly drains to the subsurface, making water access a major hardship. The research for this study focused on the seasonal influences that the climate of southwest China poses for water quality, including differences in

pesticide concentrations between agricultural and residential areas hydrologically linked by karst conduits. In late 2007 the fluvial connections in a simple karst system near Chongqing were confirmed using dye tracing techniques. Once these connections were established and the flow of the subterranean stream was assessed, the transport of agricultural runoff in the system was studied. Data loggers were used to record continuous data of the water conditions, including nitrate concentrations. The pesticides in the agricultural runoff entering and exiting the subterranean stream were quantified using ELISA methods. The concentrations were found to be within safe limits for drinking water. The hypothesis that there is a close relationship between concentrations of the pesticides glyphosate, chlorothalonil, and triazines in the input and the output of the system was supported by the results. When considering the hydrology and water chemistry data of the site, along with the water samples tested for pesticides, non-parametric statistical testing showed the correlations between these factors to be significant with  $p < 0.01$ . The percent difference between the input and the output concentrations of glyphosate, chlorothalonil, and triazines were 31, 43, and 57% respectively. Taking into account the rapid and direct flows in this karst system, the concentrations of the pesticides found in the output were more similar to the input than would be expected in a surface stream. This suggests that there are fewer natural remediation effects reducing contamination in subsurface karst rivers of southwest China than in surface rivers. Therefore, these systems should be handled with extra attention to possible contamination of water resources. The research was conducted in the spring and summer of 2007-2008 and funded by the U.S. Agency for International Development.

## CHAPTER 1. INTRODUCTION

Fluvial connections between areas of different land use types can sometimes be difficult to discern. This is especially true when water sources for an area cannot easily be connected visually to the water flows from surrounding areas –such as in water from springs. Areas that share hydrologic connections also share the same water quality. Human land use can affect water quality in springs that are recharged from a great distance away or presumed disconnected from human impacted areas. Springs in areas characterized by karst geology can be outlets of not just stored groundwater but surface water that can drain from locations in adjacent watersheds in some instances (White 1988, Ford and Williams 1989, Lu 2007).

Pollutants in karst groundwater systems tend to move rapidly through conduits. In low-permeability zones with rapid flows through conduits, the pollutant concentrations going into subsurface fluvial systems are very similar to the pollutant concentrations coming out (Vesper et al. 2001, Groves et al. 2002). In agricultural regions land-use can have a number of effects on water quality, including pesticide runoff contaminating water resources. The southwest (SW) region of China is a major agricultural area in the country. The area also contains one the highest concentrations of karst geology in the country (Figure 1) with distinctive karst towers and large caves. The combination of these factors requires special concern when dealing with water resources (Groves 2007).

China is the most populous country in the world, although it is the 4th largest geographically and only 10% of the country is arable land (Turner 2006). Due to a need to utilize the land intensively to feed its people, China is also one of the largest

manufacturers and users of pesticides in the world (Yang 2007). Land use for agriculture in China has increased significantly over the past 50 years (Hajahhasi et al. 1997, Zheng et al. 2005, Jiang et al. 2007). China produces many of its own pesticides and, although recent events have spurred steps toward further regulation, they have comparatively lax regulations and monitoring of pesticide use. As a result pesticides are often applied in excess and not handled properly (Reuters 2007, Yang 2007). After decades of high pesticide application the environment has been degraded and major economic losses have resulted. “Many of the pesticides used are highly toxic, resulting in tens of thousands of users being injured or dying every year. Consequently, it is essential to control pesticide use and at the same time develop China's agricultural economy” (Xu et al. 2003).

This study addresses the effects of agricultural land-use on the water quality in karst fluvial systems of SW China. An initial question addressed by the study was whether the pesticide levels exiting a groundwater basin posed any human health or ecological concerns and under what different hydrologic conditions such levels could be a concern. Available published information and the opinions of local scientists suggest that the system chosen for this study serves as a good representation of the nature of subsurface fluvial karst systems in this area of SW China. My hypotheses are that the input and output of the system will be closely correlated with respect to changes in pesticide levels, discharge, and other water parameters and that change in these factors will be correlated over time within each location, as well as between each location. The hypothesis that the levels of contaminants found in the inputs verses the outputs would not be significantly different is based on previous studies that have been conducted in other locations (Vaute et al. 1997, Lang et al. 2006, Liu et al. 2007, Guo F et al. 2007).

## CHAPTER 2. BACKGROUND

### 2.1. Karst Water Issues

Karst aquifers “contain dissolution-generated conduits that permit the rapid transport of ground water, often in turbulent flow. The conduit system receives localized inputs from sinking surface streams and as storm runoff through sinkholes. The conduit system interconnects with the ground water stored in fractures and in the granular permeability of bedrock” (White 2002). In order to understand the transport of dissolved compounds in karst groundwater the various aspects of the hydrology of these systems must be studied (Quinlan and Ewers 1985).

A detailed understanding of the various fluvial connections in karst groundwater basins can be difficult to obtain. As mentioned, subsurface conduits can flow under ridges normally used to delineate watershed boundaries. Such a case can require an adjustment in the definition of the effective watershed boundaries that have been defined following on the standard methods (Croskrey and Groves 2008, Hao et al. 2006). In a 2002 review of the current state of karst research claimed that the modeling of groundwater flow in karst aquifers had not progressed very much over the previous 20 years. In recent years water budgets, tracer studies, hydrograph analysis and chemograph analysis have been used in further characterizing karst aquifers (White 2002). Meanwhile, there is still a need to direct attention toward quantifying processes and mechanisms of contaminant transport in karst aquifers (White 2002, Barfield et al. 2004).

Water resources are especially sensitive to contamination and pollution in karst regions (Taraba et al. 1997, Vaute et al. 1997, Vega et al. 1998, Vesper et al. 2001, Hao et al. 2006, Zhang et al. 2006, Groves 2007, Kambesis 2007, Lu 2007). Normally in non-karst areas precipitation and overland flows that pick up contaminants can be filtered by soils before entering groundwater storage. Contaminants in environmental waters often come from human uses such as irrigation and industry and can consist of fertilizers, pesticides, harmful bacteria, and industrial wastes. Interaction with soils as water slowly percolates into groundwater aquifers allows for microbes to use or buffer these water contaminants through their reactive and metabolic processes (Vesper et al. 2001, Van Eerd et al. 2003, Aquilina et al. 2006). The slow filtering of surface water into groundwater, dilution into the vast reserves of aquifers, and long residence times therein also provides time for harmful bacteria to perish from lack of nutrients and generally dampen the possible toxicity of contaminants (Vesper et al. 2001, Zhang et al. 2006).

Properties of soil chemistry and microbiology are important for maintaining soil quality and consequently water quality. There may be less interaction of water with soils in karst regions as water flows quickly through fissures in the bedrock and are then often directed into concentrated subsurface conduit flows in the rock with relatively low effects from ameliorating reactions (Vesper et al. 2001, Barfield et al. 2004, Aquilina et al. 2006). This can lead to substantial water pollution. This is even more troubling considering that these flows often resurface in springs which are drinking water sources (White 1988, Ford and Williams 1989, Zhang et al. 2006).

Pollutants in karst waters tend to move rapidly through conduits. When karst bedrock has low-permeability and there are rapid flows through conduits, the pollutant

concentrations going into subsurface flows are very similar to the pollutant concentrations coming out at locations such as springs (Vesper et al. 2001, Groves et al. 2002). If there is little or no interaction with sediment along the conduit length and the flow is slow, pollutants tend to become more concentrated in the water. In contrast to flowing surface water, in flowing subsurface water in karst systems there is little to no effect on contaminant loads from plant interaction and uptake, photolytic effects, and processes requiring more oxygen availability (Van Eerd et al. 2003). An additional concern can arise in systems with small conduits where a restriction of the flow can occur more easily during high water input periods. This can lead to backflooding and a return of contaminants in the reverse flow direction, possibly to the source (Vaute et al. 1997).

## 2.2. China Water Quality Issues

Water acquisition and quality in China are major hindrances to sustainable development throughout the country (World Bank 2003). Almost 700 million people in China do not have access to safe water. They often consume water that exceeds what is considered the maximum permissible levels for fecal coliform bacteria, an indicator of microbes that spread a variety of illnesses (Turner 2006). Each year one-third of industrial wastewater and two-thirds of household sewage is returned to water resources untreated. More than 75 percent of the rivers flowing through Chinese cities are unsuitable for drinking or fishing. Almost half of China's surface rivers are so polluted that they are not even suitable for agriculture or industry (Turner 2006). Water scarcity concerns have also led to the use of industrial wastewater to irrigate farmland. In urban areas 70% of drinking water comes from groundwater sources, 50-90% of which is

contaminated by agricultural runoff, industrial and municipal wastewater, and in some municipalities even toxic mine tailings (Hamburger 2005, Turner 2006, Turner and Osaka 2006, Guo and Ma 2007, Ministry of Water 2007). Efforts to improve the environmental quality in China are not just significant for improving the quality of life in China itself, but for other countries as well. This can be due to the environmental influences on numerous interconnected ecological systems, or even environmental impacts on the quality of Chinese products intended for international trade (Liu and Diamond 2005, Bradsher and Barboza 2006).

The severity of China's water problems and particular issues of concern vary depending on the local climate and economy, as well as the character of each geographic region. Karst areas of China have unique problems in dealing with water issues. Approximately one-third of China's terrain is made up of karst regions containing some of the most well developed karst landforms observed on earth. The southern karst region covers approximately 500,000 km<sup>2</sup> over eight provinces (Figure 10).

Of the 80 million Chinese who live in the SW China karst region, about 8 million live below the area's poverty level (Groves 2007). Due to prevailing seasonal winds from the Indian Ocean, a monsoonal climate affects most of this area with most annual precipitation falling May-August, the typical summer monsoon season. Very dry conditions are common throughout the remainder of the year (WRI 2007). The dry season is especially severe in karst regions as surface water is quickly directed into subsurface flows, making it hard to access for populations with very limited means. Therefore, poor rural residents can spend a large portion of their time collecting water in the dry months, traveling long distances over difficult terrain (Groves 2007).



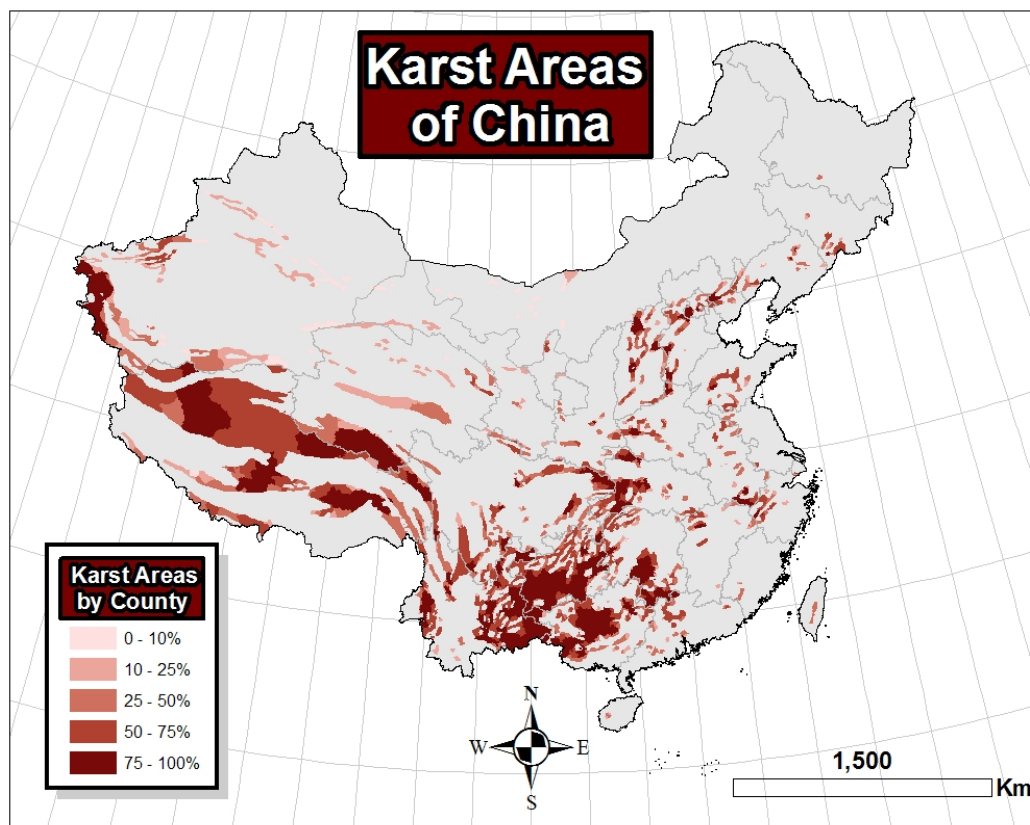


Figure 1. This map depicts the areas of China with karst geology. The darker areas indicate higher percentage of karst area in different counties. The map was created from data of county areas from the USGS and a map created through digitization by Mark Graham at Western Kentucky University.

The monsoon climate of SW China provides important additional considerations of the controls of contaminant transport in affected areas. High pulses of rainfall and runoff can lead to a corresponding pulse in some dissolved ions. Sulfate and nitrate concentrations have increased significantly in the past two decades in SW China and they usually peak during the rainy season (Chena et al. 2005). Anthropogenic inputs have major effects on water chemistry. Nitrate and chloride are two ions related to these inputs which are main contributors to groundwater pollution in SW China (Guo F et al. 2007).

In agricultural areas the main pollutants are fertilizers and pesticides, as well as fecal coliform and more harmful bacteria in areas of high animal use and poor sewage treatment (Nadav et al. 1987). In China's southern karst region, nitrates can often readily contaminate ground and surface water. Sewage effluent is the primary source of nitrates in urban areas, while chemical fertilizers and domestic animal wastes are stronger influences on nitrate levels in the water resources of rural areas (Jeong 2001, Lu 2007). Anthropogenic sources of nitrates elevate the overall levels of nitrates in the natural environment (Liu et al. 2006). The natural background level of nitrates in most water resources ranges from 1.8 to 2.0 ppm in non-agricultural areas (USEPA 2008). High nitrate levels in water resources can also lead to eutrophic and anaerobic conditions. Such conditions lead to the loss of wildlife resources such as fish, as well as providing great difficulties for water purification. Negative human health effects have been tied to frequent consumption of water containing nitrates concentrations in excess of maximum contaminant levels, usually 10 ppm (Li et al. 2005, Lang et al. 2006). Because nitrates are very soluble and easily dissociate from soil adsorption, they have a high potential to move into groundwater. Since they do not evaporate, nitrates can remain in water until consumed by plants or other organisms; which happens much less in subsurface rivers than surface rivers (Van Eerd et al. 2003). When comparing nitrate in groundwater and surface water, a higher content of nitrate is found in groundwater during the summer and winter seasons (Liu et al. 2006). This suggests that denitrification is not a significant factor in karst groundwater systems. Therefore, groundwater systems in karst areas do not easily recover when contaminated with nitrates (Almasri and Kaluarachchi 2007).

In addition to contributions from fertilizer use in China, high pesticide levels found in water that humans and other organisms are exposed to can also be a problem. High agricultural land-use with the related pesticide use in China can lead to pesticide contamination in water resources (Figure 2). This contamination can be difficult to ameliorate and can lead to significant human health and environmental concerns. These include severe impacts to ecosystems and persistence in soils, as with DDT and other organochlorines used in the past, or carcinogenic properties and dangers of acute and chronic toxicity like some organophosphates used in the present (Reuters 2007, Wang et al. 2007, Yang 2007).



Figure 2. In the Yankou valley of the Qingmuguan groundwater basin, small scale pesticide application methods are primarily used as seen here. Rice, and the corn and tomatoes growing adjacent to it, are the main crops in the area.

### 2.3. Properties of Study Pesticides

As case study of the possible impacts from pesticide transport in water resources of karst areas in SW China, the concentrations of four pesticides found in water resources were chosen for study at a field site in the region. Details of this site are described in Chapter 3. These pesticides were: glyphosate, chlorothalonil, atrazine, and chlorpyrifos. An overview of these pesticides is shown in Table 1 and additional information on each pesticide is found in the Appendix. Glyphosate is very widely used worldwide and in the area addressed in this study but is not considered a great concern for groundwater contamination or human health. Chlorothalonil is considered a possible concern for groundwater contamination and human health effects and while it is used significantly in areas of the U.S., is not widely used worldwide, while the extent of use in the study area is unknown. The residents claimed they use little to no pesticides on corn crops in recent seasons, yet atrazine is persistent in water resources and preliminary testing described in Chapter 5 indicated its presence so its levels were analyzed. Chlorpyrifos is not as great a concern for groundwater contamination in alkaline water as with more acidic to neutral water. It has possible health effects described in Tables 1 and 6 and the Appendix. Tests for it were only done in July due to limited test supplies (EXTOXNET 1996, PAN 2008).

Table 1. Details of the pesticides analyzed in water samples taken during the study. Additional details can be found in the Appendix (EXTOXNET 1996, PAN 2008).

<p><b><i>Chlorothalonil</i></b> – Fungicide (organochlorine)</p> <ul style="list-style-type: none"> <li>• Low solubility=0.6 mg/L at 25°C</li> <li>• High adsorbance coefficient=1380</li> <li>• In very basic water (pH 9.0) 65% degrades within 10 weeks</li> <li>• Soil half-life is 1-3 months</li> <li>• Degrades faster with increased soil moisture and/or higher temperature</li> <li>• High binding and low mobility in silty soil</li> <li>• Low binding, moderate mobility in sandy soil</li> <li>• High acute toxicity and highly toxic to fish</li> <li>• Possible carcinogen</li> <li>• Potential groundwater contaminant</li> <li>• Health Advisory Level (HAL)=1.5 ppb</li> </ul>	<p><b><i>Glyphosate</i></b> – Herbicide</p> <ul style="list-style-type: none"> <li>• Very common nonselective broad-spectrum product (Roundup)</li> <li>• High solubility=12,000 mg/L at 25°C</li> <li>• Very high adsorbance, even with low organic matter and clays=24,000 (estimated)</li> <li>• Moderately persistent in soils, half-life ~ 47 days, subject to microbial breakdown</li> <li>• Low potential for runoff (except colloidal)</li> <li>• Low to slight acute toxicity</li> <li>• Debated as a possible endocrine disruptor</li> <li>• MCL=700 ppb</li> </ul>
<p><b><i>Atrazine</i></b> – Herbicide (triazine), broadleaf/grasses</p> <ul style="list-style-type: none"> <li>• Most used U.S. pesticide, favored for corn</li> <li>• Claimed not currently used in QMG</li> <li>• Low to moderate solubility=28 mg/L at 20°C</li> <li>• Low to moderate adsorbance coefficient =100</li> <li>• Half life=60 to &gt;100 days</li> <li>• High hydrolysis breakdown</li> <li>• High breakdown in acidic and basic conditions low breakdown in neutral</li> <li>• Prominent groundwater contaminant</li> <li>• Slight acute toxicity</li> <li>• Debated as a carcinogen</li> <li>• Suspected endocrine disruptor</li> <li>• Maximum Contaminant Level (MCL)=3 ppb</li> </ul>	<p><b><i>Chlorpyrifos</i></b> – Insecticide (organophosphate)</p> <ul style="list-style-type: none"> <li>• Low solubility=2 mg/L at 25°C</li> <li>• High adsorbance = coefficient 6070</li> <li>• Moderate soil persistence=2 weeks -1 year or more, depending on the soil type, climate, etc.</li> <li>• High volatilization</li> <li>• High hydrolysis, especially in alkaline waters</li> <li>• Low persistence in high pH conditions</li> <li>• Moderate acute toxicity</li> <li>• Suspected endocrine disruptor</li> <li>• Significant Neurotoxin (Cholinesterase inhibitor)</li> <li>• HAL=21 ppb</li> </ul>

## CHAPTER 3. STUDY AREA

### 3.1. Overview

The United States Agency for International Development (USAID) funded a grant to develop cooperative efforts between the U.S. and China. A primary component of this grant is to address issues of water access and quality in rural SW China. As part of this effort, the water quality in a watershed of interest in this area was examined, specifically focusing on pesticide levels in water sources. The particular groundwater basin of interest is Qingmuguan (QMG), as it supplies water for the city of Qingmuguan at the southern end of the basin. The area is located 25 km northwest of the major city of Chongqing. The watershed is approximately 13.4 km<sup>2</sup>, 11.2 x 1.1 km (Figures 3 and 4). As mentioned, the study involves comparing the pesticide levels exiting QMG from the Qingmuguan subterranean river system (QSRS) (Figures 3, 4, and 5) at the Jiangjia spring (JJS) in the south (Figures 7, 15, and 16) to the levels entering the QSRS in the north at the Yankou sinking stream (YK) (Figure 32).

The northern section of QMG contains the largest agricultural valley in the basin. Here, as in other areas of the basin, rice is the primary crop, with corn and other crops grown on the margins of the valley floor (Figure 6). Other areas of agriculture are scattered throughout the basin, including significant fields of tomatoes. A variety of other small crops are grown for personal use within the basin. Still, where water resources are concerned, it is the stream draining the rice fields and this northern agricultural area that is of primary interest for this study (Nakano et al. 2004a).

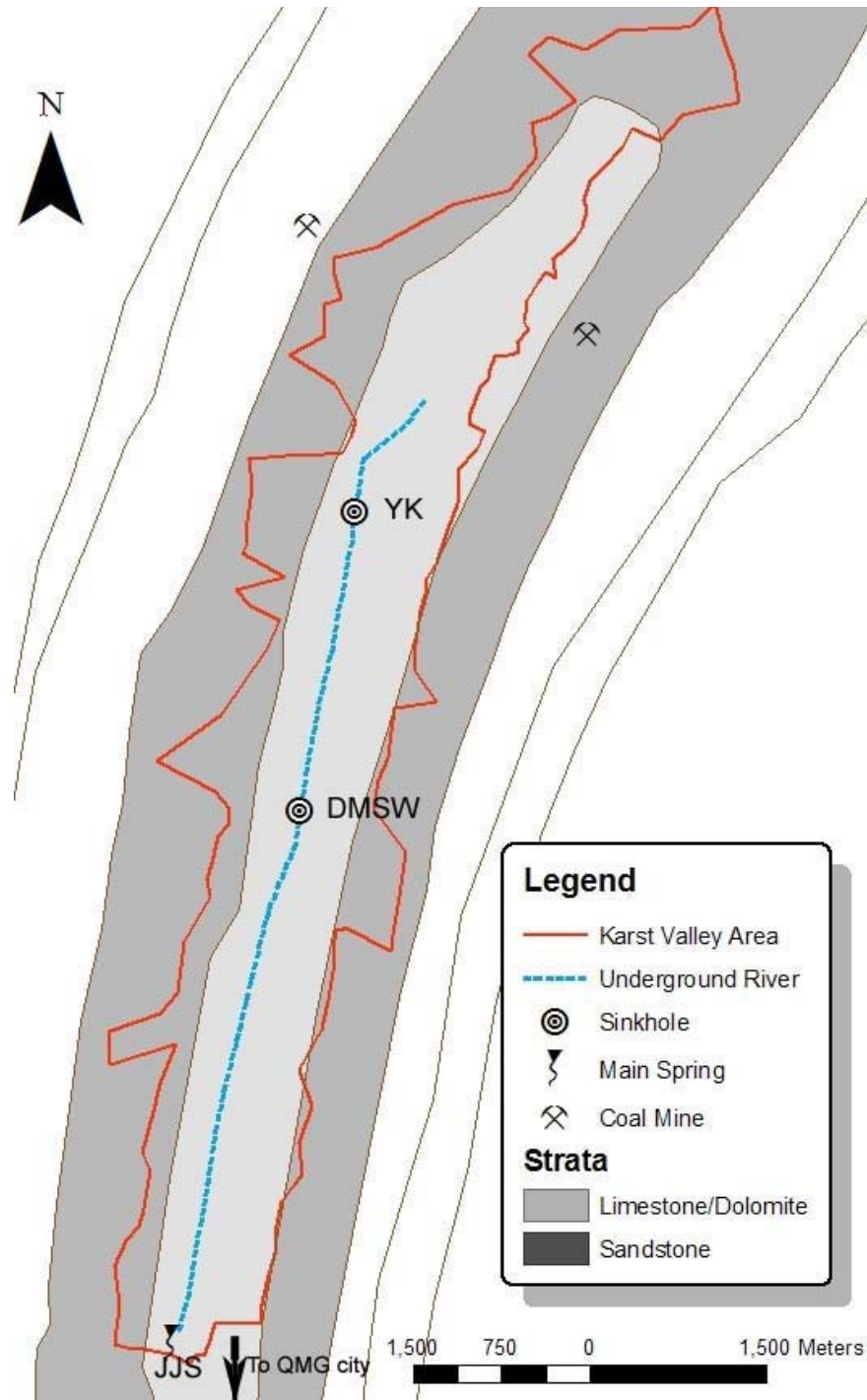


Figure 3. The Qingmuguan (QMG) groundwater basin. The Yankou sinkhole (YK) drains an agricultural valley and the Damushuiwo sinkhole (DMSW) drains an ephemeral lake to Jiangjia spring (JJS). YK and JJS were the main sample sites. The basin lies in a mountainous area formed by an anticline with valleys at the center of the basin consisting of limestone, while the ridges on the margins are sandstone separated by a coal layer that has been mined within the last 20 years.



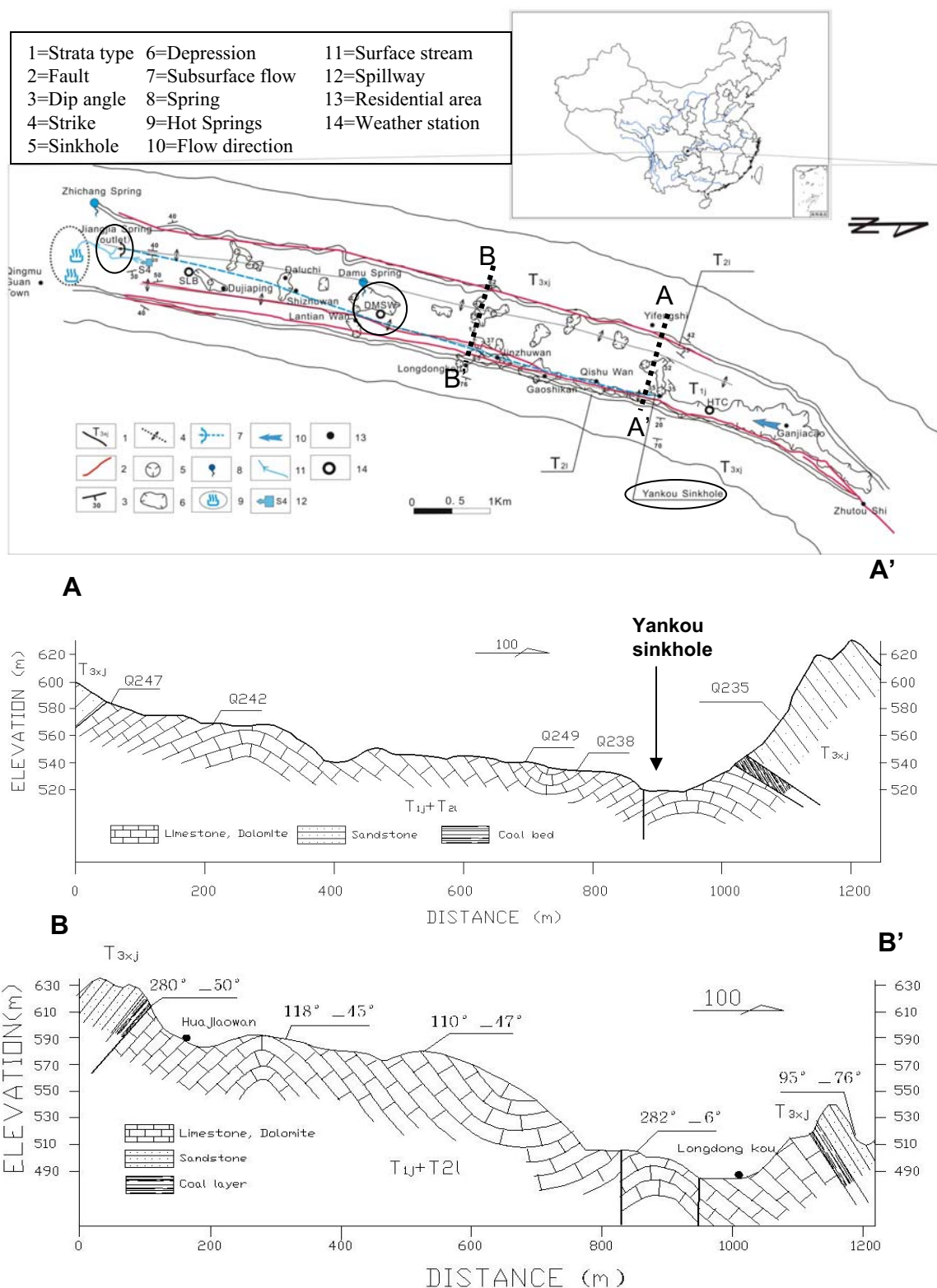


Figure 4. A detailed map of the Qingmuguan groundwater basin with prominent features is shown here with two cross-sections included, the data for which was collected by Chinese and U.S. scientists in 2007 (Adapted from Yang 2008).



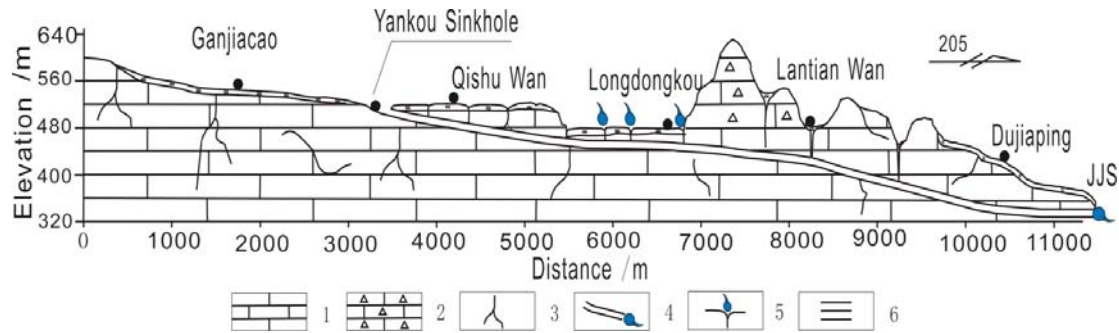


Figure 5. A simplified model of the vertical profile of QSRs. The profile was determined through a combination of travel times for water and cross-sections accounting for bedding planes and faults (Yang 2008, used by permission).

The valley depicted in Figures 3 and 4 is in the middle of a series of anticlines and synclines across the region. It lies in an anticline so it is at a higher elevation than the surrounding area. But, the anticline has been eroded into the formation of a few valleys and hills in between two major ridges. The lower center part of the basin is where the limestone is found, with sandstone layers lying in the ridges surrounding it. The limestone and sandstone are separated by a layer of coal (Figure 4). There is a noticeable vegetation difference between limestone and sandstone dominated areas in China (Li and Walker 1986). In QMG bamboo with thick shrubs and undergrowth are found on the lower part of the hillslopes, but stands of pine with ferns and thinner undergrowth are observed when crossing to the sandstone. Some of the slopes in QMG are cultivated and nearly all the flat areas. The land is used for a few other purposes including: ponds for fish farming, small areas for livestock and general residential use throughout the basin. Additionally, the coal seams in the area were mined significantly and limestone quarries are found in the basin, which leave steep sandstone slopes exposed to erosion into the valleys (Hajahhasi et al. 1997, Zheng et al. 2005, Li 2007).



Figure 6. Crops in the north end of the Yankou valley. This displays the method used in the valley of planting rice with corn intermixed and on the slopes above the valley.

Siliclastics from erosion runoff coming from these slopes and entering sinkholes can be an indicator of surface sediment transport in the QSRS (Figures 7 and 8). During two storm events in April 2008 the flux of soil erosion was calculated at approximately 9.7 tons, not including the sediment less than 0.45 micrometers in diameter and the bed-load material (Yang 2008). As mentioned, bacteria, pesticides and other potential pollutants are adsorbed on sediment, which contributes to water quality problems (Malmon et al. 2002, Hilscherova et al. 2007).

The approach used for this study in China to further understand the transport and persistence of pesticides, especially atrazine, in karst fluvial systems draws from previous work done in Kentucky and Iowa by researchers at Western Kentucky University (WKU) (Anthony 1998, Glennon 2001, Anderson 2002, Seadler 2004, Sharp 2006, Kambesis 2007, Croskrey and Groves 2008).

The systems dealt with in these studies have similar concerns to those of SW China. Although the basic concerns dealing with water quality in SW Kentucky and SW China karst areas are the same, the conditions are quite different in a number of aspects. These differences include the soils and geology, as well as the vast climate differences. The limestone strata in QMG are from the Triassic period of the Mesozoic Era that extends from about 250 to 200 million years ago. SW Kentucky consists mainly of strata dating from the Mississippian epoch extending from about 360 to 325 million years ago and is part of the Carboniferous period of the Paleozoic Era. The sandstone in Kentucky is also from the younger Pennsylvanian epoch of the Carboniferous period, while the sandstone in QMG is from the Jurassic period (Liu et al. 2004). Yet, even with different geologic histories the processes involved in the contents of the karst waters should not be significantly different. For this study the main differences of interest between SW Kentucky and SW China are the contrasts of climate, topography, hydrology, and the crops grown, along with the treatments used.

### 3.2. Water Resources

In an effort to understand controlling water and soil condition in QMG, Southwest University of China researchers began detailed investigations into the groundwater hydrochemistry and microbe activity in the area in early 2007. Water and soil samples were taken every two weeks at a number of sites in QMG from March to July 2007 and tested for a number of conditions (Figure 9).



Figure 7. Here turbulent discharge is being measured at the JJS gaging station with high turbidity seen in the discharge. The level observed was in July 2007 during a 100-year flood.

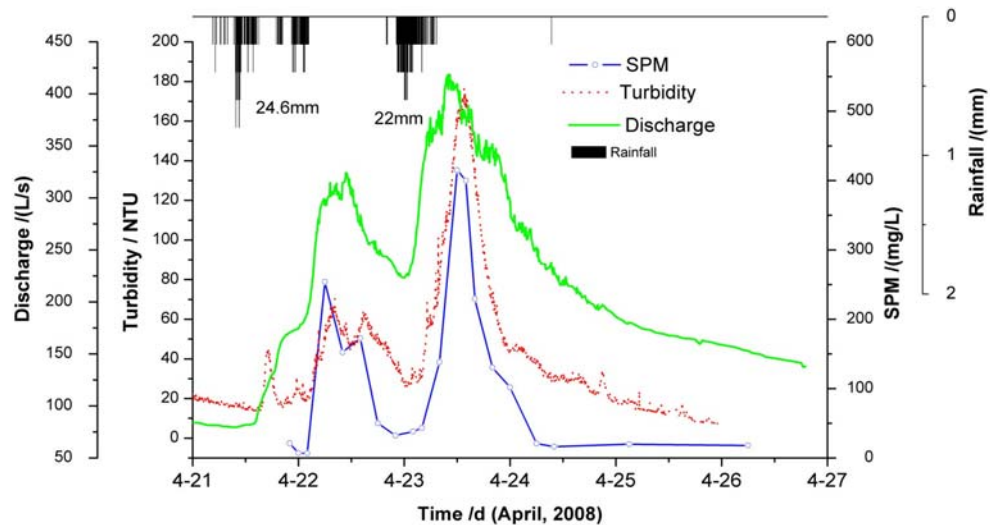


Figure 8. Data from two storm events at JJS in QMG shows the relationship between discharge, turbidity, and suspended particulate matter (SPM) during storm events in the QMG subterranean river system (QSRs). The strong response and high levels can be associated with water contamination concerns (Used with permission from Yang 2008).

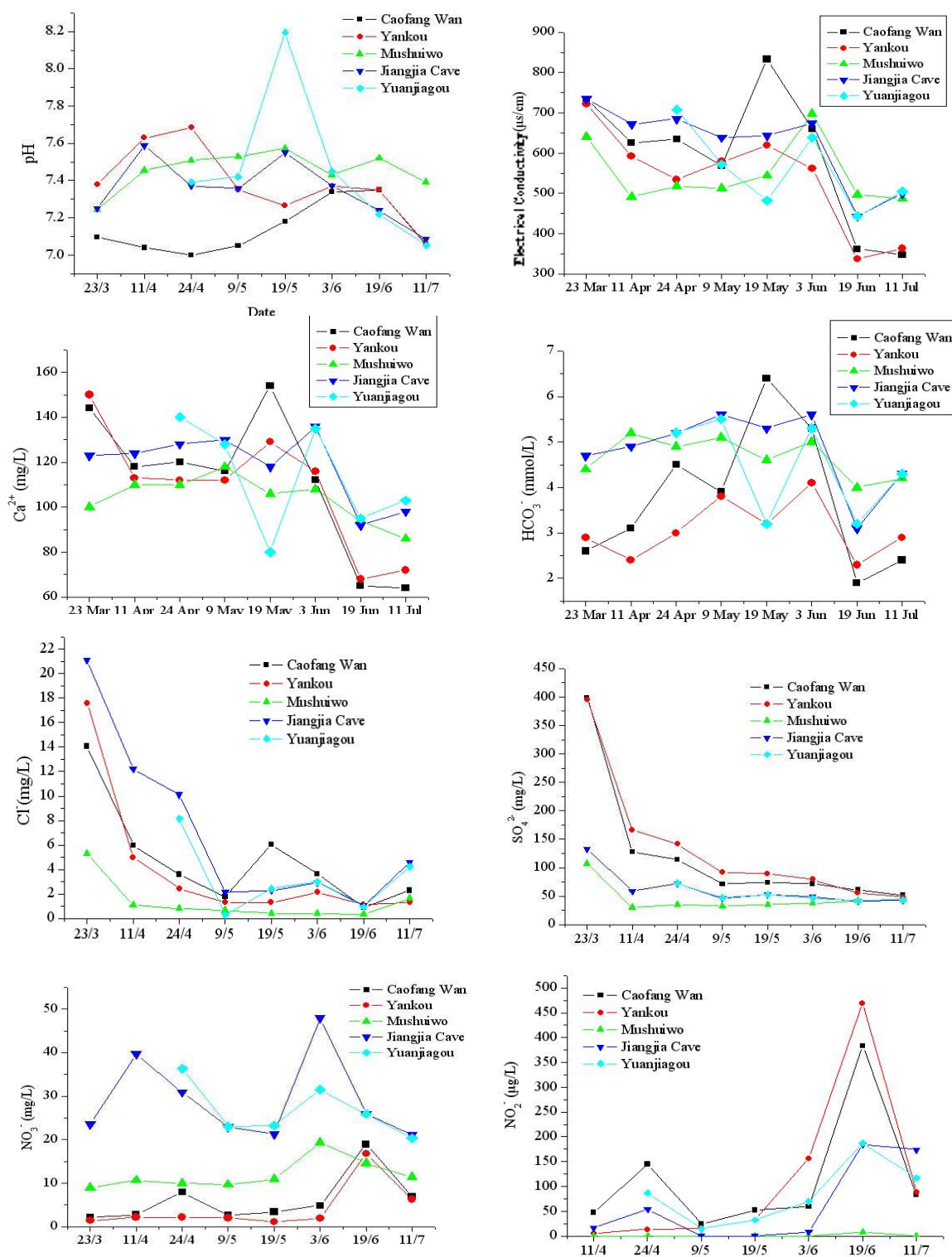


Figure 9. The results of tests for ions in water samples collected in Qingmuguan from March-July 2007. Discharge readings at these locations were unavailable. Mushuiwo is the spring leading to DMSW, Yuanjiagou is JJS, and Caofang Wan is an adjacent outlet in the middle of the YK valley (from He 2008).

Rainfall and discharge data are not available from this time, but data from JJS taken in April 2008 also express the water chemistry response to rainfall in the QSRS (Figure 10). This data indicates sudden shifts in ion concentrations, partial pressure of carbon dioxide and EC (spc) shortly following an increase in rain (Yang 2008). This leads to an increase in soluble ions in runoff and a decrease in ions dominant during baseflow conditions as they become diluted by the higher flows such as seen on 19 May in Figure 9 (Liu et al. 2004, Nakanoa et al. 2004a).

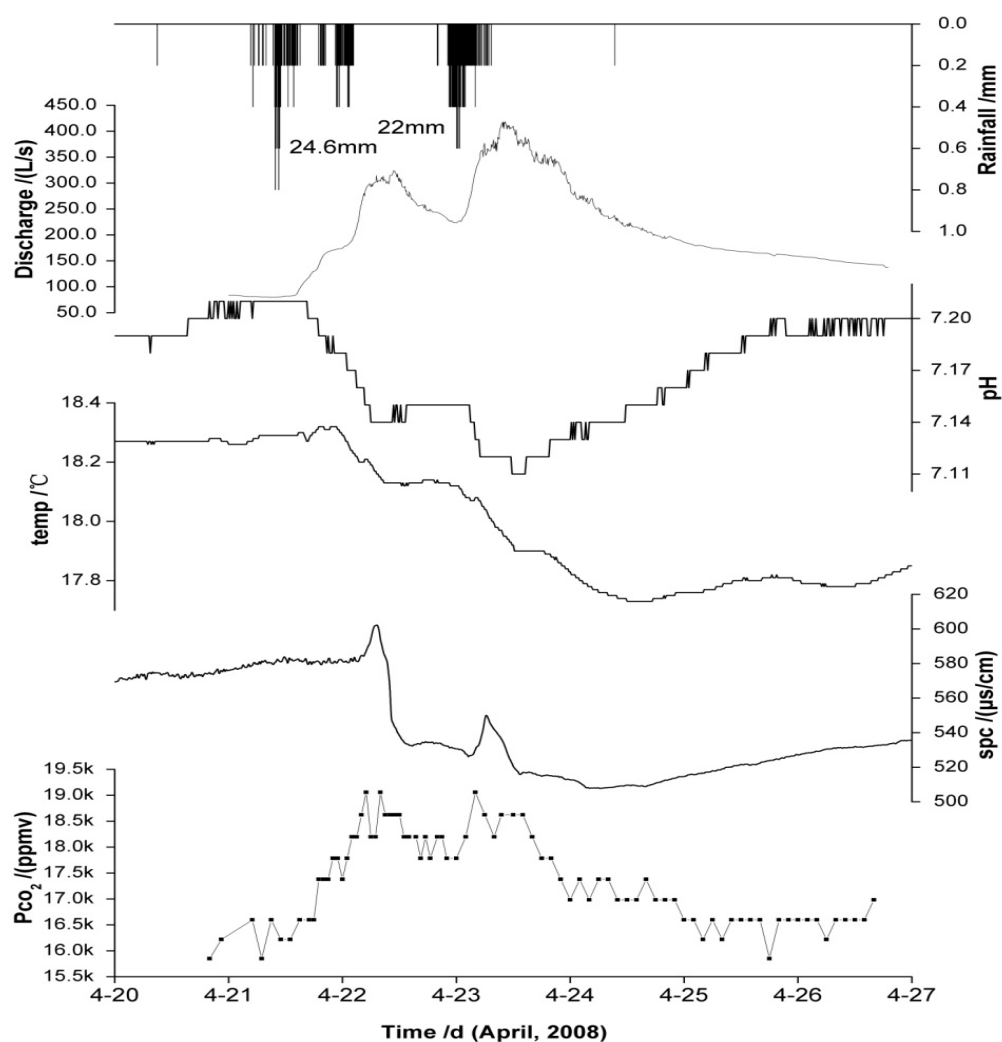


Figure 10. JJS water parameters taken in April 2008. The response to the rain events in discharge, pH, specific conductance (spc), and partial pressure of carbon dioxide are rapid and the water temperature goes down steadily over the period.



Water chemistry results from the 2007 samples showed that sulfate was quite high and both sulfate and chloride decrease as the runoff increases when the rainy season comes. Nitrate levels at JJS during this time reached as high as 50 ppm  $\text{NO}_3^-$  and never dropped below 20 ppm. (USEPA 2008).

The discharge in JJS is also greatly affected by dilution from additional inputs following large storm events. The small DMSW valley fills with water forming an ephemeral lake during large precipitation periods (Figures 11 and 12).



Figure 11. DMSW valley during flooded conditions with a level of 3-7 meters.



Figure 12. DMSW valley a week later. Flooding has drained into DMSW sinkhole.

This lake drains into the DMSW swallet which leads to JJS in a matter of days after the heavy rain stops. Consequently there is little agricultural activity in this valley during the rainy season with very high grasses dominating the valley bottom. The large inputs of water from the DMSW area with its differing land use from YK can present a complicating factor when trying to understand the patterns of hydrology and water chemistry at JJS. When the DMSW valley is not flooded there is a small water flow leading through the valley into a sinkhole going to the QSRS. The sinkhole is a passage

that has been improved with rock-brick walls and leads into a slope before draining to the QSRS. This may have been done to keep the valley drained for agriculture or made for mining. The effects of the water content of this small flow must be addressed as well.

Variation between concentration of ions or pesticides in YK and DMSW will tend to be a confounding factor when trying to understand if the pesticide levels between the inputs and outputs of the QSRS are related.



## CHAPTER 4. METHODS

### 4.1 Background Data

In order to understand pesticide transport in the QSRS it was necessary to establish specific details of the hydrology and pesticide use in QMG. Preliminary data collection on the water resource conditions in the QMG began in July 2007. Assessment of the conditions of the area began with the extensive study of map resources on the groundwater basin. This was followed by a karst hydrogeologic inventory which involved hiking throughout the watershed and cataloging the karst features contained in the study area. GPS locations and elevations were recorded for each of the features inventoried. If water was present in the feature the temperature, pH, specific conductance and an estimate of the discharge were recorded. Dissolved oxygen measurements were also recorded at some sites. Data loggers were established at YK and JJS in June 2007 continuing on through 2008 (Figure 13).



Figure 13. JJS is seen here during high discharge levels. The brick structure above the spring houses the water quality data loggers.

The data loggers recorded stage, temperature, pH, and specific conductance every 15 minutes, along with nitrate concentrations at JJS. There were 3 stations throughout the basin recording precipitation. For initial assessment of the general water quality in the area, water samples were collected at YK and JJS, along with a number of other sites of interest within the groundwater basin. These were brought back to Western Kentucky University (WKU) on ice within two days and tested for anions, cations, metals, total organic carbon, chemical oxygen demand, turbidity and atrazine.

In addition to hydrology data, information was collected on the use of pesticides in QMG. An initial list of the pesticides used in the area was also generated by conducting interviews with the local farmers. The majority of interviews were conducted in the valley draining to YK. More information on pesticide use in QMG was collected by retrieving empty pesticide packages from throughout QMG and identifying the acting pesticide compound used in the products. The retrieved packages are typically discarded at whatever location in the field the product happened to be mixed –usually near a water source.

#### 4.2 Hydrogeologic Inventory

There were 20 different karst features inventoried in QMG in July 2007. Most of them were sinkholes or springs draining from points well above the elevation of YK. The karst features inventoried included some used in additional soil and hydrology studies by researchers based near QMG at Southwest University (SWU) in Beibei, Chongqing, the WKU partner institution (He 2008, Yang 2008). These features, along with a few others that were inventoried, were dealt with in considering possible fluvial connections in the

QSRS. To assess these possible connections, a dye trace was conducted in August 2007, as well as another in September. The traces were done after many days of assessing and re-assessing the QMG hydrology for the ideal flow conditions for a clear result to be observed.

Dye was injected at the Yankou sinkhole and sinking stream (YK) for the first trace. The sites dye receptors were placed for this trace are listed from upstream to down as follows (Figures 3 and 23):

- Yankou Rong Dong (Cave) (adjacent cave to sinking stream injection point)
- Chishuguan (blue hole) (Figure 14)
- Damushuiwo spring (midway spring, drains to the sinkhole designated DMSW)
- Yihongkou (spillway)
- Jiangjia Rong Dong (karst window) (Figure 20)
- Jiangjia Spring (main spring designated as JJS) (Figures 7, 13 and 15)
- Zhichang (overpass spring)



Figure 14. Chishuguan blue hole seen here at high level.

A background analysis of the dye levels normally found at the sites at detectable levels was taken for the dye receptor locations. The background was also sampled for the spillway, which is an overflow system used for irrigating crops above the JJS outlet in the southern valley before reconnecting with the JJS flow. By the time the dye trace was conducted this flow was dry.

802.4 grams Uranine (Fluorescein) dye was injected at Yankou sinkhole (YK) on 1 August 2007 (Figure 16). The receptors were changed on days 2, 5, and 9. The receptors were kept on ice and returned to the Crawford Hydrology Laboratory at WKU for spectrofluorophotometer analysis. In addition to data from the charcoal receptors from the first trace, continuous dye levels were recorded at JJS for both of the dye traces. This was done using a flow-through field fluorometer, a dye receptor instrument made by Swiss research partners (Figure 15). This allowed for a determination of the time of the initial dye recovery and a calculation of the percent of the dye recovered.



Figure 15. Yang Pingheng installs the flow-through field fluorometer at the JJS gaging station during 2008 summer baseflow conditions. This was also the method used in the dye traces conducted in late summer 2007.

For the second dye trace 200 grams of Uranine was injected at Damushuiwo (DMSW) swallet on 14 September 2007 with data collected through 23 September. For this dye trace only the field fluorometer was used only at JJS as the sole only method of determining the connection and quantifying the dye travel time.

Additional work of assessing the hydrogeology of the area involved an in-depth assessment of the geology of QMG. This was accomplished by developing more detailed geologic cross-sections than available at the time. These cross-sections were developed by hiking the length of designated cross-sections, essentially east to west (Figure 3) and taking measurements of the dip of any outcrop layers of rock with a Brunton compass (Figure 17). These cross-sections indicate what should be the likely path of the QSRS flow based on calculations of travel times and bedding planes (Figures 3 and 4). From this it can be better understood which sections of the basin most strongly affect the QSRS surface water and sediment input (Yang 2008).



Figure 16. Shown here is the dye injection at YK that was accomplished in August 2007.



Figure 17. Shown here is an example of the method for recording the dip for cross-section.



### 4.3. Sampling and Testing

During the summer of 2008 water samples were collected from YK and JJS 4 June-28 July using USGS protocols. The water samples were collected 2-3 times per week in 40 mL amber glass bottles designated for use in holding volatile organic compounds. These samples were then usually tested for pesticide concentrations within 24-48 hours of their collection, but within 1-2 weeks in all cases (Quinlan and Alexander 1987, USGS 2006). They were tested for each specific pesticide using quantitative test kits that are highly sensitive and are produced for this analysis by Strategic Diagnostic Inc. and Abraxis. The methods used by these kits are Enzyme-Linked Immuno-Sorbent Assay (ELISA). They are normally competitive ELISA tests which use magnetic particles bound to for extraction from solution. The analysis of the assay results were conducted using a Shimadzu UV-2450 spectrophotometer. The ELISA kits needed for the analytical instruments available were test tube based as opposed to microtiter plate kits. ELISA kits of either kind were not available for most of the pesticides of interest in used in the QMG study area. The pesticides analyzed, as well as procymidon, were the only kits available for use with the accessible analytical equipment.

The competitive ELISA technique involves adding an enzyme conjugate to water samples that contain specific pesticide or compound. A solution with antibodies attached to magnetic particles is then added and the enzyme conjugate competes with the pesticide that may be in the sample to bind to these antibodies. For this test, the magnetic solution contained an antibody derived from rabbits and paired to match each different pesticide. These antibodies were then covalently bound to paramagnetic particles and suspended in a buffered solution with preservative and stabilizers. For this test the enzyme conjugate

was a diluted peroxidase derived from horseradish and labeled with each specific pesticide analog. A magnetic field is then applied once these antibody particles are bound and the pesticide is drawn out of solution and then the remaining solution is decanted. After the particles are washed a color solution is added which contains the enzyme substrate (hydrogen peroxide) and the chromogen (3, 3', 5, 5'-tetramethylbenzidine). The enzyme conjugate catalyzes the conversion of the substrate and chromogen mixture to a colored product, which expresses a stronger color if more antibody sites were taken up by the conjugate because not as much pesticide was in the water to bind and take up those sites. So, the color development is inversely proportional to the concentration of the pesticide in the water. The color saturation is then detected by a UV spectrophotometer.

The results for these tests are in micrograms (ug) per liter (L) or parts per billion (ppb). There is a limit to what the test can detect or quantify. Tables 2-5 show for each pesticide the method detection limit (MDL) or the lowest concentration detected by the assay, the limit of quantitation (LOQ) or the lowest concentration of the compound that can be quantified by the assay. The IC<sub>50</sub> is the concentration required to inhibit one half of the color produced by the negative control, which is essentially the upper limit of quantitation for a standard sample, beyond which the sample should be diluted before testing. IC<sub>50</sub> is also used to find cross-reactivity to similar compounds (SDI 2008).

The procedure for each ELISA test involved the following:

Test solutions were stored at 4 °C and then allowed return to room temperature at least one hour before the test was conducted. For each test there were four standards solutions and a control of known concentration provided that were along with the samples using the same procedures for each particular round of tests. This allowed for a

standard curve to be developed and confirmation of accurate testing via comparison to the control. For each test a special test tube rack was used with a base containing magnets for separation of the magnetic particles from the solution.

Table 2. Glyphosate ELISA test limits and cross-reactivity.

Compound	MDL (ppb)	LOQ (ppb)	IC50 (ppb)
Glyphosate	0.10	0.10	2.40
Glyphosine	50	50	3,000
Glufosinate	2000	2000	70,000
AMPA	35,000	35,000	>1,000,000

Table 3. Chlorpyrifos ELISA test limits and cross-reactivity.

Compound	MDL (ppb)	LOQ (ppb)	IC50 (ppb)
Chlorpyrifos	0.10	0.22	0.94
Diazinon	0.12	1.77	7.56
Chlorpyrifos-methyl	0.14	0.84	3.58
Pirimiphos-ethyl	0.32	13.4	57.1

Table 4. Chlorothalonil ELISA test limits and cross-reactivity.

Compound	MDL (ppb)	LOQ (ppb)	IC50 (ppb)
Chlorothalonil	0.07	0.1	1.12
2,4,5,6-Tetrachloro3-cyanobenzamide	0.29	0.94	10.5
2,5,6-Trichloro-4-hydroxy isophthalonitrile	18.7	129.5	1450
Pentachloronitro Benzene	0.14	0.17	1.90
Hexachloro-benzene	0.16	0.179	2.00
Pentachloro-phenol	29.2	151.8	1700

Table 5. Atrazine ELISA test limits and cross-reactivity.

Compound	MDL (ppb)	LOQ (ppb)	IC50 (ppb)
Atrazine	0.046	0.1	0.72
Propazine	0.033	0.1	0.74
Ametryn	0.053	0.05	0.39
Prometryn	0.054	0.09	0.64
Prometon	0.056	0.31	2.22
Desmethyl Atrazine	0.062	0.45	3.21
Terbutryn	0.090	0.76	5.50
Terbutylazine	0.310	2.15	15.5
Simazine	0.340	0.68	4.90
Desisopropyl Atrazine	0.800	30.1	217
Cyanazine	1.0	>10000	>10000
6-Hydroxy Atrazine	1.1	20.6	148



The glyphosate test first required extra derivation steps for the standards, control, and samples. This was accomplished by diluting a derivatization reagent with 3.5 mL of diluent. 50 uL of standard, control, and samples were then pipetted in duplicate into disposable assay test tubes. All pipetting for all tests was done by adding solutions down the side of the test tube just below the rim. 200 uL of a buffer was added to each tube and then vortex mixed. 20 uL of the diluted derivatization reagent was then added to each tube and they were again mixed with a vortexer immediately after addition of reagent. They were then incubated at room temperature for 10 minutes and the further procedures were then conducted the same as for the other tests. The derivatization steps of the glyphosate test yielded 300 uL of the standards, control, and samples to begin the next steps, while the amount of these used to begin the tests for triazines and chlorothalonil were 200 uL and 250 uL for chlorpyrifos. All sample solutions were placed in the test tubes with the magnetic base separate at this point. After the samples were added to the test tubes, 250 uL of the enzyme conjugate was then added to each test tube and 500 uL of the antibody magnetic particles that had been premixed. Each test tube was immediately vortex mixed for 1 to 2 seconds at low speed to minimize foaming. They were then incubated at room temperature for 15 minutes for triazines and chlorpyrifos and 30 minutes for chlorothalonil and glyphosate.

Subsequently the upper test tube rack was combined with the magnetic base and 2 minutes were allowed for the particles to separate. The test tube contents were then smoothly poured out of the combined rack into the sink making sure the base was still well seated on the tubes. The tops of the test tube in the still inverted rack were then gently blotted on paper towels, removing as much extra liquid as possible while being

careful not to dislodge the particles from the tubes. The particles in the tubes were then washed with 1 mL of deionized water washing solution and decanted again as described, after again waiting 2 minutes. This washing step was followed twice for all tests except for glyphosate which was done three times. The base was removed from the upper rack again and 500 uL of color solution was added to all tubes and vortex mixed at low speed. The solutions were then incubated for 20 minutes at room temperature at which time a stopping solution of 2 M sulfuric acid was added. The contents of the test tubes were then each added to a cleaned 1 mL cuvette and analyzed at 450 nm by UV spectrophotometer. This last step was required because a UV spectrophotometer that could normally be used with the test tubes directly was not available.

The spectrophotometer available also could not convert to absorbance value results from the standards onto a graph with the proper scales needed to provide a standard curve. A transformation of the axes for the proper regression was needed to allow calculations of the concentrations of pesticides for each sample. The scale transformation that was required for glyphosate, triazines, and chlorpyrifos was a natural logarithm (ln) scale on the x-axis representing the concentration which is the dependent variable determined from the independent variable on the y-axis. The y-axis represents the percent absorbance of the sample divided by the absorbance of the standard zero solution and must be transformed to a LogitB scale. LogitB indicates that the axis represents an inverse sigmoidal (S-curve) logistic curve which is transformed using the Bell method logistic regression. This means the transformation is more exponential at the higher and lower values, which reflects the tendency of the absorbance values to be less accurately detected at higher and lower values of the standards used for these particular

tests. For chlorothalonil the scale transformation was a ln scale on the x-axis and a linear scale on the y-axis. All graphs then used linear regression through the results of the standards plotted on the graph with these axes to determine how the absorbance readings of the pesticides in the water samples should be calculated to find the concentrations in the samples. This was accomplished by comparing the sample results in respect to the standard curve to find the pesticide concentrations in the samples. These calculations were all done with a spreadsheet available from SDI, Inc. where the absorbance numbers were input into the sheet and the resulting concentrations were provided. Since each standard, control, and sample were done in duplicate, the average of the two concentration results were then used to represent the concentration in the sample (SDI 2008, Abraxis 2008).

Methods have not been developed for testing the combination of all the specific pesticides of interest through standard HPLC/UV and GC/MS and developing such methods was beyond the scope of this project. Testing expertise was not available to develop a new method for testing all of these for this research project and it was not possible to test for each individually with the resources available. Standard solution concentrations for use with these instruments to test for individual pesticides of interest were not available within the time frame available for water sample collection and testing. Regardless of this, work during the sample analysis portion of the research also involved efforts to acquire these standards and apply available published methods for their detection. This was due to a strong interest towards determining the concentrations of some of the pesticides in the water that do not have ELISA kits available. For example, a package of Metsulfuron-methyl was found on the ground right next to the

runoff going into YK on the first day of the 2008 sampling. Some of the pesticide listed in Table 7 were used more extensively in the study area and had properties of greater interest in respect to water quality. The pesticides of most concern are those that have the strongest capacity for groundwater contamination along with the greatest concern from human health effect following exposure or ingestion in water (Table 7). Nonetheless, the ELISA method was the only viable option under the circumstances.

## CHAPTER 5. RESULTS

### 5.1. Background Analysis

The results of the initial water samples collected for a preliminary assessment of the water conditions in QMG in July 2007 are displayed in Table 6. The ion concentrations shown in the table are common for a karst groundwater basin. However, nitrate in the spring was 15.41 ppm when considering the weight represented by only the nitrogen portion of nitrate ( $\text{NO}_3^-$ -N). This is above the limit of concern for drinking water set at 10 ppm in China and by the USEPA. Additionally, iron was rather high; although high iron in water supplies is not considered a health hazard as much as an aesthetic problem. Results also show that triazines had been used in the upper watershed with 0.6 ppb reported in the runoff draining the YK agricultural valley, which is below the USEPA recommended safe limit for drinking water of 3 ppb for atrazine.

Figures 18 and 19 are the results of the data from the field data loggers. Since some different data loggers were reported at a different time scales, all data were adjusted to match a 15 minute reporting time scale. The rain gage data used for analysis was in the YK agricultural valley and data were recorded every five minutes and each time section was added to fit the 15 minute time scale. Data from the stage recorders was reported each time there was a significant and/or continuous change. Therefore, the last recorded level was substituted into all the 15 minute increments that were not recorded. The data is reported starting at 2 weeks before the sampling period to get an idea of conditions prior to the sampling that may have influenced the pesticides levels in the first few samples.

Table 6. The results of single water samples taken at 4 locations in QMG on 10 August 2007. The results show that atrazine is used in the upper watershed. The levels were below the recommended safe limit for drinking water of 3 ppb used by the United States EPA and China. Nitrate in the spring was above the limit of concern for drinking water of 10 ppm or mg L<sup>-1</sup>. Iron was rather high; although high iron in water supplies is not considered a health hazard as much as an aesthetic problem. Other results from these samples were within normal ranges (Huang and Li 2003, EPA 2008).

	OD - Chemical Oxygen Demand (ppm)	TOC – Total Organic Carbon (ppm)	Turbidity (Nephelometric) (NTU)	Atrazine (ppb)
Yankou -Sinking Stream	11.29	2.482	3	0.6
Jiangjia -Main Spring	<5	0.626	7.29	<0.05
Damushuiwo	<5	0.2	<1	<0.05
Zhichang	5.83	0.343	<1	<0.05

	NH <sub>4</sub> (ppm)	NO <sub>3</sub> (ppm)	NO <sub>2</sub> (ppm)	PO <sub>4</sub> (ppm)	SO <sub>4</sub> (ppm)
Yankou -Sinking Stream	0.35	0.38	<0.03	<0.11	37.66
Jiangjia -Main Spring	0.28	15.41	<0.03	<0.11	42.7
Damushuiwo	0.14	7.49	<0.03	<0.11	41.55
Zhichang	0.16	9.13	<0.03	<0.11	68.5

	Ca (ppm)	Na (ppm)	K (ppm)	Cl (ppm)	F (ppm)	Br (ppm)	Mg (ppm)	Li (ppm)
Yankou -Sinking Stream	91.17	3.07	1.16	1.9	0.22	<0.07	10.49	<0.01
Jiangjia -Main Spring	107.51	3.3	1.9	5.36	0.14	<0.07	11.44	<0.01
Damushuiwo	92.03	1.07	0.94	1.56	0.13	<0.07	12.59	<0.01
Zhichang	110.68	1.76	2.02	3.26	0.21	<0.07	15.57	<0.01

	Fe (ppb)	Pb (ppb)	Cr (ppb)	Cu (ppb)	Ni (ppb)	Ag (ppb)
Yankou -Sinking Stream	283.44	1.71	1.43	1.53	4.47	1.84
Jiangjia -Main Spring	357.264	1.37	4.57	2.16	4.95	2.01
Damushuiwo	14.88	1.26	1.64	1.45	4.79	1.74
Zhichang	47.79	1.66	1.83	1.58	6.53	1.91

The discharge in the QSRS was calculated by using Manning's equation with the stage to find the velocity and then multiplied by the channel area. The channels at both YK and JJS were rectangular with JJS at 1.8 m wide and YK at 0.8 m wide. At both locations for the roughness coefficient of  $n=0.025$ , slope of  $S=0.003$ , and  $k=1$  was used.

$$V = \frac{k}{n} R_h^{\frac{2}{3}} \cdot S^{\frac{1}{2}}$$

The hydraulic radius is the area divided by the wetted perimeter (Hornberger et al. 1998).

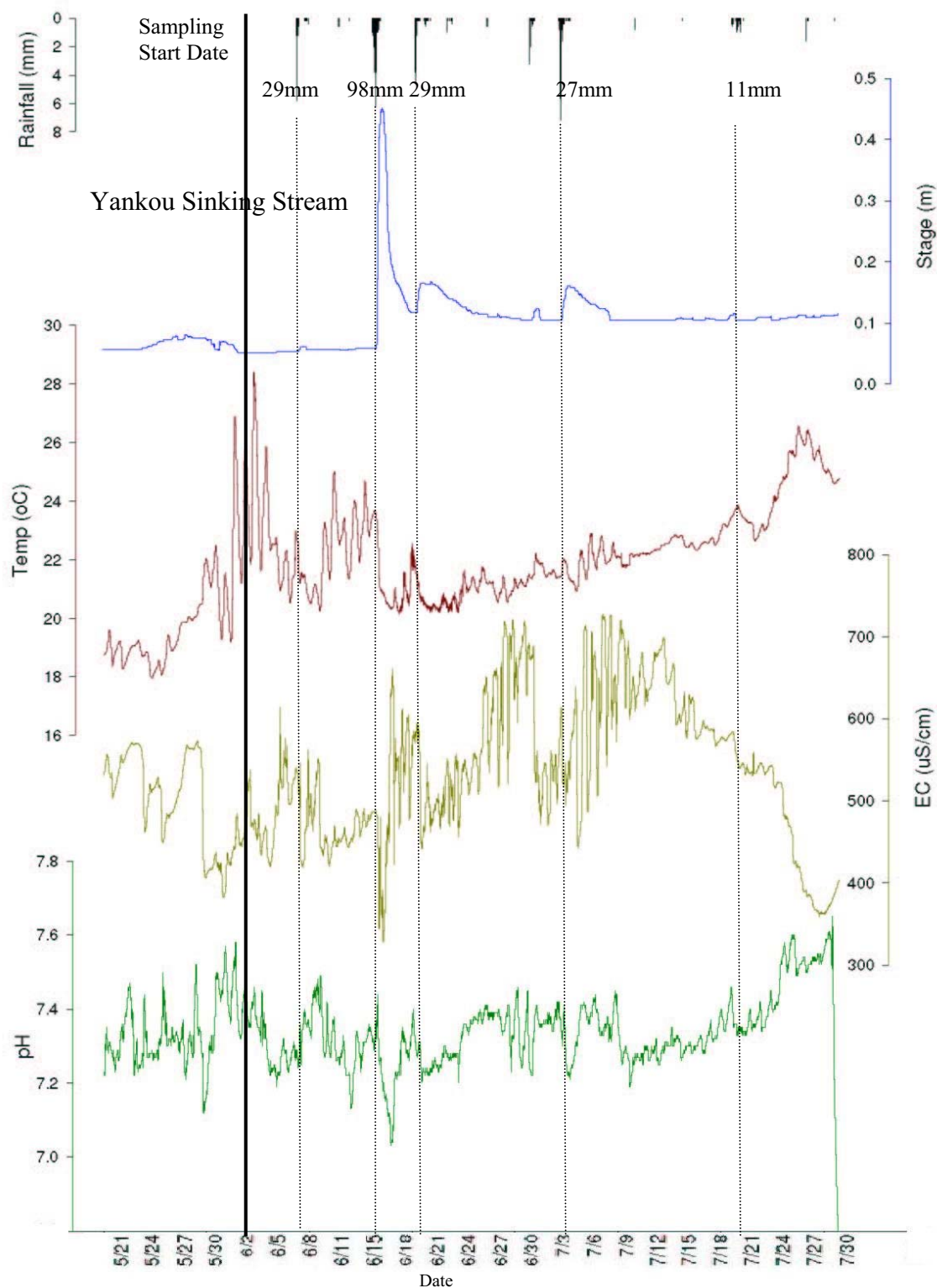


Figure 18. Water parameters from data loggers at YK, 18 May-30 July. Water samples were first taken for analysis of pesticides concentration on 2 June. The dotted lines represent rain events and resulting discharge changes.

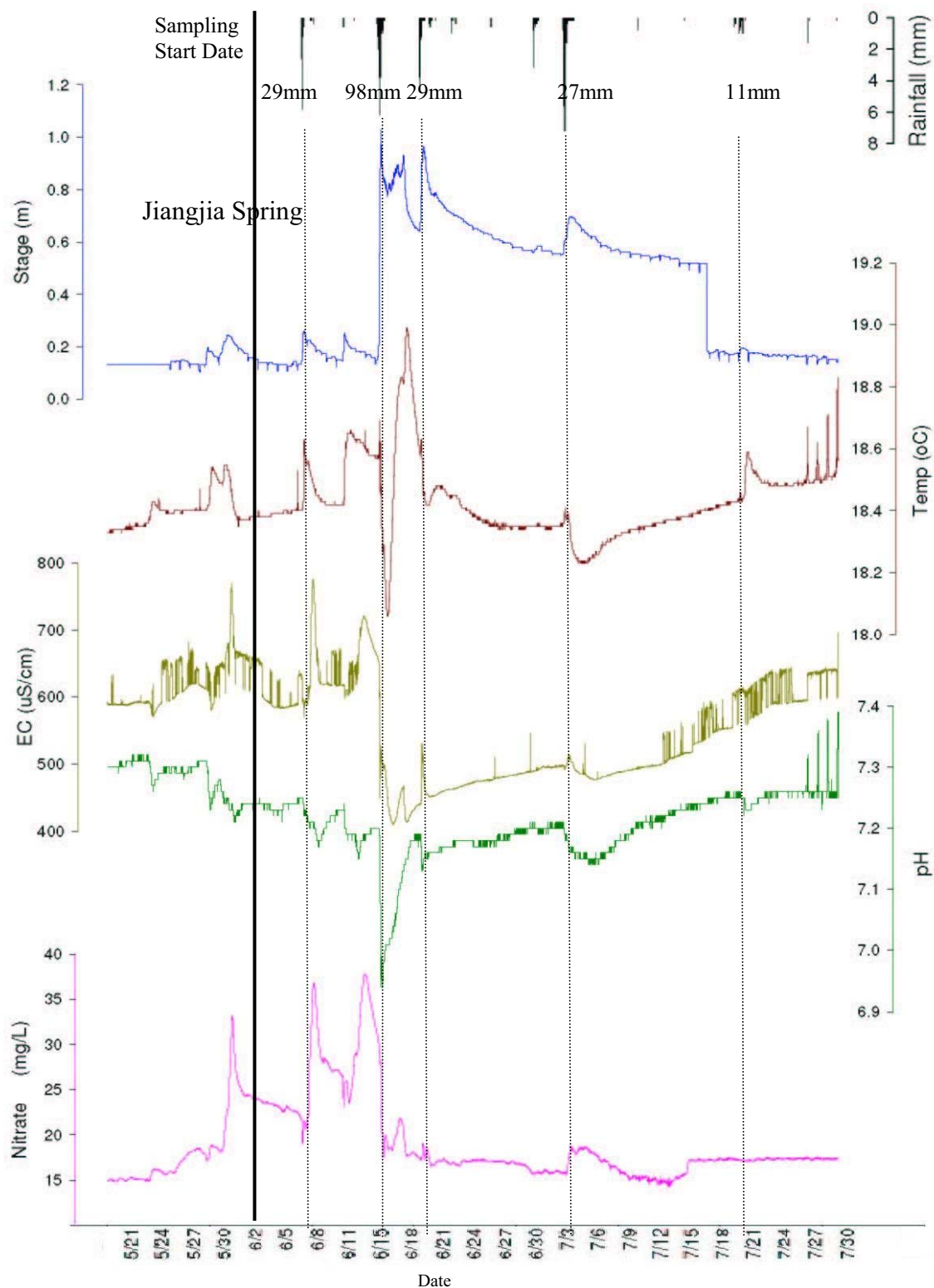


Figure 19. Water parameters from data loggers at JJS, 18 May-30 July. Water samples were first taken for analysis of pesticides concentration on 2 June. The dotted lines represent rain events and resulting discharge changes.



## 5.2. Hydrogeology

The results of the dye traces are displayed in Figures 21, 22, and 23. JJS showed a positive result for dye following both the injection at YK and at DMSW. During the YK injection 93.4% of the Uranine arrived at JJS 33.3 hours after injection. The flows were lower during the DMSW injection and dye arrived about 42 hours after injection.

The karst window (Figure 20) was the only other feature besides the cave adjacent to YK that showed a positive result for dye following the injections. The spillway was not tested during the trace but was visually confirmed as connected to the QSRS after the water level went down and access the passage draining the spillway discharge was possible. Additionally, dye levels above the background were found in receptors retrieved from the blue hole, though the levels were not significantly greater than the background level in order to confirm that dye from the injection arrived there. Also, there was no water found in the blue hole in 2008, so it was not sampled.



Figure 20. Initial testing for pH and EC was done in the karst window. Results closely correlated with JJS.

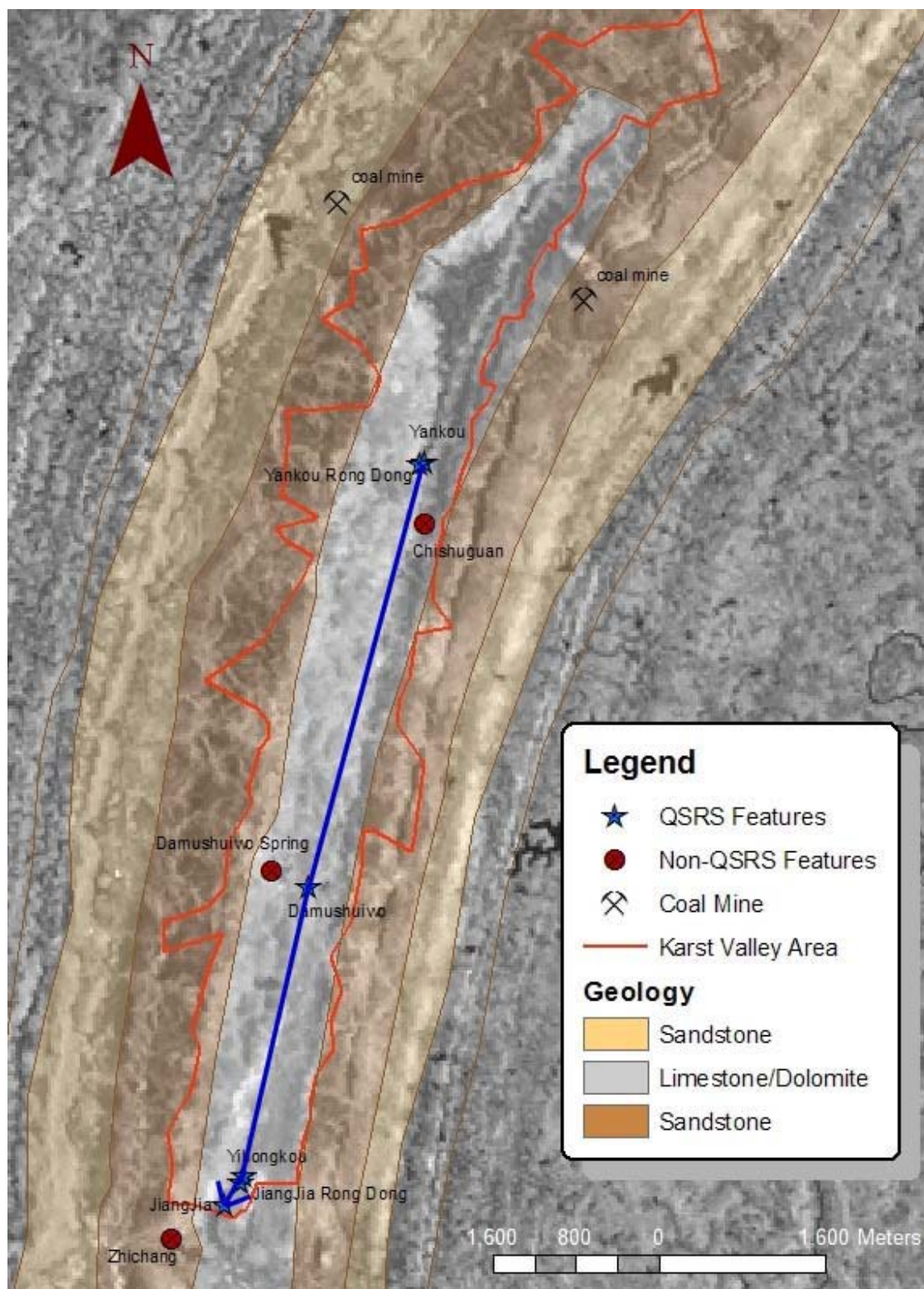


Figure 21. A map of the karst features involved in the 2007 dye traces of the QSRS. Dyes were injected at Yankou and Damushuiwo. The red circles are feature where no dye was found in the water. Blue is the QSRS and its associated features. The dark areas of the map are the lower elevations and the white are the higher elevations.

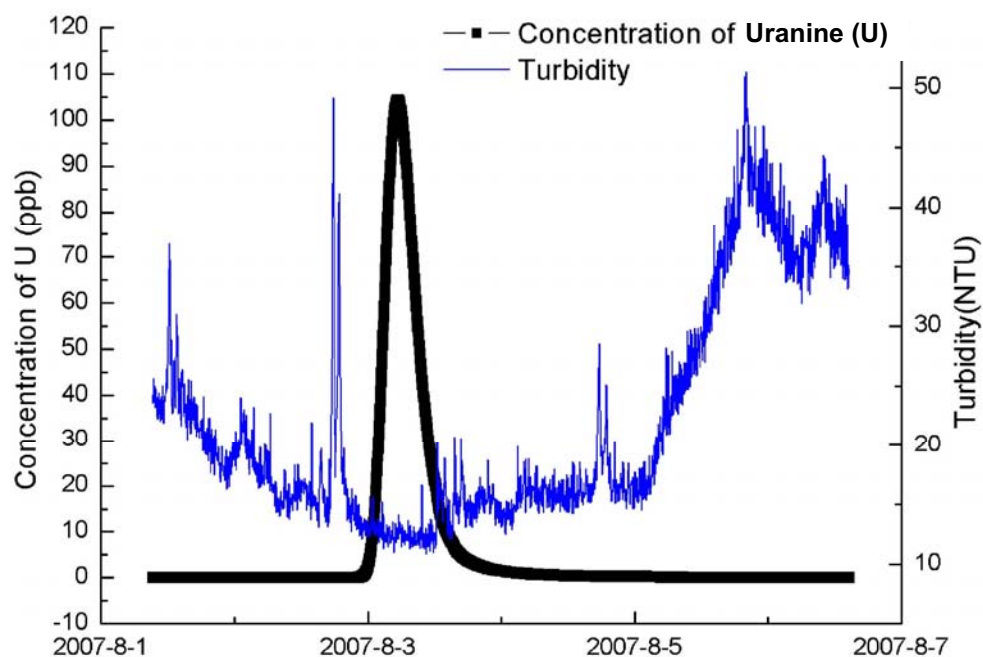


Figure 22. The breakthrough curve showing the pulse of dye arriving a JJS after injection at YK in August 2007 along with turbidity data from the flow through field fluorometer (from Ham 2007).

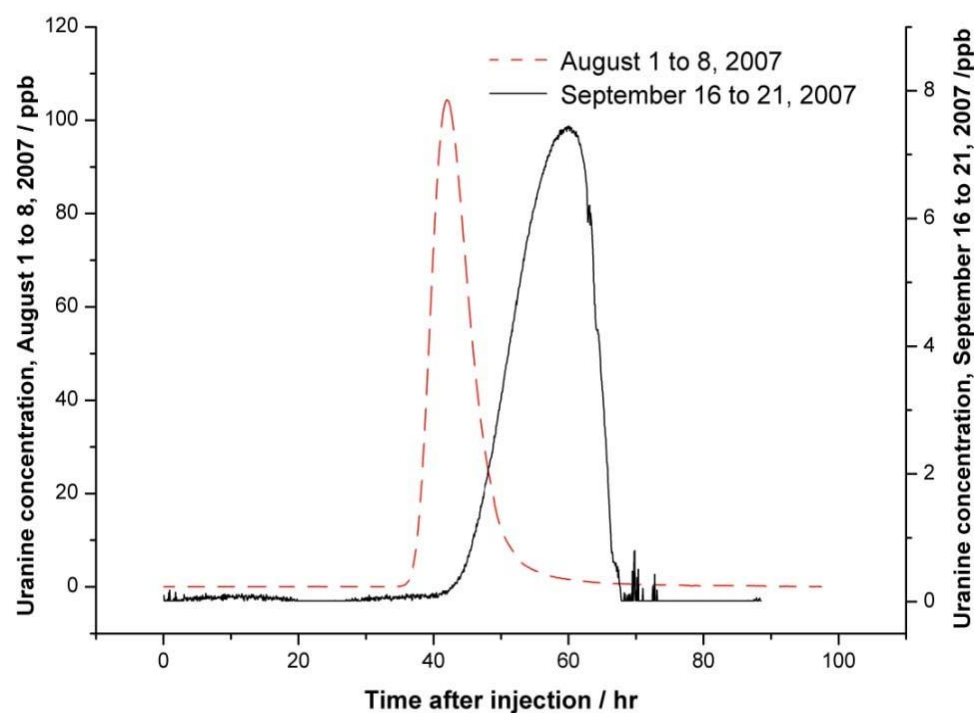


Figure 23. The breakthrough curve showing the pulse of dye arriving at JJS after injection at DMSW in September 2007 compared with the curve from the injection at YK in August 2007 (Adapted from Yang 2008).

Throughout the basin there were a number of other karst features recorded during the survey. The small cave adjacent to the sinking stream was unknown to SWU researchers until it was discovered in 2007 by climbing and cutting through some heavy vegetation. There was also a large cave inventoried during the 2007 field work that was known only to some local farmers. The mouth was quite large at about 8 m high by 15 m wide. It closed down quickly into a small passage that went about 100 m back. A thorough survey was conducted of this cave during the 2007 field work, as well as of the karst window. There were also a number of small springs recorded that drain into QMG coming from its adjacent slopes (Figure 24) into different small valleys in the QMG groundwater basin. Sinkholes are present in these valleys as well.



Figure 24. An example is shown of a small spring emerging from the bounding sandstone slopes of QMG basin.



### 5.3. Pesticides Results

Table 7 displays the results of the initial assessment of pesticide use in the QMG agricultural area. From the survey of discarded pesticide packages, a number of pesticides were used in QMG at some point. Additionally, over the course of interviews with farmers in the area, 7-8 pesticides were cited as the most prominently used in QMG. The pesticides mentioned in interviews are listed in italics in Table 7 and the pesticides chosen for analysis in QMG waters are listed in bold. The most common insecticide mentioned was dimethoate and the most common herbicide was glyphosate.

Based on potential health concerns and potential for groundwater contamination, a number of pesticides were considered for analysis in QMG water resources (Tables 1 and 7). Unfortunately, only methods for testing glyphosate, chlorothalonil, atrazine, and some samples for chlorpyrifos were feasible for analysis due to testing resources available at the time. The test used for the detection of atrazine has a close cross-reactivity with other compounds in the triazine family (Table 5). Since this is the case it cannot be determined for certain that the compound detected from the analytical test used is atrazine. Therefore, this group of compounds indicated by the test used will be referred to hereafter as triazines.

Graphs of the results of the pesticide levels are displayed in Figures 25-31. S-Plus and SPSS were used for statistical analysis and graphs were created with SigmaPlot and Excel. The data was related using the non-parametric Spearman's correlation analysis.

Table 7. Data on pesticides used in QMG obtained through interviews are listed in *italics*. Other pesticides listed were identified in use in the area via the collection of pesticide packages found on the ground in the basin. Pesticide concentrations tested for in water samples are listed in **bold** (EXTOXNET 2008, PAN 2008).

<b>Pesticides</b>	<b>Use<sup>a</sup> type</b>	<b>Groundwater Contaminant</b>	<b>Acute<sup>b</sup> Toxicity</b>	<b>Carcin-<sup>c</sup> ogen</b>	<b>Other<sup>d</sup> Health</b>
<b><i>Atrazine</i></b>	1	Yes	1	1	1
<b><i>Glyphosate</i></b>	1	Low	1	0	–
<i>Glufosinate</i>	1	--	1	--	1
<i>Metsulfuron-methyl</i>	1	Potential	1	0	–
<i>Dimethoate</i>	2	Potential	2	1	1,2,3
<i>Thiosultap disodium</i>	2	--	--	--	–
<i>Isocarbophos</i>	2	--	--	--	–
<b>Chlorpyrifos</b>	2	Conditional	2	0	1,2
Avermectin	2	Low	3	0	3
Cypermethrin beta	2	Low	1-2	1	1
Emamectin benzoate	2	Low	3	0	–
Hexaflumuron	2	--	1	0	–
<b>Chlorothalonil</b>	3	Potential	3	2	–
Carbendazim sulfur	3	No	1	1	1
Cymoxanil	3	--	1	0	–
Fosetyl aluminum	3	Potential	3	0	–
Mancozeb	3	Low	0	2	1,3,4
Mefenoxam	3	--	3	1	–
Procymidone	3	--	0	2	1
Pyrimethanil	3	--	0	1	1
Streptomycin sulfate	3	--	2	--	3
Thiram	3	Conditional	1	0	1,3,4
Ziram	3	Conditional	1	1	1,3,4
Metaldehyde	4	Potential	2	1	–

a. 1=Herbicide, 2=Insecticide, 3=Fungicide, 4=Molluscicide

b. 0=Not Toxic, 1=Slightly Toxic, 2=Moderately Toxic, 3=Highly Toxic

c. 0=Unlikely Carcinogen, 1=Possible Carcinogen, 2=Probable Carcinogen

d. 1=Suspected Endocrine Disruptor, 2=Neurotoxin (Cholinesterase Inhibitor),  
3=Developmental Toxin, 4=Reproductive Toxin

The continuous water conditions data was correlated with the pesticide sample values by using a discrete value representing their possible effect on pesticide levels prior to the sampling. This was found by averaging the values for the previous 48 hours or summing the values in the case of rainfall. A non-parametric analysis of variance (ANOVA) of the different pesticide levels and the discharge called a Wilcoxon signed-rank test was also used for analysis of the relationships between the different pesticide concentrations and loads at YK and JJS (Table 14) and comparing these to the discharge at YK and JJS (Table 13).

The loads were also calculated from discharge calculations (Figures 26, 28, and 30) to reflect the difference in the levels of discharge at the two locations and how that might reflect the relationship between the levels in the two areas, as well as what pesticides may be coming in from other areas in the basin. A Spearman's correlation was conducted between all the pesticide concentrations at each location and also between these and the discharge. The Spearman's correlation test is basically the same test as a normal Pearson's correlation which tests for linear dependence between two variables, except each set of values are ranked before the correlation is made. Tables 8 and 9 show the results of the Spearman's correlation analysis between the pesticide concentrations and between the loads at each location, as well as between the average discharge of the 48 hours prior to the sampling. Another analysis that says a lot about how the pesticide levels of YK and JJS are related to each other is how they change together. This is represented by an analysis of covariance which is shown in Table 15.

The correlation coefficients shown in Tables 8 and 9 suggest a strong relationship between both the concentrations and the loads at each site on each particular day. As determined by the statistical program, any two variables with a coefficient greater than 0.5 were strongly related, with a p-value of less than 0.01. For a coefficient between 0.4 and 0.5 the relationship was significant with a p-value of less than 0.05. The correlation between concentrations at YK and JJS of glyphosate was 0.65, chlorothalonil was 0.7, and triazines were 0.6. The correlation between loads at YK and JJS of glyphosate was 0.6, chlorothalonil was 0.55, and triazines were 0.55. Additional notable correlations were between glyphosate and chlorothalonil at YK at 0.62, and between discharge at YK and chlorothalonil at YK (0.72) and between discharge at JJS and chlorothalonil at YK.

The maximum levels of pesticides were all observed in the sample taken the day after the largest storm on 15 June. There were also high levels in samples taken just after another storm event in July during which there was a spike of rain over a short time period. This instance was not true for triazines, yet levels were high a week later which happens to coincide with elevated total dissolved solids represented by EC at YK, although not so much at JJS. The results of the load calculations show more clearly the changes in pesticide levels over the summer. For example, while the maximum concentration of triazines at both locations was observed in July, the maximum load was observed during June (Figures 27 and 28 or Tables 10 and 11). In some instances, such as most notably after the 15 and 19 July rain events, there was an increase in pesticide levels at one or both of the sites. Still, there was a fair amount of variability in the levels of pesticides at both locations not likely related to any certain water condition.



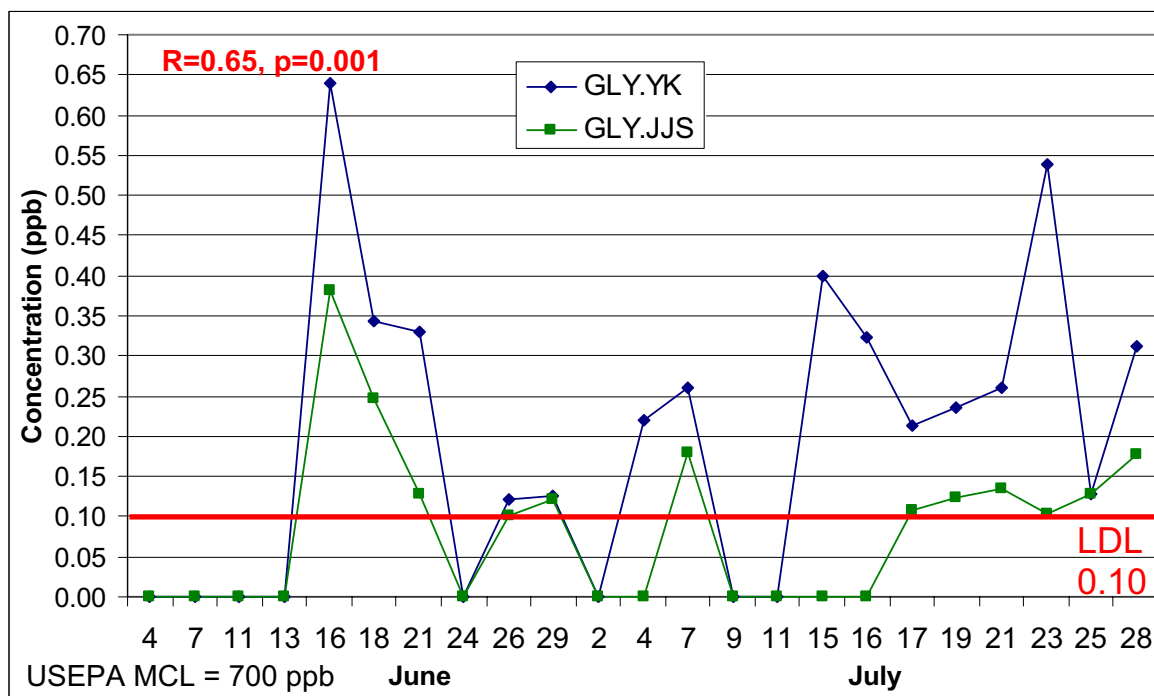


Figure 25. Glyphosate concentrations in water samples. LDL is the lower detection limit of the ELISA test. The R is the nonparametric correlation coefficient and the p is the p-value representing the strength of the correlation test.

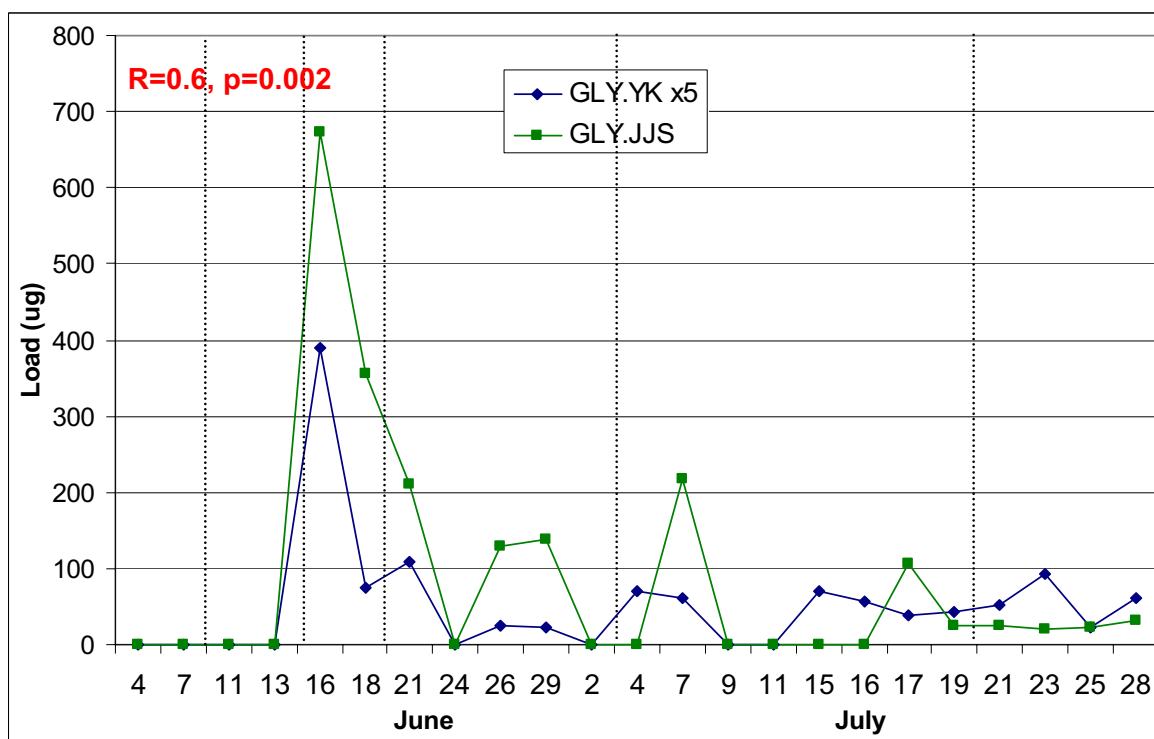


Figure 26. Glyphosate loads in water samples. The dotted line corresponds with rain events shown in Figures 18 and 19. The R is the nonparametric correlation coefficient.

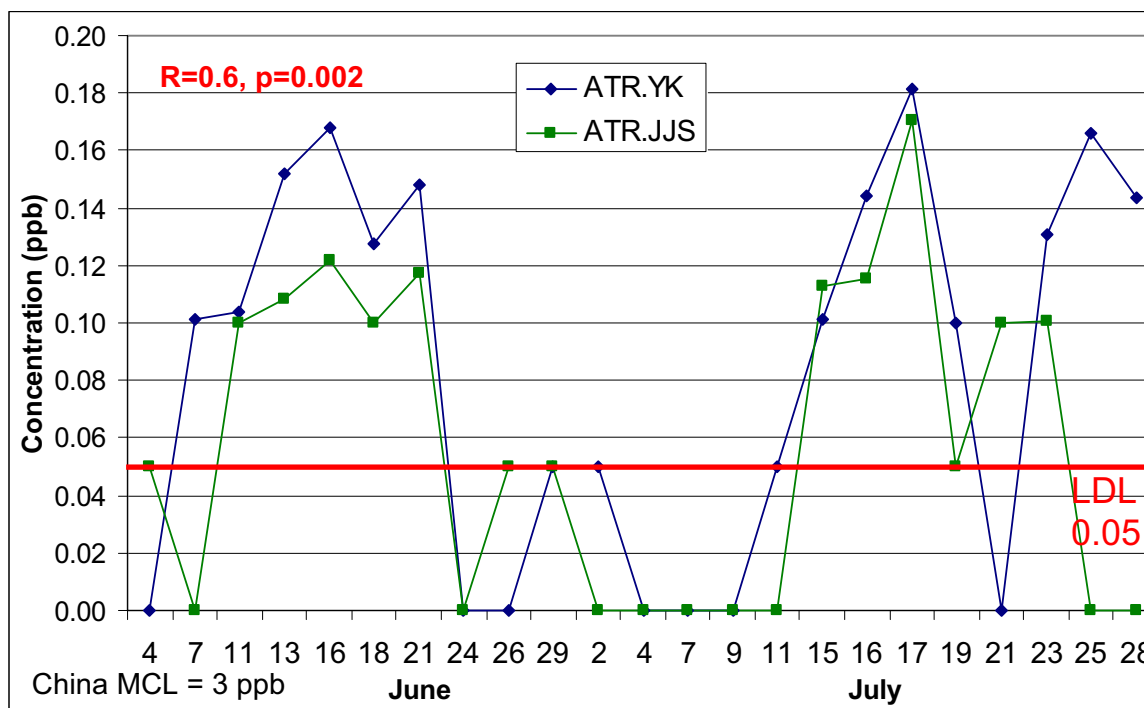


Figure 27. Triazines concentrations in water samples. LDL is the lower detection limit of the ELISA test. The R is the nonparametric correlation coefficient and the p is the p-value representing the strength of the correlation test.

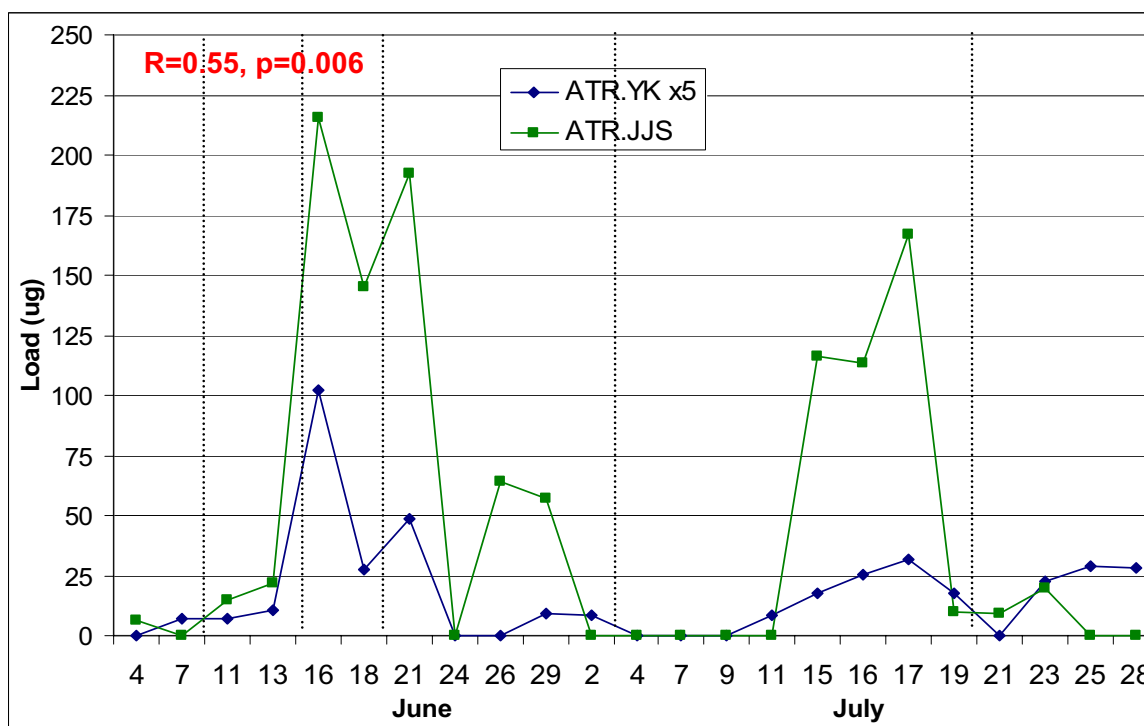


Figure 28. Triazines loads in water samples. The dotted line corresponds with rain events shown in Figures 18 and 19. The R is the nonparametric correlation coefficient.

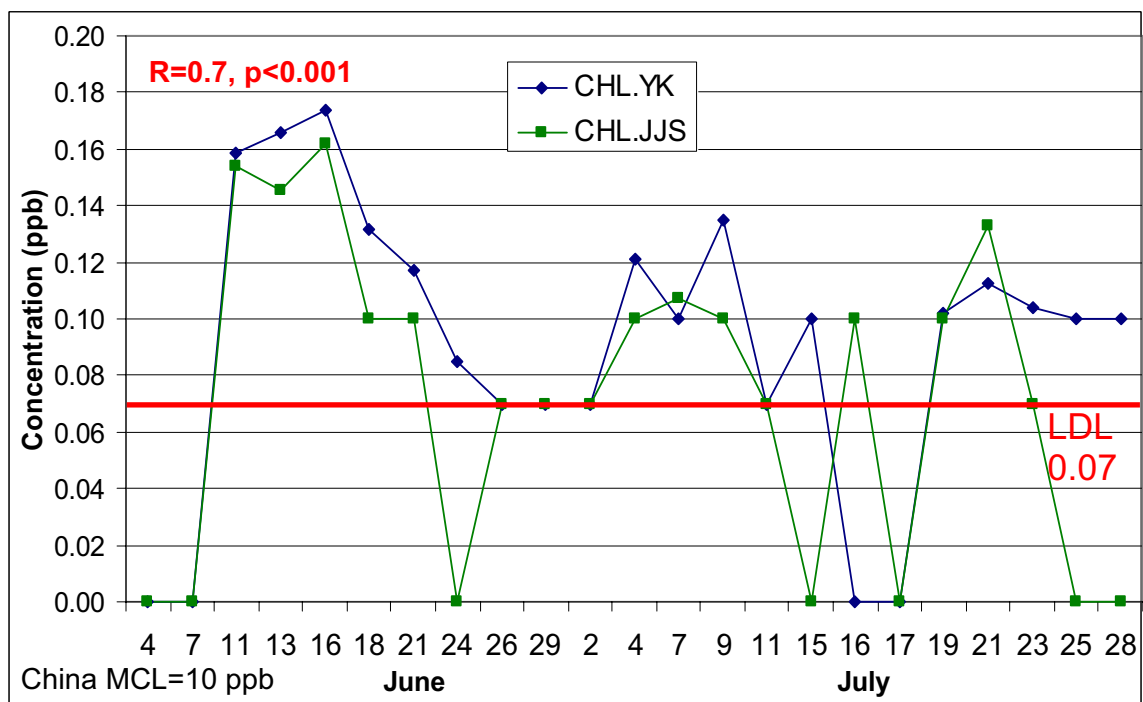


Figure 29. Chlorothalonil concentrations in water samples. LDL is the lower detection limit of the ELISA test. The R is the nonparametric correlation coefficient.

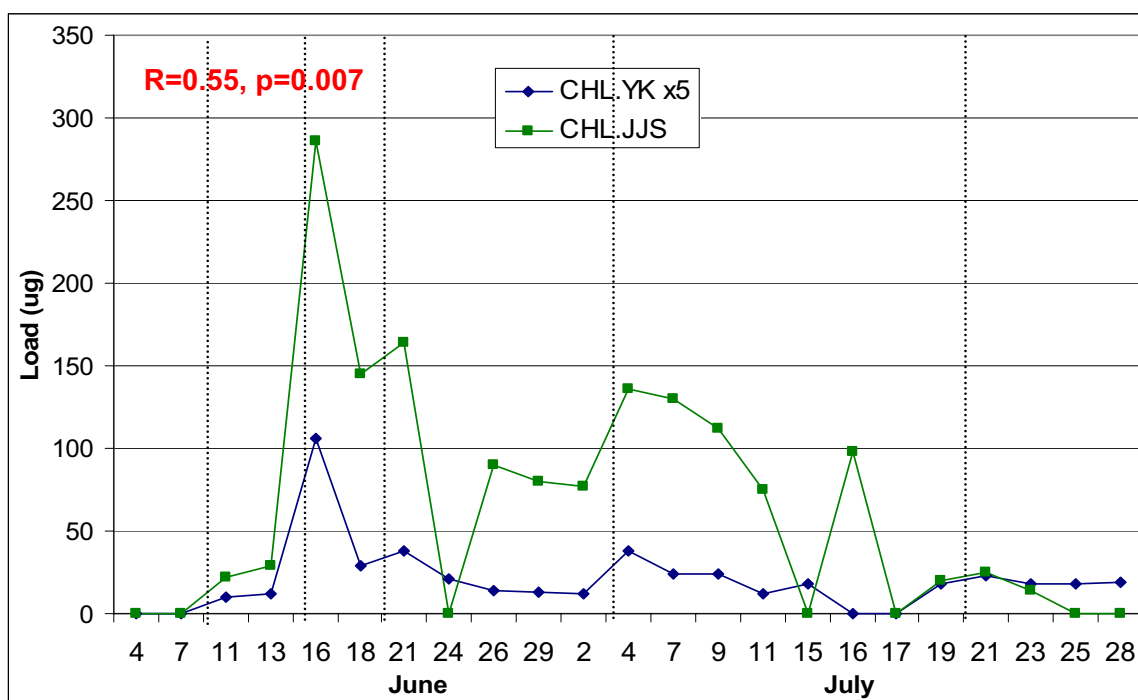


Figure 30. Chlorothalonil loads in water samples. The dotted line corresponds with rain events shown in Figures 18 and 19. The R is the nonparametric correlation coefficient and the p is the p-value representing the strength of the correlation test.

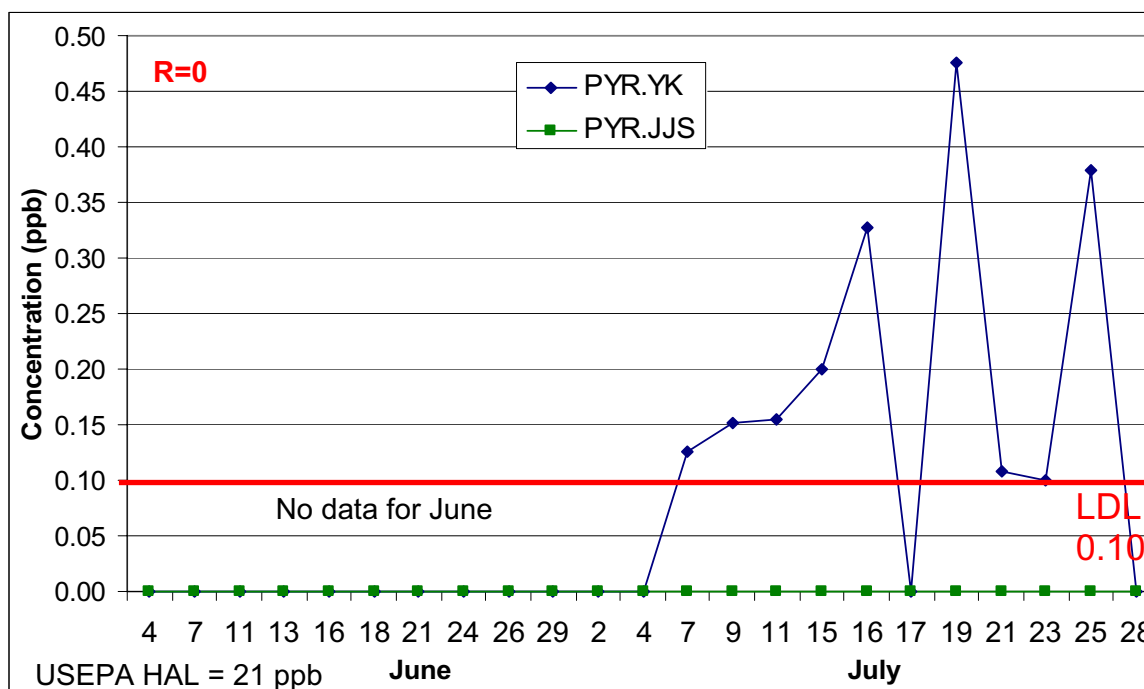


Figure 31. Chlorpyrifos concentrations in water samples. The R is the nonparametric correlation coefficient and the p is the p-value representing the strength of the correlation test. There were no tests conducted during June and there none found in JJS in July.

Table 8. Results of a nonparametric correlation test between the pesticide concentrations in samples at each site taken over the summer of 2008.

			ATR.JJS	ATR.YK	CHL.JJS	CHL.YK	GLY.JJS	GLY.YK	ST.JJS	ST.YK
Spearman's rho	Correlation Coefficient	ATR.JJS	1.000	.601**	.285	.178	.183	.513*	.200	-.170
		ATR.YK	.601*	1.000	.019	.141	.304	.399	.256	-.220
		CHL.JJS	.285	.019	1.000	.707**	.232	.191	.475*	.366
		CHL.YK	.178	.141	.707**	1.000	.265	.252	.542**	.475*
		GLY.JJS	.183	.304	.232	.265	1.000	.649**	.324	.331
		GLY.YK	.513*	.399	.191	.252	.649**	1.000	.188	.217
		ST.JJS	.200	.256	.475*	.542**	.324	.188	1.000	.272
		ST.YK	-.170	-.220	.366	.475*	.331	.217	.272	1.000

Table 9. Results of a nonparametric correlation test between the calculated pesticide loads during each sampling time at each site taken over the summer of 2008.

			ATR.JJS	ATR.YK	CHL.JJS	CHL.YK	GLY.JJS	GLY.YK	Q.JJS	Q.YK
Spearman's rho	Correlation Coefficient	ATR.JJS	1.000	.549**	.300	.039	.493*	.540**	.158	-.063
		ATR.YK	.549**	1.000	-.001	.075	.400	.480*	.175	-.119
		CHL.JJS	.300	-.001	1.000	.554**	.394	.413	.184	.600**
		CHL.YK	.039	.075	.554**	1.000	.479*	.624**	.290	.720**
		GLY.JJS	.493*	.400	.394	.479*	1.000	.602**	.262	.269
		GLY.YK	.540**	.480*	.413	.624**	.602**	1.000	.229	.321
		Q.JJS	.158	.175	.184	.290	.262	.229	1.000	.272
		Q.YK	-.063	-.119	.600**	.720**	.269	.321	.272	1.000

The complete data results of the testing are shown in Tables 10 and 11 along with the maximum, mean, standard deviation and results of chi-square tests for normal distribution of the data for each pesticide at each area and the stage or discharge. Some of the chi-square results showed a more normal distribution, most of the data of pesticide levels was not normally distributed. This also is obvious since it is not a random distribution of data, but organization by time. The sample size also indicates whether statistical tests for normally distributed data should be used. The sample size was only 23, short of a usual lower limit of 25-30 for the sample size to be appropriate for tests used under the assumption of normally distributed data. Therefore nonparametric statistical tests were used for all analyses.

Tables 10 and 11 also show the percent differences in concentrations of chlorothalonil, triazines and glyphosate for each day sampled, with the average for each shown in red. Any results of pesticide levels recorded as zero were not used for finding this average due to an inability for any proper difference to be found between a quantifiable variable and zero. The number of variables used out of the original 23 is listed as equal to n. The average percent difference of the concentrations over the months of June and July was less at JJS than YK by 31% (+/-10.8), 43% (+/-13.6), and 57% (+/-19.6) respectively. The difference in the average load over that time was greater at JJS than YK by 57% (+/-14.5), 53% (+/-11.5), and 32% (+/-17.0). The difference in the discharge over that time showed greater amounts at JJS than YK by 26% (+/-12.3).

Table 10. Pesticide concentrations and the percent difference between samples from each area. Max, mean, standard deviation and chi-squared tests for normality are also listed.

Date	CHL.YK	CHL.JJS	ATR.YK	ATR.JJS	GLY.YK	GLY.JJS	ST.YK	ST.JJS	CHL	ATR	GLY	ST
6/4	0	0	0	0.0500	0	0	0.0097	0.0577	--	--	--	200
6/7	0	0	0.1010	0	0	0	0.0160	0.1686	--	--	--	165
6/11	0.1587	0.1539	0.1037	0.1000	0	0.0002	0.0013	0.0637	3	4	--	192
6/13	0.1655	0.1453	0.1519	0.1081	0	0	0.0210	0.1157	13	34	--	138
6/16	0.1740	0.1620	0.1680	0.1220	0.6400	0.3810	0.6922	0.5691	7	32	51	20
6/18	0.1318	0.1000	0.1274	0.1000	0.3428	0.2463	0.1760	0.0884	27	24	33	66
6/21	0.1171	0.1000	0.1483	0.1175	0.3308	0.1282	0.0250	0.0796	16	23	88	104
6/24	0.1000	0	0	0	0	0	0.0475	0.0219	--	--	--	74
6/26	0.0700	0.0700	0	0.0500	0.1213	0.1000	0.0195	0.0164	0	--	19	17
6/29	0.0700	0.0700	0.0500	0.0500	0.1253	0.1210	0.0171	0.0168	0	0	4	2
7/2	0.0700	0.0700	0.0500	0	0	0	0.0679	0.0134	0	--	--	134
7/4	0.1214	0.1000	0	0	0.2205	0	0.1287	0.0507	19	--	--	87
7/7	0.1000	0.1075	0	0	0.2609	0.1800	0.0561	0.0288	7	--	37	64
7/9	0.1346	0.1000	0	0	0	0	0.0737	0.0195	29	--	--	116
7/11	0.0700	0.0700	0.0500	0	0	0	0.0042	0.0105	0	--	--	84
7/15	0.1000	0	0.1012	0.1129	0.4000	0	0.0048	0.0086	--	11	--	58
7/16	0	0.1000	0.1440	0.1157	0.3230	0	0.0096	0.0188	--	22	--	65
7/17	0	0	0.1812	0.1703	0.2140	0.1080	0.0070	0.0148	--	6	66	71
7/19	0.1018	0.1000	0.1000	0.0500	0.2360	0.1235	0.0079	0.4391	2	67	63	193
7/21	0.1125	0.1331	0	0.0500	0.2600	0.1350	0.0317	0.0481	17	--	63	41
7/23	0.1041	0.0700	0.1310	0.1009	0.5380	0.1040	0.0286	0.0618	39	26	++	73
7/25	0.1000	0	0.1663	0	0.1280	0.1280	0.0149	0.0243	--	--	0	48
7/28	0.1000	0	0.1438	0	0.3129	0.1770	0.0170	0.0220	--	--	55	25
Max	0.1740	0.1620	0.1812	0.1703	0.6400	0.3810	0.6922	0.5691	n=15	n=11	n=11	n=15
Mean	0.0914	0.0718	0.0834	0.0564	0.1936	0.0840	0.0642	0.0851	12	23	43	89
Stdev	0.0514	0.0548	0.0665	0.0544	0.1857	0.1001	0.1433	0.1392	12	19	28	58
X^2	0.2486	0.0174	0.0795	0.0010	0.0065	0	1	1	0.02	0	0.02	1

Table 11. Pesticide loads and the percent difference between samples from each area.

Date	CHL.YK	CHL.JJS	ATR.YK	ATR.JJS	GLY.YK	GLY.JJS	Q.YK	Q.JJS	CHL	ATR	GLY	Q
6/4	0	0	0	6.5	0	0	0.8	32.6	--	--	--	191
6/7	0	0	1.4	0	0	0	1.7	181.0	--	--	--	196
6/11	2.1	22.5	1.4	14.6	0	0.0	0.0	38.3	166	166	--	200
6/13	2.3	29.1	2.1	21.7	0	0	2.7	100.0	171	164	--	189
6/16	21.2	286.3	20.4	215.6	77.8	673.3	485.9	1111.6	172	165	159	78
6/18	5.7	144.8	5.5	144.8	14.9	356.7	76.0	65.0	185	185	184	15
6/21	7.7	163.6	9.7	192.2	21.6	209.7	3.6	54.9	182	181	163	175
6/24	4.3	0	0.0	0	0	0	10.1	6.6	--	--	--	42
6/26	2.8	89.7	0	64.1	4.8	128.2	2.4	4.1	188	--	186	53
6/29	2.5	80.3	1.8	57.4	4.5	138.8	1.9	4.3	188	188	187	76
7/2	2.5	77.0	1.8	0	0	0	17.8	3.0	188	--	--	143
7/4	7.6	135.9	0	0	13.9	0	47.7	26.4	179	--	--	58
7/7	4.7	130.0	0	0	12.4	217.5	13.2	10.4	186	--	179	24
7/9	4.7	111.7	0	0	0	0	20.3	5.5	184	--	--	115
7/11	2.4	74.9	1.7	0	0	0	0.2	2.0	187	--	--	164
7/15	3.5	0	3.5	116.2	14.0	0	0.2	1.4	--	188	--	143
7/16	0	98.1	5.1	113.5	11.5	0	0.8	5.2	--	183	--	149
7/17	0	0	6.4	166.6	7.5	105.7	0.4	3.5	--	185	173	154
7/19	3.6	20.4	3.6	10.2	8.4	25.2	0.5	767.7	140	97	100	200
7/21	4.5	25.3	0	9.5	10.5	25.7	5.3	24.2	139	--	84	128
7/23	3.6	13.5	4.5	19.5	18.6	20.1	4.5	36.4	116	125	8	156
7/25	3.5	0	5.8	0	4.5	23.7	1.5	7.9	--	--	136	135
7/28	3.9	0	5.6	0	12.1	31.3	1.9	6.7	--	--	88	111
Max	21.2	286.3	20.4	215.6	77.8	673.3	485.9	1111.6	n=15	n=11	n=12	n=15
Mean	4.0	65.4	3.5	50.1	10.3	85.0	30.4	108.6	171	166	137	126
Stdev	4.3	73.1	4.6	70.5	16.2	158.9	100.9	270.4	22	30	56	59
X^2	0.9844	0.1	0.4	0.0004	0.0065	0	1	1	0.54	0	0.15	1

In addition to correlation analysis of the pesticides, a nonparametric correlation analysis was done for all water parameter results along with the results of the concentrations and loads of the pesticides in YK and JJS. The value from water parameters used for the correlation comes from the mean of data over the 48 hour period prior to the sampling. The results of these correlation analyses are displayed in Table 12. These results show expected correlations between factors such as water temperature, specific conductance (EC), pH, and nitrate. But, some of these factors were not as closely correlated as expected. This may lend some insight into how well the time period chosen to represent the system fits with how the conditions are actually changing together.

Some other correlations that stand out in the analysis shown in Tables 8, 9, and 12 include: a correlation between the concentrations and loads of glyphosate and chlorothalonil at YK and JJS; a correlation between the concentrations and loads of glyphosate and triazines at YK and JJS; but there is no significant correlation between the concentrations and loads of chlorothalonil and triazines at YK and JJS. Another correlation is seen between the concentrations of triazines at YK and JJS and the concentration of nitrates at JJS, as well as specific conductance in general.

An ANOVA test basically tests two data sets to see if they are significantly different. This may not be too helpful since how similar two groups is the question of interest. But it can serve to support the results show by the correlation testing.

Instead, an ANCOVA test or analysis of covariance results should provide more valuable information about the data. ANCOVA results are shown in Table 15. In this case, these results can show how the data might represent the lag in correlated values due

Table 12. Spearman's correlation results between pesticide concentrations and loads and the mean of water parameters over the 48 hour period prior to the sampling. The CHL, ATR and GLY are the pesticides; the C=concentration, L=load, and NO3=Nitrate.

Correlation	Rainfall	Stage.YK	Temp.YK	EC.YK	pH.YK	C.CHL.YK	C.AT.R.YK	C.GLY.YK	L.CHL.YK	L.AT.R.YK	L.GLY.YK	Stage.JJS	Temp.JJS	EC.JJS	pH.JJS	NO3.JJS	C.CHL.JJS	C.AT.R.JJS	C.GLY.JJS	L.CHL.JJS	L.AT.R.JJS	L.GLY.JJS
Rainfall	1	0.122	-0.235	-0.339	-0.352	0.089	0.150	0.122	0.153	0.099	0.192	0.007	0.117	0.048	-0.032	0.019	0.109	0.217	-0.090	0.148	0.138	-0.120
Stage.YK	0.122	1	-0.609	-0.040	0.055	0.316	-0.149	0.357	0.771	0.062	0.454	0.816	-0.115	-0.725	-0.654	-0.051	0.333	-0.166	0.556	0.683	0.071	0.570
Temp.YK	-0.235	<b>-0.609</b>	1	-0.131	0.378	-0.040	0.262	0.034	-0.379	0.101	-0.110	-0.808	0.228	0.827	0.735	0.144	-0.156	0.106	-0.050	-0.575	-0.167	-0.224
EC.YK	-0.339	-0.040	-0.131	1	0.085	-0.292	-0.279	0.035	-0.097	-0.138	-0.028	0.274	-0.589	-0.416	-0.036	-0.738	-0.110	-0.070	-0.146	0.066	0.025	-0.111
pH.YK	-0.352	0.055	0.378	0.085	1	-0.177	-0.434	-0.087	0.009	-0.429	-0.094	-0.189	-0.217	0.135	0.374	-0.111	-0.148	-0.562	0.147	-0.157	-0.535	0.058
C.CHL.YK	0.089	0.316	-0.040	-0.292	-0.177	1	0.123	0.264	0.668	0.045	0.320	0.168	0.251	0.072	-0.358	0.397	0.753	0.145	0.287	0.485	0.109	0.240
C.AT.R.YK	0.150	-0.149	0.262	-0.279	<b>-0.434</b>	0.123	1	0.384	-0.158	0.911	0.300	-0.253	0.495	0.389	0.157	0.281	-0.063	0.616	0.294	-0.130	0.530	0.291
C.GLY.YK	0.122	0.357	0.034	0.035	-0.087	0.264	0.384	1	0.507	0.553	0.969	0.209	0.178	-0.140	-0.024	-0.039	0.137	0.483	0.649	0.275	0.541	0.569
L.CHL.YK	0.153	<b>0.771</b>	-0.379	-0.097	0.009	<b>0.668</b>	-0.158	<b>0.507</b>	1	0.038	0.601	0.562	0.043	-0.451	-0.435	0.051	0.421	-0.124	0.551	0.570	0.001	0.443
L.AT.R.YK	0.099	0.062	0.101	-0.138	<b>-0.429</b>	0.045	<b>0.911</b>	<b>0.553</b>	0.038	1	0.469	-0.032	0.406	0.124	0.091	0.091	-0.175	0.540	0.432	-0.054	0.541	0.403
L.GLY.YK	0.192	<b>0.454</b>	-0.110	-0.028	-0.094	0.320	0.300	<b>0.969</b>	<b>0.601</b>	<b>0.469</b>	1	0.316	0.134	-0.238	-0.140	-0.025	0.197	0.439	0.643	0.404	0.524	0.603
Stage.JJS	0.007	<b>0.816</b>	<b>-0.808</b>	0.274	-0.189	0.168	-0.253	0.209	<b>0.562</b>	-0.032	0.316	1	-0.285	-0.929	-0.839	-0.289	0.253	-0.048	0.222	0.696	0.213	0.362
Temp.JJS	0.117	-0.115	0.228	<b>-0.589</b>	-0.217	0.251	<b>0.495</b>	0.178	0.043	0.406	0.134	-0.285	1	0.370	0.304	0.531	-0.063	0.286	0.280	-0.312	0.219	0.170
EC.JJS	0.048	<b>-0.725</b>	<b>0.827</b>	<b>-0.416</b>	0.135	0.072	0.389	-0.140	<b>-0.451</b>	0.124	-0.238	<b>-0.929</b>	0.370	1	0.692	0.425	-0.055	0.173	-0.149	-0.564	-0.103	-0.278
pH.JJS	-0.032	<b>-0.654</b>	<b>0.735</b>	-0.036	0.374	-0.358	0.157	-0.024	<b>-0.435</b>	0.091	-0.140	<b>-0.839</b>	0.304	<b>0.692</b>	1	-0.079	-0.495	-0.064	-0.107	-0.767	-0.254	-0.299
NO3.JJS	0.019	-0.051	0.144	<b>-0.738</b>	-0.111	0.397	0.281	-0.039	0.051	0.091	-0.025	-0.289	<b>0.531</b>	<b>0.425</b>	-0.079	1	0.357	0.177	0.373	0.032	0.125	0.365
C.CHL.JJS	0.109	0.333	-0.156	-0.110	-0.148	<b>0.753</b>	-0.063	0.137	<b>0.421</b>	-0.175	0.197	0.253	-0.063	-0.055	<b>-0.495</b>	0.357	1	0.209	0.240	0.725	0.203	0.287
C.AT.R.JJS	0.217	-0.166	0.106	-0.070	<b>-0.562</b>	0.145	<b>0.616</b>	<b>0.483</b>	-0.124	<b>0.540</b>	<b>0.439</b>	-0.048	0.286	0.173	-0.064	0.177	0.209	1	0.153	0.082	0.922	0.291
C.GLY.JJS	-0.090	<b>0.556</b>	-0.050	-0.146	0.147	0.287	0.294	<b>0.649</b>	<b>0.551</b>	<b>0.432</b>	<b>0.643</b>	0.222	0.280	-0.149	-0.107	0.373	0.240	0.153	1	0.295	0.301	0.919
L.CHL.JJS	0.148	<b>0.683</b>	<b>-0.575</b>	0.066	-0.157	<b>0.485</b>	-0.130	0.275	<b>0.570</b>	-0.054	0.404	<b>0.696</b>	-0.312	<b>-0.564</b>	<b>-0.767</b>	0.032	<b>0.725</b>	0.082	0.295	1	0.264	0.408
L.AT.R.JJS	0.138	0.071	-0.167	0.025	<b>-0.535</b>	0.109	<b>0.530</b>	<b>0.541</b>	0.001	<b>0.541</b>	<b>0.524</b>	0.213	0.219	-0.103	-0.254	0.125	0.203	<b>0.922</b>	0.301	0.264	1	0.480
L.GLY.JJS	-0.120	<b>0.570</b>	-0.224	-0.111	0.058	0.240	0.291	<b>0.569</b>	<b>0.443</b>	<b>0.403</b>	<b>0.603</b>	0.362	0.170	-0.278	-0.299	0.365	0.287	0.291	<b>0.919</b>	<b>0.408</b>	<b>0.480</b>	1

<<Table 14. Pesticide-location non-parametric ANOVA results of concentrations and loads.

ANOVA	CHL	ATR	GLY
Conc.	YK vs. JJS	0.0145	0.0318
Load	YK vs. JJS	0.0006	0.0028

Table 15. ANCOVA results between pesticides.

Cov.	CHL.YK	CHL.JJS	ATR.YK	ATR.JJS	GLY.YK	GLY.JJS
CHL.YK		0.00253				
CHL.JJS	0.001744					
ATR.YK	0.000281	-3.8E-05	0.004232			
ATR.JJS	0.000211	0.00086	0.001946	0.002902		
GLY.YK	0.002382	0.002032	0.005272	0.004944	0.032977	
GLY.JJS	0.001787	0.001429	0.002245	0.001418	0.012429	0.009593

<<Table 13. Pesticide-stage non-parametric ANOVA results of concentrations and a value representing the stage over the previous 48 hour period. ST=Stage, C=concentration, and L=load.

ANOVA	ST.YK	ST.JJS
C.CHL.YK	0.014	<0.001
C.AT.R.YK	<b>0.117</b>	<0.001
C.GLY.YK	0.033	<0.001
L.CHL.YK	<0.001	<0.001
L.AT.R.YK	<0.001	<0.001
L.GLY.YK	0.002	0.002
C.CHL.JJS	0.003	<0.001
C.AT.R.JJS	0.002	<0.001
C.GLY.JJS	<b>0.78</b>	<0.001
L.CHL.JJS	0.001	<0.001
L.AT.R.JJS	0.002	0.002
L.GLY.JJS	0.029	0.029



to travel time through the QSRS. An interesting point is that even though it takes at least 24-48 hours for flows to reach JJS from YK, similar correlations done between selected samples offset by 2 days of collection timing still showed that the samples were not significantly correlated like the samples taken from the same day were.

### 5.5. Sampling Quality Control

As a control that the data was an accurate representation of the pesticide levels in the QSRS, some additional samples from the areas were retrieved over even intervals throughout the summer and also analyzed for pesticides. Six samples were taken from a canal draining a number of rice fields further up in the YK valley which exits the valley at a different location than the YK sinking stream. These were mostly very similar to the samples taken in YK for each day. This suggests that the flow leading into the YK sinking stream is a good representation of the pesticide level in runoff throughout the YK valley.

Three samples were taken over the summer from the karst window (Figure 20) just upstream from JJS and they were all quite similar to the same levels as the samples taken from JJS that day. This shows that the results from JJS were reliably accurate and lends support to the notion that photolytic effects may not play an important role in the breakdown of these pesticides.

Three samples were taken from the small flow going into DMSW, including one just after the 15 June storm. These were all below the detection limits of the tests, except for a sample following 15 June, which showed a result only for triazines at 0.11 ppb. This may indicate triazines have been used around the DMSW valley.

## CHAPTER 6. DISCUSSION

### 6.1. Background

2007 was a very wet year with a 100 year flood in the area that season, while 2008 was an unusually dry year in QMG. There were five main rain events over the summer season of 2008 (indicated by vertical dotted lines in Figures 18, 19, 25, 27, and 29) which had a noticeable effect on temperature and other factors regardless of whether the stage was greatly affected. The stage was low at both locations for this time of year until the large rain event on 15 June when there was a very significant increase in both locations. YK returned to levels only slightly higher than before the rain event within a few days, while the stage at JJS went down much slower and was amplified by the rain event of 19 June. This reflects that inflow from through the basin is directed to JJS. The cause of the sharp drop in stage at JJS on 15 July is unknown, but the time between the two very different readings was 15 hours and a significant reduction in the stage level from the previous day was observed during sampling on 16 July. It may have been that they released some flow from the underground spillway just upstream of the karst window for water for irrigation of the crops growing upstream from the spring.

Figures 18 and 19 show that the specific conductance was much more variable at YK, as is expected with lower discharge, and it went down significantly in both locations with the increased discharge on 15 June reflecting more dilution of total dissolved solids. As the water levels at both locations got very low toward the end of July there was a resulting increase in variability of water temperature, specific conductance (EC), and

pH at JJS. This is attributed to greater resolution of response to factors influencing these parameters when higher flows are drowning out the concentration signals. At YK at the end of July the water was almost gone, which is why the specific conductance dropped, the temperature and pH increased, and then the pH dropped sharply as the recording channel began to dry.

The concentration of nitrate reached high levels in response to small rain events prior to 15 June due to a greater response when the discharge still stays relatively low. But, during the 3 July rain event there was less rain over a longer time resulting in a more even change in discharge that closely follows the change in nitrate concentration at JJS. The water temperature at JJS showed a sharp drop as the discharge jumped much higher and then shifted to a much higher level than before the initial drop and then went down again as the next rain event came a few days later. The large fluctuation in temperature reflected the initial rainfall and then more surface runoff arriving at JJS soon thereafter.

## 6.2. Hydrogeology

The primary fluvial feature of interest in QMG was JJS because it affects the quality of one of the water supplies for the city of Qingmuguan and is a source of drinking water for approximately 500 local residents. Based on the dye traces conducted in the fall of 2007, and after consideration of the nature of the items in the hydrogeologic inventory, it was determined that the primary features in QMG that supply water flows to JJS were YK and, during large storms, DMSW (Figure 3). During large storm events the valley at DMSW floods and then drains rapidly into the swallet connected to JJS. Consequently there is extra high discharge observed at JJS until this valley is drained.

Because this valley floods often in the rainy season no crops are usually grown in it. However, corn is grown on the slopes surrounding the valley which may allow pesticides to runoff to the DMSW swallet.

Continuous data of the results of the dye traces were collected that showed the fluvial connections between JSS, DMSW and YK. This allowed for further understanding about the transport speed and nature of the conduit in the QSRS. The second dye trace took longer to reach JSS even though the dye was injected closer in the groundwater basin to JSS. This may have been due to less rain and resulting in runoff during the second dye trace compared to the first. Another explanation could be that the flow coming from DMSW is not normally as strong or direct, or that the conduit and channel gradients are less at the DMSW input (Figure 5). In the case of both dye traces, the single strong peak of the breakthrough curve (Figure 22) suggests that a well-developed and connected conduit system exists for underground flow in a direct conduit path between the locations in the QSRS. The results also suggest that transport time is rapid, especially during higher flows.

The small springs draining into different small valleys in QMG from the adjacent slopes (Figure 24) are likely fed from runoff from the steep sandstone slopes above. During storm events it is likely that these springs and other runoff sources drain into associated sinkholes that may lead into the QSRS. If this is the case then there may not be any significant input into the QSRS coming from these valleys except after large storm events. This situation would lead to a strong dilution effect on the movement of contaminants into the QSRS from these sources. Also, none of the flow paths of these

springs pass through any large agricultural areas so there may not be a significant contaminant load coming into the QSRS from these sources either.

### 6.3. Water Chemistry

The water samples that were taken at JJS between March and July of 2007 represent a good overview of water conditions over the monsoon season in QMG (Figure 9). Rainfall and discharge data are not available from this time, but data from September 2007 and April 2008 (Figure 29) indicate that sudden shifts in ion concentrations and EC (spc) shortly follow an increase in rain (Yang 2008). This should lead to an increase in soluble ions in runoff and a decrease in ions dominant during baseflow conditions as they become diluted by the higher flows (Liu et al. 2004, Nakanoa et al. 2004a).

$\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_4^+$  changed regularly corresponding to impacts from human activities, i.e. higher nitrates during fertilization and higher  $\text{Cl}^-$  near residential areas. Sulfate and chloride decreased as the runoff increased when the rainy season came. Nitrate levels at JJS during this time reached as high as 50 ppm  $\text{NO}_3^-$  and never dropped below 20 ppm. Levels were lower in YK; usually less than 3 ppm (He 2008). The MCL is 10 ppm for the nitrogen part of nitrate's level in drinking water ( $\text{NO}_3^-$ -N), or 44.3 ppm  $\text{NO}_3^-$ , which is how it is reported in this data (MEP 2002, USEPA 2008). High nitrate levels are largely influenced by inputs of irrigation water in agricultural areas (Almasri and Kaluarachchi 2007). The high nitrate levels at JJS also suggest surface runoff is its main source instead of stored groundwater, unless that the groundwater is contaminated with nitrates. This data also suggests that YK is not a primary source of nitrates to JJS and large amounts of fertilizers may not be used in the area. Once nitrates levels are high

from leaching in higher flows, an increase in nitrate occurs when discharge decreases during drier conditions leading to concentrating of the ion. This is due to the nature of karst systems. In surface streams with vegetation interactions nitrate is taken up by plants in slower and lower flow periods (Hill 1981).

Water chemistry results from these 2007 samples showed that sulfate was quite high, which is likely impacted by the coal mine near the underground river. Because the mine is upriver, the content of sulfate decreased from upriver to downstream but the chloride increased as more sewage was added from farmers throughout the watershed. Nitrates and ammonium were also affected by the runoff and agriculture. There were two peaks in the nitrate corresponding to runoff decreasing in the dry season and a larger corresponding to fertilization by local farmers, which here included also a prominent increase in ammonium. In addition to pesticide levels that that were focused on in the study, this study expresses that these ions are important to consider in assessing water quality in QMG and how these ions may also be related to the transport of pesticides in the area (He 2008, Yuan 1990).

The water samples taken in July 2007 showed high nitrate levels at JJS, but not at YK. As mentioned, this could suggest a strong input of agricultural runoff from another location in QMG draining into the QSRS. The nitrate data collected bimonthly in 2007 supports that the large difference in levels between YK and JJS was not just isolated to the July 2007 data collected during this study, but that nitrate at JJS is often high, with levels sometimes approaching or even exceeding China's MCL (MEP 2002). The data from early 2007 also show an increase in nitrate coinciding with a decrease in calcium and bicarbonate (He 2008). This indicates that, during initial high flow pulses in spring

when fertilizers are being applied, the nitrates are easily transported to JJS leading to high concentrations in the spring (Jiang 2006). It then follows that other compounds such as pesticides that are normally applied during the springtime can become concentrated at JJS in high flows. The sudden shifts in ion concentrations and specific conductance in late May and early June seem to signal an increase in rain. This could lead to leaching of these compounds from the soil into the streamflow. The reduction in overall ion concentrations in mid-June likely indicates a great increase in rain and the resulting runoff going into streams during the strongest part of the monsoon season. The higher discharge would dilute the representation of these ions in the concentrations reported. The increase in nitrate and particularly nitrite in samples taken on 19 June contrasted with the decrease in specific conductance and other ions may be a cause for water quality concerns. If other ions are diluted and the concentrations of nitrate and nitrite remain high then there must be more of these in the system to transport and the flows may be too great for them to be used up by biological and chemical processes. An assessment of the microbial activity in the area soils is not yet available, but this information should provide some valuable insight into what types of processes are significant in leading to the breakdown of pollutants.

JJS could have also received a strong pulse from storm events 1-2 days prior to some of the sampling which could explain some of the high levels. Data logger records will need to be obtained to address this. Alternatively, this may have come from DMSW since it was often flooded during the season, but it is likely that there are a few other discrete inputs to the QSRS near agricultural field sites in QMG that were not located. Triazines were recorded in YK but not in JJS could indicate processes are breaking down

pesticides along the length of the QSRS. Corn is grown most prominently in the YK valley, so not many triazines are likely used in the areas of additional agricultural water input throughout the basin. So, if the discharge is much higher at JJS than at YK, which suggests more input from throughout the basin, then the concentration would be too dilute to quantify. Yet, considering that the QSRS flows through a substantial conduit, it may be during the initial runoff pulse from YK to JJS that pesticide loads could be a concern.

The potential for groundwater contamination and the persistence of compounds in the environment depends on their water solubility, soil adsorption, potential for breakdown in water based on the hydrolysis half-life of the compound, and potential for breakdown in soil based on its aerobic and anaerobic soil half-life (Tables 1 and 6). These properties can also be affected by the interacting conditions, such as changes in pH or oxygen availability.

Turbidity is also high during high discharge pulses (Figures 8 and 10) As seen in Figures 18 and 19, levels observed at JJS are usually twice that of YK, even though the discharge is three times greater on average (also Figures 7, 15, and 31) (Yang 2008, Malmon et al. 2002).

So, for example, even though glyphosate is quickly adsorbed and retained on soils, under the conditions of high discharge and direct conduit flow, glyphosate could easily be transported to JJS at levels close to the same as that of concentrations found in the area of application at YK. This would hold true whether it was dissolved in the discharge or adsorbed to the sediment in the water column. Glyphosate is not a significant human health threat partly because it is rapidly excreted from the body. But



this scenario just as easily applies to pesticides or other compounds with similar behavior in the environment that may be a health concern. This is especially true since the sediments are not filtered by any water treatment facilities or other means in QMG before human consumption.

In considering these factors there is still cause for concern over possible pollution of the JJS water during the early monsoon season (Chena et al. 2005, Liu Z et al. 2007). High nitrate likely comes from fertilizers used by local farmers. If the nitrate is so high this could signify that pesticides applied during this time that can also readily be transported in surface water can contaminate the water also. Still, there could be less cause for concern from pesticide contamination in some cases. Whereas all agricultural areas likely apply chemical fertilizers, only certain areas or farmers apply certain pesticides. This could keep any one product from reaching too high of a load, although not rule out possible compounding pesticide combinations. Again, there is also the factor of dilution from other non-agricultural inputs along the length of the basin. But, for example, if many farmers are applying glyphosate at the same time before the planting season to clear out grasses for rice field access then, given the nature of the karst conduit system, high levels of glyphosate or many other pesticides could certainly become concentrated at dangerous levels in JJS (Li and Zhang 1999, Li et al. 2002).

The chemical oxygen demand is much higher in YK than in JJS judging from water samples collected in July 2007 for this study (Table 6), which goes along with the same data set showing higher total organic carbon. That is because these are both associated with more microbial activity and interaction with the water system. Microbial data is not yet available for QMG, but the water chemistry results show that there were

strong pulses of water going through the system. Specific conductance is correlated with discharge, as evidenced in Table 12. More contaminants can be transported by these large discharge pulses and would likely be represented in the initial flow increase as contaminants are initially dissolved into runoff and transported through the system. Also, the higher amounts of sediment in the water in these conditions could encourage higher microbial interaction with compounds adsorbed to these sediments and a reduction in contaminants loads (Zhang et al. 2006). But, the high turbulent flows could also suggest that there could be low microbial interaction due to the harsh environment. This could also lead to a lower amount of sediment remaining in the QSRS as it is flushed out by the high flows. Hence, the conduit system may not retain effective amounts of sediment with its associated nutrients to support comparatively high microbial interactions with the contents of the water (Reneauk et al. 2004, Hilscherova et al. 2007). If there was low water interaction with microbial processes in subsurface conduits following high flow events, then there should not be as much biological breakdown of contaminants entering the system. Microbial processes are a major factor in the breakdown of contaminants (Van Eerd et al. 2003). This condition could lead to a diminished capacity for natural processes to ameliorate contaminant problems in karst systems.

Judging from discharge observations, dye trace results, and other data collected by colleagues, there are high pulses of water traveling through a main conduit in the QSRS at a rapid rate. As discharge rises within a few hours of initial storm events, specific conductance, and CO<sub>2</sub> partial pressure promptly go up in response and pH goes down (Figure 10). This indicates surface runoff coming into the spring as the water interacts with the silicate slopes. Water temperature gets continuously lower over time,

especially over repeated events. This may suggest that there is significant recharge to groundwater sources connected to the spring (Yang 2008, Li et al. 2005).

#### 6.4. Pesticide Levels

A number of possible health effects are associated with the different compounds listed in Table 7, as well as potential groundwater contaminants in a few cases. The pesticides which were mentioned by farmers as the primary ones used in QMG were given special attention in considering testing for pesticides in the QSRS. After reviewing the other pesticides used in the area, their properties were considered and the ones which had the strongest potential for groundwater contamination and/or human health effects were next given special consideration for testing. But, in the end the decision of which pesticide to test for came down to which ones had test kits available for the method that was an option for the available analytical resources.

Since the logger data was continuous every 15 minutes and the pesticide samples are only for once a day 2 or 3 days a week over the summer, in order to get an idea of how water conditions may have affected the pesticide levels, a single value assessment for each day was the best way to make the comparisons. In determining a figure to represent what the conditions in YK and JJS were prior to the sampling dates, the mean and sum of the data over 48, 24, 12, and 4 hour time periods were calculated. Each of these were also related through how much they have been fluctuating over that time period by dividing them by their standard deviations. Additionally, for each of the relationships an idea of what direction they were changing over that time period was assessed by subtracting the particular time interval by the previous time interval. The

strength of each of these models was then reviewed by comparing the correlation results. In the end, the best model that represented the water condition changes prior to the sampling and the possible effects of this on pesticide levels was simply that of the mean over the period of 48 hours prior to the pesticide sampling for each day sampled in June and July.

These analyses provided significant correlation values between the pesticide levels at each location. The additional correlation observed between glyphosate and chlorothalonil at YK is likely a factor influenced by how much runoff is coming into YK. In this instance, both would be well represented in the flow from the fields because of the low flows at YK that respond clearly to inputs of compounds from agricultural runoff. Whereas, triazines may not have been applied this year and the signal showing up at the time is coming from what may already be in the groundwater or coming from runoff input at other locations in QMG. The strongest correlation was between discharge at YK and chlorothalonil at YK, which may be an indicator that chlorothalonil is the compound coming in from runoff the most of those tested, which seems unexpected since it has the lowest water solubility of the pesticides tested. Perhaps it is effectively transported undissolved in runoff and water sampling is able to detect it in this form.

Even though there was only one major storm event during sampling period, in conditions of low flow and reduced transport through the QSRs, ELISA tests still showed a noticeable response in pesticide concentrations in water samples at both locations around 15 June as well as around the other smaller storm events. Otherwise, during baseline flow conditions there was somewhat random fluctuation in pesticide concentrations in the water at the locations. Yet, even under low flow conditions the

concentrations of the pesticides found at JJS were quite similar to those found at YK and reflected aspects of hydrology and water chemistry changes observed over the 2008 summer season.

The average percent differences reported in Tables 10 and 11 can be related to data on the percent reduction in pesticide levels reported in vegetated surface streams. Such a comparison suggests that differences in levels of the pesticides studied in the QSRS are only slightly higher than would be expected in a surface stream. The results reported from most studies are not at such a great distance along streams from sampling points, but usually report reduction in pesticide levels over a greater time, usually 15 days. How these counterbalancing effects of time and space may impinge upon comparisons of this study data to data from surface stream studies is unknown. Studies showed that, especially at slower flows, vegetation and soils along stream lengths are the strongest factors in the reduction of contaminants in runoff (Briggs et al. 1998, Di et al. 1998, Kadlec et al 1994, Reichenberger et al. 2007, Iwakuma et al. 1993, Capel et al. 2001, Patty et al. 1997, Syversen and Bechmann 2004).

## 7. CONCLUSIONS AND FUTURE DIRECTIONS

All pesticide concentrations in the samples taken were well below the Maximum Contaminant Levels (MCL) and Health Advisory Levels (HAL) used in the United States and China (MEP 2002, USEPA 2008). The pesticide levels observed were mostly taken during low flow conditions. The results of this study support the hypothesis that the pesticide levels in YK and JJS are similar and there is not a significant reduction in levels from YK to JJS. Regarding how DMSW inputs may have affected the pesticide levels in JJS, there were not many detectable levels of the pesticides found in DMSW to use for comparison. There was only one storm event large enough to flood the DMSW valley and send a considerable amount of water into the sinkhole over a short period. While this flooding certainly affected the water parameter at JJS, results of pesticide sampling following the storm event suggest that DMSW is not a significant contributor to pesticide levels at JJS. Still, results of pesticide loads in JJS show that there are certainly other sources of pesticides going into the QSRS. The other inputs are more than likely nonpoint source in origin.

Regardless of load calculations, in this case under low flow conditions, there is little call for concern over high levels of pesticides coming out of JJS, even though there are excessive nitrates found in JJS during high discharge events. The average percent difference in the concentrations of chlorothalonil, triazines and glyphosate were calculated as JJS less than YK by 31, 43, and 57% respectively. The variations in the levels of pesticides, the number of samples that had a pesticide value of zero,

and the numerous factors that influence uncertainty in an environmental system all make it difficult to strongly claim that these differences are actually significant.

Based on the studies reviewed, it is also difficult to say that pesticide concentration differences between YK and JJS are less than in surface streams. But, based on the data addressed in this study, it is certainly reasonable to claim that in low flow conditions the pesticide levels from YK to JJS are not more reduced than in surface streams over a similar distance and time.

Even though the samples had rather low levels of the pesticides in them and were reduced noticeably between YK and JJS, there could still be cause for health concerns from drinking the water from this spring without proper treatment. This is because the levels are expected to be much higher during application periods and significant rain events. Karst systems are sensitive to water pollution with lower mitigating effects, especially in the well-developed systems of SW China (Yuan et al. 1990). Discharge observations, the dye traces, water chemistry, and sediment data all indicate that a well-developed conduit connects the YK and JJS and that DMSW drains directly into the QSRS. Based on this information and additional QMG water data collected in 2007, perhaps other inferences can be made in the future from this data about possible high pesticide loads in JJS. Until then, continuing this work will involve sampling pesticides in QMG water resources under a broader range of seasonal and hydrologic conditions over the length of a whole year. Sampling more closely coordinated with the farmers' application schedule and more sampling done surrounding storm events will serve to provide a better understanding of the levels of pesticides in QMG and how they are related to various water conditions. Yet, from the results it seems that higher pesticide

concentrations are apparent during high discharge levels, especially when a strong pulse is delivered over a short time. Of course one thing to mention is that even though karst fluvial systems can carry contaminants to springs very quickly and efficiently, this also means that if the source of these contaminants are remediated or eliminated then the system will likely quickly pass these contaminants on through and out of the system. This would be given that the system has low interaction and recharge from storage groundwater sources.

Data from these results will be used for further studies aimed at modeling of the transport of agricultural runoff in the system using the correlated water parameters addressed here, along with further data on the hydrology and transport of compounds in the system throughout the year. Detailed land-use data was collected during the field work of this study and continues on with graduate student work at SWU through 2009 and longer. Factors from this land-use analysis, knowledge of the hydrology and geology of QMG, and the inclusion of data of soil microbial activity, will all come together as factors included in this model. Such a model should allow for assessing the conditions in similar karst areas that will be cause for concern from negative human health or ecological impacts from agricultural or other land-use. (Kang and Lin 2007, Li et al. 2002 Nakano et al. 2004 a and b, Han et al. 2006, Hao et al. 2006, Barfield et al. 2004).

USAID work that supports this research has provided an opportunity for some of the best karst scientists in the world to come together in addressing the particular environmental and social issues affecting citizens in SW China (Figure 32).





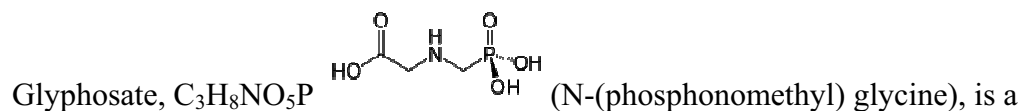
Figure 32. Will White, Yuan Daoxian, and Nico Goldscheider discuss karst issues while observing conditions at the YK gaging station. The difference in the normal discharge from JJS can be seen here when comparing Figure 15.

No researchers or agencies are known to have monitored the pesticide levels in the QMG water prior to this study. WKU academic partners at SWU have recently expanded their laboratories with more analytical instruments to accurately test for a number of geochemical parameters and pesticides. The Chinese government has shown increased interest in recent years in lowering national pollution and raising the quality of life for all of their people (Reuters 2007, Turner and Osutku 2006, Xinhua 2007, WRI 2007, AEC 2006). Research such as this provides support for these efforts to continue. Collaboration with our Chinese colleagues on karst scientific methods (Figure 30) has brought closer attention of local researchers to the special concerns dealing with impacts from excessive agricultural chemical usage in karst regions. During the summer of 2008 visiting specialists from another collaborating university in China also came to the field

site to collect samples for a broad-spectrum analysis of the pesticides found in a number of water resources in QMG. Recent efforts by local researchers to focus on land-use issues in China and to expand the scope of science being conducted in the SW China karst region have been quite successful.

## APPENDIX

### Extended Details of Study Pesticides



broad-spectrum, nonselective, systemic herbicide used to control annual and perennial plants including grasses, sedges, broad-leaved weeds, and woody plants. It can be absorbed through the leaves, injected into the bole, or applied to the stump of a tree as a forestry herbicide. It can be used on many different crops and in non-croplands.

Glyphosate itself is an acid, but it is commonly used in salt form and is supplied in several formulations in its acid form or as salts for different uses. It is usually sold as water-soluble concentrates and powders. By volume, it is one of the most widely used herbicides in the U.S. and the world. Application rates of  $3 \text{ L ha}^{-1}$  are most common for the control of annual weeds infecting crops. Glyphosate kills plants by interfering with the synthesis of amino acids. This comes through inhibiting an enzyme that leads to the formation of amino acids. Glyphosate was first sold by Monsanto in a product called Roundup, but it is no longer under patent. Glyphosate is a colorless crystal at room temperature. Its water solubility is  $12,000 \text{ mg L}^{-1}$  at  $25^\circ\text{C}$ , its adsorption coefficient is estimated at 24,000, while its vapor pressure is negligible. Its USEPA Maximum Contaminant Level (MCL) is  $700 \text{ mg L}^{-1}$  (EXTOXNET 1996, USEPA 2006).

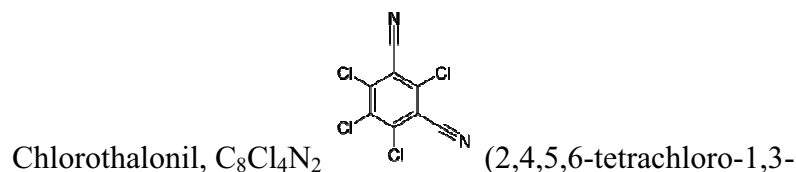
Even though glyphosate is highly soluble in water it does not leach appreciably and has low runoff potential. This is because it is very strongly adsorbed to most soils, including those with lower organic and clay content. So, unless large amounts of colloidal

material are carried in runoff it will not be very mobile. Glyphosate is moderately persistent in soil with a 47 day estimated half-life under many conditions, while field half-lives have been reported between 1 to 174 days under various conditions. Microbes mostly break it down in soil and water, while volatilization or photodegradation losses are negligible. Its half-life in pond water is 12 days to 10 weeks. It is broken down to a great extent by some plants but not others (de Andréa et al. 2003).

Some microorganisms are resistant to glyphosate inhibition. A strain of these was used to genetically modify crops such as soybeans to seed products known as Roundup Ready. 87% of U.S. soybean fields were planted with glyphosate resistant varieties in 2005. Roundup Ready crop use has reduced the use of some other herbicides such as atrazine, which has reduced dangers of herbicide runoff into drinking water. (USDA/APHIS, NASS 2005, Shipitalo et al. 2008).

Glyphosate acid and its salts are moderately toxic compounds. It is not toxic by ingestion and skin exposure, but in some forms it may have high acute inhalation toxicity. Testing of glyphosate has shown little to no organ toxicity and chronic toxicity. It also shows no mutagenic, teratogenic, carcinogenic effects and animal testing has suggested that is unlikely it would have reproductive effects in humans. Glyphosate does not have significant potential to accumulate in animal tissue; it is not absorbed well in the digestive tract and is mostly excreted unchanged. Some formulations have different effects on organisms because of the additional ingredients, but the acid form of glyphosate is not toxic to fish and honeybees, though it is slightly toxic to wild birds and aquatic invertebrates. There is a very low potential for it to bioaccumulate in the tissues of aquatic organisms. Some studies indicate certain glyphosate formulations could harm

earthworms and beneficial insects (Hassan 1991, EXTTOXNET 1996). A 2000 review of the literature said that "there is no potential for Roundup herbicide to pose a health risk to humans." This included possible high exposure groups such as herbicide applicators and children aged 1-6 (USEPA 1993, Williams 2000). Some studies classify glyphosate as an endocrine disruptor, which inhibits proper development and regulation of the body. In vitro studies have shown that glyphosate affects progesterone production in the cells of mammals and can increase the mortality of placental cells. This has been debated as sufficient evidence that it is an endocrine disruptor since a change in a single cell line may not occur in an entire organism and because in vitro studies involve concentrations much greater than would be found in real conditions and through pathways that organisms don't actually use (Walsh et al. 2000, Richard et al. 2005).

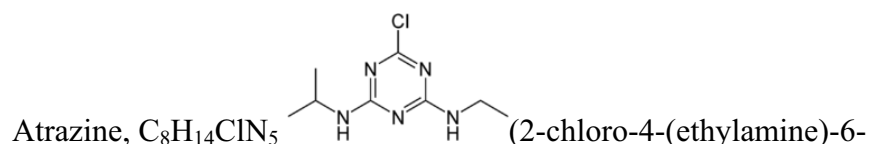


benzenedicarbonitrile), is also known as tetrachloroisophthalonitrile and international products that contain it include Bravo, Echo, and Daconil. It is a broad spectrum, non-systemic organochlorine fungicide used for vegetables, trees, small fruits, turf, ornamentals, and other agricultural crops. In the U.S., chlorothalonil is used mostly on peanuts, potatoes, cranberries, and tomatoes. In 1997 it was the third most used fungicide in the U.S., behind only sulfur and copper, with some 12 million pounds used in agriculture alone that year. Including non-agricultural uses, the USEPA estimates that on average almost 15 million pounds were used in the U.S. annually from 1990-1996. Chlorothalonil is moderately toxic and causes severe eye irritation. Chlorothalonil is an

aromatic halogen compound and a member of the chloronitrile chemical family. It is a grayish to colorless crystalline solid that is odorless to slightly pungent. Its water solubility is  $0.6 \text{ mg L}^{-1}$  at  $25^\circ\text{C}$ . Its adsorption coefficient is estimated at 1380, while its vapor pressure is  $1.3 \text{ mPa}$  at  $40^\circ\text{C}$ . It has a long term Health Advisory Level (HAL) of  $0.5 \text{ mg L}^{-1}$  (EXTOXNET 1996).

In water and soil it breaks down under basic conditions but is stable in neutral and acidic media. Chlorothalonil is moderately persistent in soils, with a half-life from 1 to 3 months and higher soil moisture or temperature increases its degradation. It is not degraded by sunlight on the soil surface. It has a high adsorption coefficient and low mobility in silty loam and silty clay loam soils, and has a low adsorption coefficient and moderate mobility in sand.

Chlorothalonil is a severe eye and skin irritant and is toxic when inhaled, but is not considered to be acutely toxic by ingestion. It is labeled as a probable carcinogen by the USEPA. Long term exposure may lead to impaired kidney function, but studies suggest that it will not affect human reproduction, produce birth defects, or be mutagenic at expected exposure. There has been carcinogenic potential claimed in some research, but its actual potential for this is not clear (PAN 2008). Chlorothalonil is rapidly excreted from the body (within 24 hours in low concentrations) and it is not stored in animal tissues, thus its bioaccumulation factor is low. It is highly toxic to fish, aquatic invertebrates, and marine organisms, but not toxic to birds or bees, although its metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile is 30 times more acutely toxic in effects to organisms than chlorothalonil and more persistent and mobile in soils (EXTOXNET 1996, WHO 1996, Cox 1997).

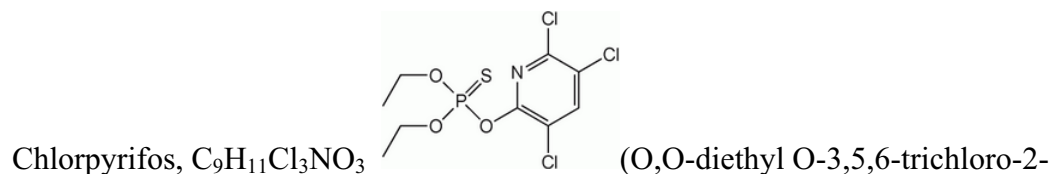


Atrazine is a Restricted Use Pesticide due to its potential for groundwater contamination. This means it may only be purchased and used by certified applicators. Atrazine is highly persistent in soil; its breakdown occurs first by hydrolysis in water and then by degradation by soil microorganisms. Hydrolysis is rapid in acidic or basic environments and those with more organic matter, but is slower at neutral pH. Atrazine is moderately to highly mobile in soils with low clay or organic matter content. It has a high potential for groundwater contamination despite its moderate solubility in water. Atrazine

adsorbs strongly to soil particles and has a half-life of 60 to 260 days and can extend to longer than a year under dry or cold conditions. Atrazine is not expected to strongly adsorb to sediments (Adams and Thurman 1991). Volatilization of atrazine is not significant. Inorganic nitrogen accelerates atrazine catabolism whereas organic nitrogen decreases it (EXTOXNET 1996).

Atrazine is slightly to moderately toxic to humans and other animals and is a mild skin irritant. It can be absorbed orally, dermally, and by inhalation. It is readily absorbed through the gastrointestinal tract and in studies 65% left the bodies of test subjects in the urine over 72 hours, while 15% was retained in body tissues, mainly in the liver, kidneys, and lungs. Animal testing suggests there may be cause for concern of chronic toxicity and possible carcinogenic potential in the long-term, though the USEPA currently regards the most current testing of its carcinogenic potential as inconclusive. There have been no mutagenic effects found. Tests have suggested an epidemiological connection to low sperm levels in men. Studies have pointed to possible endocrine disruption, reproductive and teratogenic effects (Hayes et al. 2003). Atrazine is practically nontoxic to birds and bees, slightly toxic to fish and other aquatic life, and has a low level of bioaccumulation in fish. Due to health effects several researchers have called for banning it in the U.S. (Akerman 2007).





pyridyl phosphorothioate) is a broad-spectrum organophosphate insecticide that inhibits acetylcholinesterase and acts on pests primarily as a contact poison with some action as a stomach poison. Products containing it include Dursban, Lorsban, Brodan, Scout, and Stipend. Chlorpyrifos is effective in controlling a wide range of insects and was first used primarily for controlling mosquitoes but is no longer registered for this use. It is used for grain, cotton, field, fruit, nut and vegetable crops, as well as on lawns and ornamental plants. It is also registered for direct use on structures and various animals in controlling insect pests. Chlorpyrifos is registered only for agricultural use in the U.S. where it is one of the most widely used organophosphate insecticides (USEPA 2008). It was one of the most widely used household pesticides in the U.S. sometime after it was first marketed by the Dow Chemical Company in 1965. It was restricted from use in homes and other places where children could be exposed and severely restricted for use on crops in the U.S. at the end of 2001 sometime after its health dangers were detailed (Lu et al. 2008). It is an amber to white crystalline solid with a mild sulfur odor. Its water solubility is 2 mg L<sup>-1</sup> at 25 C. Its adsorption coefficient is estimated at 6070, while its vapor pressure is 2.5 mPa at 25 C. It has a Health Advisory Level (HAL) of 0.02 mg L<sup>-1</sup> over a lifetime (EXTOXNET 1996).

Chlorpyrifos adsorbs strongly to soil particles and it is not readily soluble in water, therefore it is generally immobile in soils and unlikely to leach or to contaminate groundwater. The concentration and persistence of chlorpyrifos in water will vary

depending on the type of formulation. Studies suggest that it is unstable in water; the rate at which it is hydrolyzed increases with temperature and is constant in acidic to neutral waters, but increases in alkaline waters. It is moderately persistent in soils with a half-life usually 60-120 days, but can be as much as a year depending on the soil types, climate, and other conditions. It is less persistent in the soils with a higher pH, while the soil half-life is not affected by soil texture or organic matter content. The soil half-life is lower in anaerobic soils. It can be broken down by UV light, chemical hydrolysis and by soil microbes. Volatilization is probably the primary route of loss of chlorpyrifos from water, so since it can be taken up in the lungs it has caused some concern over concentrations in the air. Air monitoring studies in California suggest concentrations are not high enough to cause significant exposure or adverse effects, but a biomonitoring study has shown that people living near where it is used in high amounts have higher than normal chlorpyrifos levels in their bodies. It may also be toxic to some plants; data indicate that the insecticide and its soil metabolites can accumulate in certain crops (EXTOXNET 1996, Lu et al. 2008).

Chlorpyrifos is a skin and eye irritant and is moderately toxic to humans with numerous acute exposure symptoms along with similar chronic exposure symptoms. Chlorpyrifos is readily absorbed into the bloodstream through the gastrointestinal tract if it is ingested, through the lungs if it is inhaled, or through the skin if there is dermal exposure. Chlorpyrifos and its principal metabolites are eliminated rapidly in humans, with the half-life about 1 day, being mainly eliminated through the kidneys. Even though some is stored in fat tissues, it is eliminated in humans, with a half-life of about 62 hours; thus, bioaccumulation of chlorpyrifos is not significant. Tests suggest it is not

teratogenic, mutagenic or carcinogenic. However, it is a neurotoxin inhibiting an enzyme required for proper nerve functioning called acetylcholinesterase. It is also suspected endocrine disruptor, and can affect the cardiovascular system, and the respiratory system, with research associating it with asthma (AOEC 2008). Recent research indicates that children exposed to chlorpyrifos while in the womb have an increased risk of delays in mental and motor development and an increased occurrence of pervasive developmental disorders. Studies have also shown correlation between prenatal chlorpyrifos exposure and lower weight and smaller head circumference at birth (Whyatt et al 2004, Rauh et al 2006).

Chlorpyrifos is moderately to very highly toxic to birds, bees, freshwater fish, aquatic invertebrates and estuarine and marine organisms. Its properties as a neurotoxin are also seen in these organisms even at low exposure levels with smaller organisms more susceptible. Toxicity to fish may be related to water temperature based on USEPA findings that the lethal concentrations were lower in fish more commonly found in colder waters (EXTOXNET 1996).

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