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Water Quality Impacts from Agricultural Land Use in Karst Drainage Basins of SW Kentucky and SW China

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Abstract

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 karst subsurface fluvial systems are often very similar to the concentrations surfacing 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. In the temperate climate of southwest Kentucky precipitation is mostly evenly distributed throughout the year. 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 unhealthy loads, while the dry seasons can be particularly severe in karst areas as water quickly drains to the subsurface, making water access a major hardship. Our research focuses on the seasonal differences 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. The concentration of pesticides in agricultural runoff going into and coming out of the subterranean stream studied were within safe limits. Results supported that there was a close relationship among concentrations of the pesticides glyphosate, chlorothalonil, and atrazine in the input and the output of the system. Taking into account the rapid and direct flows in the karst system, the concentrations of the pesticides found in the output was more similar to the input than would be expected in a surface stream. Analysis of hydrology data of the site will be required before further conclusions can be developed. The research was conducted in the spring and summer of 2007–2008 and funded by the U.S. Agency for International Development.

Keywords: karst, water, pesticides, ELISA

Introduction

Karst water issues

Water connections between areas of different land uses 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 fluvial connections also share the same water quality. Human land use can affect water quality in springs recharged from a great distance away or presumed disconnected from areas with human impact. Springs in areas characterized by karst geology can be outlets of not just groundwater but also surface water draining from points sometimes located in adjacent surface watersheds (White 1988, Ford and Williams 1989, Lu 2007).

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Karst aquifers are those that "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, p. 85). Consideration of the flows in karst groundwater systems is necessary for understanding the transport of dissolved compounds in these waters (Quinlan and Ewers 1985).

A detailed understanding of the various flow 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 would require an adjustment in the definition of the effective watershed boundaries (Hao et al. 2006, Croskrey and Groves 2008). Modeling of groundwater flow in karst aquifers has not progressed very much over the last 20 years, though recently water budgets, tracer studies, hydrograph analysis and chemograph analysis have been used for characterizing karst aquifers. Yet, there is still a need to direct attention toward working out processes and mechanisms for contaminant transport in karst aquifers (White 2002, Barfield et al. 2004).

In karst regions water resources are especially sensitive to contamination and pollution (Hao et al. 2006). Normally in nonkarst areas, when precipitation and overland flows pick up contaminants, they can be filtered by soils before entering groundwater storage. These contaminants often come from human uses such as irrigation and industry and can consist of fertilizers, pesticides, toxic bacteria, and industrial wastes. Interaction with soils as water slowly percolates into groundwater aquifers allows for microbes to use or buffer some of 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 water into groundwater, long residence times therein and dilution into the vast reserves of aquifers 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).

Considerations of the soil's chemical, biochemical, and microbiological properties are important for maintaining soil quality and consequently water quality. There can 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 that are typical drinking water sources (White 1988, Ford and Williams 1989, Zhang et al. 2006).

Pollutants in karst waters 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). If there is little or no interaction with sediment along the conduit length and the flow is slower, pollutants tend to become more concentrated in the water, as reflected in the discharge. In contrast to surface water flows, karst subsurface flows see 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). Also, in systems with small conduits a restriction of the flow can occur more easily during high water input periods, which can lead to backflooding and a return of contaminants in the reverse flow direction, possibly even to the source (Vaute et al. 1997).

General water quality of Kentucky and China

More than a million people in Kentucky use public water supplies that use groundwater, and around half a million people there use groundwater as a private water source. Half of Kentucky's groundwater is estimated to be contaminated by bacteria. Most karst springs in Kentucky have been abandoned as municipal water sources because of groundwater contamination, but 11 percent of Kentucky karst springs are still used as rural water sources by local residents. Yet, abandoned or not, springs still often drain to streams used as water sources. Estimates of the people using surface water fed from groundwater sources are not available and may be too complex to properly establish. The true extent of the problem is difficult to determine once groundwater resources have been contaminated (Taraba et al. 1997, Croskrey and Groves 2008).

The southwest (SW) Kentucky karst region has been studied extensively and includes the Mammoth Cave system, the longest known cave in the world, and the Pennyroyal Sinkhole plain, well known for its high concentration of sinkholes covering a primarily agricultural area. Water quality is a principal focus in the area, especially in recent years. The difference in climate creates a major difference in the karst water considerations of SW Kentucky and those of SW China (Shuster and White 1971, Anthony et al. 2003, Liu et al. 2007).

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 contains excess of 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 percent of drinking water comes from groundwater sources, 50–90 percent 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 Otsuka 2006, Guo and Ma 2007, Ministry of Water Resources 2007).

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 here pose 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^2 over eight provinces. 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). 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 through the rest of the year (World Resources Institute 1998). 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).

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 past two decades in SW China and they peak in the rainy season (Chena et al. 2005). Anthropogenic inputs have major effects on water chemistry. Nitrate and chlorine are two ions affected by this and are the main contributors to groundwater pollution in SW China (Guo et al. 2007). Sewage effluent is the primary source of nitrates in urban areas, while chemical fertilizers and domestic animal wastes are the primary source in rural areas (Lu 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 (Aharonson et al. 1987). Because nitrates are very soluble, they do not readily bind to soils and 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. This suggests that denitrification is not a significant factor in karst groundwater systems. Therefore, karst groundwater systems do not easily recover when they are contaminated with nitrates (Almasri and Kaluarachchi 2007).

China is the most populous country in the world, although it is the fourth largest geographically and only 10 percent of it 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 producers and consumers of pesticides (Yang 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). Therefore, pesticide contamination in water resources is a concern in China. 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, as with some organophosphates used in the present (Wang et al. 2006, Reuters 2007, Yang 2007).

The use of land for agriculture in China has increased significantly over the past 50 years (Hajahhasi et al. 1997, Zheng et al. 2005, Jiang et al. 2007). After decades of high pesticide application the environment has been degraded and enormous 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, p. 78).

Study Area

The United States Agency for International Development (USAID) funded a grant to develop cooperative efforts between the United States 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 we examined the water quality in a watershed of interest in this area, specifically focusing on pesticide levels in water sources. The particular watershed of interest is Qingmuguan (QMG), as it supplies water for the city of Qingmuguan at the southern end of the basin. It is located 25 km northwest of the major city of Chongqing. The watershed is approximately 13.4 km^2 stretching 11.2 km long and 1.1 km wide (Figure 1). The initial question we sought to address was whether the pesticide levels exiting the groundwater basin posed any human concerns and under what different hydrologic conditions the levels could be a concern.

The northern section of the basin contains the main agricultural valley. 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. 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 our primary interest (Nakanoa et al. 2004).

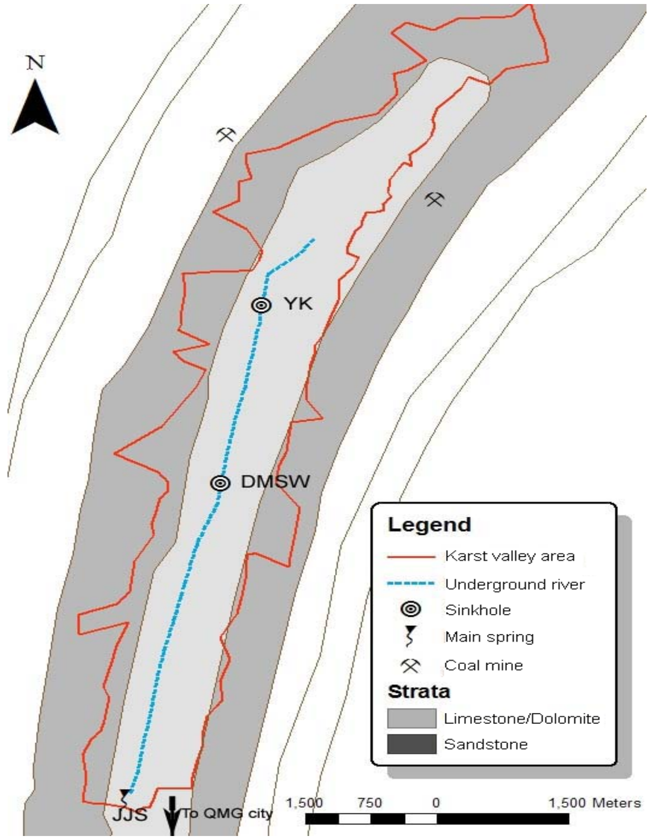

Figure 1. The Qingmuguan (QMG) groundwater basin. The Yankou sinkhole (YK) drains an agricultural valley, and the Damushuiwo sinkhole (DMSW) drains an ephemeral lake to Jiangjia spring (JJS). The basin lies in a mountainous area formed by an anticline with valleys at the center of the basin consisting of limestone, while the ridges on the margins are sandstone separated by a coal layer that has been mined within the last 20 years

The valley is in the middle of a series of anticlines and synclines in the landscape. It is situated in an anticline that has been eroded into the formation of a few valleys and hills in between two major ridges. This also means that it sits at a higher elevation than the surrounding area, a valley in the mountains. The center low part of the basin is where the limestone is found. The basin is lined by sandstone layers in the ridges surrounding it. The limestone and sandstone are separated by a layer of coal. There is a noticeable vegetation difference between the limestone and sandstone. Bamboo and thick shrubs and undergrowth are found lower on the hills, but stands of pine with ferns in the undergrowth are observed when crossing to the sandstone. Nearly all flat areas in QMG and some slopes are cultivated. The coal seams in the area have been mined significantly, and a few limestone quarries are in the basin, which leave steep sandstone slopes exposed to erosion into the valleys (Hajahhasi et al. 1997, Zheng et al. 2005).

Silicates from erosion runoff coming from these slopes and entering sinkholes can be an indicator of surface sediment transport in the QMG subterranean river system (QSRS). 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 µm in diameter and the bed-load material (Figure 2). Bacteria, pesticides, and other potential pollutants are adsorbed on sediment, which contributes to water quality problems and can lead to human health problems (Malmon et al. 2002, Hilscherova et al. 2007). There are few water treatment facilities in rural areas of China including in the QMG area.

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 respects. These conditions 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. Southwest 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 on them.

Methods

Preliminary data collection on the water resources 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 that involved hiking throughout the watershed and

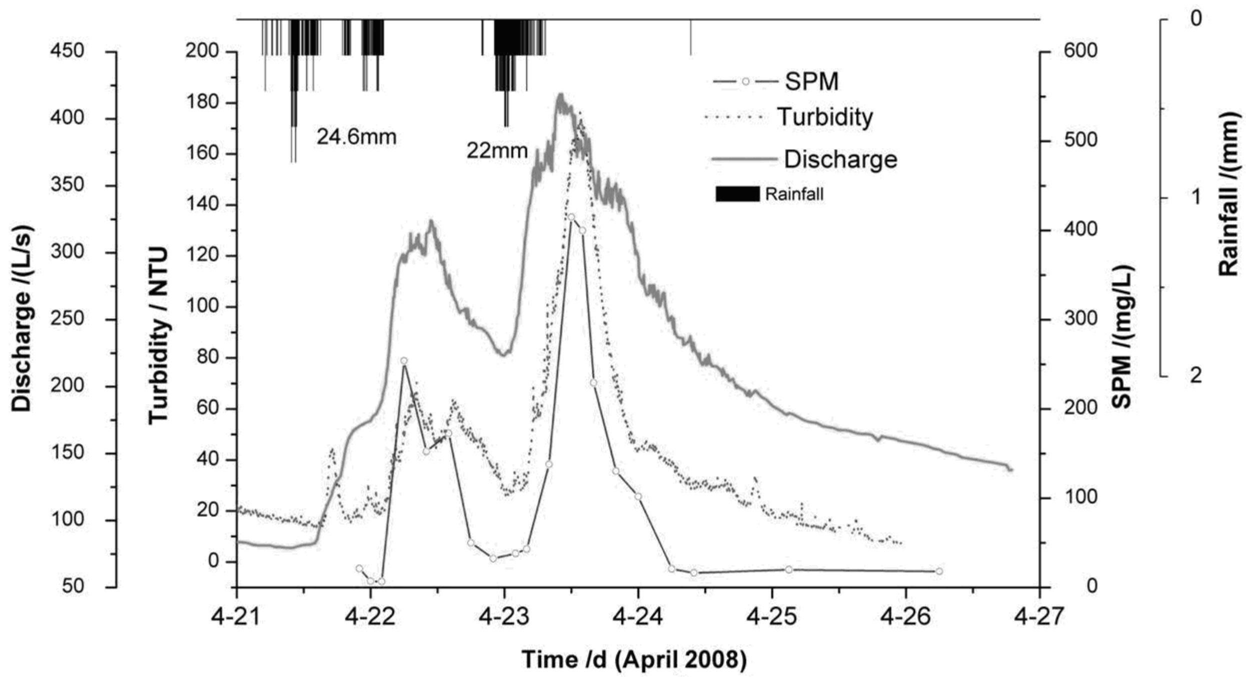

Figure 2. Data from two storm events at JJS in QMG show the relationship between discharge, turbidity, and suspended particulate matter (SPM) during storm events in the QMG subterranean river system (QSRS). The strong response and high levels can be associated with water contamination concerns (adapted from Yang, in press)

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.

Water samples were collected at the sinking stream and the main spring, 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. The results showed standard ion concentrations for a karst groundwater basin. Yet, nitrate in the spring was 15.41 mg/L, which is above the U.S. Environmental Protection Agency (USEPA) 10 mg/L limit of concern for drinking water. Additionally, iron was rather high, but high iron in water supplies is not considered a health hazard as much as an aesthetic problem. Results also show atrazine, used in the upper watershed, with 0.6 ppb reported in the runoff draining the northern agricultural valley, which is below the USEPA recommended safe limit for drinking water of 3 ppb.

Two dye traces were also conducted to determine the connections between karst fluvial features in the basin. This was done after many days of assessing and re-assessing the flow conditions in the area. Charcoal receptors were placed at six karst water features of interest within the watershed. Background receptors were obtained prior to injection of dye. Uranine (Fluorescein) dye, 802.4 grams, was injected at Yankou sinkhole (YK) on August 1, 2007. 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. Additionally, 200 grams of Uranine was injected at Damushuiwo (DMSW) swallet on September 14, 2007, with data collected through September 23. In addition to data from the charcoal receptors from the first trace, continuous dye levels were recorded at Jiangjia spring (JJS) for both of the dye traces. This was done through the use of a flow-through field fluorometer, a dye receptor instrument developed by Swiss research partners, and allowed for a more accurate determination of the time of the initial dye recovery and a calculation of the percent of the dye recovered. During the YK injection, 93.4 percent of the Uranine arrived at JJS 33.3 hours after injection. The flow conditions were lower during the DMSW injection, and the dye arrived about 42 hours after injection.

Additional work of assessing the area was also done by developing more detailed geologic cross-sections than available at the time. These were conducted by hiking the length of designated cross-sections and taking measurements of any outcrops with a Brunton compass. An initial list of the pesticides used in the area was also generated by conducting interviews with the local farmers and the retrieval of empty pesticide packages from QMG. These packages are typically discarded at whatever location in the field the product happened to be mixed, usually near a water source. This list is shown in Table 1, but it likely represents the minority of pesticide concentration going into the QSRS system.

Table 1. Data on pesticides used in QMG obtained through interviews are listed in italics. Other pesticides listed were identified as being in use in the area via the collection of pesticide packages found on the ground in the basin. Pesticide concentrations tested in water samples are listed in bold (EXTOXNET 2008, Pesticide Action Network North America 2008).

Pesticides	Use type[a]	Groundwater contaminant	Acute toxicity[b]	Carcin-ogen[c]	Other health[d]
Atrazine	1	Yes	1	2	1
Glyphosate	1	Low	1	1	--
Glufosinate	1	--	1	--	1
Metsulfuron-methyl	1	Potential	1	1	--
Dimethoate	2	Potential	2	2	1,2,3
Thiosultap disodium	2	--	--	--	--
Isocarbophos	2	--	--	--	--
Chlorpyrifos	2	Conditional	2	1	1,2
Avermectin	2	Low	3	1	3
Cypermethrin beta	2	Low	1-2	2	1
Emamectin benzoate	2	Low	3	1	--
Hexaflumuron	2	--	1	1	--
Carbendazim sulfur	3	No	1	2	1
Chlorothalonil	3	Potential	3	3	--
Cymoxanil	3	--	1	1	--
Fosetyl aluminum	3	Potential	3	1	--
Mancozeb	3	Low	0	3	1,3,4
Mefenoxam	3	--	3	1	--
Procymidone	3	--	0	3	1
Pyrimethanil	3	--	0	2	1
Streptomycin sulfate	3	--	2	--	3
Thiram	3	Conditional	1	1	1,3,4
Ziram	3	Conditional	1	2	1,3,4
Metaldehyde	4	Potential	2	2	--

a. 1=Insecticide, 2=Fungicide, 3=Herbicide, 4=Molluscicide
b. 0=Not toxic, 1=Slightly toxic, 2=Moderately toxic, 3=Highly toxic
c. 1=Unlikely carcinogen, 2=Possible carcinogen, 3=Probable carcinogen
d. 1=Suspected endocrine disruptor, 2=Neurotoxin (Cholinesterase inhibitor), 3=Developmental toxin, 4=Reproductive toxin

Additionally, over the course of interviews with 4–5 farmers in the area, 7–8 pesticides were cited as the most prominently used in QMG. The majority of interviews were conducted in the YK valley. 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 (Table 1). 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. Glyphosate is very widely used in QMG and worldwide 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 but is not widely used worldwide, while the extent of use in QMG is unknown. The residents claimed they use little to no pesticides on their corn crops in recent seasons, yet atrazine is known to be quite persistent in water resources. Our preliminary testing indicated its presence, so we decided to test for it as well. Chlorpyrifos is not as great a concern for groundwater contamination in alkaline water as with more acidic to neutral water; it has some possible health effects (Tables 1, 2). It was not cited as used in QMG until June 2008, so it was only tested for in July (EXTOXNET 2008, Pesticide Action Network North America 2008).

During the summer of 2008, water samples were collected from YK and JJS June 4–July 28 using U.S. Geological Survey (USGS) protocols (U.S. Geological Survey 2006). The water samples were collected 2–3 times per week in 40 ml volatile organic compound amber glass bottles and usually tested within 24–48 hrs of their collection, but within 1–2 weeks in all cases (Quinlan and Alexander 1987). They were tested for each specific pesticide using highly sensitive quantitative test kits produced for this study by Strategic Diagnostic Inc. and Abraxis. The methods used by these kits are Enzyme-Linked Immuno-Sorbent Assay (ELISA) tests. They are normally magnetic particle-based competitive ELISA tests. The analysis of the assay results were conducted using a Shimadzu UV-2450 spectrophotometer at 450 nm by using a micropipettor to transfer the assay solutions to 1 mL cuvettes acquired for use in this particular spectrophotometer. The ELISA kits needed for the analytical instruments available used test tubes, as opposed to microtiter plate kits. ELISA kits of either kind were not available for most of the pesticides of interest used in the QMG study area. The pesticides mentioned, as well as procymidon, were the only ones with kits available for use with the accessible analytical equipment.

Data loggers were established at YK and JJS recording stage, temperature, pH, specific conductance, and at JJS the nitrate concentration every 15 min. There were three stations throughout the basin recording precipitation. Unfortunately, those results were not yet available for this analysis. Analysis of pesticide loads and comparisons based on these conditions will be reported in 2009.

Results and Discussion

The primary feature of interest is 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, we determined that the primary features in QMG that supply flows to JJS were YK and, during large storm events, DMSW. 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 swallet.

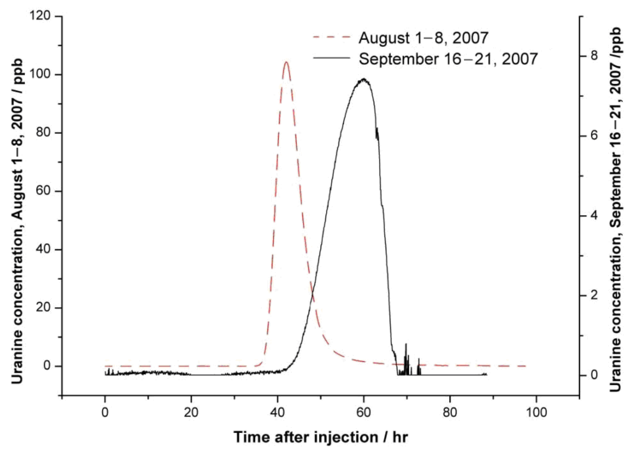

Figure 3. The breakthrough curve showing the pulse of dye arriving a JJS after injection at YK in August and DMSW in September 2007 (adapted from Yang, in press).

In the case of both dye traces, the single strong peak of breakthrough curve (Figure 3) suggests that a well-developed and connected conduit system exists for underground flow in a direct conduit path between the locations in the QMG subterranean river system (QSRS). The results also suggest that the transport time is rapid, especially during higher flows.

The results of our detailed cross-section efforts indicate the likely path of the QSRS flow, as it normally follows bedding planes. This may also allow us to understand which sections of the basin most strongly affect QSRS surface water and sediment input.

There are also a number of small springs draining into different small valleys in the QMG groundwater basin from the adjacent slopes. These are likely fed from runoff from the steep sandstone slopes above. We documented sinkholes in these valleys as well. During storm events it is likely that these springs, along with other runoff sources, also drain into these sinkholes, which may then flow into the QSRS. If this were so, it is not likely there would be any significant input coming from these valleys except after large storm events. In this case there would be a strong dilution effect on the movement of contaminants into QSRS from these sources. Also, none of the flow paths of these springs passed through any significant agricultural areas, so there may not be a significant load of contaminants coming into the QSRS from these sources either.

We suspected that the amount of contaminants found in YK and DMSW and the amount found in JJS would not be significantly different based on previous related studies that have been conducted in other locations (Vaute et al. 1997, Lang et al. 2006, Liu et al. 2007, Guo et al. 2007).

The potential for groundwater contamination and persistence of each compound in the environment depends on their water solubility, soil adsorption, potential for breakdown in water based on hydrolysis half-life of the compound, and potential for breakdown in soil based on aerobic and anaerobic soil half-life of the compound (Table 2).

Table 2. Details of pesticides sampled in QMG, June 4–July 28, 2008 (EXTOXNET 2008, Pesticide Action Network North America 2008).

Chlorothalonil—Fungicide (organochlorine) • Low solubility = 0.6 mg/L at 25°C • High adsorbance coefficient = 1380 • In very basic water (pH 9.0) 65% degrades within 10 weeks • Soil half-life is 1–3 months • Degrades faster with increased soil moisture and (or) higher temperature • High binding and low mobility in silty soils • Low binding, moderate mobility in sandy soils • High acute toxicity and highly toxic to fish • Possible carcinogen • Potential groundwater contaminant • Health Advisory Level (HAL) = 1.5 ppb	***Atrazine***—Herbicide (triazine), broadleaf/grasses • Most used pesticide in the U.S., favored for corn • Claimed not to be used currently in QMG • Low to moderate solubility = 28 mg/L at 20°C • Low to moderate adsorbance coefficient =100 • Half life = 60 to >100 days • High hydrolysis breakdown • High breakdown in acidic and basic conditions, low breakdown in neutral • Prominent groundwater contaminant • Slight acute toxicity • Debated as a carcinogen • Suspected endocrine disruptor • Maximum Contaminant Level (MCL) = 3 ppb
Glyphosate—Herbicide • Very common nonselective broad-spectrum product (Roundup) • High solubility = 12,000 mg/L at 25°C • Very high adsorbance, even with low organic matter and clays = 24,000 (estimated) • Moderately persistence in soils, half-life ~47 days, subject to microbial breakdown • Low potential for runoff (except colloidal) • Low to slight acute toxicity • Debated as a possible endocrine disruptor • MCL = 700 ppb	***Chlorpyrifos***—Insecticide (organophosphate) • Low solubility = 2 mg/L at 25°C • High adsorbance = coefficient 6070 • Moderate soil persistence = 2 weeks to 1 year or more, depending on soil type, climate, etc. • High volatilization • High hydrolysis, especially in alkaline waters • Low persistence in high pH conditions • Moderate acute toxicity • Suspected endocrine disruptor • Significant neurotoxin (Cholinesterase inhibitor) • HAL = 21 ppb

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^2 partial pressure promptly go up in response and pH goes down. 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 (Li et al. 2005; Yang, in press).

Nitrate levels at JJS were high in bimonthly samples March–July 2007, never dropping below 20 ppm and reaching as high as 50 ppm. Levels were lower in YK, usually less than 3 ppm (He Qiufang, 2007, Southwest University of China, unpublished data). The USEPA MCL is 10 ppm (U.S. Environmental Protection Agency 2003). High nitrate levels are largely influenced by inputs of irrigation water in agricultural areas (Almasri and Kaluarachchi 2007). The high nitrate levels at JJS suggest that groundwater is not its main source; it seems its other significant agricultural water inputs in QMG.

The year 2007 was very wet with a 100-year flood in the area that season. 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, it may have come from DMSW since it was often flooded during the season, but it is likely that there are a few other discreet inputs to the QSRS system near agricultural field sites in QMG that we did not locate. The presence of atrazine at the YK but not at JJS could indicate processes are breaking down pesticides along the length of the underground river. Corn is grown most prominently in the YK valley, so it is not likely that much atrazine is 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 large conduit, it may be during the initial runoff pulse YK to JJS that pesticide loads could be a concern.

The year 2008 was unusually dry for QMG. There was only one major storm event (June 15) during the sampling period. There were a few other very small rain events, including on July 17, but none that likely greatly impacted the discharge at JJS. As mentioned, rainfall and discharge data are not available at the present time. Still, the ELISA test results show a definite response in pesticide concentrations in water samples at both locations around June 15 and other smaller storm events. Otherwise, during base 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 similar to those found at YK and reflected similar changes in the levels observed over the 2008 summer season.

Conclusions

The pesticide levels observed were mostly taken during low-flow, baseline conditions. There was still a distinct relationship seen between the concentrations of pesticides in YK and JJS. There were not many detectable levels of the pesticides found in DMSW, yet there was only one storm event large enough to flood the valley and send a considerable amount of water into the sinkhole over a short period. It is difficult to claim that there was a significant amount of more pesticides found in JJS compared to YK than would be normally observed in a surface stream. This is especially true since the actual loads cannot be known until discharge measurements are available. Still, all pesticide concentrations in the samples taken were well below the maximum contaminant levels (MCLs) and health advisory levels (HALs) used in the United States (U.S. Environmental Protection Agency 2003). Regardless of load calculations, in this case under base 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.

Still, 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 about possible high pesticide loads in JJS.

Southwest University of China researchers began detailed investigations into the groundwater hydrochemistry and microbe activity in the QMG area in early 2007. As mentioned earlier, water and soil samples were taken every two weeks from March–July of 2007. Rainfall and discharge data are not available from this time, but data from September 2007 and April 2008 indicate that sudden shifts in ion concentrations and specific conductance shortly follow an increase in rain (Yang, in press). This should lead to an increase in soluble ions in runoff and a decrease in ions dominant during base flow conditions as they become diluted by the higher flows (Liu et al. 2004, Nakanoa et al. 2004).

The data from early 2007 show an increase in nitrate coinciding with a decrease in calcium and bicarbonate (He Qiufang, 2007, Southwest University of China, unpublished data). 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. Turbidity is also high during these pulses, as seen in Figure 2 (Malmon et al. 2002; Yang, in press). So, for example, even though glyphosate is quickly adsorbed to soils, during such events it could easily be transported to JJS at levels close to the same as that of application concentrations at YK. This would hold true whether it was dissolved in the discharge or, almost as significantly, adsorbed to the sediment in the water column. Glyphosate is not a significant human health threat, but this scenario just as easily applies to pesticides or other compounds with similar properties 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 et al. 2007). High nitrate likely comes from fertilizers used by local farmers. If the nitrate is so high, then pesticides applied during this time that can readily be transported in surface water can also contaminate the water. Still, there could be less cause for concern for 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 it would not rule out possible compounding pesticide combinations. There is also the factor of dilution from other nonagricultural inputs along the length of the basin. But, for example, if everyone is applying glyphosate to clear out grasses for rice fields, 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).

Microbial data are not yet available for QMG, but the water chemistry results show that there were strong pulses of water going through the system. More contaminants can be transported by these flows 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). However, 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 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 (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). Therefore, this condition could be a factor leading to a diminished capacity for natural processes to ameliorate contaminant problems in affected karst systems.

No researchers or agencies are known to have monitored the pesticide levels in the QMG water prior to this study. Our academic partners at the Southwest University of China 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 (World Resources Institute 1998, Turner and Otsuka 2006, U.S. Embassy in Beijing, China 2006, Reuters 2007, Xinhua News Agency 2007). Research such as this will provide support for these efforts to continue. Collaboration with our Chinese colleagues on karst scientific methods has brought the 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 our 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.

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References

Aharonson, N., S.Z. Cohen, N. Drescher, T.J. Gish, S. Gorbach, P.C. Kearney, S. Otto, T.R. Roberts, and J.W. Vonk. 1987. Potential contamination of ground water by pesticides. Pure and Applied Chemistry 59(10):1,419–1,446.

Almasri, M., and J. Kaluarachchi. 2007. Modeling nitrate contamination of groundwater in agricultural watersheds. Journal of Hydrology 343:211–229.

Anthony, D., C. Groves, and J. Meiman. 2003. Preliminary investigations of seasonal changes in the geochemical evolution of the Logdson River, Mammoth Cave, Kentucky. Speleogenesis and Evolution of Karst Aquifers 1(4):1–6. [online] URL: http://www.speleogenesis.info/archive/publication.php?PubID=3257&Type=publication. Accessed 30 May 2008.

Aquilina, L., B. Ladouche, and N. Dörfliger. 2006. Water storage and transfer in the epikarst of karstic systems during high flow periods. Journal of Hydrology 327:472–485.

Barfield, B., G. Felton, E. Stevens, and M. McCann. 2004. A simple model of karst spring flow using modified NRCS procedures. Journal of Hydrology 287:34–48.

Chena, M., D. Pollard, and E. Barron. 2005. Hydrologic processes in China and their association with summer precipitation anomalies. Journal of Hydrology 301:14–28.

Croskrey, A., and C.G. Groves. 2008. Groundwater sensitivity mapping in Kentucky using GIS and digitally vectorized geologic quadrangles. Environmental Geology 54:913–920.

EXTOXNET. [2008]. ETOXNET: The Extension Toxicology Network. University of California–Davis, Oregon State University, Michigan State University, Cornell University, University of Idaho. [online] URL: http://extoxnet.orst.edu/ghindex.html . Accessed 5 March 2008.

Ford, D.C., and P.W. Williams. 1989. Karst Geomorphology and Hydrology. Unwin Hyman Ltd. Winchester, MA, pp 120-135.

Groves, C.G. 2007. Water resource challenges in karst regions of southwest China. China Environment Series 9:139–148.

Groves, C.G., J. Meiman, J. Despain, Z. Liu, and D.X. Yuan. 2002. Karst aquifers as atmospheric carbon sinks: An evolving global network of research sites. In E.L. Kunlansky, ed., U.S. Geological Survey Karst Interest Group Proceedings, Shepherdstown, WV, August 20–22, 2002, pp. 32–39. U.S. Geological Survey Water-Resources Investigations Report 02-4174.

Guo, C., and T. Ma. 2007. The optimum allocation of water resources in the karst rock areas of Southwest China. In Groundwater: Present Status and Future Task: Full papers of the 34th Congress of the International Association of Hydrogeologists, Beijing, 9–13 October 2006. Ministry of Land and Water Resources, China Geological Survey, Beijing. [online] URL: http://old.cgs.gov.cn/zt_more/34/zhaiyao/html/05/525.htm. Accessed 3 January 2008.

Guo, F., G. Jiang, and D.X. Yuan. 2007. Major ions in typical subterranean rivers and their anthropogenic impacts in southwest karst areas, China. Environmental Geology 65:664–672.

Hajahhasi, M., A. Jalalian, and H. Karimzadeh. 1997. Deforestation effect on soil physical and chemical properties, Lordegan, Iran. Plant and Soil 190:301–308.

Hamburger, J. 2005. Pesticides in China: A growing threat to food safety, public health, and the environment. China Environment Series 5:29-44.

Hao, Y., T. Yeh, C. Hu, Y. Wang, and X. Li. 2006. Karst groundwater management by defining protection zones based on regional geological structures and groundwater flow fields. Environmental Geology 50: 415–422.

Hilscherova, K., L. Dusek, V. Kubik, P. Cupr, J. Hofman, J. Klanova, and I. Holoubek. 2007. Redistribution of organic pollutants in river sediments and alluvial soils related to major floods. Journal of Soils and Sediments 7(4):67–177.

Jiang, T., Y.D. Xu, C-Y Chen, X.H. Chen, X. Chen, and V.P. Singh. 2007. Comparison of hydrological impacts of climate change simulated by six hydrological models in the Dongjiang Basin, South China. Journal of Hydrology 336: 316–333.

Jiang, Y. 2006. The impact of land use on soil properties in a karst agricultural region of southwest China: A case study of Xiaojiang watershed, Yunnan. Journal of Geographical Sciences 16(1):69–77.

Lang, Y.C., C.Q. Liu, Z.Q. Zhao, S.L. Li, and G.L. Ha. 2006. Geochemistry of surface and ground water in Guiyang, China: Water/rock interaction and pollution in a karst hydrological system. Applied Geochemistry 21:887–903.

Li, S.L., C.Q. Liu, F.X. Tao, Y.C. Lang, and G.L. Hanet. 2005. Carbon biogeochemistry of ground water, Guiyang, Southwest China. Ground Water 43:494–499.

Li, Y., and J. Zhang. 1999. Agricultural diffuse pollution from fertilizers and pesticides in China. Water Science and Technology 39:25–32.

Li, Y.R., G.H. Huang, Y.F. Li, J. Struger, and J.D. Fischer. 2002. A pesticide runoff model for simulating runoff losses of pesticides from agricultural lands. Water Science and Technology 47(1):33–40.

Liu, Z., C. Groves, D. Yuan, J. Meiman, G. Jiang, S. He, and Q. Li. 2004. Hydrochemical variations during flood pulses in the South-west China peak cluster karst: Impacts of CaCO3–H2O–CO2 interactions. Hydrological Processes 18:2,423–2,437.

Liu, Z., Q. Li, H. Sun, and J. Wang. 2007. Seasonal, diurnal and storm-scale hydrochemical variations of typical epikarst springs in subtropical karst areas of SW China: Soil CO2 and dilution effects. Journal of Hydrology 337:207–223.

Lu, Y. 2007. Karst water resources and geo-ecology in typical regions of China. Environmental Geology 51:695–699.

Malmon, D., T. Dunne, and S. Reneau. 2002. Predicting the fate of sediment and pollutants in river floodplains. Environmental Science and Technology 36:2,026–2,032.

Ministry of Water Resources. 2007. China to make more efficient use of mine water. 26 Feb 2007. People's Republic of China, Ministry of Water Resources. [online] URL: http://www.mwr.gov.cn/english1/20070226/82423.asp. Accessed 20 February 2008.

Nakanoa, Y., A. Miyazaki, T. Yoshida, K. Ono, and T. Inoue. 2004. A study on pesticide runoff from paddy fields to a river in rural region—1: Field survey of pesticide runoff in the Kozakura River, Japan. Water Research 38:3,017–3,022.

Pesticide Action Network North America. 2008. The Pesticide Action Network Pesticides Database. PANNA. [online] URL: http://www.pesticideinfo.org/. Accessed 5 March 2008.

Quinlan, J., and E. Alexander. 1987. How often should samples be taken at relevant locations for reliable monitoring of pollutants from an agricultural, waste disposal, or spill site in a karst terrane? A first approximation. In B. Beck and W. Wilson, eds., Proceedings of Multidisciplinary Conference on Sinkholes and Environmental Impacts of Karst, pp. 277–293. A.A. Balkema, Rotterdam.

Quinlan, J., and R. Ewers. 1985. Ground water flow in limestone terranes: Strategy rationale and procedure for reliable, efficient monitoring of ground water quality in karst areas. In Proceedings of Fifth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring, Columbus, OH, 21–24 May 1985, pp. 197–234. National Water Well Association, Worthington, OH.

Reuters. 2007. China to crack down on banned pesticide use. 7 Aug 2007. Thomson Reuters. [online] URL: http://www.reuters.com/article/latestCrisis/idUSPEK92660. Accessed 11 August 2007.

Shuster, E., and W.B. White. 1971. Seasonal fluctuations in the chemistry of limestone springs: A possible means for characterizing carbonate aquifers. Journal of Hydrology 14:93–128.

Taraba, J.L., J.S. Dinger, L.V.A. Sendlein, and G.K. Felton. 1997. Land use impacts on water quality in small karst agricultural watersheds. In T.M. Younos, ed., Proceedings: Karst-water Environment Symposium, Roanoke, VA, 30–31October 1997, pp. 127–140. Virginia Water Resources Research Center, Blacksburg, VA.

Turner, J. 2006. New ripples and responses to China's water woes. The Jamestown Foundation: China Brief 6(25):8–12. [online] URL: http://www.jamestown.org/images/pdf/cb_006_025.pdf. Accessed 10 May 2007.

Turner, J., and K. Otsuka. 2006. Reaching Across the Water: International Cooperation Promoting Sustainable River Governance in China. Woodrow Wilson International Center for Scholars, China Environment Forum. [online] URL: www.wilsoncenter.org/cef/. Accessed 5 March 2008.

U.S. Embassy in Beijing, China. 2006. Beijing environment, science, and technology update, January 2006. U.S. Embassy of Beijing, China; Environment, Science, Technology, and Health Section. [online] URL: http://beijing.usembassy-china.org.cn/esth0106.html Accessed 15 June 2009.

U.S. Environmental Protection Agency. 2003. Drinking water contaminants: Maximum contaminant levels. U.S. Environmental Protection Agency, EPA 816-F-03-016. [online] URL: ehttp://www.epa.gov/safewater/contaminants/index.html#listmcl. Accessed 10 August 2008.

U.S. Geological Survey. 2006. National field manual for the collection of water-quality data: Chapter A4. Collection of water samples. U.S. Geological Survey Techniques of Water-Resources Investigation book 9. [online] URL: http://water.usgs.gov/owq/FieldManual/chapter4/html/Ch4_contents.html. Accessed 20 April 2007.

Van Eerd, L.L., R.E. Hoagland, R.M. Zablotowicz, and J.C. Hall. 2003. Pesticide metabolism in plants and microorganisms. Weed Science 51(4):472–495.

Vaute, L., C. Drogue, L. Garrelly, and M. Ghelfenstein. 1997. Relations between the structure of storage and the transport of chemical compounds in karstic aquifers. Journal of Hydrology 199(3):221–238.

Vesper, D.J., C.M. Loop, and W.B. White. 2001. Contaminant transports in karst aquifers. Theoretical and Applied Karstology 13–14:101–111.

Wang, T.Y., Y.L. Lu, R.W. Dawson, Y.J. Shi, H. Zhang, and Y. Xing. 2006. Effects of environmental factors on organochlorine pesticide residues in soils of the Guanting Reservoir area, China. Journal of Environmental Science and Health, Part B 41:309–321.

White, W.B. 1988. Geomorphology and Hydrology of Karst Terrains. Oxford University Press.

White, W.B. 2002. Karst hydrology: Recent developments and open questions. Engineering Geology 65:85–106.

World Bank. 2003. China: Southwest poverty reduction program project. The World Bank, Implementation Completion and Results Report no. 2613230. [online] URL: http://go.worldbank.org/H6YV3XZ960. Accessed 20 May 2008.

World Resources Institute. 1998. Regional profile: China's Health and Environment. In World Resources 1998–99: Environmental Change and Human Health, pp. 115–126. World Resources Institute, United Nations Environment Programme, United Nations Development Programme, and The World Bank. [online] URL: http://www.wri.org/pubs/pubs_description.cfm?pid=2889. Accessed 10 September 2007.

Xinhua News Agency. 2007. 'Officials should be held responsible for pollution.' China Daily 27 Feb 2007. [online] URL: http://www.chinadaily.com.cn/china/2007-02/27/content_814500.htm. Accessed 2 March 2008.

Xu, H., Y. Qian, B.Z. Peng, X. Jiang, and X.M. Hua. 2003. Environmental pesticide pollution and its countermeasures in China. AMBIO 32(1):78–80.

Yang, P. In press. Study on characteristics of aquifer media of Qingmuguan karst subterranean river system, Southwestern China. In Proceedings of the 33rd International Geological Congress: International Perspectives on Karst Aquifers and Water Resources (Symposium HYH-09), Oslo, Norway, 6–14 August 2008. IGC, International Union of Geological Sciences.

Yang, Y. 2007. Pesticides and Environmental Health Trends in China: A China Environmental Health Project Factsheet. Woodrow Wilson International Center for Scholars, China Environment Forum. [online] URL: www.wilsoncenter.org/cef. Accessed 5 May 2008.

Yuan, D.X., C. Drogue, A. Dai, W.K. Lao, W.T. Cai, P. Bidaux, and M. Razack. 1990. Hydrology of the karst aquifer at the experimental site of Guilin in Southern China. Journal of Hydrology 115:285–296.

Zhang, P., L. Li, G. Pan, and J. Ren. 2006. Soil quality changes in land degradation as indicated by soil chemical, biochemical and microbiological properties in a karst area of Southwest Guizhou, China. Environmental Geology 51:609–619.

Zheng, F., X. He, X. Gao, C. Zhang, and K. Tanget. 2005. Effects of erosion patterns on nutrient loss following deforestation on the loess plateau of China. Agriculture, Ecosystems and Environment 108:85–97.