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# Pesticide use in the wheat-maize double cropping systems of the North China Plain: Assessment, field study, and implications

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## Abstract

In the North China Plain (NCP), rising inputs of pesticides have intensified the environmental impact of farming activities in recent decades by contributing to surface water and groundwater contamination. In response to this, the Chinese government imposed stricter regulations on pesticide approval and application, and better monitoring strategies are being developed. However, sufficient and well-directed research on the accumulation and impact of different pesticides is needed for informed decision-making.

In this study, current pesticide use, and recent and current research on water contamination by pesticides in the NCP are reviewed and assessed. Additionally, a small-scale field study was performed to determine if residuals from currently-used pesticides in the NCP can be detected in surface water, and in connected shallow groundwater. The contaminants of interest were commonly used pesticides on winter wheat-summer maize fields (the dominant cropping system in the NCP), such as 2,4-D and atrazine. Sampling took place in May, July, and October 2013; and March 2014.

Results from our literature research showed that sampling is biased towards surface water monitoring. Furthermore, most studies focus on organic chlorinated pesticides (OCPs) like the isomers of dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH), which were banned in China in 1983. However, currently-used herbicides like 2,4-D and atrazine were detected in river water and groundwater in all samplings of our field study. The highest concentrations of 2,4-D and atrazine were found in the river water, ranging up to 3.00 and 0.96 µg/L, respectively.

The monitoring of banned compounds was found to be important because several studies indicate that they are still accumulating in the environment and/or are still illegally in use. However, supported by our own data, we find that the monitoring in groundwater and surface water of currently permitted pesticides in China needs equal attention, and should therefore be increased.

**Keywords**: North China Plain; Surface water – groundwater interaction; Pesticides; Atrazine; 2,4-D

## 1. Introduction

The North China Plain (NCP) has an output of the national maize and wheat production of about 60% and 40%, respectively (Zhao and Guo, 2013), which makes it a crucial area for China’s domestic food supply. It is therefore also referred to as China’s *bread basket*. In recent decades, the total cultivated area in the NCP has decreased due to competition for land use from industry and urbanization. To continue meeting the food demands of the rapidly growing Chinese population, higher production efficiencies needed to be achieved, so that the loss of production areas could be compensated. This goal was successfully met by introducing modern agricultural practices in the 1970s and 1980s (such as the use of fertilizers and pesticides) and by increasing irrigated agriculture. On the down-side, pesticide overuse has nowadays become common and poses a risk to valuable surface water and groundwater resources (Zhang et al., 2011). This negative effect of the agricultural activities on potential drinking water is especially problematic in the provinces of the NCP because of its high population density and its relatively low amounts of available water resources (Varis and Vakkilainen, 2001). Therefore, further decline in water quantity and quality is an imminent challenge for the area (van Oort et al., 2016; Sun et al., 2012; Zheng et al., 2015).

To address the problem of agricultural water pollution by pesticides, studies in recent years have dealt with the optimization of applied pesticide doses (Zhang et al., 2013), the need to develop a systematic risk assessment approach for water pollution by pesticides (Zhao and Pei, 2012), and the enhancement of pesticide management in general (Hamburger, 2002; Wei et al., 2007; Zhen et al., 2005). Further studies on pesticide residues in waterways and agricultural soils have repeatedly detected banned organochlorine insecticides, such as hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) (Feng et al., 2011; Sun et al., 2010). Risk mapping of these compounds, and the detection of potentially still active application and bioaccumulation, are important tasks. However, other disputed pesticides such as atrazine (which has been banned in the EU since 2004, but is legally used in China) may potentially accumulate in the environment and cause negative environmental impacts, too. Therefore, monitoring of currently permitted and applied pesticides should also be considered. This includes obtaining knowledge about pesticide choices, means of application and disposal, environmental loads, and potential environmental impacts. Based on this information, upcoming problems can be better identified, and pesticides can be chosen and applied more wisely by the farmers. However, a comprehensive overview and review of commonly applied pesticides on Chinese winter wheat-summer maize rotations (and their loads in regional water resources) are very limited, and the availability of detailed statistics on pesticide use in China is extremely low (World Bank, 2010).

Upon this background, the aim of this study was (a) to review the current use of pesticides within the NCP, (b) to assess the recent and current research and monitoring of pesticides in water resources in the NCP, (c) to perform a small-scale field study on the occurrence of currently-used pesticides in surface water and connected groundwater, (d) to assess (supported by our findings in the field study) if currently used pesticides might cause environmental problems and if this is sufficiently addressed in the current monitoring efforts , and (**e**) to give recommendations for future study focus within the region.

The paper includes a comprehensive review part based on publicly available information and a field investigation at Fu River (Hebei Province) in order to investigate the current pesticide use and occurrence in the NCP. The agricultural cultivation at the field site is typical for this region, and although the study is limited in time, the findings presented illustrate the limitations in the current monitoring programs and are thereby an important contribution to the recommendations and conclusions of this paper.

## 2. Material and methods

### 2.1. Field site

A field site located at Fu River, the main incoming river to the Baiyang Lake area in Hebei Province, China, was selected as an example for the wheat-maize double cropping system in the NCP (Figure 1a-b). The vicinity of the field site to surface water was chosen in order to investigate surface water-groundwater interactions and pollution exchange between the environmental compartments. A monitoring network (consisting of four shallow groundwater wells of which three were used for pesticide sampling) was set up on an agricultural field (about 70x240 m) that extends to about 5 m to the river bank (Figure 1c). The agricultural plot (owned by one household) is surrounded by other fields with different ownership, but the same cropping system.

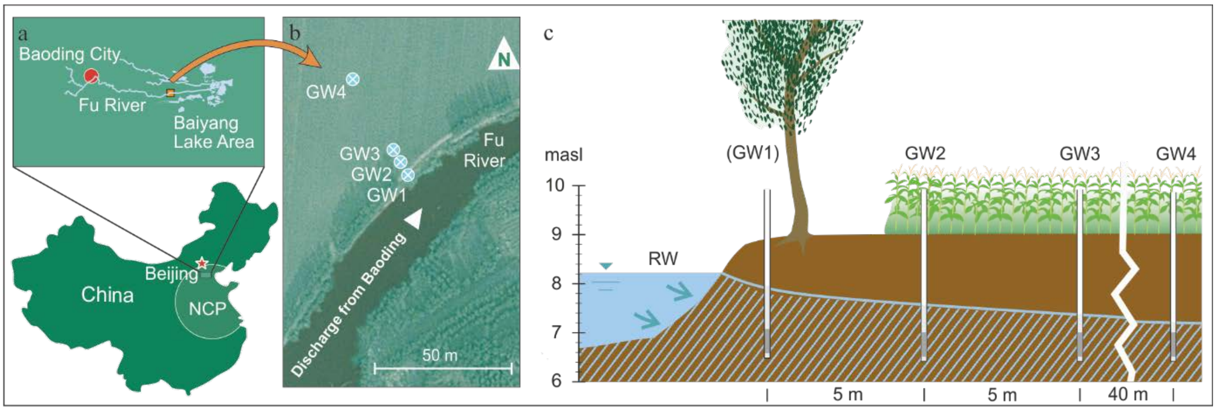



**Fig. 1** (a) Location of the study site, (b) aerial view of the field site, and (c) cross-section of the sampling wells (GW1 only used for ion-analysis and general water chemistry) SINGLE-COLUMN COLOUR FIGURE

The area around Fu River is characterized by pressures from agricultural, domestic, and industrial water users. Numerous paper mills, and chemical, battery and petrochemical plants are located in the upstream part of Fu River (Hu et al., 2010a), and it receives an approximate amount of over 100 000 $m^3$ of sewage and treated wastewater from Baoding city per day (Qi et al., 2012). Previous studies show that the point and non-point pollution sources along the flow path of Fu River increase levels of organic chlorinated pesticides (OCPs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) in the river—especially near industrial areas (Hu et al, 2010b). Studies at the river mouth (entering into Baiyang Lake) show extremely high loads of the nutrients ammonium and potassium (e.g. Zhao et al., 2012). This indicates contamination from poorly treated sewage that is led into the river (Xu et al., 2012), or possibly from direct discharge of animal manure as observed in other regions of China (Strokal et al., 2016). Temporal nitrate peaks that occur simultaneously with increased sediment loads in the river imply contamination by surface runoff of agricultural pollutants (possibly also pesticides) from adjacent field areas after rainstorms (Yan et al., 2005).

## 2.2. Field site management and pesticide application

The field site was managed according to the local customs of the area (described in more detail in Brauns et al., 2016). The successive winter wheat–summer maize rotation encompassed the growing season for wheat from October 2012 to June 2013 and that of maize from June 2013 to October 2013. Irrigation with surface water took place three times during the growing period of winter wheat. Towards the end of the study period, the region from about 1 -2 km upstream of the field site until the entrance of Fu River into the Baiyang Lake system was expected to become flooded due to unusually high summer rainfalls, which exceeded the 10-year average by 57%. Therefore, the farmers along this section of the river refrained from planting winter wheat, and the land became fallow (and flooded) during the remaining study period.

Based on interviews with the farmer, pest and weed management at the sampling site itself was done via chemical crop protection which took place twice in the winter wheat growing season (with tribenuron-methyl and dimethoate) and twice during the growing season of the summer maize (paraquat and acetochlor) via knapsack spraying. More detailed information on planting times, irrigation, and times and amounts of pesticide application can be found in Appendix A Table A.2. The pesticide application in the study year was not identical to the one in previous years, where atrazine had been used instead of acetochlor, and additional insecticides had been applied in the fall. Application rates in the study year were mostly in accordance to the recommendations on the labels of the pesticide containers. According to statements from the farmer however, it seemed that the exact application amount was sometimes based on avoiding leftovers in pesticide packages/bottles, rather than on judging the actual needed application rate based on observation in the field, e.g. the amount of weed sprouting.

Additional farmer interviews indicated that treatment with other substances in neighboring fields was likely. For example, either 2,4-D or atrazine is often also used as post emergence pesticide on winter wheat in early spring (March to April).  The discovery of empty containers from other substances (e.g. triadimefon) in the ambient environment of the study field also indicated that additional compounds were used, at least in the surrounding area (Figure 2).


**Fig. 2** (a) Improperly disposed insecticide/fungicide bags that were found at the field site (tribenuron-methyl and triadimefon, respectively), (b) pollution in the adjacent river, and (c) empty insecticide bottle (8% dimethoate and 2% cyhalothrin) found in the river next to the sampling site. SINGLE-COLUMN COLOUR FIGURE

## 2.3. Field sampling and chemical analysis

1 L water samples were obtained from river and from groundwater wells at a distance of 6, 11, and 41 m from the river (corresponding to GW2, GW3, and GW4 on Figure 1c) in May,

July and October 2013, and in March 2014. The sampled water was filled to the rim into brown glass bottles, immediately cooled to 4°C, insulated, and shipped by courier to the laboratory in Denmark (Eurofins, Glostrup). The samples were analyzed for a standard package of different pesticides, which included some of the most universally used herbicides in the NCP (and at the field) site as identified in section 3.2. (a full list of analytes is given in Appendix A Table A.2). Analysis was done via gas chromatography mass spectrometry (GC/MS) for chlorphenols and dichlobenil, and via liquid chromatography tandem mass spectrometry (LC-MS/MS) for all other pesticides. The detection limit was 0.01 µg/L for all compounds.

# 3. Results and discussion

## 3.1. Detected pesticides in the field study

Detected pesticides and their degradation products (or, in the case of 2,6-dichlorphenol, intermediates) in the field study included mainly 2,4-D, 2,4-dichlorphenol (metabolite of 2,4-D), 2,6-dichlorphenol (intermediate to 2,4-D), atrazine and the atrazine-metabolites hydroxyatrazine, deethylatrazine, and deisopropylatrazine, terbutylazine, MCPA, bentazone, DNOC, BAM (metabolite of chlorthiamid, dichlobenil and fluopicolide), and dichlorprop (see Table 1).

**Table 1** Detected concentrations in µg/l of selected herbicides in river water (RW) and groundwater (GW) samples (see Figure 1 for the location of the sampling points), and drinking water limits (DWL) for China and for the USA (for comparison, the standard of the European Drinking Water Directive is 0.1µg/L for each individual pesticide, and 0.5µg/L for the sum of all pesticides detected in the sample). Data for the Chinese standard is according to the guideline GB 5749-2006.

| **Pesticide** (all values in µg/L) | **29 May 2013** | | | | **22 July 2013** | | | | **07 October 2013** | | | | **25 March 2014** | | | | **DWL** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | RW | GW2 | GW3 | GW4 | RW | GW2 | GW3 | GW4 | RW | GW2 | GW3 | GW4 | RW | GW2 | GW3 | GW4 | CN | USA |
| **2,4-D and related compounds** | | | | | | | | | | | | | | | | | | |
| 2,4-D[1] | **3.00** | 0.41 | **2.30** | 0.70 | 0.27 | 0.09 | 0.10 | 0.31 | 0.51 | 0.03 | 0.03 | 0.01 | 0.65 | 0.01 | 0.05 | 0.02 | 30 | 70* |
| 2,4-dichlorophenol (M) | 0.09 | 0.14 | 0.09 | 0.14 | 0.02 | 0.10 | 0.09 | 0.07 | 0.06 | 0.03 | 0.04 | 0.03 | 0.01 | ND | ND | ND | - | 20** |
| 2,6-dichlorophenol (I) | ND | 0.02 | ND | 0.01 | 0.01 | 0.03 | 0.16 | 0.02 | 0.01 | ND | ND | ND | 0.01 | ND | ND | ND | - | 4*** |
| **Atrazine and related compounds** | | | | | | | | | | | | | | | | | | |
| Atrazine | 0.96 | 0.33 | 0.91 | 0.40 | 0.32 | 0.29 | 0.29 | 0.49 | 0.49 | 0.19 | 0.20 | 0.20 | 0.54 | 0.12 | 0.19 | 0.15 | 2 | 3* |
| Hydroxyatrazine (M) | **9.70** | 0.46 | 0.37 | 0.47 | 0.31 | 0.59 | 0.54 | 0.49 | **3.00** | 0.55 | 0.39 | 0.48 | **1.60** | 0.26 | 0.33 | 0.20 | - | - |
| Desethylatrazine (M) | 0.07 | 0.04 | 0.05 | 0.04 | 0.17 | 0.09 | 0.07 | 0.16 | 0.03 | 0.01 | 0.02 | 0.04 | 0.05 | 0.03 | 0.04 | 0.08 | - | - |
| Deisopropylatrazine (M) | 0.07 | 0.05 | 0.05 | 0.04 | 0.04 | 0.16 | 0.08 | 0.09 | ND | ND | ND | 0.01 | 0.13 | 0.01 | 0.02 | 0.02 | - | - |
| **Other compounds** | | | | | | | | | | | | | | | | | | |
| Terbuthylazine | ND | ND | 0.02 | 0.01 | ND | ND | ND | 0.02 | ND | ND | ND | ND | ND | ND | ND | ND | - | - |
| MCPA[2] | 0.06 | 0.03 | 0.05 | 0.02 | 0.03 | ND | ND | 0.01 | ND | ND | ND | ND | 0.04 | ND | ND | ND | - | 10** |
| Bentazone | 0.03 | 0.02 | ND | 0.02 | 0.01 | ND | ND | ND | 0.03 | 0.08 | 0.07 | 0.07 | 0.01 | 0.03 | 0.03 | 0.04 | 300 | 20** |
| DNOC[3] | 0.06 | ND | ND | ND | 0.04 | ND | ND | ND | 0.02 | ND | ND | ND | 0.11 | ND | ND | ND | - | - |
| BAM[4] | 0.06 | 0.01 | ND | 0.04 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | - | - |
| Dichlorprop | ND | ND | ND | ND | 0.02 | ND | ND | ND | 0.04 | ND | ND | ND | ND | ND | ND | ND | - | - |

Values >1 µg/L are highlighted in bold; ND = Not detected (< 0.01 µg/L ); M = Metabolite; I = Intermediate 1 = 2,4-Dichlorophenoxyacetic acid; 2 =2-methyl-4-chlorophenoxyacetic; 3= Dinitro-ortho-cresol; 4=2,6-dichloro-benzamide; *=National standard; **=Federal guideline; ***State guideline

The pre and post emergence herbicides 2,4-D, atrazine, and its metabolite hydroxyatrazine were the most abundantly detected species. They were found throughout all four samplings and in all of the samples, with peak values of 3.00 µg/L (2,4-D), 0.96 µg/L (atrazine), and 9.70 µg/L (hydroxyatrazine). The range of our measured concentrations is similar to results from a study in the Beijing area, where herbicides in surface water were detected in concentrations up to 5.1 µg/L (Deuerlein et al. 2001a). All of the observed peak concentrations occurred in river water in May 2013. This peak time in May might be due to runoff from field irrigation after the spring application of herbicides (see Figure 3 for irrigation times, rainfall events, and herbicide application times), and possibly from spray drift during application. Discarded containers adjacent to—or even directly into—the river might be an additional cause of the rather surprising peak in river water before the actual raining season (when a stronger effect of surface runoff due to heavy rainfall events could be expected).

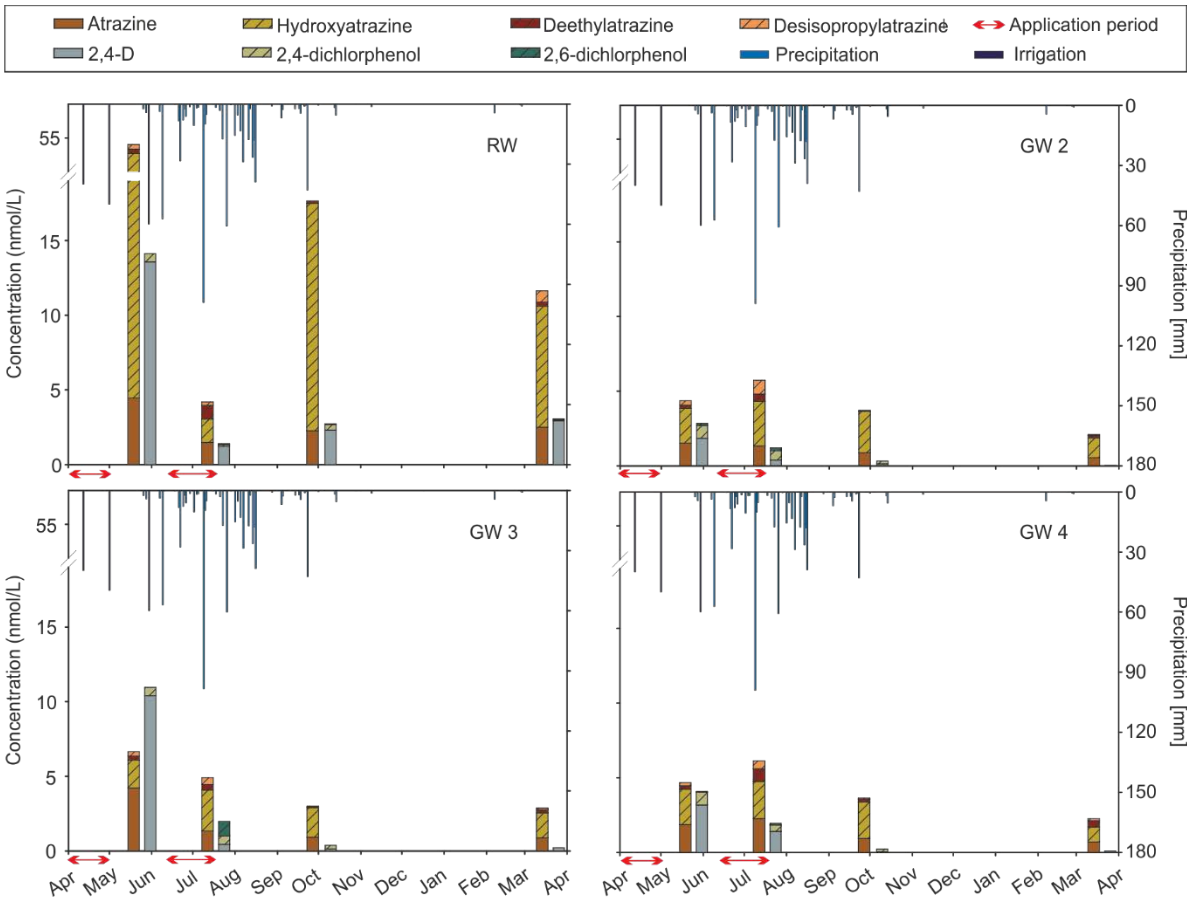



**Fig. 3** Detections of atrazine and 2,4-D and selected degradation products and isomers for river water (RW) and groundwater (GW) samples, application periods of the herbicides, and precipitation from April 2013-April 2014. Precipitation is indicated as inverted bars on the secondary Y-axis. SINGLE-COLUMN COLOUR FIGURE

During fall and early spring, 2,4-D concentrations in river water were mostly one order of magnitude higher than in the sampled groundwater. Generally, the 2,4-D concentrations in surface remained relatively high in all samplings, and did not drop below 0.27 µg/L (July 2013). A sharp decrease in concentration was however observed after the peak detected in May (3.00 µg/L). This drop was likely caused by the high dilution of the river water that occurred just before the sampling in July (20% of the annual rainfall). Atrazine and hydroxyatrazine also peaked in  river water, but the concentrations in groundwater and river water samples were generally more similar to each other than in the case of 2,4-D, meaning that 2,4 removal along the flow path was slightly more rapid than for atrazine and its metabolites. This might indicate a higher degradation rate of 2,4-D.

Another interesting finding was that the atrazine degradation product hydroxyatrazine exceeded that of the mother compound atrazine in nearly all samples (see Figure 1 for comparison in µmol/L); even in groundwater. Other studies have found this dominance of hydroxyatrazine only in surface water, where chemical hydrolysis dominates the atrazine degradation process (Ren and Jiang, 2002a), while close to no hydroxyatrazine is usually detected in groundwater (Geng et al., 2013). Furthermore, the molar ratio of deethylatrazine over atrazine, also called DAR, in the groundwater samples was much lower than 1.0 (only 0.24 on average), which indicates that no transport through the unsaturated zone has taken place (Adams and Thurman, 1991). We therefore conclude that the much of the groundwater contamination originated from the polluted river.

Compared to the distinct peak concentrations observed after the first application period, pesticide concentrations after the summer application did not peak as considerably. This is likely due to the higher dilution factor caused by the summer rainfalls. The fact that no application of pesticides took place from about 1-2 km upstream of the study site (due to flooding of the lower reach of Fu River) might also have reduced the signal slightly. However, the fallow stretch upstream of the site only accounts for a very small proportion of the expected source area for pesticide contamination along the river, so that it is unlikely that this caused high differences in surface water concentration compared to a year with regular farming activities. Higher vertical input of pesticides from transport through the unsaturated zone under normal field conditions could have been possible, but as the lateral inflow of the river water seemed to be the dominant influence at this site, this also would only have changed the study results to a minor extend.

In summary, the high concentration of most of the detected pesticides in river water demonstrates that there is a high potential for groundwater contamination by polluted surface water — despite the high dilution factor in rivers. The peak concentrations in the river water are mostly observed after the pesticide application on sparse vegetation before the beginning of the raining season, indicating pollution by spray drift during application (especially during application on sparse vegetation in the spring time), surface runoff, and possibly also by point sources, such as improperly disposed containers.

## 3.2. Agriculture and pesticide use in the NCP

The NCP (extending over much of the provinces Beijing, Tianjin, Hebei, Henan, Shandong, Jiangsu, and Anhui in the Eastern part of China) supports 14% of China's arable land and 11% of its population with only 2% of the nation's total groundwater resources (Frenken, 2012). The relatively fertile alluvial soils of the NCP and its mild winters with long sunshine hours allow for double-cropping systems, such as the cultivation of winter wheat (October-June) and summer maize (June-October). This is the dominant agricultural activity in this area (Li et al., 2015). However, the strong seasonality of rainfall—of which 70-80% occurs from July to September—makes irrigation a necessity to sustain a good harvest of the winter wheat (but is usually not necessary for the summer maize). Furthermore, the intense use of the soils requires a major input of fertilizers to sustain high yields (Gao et al., 2014).

Due to the heavy promotion of agrochemicals by the government in the 1980s, and the increase in time constraints of farmers due to new job opportunities outside of the agricultural sector, a major shift from traditional hand weeding to the use of pesticides took place in recent decades. At present, about 800 pesticide products are approved for use in China, of which herbicides had an increasing share from 20% in 1960 to 56% in 2009 (Devi et al., 2009; Zhang et al., 2011). This relative increase in the share of applied herbicides from the total applied pesticides has previously been observed in the United States (US). Here, the percentage of applied herbicides rose from 18% to 76% between 1960 and 2008 (Fernandez-Cornejo et al., 2014).

In the provinces of the NCP, a particularly strong trend of increasing pesticide utilization can be observed. According to data from representative regions in the NCP, 93.5% of the sown area is treated with pesticides, which is well above the national average of 70.4% (Löw, 2003). In the specific case of winter wheat-summer maize fields, it is estimated that about 80% of the farmers in the NCP are using herbicides, and that only little weeding is still done by hand (Menegat, 2013). Average application rates of pesticides for wheat-maize systems in the NCP at the turn of the century were reported to be 2.82 kg a.i./ha/year (Li and Zhang, 1999), but more recent publications report current application rates of 5.87 kg a.i./ha/year (Wang et al., 2014).

## 3.3. Pesticide handling, application, occupational risk, and farmer's knowledge

A common method of pesticide application in China (and also in the NCP) is via spraying from knapsack sprayers; often while wearing little protective clothing (Yang et al., 2014). Consequently, a survey of 270 households in the NCP showed that 20% of the interviewed farmers experience health impacts such as headache, dizziness, nausea, stomach ache, skin rashes, fatigue, and increased visits to the doctor during times of pesticide application (Zhen et al., 2005). On the country level, 300-500 farmers die each year because of pesticide poisoning (Devi et al., 2009). A follow-up study on registered intoxications with the herbicide paraquat found that—despite the widespread use of the chemical—its hazard to health is not fully conceived by farmers, and many believe the compound to be less toxic than it is (Yin et al., 2013). This stresses that the occupational risk from pesticides still needs to be clearly understood.

Furthermore, it is reported that pesticides are applied in very high doses, and “over application is a common phenomenon in China” (Zhao, 2013). In a study on pesticide overuse on cotton, about 87% of the surveyed farmers used double or more than the recommended doses even though they claimed to have read the instructions in the manual (Jin et al. 2015). Another example is that many farmers that grow genetically modified Bt (*Bacillus thuringiensis*) cotton still add pesticides for pests, against which the Bt cotton is resistant (Chen et al., 2013). This overuse of pesticides has been related to a variety of reasons. Hamburger (2002) argues that mistrust into the exact composition and effectiveness of the compounds, and the misconception that higher application doses will give more protection against pest outbreaks are major causes for the observed over applications. Other studies imply that untimely spraying (when pests and diseases had already broken out), and a strong tendency *to do as the neighbor does* might be the cause (Liang et al., 2011). Overall, the over application indicates a lack of farmer education. Indeed, a study of 64 farming household in Hebei province discovered that 86% had never received any agricultural training (Kühl et al. 2009).

Another observed phenomenon is that emptied pesticide containers are often disposed of by simply leaving them in the field, or even in ditches and waterways. According to the China Crop Protection Industry Association (CCPIA, 2014), more than 5-10 pesticide packages per mu of farmland (1 mu =0.06ha) can be found on average. This may create an additional source of pesticide pollution in soil and water, and current studies propose that an enhanced farmer education as well a better infrastructure for proper disposal are needed to change the situation (Geng and Ongley, 2013; Jin et al. 2015).

### 3.4. Recent and current research focus on pesticides in the NCP

A literature review was undertaken to assess the recent and current research and monitoring of pesticides in the NCP. As of today, no public national database on systematic governmental monitoring of pesticides in surface and/or groundwater could yet be found, and recent publications point out the need for the establishment of a detailed governmental environmental monitoring and risk assessment system (Han and Jin, 2016; Zhao and Pei, 2012).

In 1997, some data on sites contaminated with persistent organic pollutants (POPs), such as DDT and HCH, was published in *The National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants* (The People's Republic of China, 2007). However, all data from mainland China was derived from published scientific studies only. The plan therefore highlights that a national monitoring system for persistent organic pollutants (POPs) needs to be established. The Chinese Geological Survey (CGS) conducted a groundwater quality survey from 2005-2015. Over 36,000 samples were taken and more than 70 components (including a wide range of banned and currently-used pesticides, listed in CGS, 2008) were measured over an area about 4,400,000 $km^2$. However, this data is not publicly accessible. For routine measurements of groundwater quality, about 4000 monitoring wells (operated by CGS and the provincial government monitoring institutes) are currently in use, but pesticides are not considered for most of the wells. A more comprehensive national groundwater monitoring network (about 20,000 professional monitoring wells) is constructed at present, and over 80 components including pesticides will be measured (Hao Aibing, personal communication December 13, 2016).

Results from our literature study on non-governmental pesticide research in the NCP (Table 2, sorted by sampling year), show that ten out of seventeen studies focused on surface water pollution by HCH and DDT. These compounds had been the most widely applied pesticides in China between the 1950s and 1980s (Dai et al. 2011), but have been banned for most uses (including agriculture) by the Chinese government since 1983. A strong research focus on HCH and DDT between 1970 and 1980 has previously been observed by Li and Zhang (1999). Only six of our reviewed studies primarily concentrated on pesticides that are currently in use. Out of these six studies, four are limited to the analysis for atrazine residues only, and all the six studies have been published before or in 2004 (Deuerlein et al., 2001a; Domagalski et al., 2001; Ren and Jiang, 2002a; Ren and Jiang, 2002b; Ren and Jiang, 2004; Ye et al., 2001).

**Table 2** List of recent studies (1995-2013) on pesticide pollution in surface water (SW) and groundwater (GW) in the North China Plain. The studies are sorted by sampling year. Concentrations highlighted in bold exceeded the Chinese drinking water limit (according to guideline GB 5749-2006).

| Study # | Pesticide | SCPOP | Study region | Sampling time | SW – sampling | | GW - sampling | | GW depth | Author/year |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | (year/month) | Mean (µg/L) | Range (µg/L) | Mean (µg/L) | Range (µg/L) | (m) | |
| 1 | DDT (I) | x | Baiyangdian | 1995/06 | 0.100 | - | - | - | - | Dou and Zhao, 1997 |
| | BHC (I) | x | " | " | 0.300 | - | - | - | - | " |
| 2 | Various[1] | | Tangshan | 1996 | - | - | ND | ND | no data | Domagalski et al., 2001 |
| **3** | **Atrazine (I)** | | **Baiyangdian** | 1998 | - | - | 1.33 | 0.40-**3.29** | 15-50 | Ye et al., 2001 |
| **4** | **Atrazine (I)** | | **Yanghe** | 1999-2000 | - | ND-**26.1** | - | ND-0.69 | 30-300 | Ren and Jiang, 2002b |
| **5** | **Atrazine (I)** | | **Yanghe** | 2000/12 | **6.7** | - | 0.36 | ND-0.72 | 130 & 380 | Ren and Jiang, 2002a |
| 6 | Various[2] | | Beijing | 2001 | - | <0.1-5.1 | ND | ND | 100 | Deuerlein et al., 2001a |
| **7** | **Atrazine (I)** | | **Guanting*** | 2002/03 | **3.0** | **2.0 – 4.8** | | | | Ren and Jiang, 2004 |
| 8 | Aldrin (I) | x | Huai'an | 2002/07 | $0.005^{G}$ | 0.002-0.033 | - | - | - | Wang et al., 2009 |
| | DDT (I) | x | " | -2003/03 | $0.011^{G}$ | 0.003-0.081 | - | - | - | " |
| | Dieldrin (I) | x | " | " | $0.001^{G}$ | <0.001-0.002 | - | - | - | " |
| | Endosulfan (I) | x | " | " | $0.003^{G}$ | <0.001-0.010 | - | - | - | " |
| | Endrin (I) | x | " | " | $0.002^{G}$ | 0.001-0.064 | - | - | - | " |
| | HCB (F) | x | " | " | $0.003^{G}$ | <0.001-0.001 | - | - | - | " |
| | HCH (I) | x | " | " | $0.003^{G}$ | 0.001-0.009 | - | - | - | " |
| | Heptachlor (I) | x | " | " | $0.008^{G}$ | <0.001-0.003 | - | - | - | " |
| | Methoxychlor (I) | | " | " | $0.003^{G}$ | 0.001-0.013 | - | - | - | " |
| 9 | Acetochlor (H) | | Guanting* | 2003/09&11 | 0.001 | ND-0.002 | - | - | - | Xue and Xu, 2006 |
| | Alachlor (H) | | | & 2004/05&08 | 0.002 | ND-0.006 | - | - | - | " |
| | Aldrin (I) | x | " | " | 0.023 | 0.002-0.032 | - | - | - | " |
| | Chlordane (I) | x | " | " | 0.010 | 0.001-0.039 | - | - | - | " |
| | Chlorpyrifos (I) | | " | " | 0.002 | <0.001-0.002 | - | - | - | " |
| | Cypermethrin (I) | | " | " | 0.001 | ND-0.002 | - | - | - | " |
| | DDT (I) | x | " | " | 0.093 | 0.006-0.364 | - | - | - | " |
| | Deltamethrin (I) | | " | " | 0.004 | ND-0.006 | - | - | - | " |
| | Dicofol (I) | | " | " | 0.001 | ND-0.003 | - | - | - | " |
| | Dieldrin (I) | x | " | " | 0.001 | ND-0.005 | - | - | - | " |
| | Endosulfans[3] (I) | x | " | " | 0.025 | 0.005-0.077 | - | - | - | " |
| | Endrins[4] (I) | x | " | " | 0.009 | ND-0.0019 | - | - | - | " |
| | Fenvalerate (I) | | " | " | 0.002 | ND-0.003 | - | - | - | " |
| | HCB (F) | x | " | " | 0.012 | 0.001-0.027 | - | - | - | " |
| | HCH (I) | x | " | " | 0.071 | 0.007-0.051 | - | - | - | " |
| | Heptachlor (I) | x | " | " | 0.005 | 0.002-0.021 | - | - | - | " |
| | Methoxychlor (I) | | " | " | 0.004 | ND-0.022 | - | - | - | " |
| | Metolachlor (H) | | " | " | 0.023 | 0.016-0.027 | - | - | - | " |
| | Nitrofen (H) | | " | " | 0.001 | ND-0.002 | - | - | - | " |
| | Trifluralin (H) | | " | " | 0.005 | 0.003-0.005 | - | - | - | " |
| 10 | DDT (I) | x | Huaihe | 2007/03 | 0.011 | 0.004-0.034 | - | - | - | Feng et al., 2011 |
| | HCH (I) | x | " | " | 0.004 | ND-0.013 | - | - | - | " |
| 11 | DDT (I) | x | Baiyangdian | 2007/07 | 0.002 | - | - | - | - | Hu et al., 2010a |
| | HCH (I) | x | " | " | 0.002 | - | - | - | - | " |
| 12 | DDT (I) | x | Baiyangdian | 2007/10 | ND | ND | - | - | - | Wang et al., 2013 |
| | HCH (I) | x | " | " | 0.002 | 0.001-0.008 | - | - | - | " |
| 13 | DDT (I) | x | Baiyangdian | 2008/07 | 0.011 | 0.004-0.021 | - | - | - | Dai et al., 2011 |
| | HCH (I) | x | " | " | 0.006 | 0.003-0.011 | - | - | - | " |
| 14 | DDT (I) | x | Weishan Lake | 2009/06 | 0.096 | 0.035-0.157 | - | - | - | Ge et al., 2010 |
| | HCH (I) | x | " | " | 0.036 | 0.013-0.195 | - | - | - | " |
| 15 | HCH (I) | x | Baiyangdian | 2010/03-12 | 0.024 | 0.006-0.054 | - | - | - | Dai et al., 2013 |
| 16 | DDT (I) | x | Baiyangdian | 2010/03-12 | 0.008 | 0.002-0.034 | - | - | - | Dai et al., 2014 |
| 17 | DDT (I) | x | Baiyangdian | 2012/10 | 0.006 | 0.003-0.017 | - | - | - | Guo and Feng, 2014 |
| | HCH (I) | x | " | " | 0.005 | 0.003-0.012 | - | - | - | " |

x indicates that the compound is listed in the SCPOP (Stockholm Convention on Persistent Organic Pollutants); Guanting* = Guanting Reservoir; BHC = Benzene hexachloride; DDTs = Dichlorodiphenyltrichloroethanes; HCB = Hexachlorobenzene; HCHs = Hexachlorocyclohexanes; H = Herbicide; I = Insecticide; F = Fungicide; G = Geometric mean; ND = Not detected; 1 = Complete list of analytes not known, but included the herbicides atrazine, cyanazine, simazine, alachlor, metolachlor, dicamba; 2 = Analysis for 31 pesticides. Detected in SW: Butachlor (H), metolachlor (H), molinate (H), chlorpyrifos (I), diazinon (I), and dichlorvos (I). No fungicides were detected in GW; 3 = Endosulfan I & II + Endosulfan sulfate; 4 = Endrin + Endrin aldehyde

From 2002 onward, only studies that focused primarily on HCH and DDT were found—despite the fact that detected concentrations were continuously by at least one order of magnitude below the Chinese drinking water limit (1 µg/L). One reason for the observed sampling bias might be that DDT and HCH were listed as persistent organic pollutants (POPs) by the Stockholm Convention on Persistent Organic Pollutants (SCPOP) in 2004, which could have incentivized scientists to primarily publish studies on this topic. Additionally, there seems to be a stronger focus on surface water than on groundwater sampling. In fact, the authors could not find a published study on pesticides in groundwater in the NCP after 2002 – despite the fact that Ye et al. had detected atrazine concentrations in groundwater samples that exceeded the national threshold for drinking water of 2 µg/L in 2001. This indicates that pesticide research in the NCP has not only narrowed down to studies related to the SCPOP, but also that sampling in the easier accessible surface water is preferred over groundwater sampling.

### 3.5. Applied pesticides in the NCP and their potential environmental impact

At present, statistics on pesticide use in China are neither easily obtainable nor greatly detailed (World Bank, 2010). The authors therefore identified the most commonly applied pesticides for wheat-maize cropping in the NCP by means of a literature search, in which ten studies were considered that referenced to specific pesticides as being “the most typically applied” in the region (Table 3).

**Table 3** Most commonly applied pesticides in the North China Plain (NCP) for winter wheat and summer maize. The presented pesticide list is based on the identification of different herbicides, insecticides, and fungicides in recent literature as most abundantly used pesticides in the wheat-maize systems of the NCP.

| **Pesticide** | **Citation** | **Applied on** | **Emergence** | |
|---|---|---|---|---|
| | | | Pre | Post |
| **Herbicides** | | | | |
| 2,4-D | 1, 2, 4, 6,10 | W / M | | x |
| Acetochlor | 1, 3, 8,9 | M | x | |
| Atrazine | 1, 5, 7, 8,9 | W / M | x | x |
| Butachlor | 1,8 | W / M | x | |
| Chlortoluron | 1 | W / M | | x |
| Glyphosate | 1 | W / M | | x |
| Iodosulfuron | 6 | W | | x |
| MCPA | 1 | W / M | | x |
| Mesotrione | 8 | M | x | x |
| Metolachlor | 8 | M | x | |
| Metribuzin | 8 | M | x | x |
| Molinate | 1 | W / M | x | x |
| Nicosulfuron | 8 | M | | x |
| Paraquat | 1 | W / M | | x |
| Tribenuron-methyl | 6 | W | | x |
| Trifluralin | 1 | W / M | x | |
| Topramezone | 8 | M | | x |
| **Insecticides** | | | | |
| Acephate | 7 | W | | |
| Carbofuran | 3 | M | | |
| Chlorpyrifos | 5 | M | | |
| Dichlorvos | 3 | W / M | | |
| Dimethoate | 2, 3, 4,10 | W / M | | |
| Emamectin benzoate | 5 | M | | |
| Omethoate | 4 | M | | |
| **Fungicides** | | | | |
| Carbendazim | 4 | M | | |
| Chlorothalonil | 7 | W | | |

W = Wheat; M = Maize; 1 = Deuerlein et al., 2001b; 2 = Hou et al., 2012; 3 = Huang et al., 2013; 4 = Li and Zhang, 1999; 5 = Liu et al., 2012; 6 = Menegat et al., 2013; 7 = Wang et al., 2014; 8 = Ye et al., 2001; 9 = Zhang et al., 2013; 10= Huang et al., 2015

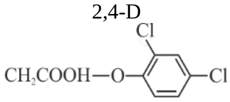
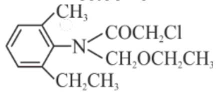
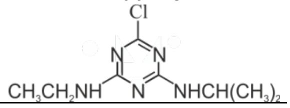
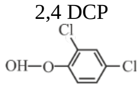
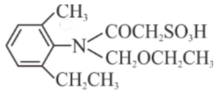
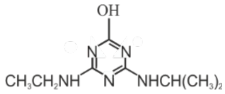
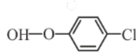
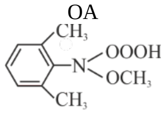
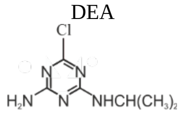
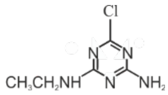
The results show that the different studies observed a relatively broad range of different pesticides of being used in the same wheat-maize cropping systems in the NCP. Within the group of herbicides, 2,4-D, acetochlor, and atrazine seem to be the most widely applied compounds for weed control. This is similar to the five most used herbicides in the US: glyphosate, atrazine, acetochlor, metolachlor, and 2,4-D (Fernandez-Cornejo et al., 2014).

Potential pesticide pollution of surface water and groundwater depends on the means and rate of application, environmental factors, the physicochemical properties of the pesticide, and its degradability in aquatic systems and soil. For example, high adsorption coefficients ($K_{OC}$) of insecticides like chlorpyrifos lead to accumulation in soil and river sediments (McKnight et al., 2015; Rasmussen et al., 2015). Many herbicides on the other hand have a higher potential for leaching and runoff – not only because of their different chemical properties, but also due to their early application when little vegetation is present (insecticides and fungicides are normally applied on foliage). This can lead to a higher impact of spray drift during, and surface runoff after the application. Accordingly, the majority of detected pesticides in large-scale investigations are usually herbicides (e.g. Kolpin et al., 1998; Steele et al., 2002).

### 3.6. Transport, fate, and expected impact of 2,4- D, acetochlor and atrazine

Table 4 summarizes the main physicochemical properties of 2,4-D, acetochlor, and atrazine; their environmental behavior that derives from these properties; and their main degradation products. Acetochlor binds strongly to organic matter in the soil (Hiller et al, 2008), which makes it unlikely to leach into groundwater. Additionally, studies have shown that acetochlor is readily degradable in topsoil and in the subsurface (Janniche et al., 2010). Accordingly, it has only rarely been detected in surface water and groundwater (Barbash et al., 1999; Kolpin et al. 1996).

**Table 4** Physicochemical properties of the three herbicides 2,4-D, acetochlor, and atrazine, derived behavior in aquatic and soil systems, and main degradation products.

| | 2,4-D | Acetochlor | Atrazine |
|---|---|---|---|
| |  |  |  |
| Physicochemical properties[1] | | | |
| Molecular formula | $C_9H_8Cl_2O_3$ | $C1_4H_20ClNO_2$ | $C_8H_{14}ClN_5$ |
| Molar weight (g/mol) | 221.0 | 269.8 | 215.7 |
| Solubility (mg/L) | 23 180 (pH 7) | 282 | 33 |
| Vapor pressure (mPa) at 25°C | 1.9 $E^{-2}$ | 4.6 $E^{-2}$ | 3.6 $E^{-2}$ |
| log $K_{OW}$ at 20°C | 2.58-2.83 | 4.14 | 2.5 |
| Ecosystem behavior and mobility[2] | | | |
| Potential for bioaccumulation | Low | Low | Low |
| Persistency in aquatic systems | High | High | Low |
| Persistency in soil systems | Low | Low | Medium |
| Soil mobility | Mobile | Moderately mobile | Moderately mobile |
| Leachability into groundwater | Low/moderately | Low | Possible |
| Main degradation products[3] | 2,4 DCP  | ESA  | HA  |
| | 4-CP  | OA  | DEA  |
| | | | DIA  |

2,4-DCP = 2,4-Dichlorophenol; 4-CP = 4-Chlorophenol; ESA = Acetochlor ethanesulfonic acid; OA = Acetochlor oxanilic acid; HA = Hydroxyatrazine; DEA = Deethylatrazine; DIA = Deisopropylatrazine; 1 =Tomlin, 2009; 2 = IUPAC, 2015; 3 = Modified from Reitzel et al. 2004 (2,4-D), Janniche et al., 2010 (Acetochlor), and Vonberg et al., 2014 (Atrazine).

2,4-D is expected to show higher mobility in soil than acetochlor (Hiller et al., 2008), but generally has good degradability in soil, unsaturated zone and aquifer conditions (Johnson et al. 1995; Tuxen et al., 2000; Willems et al. 1996). The persistence of 2,4-D in surface water is relatively high due to its non-volatility and limited chemical and photochemical degradation (Aly et al., 1964; Loos et al., 2009; Zepp et al., 1975). 2,4-D has been sparsely detected in surface water and groundwater (Domagalski et al., 2001, Rawn et al. 1999).

Atrazine has a moderate mobility, but higher persistence in soil, and is prone to groundwater leaching (Barbash and Resek 1996; Graymore et al. 2001). This is in accordance with many studies worldwide that detected atrazine and atrazine metabolites in surface water and groundwater (Crocker et al., 2002; Domagalski et al., 2001; Maloschik et al., 2007; Sparling et al., 2010; Székács et al. 2015). The degradation process in the subsurface is slow, so that atrazine residues can occasionally still be detected at the 0.1 µg/L threshold even 20 years after the last application (Vonberg et al., 2014). In groundwater and in the vadose zone, the degradation products hydroxyatrazine, deethylatrazine, and deisopropylatrazine usually occur in concentrations of deethylatrazine > deisopropylatrazine > hydroxyatrazine (Bayless, 2001). In surface water, hydroxyatrazine is usually detected in higher concentrations than deethylatrazine and deisopropylatrazine, and often also in higher concentrations than the parent compound atrazine (Lerch et al., 1998; Ren and Jiang, 2002a). Under loosing stream conditions, the hydroxyatrazine concentrations in the water entering the aquifer is expected to be quickly lowered because hydroxyatrazine has been shown to readily sorb to soil and organic matter in several studies (Brouwer et al., 1990; Mandelbaum et al., 1993; Mersie and Seybold, 1996).

The pesticides atrazine and 2,4-D are regulated in both the US and the Chinese Drinking Water Guidelines. In case of long-term exposure above the maximum contamination level (MCL), atrazine is expected to cause cardiovascular and reproductive problems, and 2,4-D may cause damage to kidney, liver, adrenal glands (EPA, 2009). The two chlorinated metabolites of atrazine (deethylatrazine and deisopropylatrazine) have similar properties as atrazine, and are likewise suspected endocrine disruptors (Stanko et al., 2010; Stoker et al., 2002) with slight ecotoxicity. In terms of non-human impact, atrazine residues have been recognized as a threat to consecutive crops in double cropping systems and wild plants due to the phytotoxicity of the pesticide residues (Ren and Jiang, 2002b). This risk may be increased if surface water or groundwater used for irrigation contains atrazine residues. However (as discussed in 3.4.), only little monitoring of atrazine has recently taken place in the NCP.

### 3.7. Implications for pesticide handling, management and monitoring

Combined findings from our literature review and our own observations at our field site imply that little knowledge of active ingredients in pesticide products and improper handling of pesticides is common in many farming households in China. Point sources from carelessly disposed containers remain a problem, and can be a source for soil, surface water, and groundwater pollution. Therefore, more educational activities more easily accessible disposal sites for pesticide containers should be offered.

Our field study has further shown that some of the currently applied pesticides can be detected throughout different times of the year in both surface water and groundwater. Polluted surface water that infiltrates into groundwater can be a source of pollution, and it is advisable to treat surface water and groundwater as a joint resource by using appropriate monitoring in both environmental compartments. Compared to the results from our literature research, there seems to be a lacking scientific focus on currently used pesticides. We therefore see a need for comprehensive monitoring program of surface water and groundwater. The program should include both currently applied and banned pesticides, and should be able to capture temporal variation.

Shallow groundwater wells and river water are often used for irrigation in the NCP. The main irrigation period is typically from March to May, which coincides with our detected peak concentrations of pesticides in river. Ren and Jiang (2002a) reported a decline in crop yield (caused by phytotoxicity) when fields were irrigated with groundwater from 130m depth, where deethylatrazine dominated as degradation product, and the total residue of atrazine and chlorinated atrazine metabolites (atrazine+deethylatrazine+deisopropylatrazine) was about 9 µg/L. In our field investigation, the total chlorinated residue was comparatively low (with a maximum concentration of 1.1 µg/L in surface water in May 2013) because hydroxyatrazine was the main degradation product. Both surface water and shallow groundwater may therefore still be suitable for irrigation (at least in terms of atrazine and atrazine residues), but monitoring of atrazine and 2,4-D is nevertheless advisable. Furthermore, the most crucial time for monitoring of surface water is after the spring application of herbicides. This is in accordance with the results on herbicide study in the Midwestern United States, which concluded that the spring flush of herbicides in surface water might be a major contributor to alluvial groundwater pollution (Thurman et al., 1991).

## 4. Conclusion

Our findings show that the three most widely used herbicides on winter wheat-summer maize fields in the NCP are 2,4-D, acetochlor, and atrazine. All of these compounds are suspected to have potential negative impacts on the environment, and two of them (acetochlor and atrazine) have been banned for this reason in Europe. In our field study, 2,4-D, atrazine, and atrazine metabolites could be detected in river water and groundwater throughout the year, with peak values of 3.00 µg/L, 0.96 µg/L, and 9.84 µg/L, respectively. Though our study has limited repetition in time and space, we still see it as a relevant indication for the need to monitor these compounds.

Indeed, we found that the monitoring gap on herbicides in groundwater systems is currently closing by the on-going development of a national groundwater monitoring network, which will also be used for the monitoring of pesticides (including compounds such as atrazine and 2,4-D). Nevertheless, there is a current research bias on surface water pollution by the legacy pesticides DDT and HCH, which were banned in China in the 1980s. Even though it is important to monitor if these compounds are still accumulating in the environment and/or are still illegally in use; we think that more research on currently-used pesticides should also be encouraged. This research should ideally include both surface water and groundwater monitoring, and should be able to catch temporal variations.

In addition to this, overuse and improper handling of pesticides have been observed in China for a long time, and studies have been pointing out since the 1980s that better management needs to be implemented. Farmer education is still poor in many areas, and infrastructure for proper pesticide disposal is missing. Better farmer education, enhanced quality control, and a sufficient disposal system for pesticides are highly recommended to avoid occupational risks, pesticide overuse, and environmental pollution.

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# Appendix A – Supplementary information

**Table A.1** Crop activities, irrigation, and pesticide application during wheat and maize cultivation in 2012/2013.

| | Date | Crop activities | | Irrigation | Pesticide application (g/ha of active ingredient) | | |
|---|---|---|---|---|---|---|---|
| | | Seeding | Harvest | (mm) | Type of pesticide | Application | Recommended application* |
| Winter wheat | 10 Oct 2012 | + | | | | | |
| | 12 Apr 2013 | | | 40 | | | |
| | 20 Apr 2013 | | | | Tribenuron-methyl (H) | 18 | 9-18 |
| | 01 May 2013 | | | 50 | | | |
| | 30 May 2013 | | | 60 | | | |
| | 03 June 2013 | | | | Dimethoate (I) | 75 | 50-100 |
| | 10 June 2013 | | + | | | | |
| Summer maize | 12 June 2013 | + | | | | | |
| | 07 June 2013 | | | | Paraquat (H) | 1000 | 600-900 |
| | | | | | Acetochlor (H) | 2100 | 1800-3750 |
| | 05 Oct 2013 | | + | | | | |

*recommendation as stated on the pesticide container

**Table A.2** Full set of analyzed compounds from the four field campaigns for river water (RW) and groundwater (GW) samples. All detection limits were 0.01 µg/L.

| **Pesticide** (all values in µg/L) | **29 May 2013** | | | | **22 July 2013** | | | | **07 October 2013** | | | | **25 March 2014** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | RW | GW2 | GW3 | GW4 | RW | GW2 | GW3 | GW4 | RW | GW2 | GW3 | GW4 | RW | GW2 | GW3 | GW4 |
| **Triazine-herbicides** | | | | | | | | | | | | | | | | |
| Atrazine | 0.96 | 0.33 | 0.91 | 0.40 | 0.32 | 0.29 | 0.29 | 0.49 | 0.49 | 0.19 | 0.20 | 0.20 | 0.54 | 0.12 | 0.19 | 0.15 |
| - Desethylatrazine (M) | 0.07 | 0.04 | 0.05 | 0.04 | 0.17 | 0.09 | 0.07 | 0.16 | 0.03 | 0.01 | 0.02 | 0.04 | 0.05 | 0.03 | 0.04 | 0.08 |
| - Deisopropylatrazine (M) | 0.07 | 0.05 | 0.05 | 0.04 | 0.04 | 0.16 | 0.08 | 0.09 | ND | ND | ND | 0.01 | 0.13 | 0.01 | 0.02 | 0.02 |
| - Hydroxyatrazine (M) | 9.70 | 0.46 | 0.37 | 0.47 | 0.31 | 0.59 | 0.54 | 0.49 | 3.00 | 0.55 | 0.39 | 0.48 | 1.60 | 0.26 | 0.33 | 0.20 |
| Cyanazine | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Simazine | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Terbutylazine | ND | ND | 0.02 | 0.01 | ND | ND | ND | 0.02 | ND | ND | ND | ND | ND | ND | ND | ND |
| **Phenoxy-herbicides** | | | | | | | | | | | | | | | | |
| 2,4-D[1] | 3.00 | 0.41 | 2.30 | 0.70 | 0.27 | 0.09 | 0.10 | 0.31 | 0.51 | 0.03 | 0.03 | 0.01 | 0.65 | 0.01 | 0.05 | 0.02 |
| - 2,4-dichlorphenol (M) | 0.09 | 0.14 | 0.09 | 0.14 | 0.02 | 0.10 | 0.09 | 0.07 | 0.06 | 0.03 | 0.04 | 0.03 | 0.01 | ND | ND | ND |
| - 2,6-dichlorphenol (I) | ND | 0.02 | ND | 0.01 | 0.01 | 0.03 | 0.16 | 0.02 | 0.01 | ND | ND | ND | 0.01 | ND | ND | ND |
| MCPA[2] | 0.06 | 0.03 | 0.05 | 0.02 | 0.03 | ND | ND | 0.01 | ND | ND | ND | ND | 0.04 | ND | ND | ND |
| - 4-chlor-2-methylphenol (M) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Dichlorprop | ND | ND | ND | ND | 0.02 | ND | ND | ND | 0.04 | ND | ND | ND | ND | ND | ND | ND |
| Mecoprop | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| **Other herbicides** | | | | | | | | | | | | | | | | |
| Bentazon | 0.03 | 0.02 | ND | 0.02 | 0.01 | ND | ND | ND | 0.03 | 0.08 | 0.07 | 0.07 | 0.01 | 0.03 | 0.03 | 0.04 |
| Dichlobenil | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| - BAM[3] (M) | 0.06 | 0.01 | ND | 0.04 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Dinoseb | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| DNOC[4] | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Hexazinone | 0.06 | ND | ND | ND | 0.04 | ND | ND | ND | 0.02 | ND | ND | ND | 0.11 | ND | ND | ND |
| Isoproturon | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Metamitron | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Pendimethalin | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |

M = Metabolite; I = Intermediate; ND = Not detected (<0.01 µg/L); 1= 2,4-Dichlorophenoxyacetic acid; 2 = 2-methyl-4-chlorophenoxyacetic; 3= Dinitro-ortho-cresol; 4=2,6-dichloro-benzamide