

The detection of aquatic contamination with plant protection products in amphibian reproduction sites

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Abstract

Environmental pollution is a major problem the world is currently facing and which affects ecosystems and human health adversely. Furthermore, it is one of the causes for the global decline in many taxonomic species, including amphibians. Due to their complex life cycle, amphibians are very sensitive towards chemical contamination. As many amphibian species inhabit agricultural land, the most relevant chemical group for them are plant protection products (PPPs). Through drift or deposition, PPPs can also end up in water habitats, where they might affect the embryonic or larval stages and adult individuals. The risk of PPPs is determined by comparing exposure with effects. Many studies provided evidence that PPPs can have severe toxic effects on amphibians. However only few data exist about the exposure amphibians are facing in the environment. It is largely unknown, which PPPs occur in which concentrations in the field and which species are affected. But to minimize the decline of amphibian species caused by habitat pollution, it would be highly important to have data about the exposure, so that a risk assessment can be conducted and safety measures undertaken.

Therefore, I did a field study in this bachelor thesis. The goal was to earn an impression how contaminated amphibian reproduction sites are. Furthermore, I was interested, whether the presence of PPPs could be explained by the amount of surrounding agricultural land use, by the width and spatial structure of the buffer zone or by the amount and type of aquatic vegetation. A further question I posed was, whether a water contamination with PPPs could explain the absence of a stable *Hyla arborea* population in some reproduction sites.

The field study involved twelve reproduction sites. To examine a possible water contamination, water samples were collected from each pond on three days in May. Furthermore, I investigated visually the use of the surrounding landscape, the buffer zone and the aquatic vegetation. Then the collected data were analyzed in R and Excel.

In the water samples could be proven a total of 55 different PPPs, 14 occurred even above the critical value of 100 ng/l set by the WPO. Each water sample contained a mixture of various PPPs. Chemical mixtures can be very dangerous to water organisms due to synergistic effects. Furthermore I detected that the majority of the substances didn't fluctuate between the three sampling days. This means that high concentrations remained high during the whole month of May.

The most important conclusion of this research is that the amphibians inside two of the analyzed reproduction sites face high exposure. In each water samples of the two ponds could be detected over 40 different PPPs and a total concentration between 2800 and 6300 ng/l. These results indicates, that amphibian species are exposed to very high concentrations and to a mixture of various substances over a time period of three weeks. Therefore it is likely that PPPs pose a high risk for the amphibian species in these waters.

One possible source for the contamination inside these two ponds are drainages. Drainages from the nearby fields or partly from the nearby main road or industrial zone are directly diverted into the waters. Furthermore these ponds don't possess a discharge like the other ponds in the area. This results in an accumulation of PPPs in the water.

In my study was shown, that the ponds surrounded by a dam contained lower concentrations of PPPs than the ponds without a dam. Therefore a dam might have a protective effect against input via drift or runoff. The instalment of a dam might presents a good measure against contamination that can easily be realized in the construction of future ponds.

Introduction

One of the problems the world is currently facing and that can have severe effects on human health, biodiversity and ecosystems is the pollution of the environment. It is caused by synthetic contaminants, which end up in ecosystems and affect them adversely. A variety of anthropogenic sources for chemicals is known, including agriculture, traffic, private households and industry (Hill 2004). The contaminants enter the environment via different ways: they can be transported through waste water or through the atmosphere, they are washed out of agricultural land or paved surfaces into the surrounding landscape with rainfalls or they enter the environment through leachate from disposal sites (Hill 2004).

Plant protection products (PPPs) are synthetically produced, organic micro pollutants (Braun et al. 2015). Micro pollutants occur in the environment in very low concentrations between µg/liter and ng/liter (Braun et al. 2015). PPPs are used in agriculture to protect the yield against losses through pests, fungi or strong weeds (Braun et al. 2015). At the moment, several thousand pesticide products are released (Brühl et al. 2013) and about 2.3 million tons of PPPs are applied worldwide each year (Grube et al. 2011). In Switzerland, more than 2000 tones are annually used (Bossard 2016). However the global application rate is rising (Köhler & Triebkorn 2013). As the human population increases steadily, the pressure on the food supply tightens and a higher amount of PPPs is used to ensure more yield (Köhler & Triebkorn 2013).

Although the new generation of PPPs are formulated to degrade quickly and to be effective in lower concentrations and application rates, they still accumulate in soils and waters in amounts high enough to affect other organisms (Lehman & Williams 2010). This can happen in agricultural land as well as in regions which aren't directly concerned with agricultural pesticide application (Lehman & Williams 2010).

PPPs are biological active substances (Aldrich et al. 2016). Therefore they can have besides the intended effects on plants, pests or fungi also a variety of negative effects on other, non-target organisms (Aldrich et al. 2016). Amphibia is one vertebrate class which is often affected by contamination with PPPs, because many species occupy habitats in agricultural land.

The future of the amphibian class is worldwide highly in danger. The Red List composed 2004 by the International Union for Conservation of Nature shows that 32% of all amphibian species are threatened with extinction (Stuart et al. 2004). With this high percentage, amphibians are the most endangered class of vertebrates (Stuart et al. 2004). The actual situation of the amphibians in Switzerland is precarious as well. The Red List of endangered species in Switzerland released 2005 indicates that one out of twenty evaluated species is extinct in Switzerland, namely *Bufo viridis* (Schmidt & Zumbach 2005). Furthermore nine species are classified as endangered and four as vulnerable (Schmidt & Zumbach 2005).

Several factors lead to the global decline in amphibian population sizes, including overexploitation, introduction of invasive species, emerging of infectious diseases or pathogens, climate change and habitat destruction due to change in land use or pollution (Collins & Storfer 2003). These factors are mostly caused by humans and act often cumulative and synergistic (Collins & Storfer 2003).

Amphibians are very sensitive for pollution with PPPs (Wagner & Viertel 2016). Due to their partly aquatic and partly terrestrial life cycle, amphibian species make contact with PPPs in the

water during their embryonic and larval stages, but also on land as juveniles and adults (Cothran et al. 2013).

As the PPPs are directly applicate on agricultural fields (Brühl et al. 2013), amphibian species which occupy or migrate through agricultural land are inevitably exposed. Owing to their highly permeable skin (Brühl et al. 2013), amphibian juveniles and adults are more delicate to dermal uptake of chemicals than birds or mammals (Quaranta et al. 2009). The sensitivity towards PPPS of terrestrial living species haven't been accurately investigated yet (Aldrich et al. 2016). Though experiments with direct overspray of different PPPs in environmental relevant doses on juveniles showed that the mortality rate of the amphibians increases enormously when they are facing exposure (Brühl et al. 2013, Releya 2005).

In agricultural landscapes, the reproduction habitats of amphibians like wetlands or ponds are often completely surrounded by cultivated land (Lenhard et al. 2014). The PPPs which end up in water can affect larval or embryonic stages as well as adult individuals. The exposure to contaminants during the amphibian development can have severe outcomes. Many laboratory or semi field studies showed that they can cause reduced growth, delayed metamorphose, malformations, increased mortality rate and changes in the behavior (Larsen & Sorensen 2004, Larsen et al. 2004, Bernabò et al. 2013, Brunelli et al. 2009, Mandrillon & Saglio 2007, Saym 2010, Howe et al. 2004, Lavorato et al. 2013).

As indicated above, numerous laboratory studies, showed, that PPPs can have lethal and a lot of sub lethal effects on amphibians. But little is known about the exposure amphibians are facing in their land habitats or breeding sites. For the lack of data, it is unclear to which substance or mixtures of substances species are exposed, nor in what concentration they occur or how long they are present (Aldrich et al. 2016).

Due to this knowledge gape, no substantive conclusion could be made about the risk that poses the use of PPPs on amphibians. The risk is estimated by comparing the effects with the exposure (Aldrich et al. 2016). It is essential to earn data about the exposure amphibians are facing, so that a risk assessment could be conducted. Then appropriate safety measurements could be undertaken to minimize the decline of amphibian species caused by habitat pollution.

To reduce this knowledge gap, I examined twelve breeding sites in a field study. In this study, I tested mainly two topics:

The first topic I was interested in was the possible contamination of the breeding sites with PPPs. I wanted to know whether the amphibians in the ponds face exposure to PPPs and specifically which substances occur in which concentration in the water.

As their presence in the environment differs temporally and spatially, PPPs aren't consistent stressors. In general, the highest input of PPPs into surface waters happens during the first rainfalls after the application (Braun et al. 2015). The duration between two PPPs concentration peaks in water can decide whether aquatic organisms can recover themselves from the exposure or not (Ashauer 2009). Therefor I wanted to test if the found concentrations show any fluctuations.

To explain the possible presence of PPPs, I analyzed three factors which could cause or inhibit a pollution with PPPs:

- The first factor was the agricultural land. I searched for correlation between different crops and PPPs concentrations. I had the hypothesis, that with increasing amount of agricultural land use around the pond, the concentrations of PPPs inside the water would rise.
- The second factor I investigated and which could protect the water against contamination is the buffer zone. It is known that a broader buffer zone or hedges can reduce the input of PPPs via spray drift (De Snoo & De Wit 1998, Brown et al. 2004, Lazzaro et al. 2008). I hypothesized, that the reproduction sites contain fewer PPPs in the water when they are surrounded by a broad buffer zone or a by a buffer zone with hedges.
- The third factor I analyzed and which could inhibit the pollution of the ponds with PPPs is the vegetation inside the water. Several researches focus on macrophytes as a method to mitigate pesticide pollution in agricultural surface waters. It was shown that emerged aquatic macrophytes can reduce the entering of spray drift in waters by intercepting the pesticide droplets (Dabrowski et al. 2005). Furthermore, macrophytes can reduce the concentration of insecticides or other contaminants by adsorption, by assimilation or by providing area for microbial attachment (Kröger et al. 2009, Schultz et al. 2003). Therefor I hypothesized that with increasing amount of water vegetation the concentrations of PPPs in the water would be lower.

The second topic I wanted to investigate concerned a specific amphibian species. The twelve examined ponds can be divided into two groups with six ponds each. The first group are the ones which are used as breeding sites and the second group are the ones which aren't used as breeding sites by the species *H. arborea*. However all twelve ponds satisfy the physical requirements of the species for a suitable reproduction site. Therefor I hypothesized that a contamination of the water might be the reason for the absence of *H. arborea* in some ponds.

Methods and Measurements

Study species

A sub question of my research concerns the species *Hyla arborea* (European tree frog). In Switzerland the species colonizes regions north of the Alps in the midland until an altitude of 700 meter above sea level (Meyer et al. 2014). It lives in metapopulations (Schmidt et al. 2015). *H. arborea* appears only during the reproduction in waters. The bigger part of the year, it spends in terrestrial habitats (Meyer et al. 2014). The summer habitat is located maximal one km away from the spawn waters (Cigler & Cigler 1996). There it lives on tall forbs or shrubberies (Meyer et al. 2014). In September or October, the frog moves back to its winter habitat in roots, clefts, earth wholes (Meyer et al. 2014) or under leaf piles (Cigler & Cigler 1996). It spends the cold months in dormancy until the reproduction time begins in spring (Meyer et al. 2014).



Figure 1: *Hyla arborea* individual

As it is a warmth-loving species, *H. arborea* leaves the winter habitat late in spring (Meyer et al. 2014). The reproduction takes place from April until the beginning of July (Meyer et al. 2014). Under ideal conditions the embryonal development lasts 7-14 days' time, then the larvae hatches (Meyer et al. 2014). The larval development needs 2-3 months, depending on the water temperature (Meyer et al. 2014). After two years, the juveniles turn into sexually mature adults (Friedl & Klump 1997). Although their lifespan can last seven years, most of the individuals reproduce themselves only once due to the high mortality rate (Meyer et al. 2014).

An ideal spawn pond for *H. arborea* is sunny, what leads to increased water temperature (Meyer et al. 2014). Furthermore, it dries out temporarily, what inhibits the establishment of stable predator populations for instance fish (Schmidt et al. 2015, Bronmark & Edenhamn 1994). As males can change the spawn waters several times during the same reproduction season, the ponds should be well connected to each other, as well as to the summer habitats (Cigler & Cigler 1996). Typical reproduction sites of the *H. arborea* are flooded meadows (Schmidt et al. 2015), wetlands or gravel-pits (Baumgartner 1986).

H. arborea is classified on the red list of Switzerland as an endangered species (Schmidt & Zumbach 2005). Once its distribution range covered the whole midland from the western to the eastern part of Switzerland. Today the species appears only in several isolated metapopulations (Pellet et al. 2003), as the following figure indicates.

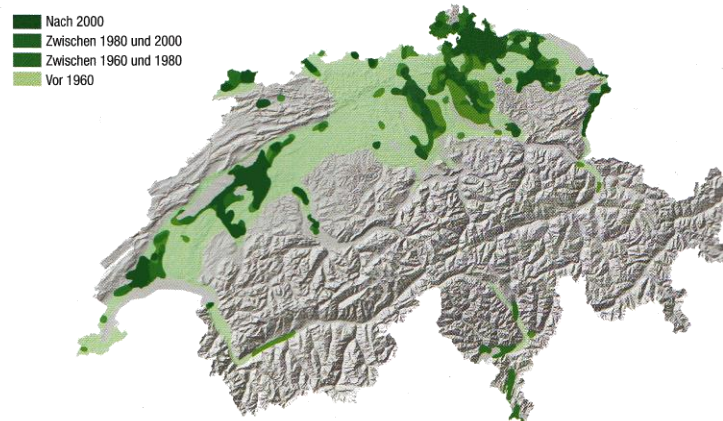


Figure 2: Distribution map of *H. arborea* in Switzerland. Before 1960 the species occurred in most parts in the midland, but after 2000 their distribution range was minimized. Now they occur only in isolated metapopulations.

The most important reason for the decline of *H. arborea* in Switzerland is the loss of intact and suitable reproduction waters (Cigler & Cigler 1996). About 90% of the wetlands in the midland have vanished (Schmidt et al. 2015) mostly due to river corrections (Imboden, 1976). Furthermore, around 20% of the agricultural land are drained today (Béguin & Smola 2010). This leads to a drier landscape and the disappearance of temporal waters (Schmidt et al. 2015). Sometimes, the damage of the spawn waters isn't physical but in connection with the water condition. The water quality decreases due to infiltration of agricultural contaminants (Cigler & Cigler 1996) or the change of the water temperature. The artificial introduction of fishes leads also to losses of suitable spawn waters (Bronmark & Edenhamn 1994). *H. arborea* migrate several times during their life cycle. However the landscape today is fragmented through barriers the frog can't conquer (Andersen et al. 2004). These barriers are mostly anthropogenic: streets, railways, agricultural land or settlements. The consequence is that the frogs can't colonise new waters, move between different habitats or interact with other populations. This leads to an isolation of the population, what can cause inbreeding and bottle neck effects and what makes this population even more vulnerable to extinction (Anderson et al. 2004).

Study areas

The ponds of our research are located in the Saanetal and the Seeland in Switzerland. For the field study, Silvia Zumbach, overall director and director for the sector amphibians in the Swiss amphibian and reptile conservation program (karch), took a preselection of eligible ponds. Her preselection is based on regular observations of *H. arborea* occurrences carried out by herself since we'd like to compare the water quality between ponds with a *H. arborea* population and ponds without a *H. arborea* population. Thereafter twelve ponds were chosen out of this preselection together with the lab for water and soil protection Berne (GBL). Only in half of the chosen ponds *H. arborea* reproduces itself, though the physical characters of all ponds seem to accord with the habitat requirements of the species.

Nine of the ponds are located in the Seeland and three in the Saanetal.

The information about the ponds in the Seeland derive from private messages with Silvia Zumbach and Robert Stegemann, director of the engineering office Lüscher & Aeschlimann or my personal observations.

Leuschelzmoos (1) has one of the largest surface area of the ponds in our research. Nevertheless it dries out annually apart from a little zone in the center. It is supplied by rainwater and drainage water from the nearby fields. It has developed naturally and its age is unknown.

Fofere (2) was built in 2006 as a compensation measure for a road project. As no natural water fluctuations occur in that area, the pond possesses an artificial discharge. Thereby the water level can be regulated. It is supplied by a streamlet.

The pond Ziegelmoos (3) is a naturally developed pond in a former turf mining site. It dries out sometimes, but not annually. It is supplied by groundwater and a streamlet.

The ponds Hofmatte (4), Erlacher Rundi (5), Gritzimoos (6), and Heumoos (8) were all build in 2001 as a compensation measure for a road project. They are supplied by surface water and groundwater. They dry out only in very warm years.

Panzersperre (7) exists since 1918. It is supplied by surface water and groundwater and can dry out only in very warm years.

The pond Muttli (9) developed naturally probably out of a former gravel pit, however its age is unknown. It is the pond with the biggest surface area in our research and doesn't generally dry out.

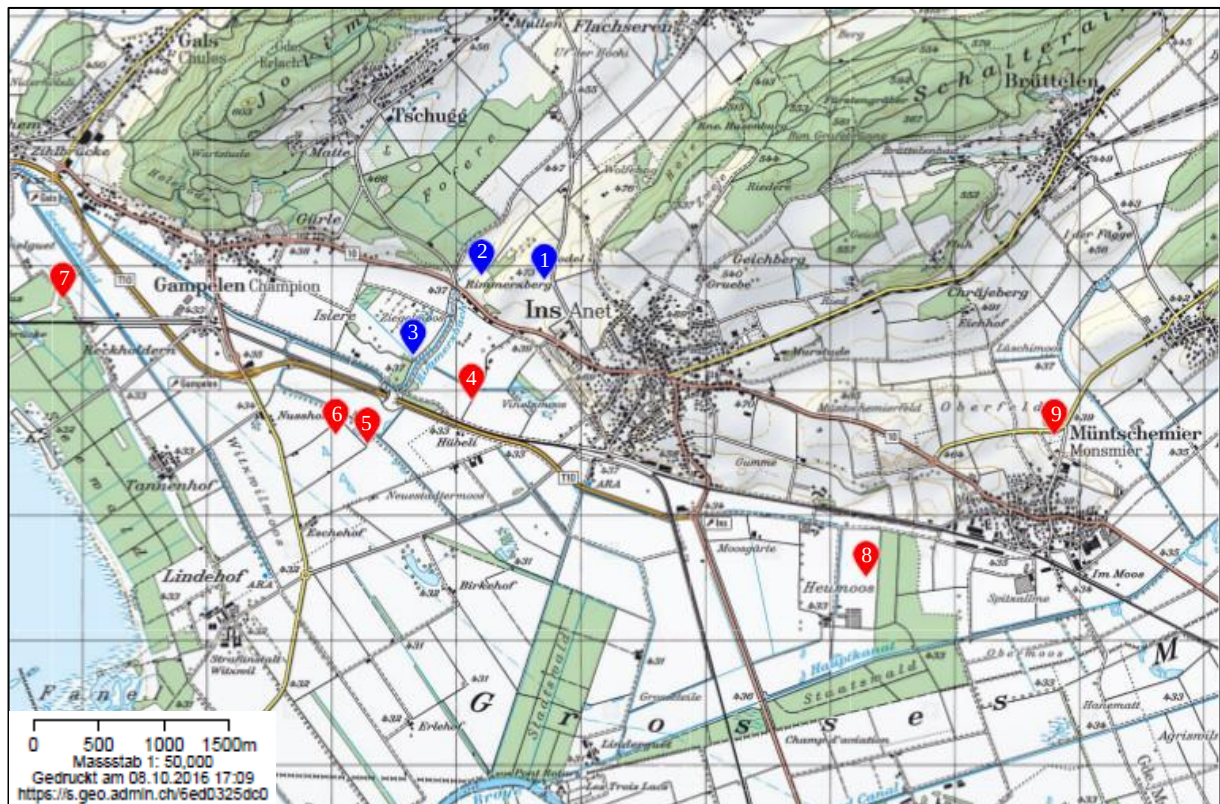


Figure 3: Map of the examined ponds in the Seeland. The blue dots refer to ponds with a *H. arborea* population. The red dots refer to ponds without a *H. arborea* population. 1.Leuschelzmoos, 2.Fofere, 3.Ziegelmoos, 4.Hofmatte, 5.Erlacher Rundi, 6.Gritzimoos, 7.Panzersperre, 8.Heumoos, 9.Muttli

The three ponds Chatzestiig (10), Viadukt (11) and Laupenau (12) have been built recently. Their construction was part of a project carried out between 2001 and 2007 (Schmidt et al. 2015). It aimed the connection of two isolated *H. arborea* populations in Auried and Oltigenmatt (Schmidt et al. 2015). The course of the river Saane was mend to be a passage between this two areas. Therefor 14 new spawn ponds were built as connectors next to the river bank including Chatzestiig (10), Viadukt (11) and Laupenau (12). Since natural water fluctuations doesn't occur anymore in this region, the newly constructed ponds in the project were equipped with an artificial discharge (Schmidt et al. 2015). Thereby the ponds can be drained in autumn and refilled by rainwater in spring. This enables the creation of temporal waters, which are highly valuable for *H. arborea* (Schmidt et al. 2015). The efficiency control showed that the project was successful. All the ponds were used as reproduction sites already one year after the construction and the total number of individuals grew (Schmidt et al. 2015).

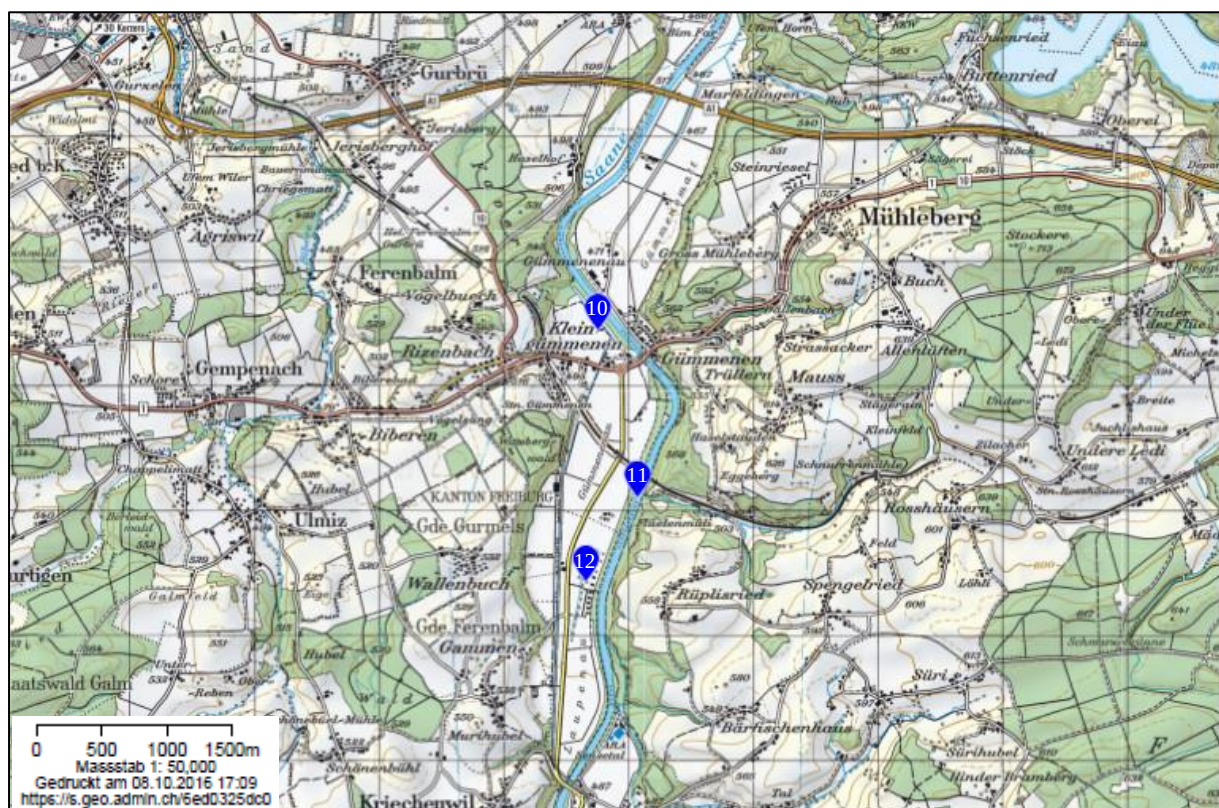


Figure 4: Map of the examined ponds in the Saanetal. The blue dots refer to ponds with a *H. arborea* population. The red dots refer to ponds without a *H. arborea* population. 10.Chatzestiig, 11.Viadukt, 12.Laupenau

Water sampling

To prove a contamination of spawn waters with PPPs, Silvia Zumbach, Nicolas Dulex, who fulfilled his civilian service at the karch and I took water samples on three days distributed in the month of May: the 09 May, the 23 May and the 29 May 2016. We chose May, because then the *H. arborea* populations are most vulnerable to water contamination. In this time, individuals of all lifecycle states are present in the ponds (Meyer et al. 2014). Spawn, larvae and adult frogs occur (Meyer et al. 2014) and they all can be affected by contaminated water.

On each sampling day, a total of seven water samples of each pond have been collected from the pond side: twice 1l to measure the insecticide concentrations, 1l for possible further studies, 0.5l for measuring the content of nutrients, 250ml for measuring the pesticide concentrations and twice 14ml Greiner Tubes for measuring the concentration of glyphosate. In the field, several supplementary measurements were taken: the PH, the saturation [% and mg/l], the conductivity [$\mu\text{S}/\text{cm}$] and the temperature of the water [$^{\circ}\text{C}$]. As this measurements can vary during a day, the time when the measurements were taken was noted.

We put the collected water samples into a refrigerated box to transport them to Berne, where they were evaluated by the lab for water and soil protection GBL. The water was examined on 86 micro pollutants, mostly PPPs and their metabolites, but also chemicals used in private households or industry and pharmaceuticals. These are micro pollutants often applied in Switzerland and therefor appear regularly in waters. Additionally, the concentration of 26 metals and semimetals was determined. The samples were also investigated on the content of chloride, phosphor, nitrogen and sulfate.

The concentration of these substances and measurements for each pond and sampling day can be found in the appendix table A1- A7.

Characterization of the ponds and their surroundings

I tried to explain the possible presence of PPPs with three factors which may cause or inhibit a pollution in the ponds. The three factors were the land use around the ponds, the buffer zone surrounding the ponds and the aquatic vegetation inside the ponds.

To investigate correlations between the pollution and the land use, I analyzed the surrounding landscape during May and June. To have a precise impression of the land use, I determined the vegetation on 16 different positions around the pond, as indicated in the following figure. I considered eight cardinal directions: North, Northeast, East, Southeast, South, Southwest, West and Northwest. In each direction two sites were analyzed: in 50 m distance (points 1-8) and in 100 m distance (points 9-16) from the pond bank.



Figure 5: Example of a printed map of Erlacher Rundi with the marked points that should be investigated in the field. Points 1-8 are located in a distance of 50 m of the ponds bank, points 9-16 in a distance of 100 m.

Before the investigation in the field, I printed out an aerial picture of each pond from the website swisstopo in a scale of 1:2500. Then I marked the points 1-16 with a deviation of 1 mm, what would be 2.5 m in the field. In the field, I determined visually the position of the points 1-16 and the land use on this points. I distinguished between nine different uses: cultivations of crops, cultivation of sugar beets, cultivation of potatoes, cultivation of vegetables, intensive meadow, extensive meadow, wood, waters and fallow land.

For the statistical analysis I simplified the collected data. I assumed that the eight points in 50m distance (points 1-8) were 100%. Then I calculated the percentage for the occurrence of each land use. I did the same for the points in 100m distance (points 9-16).

The second factor was the buffer zone around the ponds. I hypothesized that a buffer type with high bushes and a broader buffer zone could prevent the runoff or drift of PPPs into the ponds. I characterized therefor the buffer zone around the ponds. On the website swisstopo, I measured the buffer width in meters in eight cardinal directions (North, Northeast, East, Southeast, South, Southwest, West and Northwest). This was done on aerial pictures with the tools provided by the website, with a deviation of 2.5 m. For the statistical analysis the mean of these eight measurements was calculated.

The buffer type was analyzed visually in the field. Two types of buffers were differentiated: high buffers consisting of hedges or trees and low buffers consisting of meadows. I determined which buffer type is present in eight cardinal directions (North, Northeast, East, Southeast, South, Southwest, West and Northwest). For the statistical analysis, I assumed, that these eight observed directions were 100%. Then I calculated in which percentage the two buffer types occurred.

I also analyzed, whether the ponds are surrounded by a dam, who could protect them against wind drift, or not.

The third factor was the vegetation inside the water. To test whether there is a correlation between the PPPs and the aquatic vegetation, the amount of vegetation inside the ponds was estimated visually. I distinguished between cane brake, floating leaf and submerged vegetation. I looked at each type of vegetation separately and estimated, what percentage of the surface area they cover. The highest percentage for each vegetation type separately is therefor 100 %.

Furthermore, I wanted to test if spatial characteristics of the pond could explain the presence of the PPPs. I measured the range and the surface area of each pond. I did this on the website swisstopo on aerial pictures with the tools provided by the website. In the field, four measurements of the water depth were taken in a distance of 2m away from the pond bank in four cardinal directions (North, East, South and West). Then the mean of this measurements was calculated. For my research, I assumed that each pond is perfectly round and has a volume of a spherical sector. With this data, the volume of the spherical sector was calculated with the program vectorworks 2015.

Statistical Analysis

The lab for water and soil protection GBL tested the water samples on 86 different micro pollutants, most of them PPPs and their metabolites but also pharmaceuticals and chemicals used in private households and industry. In this analyses I considered only the PPPs.

The found concentrations of each PPP were assigned to 6 classes, numbered from 0 to 5:

- Class 0: no concentration could be detected
- Class 1: the found concentration is lower than 5 ng/l
- Class 2: the found concentration lies between 5 ng/l and 100 ng/l
- Class 3: the found concentration lies between 100 ng/l and 500ng/l
- Class 4: the found concentration lies between 500ng/l and 1000 ng/l
- Class 5: the found concentration is higher than 1000ng/l

In Switzerland, the surface water and the groundwater are secured by the Federal Act on the Protection of Waters WPA. The goal of this act is to protect the waters against adverse effects, to ensure their function as ecosystem and to enable their sustainable use (§ 1 WPA). The Waters Protection Ordinance WPO defines in its appendix numerical requirements of different parameters in surface water including heavy metals, pesticides and nutrients. The maximal value for pesticides is set on 0.1 µg/l for single substances (Annex 2 WPO).

Therefor the classes 3 – 5 in my research refer to concentrations above the maximal value set by the WPO.

All the concentration classes of the found PPPs for each pond and each sampling day were summarized. This results in three “sums of all concentration classes” per pond, one for each sampling day. Apart from the “sum of all concentration classes” I used in my analyses these PPPs, which occurred at least in one water sample over the maximal value of 0,1 µg/l set by the WPO. The analysis of these substances was conducted with real concentrations and not with the concentration classes. The referring substances are briefly presented in table 1. Seven substances are herbicides, three are fungicides. For many of these substances could be found side effects on amphibian species as well (Johansson et al. 2006, Releya 2005).

Table 1: All substances found in the ponds in concentrations above the limiting value of 100 ng/l set by the WPO. The sixth column is referring to the WHO toxicity classes. The WHO have a scale of five classes which shows the possible effects on humans: U = unlikely to present acute hazard, III = slightly hazardous, II = moderately hazardous, Ib = Highly hazardous, Ia = extremely hazardous (World Health Organization WHO, 2009). The information to chloridazon derive from the open chemistry database o The data about the other substances derive all from the book “the pesticide encyclopedia” (Paranjape et al. 2014) or from the EU Pesticides database.

substances	chloridazon metabolites: desphenyl chloridazon and methyl desphenyl chloridazon	ethofumensate	linuron	metamitron metabolite: desamino metamitron	metolachlor
function	herbicide	herbicide	herbicide	herbicide	herbicide
mode of action	blocks the photosystem II electron transport in the photosynthesis	blocks mitosis, photosynthesis and respiration	blocks the photosynthesis	blocks photosynthesis Absorbed by all plant parts	blocks protein production and photosynthesis
applicate in:	sugar beet, crops	carrots, spinach and sugar beet	soybean, cotton, potato, maize, onion, winter wheat, legumes, vegetables and fruits	sugar and fodder beets, non-crop areas like industrial districts, lawn and irrigation canals	Cereals, sorghum, groundnuts, cotton and ornamental plants
toxicity	• acute rat LD ₅₀ oral: 647 mg/kg	• acute rat LD ₅₀ oral: > 5000 mg/kg bw • LC ₅₀ in fish: 38,50 mg/l • toxic to algae and daphnia	• acute rat LD ₅₀ oral: 1500 mg/kg • toxic to fishes	• acute rat LD ₅₀ oral: 1183mg/kg.	• 96 h LC ₅₀ in fish: 2 - 15 mg/l
WHO class		U (unlikely to be hazardous)	U (unlikely to be hazardous)	III (slightly hazardous)	III (slightly hazardous)
DT50 in soil		mean DT ₅₀ = 77 d (n=13)	DT ₅₀ = 13 - 82 d		DT ₅₀ : 11-31 d
DT50 in water		• in water: DT ₅₀ = 7-50 d • in whole aquatic system: DT ₅₀ = 507 and 550	• in water: DT ₅₀ = 48 d • in whole aquatic system: DT ₅₀ = 46 d		• in water: DT ₅₀ = 6-12 d • in whole aquatic system: DT ₅₀ = 42-53 d
photolysis in soil		DT ₅₀ = 65 d; 300-800 nm, light 12h per day, 15 mg as/kg.	not significant		no photolysis observed
photolysis in water		• DT ₅₀ = 37-62 d (summer, 40-60°N) • DT ₅₀ = 4.6 d (on a year basis) / 2.6 d (for month May)	stable		pH 7, 25°C, Xenon lamp : DT ₅₀ = 75 d
hydrolysis		pH 5.0, 7.0, 9.2: negligible	stable		stable
remarks			potential groundwater contaminant, for human irritating to eyes and skin, possible carcinogen	allowed in the EU, but in the USA prohibited	proven groundwater contaminant,

substances	Metribuzin metabolite desamino metribuzin	glyphosate metabolite AMPA	azoxystrobin	metalaxyl	propamocarb
function	herbicide	herbicide	fungicide	fungicide	fungicide
mode of action	blocks the electron transport in the photosystem II	affects the amino acid synthesis by blocking EPSPS and therefore acts on a lot of enzymatic reactions	blocks the respiration in the mitochondria of the fungi by stopping the electron transfer. This affects the spore germination and the growth of the mycelium	blocks the RNA production in fungi, especially the ribosomal RNA	interferes the cell wall synthesis, disrupts the phospholipid production and fatty acids and affects the mycelial growth and spore production
applicate in:	soybean, potatoes, tomatoes, sugarcane, asparagus, maize and turf grass	cereals, peas, beans, canola, flax and mustard	cereals, grapes, rice, potatoes, tomatoes, citrus, bananas, coffee	potatoes, peas, tomatoes, tobacco, vines In mixture with other fungicides: maize, sorghum, cotton, onions, cucurbits and citrus	strawberries, potatoes, tomatoes, lettuce and cabbage
toxicity	- acute rat LD₅₀ oral: 1090-2300 mg/kg 4h inhalation rat LD₅₀: >65/l, moderate toxic via respiration route - slightly toxic to fish	- acute rat LD₅₀ oral: 4230-5600 mg/kg, - for fish and tadpoles: very toxic in combination with surfactants	- acute rat LD₅₀ oral: > 5000 mg/kg - acute LC₅₀ for various fish: 0.47 - 1.6 mg/l - very toxic to bees	acute rat LD₅₀ oral: 633mg/kg	- acute rat LD₅₀ oral: 2000 - 8550 mg/kg, 96 h LD₅₀ in fish: 235 - 616 mg/l
WHO class	II (Moderately toxic)		U (unlikely to present acute hazard)	III (slightly hazardous)	
DT50 in soil		DT ₅₀ = 21 d; in Switzerland	DT ₅₀ = 3 - 39 d	median DT ₅₀ = 38.7 d	
DT50 in water		- in water: DT₅₀ = 1 and 4 d - in whole aquatic system: DT₅₀ = 27 and 146 d	- in water: DT₅₀ = 34 d - 57 d - in whole aquatic system: DT₅₀ = 170 d - 294 d	in water: DT₅₀ = 22.4 d - 47.5 d	
photolysis in soil		DT ₅₀ = 96 (90 d dark); 101 d (1236 d dark)	DT ₅₀ = 11 d	stable	
photolysis in water		DT ₅₀ = 33 d (pH 5), 69 d (pH 7), 77 d (pH 9)	DT ₅₀ = 8.7 - 13.9 d at pH 7	not significant	
hydrolysis		stable	stable	not significant	
remarks	possible source of endocrine damage	non selective herbicide, probably carcinogenic	potential groundwater contaminant		potential groundwater contaminant

The collected data were evaluated in Excel and R.

To test whether the content of PPPs inside the ponds fluctuates, I searched for differences in the concentrations between the sampling days. I used the lmer function of the R package lme4. This function fits a linear mixed effect model. It allows me to consider that the measurements aren't independent due to the fact that three measurements were taken of the same pond. I defined the name of the pond as random effect and the sampling dates as fixed effect. I made several linear mixed effect models with changed dependent measures: one for each PPPs' concentration named in table 1 and one for "the sum of all concentration classes":

$\text{lmer}(\text{PPPs' concentrations} \sim \text{sampling date} + (1|\text{name}))$

I wanted to test whether the surrounding land use, the buffer type and width and the aquatic vegetation could explain the presence of PPPs inside the ponds. For this reason I defined a variety of explanatory variables which could affect the concentration of PPPs. These variables were:

- the percentage of each of the nine defined land uses (crops, sugar beets, potatoes, vegetables, intensive meadow, extensive meadow, wood, waters and fallow land) 50m and 100m away from the ponds bank [%]
- the percentage of high buffer surrounding the pond [%]
- the average buffer width [m]
- the presence of a dam around the pond
- the percentage of aquatic vegetation for each vegetation type (cane brake vegetation, underwater vegetation and floating leave vegetation) [%]

Furthermore I wanted to test whether spatial characteristics of the pond could explain the presence of the PPPs. Therefore three spatial explanatory variables were defined:

- the surface area of the pond [m²]
- the range of the pond [m]
- the water volume of the pond [m³]

For these tests, I used linear mixed effect models with the ponds name as a random factor to consider the non-independence of the pesticide measurements. The fixed effect were the defined explanatory variables. The dependent measures were the concentrations of the PPPs in table 1 or the "sum of all concentration classes".

$\text{lmer}(\text{PPPs' concentrations} \sim \text{variable n} + (1|\text{name}))$

Additional to the presence of PPPs in the water, I was interested whether a water contamination might explain the absence of a *H. arborea* population in six of the twelve investigated ponds. To test this, I fitted again linear fixed effect models with the name of the pond as random factor and the presence of a *H. arborea* population as fixed effect. To test a possible influence of the different contaminants on the presence of *H. arborea*, I fitted models with changed dependent measures: the concentrations of the pesticides in table 1 [ng/l], "the sum of all pesticide classes", DOC [mg/l], chloride [mg/l], phosphor [mg/l], nitrogen [mg/l], nitrate nitrogen [mg/l], nitrite nitrogen [µg/l], ortho phosphate [µg/l] and sulfate [mg/l].

$\text{lmer}(\text{concentrations of substances} \sim \text{presence of } H. \text{ arborea} + (1|\text{name}))$

Other parameters that might change the water quality and therefor explain the absence of the species were the conductivity [$\mu\text{S}/\text{cm}$], the PH, the water temperature [$^{\circ}\text{C}$] and the oxygen saturation [mg/l and %].

`lmer (other parameters ~ presence of H. arborea + (1|name))`

I thought that also a water contamination with metals could affect *H. arborea*. As only one measurement per pond was taken of the metals, no random effect had to be considered. Therefor I used the `lm` function, which fits a linear model.

`lm (concentration of metals ~ presence of H. arborea)`

Results

Found PPPs concentrations inside the ponds

The lab for water and soil protection Berne (GBL) tested the water samples for the presence of 86 different micro pollutants. 62 of the analyzed pollutants were PPPs or their metabolites, 20 pollutants were pharmaceuticals or their metabolites and 4 pollutants were chemicals used in private households or industry.

Table 2: Overview of the investigated and proved substances

pollutant type	number of investigated substances	number of found substances in the water	number of substances occurring over the critical value of 100 ng/l set by the WPO
PPPs and their metabolites	62	55	14
pharmaceuticals and their metabolites	20	15	3
chemicals of private households or industry	4	4	2

In this thesis I focus mainly on a contamination with PPPs. From 62 tested PPPs, 55 were detected in at least one water sample (table 2).

The number of detected PPPs in each water sample varies between 29 and 48. Figure 6 presents the number of detected PPPs for each water sample, grouped by originating pond. It is conspicuous that the number in the three water samples of the same pond doesn't differ significantly. Between the ponds however can be seen clear differences. Panzersperre is the pond with the lowest number, while Mutkli is the pond with the highest number of found PPPs.

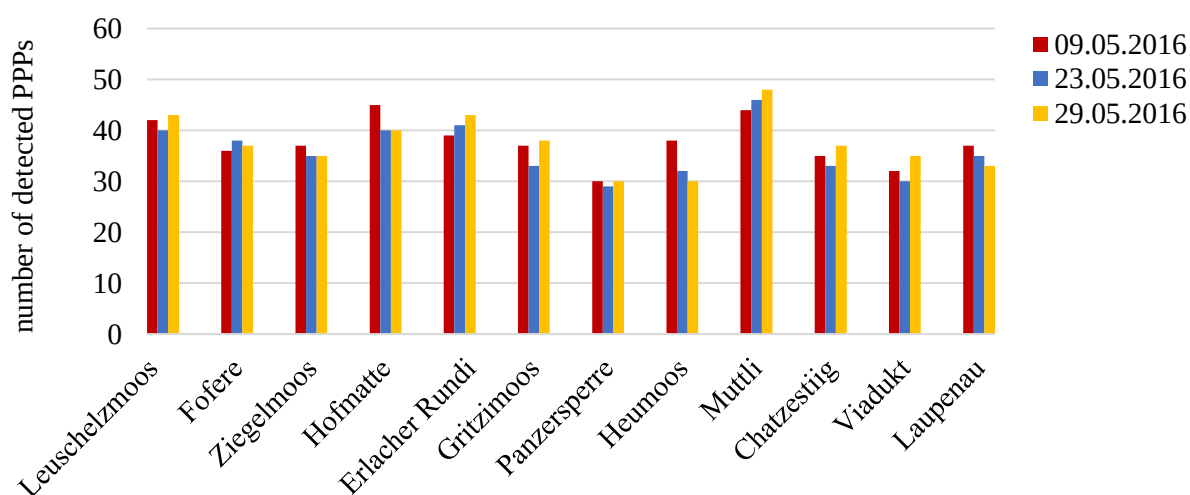


Figure 6: Bar plot. The 36 water samples are presented on the x-axis, grouped by originating pond. The number of PPPs found in each sample are presented on the y-axis. Differences between the ponds are more distinctive than between the three samples of the same pond.

In order to protect the surface waters against adverse effects, the water protection ordinance set a maximal value of certain substances. The maximal value of PPPs is 100ng/l. In figure 7 is shown, how many of the found PPPs occurred in concentrations over this critical value per sampling day. The ponds Fofere, Panzersperre, Heumoos and Chatzestiig don't contain any. However in the water samples of Leuschelzmoos and Muttli were several PPPs in high concentrations detected. In their waters samples lied the number of substances over the critical value between 7 and 11.

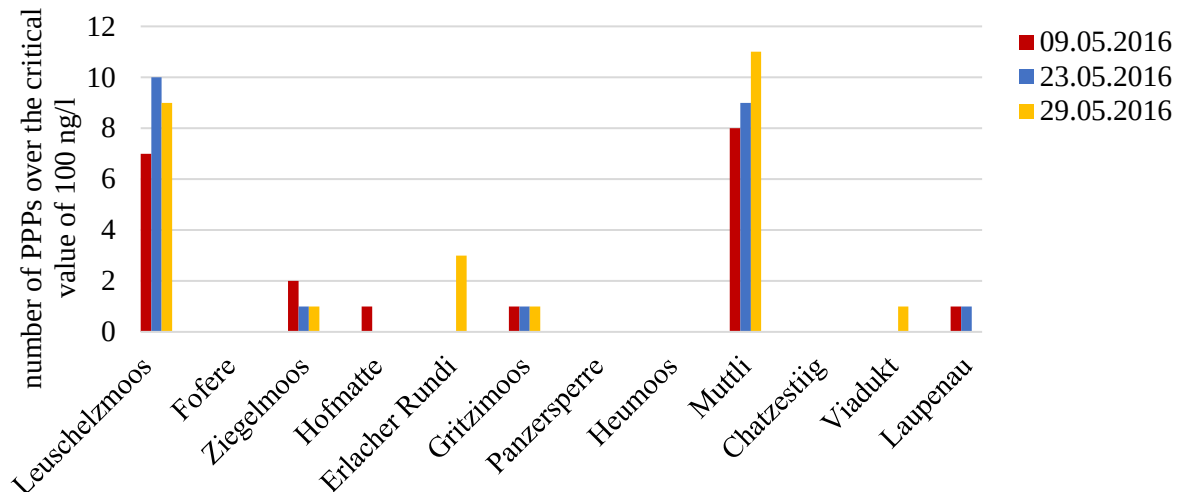


Figure 7: Bar plot. The 36 water samples are presented on the x-axis, grouped by originating pond. The number of PPPs which were detected over the critical value of 100 ng/l set by the WPO are presented on the y-axis. The ponds Muttli and Leuschelzmoos contains the highest variety of PPPs over the critical value.

Figure 8 presents the sum of all the detected concentrations per water sample. Muttli and Leuschelzmoos contain very high concentrations, between 2800 and 6300 ng/l.

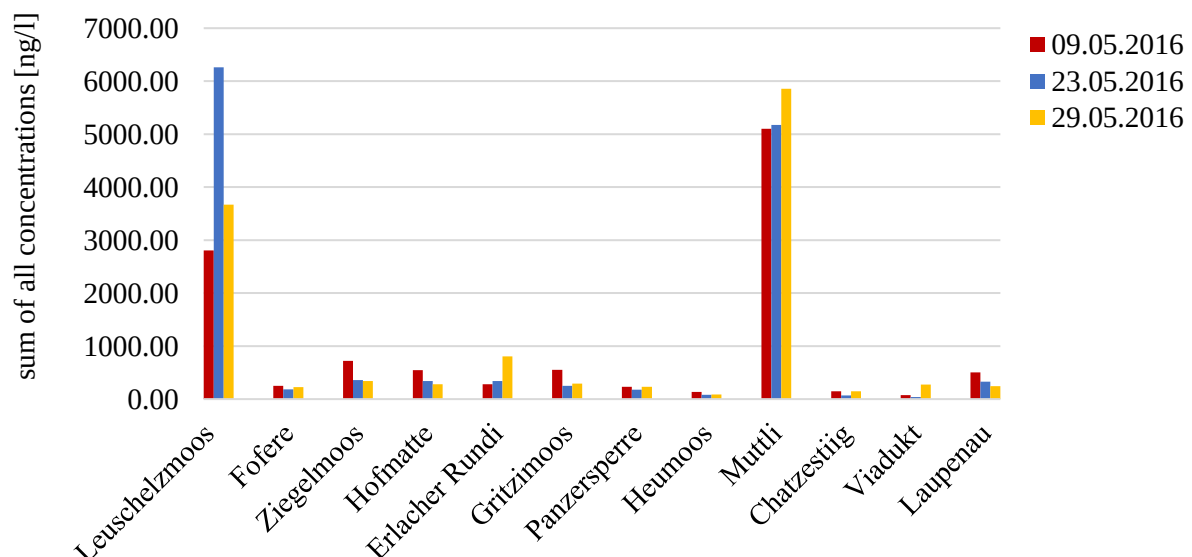


Figure 8: Bar plot. The 36 water samples are presented on the x-axis, grouped by originating pond. The sum of all PPPs concentrations found in one water sample is presented on the y-axis. The figure shows that the ponds Muttli and Leuschelzmoos contains the highest sum of concentrations.

Fluctuations of the PPPs concentrations between the three sampling days

I conducted the function: lmer (PPPs' concentrations ~ sampling day + (1|name)) with the concentrations of the PPPs occurring at least in one water sample over the critical value of 100 ng/l (table 1) or the “sum of all concentration classes” as dependent measures.

Methyl desphenyl chloridazon, the metabolite of the herbicide chloridazon and the herbicide glyphosate showed correlations between the three sampling days (09.05.2016, 23.05.2016, 29.05.2016), as indicated in table 3, ID 1 and 2. The glyphosate concentration of the first sampling day (09.05.16) was significantly higher, than the concentrations of the following sampling days. The concentration of methyl desphenyl chloridazon of the second sampling day (23.05.2016) was significantly lower than of the first sampling day.

Table 3: Correlations between the different sampling days (09.05.2016, 23.05.2016, 29.05.2016) and the concentrations of the PPPs occurring at least in one water sample over critical value of 100 ng/l set by the WPO (table 1) or the “sum of all concentration classes”.

ID	Variable	Correlates with the substance	Estimate	Std. error
1	sampling day: 23.05.2016	methyl desphenyl chloridazon	-9.988	4.916
	sampling day: 25.05.2016		-6.187	4.916
2	sampling day: 23.05.2016	glyphosate	-132.40	46.74
	sampling day: 25.05.2016		-128.70	46.74

The “sum of all concentration classes” and the other substances named in table 1 showed no correlations.

Factor one: land use

Land use in 50 m distance from the ponds bank

I conducted the function: lmer (PPP's concentrations ~ the percentage of land use in 50 m distance from the pond's bank [%] + (1|name)) with the concentrations of the PPPs occurring at least in one water sample over the critical value of 100 ng/l (table 1) or the “sum of all concentration classes” as dependent measures. The concentrations of desphenyl chloridazon and methyl desphenyl chloridazon showed a positive correlation with the amount of crop cultivation [%] (table 4, ID 1 and 2). Both of this substances are metabolites of the herbicide chloridazon which is often used in crop and sugar beet cultivation.

Table 4: Correlations between the different land uses (crops, sugar beets, potatoes, vegetables, intensive meadow, extensive meadow, wood, waters and fallow land) in 50 m distance of the ponds bank and the concentrations of the PPPs occurring at least in one water sample over critical value of 100 ng/l set by the WPO (table 1) or the “sum of all concentration classes”.

ID	Variable	Correlates with the substance	Estimate	Std. error
1	amount of crop cultivation [%]	desphenyl chloridazon	482.80	225.68
2	amount of crop cultivation [%]	methyl Desphenyl chloridazon	139.897	60.633

I fitted also linear mixed effect models with the combination of two different land uses as explanatory variables. The significant results can be found in the appendix table A9.

Land use in 100 m distance from the ponds bank

I conducted the function: lmer (PPP's concentrations ~ the percentage of land use in 100 m distance from the pond's bank [%] + (1|name)) with the concentrations of the PPPs occurring

at least in one water sample over the critical value of 100 ng/l (table 1) or the “sum of all concentration classes” as dependent measures. The “sum of all concentration classes” showed a negative correlation with the amount of wood [%]. The concentrations of azoxystrobin, ethofumesate, met amitron and its metabolite des amino met amitron, metalaxyl, metolachlor and the two metabolites of chloridazon desphenyl chloridazon and methyl desphenyl chloridazon showed positive correlations with the amount of sugar beet cultivation [%] (table 4, ID 2-9). Azoxystrobin and metalaxyl are fungicides, the others are herbicides.

Table 5: Correlations between the different land uses (crops, sugar beets, potatoes, vegetables, intensive meadow, extensive meadow, wood, waters and fallow land) in 100 m distance of the ponds bank and the concentrations of the PPPs occurring at least in one water sample over critical value of 100 ng/l set by the WPO (table 1) or the “sum of all concentration classes”.

ID	Variable	Correlates with the substance	Estimate	Std. error
1	amount of wood [%]	“sum of all concentration classes”	-77.111	31.841
2	amount of sugar beet cultivation [%]	azoxystrobin	318.57	140.88
3	amount of sugar beet cultivation [%]	ethofumesate	1704.499	539.024
4	amount of sugar beet cultivation [%]	met amitron	644.70	186.56
5	amount of sugar beet cultivation [%]	des amino met amitron	995.87	408.70
6	amount of sugar beet cultivation [%]	metalaxyl	336.380	96.681
7	amount of sugar beet cultivation [%]	metolachlor	272.739	77.825
8	amount of sugar beet cultivation [%]	desphenyl chloridazon	1025.85	351.73
9	amount of sugar beet cultivation [%]	methyl desphenyl chloridazon	290.917	94.395

I fitted also linear mixed effect models with the combination of two different land uses as explanatory variables. The significant results can be found in the appendix table A10.

Factor two: Buffer zone

Testing correlations between high buffer and the PPPs concentrations

I conducted the function: lmer (PPP’s concentrations ~ the percentage of high buffer surrounding the pond [%] + (1|name)) with the concentrations of the PPPs occurring at least in one water sample over the critical value of 100 ng/l (table 1) or the “sum of all concentration classes” as dependent measures. None of the linear mixed effect models showed any correlation between the amount of high buffer and the concentrations of the different PPPs.

Muttli is the pond with the highest sum of all PPPs concentrations and it contains a huge variety of different substances over the critical value. Moreover, it is completely surrounded by woods. Therefore, the data of Muttli could disguise possible correlations in our analysis. I fitted again the same linear mixed effect models as before excluding Muttli. No model showed any correlations.

Testing correlations between buffer width and the PPPs concentrations

I conducted the function: lmer (PPP’s concentrations ~ the average buffer width [m] + (1|name)) with the concentrations of the PPPs occurring at least in one water sample over the critical value of 100 ng/l (table 1) or the “sum of all concentration classes” as dependent measures.

The substances des amino metribuzin, a metabolite of the herbicide metribuzin and the herbicide glyphosate showed positive correlation (table 6, ID 1 and 2). This would indicate, that with rising buffer width, the concentration of these two substances would rise too. The pond Muttli contains by far the highest concentrations of des amino metribuzin and glyphosate. Moreover,

it is surrounded by the widest buffer zone in our analysis. These facts could explain the positive correlations. Possible protective effects of the buffer width would be disguised through the data of the pond Muttli. Therefore we fitted again linear mixed effect models excluding the data of Muttli. No models showed any correlations.

Table 6: Correlations between the buffer width and the concentrations of the PPPs occurring at least in one water sample over critical value of 100 ng/l set by the WPO (table 1) or the “sum of all concentration classes”.

ID	Variable	Correlates with the substance	Estimate	Std. error
1	The average buffer width [m]	desamino metribuzin	12.874	6.748
2	The average buffer width [m]	glyphosate	5.233	2.191

Testing correlations between a dam and the PPP's concentrations

I conducted the function: lmer (PPP's concentrations ~ the presence of a dam around the pond + (1|name) with the concentrations of the PPPs occurring at least in one water sample over the critical value of 100 ng/l (table 1) or the “sum of all concentration classes” as dependent measures.

The linear mixed effect model with “the sum of all concentration classes” as dependent measure showed a negative correlation (table7, ID 1). This result indicates that the ponds surrounded by a dam have a lower “sum of all concentration classes”. Therefore, the dam might have a protective function.

Table 7: Correlations between the presence of dam and the concentrations of the PPPs occurring at least in one water sample over critical value of 100 ng/l set by the WPO (table 1) or the “sum of all concentration classes”.

ID	Variable	Correlates with the substance	Estimate	Std. error
1	presence of a dam	the sum of all concentration classes	-17.876	8.453

In the following figure the “sums of all concentration classes” are presented, divided into two groups: one group are the sums in ponds surrounded by a dam, the other group are the sums in ponds without a dam. For this figure, I didn't consider all three measurements of the different sampling days per pond, but used the mean of the three measurements. It is shown that there the ponds without a dam contain more PPPs or PPPs in higher concentration.

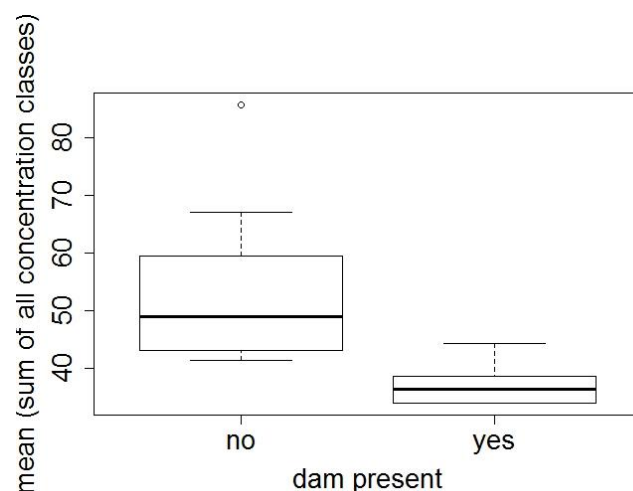


Figure 9: Box plot. On the x-axis are the grouped ponds represented: one group are the ponds surrounded by a dam, the other group are the ponds without a dam. The “sum of all concentration classes” is shown on the y-axis. For this figure, the mean of the three “sums of all concentration classes” was calculated.

The models with the other PPPs as dependent measures showed no correlations.

Factor three: aquatic vegetation

I conducted the function: `lmer (concentrations ~ the percentage of aquatic vegetation for each vegetation type [%] + (1|name))` with the concentrations of the PPPs occurring at least in one water sample over the critical value of 100 ng/l set by the WPO (table 1) or the “sum of all concentration classes” as dependent measures. I differed between three types of aquatic vegetation: cane brake vegetation, floating leaf vegetation and submerged vegetation.

The linear mixed effect models with the vegetation types cane brake and floating leaf vegetation showed no correlations between amount of vegetation and PPPs concentrations.

For the underwater vegetation analysis, I had to remove the pond Muttli from the analysis, because during field work the water was very muddy and it was not possible to determine reliably the amount of underwater vegetation. The linear mixed effect models showed no correlation between amount of underwater vegetation and PPPs concentrations.

Spatial characteristics of the ponds

I conducted the function: `lmer (PPP's concentrations ~ spatial variables + (1|name))` with the concentrations of the PPPs occurring at least in one water sample over the critical value of 100 ng/l set by the WPO (table 1) or the “sum of all concentration classes” as dependent measures. The three spatial variables were: the surface area of the ponds [m²], the range of the pond [m] and the water volume [m³].

The linear mixed effect models with the surface area [m²] and the water volume [m³] showed positive correlations for eleven of the substances named in the table 1 and the “sum of all concentration classes” (table 8, ID 1-12 or ID 22-33). These results indicate that the concentration of these eleven substances and the “sum of all concentration classes” rises with the surface area or water volume.

The linear mixed effect models with the range of the pond showed positive correlations for eight substances and the “sum of all concentration classes” (table 8, ID 13-21). These results indicate that the concentration of PPPs in the pond rises with its range.

An explanation for these positive correlations might be that the ponds with the highest contamination are the ones with the biggest surface area, the widest range and the highest water volume, namely Muttli and Leuschelzmoos. I fitted linear mixed effect models for all three spatial variables excluding the data of the two ponds. No correlation could be proven.

Table 8: Correlations between the variables concerning the spatial characteristics of the ponds and the concentrations of the PPPs occurring at least in one water sample over critical value of 100 ng/l set by the WPO (table 1) or the “sum of all concentration classes”.

ID	Variable	Correlates with the substance	Estimate	Std. error
1	the surface area of the ponds [m ²]	sum of all concentration classes	12.903	2.051
2	the surface area of the ponds [m ²]	azoxystrobin	50.497	9.942
3	the surface area of the ponds [m ²]	chloridazon	84.09	19.43
4	the surface area of the ponds [m ²]	desamino metatritron	154.83	27.25
5	the surface area of the ponds [m ²]	desamino metribuzin	193.30	54.68
6	the surface area of the ponds [m ²]	ethofumesate	163.14	60.43
7	the surface area of the ponds [m ²]	linuron	87.97	25.31
8	the surface area of the ponds [m ²]	metalaxyl	28.88	12.66
9	the surface area of the ponds [m ²]	metolachlor	21.184	9.168
10	the surface area of the ponds [m ²]	propamocarb	63.74	21.77
11	the surface area of the ponds [m ²]	glyphosate	69.32	19.67
12	the surface area of the ponds [m ²]	AMPA	193.92	43.88
13	the range of the pond [m]	sum of all concentration classes	18.696	7.329
14	the range of the pond [m]	azoxystrobin	70.95	31.64
15	the range of the pond [m]	chloridazon	131.41	53.71
16	the range of the pond [m]	desamino metatritron	230.28	89.71
17	the range of the pond [m]	desamino metribuzin	297.3	140.6
18	the range of the pond [m]	linuron	135.63	64.61
19	the range of the pond [m]	propamocarb	98.01	47.33
20	the range of the pond [m]	glyphosate	126.53	43.24
21	the range of the pond [m]	AMPA	294.8	124.4
22	the water volume [m ³]	sum of all concentration classes	7.703	1.575
23	the water volume [m ³]	azoxystrobin	31.526	6.584
24	the water volume [m ³]	chloridazon	51.58	13.10
25	the water volume [m ³]	desamino metatritron	95.76	18.70
26	the water volume [m ³]	desamino metribuzin	118.41	36.22
27	the water volume [m ³]	ethofumesate	102.44	38.48
28	the water volume [m ³]	linuron	53.91	16.73
29	the water volume [m ³]	metalaxyl	18.452	8.017
30	the water volume [m ³]	metolachlor	12.995	5.854
31	the water volume [m ³]	propamocarb	39.07	13.95
32	the water volume [m ³]	glyphosate	41.87	12.71
33	the water volume [m ³]	AMPA	119.05	29.61

Hyla arborea

PPPs

I conducted the function: lmer (PPP's concentrations ~ presence of *H. arborea* population + (1|name)) with the concentrations of the PPPs occurring at least in one water sample over the critical value of 100 ng/l set by the WPO (table 1) or the “sum of all concentration classes” as dependent measures. The linear mixed effect models showed no correlation between the presence of *H. arborea* population and the concentrations of PPPs.

Metals and semimetals

I conducted the function: `lm (metal concentrations ~ presence of H. arborea population)`. The concentrations of the metals and semimetals can be found in the appendix table A3. As I only had one measurement of the metals or semimetal per pond, no random effect needed to be considered. The linear models showed no correlation between the presence of *H. arborea* and the concentration of the metals or semimetals.

Further measurements

I conducted the function: `lmer (concentrations ~ presence of H. arborea population + (1|name))` with the concentrations of DOC [mg/l], chloride [mg/l], phosphor [mg/l], nitrogen [mg/l], nitrate nitrogen [mg/l], nitrite nitrogen [µg/l], ortho phosphate [µg P/l] and sulfate [mg/l].

Sulfate showed a negative correlation with the presence of a *H. arborea* population. This result indicates that ponds without a *H. arborea* population contains more sulfate and it leads to the conclusion that sulfate might be responsible for the absence of the species.

Table 9: Correlations between the presence of a *H. arborea* population and the concentrations of the PPPs (table x), the “sum of all concentration classes”, metals and semimetals or further measurements.

ID	Variable	Correlates with the substance	Estimate	Std. error
1	the presence of a <i>H. arborea</i> population	sulfate	-24.134	9.387

In the following figure the sulfate concentrations are presented, divided into two groups: one are the sulfate measurements in ponds with a *H. arborea* population, the other group without a *H. arborea* population. For this figure I didn't consider all three measurements of the different sampling days per pond, but used their mean. It is shown that there is a difference between the two pond groups in the sulfate concentration.

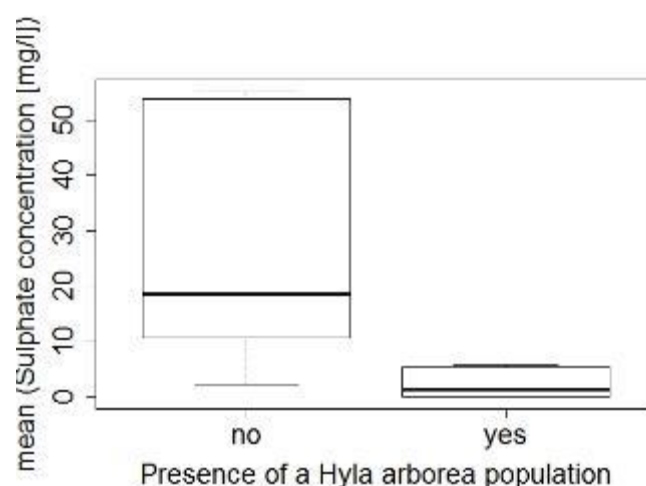


Figure 10: Box plot. On the x-axis are the grouped ponds represented: one group are the ponds which are populated by *H. arborea*, the other group which aren't populated. The sulfate concentration is shown on the y-axis. For the figure, the mean of the three measurements per pond was calculated. The figure indicates that the ponds without a *H. arborea* population contain higher concentrations of sulfate.

I conducted the function: `lmer (parameters~ presence of H. arborea population + (1|name))`. The parameters were the conductivity [µS/cm], the PH, the oxygen saturation [mg/l and %] or the water temperature [C°]. These parameters might change the water quality and therefor

explain the absence of the *H. arborea* species. The linear mixed effect models however didn't show any correlation.

Discussion

In this dissertation, the water of twelve reproduction sites distributed in the Seeland and Saanetal were analyzed. The goal was to find out whether the amphibians populating this reproduction sites face exposure to chemical contamination with plant protection products. I was interested, in which concentrations different substances occur and whether there could be observed any temporal fluctuation in them. Furthermore, I wanted to determine, whether the amount of surrounding agricultural land use, the width and spatial structure of the buffer zone or the amount and type of aquatic vegetation inside the ponds could explain the presence of the found PPPs. Finally, I posed the question, whether a possible water contamination could explain the absence of a stable *H. arborea* population in half of the ponds. To test this questions, water samples of each pond were collected on three days in May and investigated on 62 PPPs or their metabolites. Furthermore the use of the surrounding landscape, the buffer zone and the aquatic vegetation were examined visually. Then the collected data were analyzed in R and Excel.

In total, 55 of 62 tested PPPs were detected. Most of the concentrations lied between 1 -100 ng/l, but fourteen substances occurred in concentrations over the critical value of 100 ng/l set by the WPO. Besides, my results showed that each water sample contains a mixture of between 29 and 48 different PPPs. Mixtures of different chemicals in the water can get very dangerously to aquatic organism due to additive or synergistic affects (Schwarzenbach et al. 2006). Several studies already underlined this phenomenon (Hayes et al. 2006, Boone & Bridges-Britton 2006).

Furthermore I detected that the majority of the tested substances didn't fluctuate between the three sampling days in May. Only two substances showed fluctuations: the metabolite methyl desphenyl chloridazon and the herbicide glyphosate. The concentration of methyl desphenyl chloridazon of the second sampling day was significantly deeper than the concentration of the first. The concentration of glyphosate was higher in the first sampling day than in the other days, what might be explained be the short degradation time of glyphosate in water of $DT_{50} = 1 - 4$ days (table 1). All the other substances didn't fluctuate between the sampling days. The reason for this result might be, that these substances degrade very slowly or that a constant input of PPPs into the water happens. The conclusion of no fluctuations between the sampling days is, that water organisms inside strongly polluted ponds face this contamination for a time period of at least three weeks. Chronical exposure during the development of amphibians can have severe outcomes. It can cause malformations (Bernabò et al. 2011) or an increased mortality rate (Hartmann et al. 2014).

As data about the water quality in amphibian reproduction sites are rare, the results of this field study provide us an idea, how high the exposure amphibians are facing is: two of the twelve analyzed ponds were strongly contaminated with PPPs, namely Muttli and Leuschelzmoos. In their water samples could be detected over 40 different PPPs. The sum of all concentrations per sample made a total value between 2800 and 6300 ng/l. These results indicates, that amphibian species populating this two reproduction sites are exposed to a contamination in a composition of various PPPs in high concentrations over a time period of three weeks. Therefor the goals of the WPO aren't fulfilled and it is likely, that PPPs pose a high risk on the amphibian species and other water organisms in this ponds.

I analyzed three factors that may cause or inhibit a water pollution with PPPs.

- The first factor is the use of the surrounding land scape. The amount of agricultural land did not correlate significantly with the PPPs concentrations. But when I split up the agricultural land use in various cultivation types, correlations could be seen between some cultivations and some PPPs. The amount of sugar beet cultivation in 100 m

distance from the ponds bank correlates positively with the herbicides metamiltron, ethofumesate, metolachlor, with the herbicide metabolites desamino metamiltron, desphenyl chloridazon, metyl desphenyl chloridazon and with the fungicides azoxystrobin and metalaxyl. The amount of crop cultivation in 50 m distance from the ponds bank correlates positively with the metabolites of the herbicide chloridazon: desphenyl chloridazon and methyl desphenyl chloridazon.

These results indicate that in these two cultivations the application rate of these specific PPPs is higher than in the other cultivations. Furthermore it is shown, that in sugar beet cultivation a variety of different PPPs are applied. Due to crop rotation, it is quite difficult to protect the ponds against the input of specific land uses. A general decline in PPPs application in the crop and sugar beet cultivation might be achieved by the instalment of direct support schemes. One program that already exists is Extensio. In this program, the production of crops, sunflowers, broad beans, rape and peas without fungicide and insecticide use is encouraged by direct payments to the farmers (Eidgenössisches Departement für Wirtschaft, Bildung und Forschung WBF 2016). To provide a higher incentive for an extensive production in the sugar beet cultivation, sugar beet should be included to this program. Most of the substances that correlated in my analysis with sugar beet or crops are herbicides or their metabolites. Therefore, also some direct support programs should be installed that promote the cultivation without herbicides.

A reduction in the water contamination with PPPs might also be achieved by inhibiting the input ways. Studies have shown, that a broad buffer zone or hedges can reduce the input of PPPs via spray drift (De Snoo & De Wit 1998, Brown et al. 2004, Lazzaro et al. 2008). I found out, that a dam could present a possible protective measurement. It might work by inhibiting aerial drift or runoff of agricultural land after rainfalls. The dams in my investigation are differently shaped. The pond Panzersperre is situated next to a several meter high stone wall, a relict of the former military area. However a stone wall as a possible protective measurement can be excluded. Though it would indeed prevent the PPPs from entering the water, it would represent a barrier amphibians can't conquer. The dams next to Heumoos and Fofere are earthworks of about 1 m height. The dams next to Viadukt and Chatzestiig are also earthworks, but of several meters height. Earthworks would present a good protective measurement that can easily be realized in the construction of future ponds. Further researches should be made to find out, how high the dam should be to shelter the pond, but not to impede amphibians.

- Another factor that might inhibit a water pollution is the aquatic vegetation inside the ponds. In my study, no correlations were proved between the amount of the different aquatic vegetation types and the concentrations of PPPs. However, this result wasn't surprisingly, as the data about the aquatic vegetation were too fragmentary to conduct an adequate statistical analysis. The vegetation type floating leaf is only in one pond represented. Furthermore during field work it transpired that a visual examination of the submerged plants was very difficult, as the water was partly very muddy.
- The last factor I analyzed was the buffer zone. No correlations could be detected neither between the buffer width and the PPPs concentrations nor between the amount of wooded buffer and the PPPs concentrations. It seems that the buffer zone in my research didn't protect the ponds against a contamination. This result came as a surprise, because many studies have already proven the protective effect of buffer zones (De Snoo & De Wit 1998, Brown et al. 2004, Lazzaro et al. 2008). Leuschelzmoos and Muttli were the most contaminated ponds in my research. However they are surrounded by a buffer zone with an average width of 37 m and 58m respectively. A zone broad enough to inhibit input of drift (De Snoo & De Wit 1998, Brown et al. 2004). Therefore the question that

remains is, why are the ponds Leuschelzmoos and Muttli despite their broad and structured buffer zone so strongly contaminated and how do the PPPs enter them?

One possible solution might be, that the PPPs enter the ponds via the drainages from the surrounding landscapes. In drainages, the seeped rainwater is collected in the field, and then diverted to nearby waters (WBF 2016). In Switzerland, about 20% of the agricultural land is drained today (Béguin & Smola 2010). Therefore they might present a possible input way for PPPs into amphibian reproduction sites.

I contacted the engineering office Lüscher & Aeschlimann in Ins and it provided me maps where the drainages are marked of some investigated ponds in the Seeland and their surroundings. All the maps can be found in the appendix. Furthermore Mr. Stegemann Robert, director of the engineering office, gave me some valuable information about the ponds, which I used for the following sections.

The map below shows the drainages in the surroundings of Leuschelzmoos. Thanks to structural measurements in 2010 only a part of the drainage water of the main road end up in the pond. But what stands out is, that the drainages of the nearby fields are diverted directly into the ponds. Leuschelzmoos doesn't possess an efflux, only an artificial overflow when the water surface is too high.

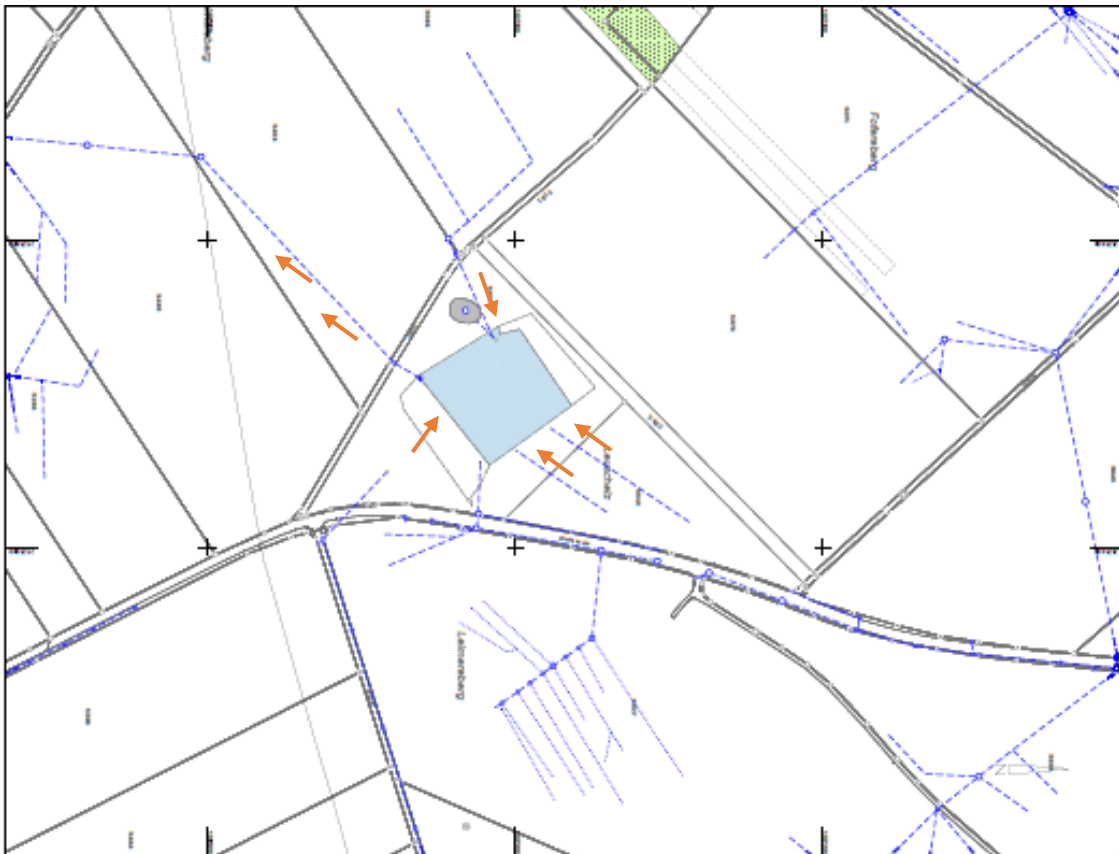


Figure 11: Drainages in the surrounding landscape of Leuschelzmoos (1:8000). The red arrows indicate, in which direction the water is flowing.

The following map shows the drainages around Muttli. Several drainages from the nearby fields enter the pond, but also the drainage from the road is diverted directly into the water. The separate sewer system from the football pitch, a nearby horse farm and the industrial zone is connected with the water as well. Like Leuschelmoos, Muttli doesn't have an efflux.



Figure 12: Drainages in the surrounding of Muttli (1:8000). The red arrows indicate, in which direction the water is flowing.

Therefore the reason for the high PPPs concentration inside Muttli and Leuschelzmoos is, that the drainages from the surroundings are diverted directly into the water. Furthermore they don't have an efflux, what differs them from the other ponds in my research. Fofere possesses an artificial discharge. Heumoos, Hofmatte, Gritzimoos, Panzersperre and Erlacher Rundi are in contact with the groundwater, which regulate their water surface. So in this ponds a washout of the PPPs is possible. In contrast, the water of Leuschelzmoos and Muttli doesn't flow off what leads to an accumulation of PPPs inside the water.

Up to the present, no effective measures are known to reduce the input of PPPs via drainages (WBF 2016). The action schedule of PPS showed however, that the discovering of measures is of high importance (WBF 2016). I guess the instalment of an efflux would inhibit the accumulation of PPPs inside Muttli and Leuschelzmoos, but this would be connected with complex or even impossible construction measures.

The last sub question I tried to answer was, whether the absence of a *H. arborea* population could be explained with a water contamination. Neither the concentrations of PPPs nor the concentrations of metals or semimetals showed any differences between ponds with and ponds without a *H. arborea* population. The only substance that differed between this two pond groups in its concentration was sulfate. Higher concentrations were detected in the ponds without *H. arborea*. Sulfate can occur in runoff from agriculturally used landscapes, in industrial waste water or in waters with a catchment basin with elevated mineralization (Elphick et al. 2011). In the agriculture, different sulfates are used as fertilizers or added to PPPs, like copper sulfate, iron sulfate or magnesium sulfate. One study tested the effects of sulfate on the larvae of the amphibian species *Pseudacris regilla* (Elphick et al. 2011). Interestingly, sulfate affected the larval growth positively. Larvae which were exposed to concentrations until 1000 mg/l were

about 30% heavier than the larvae of the control group. So sulfate might be used beneficially in their metabolism (Elphick et al. 2011). The concentrations in my research are far below 1000 mg/l. The maximal concentration is reached in the pond Panzersperre with 70, 23 mg/l. Therefore the sulfate concentration as a possible explanatory variable for the absence of *H. arborea* is doubtful. It can't be excluded though, because different amphibian species can differ in their sensitivity towards environmental chemicals (Boone et al. 2009).

More likely, there is another cause for the absence of *H. arborea* in half of the ponds - a certain mixture of PPPs. As indicated above, chemical mixtures can get very dangerous to aquatic organisms through synergistic effects (Schwarzenbach et al. 2006). A statistical test might be conducted, to prove whether a certain mixture of different PPPs occur in the ponds without *H. arborea*. A laboratory experiment could give more evidence, which role chemical contaminants in the unpopulated waters have. Tadpoles could be risen under identical conditions in water taken from the ponds without a *H. arborea* population and in clean water, and their development be compared.

H. arborea is one of the species threatened with extinction in Switzerland. It is therefore highly important to know, why they don't occur in reproduction sites which would satisfy their physical demands. Then adequate safety measurements could be conducted and the populations stabilized.

Conclusion

In my study I proved, that two ponds are strongly contaminated, with pesticides in high concentrations and in mixtures. This indicates, that the targets of the WPO aren't fulfilled and that there might be a risk for amphibians and other water organism.

I found out, that drainages are an important input way for PPPs that should be investigated more, so that inhibiting measures could be undertaken.

Furthermore I detected, that a dam might be a possible protective measurement against water contamination, as it shelters the pond against drift and runoff.

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First of all, I would like to give my thanks to Dr. Benedikt Schmidt and Dr. Katja Räsänen. Both of them supported me during the whole process of this thesis, answered my numerous questions and gave me a lot of good advices. Special thanks goes to Silvia Zumbach who supported me with the water sampling, taught me a lot about local anuran species and gave me valuable tips for writing this dissertation. Furthermore, I would like to thank the GBL Berne for analyzing the water samples and for providing me the data of the detected chemicals, to Dr. Claudia Minkowski for answering my questions about the data and Dr. Markus Zeh for giving me private photos of the analyzed ponds. I want to thank the engineering office Lüscher & Aeschlimann AG in Ins for providing me the maps of the ponds and the surrounding landscape in the Seeland and Robert Stegemann for the useful information and explanation about the ponds. Last but not least I want to thank Nicolas Dulex for helping me with the water sampling.

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Picture references

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Figure 6-10: created with R and Excel

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Figure 12: p.30. Map. Provided by the office of engineering Lüscher & Aeschlimann Ins

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Appendix

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Table A 1: Concentrations of the found PPPs in ponds with a *H. arborea* population [ng/l]

	Leuschelzmoos			Fofere			Ziegelmoos			Chatzestiig			Viadukt			Laupenau		
	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016
2_OH_Atrazin.1	3.67	6.61	3.15	1.41	5.27	1.84	17.79	14.68	14.02	0.66	0.60	0.66	1.00	0.88	0.89	1.73	2.16	5.69
2OH-Propazin.1	0.31	0.37	0.32	0.00	0.12	0.00	1.22	0.84	0.92	0.16	0.12	0.12	0.11	0.08	0.09	0.18	0.26	0.51
2OH-Terbutylazin.1	10.46	5.45	7.43	2.12	5.70	2.05	47.16	38.68	32.85	3.07	2.37	2.42	1.57	1.35	1.39	1.92	2.28	3.98
Alachlor.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Atrazin.1	0.30	0.36	0.22	0.46	0.38	0.41	0.06	0.08	0.10	0.14	0.08	0.16	0.10	0.00	0.14	2.60	1.58	1.11
Azoxystrobin.1	224.76	103.06	324.24	15.28	9.88	9.67	1.92	1.92	2.03	1.39	1.44	17.95	1.43	1.48	5.20	1.22	1.27	17.31
Boscalid.1	5.56	4.92	4.41	2.23	1.91	2.08	2.10	1.63	1.58	1.49	1.90	2.26	1.77	1.82	1.89	1.39	1.57	1.27
Carbendazim.1	4.15	4.28	4.86	0.66	0.78	0.83	1.25	0.67	0.63	1.39	0.49	0.62	1.27	0.52	0.54	0.93	0.31	0.54
Chloridazon.1	61.63	43.44	52.40	1.08	1.25	1.38	21.44	19.54	23.27	0.73	0.83	0.71	0.84	0.85	0.96	0.00	1.30	0.73
Chlorpropham.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.75	0.00	0.00	0.00
Chlorpyrifos.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chlorpyrifos-Methyl.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chlortoluron.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cyanazin.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cyproconazole.1	23.63	14.74	18.15	39.36	18.49	20.59	3.61	2.12	1.71	0.74	0.48	0.48	0.53	0.33	0.41	0.45	0.16	0.20
Cyprodinil.1	2.15	0.00	0.00	1.53	1.58	0.00	2.00	0.00	0.00	2.49	0.00	8.03	1.76	0.00	4.24	2.03	0.00	16.42
DEET.1	95.24	7.43	10.96	6.65	17.14	4.40	3.21	15.10	2.94	6.04	8.03	4.64	3.51	6.07	194.68	4.37	4.09	9.12
Desamino_Metamitron.1	319.24	1017.88	617.66	30.41	17.65	22.03	134.79	120.74	143.97	6.77	9.20	8.45	5.95	5.58	6.12	11.30	8.89	5.66
Desamino_Metribuzin.1	4.76	3.68	5.65	7.65	5.20	5.27	3.72	2.81	2.64	1.34	1.13	0.93	0.60	0.76	0.93	0.46	1.69	0.68
Desethylatrazin.1	1.06	0.81	0.00	0.00	0.32	0.48	0.31	0.21	0.00	0.00	0.00	0.22	0.00	0.14	0.07	13.93	8.23	4.60
Desethylterbutylazin.1	3.35	3.24	4.93	4.17	5.02	7.41	1.64	1.72	3.08	2.41	4.13	7.66	3.82	4.21	6.73	1.82	3.68	5.06
Desisopropyl-atrazin.1	0.00	0.00	0.21	0.00	0.00	0.25	0.00	0.09	0.04	0.00	0.00	0.15	0.00	0.00	0.03	0.00	0.00	0.27

Desph.Chloridazon.1	888.09	441.73	672.60	0.00	0.00	0.00	53.03	39.50	41.76	0.00	0.00	9.56	0.00	0.00	0.00	263.79	168.87	94.57
Diazinon.1	3.52	0.88	0.86	1.11	0.84	0.86	0.89	0.00	0.84	0.00	0.94	0.88	0.00	0.83	0.82	0.83	0.87	0.83
Dichlorbenzamid.1	10.51	15.16	9.99	11.36	8.91	9.48	24.98	21.01	18.61	0.98	0.84	0.00	0.97	0.00	0.00	60.92	46.21	31.48
Diflufenican.1	0.68	0.56	0.61	1.06	0.93	1.00	7.61	6.20	5.48	0.49	0.56	0.53	0.60	0.58	0.50	0.52	0.00	0.00
Dimetachlor.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dimethenamid.1	2.73	2.23	0.42	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.70	0.00	0.00
Dimethoat.1	440.94	118.38	72.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Diuron.1	0.36	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00
Epoxyconazol.1	3.64	2.44	2.67	2.91	2.37	2.21	0.00	0.00	0.00	0.00	0.00	1.22	0.98	0.92	1.05	0.00	1.03	0.00
Ethofumesate.1	38.89	2594.10	331.20	14.03	13.16	15.31	9.39	7.17	8.81	4.21	5.10	9.55	4.44	3.31	4.23	3.48	3.03	3.71
Imidacloprid.1	14.29	218.68	26.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Iprovalicarb.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.89	2.29	0.00	0.00	0.00	0.00	0.00	0.00
Irgarol.1	0.00	1.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isoproturon.1	0.73	0.00	0.38	0.24	0.00	0.00	0.19	0.00	0.07	0.23	0.14	0.00	0.03	0.00	0.00	0.07	0.00	0.00
Linuron.1	0.85	0.70	1.24	0.22	0.34	0.38	1.94	0.48	0.59	0.17	0.28	0.51	0.25	0.19	0.26	0.16	0.74	0.22
Metalaxyl.1	181.78	173.27	241.18	0.26	0.84	0.93	0.37	0.89	0.68	0.75	8.81	31.70	0.21	0.41	0.79	0.14	0.35	0.83
Metamitron.1	12.02	903.32	49.76	1.14	2.55	0.00	0.00	0.00	0.00	2.13	0.00	2.60	1.10	0.00	0.00	4.19	2.15	0.00
Metazachlor.1	0.37	0.27	0.44	0.07	0.24	0.37	0.14	0.07	0.24	0.39	0.10	0.21	0.15	0.10	0.08	0.38	0.07	0.05
MetazachlorOA.1	1.69	0.08	1.08	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00	3.04	2.71	0.00
Methoxyfenozid.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methyl-Desph.Chlor..1	208.24	147.08	193.91	0.00	0.42	0.42	8.75	8.40	8.86	3.01	1.35	3.14	0.00	0.15	0.16	67.63	39.42	22.12
Metobromuron.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Metolachlor.1	37.51	0.00	373.82	8.28	10.78	15.45	3.35	4.37	6.78	6.98	11.59	16.98	4.16	3.78	7.08	5.29	5.07	6.59
Metribuzin.1	0.00	0.82	1.71	0.00	1.32	0.81	0.00	0.35	0.50	0.00	0.00	0.67	0.00	0.00	0.42	0.00	0.00	0.50
Napropamid.1	0.00	0.00	0.74	0.00	0.76	0.73	0.73	0.76	0.78	0.77	0.73	0.00	0.00	0.00	0.00	0.75	0.00	0.00
Nicosulfuron.1	0.00	0.00	0.00	0.89	0.00	1.46	0.00	0.00	0.00	0.13	0.00	0.00	0.18	0.00	1.96	0.00	0.90	1.65
Orbencarb.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.86	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Pirimicarb.1	0.00	0.04	0.09	0.03	0.03	0.03	0.00	0.00	0.06	0.00	0.02	0.00	0.00	0.02	0.01	0.00	0.05	0.00
Propachlor.1	1.60	1.55	0.29	5.80	1.88	0.18	3.48	1.93	0.17	0.00	0.00	0.08	0.04	0.00	0.07	0.02	0.02	0.04
Propamocarb.1	0.07	0.46	0.09	0.02	0.07	0.03	0.40	0.21	0.10	0.06	0.03	0.11	0.06	0.12	0.07	0.04	0.08	0.05
Propazin.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Propiconazol.1	0.00	0.00	0.00	1.29	0.00	0.00	0.00	0.00	0.00	1.29	0.00	1.67	0.00	0.00	0.00	0.00	0.00	1.36
Pirimethanil.1	123.91	64.00	472.28	0.99	0.65	0.54	3.48	0.67	0.72	0.57	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Simazin.1	0.20	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tebuconazol.1	1.88	1.43	2.36	0.99	1.27	1.50	1.79	1.25	1.36	1.28	1.94	2.41	1.25	1.62	1.69	1.11	1.60	1.62
Terbuthylazin.1	0.71	0.22	1.44	1.40	0.99	3.41	1.09	0.53	1.64	0.58	1.28	7.40	0.96	0.99	13.01	0.16	0.52	2.64
Terbutryn.1	0.00	0.00	0.00	0.00	0.00	1.22	4.00	3.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Thiacloprid.1	0.71	0.49	0.66	0.09	0.12	0.13	0.28	0.23	0.24	0.16	0.20	0.25	0.12	0.12	0.16	0.10	0.09	0.00
AMPA	11.405	330.97	23.912	33.248	19.805	30.5625	6.346	3.615	0	7.607	3.368	0.549	4.271	2.737	0	4.713	0.279	0
Glyphosat	56.872	25.111	133.068	51.295	22.713	60.0445	346.167	40.021	14.966	87.24	2.113	2.509	29.081	1.863	18.657	42.502	14.85	3.304
Gesamtergebnis	69	73	73	47	51	47	50	47	47	40	38	46	34	32	43	45	43	43
Summe Pestizide (ng/L)	2804.46	6261.31	3670.17	249.78	181.89	225.69	721.11	362.18	343.00	147.91	71.94	150.28	73.08	42.01	276.08	504.89	326.37	244.68

Table A 2: Concentrations of the found PPPs in ponds without a *H. arborea* population [ng/l]

	Hofmatte			Erlacher Rundi			Gritzimoos			Panzersperre			Heumoos			Muttli		
	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016
2_OH_Atrazin.1	7.71	12.18	16.53	55.96	46.93	34.48	8.15	7.40	7.84	3.06	2.52	2.42	9.37	7.14	7.80	20.92	20.18	21.51
2OH-Propazin.1	0.86	0.65	0.81	3.18	2.67	1.89	0.50	0.52	0.52	0.20	0.19	0.18	1.08	0.88	0.89	1.05	0.00	0.00
2OH-Terbutylazin.1	2.58	4.12	4.83	11.96	9.42	6.97	3.06	2.83	2.42	0.59	0.55	0.53	1.35	1.14	1.10	42.05	36.94	35.78
Alachlor.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Atrazin.1	0.88	0.24	0.12	0.09	0.19	0.12	0.19	0.00	0.21	0.13	0.00	0.08	0.57	0.52	0.63	0.37	0.41	0.30
Azoxystrobin.1	3.25	5.91	6.51	2.34	2.45	2.06	3.13	3.01	3.03	1.17	1.10	1.13	1.63	1.57	1.68	118.34	122.33	140.69
Boscalid.1	1.69	1.98	2.04	3.13	3.45	2.52	2.72	2.24	2.15	0.92	0.96	0.90	2.32	2.04	2.26	7.15	6.64	6.77
Carbendazim.1	1.56	3.16	3.42	0.82	0.42	0.39	1.14	0.71	0.60	0.78	0.48	0.00	3.39	1.97	2.24	4.96	6.61	6.45
Chloridazon.1	35.45	6.47	6.77	1.64	1.58	1.69	6.44	6.37	24.98	1.30	1.42	1.53	0.36	0.48	0.45	607.63	369.16	284.00
Chlorpropham.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.88	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chlorpyrifos.1	0.00	0.00	0.00	4.16	4.40	4.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.16	5.17	4.86
Chlorpyrifos-Methyl.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chlortoluron.1	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cyanazin.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cyproconazole.1	0.32	0.82	1.21	0.96	0.61	0.46	0.71	0.46	0.39	0.00	0.00	0.00	0.51	0.46	0.33	62.41	50.91	59.40
Cyprodinil.1	6.71	2.79	2.97	2.38	2.10	1.85	1.83	1.77	0.00	1.60	0.00	0.00	2.68	1.90	0.00	4.26	4.74	5.42
DEET.1	2.14	26.59	3.34	3.29	6.18	96.08	3.02	4.12	3.30	5.32	9.04	3.32	3.12	5.89	3.43	5.05	37.36	19.22
Desamino_Metamitron.1	7.53	13.56	18.84	17.30	28.11	198.33	42.35	42.52	68.63	5.29	5.54	3.70	10.22	9.88	9.24	98.80	622.87	493.03
Desamino_Metribuzin.1	2.38	5.97	7.13	1.00	2.07	1.24	1.40	3.38	2.76	0.00	0.17	0.00	0.89	1.14	1.38	1166.85	978.94	951.87
Desethylatrazin.1	1.20	0.29	0.21	1.26	0.00	0.17	0.00	0.13	0.04	0.00	0.18	0.00	1.07	0.72	0.79	0.00	0.34	0.00
Desethylterbutylazin.1	1.91	2.61	2.85	1.18	3.75	3.69	2.92	3.76	5.11	0.62	1.33	1.40	3.29	3.55	4.24	4.41	4.97	6.88
Desisopropyl-atrazin.1	1.29	0.00	0.17	0.00	0.00	0.23	0.00	0.00	0.42	0.00	0.06	0.15	0.06	0.00	0.12	0.00	0.04	0.08

Desph.Chloridazon.1	192.22	70.15	67.01	0.00	0.00	5.95	0.00	0.00	0.00	62.01	73.65	88.98	0.00	0.00	0.00	67.69	90.00	113.23
Diazinon.1	0.85	0.88	0.86	0.00	0.87	0.89	0.89	0.89	1.20	0.00	0.00	0.84	0.86	0.86	0.89	0.96	1.01	1.00
Dichlorbenzamid.1	52.51	22.46	26.37	36.84	41.23	37.21	0.75	0.00	0.00	10.43	10.81	12.48	19.87	17.14	19.18	39.50	43.04	45.64
Diflufenican.1	0.68	0.73	0.70	0.52	0.60	0.57	0.61	0.62	0.57	0.00	0.00	0.00	0.57	0.56	0.00	5.84	5.54	5.14
Dimetachlor.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dimethenamid.1	0.73	0.00	0.00	0.00	0.00	0.00	14.60	5.15	2.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	39.91	27.68
Dimethoat.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Diuron.1	0.06	0.00	0.00	0.10	0.13	0.07	0.01	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.65	0.00	0.70
Epoxyconazol.1	0.00	1.10	0.00	0.00	1.08	1.01	1.73	1.63	1.47	0.00	0.00	0.00	0.00	0.93	0.00	13.06	9.76	9.96
Ethofumesate.1	9.46	10.87	12.99	12.50	59.14	61.66	32.76	125.80	115.93	6.12	7.69	4.63	4.00	4.60	5.30	237.09	244.47	213.54
Imidacloprid.1	0.00	0.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9.32	8.80	11.19
Iprovalicarb.1	0.00	0.00	0.00	0.00	0.00	0.27	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Irgarol.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isoproturon.1	5.23	0.00	0.00	0.37	0.24	0.00	0.20	0.00	0.00	0.08	0.00	0.04	0.23	0.00	0.00	191.24	91.30	58.15
Linuron.1	29.45	4.42	1.57	1.40	1.59	1.02	0.82	0.73	0.89	0.41	0.14	0.89	1.00	0.68	0.89	57.73	724.51	639.54
Metalaxyl.1	0.88	2.81	2.51	1.36	2.49	1.80	0.84	1.31	1.16	0.08	0.00	0.18	1.15	1.92	1.86	20.41	22.44	23.76
Metamitron.1	4.13	0.00	0.00	16.11	6.96	210.66	2.15	17.41	3.53	1.52	6.50	0.00	0.86	0.00	0.00	0.00	26.62	16.27
Metazachlor.1	0.18	0.30	0.18	0.04	0.31	0.26	0.09	0.16	0.23	0.05	0.05	0.00	0.28	0.19	0.24	8.15	9.01	9.16
MetazachlorOA.1	53.87	15.85	12.41	6.87	7.22	5.33	0.00	0.00	0.00	0.00	0.00	0.27	2.96	1.87	2.34	39.77	37.41	39.84
Methoxyfenozid.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methyl-Desph.Chlor..1	61.10	28.99	33.12	1.48	1.28	1.29	0.00	0.10	0.06	35.26	40.78	48.07	0.00	0.05	0.18	15.87	13.46	15.77
Metobromuron.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Metolachlor.1	3.43	7.74	7.62	2.27	71.53	112.44	3.75	8.27	13.45	7.63	8.15	6.16	3.94	6.02	8.68	11.54	53.41	57.29
Metribuzin.1	5.28	3.36	1.98	0.00	1.93	0.61	0.00	0.00	0.53	0.00	0.41	0.24	0.00	0.00	0.00	312.91	208.76	236.84
Napropamid.1	0.75	0.82	0.77	0.00	0.00	0.73	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.81	2.05	2.04
Nicosulfuron.1	0.00	0.00	1.32	0.13	0.00	0.00	0.21	0.00	1.26	0.00	0.00	0.00	0.70	0.00	0.00	0.00	0.00	36.40
Orbencarb.1	0.82	0.00	0.00	0.00	0.86	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.90

Pirimicarb.1	0.00	0.05	0.12	0.04	0.23	0.85	0.00	0.10	0.59	0.24	0.21	0.16	0.00	0.02	0.00	1.94	21.42	39.77
Propachlor.1	2.37	3.07	0.06	0.37	1.25	0.27	1.00	2.18	0.52	0.36	0.15	0.25	0.78	0.00	0.53	4.18	2.59	19.26
Propamocarb.1	0.02	0.09	0.16	0.14	0.05	0.06	0.03	0.08	0.07	0.05	0.04	0.08	0.08	0.05	0.09	2.24	71.12	948.28
Propazin.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Propiconazol.1	1.31	0.00	2.47	1.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.81	1.73	1.75
Pirimethanil.1	1.21	0.73	1.00	4.81	0.67	0.64	1.61	0.58	0.00	0.50	0.00	0.00	0.95	0.00	0.00	3.66	19.17	18.68
Simazin.1	1.87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11.29	9.03	8.21
Tebuconazol.1	1.43	1.88	3.42	1.36	1.71	1.66	1.32	1.89	1.93	0.65	0.88	1.12	1.11	1.48	1.76	76.36	56.35	82.47
Terbuthylazin.1	0.67	0.23	0.61	0.00	0.36	1.00	0.94	0.90	2.35	0.00	0.00	0.55	1.23	1.00	2.27	2.99	2.52	7.44
Terbutryn.1	1.31	1.42	1.56	0.00	1.42	1.32	1.28	0.00	1.21	0.00	0.00	0.00	1.26	0.00	0.00	1.47	1.66	1.49
Thiacloprid.1	0.23	0.29	0.42	0.15	0.27	0.25	0.22	0.18	0.24	0.08	0.04	0.08	0.25	0.25	0.31	2.89	3.44	5.34
AMPA	4.396	4.96	0	7.745	2.971	0	8.35	0	0	4.603	2.13	2.394	4.842	0	0	1032.649	854.278	979.584
Glyphosat	35.586	68.46	22.218	72.433	19.118	4.302	398.075	3.683	19.248	82.779	5.842	52.73	46.321	2.173	7.207	776.2075	229.841	141.901
Gesamtergebnis	59	53	52	48	51	56	45	41	46	38	38	35	42	37	36	85	93	102
Summe Pestizide (ng/L)	549.47	339.76	279.18	278.75	339.81	808.40	549.78	250.85	292.12	233.80	180.99	235.49	135.18	79.06	88.27	5098.58	5172.22	5854.47

Table A 3: Concentrations of the found metals and semi metals

	Leuschelzmoos	Fofere	Ziegelmoos	Chatzestig	Viadukt	Laupenau	Hofmatte	Erlacher Rundi	Gritzmoos	Heumoos	Panzersperr	Murtli
Aluminium_gesamt [µg/l]	1045.80	1077.06	1452.91	569.97	1108.77	1067.32	879.90	525.81	1473.89	991.66	3434.53	1374.36
Antimon_gesamt [µg/l]	0.23	0.08	0.48	0.10	0.07	0.10	0.17	0.18	0.12	0.14	0.45	0.27
Arsen_gesamt [µg/l]	1.24	1.63	2.75	1.07	0.92	0.66	2.99	2.38	1.96	0.86	2.81	2.55
Beryllium_gesamt [µg/l]	0.02	0.04	0.04	0.01	0.02	0.01	0.04	0.01	0.02	0.01	0.11	0.07
Blei_gesamt [µg/l]	0.62	0.43	0.36	0.21	0.81	0.30	0.39	0.41	0.80	0.58	1.71	1.49
Bor_gesamt [µg/l]	22.28	10.98	20.97	19.31	12.38	8.50	22.39	41.41	11.95	20.81	19.06	19.78
Cadmium_gesamt [µg/l]	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.04	0.01
Calcium_gesamt [mg/l]	40.19	48.74	90.27	80.84	51.17	39.18	134.11	164.98	86.10	52.10	197.55	25.41
Chrom_gesamt [µg/l]	0.76	1.05	0.78	0.06	0.46	0.00	0.57	0.28	0.40	0.05	4.15	1.65
Eisen_gesamt [µg/l]	494.78	733.09	231.93	2476.81	472.24	23.54	1160.86	252.85	841.30	101.36	1998.24	1098.05
Kalium_gesamt [mg/l]	3.49	1.76	1.38	2.36	0.24	0.15	1.57	5.48	2.00	1.43	1.87	5.39
Kobalt_gesamt [µg/l]	0.31	0.21	0.21	0.20	0.17	0.07	0.29	0.24	0.22	0.08	1.08	0.49
Kupfer_gesamt [µg/l]	1.33	1.39	1.39	0.72	0.50	0.55	0.56	0.36	0.67	1.12	2.13	1.73
Lithium_gesamt [µg/l]	1.11	0.74	0.75	0.62	0.96	2.21	3.00	1.70	1.70	1.38	2.71	1.02
Magnesium_gesamt [mg/l]	5.17	2.47	6.53	2.92	1.59	8.42	9.87	8.97	4.39	7.86	5.98	1.71
Mangan_gesamt [µg/l]	121.34	81.52	93.81	127.91	90.56	41.28	342.89	376.22	59.56	16.91	80.62	175.14
Molybdän_gesamt [µg/l]	0.25	0.28	0.66	0.14	0.11	0.43	0.56	0.17	0.26	0.18	0.91	0.70
Natrium_gesamt [mg/l]	4.78	0.62	3.52	2.68	0.24	3.32	2.85	10.84	0.57	2.21	3.28	3.23
Nickel_gesamt [µg/l]	2.11	1.45	2.27	1.01	0.94	0.74	1.80	1.39	1.21	0.90	5.71	2.12
Quecksilber_gesamt [µg/l]	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.01

Selen_gesamt [µg/l]	0.05	0.10	0.23	0.10	0.05	0.03	0.07	0.22	0.06	0.07	0.27	0.30
Silber_gesamt [µg/l]	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.00
Uran_gesamt [µg/l]	0.17	0.15	7.62	0.04	0.10	0.25	10.60	2.30	1.05	1.03	13.48	0.17
Vanadium_gesamt [µg/l]	0.88	1.36	1.13	0.00	0.59	0.00	0.55	0.00	0.23	0.00	5.44	2.88
Zink_gesamt[µg/l]	3.80	3.48	1.03	3.36	1.54	0.68	1.05	3.79	1.34	0.84	5.94	3.94
Zinn_gesamt [µg/l]	0.11	0.08	0.19	0.04	0.40	0.11	0.09	0.11	0.20	0.14	0.30	0.15

Table A 4: Concentrations of further substances in ponds with a *H. arborea* population [ng/l]

	Leuschelzmoos			Fofere			Ziegelmoos			Chatzestiig			Viadiukt			Laupenau		
	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016
DOC	10.98	10.58	9.68	5.54	12.21	4.69	32.74	28.20	32.20	11.00	9.05	10.69	7.44	6.90	7.10	9.14	9.36	12.65
Chlorid	7.67	5.95	5.93	0.16	1.29	0.16	3.90	2.09	2.14	2.50	1.16	2.38	0.13	0.07	0.13	4.01	1.60	1.50
Gesamtposphor	36.96	144.82	76.45	92.52	637.93	104.77	21.42	21.60	19.41	54.98	53.04	41.02	28.54	35.01	27.30	57.55	75.21	107.05
Gesamtstickstoff	0.98	2.49	0.98	0.73	1.83	0.56	2.75	1.87	1.90	0.91	0.78	0.96	0.71	0.65	0.67	0.74	1.05	1.44
Nitrat-Stickstoff	0.00	1.31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Nitrit-Stickstoff	0.92	0.01	0.01	0.42	0.00	0.00	2.07	0.00	0.00	0.86	0.00	0.01	0.51	0.00	0.00	0.79	0.00	0.00
ortho-Phosphat	2.32	43.21	8.04	8.01	373.37	12.08	0.98	0.71	0.58	1.55	1.44	0.79	1.75	0.52	0.87	1.31	1.67	2.08
Sulfat	5.65	4.55	5.84	0.00	0.25	0.02	7.33	5.26	4.75	0.40	0.65	0.56	0.00	0.22	0.00	3.97	1.49	0.18

Table A 5: Concentrations of further substances in ponds without a *H. arborea* population [ng/l]

	Hofmatte			Erlacher Rundi			Gritzimoos			Heumoos			Panzersperre			Muttli		
	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016
DOC	9.72	17.50	17.20	20.11	18.23	18.26	10.90	9.76	10.30	11.28	12.19	12.29	33.04	31.00	31.89	9.84	8.21	8.82
Chlorid	4.77	11.87	13.11	24.53	21.47	22.72	0.25	0.28	0.30	1.29	0.95	0.82	3.63	2.87	2.72	8.13	4.51	3.65
Gesamtphosphor	6.74	27.37	32.73	123.43	25.32	55.83	20.20	8.96	34.87	13.83	17.37	19.90	78.39	43.36	69.76	175.68	243.30	0.21
Gesamtstickstoff	4.53	1.52	1.55	1.83	1.18	1.31	0.82	0.63	1.13	0.88	0.89	0.90	2.82	2.06	3.95	0.88	1.22	0.90
Nitrat-Stickstoff	2.78	0.08	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.28	0.00	0.04	0.04
Nitrit-Stickstoff	3.15	0.00	0.01	1.45	0.00	0.00	0.79	0.00	0.00	0.64	0.00	0.00	1.87	0.00	0.01	0.81	0.00	0.01
ortho-Phosphat	1.47	1.06	1.55	1.62	0.97	0.98	1.12	0.25	0.32	0.95	0.70	0.49	1.51	1.78	1.84	69.67	105.61	109.99
Sulfat	0.20	56.29	58.71	24.98	23.27	23.99	13.18	12.77	12.67	14.15	9.65	7.99	70.26	51.24	40.12	1.59	1.81	2.66

Table A 6: Further measurements in ponds with a *H. arborea* population [ng/l]

	Leuschelzmoos			Fofere			Ziegelmoos			Chatzestiig			Viadukt			Laupenau		
	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016
Leitfähigkeit	263	231	279	371	257	322	458	375	447	470	377	416	243	254	268	258	265	346
PH-Wert	7.23	7.57	7.99	7.34	7.43	7.17	7.74	7.5	7.73	7.32	7.35	7.18	8.01	7.82	8.08	9.03	8.67	7.14
Sauerstoff_Elektrode	4.71	5.86	3.08	2.83	5.7	2.4	5.56	5.07	6.32	4.66	4.14	3.97	11.23	9.94	13.79	18.98	13.28	10.19
Sauerstoffsättigung	52.4	58.4	32.9	30.5	58.7	26	61.9	52.1	68.3	50.6	41	43	129.2	100.8	153.8	214	128.6	118.1
Temperatur	17.8	12.8	16.5	16.6	13.2	16.6	18.9	14.8	16.6	16.8	12.5	16.4	19.2	14.8	18.6	18.4	13.6	20.1

Table A 7: Further measurements in ponds without a *H. arborea* population [ng/l]

	Hofmatte			Erlacher Rundi			Gritzimoos			Panzersperre			Heumoos			Mutli		
	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016	09.05.2016	23.05.2016	30.05.2016
Leitfähigkeit	853	483	692	863	670	716	434	391	456	881	803	831	329	223	258	197.8	160.6	157.5
PH-Wert	7.29	7.65	7.63	7.61	7.69	7.43	7.62	7.55	7.58	7.77	7.66	7.34	7.91	8.04	7.68	7.55	7.29	7.08
Sauerstoff_Elektrode	6.62	6.97	3.04	3.44	5.42	3.43	4.62	6.35	7.4	9.26	6.98	7.34	9.5	7.88	9.61	9.53	4.86	4.6
Sauerstoffsättigung	71.3	67.5	32.4	34.4	52.1	36.4	49.9	63.4	79.8	102.9	73.4	6.37	109.9	82.8	106.8	106.4	50.4	50.3
Temperatur	16.5	11.7	15.7	13.4	12.4	15.4	16.7	13.3	16.5	18	14.5	16.8	19.9	15.2	17.9	18.3	15	17.1

Table A 8: Land use, buffer zone, aquatic vegetation

	Leuschelzmoos	Fofere	Ziegelmoos	Chatzestiig	Viadukt	Laupenau	Hofmatte	Erlacher Runde	Gritzimoos	Panzersperre	Heumoos	Mutli
<i>Hyla arborea</i> present	yes	yes	yes	yes	yes	yes	no	no	no	no	no	no
surface [m²]	3380.000	591.910	712.500	326.830	231.530	245.560	223.540	321.680	262.580	484.490	240.220	7893.590
area [m]	218.000	124.800	213.680	72.020	59.680	75.260	99.490	69.370	101.790	224.260	110.460	323.910
water depth [m]	0.305	0.185	0.230	0.300	0.188	0.140	0.233	0.180	0.190	0.458	0.458	0.278
water volume [m³]	4345.386	202.304	329.946	138.237	52.722	42.872	62.122	81.130	63.999	372.018	135.015	13963.151
percentage crop 50m	0.500	0.250	0.000	0.000	0.250	0.125	0.625	0.000	0.000	0.000	0.000	0.000
percentage sugar beets 50m	0.125	0.000	0.000	0.000	0.000	0.000	0.000	0.250	0.125	0.250	0.000	0.000
percentage potatoes 50m	0.125	0.000	0.000	0.250	0.000	0.000	0.125	0.000	0.000	0.000	0.000	0.000

percentage vegetables 50m	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.125	0.375	0.125
percentage intensive meadow 50m	0.000	0.500	0.000	0.000	0.000	0.125	0.000	0.000	0.000	0.250	0.375	0.250
percentage uninensive meadow 50m	0.250	0.250	0.750	0.125	0.125	0.500	0.250	0.625	0.250	0.375	0.250	0.625
percentage fallow land 50m	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.250	0.000	0.000	0.000
percentage woods 50m	0.000	0.000	0.250	0.500	0.375	0.125	0.000	0.125	0.250	0.000	0.000	0.000
percentage waters 50m	0.000	0.000	0.000	0.125	0.250	0.125	0.000	0.000	0.125	0.000	0.000	0.000
percentage crop 100m	0.250	0.250	0.000	0.125	0.375	0.125	0.375	0.000	0.125	0.000	0.000	0.250
percentage sugar beeds 100m	0.375	0.000	0.000	0.000	0.000	0.000	0.000	0.250	0.125	0.125	0.000	0.000
percentage potatoes 100m	0.250	0.000	0.000	0.250	0.000	0.000	0.375	0.000	0.125	0.000	0.000	0.000
percentage vegetables 100m	0.000	0.000	0.125	0.000	0.000	0.000	0.000	0.000	0.000	0.375	0.375	0.250
percentage intensive meadow 100m	0.000	0.500	0.000	0.000	0.125	0.125	0.000	0.000	0.000	0.125	0.250	0.125
percentage uninensive meadow 100m	0.125	0.125	0.625	0.125	0.000	0.625	0.000	0.750	0.250	0.000	0.000	0.250
percentage fallow land 100m	0.000	0.000	0.000	0.000	0.000	0.000	0.250	0.000	0.250	0.000	0.125	0.125
percentage woods 100m	0.000	0.125	0.250	0.250	0.250	0.125	0.000	0.000	0.000	0.375	0.125	0.000
percentage waters 100m	0.000	0.000	0.000	0.250	0.250	0.000	0.000	0.000	0.125	0.000	0.125	0.000
sum of percentage agricultural land 50m	0.750	0.750	0.000	0.250	0.250	0.250	0.750	0.250	0.125	0.625	0.750	0.375
sum of percentage natural land 50m	0.250	0.250	1.000	0.750	0.750	0.750	0.250	0.750	0.875	0.375	0.250	0.625
sum of percentage agricultural land 100m	0.875	0.750	0.125	0.375	0.500	0.250	0.750	0.250	0.375	0.625	0.625	0.625
sum of percentage natural land 100m	0.125	0.250	0.875	0.625	0.500	0.750	0.250	0.750	0.625	0.375	0.375	0.375
percentage buffer deep	0.750	0.500	1.000	0.250	0.250	0.125	1.000	0.625	0.625	0.500	1.000	0.000
percentage buffer high	0.250	0.500	0.000	0.750	0.750	0.875	0.000	0.375	0.375	0.500	0.000	1.000
buffer width [m]	37.365	23.661	53.234	58.004	34.894	28.143	24.418	38.466	39.156	37.594	33.264	58.548
percentage floating leave	0.000	0.000	0.000	0.000	0.100	0.000	0.000	0.000	0.000	0.000	0.000	0.000

percentage underwatervegetation	0.000	0.000	0.300	0.000	0.000	0.800	0.000	0.000	0.000	0.500	0.250	NA
percentage of cane bake vegetation	0.900	0.900	0.100	0.700	0.400	0.800	0.900	1.000	0.600	0.100	0.250	0.400
wall present	no	yes	no	yes	yes	no	no	no	no	yes	yes	no

Table A 9: Correlations of land use combinations with PPPs in 50 m distance of the ponds bank

ID	Variable	Correlates with the substance	Estimate	Std. error
1	amount of crop cultivation [%]	Desphenyl Chloridazon	482.80	225.68
2	amount of crop cultivation [%]	Methyl Desphenyl Chloridazon	139.897	60.633
3	amount of crop cultivation [%]	Desphenyl Chloridazon	551.09	252.88
	amount of extensive meadow [%]		179.16	263.89
4	amount of crop cultivation [%]	Methyl Desphenyl Chloridazon	154.490	68.580
	amount of extensive meadow [%]		38.284	71.565
5	amount of crop cultivation [%]	Desphenyl Chloridazon	472.39	232.28
	amount of waters [%]		-420.75	607.83
6	amount of crop cultivation [%]	Methyl Desphenyl Chloridazon	136.67	61.85
	amount of waters [%]		-130.52	161.85
7	amount of crop cultivation [%]	Methyl Desphenyl Chloridazon	137.493	65.259
	amount of fallow land [%]		-34.686	197.746
8	amount of crop cultivation [%]	Methyl Desphenyl Chloridazon	134.76	64.35
	amount of intensive meadow [%]		-34.62	79.60
9	amount of crop cultivation [%]	Desphenyl Chloridazon	527.08	230.50
	amount of sugar beet cultivation [%]		496.90	505.51
10	amount of crop cultivation [%]	Methyl Desphenyl Chloridazon	156.066	59.046
	amount of sugar beets cultivation [%]		181.457	129.491
11	amount of crop cultivation [%]	Methyl Desphenyl Chloridazon	143.119	67.801
	amount of vegetables cultivation [%]		18.594	131.745
12	amount of intensive meadow [%]	Desphenyl Chloridazon	-649.60	339.11
	amount of wood [%]		-749.59	347.78
13	amount of intensive meadow [%]	Methyl Desphenyl Chloridazon	-183.79	90.91
	amount of wood [%]		-217.32	93.23

Table A 10: Correlations of land use combinations with PPPs in 100 m distance of the ponds bank

ID	Variable	Correlates with the substance	Estimate	Std. error
1	amount of wood [%]	“sum of all concentration classes”	-77.111	31.841
2	amount of wood [%] amount of crop cultivation [%]	“sum of all concentration classes”	-70.981 18.391	34.614 31.764
3	amount of wood [%] amount of extensive meadow [%]	“sum of all concentration classes”	-73.570 -1.102	30.594 14.569
4	amount of wood [%] amount of fallow land [%]	“sum of all concentration classes”	-87.480 -34.486	34.697 45.429
5	amount of wood [%] amount of intensive meadow [%]	“sum of all concentration classes”	-72.213 -5.391	30.250 26.475
6	amount of wood [%] amount of potato cultivation [%]	“sum of all concentration classes”	-74.706 -4.784	31.669 30.824
7	amount of wood [%] amount of sugar beet cultivation [%]	“sum of all concentration classes”	-75.465 4.939	35.788 37.5220
8	amount of wood [%] amount of vegetable cultivation [%]	“sum of all concentration classes”	84.039 26.227	30.472 26.186
9	amount of wood [%] amount of waters [%]	“sum of all concentration classes”	-62.311 -43.200	29.778 38.989
10	amount of sugar beet cultivation [%]	Azoxystrobin	318.57	140.88
11	amount of sugar beet cultivation [%] amount of crop cultivation [%]	Azoxystrobin	349.58 193.41	130.65 114.36
12	amount of sugar beet cultivation [%] amount of extensive meadow [%]	Azoxystrobin	335.47 -51.47	145.35 66.02
13	amount of sugar beet cultivation [%] amount of fallow land [%]	Azoxystrobin	320.39 13.24	150.70 188.19
14	amount of sugar beet cultivation [%] amount of intensive meadow [%]	Azoxystrobin	333.428 33.550	159.256 132.939
15	amount of sugar beet cultivation [%] amount of potato cultivation [%]	Azoxystrobin	302.276 76.249	149.021 138.345
16	amount of sugar beet cultivation [%] amount of vegetable cultivation [%]	Azoxystrobin	325.194 32.119	150.101 123.027
17	amount of wood [%] amount of fallow land [%]	Azoxystrobin	-356.71 -310.21	169.55 221.99
18	amount of sugar beet cultivation [%]	Desamino Metamitron	995.87	408.70
19	amount of sugar beet cultivation [%] amount of crop cultivation [%]	Desamino Metamitron	1065.46 434.12	402.48 352.27
20	amount of sugar beet cultivation [%] amount of fallow land [%]	Desamino Metamitron	1001.10 38.10	437.18 545.95
21	amount of sugar beet cultivation [%] amount of intensive meadow [%]	Desamino Metamitron	989.47 -14.44	463.60 386.99
22	amount of sugar beet cultivation [%] amount of potato cultivation [%]	Desamino Metamitron	969.25 124.54	437.27 405.94
23	amount of sugar beet cultivation [%] amount of vegetable cultivation [%]	Desamino Metamitron	1018.84 111.45	434.73 356.32
24	amount of sugar beet cultivation [%] amount of waters [%]	Desamino Metamitron	910.98 -370.66	438.56 547.68
25	amount of wood [%] amount of fallow land [%]	Desamino Metamitron	-1096.8 -959.9	496.5 650.1
26	amount of sugar beet cultivation [%]	Desphenyl Chloridazon	1025.85	351.73
27	amount of sugar beet cultivation [%] amount of crop cultivation [%]	Desphenyl Chloridazon	1098.20 451.33	332.68 291.18
28	amount of sugar beet cultivation [%] amount of extensive meadow [%]	Desphenyl Chloridazon	1063.04 -113.29	365.61 166.06
29	amount of sugar beet cultivation [%] amount of fallow land [%]	Desphenyl Chloridazon	1012.61 -96.35	375.46 468.88

30	amount of sugar beet cultivation [%] amount of intensive meadow [%]	Desphenyl Chloridazon	1022.517 -7.527	398.998 333.064
31	amount of sugar beet cultivation [%] amount of potato cultivation [%]	Desphenyl Chloridazon	942.554 389.706	351.449 326.269
32	amount of sugar beet cultivation [%] amount of sugar vegetable cultivation [%]	Desphenyl Chloridazon	1011.48 -69.71	375.09 307.44
33	amount of sugar beet cultivation [%] amount of waters [%]	Desphenyl Chloridazon	952.56 -320.02	377.37 471.27
34	amount of sugar beet cultivation [%] amount of woods[%]	Desphenyl Chloridazon	981.63 -120.69	393.46 375.28
35	amount of sugar beet cultivation [%]	Ethofumensate	1704.499	539.024
36	amount of sugar beet cultivation [%] amount of crop cultivation [%]	Ethofumensate	1816.5 698.6	534.8 468.1
37	amount of sugar beet cultivation [%] amount of extensive meadow [%]	Ethofumensate	1780.25 -230.78	546.20 248.08
38	amount of sugar beet cultivation [%] amount of fallow land [%]	Ethofumensate	1713.27 63.81	555.30 693.46
39	amount of sugar beet cultivation [%] amount of intensive meadow [%]	Ethofumensate	1747.11 96.25	588.48 491.23
40	amount of sugar beet cultivation [%] amount of potato cultivation [%]	Ethofumensate	1609.81 442.99	552.02 512.47
41	amount of sugar beet cultivation [%] amount of vegetable cultivation [%]	Ethofumensate	1696.474 -38.935	555.046 454.933
42	amount of sugar beet cultivation [%] amount of waters [%]	Ethofumensate	1688.0811 -71.6910	570.8900 712.9325
43	amount of sugar beet cultivation [%] amount of woods[%]	Ethofumensate	1569.95 -367.20	580.09 553.29
44	amount of woods [%] amount of fallow land [%]	Ethofumensate	-1447.8 -1337.5	704.4 922.3
45	amount of sugar beet cultivation [%]	Metalaxyl	336.380	96.681
46	amount of sugar beet cultivation [%] amount of crop cultivation [%]	Metalaxyl	357.96 134.63	89.25 78.12
47	amount of sugar beet cultivation [%] amount of extensive meadow [%]	Metalaxyl	353.701 -52.767	95.510 43.381
48	amount of sugar beet cultivation [%] amount of fallow land [%]	Metalaxyl	331.753 -33.678	103.053 128.694
49	amount of sugar beet cultivation [%] amount of intensive meadow [%]	Metalaxyl	344.059 17.344	109.457 91.369
50	amount of sugar beet cultivation [%] amount of potato cultivation [%]	Metalaxyl	312.25 112.89	95.75 88.89
51	amount of sugar beet cultivation [%] amount of vegetable cultivation [%]	Metalaxyl	332.418 -19.225	103.100 84.504
52	amount of sugar beet cultivation [%] amount of waters [%]	Metalaxyl	340.500 17.990	106.244 132.678
53	amount of sugar beet cultivation [%] amount of woods[%]	Metalaxyl	324.4798 -32.4779	108.1751 103.1767
54	amount of sugar beet cultivation [%]	Metamitron	644.70	186.56
55	amount of sugar beet cultivation [%] amount of crop cultivation [%]	Metamitron	671.60 167.83	188.32 164.83
56	amount of sugar beet cultivation [%] amount of extensive meadow [%]	Metamitron	658.336 -41.556	190.838 86.679
57	amount of sugar beet cultivation [%] amount of fallow land [%]	Metamitron	634.664 -73.010	191.942 239.699
58	amount of sugar beet cultivation [%] amount of intensive meadow [%]	Metamitron	659.12 32.58	203.68 170.02
59	amount of sugar beet cultivation [%] amount of potato cultivation [%]	Metamitron	619.00 120.22	191.88 178.14
60	amount of sugar beet cultivation [%] amount of vegetable cultivation [%]	Metamitron	633.768 -53.021	191.792 157.198
61	amount of sugar beet cultivation [%]	Metamitron	644.047	197.614

	amount of waters [%]		-2.833	246.782
62	amount of sugar beet cultivation [%] amount of woods[%]	Metamitron	618.7223 -70.8859	201.6903 192.3709
63	amount of sugar beet cultivation [%]	Methyl Desphenyl Chloridazon	290.917	94.395
64	amount of sugar beet cultivation [%] amount of crop cultivation [%]	Methyl Desphenyl Chloridazon	310.08 119.55	89.59 78.41
65	amount of sugar beet cultivation [%] amount of extensive meadow [%]	Methyl Desphenyl Chloridazon	305.78 -45.27	94.98 43.14
66	amount of sugar beet cultivation [%] amount of fallow land [%]	Methyl Desphenyl Chloridazon	288.260 -19.331	100.867 125.963
67	amount of sugar beet cultivation [%] amount of intensive meadow [%]	Methyl Desphenyl Chloridazon	289.886 -2.327	107.078 89.384
68	amount of sugar beet cultivation [%] amount of potato cultivation [%]	Methyl Desphenyl Chloridazon	264.900 121.723	91.630 85.065
69	amount of sugar beet cultivation [%] amount of sugar vegetable cultivation [%]	Methyl Desphenyl Chloridazon	290.125 -3.843	100.939 82.733
70	amount of sugar beet cultivation [%] amount of waters [%]	Methyl Desphenyl Chloridazon	270.37 -89.70	101.04 126.18
71	amount of sugar beet cultivation [%] amount of woods[%]	Methyl Desphenyl Chloridazon	290.6073 -0.8442	106.1967 101.2897
72	amount of potato cultivation [%] amount of fallow land[%]	Methyl Desphenyl Chloridazon	239.32 -217.85	115.95 155.97
73	amount of sugar beet cultivation [%]	Metolachlor	272.739	77.825
74	amount of sugar beet cultivation [%] amount of crop cultivation [%]	Metolachlor	283.237 65.489	78.714 68.895
75	amount of sugar beet cultivation [%] amount of extensive meadow [%]	Metolachlor	274.102 -4.153	79.872 36.278
76	amount of sugar beet cultivation [%] amount of fallow land [%]	Metolachlor	268.544 -30.527	80.071 99.994
77	amount of sugar beet cultivation [%] amount of intensive meadow [%]	Metolachlor	279.561 15.408	84.954 70.915
78	amount of sugar beet cultivation [%] amount of potato cultivation [%]	Metolachlor	266.985 26.920	80.440 74.676
79	amount of sugar beet cultivation [%] amount of vegetable cultivation [%]	Metolachlor	269.952 -13.521	80.096 65.649
80	amount of sugar beet cultivation [%] amount of waters [%]	Metolachlor	267.072 -24.747	82.366 102.860
81	amount of sugar beet cultivation [%] amount of woods[%]	Metolachlor	249.92 -62.28	83.54 79.68
82	amount of woods [%] amount of fallow land [%]	Metolachlor	-259.52 -273.44	93.63 122.59



Figure A 1: Drainages of the surrounding landscape of Fofere. Fofere possesses an artificial discharge. One drainage flows directly under the pond, but the as Fofere is sealed, no water can enter from underneath.



Figure A 2: Drainages of the surrounding landscape of Ziegelmoos. I investigated the pond on the left side.



Figure A 3: Drainages of the surrounding landscape of Hofmatte.

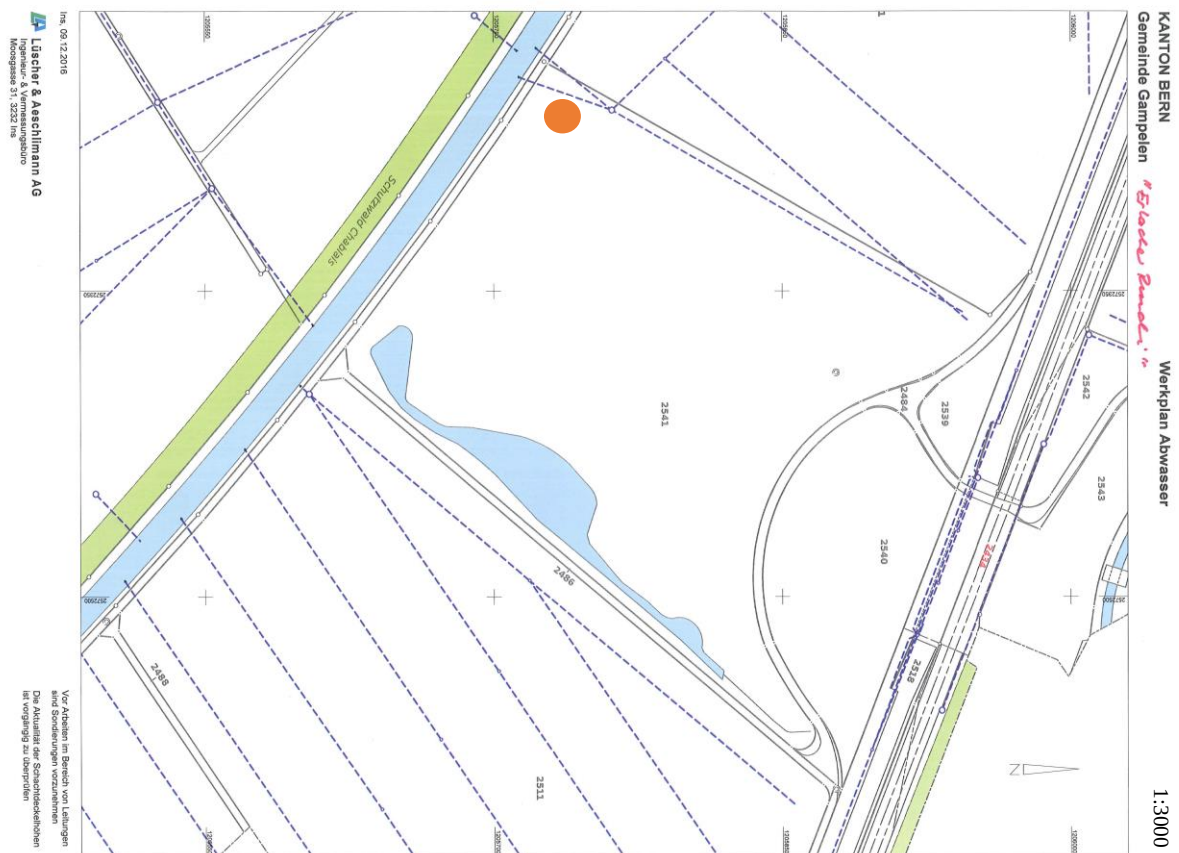


Figure A 4: Drainages of the surrounding landscape of Erlacher Rundi. The pond I investigated isn't drawn in the figure. I marked its position with an orange dot.

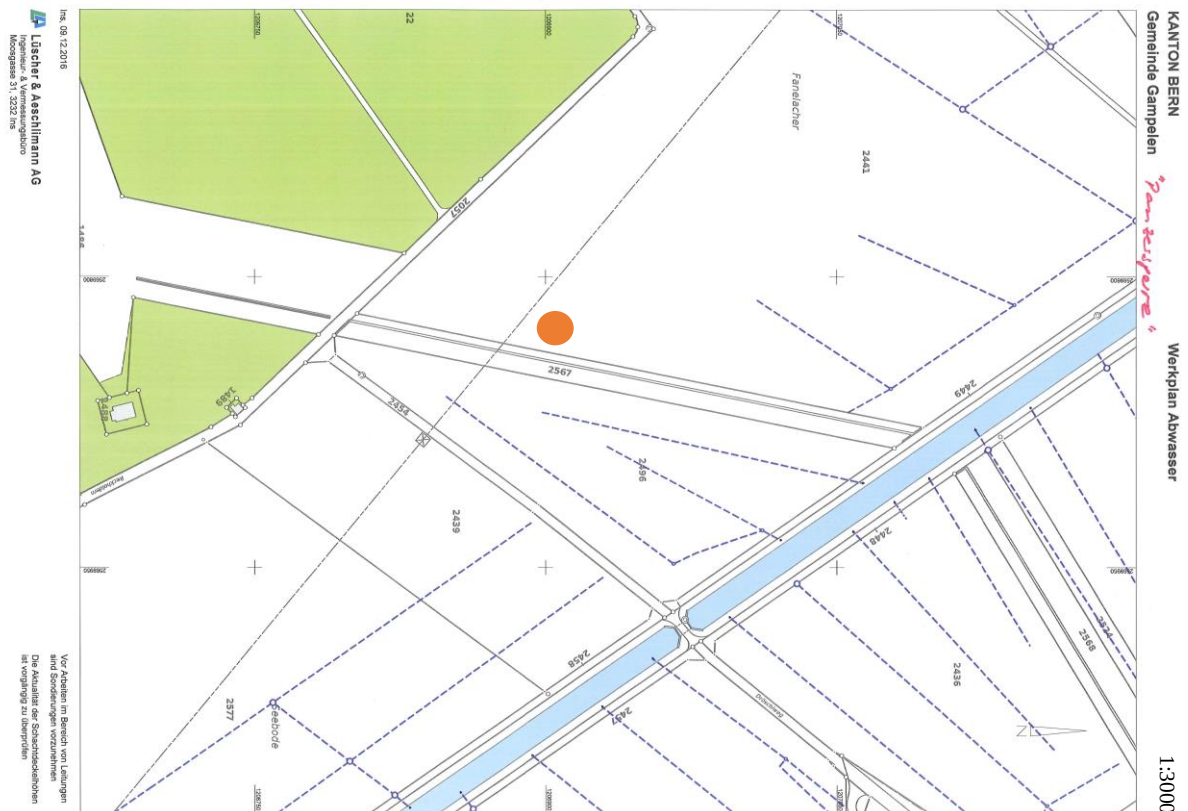


Figure A 5: Drainages of the surrounding landscape of Panzersperre. Its position is next to the stone wall 2567. I marked it with an orange dot.

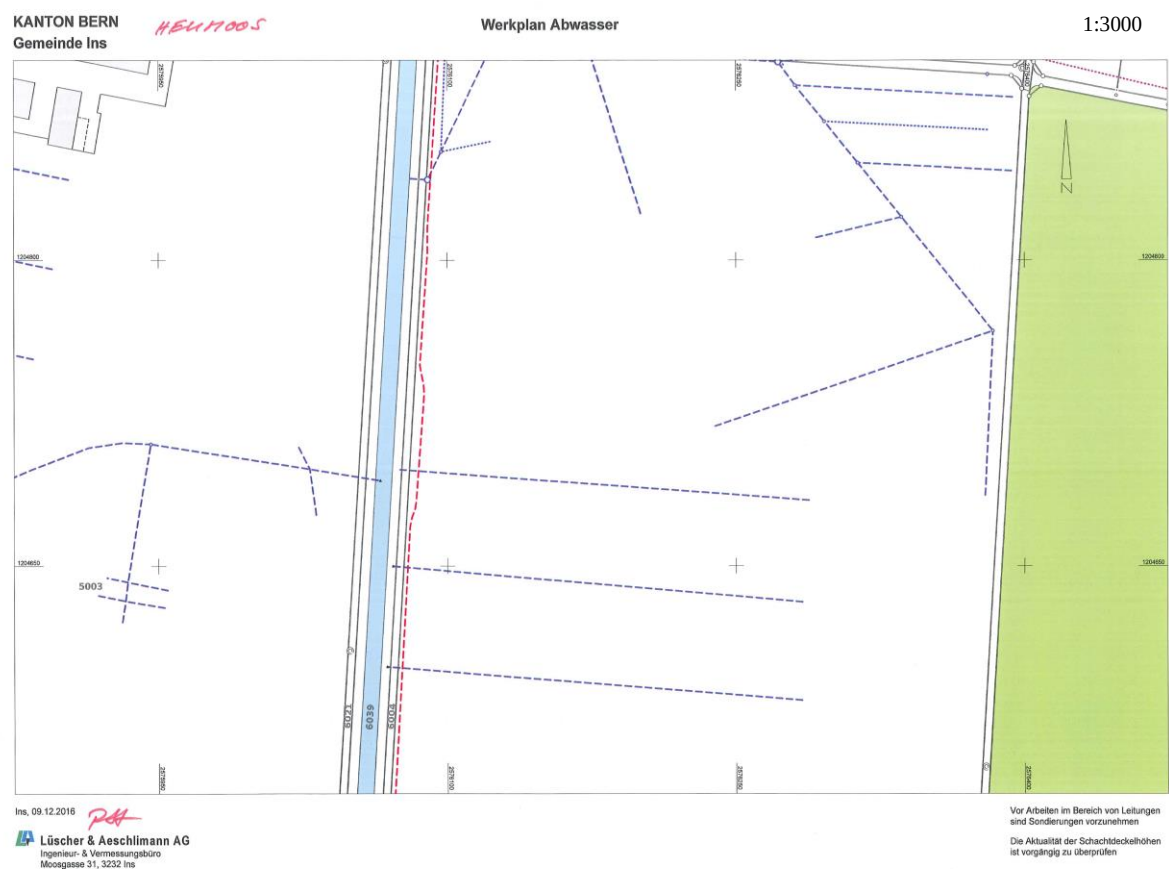


Figure A 6: Drainages of the surrounding landscape of Heumoos. The pond is approximately in the middle of the map in the field between the wood and the canal.