The impact of land use intensity on the water quality in Entlebuch, Switzerland

Catherine Hutchings

Dissertation submitted as part of the final examination for the degree of:
MA with Honours in Economics and Geography
University of Dundee, 2016

Acknowledgements

First of all I would like to thank my dissertation supervisor Andrew Black for his help and encouragement throughout this project and the time he took despite many other commitments. Furthermore I thank Florian Knaus from the UNESCO biosphere Entlebuch for his help and for giving me the opportunity of conducting this research in collaboration with the biosphere. I also want to thank Madeleine Langmeier, Denise Freudemann as well as everyone else in the AuA Labor, eawag Dübendorf for very kindly welcoming me and helping me analyse my water samples.

Abstract

This study looks at the impact of agricultural land use on water quality in the UNESCO biosphere Entlebuch (UBE), Switzerland. In Switzerland agriculture is a major contributor to nitrogen and phosphor in lakes and rivers, negatively impacting freshwater ecosystems. In UBE the agriculture is known to be unsustainable and too intensive, but no water quality data is available. This study therefore analyses the water quality in different catchments within UBE and investigates the impact of agricultural land use on water quality. Nitrite, nitrate and orthophosphate were analysed for 11 different catchments. Furthermore a GIS analysis was undertaken to calculate the mean land use intensity (as an indicator of agricultural land use) for each catchment. Test of correlation was used to investigate the relationship between mean land use intensity and the selected water quality parameters. The results show that in most streams the water quality is classified as good or high, so that the objective of the EU water framework directive of achieving good chemical status of surface waters is met. In the catchment with the highest land use intensity, the water quality did not achieve good chemical status, possibly causing localised negative impacts on the stream ecosystem. However it is unlikely to have strong further implications on the main river of UBE. Although overall the water quality is good, the study shows that intense agricultural land use has a negative impact on water quality. This finding is of significance in order to effectively target the localised effects of intensive agricultural land use on water quality.

Table of contents

List of Tables and Figures

Tables **Page**

Figures **Page**

Figures (continued) **Page**

1 Introduction

1.1 Problems and implications of excess nutrients in waters

Around 8.5-9.5 million tonnes of phosphorus enter the oceans annually. This is estimated to be approximately eight times the natural background rate of influx (Rockström et al, 2009). The over-enrichment of nutrients (mainly nitrogen and phosphor) causes eutrophication in oceans, lakes and rivers worldwide and has become a major environmental issue in recent decades. It is mainly caused by human activities such as the use of agricultural fertilizers, organic waste from livestock or release of sewage into surface waters (Dodds, 2002). Excessive nitrogen (N) and phosphorus (P) in waters is a major environmental issue due to the problem of eutrophication as well as direct health effects. Consuming water with high concentrations of nitrate (NO_3) can lead to methaemoglobinaemia in livestock and infants. Nitrate is reduced to nitrite, which interferes with the oxygen-carrying ability of the blood. Phosphorus on the other hand does not pose any direct health risks (Carpenter et al., 1998; Davie, 2008). Eutrophication is the increased growth of algae and aquatic weeds. It reduces the benefits a body of water can provide regarding recreation, fishing, industry, agriculture and the supply of drinking water. Furthermore it leads to fish kills and loss of aquatic biodiversity due to oxygen shortages. In freshwater, an excess of nutrients can lead to blooms of cyanobacteria, which lead to fish kill, foul odour, and unsuitability of drinking water. When these bacteria die they release toxic substances, which can kill livestock (Carpenter et al., 1998; Davie, 2008; Dodds, 2002).

In Europe one of the main causes of eutrophication is excess nutrients from agriculture. The agricultural contribution to total annual P loads in EU waters is often about 50% (range 25–75%) with higher proportional contributions in countries where point-source P inputs (e.g.

from sewage) have been markedly reduced by wastewater treatment (Withers and Haygarth, 2007).

Human processes, primarily the production of fertilisers and the cultivation of leguminous crops, convert annually around 120 million tons of nitrous gas (N_2) into reactive forms, which cause eutrophication when high quantities reach bodies of water. According to Rockström et al. (2009) this amount is more than the combined effects from all earth terrestrial processes. In their paper nine earth regulatory systems are explored that are essential to maintain conditions of the Holocene that enable human development. The nitrogen and phosphorus cycles are two of these systems. For both cycles a boundary is defined, which is a safe operating space for humanity. Although it is difficult to set an exact boundary it is clear that the alteration to the nitrogen cycle has far exceeded the safe boundary and phosphorus is rapidly approaching its boundary. The majority of these alterations are due to agricultural practices, which increase the amount of P and N available to causing eutrophication (Rockström et al, 2009)

The eutrophication problem is expected to increase due to the growing population, increased livestock production (due to increased meat consumption) and growth of urban areas (Carpenter et al., 1998).

1.2 Policies related to water quality

The problem of excess nutrients in waters has been recognised and European governments have taken action. Introduced in December 2000, the EU Water Framework Directive (WFD) applies to all countries in the EU or EEA (e.g. Switzerland). One of the main objectives is to achieve “good ecological status" and "good chemical status" of surfaces waters (EU, 2000). The directive provides a legislative framework to implement catchment controls on nutrient inputs to EU waters from all sources, including those from agriculture. In order to achieve good chemical status an integrated catchment management which targets agriculture is needed (Withers and Haygarth, 2007).

In Switzerland issues concerning water quality are addressed in the Waters Protection Ordinance (WPO). There are however no legally binding limit values for most trace elements. For bodies of flowing water the only nutrient with a specific limit value is ammonium: at temperatures of over 10°C: 0.2 mg/l N, under 10°C: 0.4 mg/l N (WPO, 2016).

The WPO does however provide descriptive water quality requirements based on the WFD. For example "the water quality must be such that no visible colonies of bacteria, fungi or protozoa and no unnatural proliferation of algae or higher water plants are formed in any waters" (WPO, 2016, Annex 2 (11a)). Based on these descriptions and the WFD, the Swiss Environmental Department has published values for individual nutrients categorising the water quality status (High, Good, Moderate, Poor, Bad). The values published by the Swiss Environmental Department are however not legally binding (Liechti, 2010). Table 1.1 summarises the values for the water quality parameters that were analysed in this study.

Table 1.1: summary of water quality status classification for the water quality parameters tested in this study

Water quality status		Nitrite [N/L mg] (< 10 mg/L Cl-)	Nitrate [N/L mg]	Ortho-P [P/L mg]
🟦	High	< 0.01	< 1.5	< 0.02
🟩	Good	0.01 to < 0.02	1.5 to < 5.6	0.02 to < 0.04
🟨	Moderate	0.02 to < 0.03	5.6 to < 8.4	0.04 to < 0.06
🟧	Poor	0.03 to < 0.04	8.4 to < 11.2	0.06 to < 0.08
🟥	Bad	0.04 and above	11.2 and above	0.08 and above

1.3 Aims and objectives

This study was conducted in the UNESCO Biosphere Entlebuch, (UBE), in Central Switzerland.

The aim of the study is to investigate the impact of agricultural land use on water quality by analysing the water quality in 11 different catchments.

The main objectives are:

- To investigate whether the water quality in the streams has good chemical status (according to classification of the Swiss Environmental Department, which is based on WFD)

- To test if there is a significant correlation between the land use intensity (as an indicator of agricultural land use) and the water quality (nitrite, nitrate and orthophosphate).

1.4 Structure of Dissertation

The dissertation will firstly review relevant literature regarding sources of nutrients and nutrient pathways and processes. Then, based on previous research, areas are identified in which more research is needed, which means research on water quality in the UNESCO Biosphere Entlebuch. Therefore the area of the UBE is described before the research methods are explained and evaluated. Chapter 5 presents all the results, and chapter 6 interprets these results and states how they answer the research question. Finally the findings are summarised and further implications of this study are described.

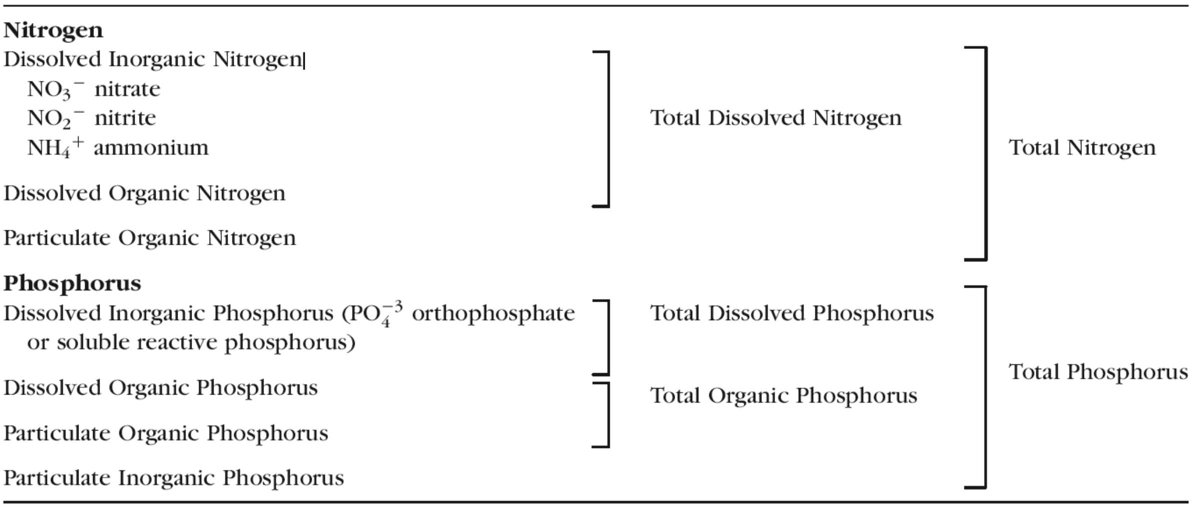
2 Literature review

This chapter first briefly describes the different chemical states of nutrients. Secondly the different types of anthropogenic sources of nutrients in rivers and their transport pathways and processes are explained. Then an overview is provided of previous research and common methods applied when examining the impact of agriculture on water quality. Finally, in relation to previous research conducted in central Switzerland, areas are identified in which more research is needed.

2.1 Different chemical states of nutrients

There are many chemical states in which nitrogen (N) and phosphorus (P) occur in freshwater ecosystems. They can occur as dissolved and particulate as well as organic and inorganic forms (see table 2.1). The form in which they occur depends on many factors such as the source, instream process of absorption and desorption as well as nutrient cycle processes such as nitrification and denitrification (Allan, 2007; Dodds, 2002). Some of these influences will be discussed later in relation to overall nutrient concentrations.

Table 2.1: Major forms of nitrogen and phosphorus found in natural waters. Nitrogen is also present as dissolved N_2 gas (not shown) (Allan, 2007)



Nitrogen		
Dissolved Inorganic Nitrogen	Total Dissolved Nitrogen	Total Nitrogen
NO_3^- nitrate		
NO_2^- nitrite		
NH_4^+ ammonium		
Dissolved Organic Nitrogen		
Particulate Organic Nitrogen		
Phosphorus		
Dissolved Inorganic Phosphorus (PO_4^{-3} orthophosphate or soluble reactive phosphorus)	Total Dissolved Phosphorus	Total Phosphorus
Dissolved Organic Phosphorus	Total Organic Phosphorus	
Particulate Organic Phosphorus		
Particulate Inorganic Phosphorus		

2.2 Sources of Nutrients

2.2.1 Natural sources

Although the focus of the dissertation is on anthropogenic land use impacts on water quality, it should be mentioned that N and P occur naturally in water.

Nitrogen gas (N_2) is abundant in the atmosphere. Through N fixation by bacteria in soil and plant nodules the two N atoms are freed and can be bound to hydrogen to form ammonium. The process of nitrification transforms ammonium into nitrite and then nitrate, which is soluble and can be absorbed by plants (Allan, 2007; Davie, 2000). Runoff from soil and vegetation is therefore a natural source of nitrogen. Furthermore some sedimentary rock can contain large amounts of fixed N. Weathering of this can add nitrate to running water (Allan, 2007). While the main reservoir for N is the atmosphere, P is stored in rocks and sediment, then released slowly by weathering (Davie, 2000). Furthermore P is generated when plants decompose and is stored in soil organic layers. It enters streams by surface runoff and subsurface pathways (Allan, 2007).

The natural contribution of both N and P to rivers is however very low: 0.1mg /L NO_3-N, 0.001mg/L NO_2-N and around 0.01 mg /L P for PO_4 (Davie, 2000).

2.2.2 Anthropogenic sources of nitrogen

A common, well-known source of Nitrogen is agriculture. Nitrate fertilizers are applied to fields to enhance plant growth. It is easy to apply since it is extremely soluble and can easily be absorbed by plants through their root system. However its high solubility means it tends to be flushed through the soil and into rivers. The other agricultural source is animal waste, which is either washed directly from pastures into rivers or applied to fields in the form of slurry. The organic nitrogen in the slurry then breaks down into nitrates (Allan, 2007; Carpenter et. al., 1998; Davie, 2000).

Other sources of nitrate in both urban and rural areas are from treated sewage, drainage from septic tanks and construction sites, lawn fertilizer and pet waste (Carpenter et. al., 1998; Davie, 2000; Hem, 1989). Finally, nutrients are deposited from the atmosphere onto the land. All energy produced by combustion engines (e.g. cars, industry) creates various forms of nitrogen oxide gases, which enter the atmosphere. When enough energy is available nitrogen gas combines with oxygen. Since these gases are water-soluble they form nitrites and nitrates in rainwater. As the source of atmospheric pollution is not well studied it is unclear how much enters rivers in this way (Davie, 2008). However it is clear that the anthropogenic N fixation (e.g. from fossil fuel and biomass combustion, manufacturing fertilizers and cultivation of leguminous crops) exceeds the natural fixation (Allan, 2007; Rockström et al., 2009).

2.2.3 Anthropogenic sources of phosphorus

Phosphorus and nitrogen have many similar sources. P also reaches rivers through treated sewage (from detergents and soaps), drainage from septic tanks and construction sites, lawn fertilizer and pet waste. Agriculture also contributes significantly with animal waste, slurry and fertilizer. Phosphorus fertilizers are however much less soluble than nitrate and are therefore applied less frequently, in solid form (Davie, 2000). Compared to N the atmospheric input is very small and can only be detected in areas where P is very scarce (Allan, 2007). P is stored in rocks and sediment and is abstracted by mining. Runoff from mining sites can also lead to increased P concentration in streams (Carpenter et. al., 1998; Hem, 1989).

2.3 Nutrient pathways and processes

This section focuses on pathways and processes of nutrients from agriculture, since the dissertation’s main aim is to investigate the impact of agricultural land use on water quality. Agriculture is categorised as a diffuse source. Generally the sources of nutrient inputs are distinguished between diffuse (non-point) and point source. With a point source the exact location of the source is known, e.g. a pipe where sewage enters a stream. However with diffuse sources the exact location of the nutrient source cannot be specified, since the source comes from a larger area (Davie, 2000). Agriculture is seen as a diffuse source since the input comes from all the agricultural fields in a catchment. The exception might be runoff from barnyards, where the source is more local (Edwards and Withers, 2008)

Since agriculture is a diffuse source the transport of N and P depends strongly on rainfall, which flushes the nutrients on the surface or in the soil into streams. Figure 2.1 illustrates the different transport processes.

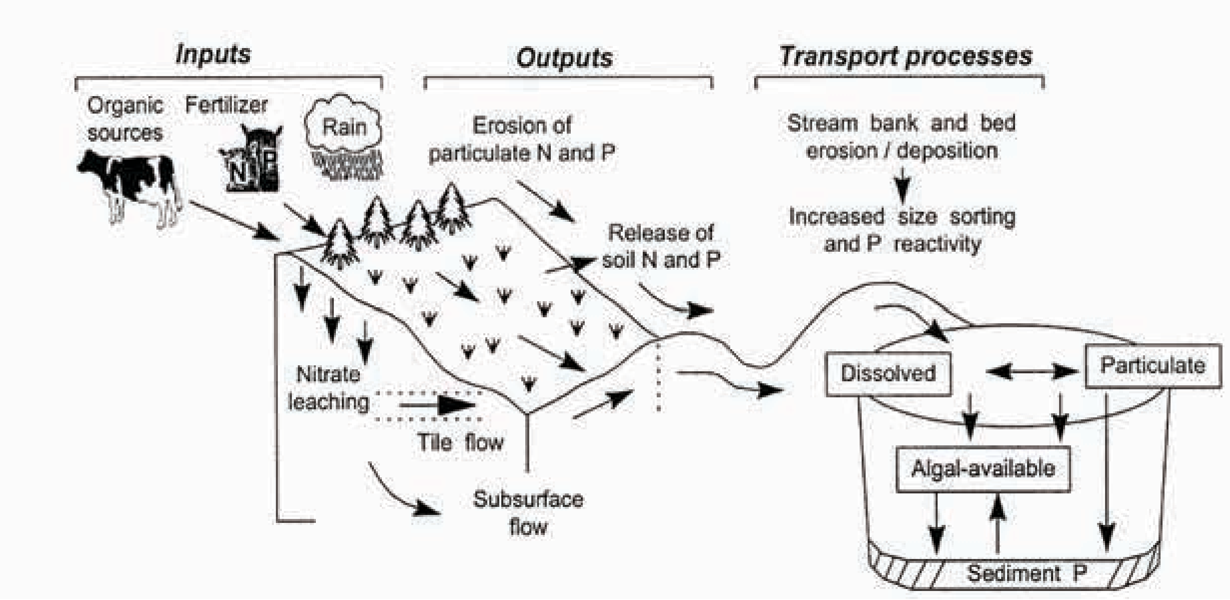


Figure 2.1: Inputs, outputs and processes of transport of P and N from agricultural land (Carpenter et. al., 1998).

As already stated P is much less soluble than N. Therefore it is often attached to particles of sediment and transported to rivers by erosion (Allan, 2007; Davie, 2000; Palmer-Felgate et al. 2009). The erosion risk of an area depends on several factors. Steep slopes, under-drained land and lack of vegetation cover lead to an effective delivery of particles to watercourses

(Jarvie et al. 2010). Furthermore agriculture increases erosion risk by disturbing the soil (Allan, 2007). Conventional tillage creates tramlines running up and down the slope, which poses a great risk of rill erosion. Furthermore high livestock numbers and heavy machinery use leads to a higher bulk density of the soil. High bulk density is an indicator of low soil porosity and high soil compaction, which reduces the movement of air and water through the soil. Therefore infiltration into the soil is reduced, which can lead to increased surface runoff (Arshad, 1996, Lal and Shukla, 2004, Petry et al., 2002). Although measures such as mole pipes potentially reduce erosion risk they increase the hydrological connectivity. This tends to accelerate and exacerbate water and sediment losses leading to a more effective supply of nutrients to watercourses (Monaghan, 2007). Generally a hydrological connectivity and close proximity of agricultural practices to watercourses increases the nutrient input.

Although primarily transported in particle form P can also travel in dissolved form, and these forms can change temporarily. For example P from fertilized grassland tends to be primarily in dissolved form during base flow and in particulate form during storm flow (Allan, 2007).

N on the other hand is more soluble than P. Although N is also transported by erosion it often leaches into the ground and reaches the watercourses through subsurface flow (Allan, 2007; Carpenter et. al., 1998, Davie, 2000; Edwards and withers, 2008).

Due to these processes of transport, the concentration of both N and P tend to increase during and after a rainfall event if the main nutrient source is diffuse (e.g. agriculture). Since P is more likely to reach watercourses through surface runoff, the instream concentration is greatest during a rainfall event and declines quickly after the event. N on the other hand is more likely to be transported via subsurface flow. Various studies therefore argue that the response is not as flashy as P: the initial proportion of subsurface flow is relatively low during a rainfall event and increases after the end (Jiang et al. 2010; Petry et al., 2002, Zhang et al., 2011).

However where the main nutrient source is from a point source, rainfall leads to a decrease in both N and P concentration. A point source usually supplies nutrients to a watercourse relatively consistently. Increased flow due to rainfall therefore leads to a dilution effect (Chapman, 1996; Jarvie 2008a and 2010). When a river's main nutrient source is from agriculture another factor influencing the timing and concentration is the timing of fertilizer application. Concentrations of nutrient are expected to rise after application, especially when application is followed by a rainfall event (Carpenter et. al., 1998).

The nutrient concentration in the water is however not solely dependent on the input (e.g. fertilizer) and rainfall, but is influenced by instream processes such as abiotic and biotic uptake and transformation mechanisms (Allan, 2007).

Sorption onto sediments has a strong influence upon phosphate, less so on ammonium and hardly any on nitrite or nitrate. When the orthophosphate concentration in streams is high, the phosphate ion attaches onto charged clays and organic particles. When concentration is however lower, compared to an equilibrium orthophosphate value of no net exchange, desorption occurs. Hence this process acts as a buffer by absorbing P when concentration is high and releasing when it is low (Allan, 2000; Palmer-Felgate et al. 2009). Furthermore nutrients tend to accumulate during lower discharge and velocity, since there are more opportunities of interaction with sediment surfaces and biofilm (Allan, 2007).

Additionally the inorganic forms (e.g. nitrite, nitrate or orthophosphate) entering a watercourse can be incorporated into organic forms by biological uptake. Nutrient uptake and cycling (e.g. denitrification) varies in response to biotic demand, which is influenced by environmental factors that control primary and microbial production (Allan, 2007). Therefore due to storage in soils and river sediment, biological uptake and denitrification in the case of N, the nutrient output (total mass of nutrients exported by river per unit time) is usually less than the input.

Due to these instream processes, agricultural practices and the variation of rainfall events throughout the year a seasonality of nutrient concentration can often be observed.

If the main nutrient source is from agriculture, nutrient levels build up in the soil in summer, meaning a low concentration in watercourses. N and P are then washed out with increasing precipitation in autumn and winter. This effect is exacerbated by ploughing in autumn, which releases large amounts of soil-bound N and P (Davie, 2008; Edwards and Withers, 2008; Jarvie et. al., 2008a). However for point sources the opposite applies: higher concentration during summer, and lower during precipitation-rich months due to dilution (Jarvie et. al, 2010). In some regions summer storms can result in rapid runoff from impervious areas such as barnyards resulting in significant delivery of nutrients (Edwards and Withers, 2008).

The seasonal timing is important. March to the end of August is the ecologically critical plant-growing season. If in this period the nutrient concentration is too high it poses a risk of eutrophication. If contributions from agricultural diffuse sources are minimal during this time, it is critical that point sources do not deliver excessive nutrient levels. However the uptake of N by terrestrial vegetation also reduces nutrient concentration in the growing season, reducing the nutrients available for undesirable plant growth such as algae. (Allan, 2007; Palmer-Felgate et al. 2009). The last factor to consider is the storage of P in stream beds. If the main nutrient source in the catchment is from agriculture, most input will be during autumn and winter. During these seasons P is more likely to be stored and might be released in the ecologically sensitive time of summer low flow, when the agricultural inputs decrease (Edwards and withers, 2008; Palmer-Felgate, 2009). To summarise, the seasonality varies depending on local conditions of the main sources of nutrients as well as precipitation patterns.

2.4 Previous research and rationale for dissertation

Much research has already been conducted worldwide showing the negative impact of agriculture on water quality. Here is a brief overview of some of the approaches and methods used in studies. Regarding land use, data is often used in some way related to the percentage cover of certain land use types (Bu et al., 2014; Jarvie et al, 2008a, 2008b and 2010; Woli et al., 2004). Sometimes an agricultural intensity measurement is used, including for example the proportion of cultivated soils, intensity of under-drainage and amount of fertiliser and manure applied (Palmer-Felgate et al., 2009). Depending how the catchments were selected, either correlation analyses or tests of difference are conducted. For example Jarvie et al. (2010) selected a set of catchments including some with low and some with high percentage agricultural land use. To compare the high with the low percentage areas, catchments with similar characteristics (catchment area, rainfall patterns, soils and underlying geology) were selected. Other studies selected catchments with wide ranges of percentage cover of certain land uses. This allows testing for correlation between water quality and for example cattle per ha, percentage cover grassland or population density (Bu et al., 2014; Jarvie et al, 2008a and 2008b, Woli et al., 2004). Furthermore the sampling frequency and timing varies between studies. While some conduct regular sampling e.g. every 7 days over 2 years (Jarvie et al, 2008a) others additionally use automatic storm sampling. Bu et al. (2014) regularly sample for one month in the dry period and one month in the rainy season in China, to detect possible differences due to the state of weather.

Most studies use flow data to test for correlation between flow height and nutrient concentration. Furthermore laboratory analyses are very similar: use of 0.45µm filter, P is

determined colorimetrically using the phosphomolybdenum blue method while nitrite and nitrate are determined with ion chromatography (Bu et al., 2014; Jarvie et al, 2008a, 2008b and 2010; Woli et al., 2004).
The results from all the studies mentioned generally support the negative impact of agriculture on water quality, although some correlation analyses or tests of difference for some water quality parameters or catchments are not significant or show a different trend. Furthermore when patterns of seasonality of nutrient concentration are found, they can be explained according to type of source and instream processes. Additionally Jarvie et al. (2010) and Woli et al. (2004) found that intensive livestock farming areas contribute significantly more nutrients than any other intensive agricultural activity.

In central Switzerland the problem of eutrophication in lakes is well studied. It is primarily caused by intensive agriculture, especially due to high livestock density (Bundesamt für Wasser und Geologie, 2005). Various measures have been undertaken and today most major Swiss lakes have good water quality. However plants and animals in Lake Baldegg and Lake Sempach in central Switzerland can only survive due to artificial aeration and circulation in the lakes (Bundesamt für Wasser und Geologie, 2005; Gemeinde Verband Sempachersee, 2016). Furthermore there is a problem of phosphor accumulation in the soils of central Switzerland, which poses a risk of future eutrophication (Bundesamt für Wasser und Geologie, 2005).

Very little is known in the UNESCO Biosphere Entlebuch (UBE) regarding water quality in streams and rivers. There is a measuring station on Kleine Emme, the main river running through the biosphere. However this lies further downstream, outside the biosphere.

Therefore UBE was interested in the water quality upstream and in tributaries of the main river.

More information is available regarding the agriculture. Knaus (2015) argues that agriculture in the UBE is unsustainable and too intensive. It can only be supported by importing 45,000 tonnes of animal feed annually. The agricultural practices are shown to have negative impacts on the environment. His study shows a negative correlation between land use intensity and biodiversity. However since there is no data on water quality, it is unclear if there is also a correlation. This dissertation examines water quality in the UBE and also tests whether there is a correlation between land use intensity and water quality.

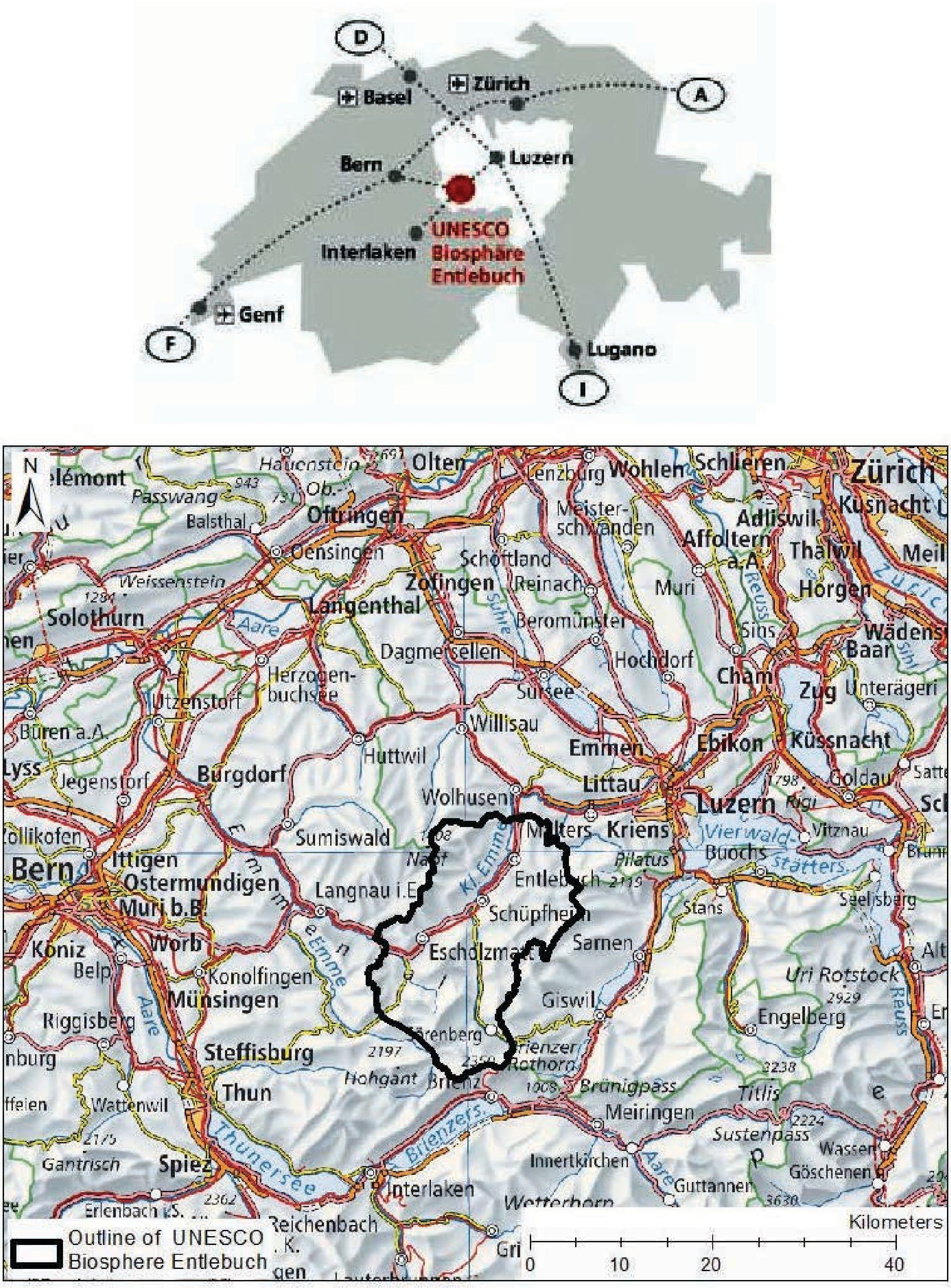
3 Study area

This chapter examines the area where the study was conducted. First the area of the UNESCO biosphere Entlebuch (UBE) is described including geology, climate and land use. Then the properties of the selected catchments and streams are outlined. Finally the selection process of the sampled catchments is explained in relation to the research aim and objectives.

3.1 UNESCO Biosphere Entlebuch

3.1.1 Location

The sampling was undertaken in the UBE, in central Switzerland (see Figure 3.1). The location is in the northern and central part (the main valley of the UBE from Escholzmatt, through Schüpfheim to Entlebuch), and the exact location of the catchments will be described later.



-Bundesamt für Landestopografie swisstopo (2012) Swiss Map Raster: [Pixel1000] Swiss Map Raster 1000 (Pixelkarte)
-Bundesamt für Umwelt BAFU (2012) Biosphärenreservate
-UNESCO Bioshpäre Entlebuch (no date) Portrait Region Entlebuch
Available at: http://www.biosphaere.ch/de/portrait/region-entlebuch

Cathy Hutchings, August 2015

Figure 3.1: Location of UNESCO Biosphere Entlebuch within Switzerland.

3.1.2 Geology

The geology in UBE is very varied due to the diverse geological history: formation and folding of the Alps, erosion and deposition of the Alps during their formation, and erosion/deposit processes during the ice age (Schlunegger, 2006). Around 15 to 35 million years ago rivers carried erosion material from the Alps and deposited them in the main valley of the UBE. These are known as Molasse from the tertiary (see figure 3.2). Other dominant features are lateral moraines and the alluvial deposits along Kleine Emme (quaternary). The lateral moraines were formed when the glaciers retreated south into the Alps after the “Last Glacial Maximum” around 10,000 years ago (Schlunegger, 2006). There are Mesozoic sediments in the south and south-eastern part of UBE, but no sampling was undertaken there.

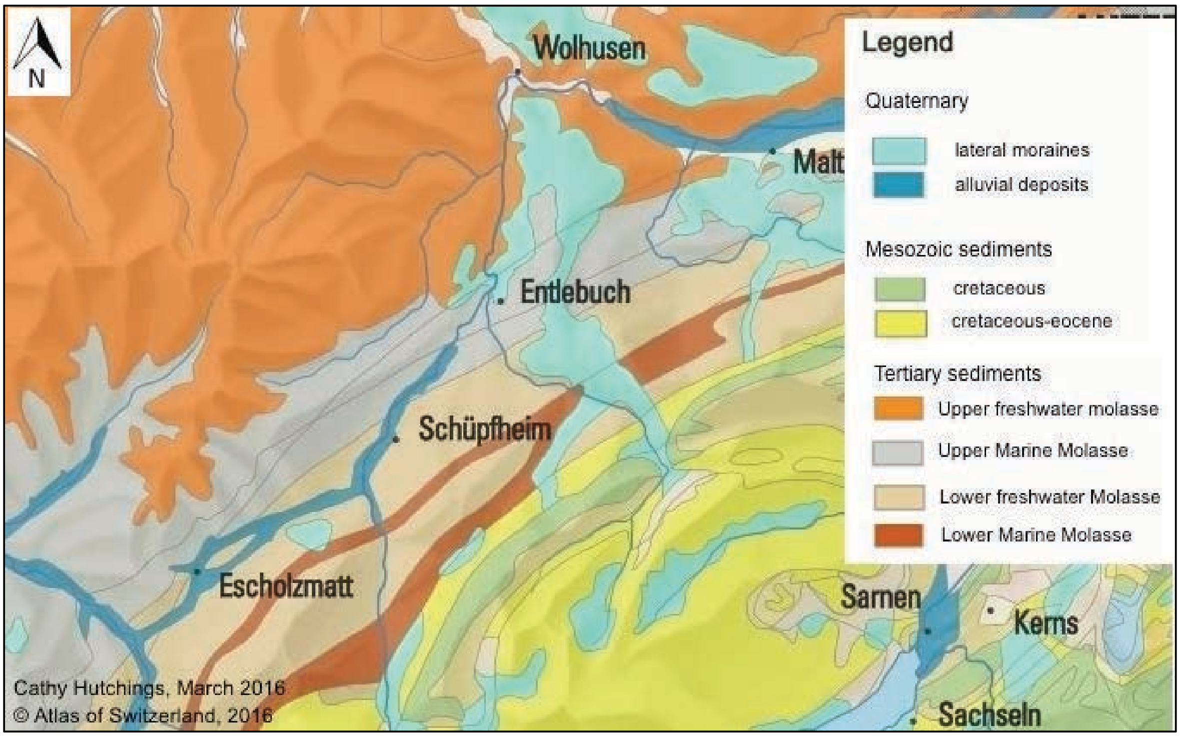


Figure 3.2: Geology of sampling location.

3.1.3 Soil types

The dominant soil types in the UBE are: brown earth, Regosol, and Gley and boggy soil (see figure 3.3).

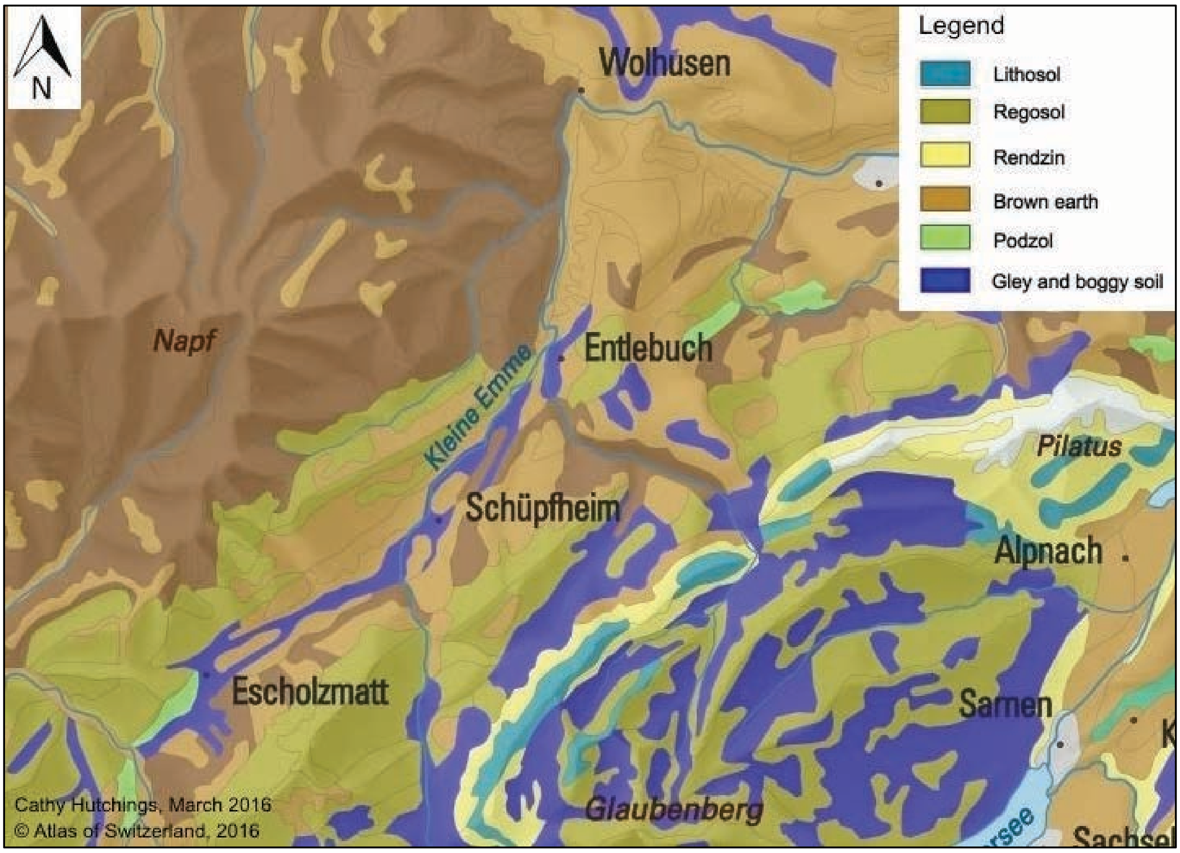


Figure 3.3: Main soil types of sampling location.

3.1.4 Climate

No official federal climate data is available for within UBE, therefore the data of the nearest station was used: Langnau i.E., which lies 745 m.a.s.l. (Schüpfheim 719 m.a.s.l.) and has roughly the same climate. Some annual figures: the mean temperature is 7.9°C, total precipitation is 1376mm, with 145 days of precipitation, and snow cover lies for 56.5 days (Bundesamt für Meteorologie und Klimatologie Meteoschweiz, 2014). Figure 4.4 shows the climate diagram for Langnau i.E.

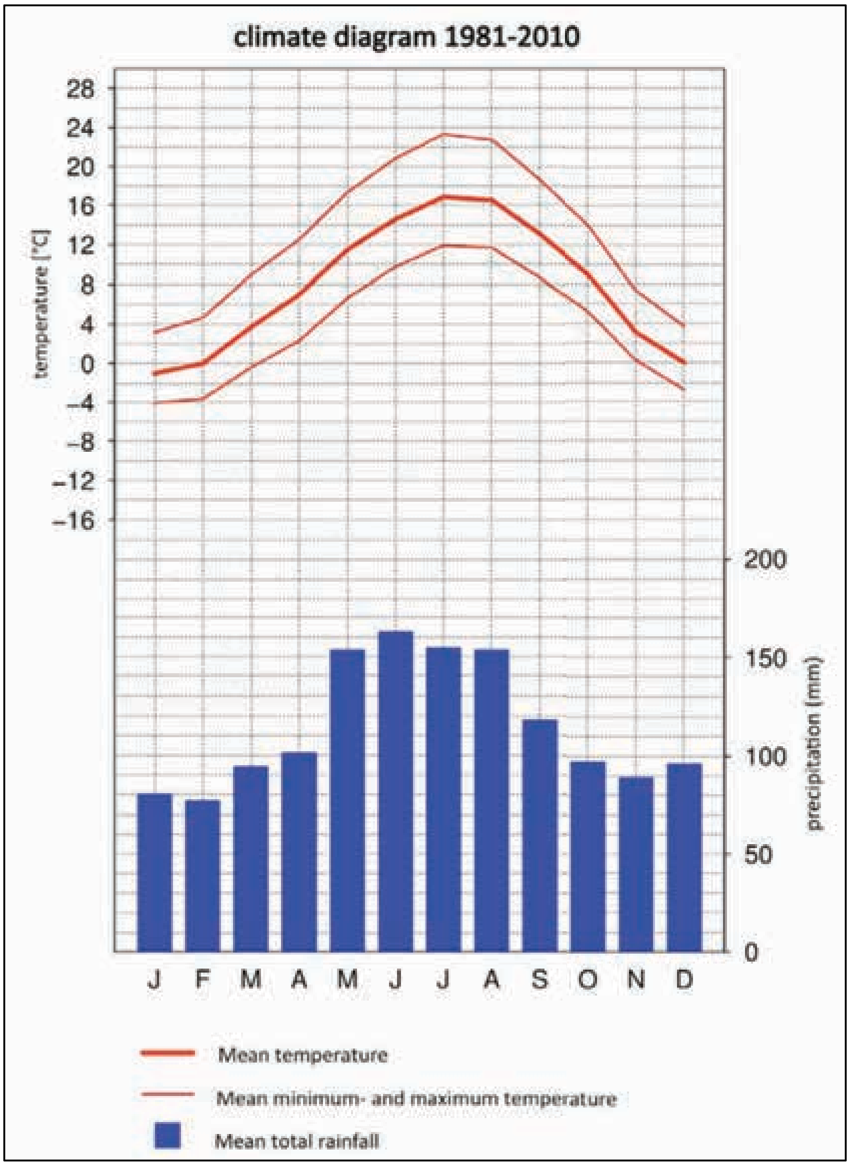


Figure 3.4: Climate diagram for Langnau i.E. showing monthly temperature and precipitation (1981-2010).

The annual total precipitation varies in the UBE (see Figure 3.5). This data is based on annual mean precipitation analyses on a 2 km grid for the whole Alpine region. The analyses are based on data from 5831 pluviometers and 259 totalisers from 1971 to 1990. The interpolation of the weather data is based on a local weighted regression, whereby various topographical parameters were taken into account (altitude, slope exposure, slope inclination, etc.) (Atlas of Switzerland, 2016).

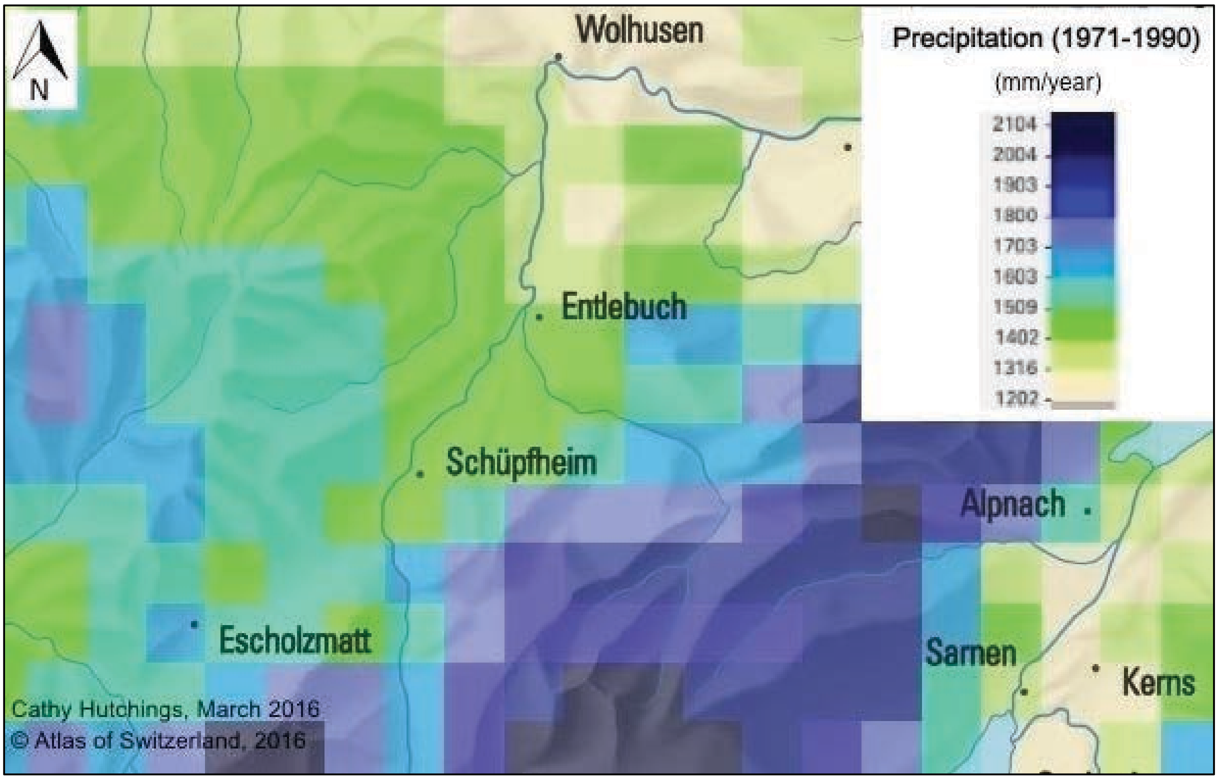


Figure 3.5: Distribution of annual precipitation (mm) in UBE.

3.1.5 Protection status and agricultural land use

There are three zones of protection status within a UNESCO biosphere (UNESCO, 2016):

- “The core area(s) comprises a strictly protected ecosystem that contributes to the conservation of landscapes, ecosystems, species and genetic variation.”
- “The buffer zone surrounds or adjoins the core areas, and is used for activities compatible with sound ecological practices that can reinforce scientific research, monitoring, training and education.”
- “The transition area is the part of the reserve where the greatest activity is allowed, fostering economic and human development that is socio-culturally and ecologically sustainable.”

The UBE core contains moors, alluvial forests and mountain ridges. 40% of the area is the buffer zone containing protected forests, moors and pastures. The transition area covers 50% of the UBE and comprises agricultural and industrial areas as well as towns and villages (UBE, 2016). Figure 3.6 shows the distribution of the different zones in UBE.

The land use is therefore strongly interlinked with the protection status, which can be seen when figure 3.6 is compared with figure 3.7 (presented on the next 2 pages).
Agriculture plays an important role in the UBE: 34% of the working population are employed in the primary sector (agriculture and forest), compared to 4% in all Switzerland (Knaus, 2011). The agriculture in the UBE is unsustainable, too intensive and can only be supported by importing 45,000 tonnes of animal feed annually (Knaus, 2015). The number of organic farms is low, at 6%. Furthermore set-aside areas exist, mostly however in remote areas, where intensive land use is impossible. In the main valley of the UBE only around 8% of the area are set asides (Knaus, 2011).

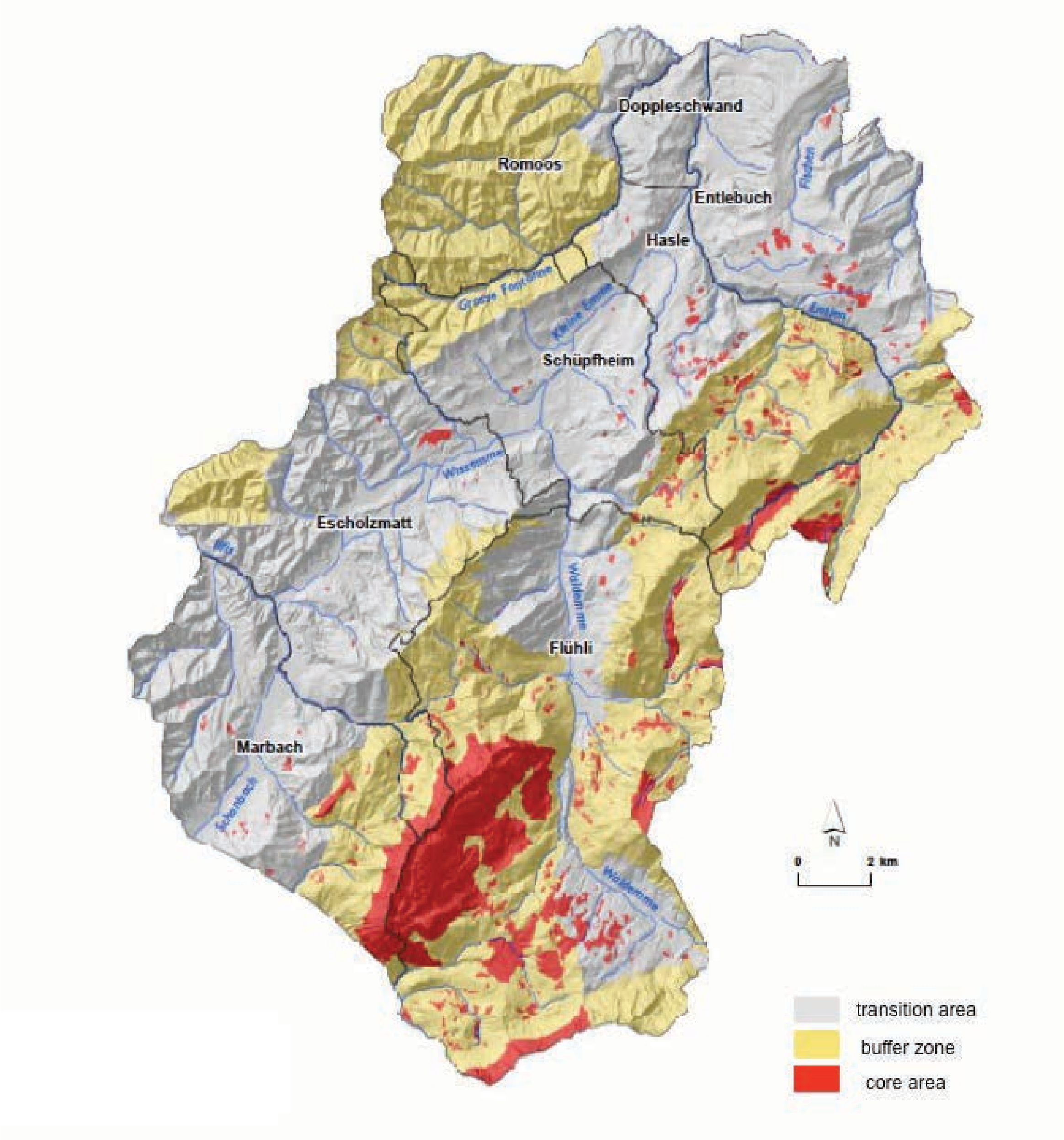


Figure 3.6: The three zones of protection status in the UBE (UBE, 2006).

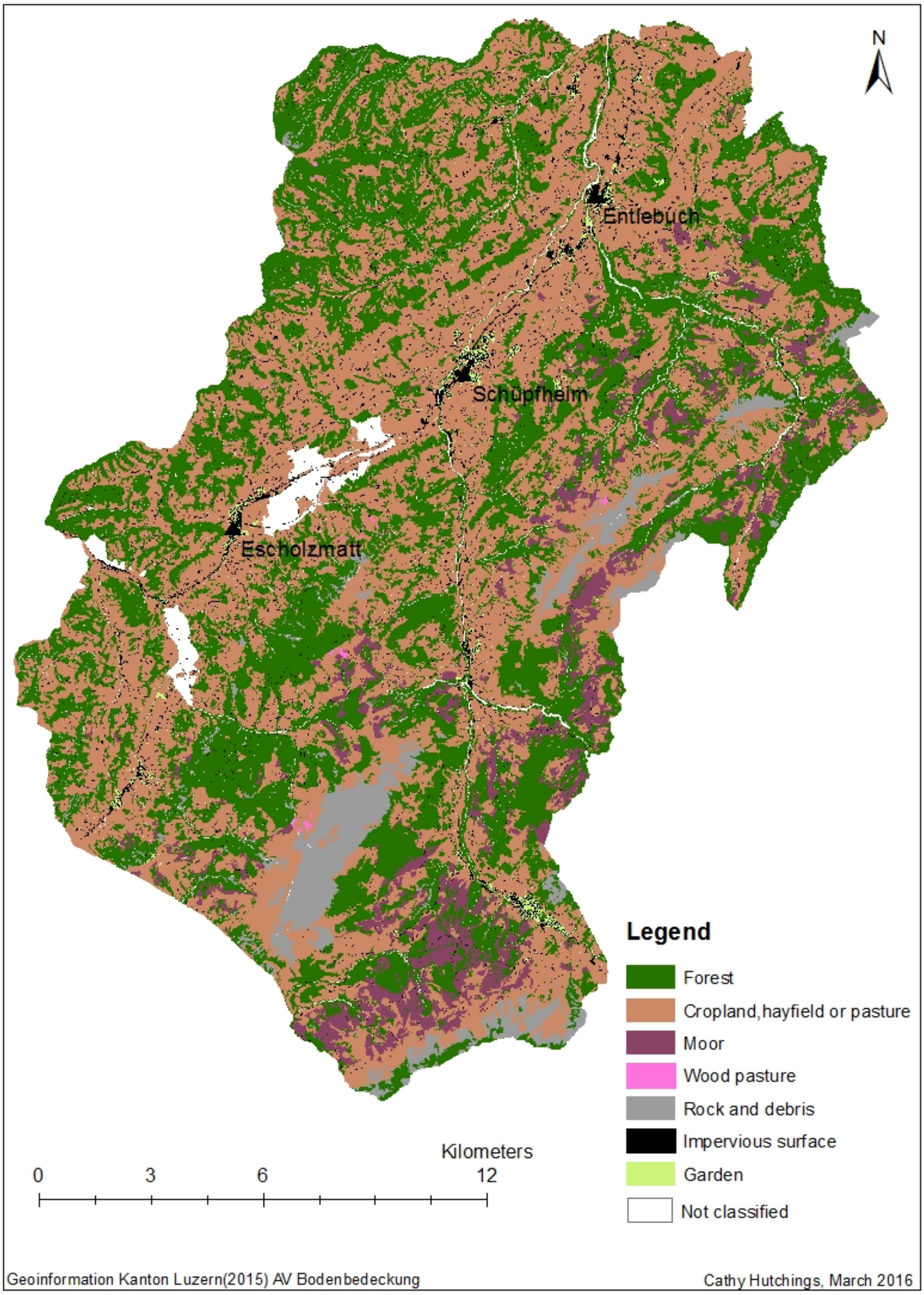


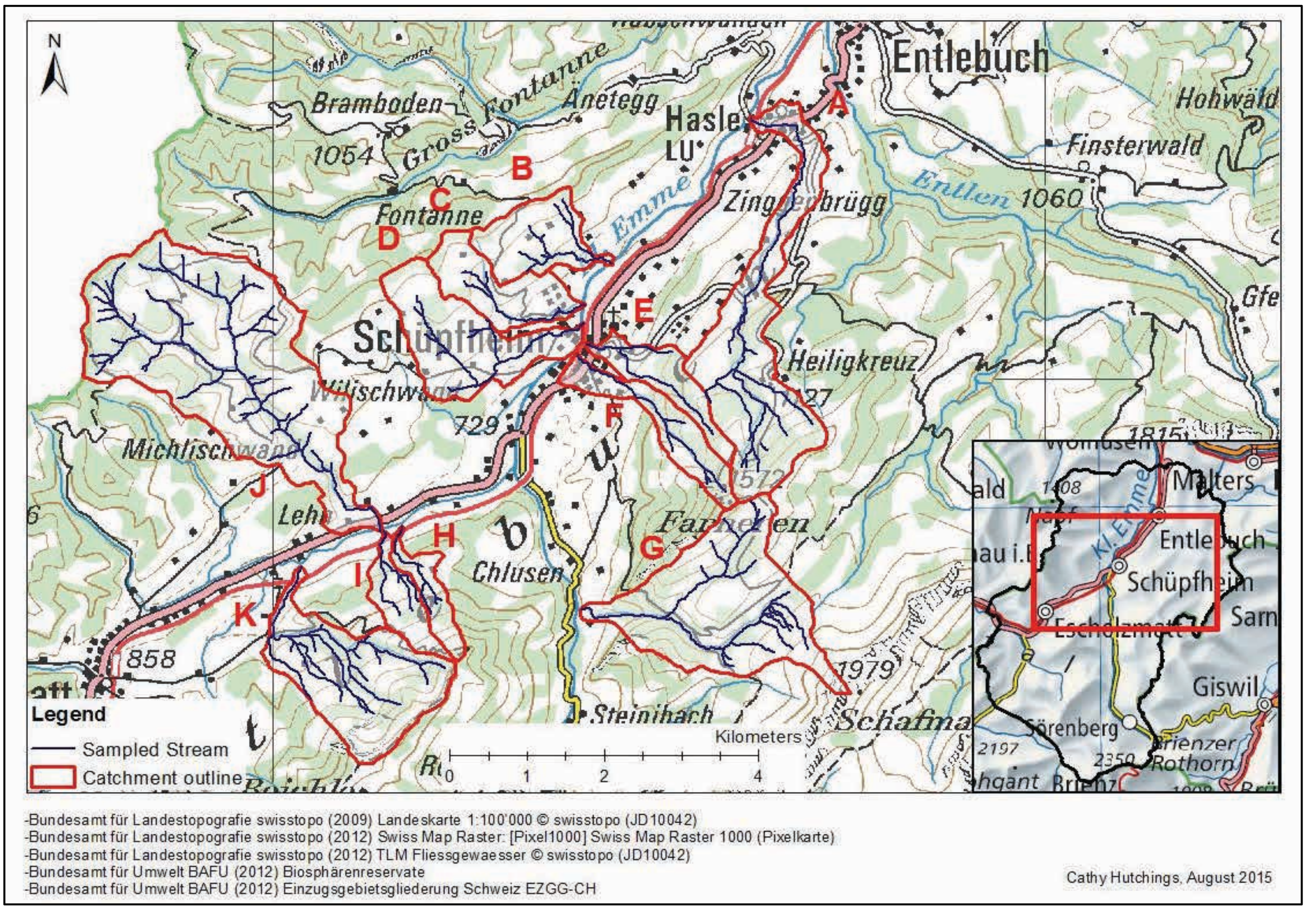
Figure 3.7: Land use in the UBE.

3.2 Properties of selected catchments

The 11 catchments all lie in the main valley of the UBE (see figure 3.8).

The sample points are in tributary streams of Kleine Emme and Wald Emme, and the water samples were taken just before the stream joins these main rivers.

The catchment areas range from 0.54 to 7.09 sq km. Table 3.1 summarises some of the characteristics of the catchments.



-Bundesamt für Landestopografie swisstopo (2009) Landeskarte 1:100'000 © swisstopo (JD10042)
-Bundesamt für Landestopografie swisstopo (2012) Swiss Map Raster: [Pixel1000] Swiss Map Raster 1000 (Pixelkarte)
-Bundesamt für Landestopografie swisstopo (2012) TLM Fliessgewaesser © swisstopo (JD10042)
-Bundesamt für Umwelt BAFU (2012) Biosphärenreservate
-Bundesamt für Umwelt BAFU (2012) Einzugsgebietsgliederung Schweiz EZGG-CH

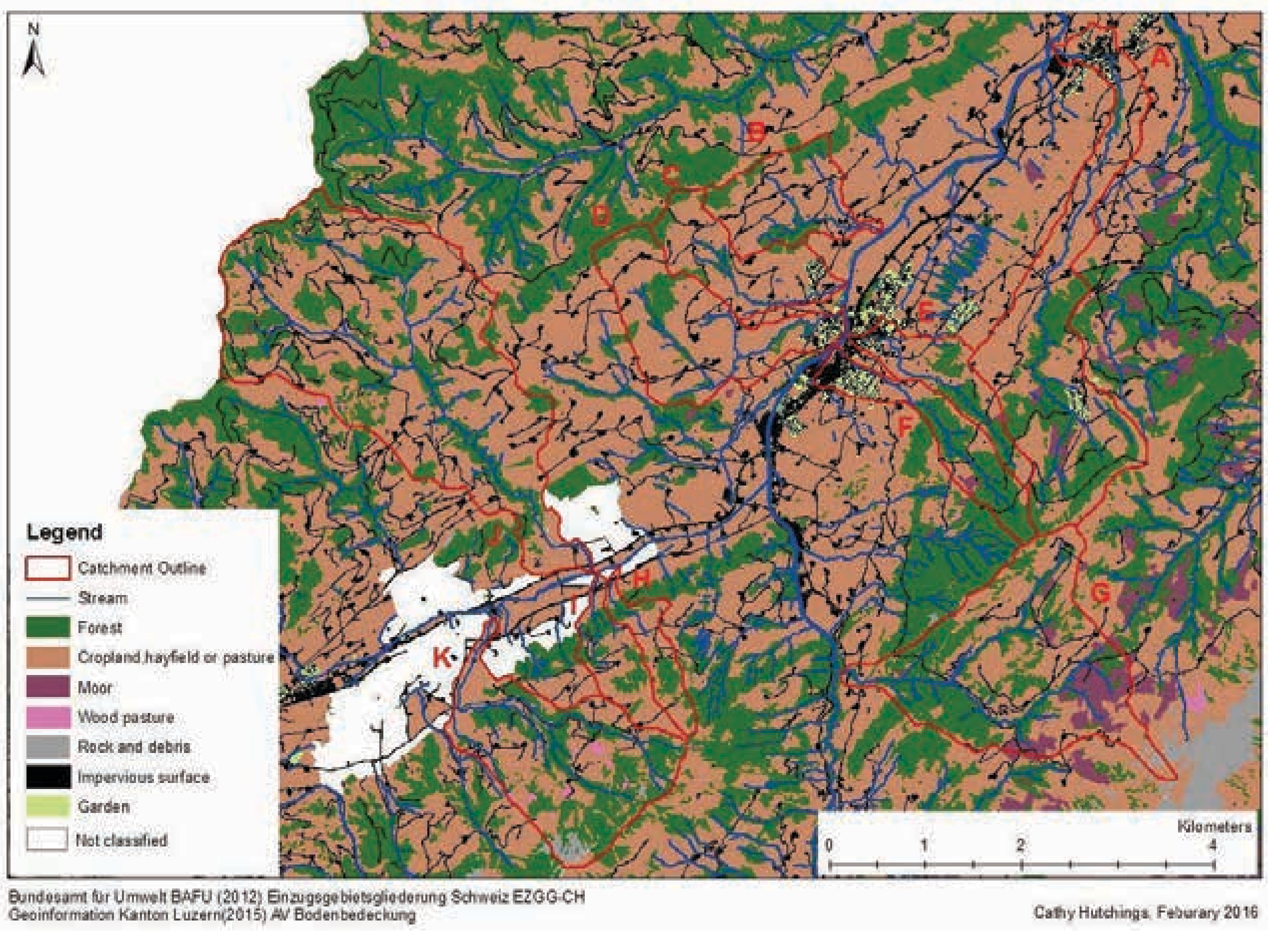
Cathy Hutchings, August 2015

Figure 3.8: Location of sampled streams and catchments within the UBE.

Table 3.1: Selected characteristics of the sampled catchments
The catchments are ranked according to mean land use intensity

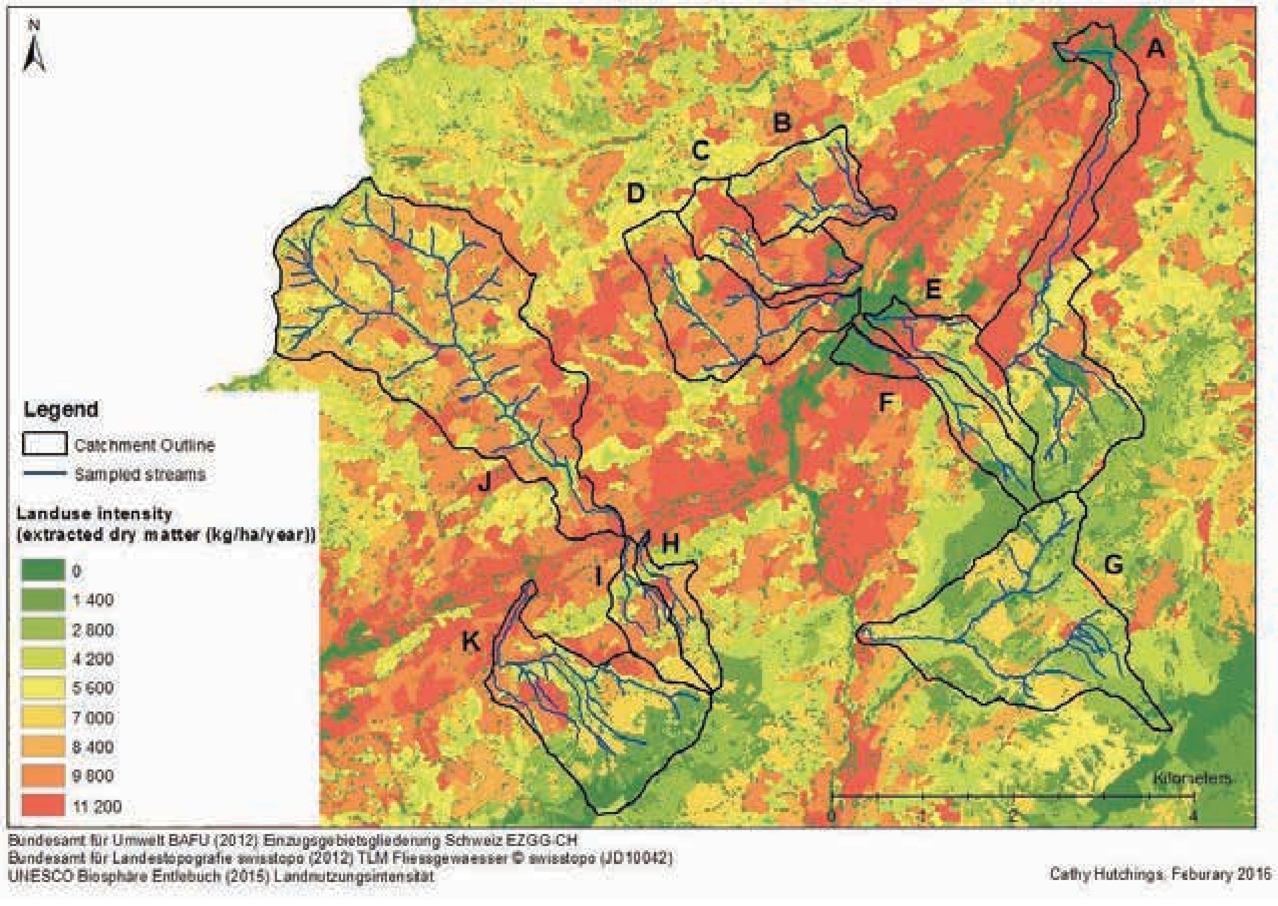
Catchment	**Area (sq km)**	**Difference in elevation**	**Mean land use intensity**
G	3.98	1134.31	4010.15
F	1.08	859.18	4310.70
K	2.91	929.71	5152.30
E	0.89	599.79	6045.59
A	3.65	860.30	6394.87
H	0.54	714.48	6567.86
I	0.71	705.81	7204.73
J	7.09	477.61	7504.16
D	2.15	422.50	8018.37
B	1.23	368.01	8040.56
C	1.25	400.91	8553.54

The catchments represent a wide range of mean land use intensities, as table 3.1 shows. Land use intensity is defined as the annual extracted dry matter in kg per ha. The data looks at intensity of agriculture and forestry, so areas such as rock surfaces or settlements (gardens and impervious surfaces such as streets and houses) are classified as no land use, since nothing is extracted (Knaus, 2015). On the next page a map of the land use (figure 3.9) is presented alongside a map of land use intensity (figure 3.10).



Bundesamt für Umwelt BAFU (2012) Einzugsgebietsgliederung Schweiz EZGG-CH
Geoinformation Kanton Luzern(2015) AV Bodenbedeckung
Cathy Hutchings, Feburary 2016

Figure 3.9: Land use in the area of sampling.



Bundesamt für Umwelt BAFU (2012) Einzugsgebietsgliederung Schweiz EZGG-CH
Bundesamt für Landestopografie swisstopo (2012) TLM Fliessgewaesser © swisstopo (JD10042)
UNESCO Biosphäre Entlebuch (2015) Landnutzungsintensität
Cathy Hutchings, Feburary 2016

Figure 3.10: Land use intensity in the area of sampling.

When looking both at the map of the land use and the land use intensity, one can see that the intensity is the highest in the lower-lying areas where the land is used for agriculture (cropland, hayfield or pasture). This is around the main valley of UBE running southwest to northeast. Furthermore land covered with forest is generally not used intensively, due to slow tree growth (Knaus, 2015).

The mean land use intensities of the catchments are strongly linked to the land use type. With increasing mean intensity the combined area of forest and moor generally decreases, while the area used for agriculture increases. Catchment F is an exception, being the only catchment where the percentage cover of forest or moor is higher than that of agriculture. Furthermore large parts of Schüpfheim are in that catchment (17.8% is covered by impervious surface and gardens).

Table 3.2 presents the percentage area covered by each land use type, while figure 3.11 visualises the percentage cover according to 3 categories of land use. The percentage area per land use intensity class for each catchment can be found in Appendix A. The lower intensity catchments are more evenly spread over all the intensity classes, while for the higher intensity catchment the majority of the area falls into the top two categories.

Table 3.2: Percentage area per land use type and number of buildings per sq km in each catchment
The catchments are ranked according to mean land use intensity

	Land use (%)							
Catchment	Forest	Cropland, hayfield or pasture	Moor	Wood pasture	Rock and debris	Impervious surface	Garden	Number of Buildings per sq km
G	36.92	48.74	10.98	0.00	0.89	1.41	0.00	13.31
F	49.34	29.72	2.35	0.00	0.00	11.35	6.45	229.03
K	40.13	50.98	0.00	1.32	3.66	1.58	0.00	16.51
E	34.04	53.13	0.78	0.00	0.00	7.61	3.82	130.39
A	31.59	58.31	1.90	0.00	0.00	5.10	2.20	90.02
H	33.09	64.57	0.00	0.00	0.00	1.58	0.00	11.13
I	32.28	62.90	0.00	0.00	0.00	2.63	0.00	19.77
J	30.42	65.74	0.13	0.27	0.00	2.45	0.00	24.12
D	19.95	73.40	0.00	0.00	0.00	4.33	1.77	76.73
B	25.57	70.77	0.00	0.00	0.00	3.07	0.09	50.25
C	16.95	75.49	0.00	0.00	0.00	4.89	2.28	100.01

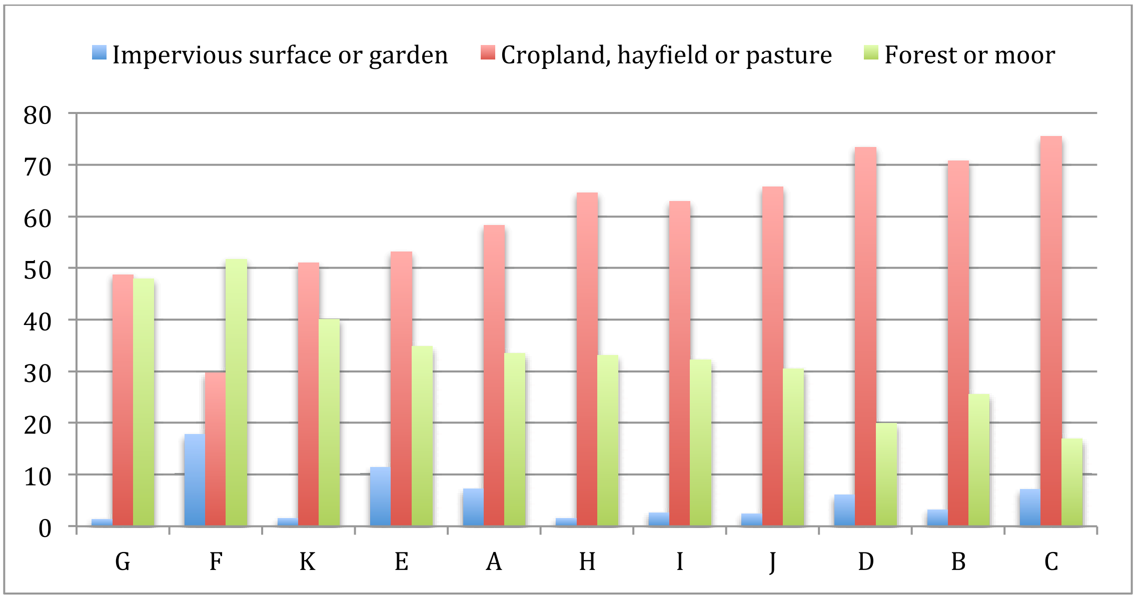


Figure 3.11 Percentage area per land use category (combined area of forest and moor, combined area of impervious surface and garden and cropland, hayfield or pasture) for each catchment.

3.3 Sampling design in relation to area

3.3.1 Selection of catchments

The catchments were chosen with the aim of obtaining a wide variety of mean land use intensities. This is necessary in order to conduct the test of correlation with water quality. Furthermore all sampling points are easily accessible and in relative proximity to each other, enabling sampling to be undertaken within one day.

3.3.2 Evaluation of catchment selection

The sampling design allows for effective correlation analysis due to the wide range of mean land use intensities of the catchments. Furthermore all samples were taken within around 3h, so that differences of nutrient concentration can be linked to land use intensity and not to the different weather or flow conditions. However this selection process means there is a convenience bias (e.g. close to roads). Remoter catchments are less likely to be selected (Clifford et al. 2010).

Furthermore the samples are not representative of the whole UBE. They represent the transition area, the low-lying, flatter region of the valley, where agriculture is possible and hence the land use intensities are higher. In the higher regions (especially northwest of Sörenberg), there is little agriculture and very low population density (see Figure 3.12). Therefore lower water quality is to be expected in the valley. Hence the UBE is interested in obtaining water quality data in that area.
However the GIS analysis was not done for all possible catchments in the transition area, so it is unclear how far the samples are representative of that area. Nonetheless when looking at Figure 3.12, they seem fairly representative.

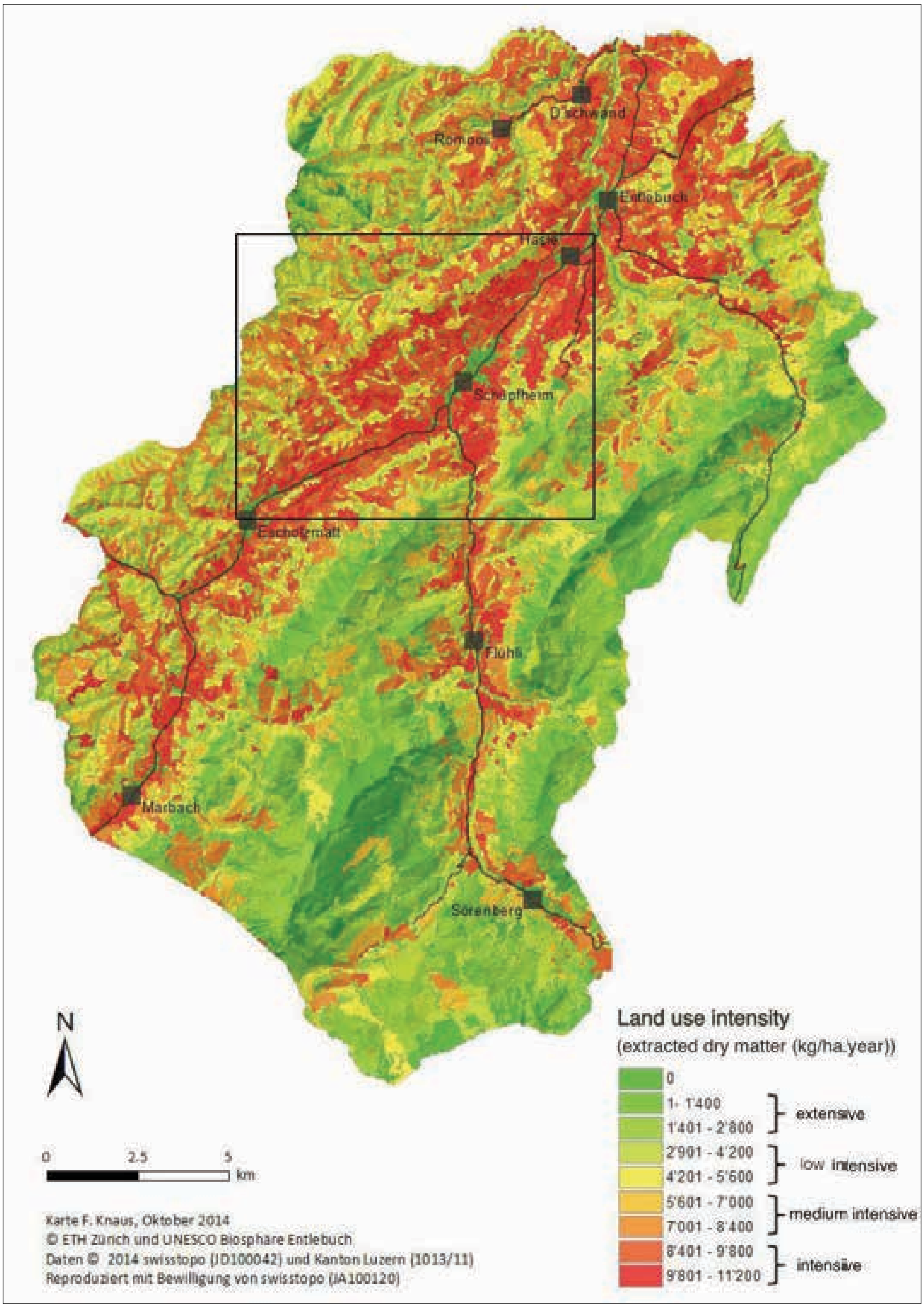


Figure 3.12: Land use intensity in the UBE showing the area of the selected catchments (represented by the black frame).

4 Methodology

Part of the sampling design, regarding the choice of catchments, has already been described and evaluated in chapter 3. This chapter firstly looks at the field and lab methods used to determine water quality in the 11 streams. Then the GIS analysis performed to obtain mean land use intensity per catchment is described. Following this is an evaluation of the usefulness and suitability of lab, field and GIS methods. Finally the statistical methods that were applied to test the impact of agricultural land use on water quality are described. The usefulness and suitability of these is evaluated in chapter 6, after the results of the statistical analysis have been presented.

4.1 Field methods

4.1.1 Sample collection and storage

The water samples were collected in 100 ml polyethylene containers. The sampling points chosen meant sampling could be achieved within 3 hours. Therefore all samples were taken under similar weather conditions, enabling reliable comparison between the catchments.

The sampling bottles were pre-washed with stream water three times prior to collection, to avoid contamination. The water was collected away from the margins in mid-stream and always at the same location. In each stream 1 grab sample was taken per visit. To gain representative samples of the whole stream, samples were taken at around mid-depth. Since most streams were very shallow, this meant placing the container just above the streambed and at or just below the surface. Furthermore sample locations were chosen to represent average stream velocity. Areas of very slow and very fast flowing water were disregarded. To avoid disturbing sediments on the streambed and so contaminating the sample, the containers did not come into contact with the streambed and the sampling point was reached from downstream.

Each sample was immediately cooled to between 3-6 C° in cool boxes. It was stored at 4 C° for 12-48 h, then taken in cool boxes for laboratory analysis.

4.1.2 Frequency and timing of sampling

All catchments were visited 7 times in total, except G, where only 6 measurements were taken. As explained in chapter 2 the state of the weather and the height of the stream flow strongly influence nutrient concentration. Sampling was therefore timed to encompass different weather conditions and flow.

4.1.3 Secondary variables

The height of flow was estimated visually in the field, since there is no flow data available in the UBE. Photographs were taken, so that once the sampling was completed they could be examined and used to support the classification made in the field.

The state of weather was noted in the field and confirmed by precipitation data from the Schüpfheim weather station. Since all catchments lie within around 5 km radius of the weather station and all the samples were collected within 3 hours, all the catchments were classified the same for a given day.

4.2 Laboratory methods

The water samples were analysed in the AuA Labor of eawag (Swiss Federal Institute of Aquatic Science and Technology) in Dübendorf. All samples were tested for orthophosphate (PO_4), nitrate (NO_3) and nitrite (NO_2).

Nitrogen is typically present in rivers as nitrate, nitrite and ammonium. Ammonium was not analysed since the values found further downstream in Werthenstein were classified as high water quality status for the previous 30 years. The values for nitrate and nitrite on the other hand showed higher nutrient concentrations at times (UWE, 2015). Since time and resources were limited, the parameters with the most significance of expressing water quality and potentially undesirable values were chosen.

Regarding phosphorus the samples were analysed for orthophosphate. The orthophosphate ion is the most thermodynamically stable and therefore most likely to occur in water (Hem, 1989). Furthermore it is considered the best indicator of what is immediately available for uptake by aquatic species (Allan, 2007).

The water samples were filtered using 0.45µm membrane filters. Following eawag standard operating procedures nitrite and orthophosphate were determined colorimetrically using a photometer. The phosphomolybdenum blue method was used for orthophosphate while nitrite formed a red azo colour (Langmeier 2012 & 2015). Nitrate was measured using ion chromatography (Langmeier and Freudemann, 2014).

4.3 GIS analysis: land use intensity per catchment

The UBE provided the land use intensity dataset. Land use intensity is defined as the annual extracted dry matter in kg per ha. The data looks at intensity of agriculture and forestry. Forestry land use is modelled according to gradient, proximity to roads and the speed of plant growth (which is reduced from 1200 m.a.s.l.). The resulting total annual used dry matter from the model is similar to the real average annual use. Therefore the model seems accurate. Agricultural intensity is based on a data set where the land use for each land parcel is known. From this data, provided by farmers, the amount of fertilizer and extracted biomass can be derived. All the forestry and agricultural parcels are allocated one of the 5 categories ranging from no use to intensive use. Forestry and agriculture covers 86% of the UBE area. Other areas such as rock surfaces or settlements (streets, houses, private gardens) are classified as no land use, since nothing is extracted (Knaus, 2015). For gardens this is strictly speaking not true. However since data is unavailable, these were classified as land use intensity 0.

The catchment outline was taken from the Federal Office for the Environment (BAFU, 2012). However the catchments were drawn for the main rivers running through the UBE and not its tributaries. Therefore for a few catchments some minor alterations had to be made using a digital elevation model.

The mean land use intensity for each catchment was calculated with ArcGIS using zonal statistics. The pixel size of the intensity data set is 25m^2, while the catchment size ranges from 0.54 km^2 to 7.09 km^2.

4.4 Evaluation of methods

4.4.1 Field methods

The grab sample is representative, since most streams are very shallow and narrow. Streams g and k were relatively wider and deeper. In those cases a depth and area-integrated sample could have been taken, meaning mixing a series of samples taken from various locations within the river (Bartram and Ballance, 1996, Chapman, 1996, Hem, 1985, Jarvie et al., 2002). However both g and k are still small streams, so any benefit gained is minimal compared to the time investment.

The short time taken to collect all samples per visit means that differences in concentrations cannot be linked varying states of weather. Errors could arise due to storage conditions of the samples. Although the water samples were stored at recommended temperatures, the time between collection and lab analysis was sometimes over 24 hours. This is especially important when analysing orthophosphate. There is a problem of absorption of P onto the container as well as desorption as the sample bottles were reused. Generally the longer samples are stored, the higher the uncertainty concerning the accuracy of the laboratory measurements. Furthermore if samples contain particles, there can be changes between particulate and dissolved concentration (Allan, 2007; Bartram and Ballance, 1996; Harmel et al., 2006; Jarvie et al., 2002). An option is to filter the sample in the field. It is also argued that glass containers and adding preservatives might reduce absorption/ desorption, although it is unclear how effective these measures are (Bartram and Ballance, 1996; Harmel et al., 2006; Jarvie et al., 2002).

Evaluation of field methods regarding frequency and timing as well as secondary variables are made in chapter 6, since their effectiveness is discussed in relation to statistical analysis.

4.4.2 Laboratory methods

Nitrate, nitrite and orthophosphate were chosen to represent the water quality. However P can change quickly between various forms, so that total P might be a better indicator of overall P availability (Allan, 2007). Regarding the laboratory analysis, contamination is possible in both filtration and analysis processes. Possible human errors include adding inaccurate amounts of chemicals to the water sample for colorimetric analysis, and errors in reporting the measurements (e.g. retrieving the wrong values from the photometer). Furthermore the interval between adding chemicals and analysing the colour was timed only for the 1st sample. Therefore the length of the colour formation process was perhaps not equal for all samples, leading to the colour possibly not representing the amount of orthophosphate/nitrite proportionally. This can lead to inaccurate photometer readings. Other errors could be due to faulty machines, photometer calibration errors or when determining nitrate via ion chromatography (Bartram and Ballance, 1996; Davie, 2008; Jarvie et al., 2002).

A limitation of the photometer is that it can only accurately measure a certain range of nutrient values. While too high concentrations can be diluted, the lower values are then capped. Therefore the values for nitrite under 1 µg N/L and nitrate under 0.25 mg N/L are inaccurate and were all stated as <1 µg N/L or <0.25 mg N/L. Therefore no variations between samples can be detected with concentrations under these values.

4.4.3 Choice of laboratory analysis compared to other available methods

The method of taking water samples and analysing in the lab was chosen since it is the most accurate and most common method in the developed world. All studies mentioned in chapter 2 used this method, although perhaps automated sampling was undertaken or the exact lab procedures varied. Other options available include paper strips or analysing water samples in the field using a field test kit (Jarvie et al., 2002). Although the option using paper strips can be done easily and quickly in the field, the results are very inaccurate especially for low concentrations (WHO, 1997, Reedyk and Forsyth, 2006). With the other option water samples are collected and then analysed using visocolor tests and a filter photometer. The advantage of this method is that chemical analysis can be made within the same day, reducing storage problems. Furthermore it provides more flexibility regarding timing of sampling, since chemical analysis can be done at any time. This method is more accurate than the test strips, the main reason being that the colour is measured by the photometer, which removes human subjectivity when comparing the colour of the sample to a colour standard (Reedyk and Forsyth, 2006). This method is however still far less accurate than laboratory analysis, and should only be chosen due to logistical or financial constraints (WHO, 1997). Analysing the samples in the lab meant that often analysis could not be done within 24h of sampling, due to the 100 km distance between UBE and eawag. However possible inaccuracies resulting from longer storage were deemed lower than any resulting from using test kits (for chemical analysis).

4.4.4 GIS methods

Since the pixel size ($25m^2$) of the land use intensity data is relatively small compared to the catchment sizes (ranges from 0.54 to 7.09 km^2) calculations made in ArcGIS are precise. However the intensity data is given in 5 classes. Using the mean value when dealing with classes is not very accurate. Nonetheless it is the only option since to test for correlation with water quality, only one other variable describing land use can be used. Hence using for example the percentage cover of each intensity class is not possible.

Although the intensity data being in classes is a minor limitation, the method of land use intensity and the calculations are valid. The model is fairly accurate since the output from forestry matches the real output. Furthermore the information for the agricultural output is provided for each field by the farmers. Unless these have provided false information or errors exist in the derivation of extracted biomass the model is accurate. The main aim of the research is to study the impact of agricultural land use on water quality, but the land use intensity data set covers both forestry and agriculture. However intensive forestry is not possible due to slow plant growth (Knaus, 2015). The intensity therefore mainly expresses agricultural land use intensity. Furthermore using the mean intensity instead of only percentage of agricultural land cover provides more information and is more accurate regarding water quality. It is expected that the bigger the area within a catchment is used for agriculture and the more intensive those practices are (e.g. fertilizer) the worse the water quality.

4.5 Statistical analysis

All analyses were performed using R (version 3.1.2, R Core Team, 2014).

The Shapiro-Wilk test was used to test the distribution:

Null Hypothesis (H_0): There is no difference between the distribution of our sample and the normal distribution.

Alternative hypothesis (H_1): There is a difference between the distribution of our sample and the normal distribution.

Depending whether the data sets were normal or not, Pearson's product-moment correlation test or the Kendall rank tau correlation and Spearman's rank correlation tests were performed.

H_0: there is no significant correlation between nitrite/nitrate/orthophosphate and the mean land use intensity

H_1: there is a significant correlation between nitrite/nitrate/orthophosphate and the mean land use intensity

Due to findings in the literature there is expected to be a significant correlation between all the water quality parameters and the mean land use intensity. If this is not the true it will be investigated why this might be the case.

5 Results

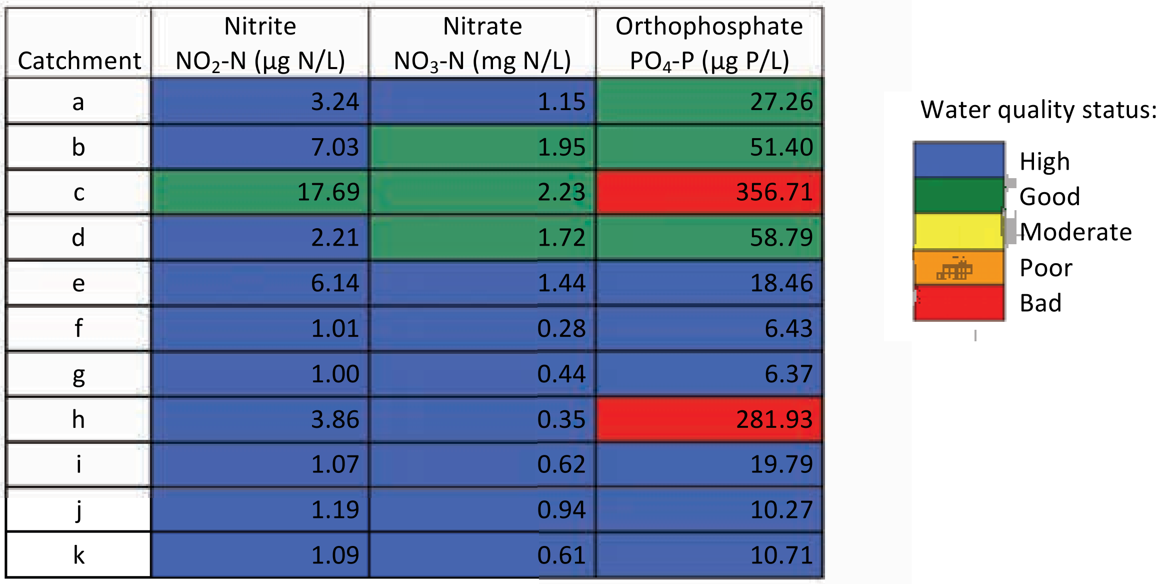
This chapter presents the data obtained through field and lab work and the results of the statistical analysis. First the water quality data are presented and assessed in the context of the classification of water quality status presented in the introduction. Then it is tested whether a significant correlation exists between water quality (nitrite, nitrate and orthophosphate) and land use intensity. The results of the GIS analysis regarding land use intensity were already presented in chapter 3.

Firstly the test of correlation was done using all data. Then to test whether outliers have an impact on the strength and significance of the correlation, the outliers were removed and the data tested for correlation. Finally the impact of the height of flow and the state of weather on the correlation was tested.

5.1 Status of water quality

The mean values of nitrite, nitrate and orthophosphate from all measurements were calculated for each catchment and are presented in Table 5.1. The values were all classified according to the classification of water quality status of the Swiss Environmental Department, which is based on the EU water framework directive (see Table 1.1). Most values show a high or good status of water quality, except orthophosphate for catchments c and h. Possible reasons for this and implications will be discussed in chapter 6.

Table 5.1: Mean water quality coloured according to water quality status



Catchment	Nitrite NO_2-N (µg N/L)	Nitrate NO_3-N (mg N/L)	Orthophosphate PO_4-P (µg P/L)
a	3.24	1.15	27.26
b	7.03	1.95	51.40
c	17.69	2.23	356.71
d	2.21	1.72	58.79
e	6.14	1.44	18.46
f	1.01	0.28	6.43
g	1.00	0.44	6.37
h	3.86	0.35	281.93
i	1.07	0.62	19.79
j	1.19	0.94	10.27
k	1.09	0.61	10.71

Water quality status:

🟦 High
🟩 Good
🟨 Moderate
🟧 Poor
🟥 Bad

5.2 Correlation between land use intensity and water quality using all data points

The mean value of nitrite, nitrate and orthophosphate from all measurements was calculated for each catchment. The Shapiro-Wilk test showed that nitrate is normally distributed (W = 0.92, p=0.31), while nitrite (W = 0.69, p= 3.04×10^{-4}) and orthophosphate (W = 0.62, p= 4.95×10^{-5}) are not normally distributed. The dataset of the mean land use intensity of the catchments is normal (W = 0.94, p= 0.53).

In order to detect if there is a significant correlation between nitrate and land use intensity Pearson's product-moment correlation test was used, since both datasets are normal. The result shows a significant strong positive correlation (r= 0.76, t= 3.55, df= 9, p= 6.23 x 10^{-3}) (see figure 5.1).

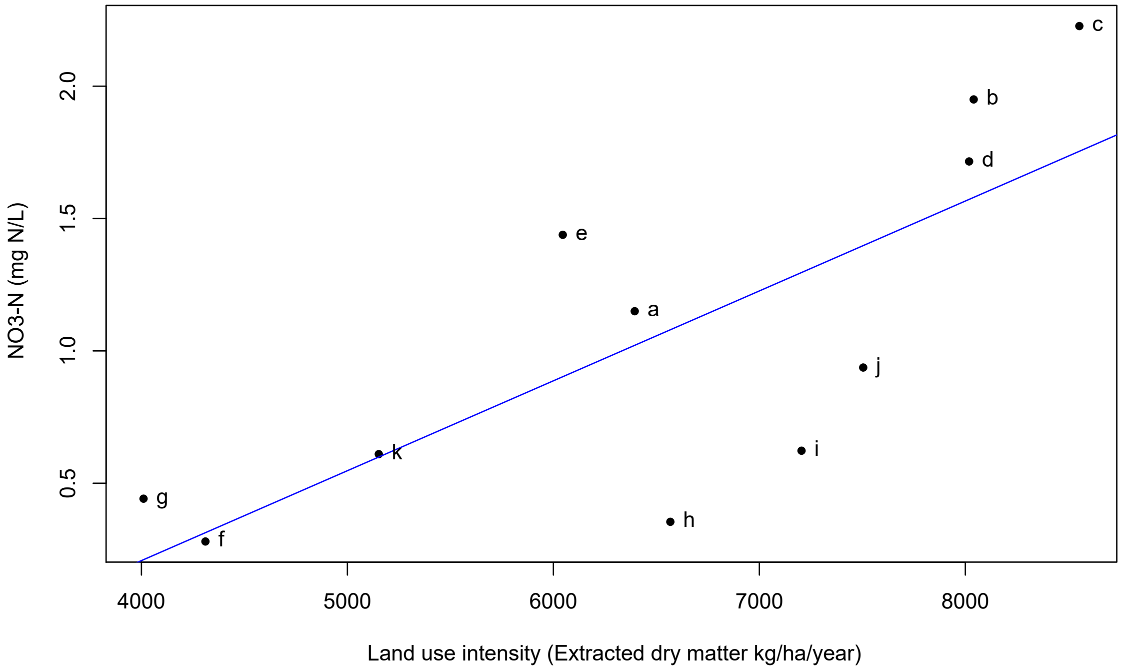


Figure 5.1: Relationship between nitrate (NO_3-N (mg N/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The blue line represents the least squared linear regression line and the points are labelled according to catchment.

The Kendall rank tau correlation and Spearman's rank correlation tests were performed for orthophosphate and nitrite. For both there is a significant moderate positive correlation with land use intensity: nitrite (Spearman's rank rho=0.69, p= 0.019 and Kendall's rank correlation tau = 0.56, z =2.41, p=0.016) and orthophosphate (Spearman's rank rho=0.76, p= 6.23 x 10^{-3} and Kendall's rank correlation tau = 0.64, z = 2.72, p= 6.43 x 10^{-3}) (see Figure 5.2 and 5.3).

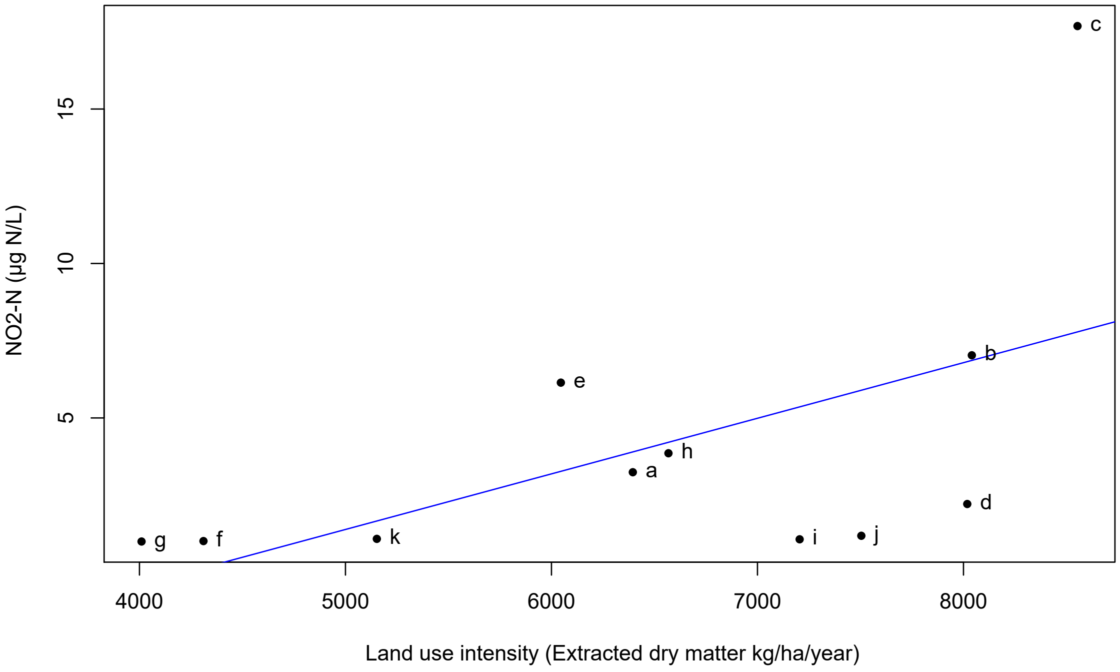


Figure 5.2: Relationship between nitrite (NO_2-N (mg N/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The blue line represents the least squared linear regression line and the points are labelled according to catchment.

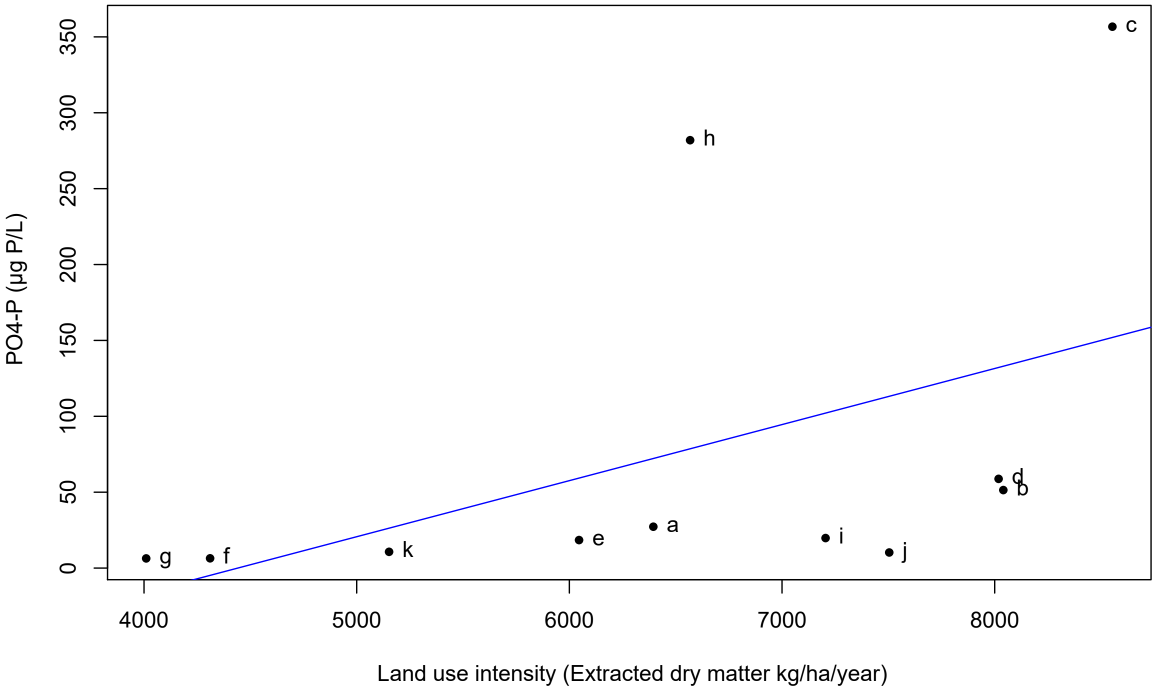


Figure 5.3: Relationship between orthophosphate (PO_4-P (µg P/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The blue line represents the least squared linear regression line and the points are labelled according to catchment.

5.3 Sensitivity of data to outliers

5.3.1 Outlier detection and removal

The data contains some exceptionally high measurements of nitrite, nitrate and orthophosphate. In order to test how sensitive the results are to these outliers they were removed.

Outliers were detected visually from boxplots. Not all outliers of each catchment were removed, rather the very extreme high values. Table 5.2 summarizes the value of all the outliers and shows the day of sampling (which is the same for some of the outliers). Possible explanations of these high measurements can be found in chapter 6.

Table 5.3 and 5.4 show the mean values with and without outliers for nitrite, nitrate and orthophosphate for each catchment. Figure 5.4, 5.5 and 5.6 show the boxplot for each water quality parameter, showing the difference between the dataset containing outliers and the one without. When comparing the boxplots with and without outliers it is important to note the different range of values on the y-axis.

Table 5.2: Overview of all the outliers (value and sampling day) according to catchment and water quality parameter

	Nitrite NO_2-N (µg N/L)		Nitrate NO_3-N (mg N/L)		Orthophosphate PO4-P (µg P/L)	
Catchment	Outlier	Sampling day	Outlier	Sampling day	Outlier	Sampling day
a	15.10	21/07/2015				
c	56.00	10/08/2015	4.82	25/08/2015	1740	10/08/2015
d			3.28	25/08/2015		
h	19.00	21/07/2015			1875	21/07/2015

Table 5.3: Mean water quality parameters with outliers.
In bold the mean values affected by the outliers

Catchment	Nitrite NO_2-N (µg N/L)	Nitrate NO_3-N (mg N/L)	Orthophosphate PO_4-P (µg P/L)
a	**3.24**	1.15	27.26
b	7.03	1.95	51.40
c	**17.69**	**2.23**	**356.71**
d	2.21	**1.72**	58.79
e	6.14	1.44	18.46
f	1.01	0.28	6.43
g	1.00	0.44	6.37
h	**3.86**	0.35	**281.93**
i	1.07	0.62	19.79
j	1.19	0.94	10.27
k	1.09	0.61	10.71

Table 5.4: Mean water quality parameters without outliers.
In bold the mean values affected by the outliers

Catchment	Nitrite NO_2-N (µg N/L)	Nitrate NO_3-N (mg N/L)	Orthophosphate PO_4-P (µg P/L)
a	**1.27**	1.15	27.26
b	7.03	1.95	51.40
c	**11.30**	**1.80**	**126.17**
d	2.21	**1.46**	58.79
e	6.14	1.44	18.46
f	1.01	0.28	6.43
g	1.00	0.44	6.37
h	**1.33**	0.35	**16.42**
i	1.07	0.62	19.79
j	1.19	0.94	10.27
k	1.09	0.61	10.71

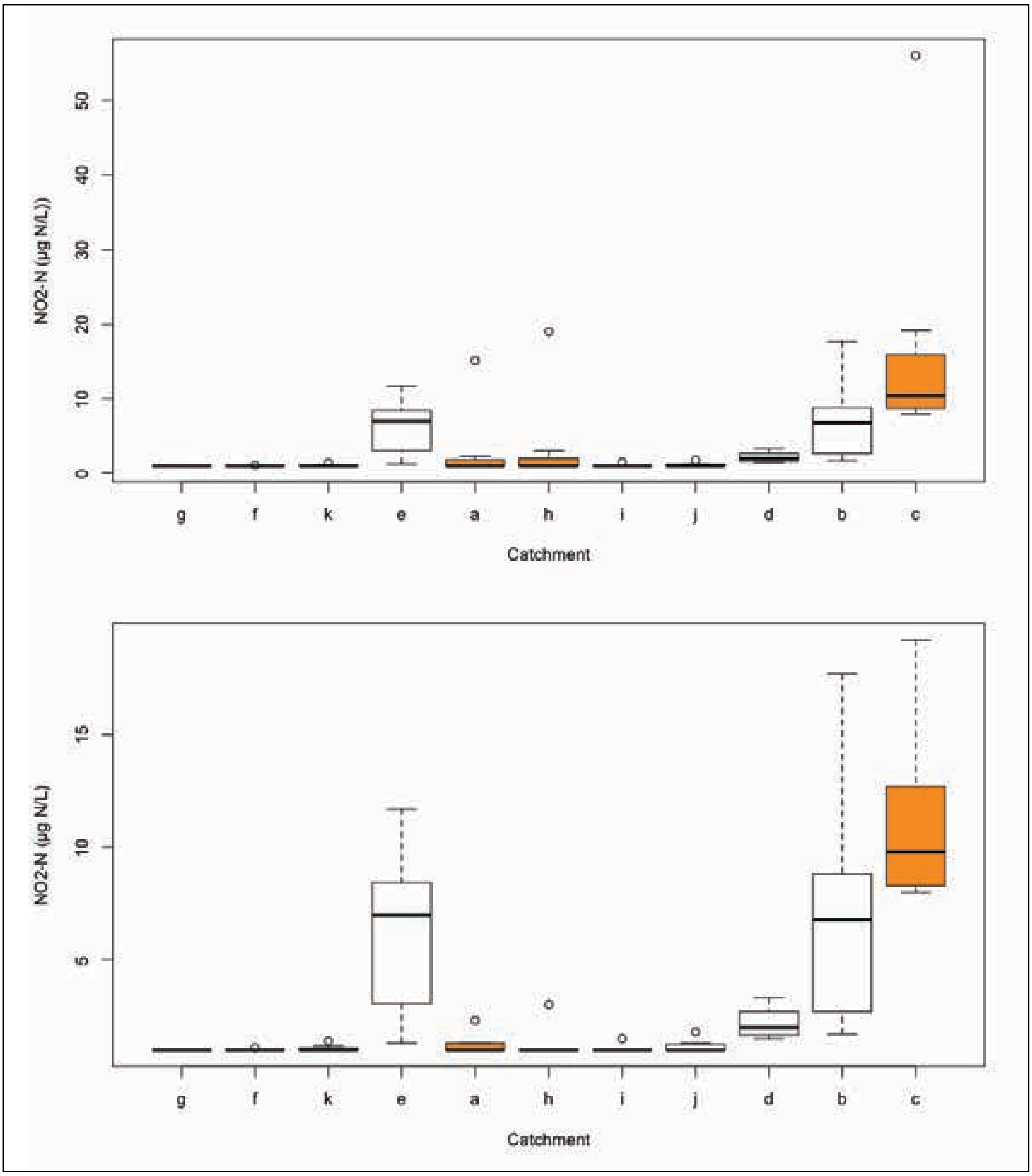


Figure 5.4: Mean nitrite (NO_2-N (µg N/L)) for each catchment (ranked according to mean land use intensity with g having the lowest value). The top boxplot represents the data including all data points, while in the bottom one the outliers have been removed. The catchments where the outliers were removed are marked orange (outliers: a=15.10, c=56.00, h=19.00).

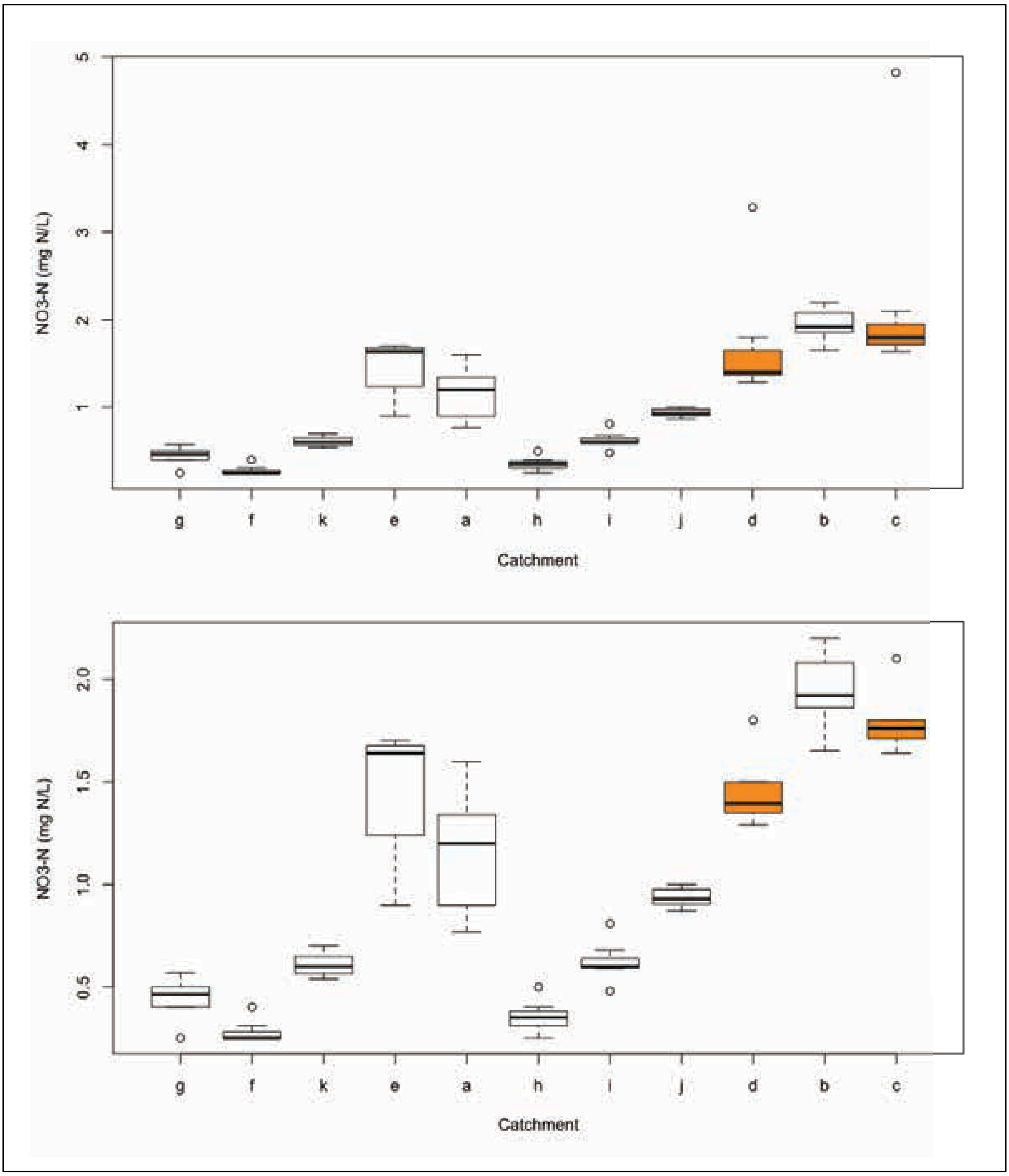


Figure 5.5: Mean nitrate (NO_3-N (mg N/L)) for each catchment (ranked according to mean land use intensity with g having the lowest value). The top boxplot represents the data including all data points, while in the bottom one the outliers have been removed. The catchments where the outliers were removed are marked orange (outliers: c=4.82, d=3.28).

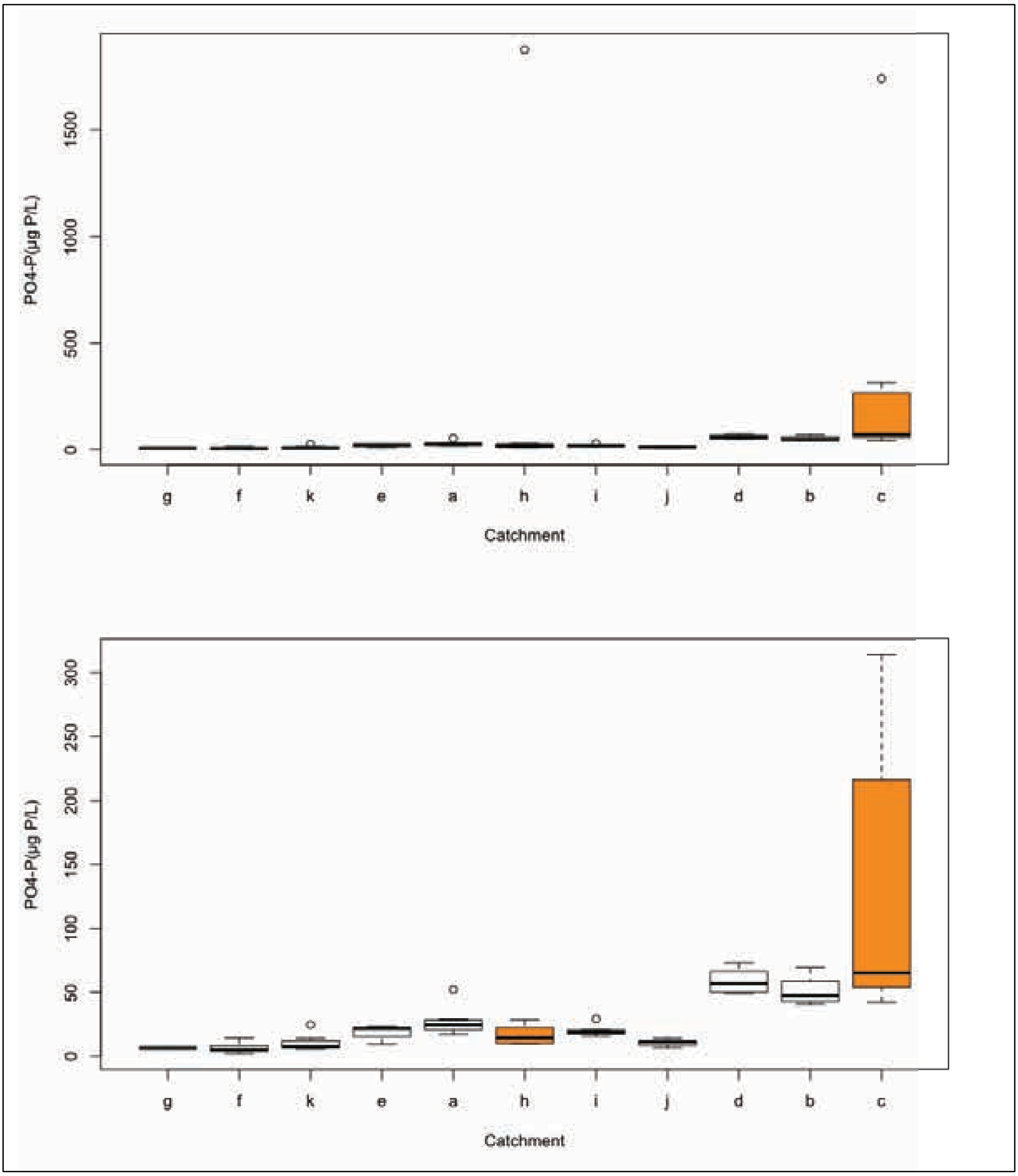


Figure 5.6: Mean orthophosphate (PO_4-P (µg P/L)) for each catchment (ranked according to mean land use intensity with g having the lowest value). The top boxplot represents the data including all data points, while in the bottom one the outliers have been removed. The catchments where the outliers were removed are marked orange (outliers: c=1740, h=1875).

5.3.2 Correlation analysis

After removing the outliers the data were tested for normality. The Shapiro-Wilk test showed that nitrate is normally distributed (W = 0.92, p= 0.34) while nitrite (W= 0.67, p= 3.32 x 10^{-4}) and orthophosphate (W= 0.73, p= 9.98 x 10^{-4}) are not normally distributed.

There is a significant moderate positive correlation between mean land use intensity and nitrite (Spearman's rank rho=0.75, p= 7.28 x 10^{-3} and Kendall's rank correlation tau = 0.64, z = 2.72, p=6.44 x 10^{-3}). There is a significant strong positive correlation for both nitrate (r= 0.74, t = 2881, df = 9, p= 9.41 x 10^{-3}) and orthophosphate (Spearman's rank rho=0.81, p= 2.56 x 10^{-3} and Kendall's rank correlation tau = 0.67, z = 2.88, p= 3.97 x 10^{-3}).

The difference in strength and significance of the correlations between using the data set with and without outliers is summarised in table 5.5 and 5.6. Furthermore these results were visualised using scatterplots (see Figure 5.7 to 5.9).

Table 5.5: Difference between the strength and significance of the correlation between dataset with and without outliers for nitrate

Outliers	Correlation Coefficient	P value
With	0.76	6.23 x 10^{-3}
Without	0.74	9.41 x 10^{-3}

Table 5.6: Difference between the strength and significance of the correlation (Spearman and Kendall rank) between dataset with and without outliers for nitrite and orthophosphate

		Spearman rank		Kendall rank	
Water quality parameter	Outliers	Correlation Coefficient	P value	Correlation Coefficient	P value
Nitrite	With	0.69	0.019	0.56	0.016
	Without	0.75	7.28 x 10^{-3}	0.64	6.44 x 10^{-3}
Orthophosphate	With	0.76	6.23 x 10^{-3}	0.64	6.43 x 10^{-3}
	Without	0.81	2.56 x 10^{-3}	0.67	3.97 x 10^{-3}

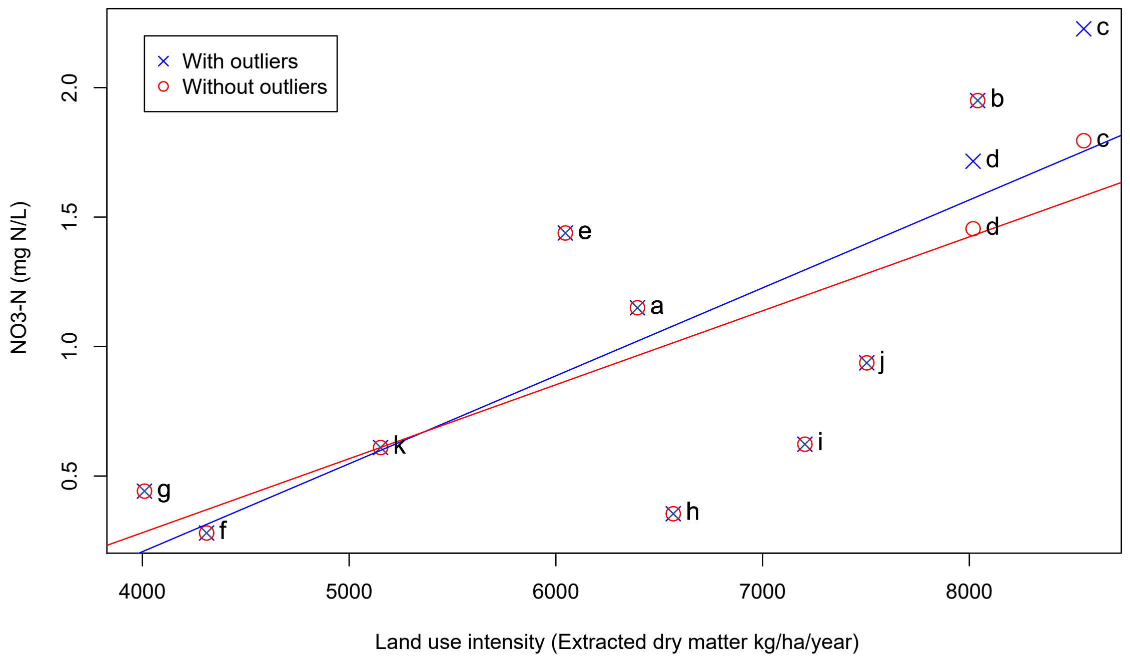


Figure 5.7: Relationship between nitrate (NO_3-N (mg N/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The crosses/circles are labelled according to catchment. The blue crosses represent the mean values of the data set containing the outliers and the blue line represents the least squared linear regression line for these data points. The red circles and line represent the same concept but for the data set where the outliers have been removed.

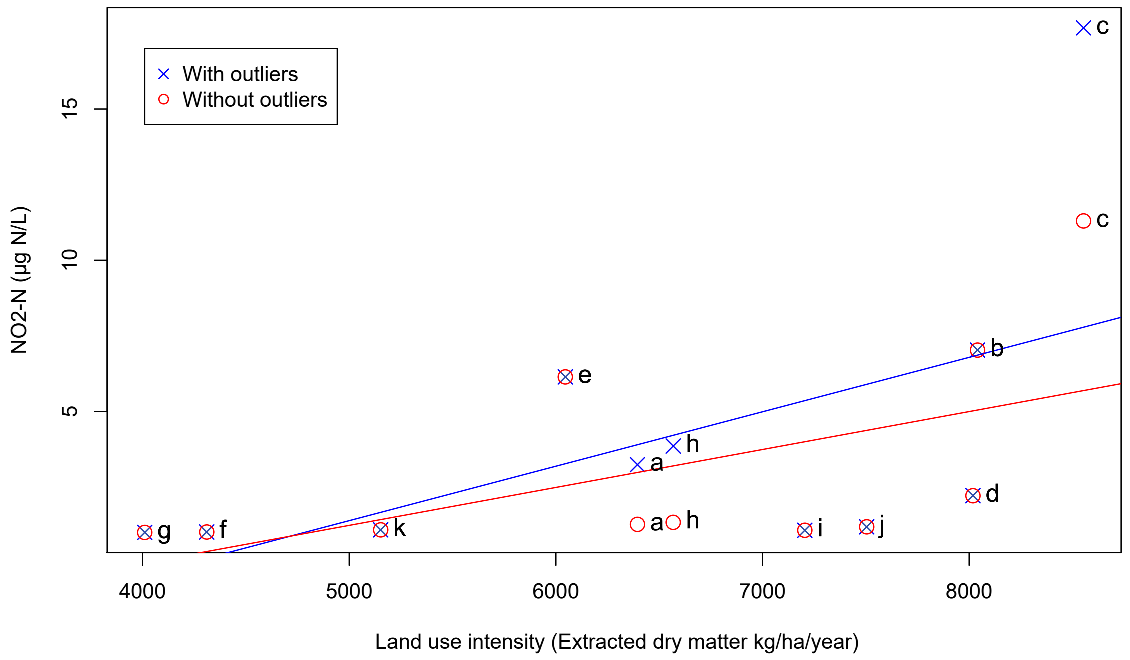


Figure 5.8: Relationship between nitrite (NO_2-N (mg N/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The crosses/circles are labelled according to catchment. The blue crosses represent the mean values of the data set containing the outliers and the blue line represents the least squared linear regression line for these data points. The red circles and line represent the same concept but for the data set where the outliers have been removed.

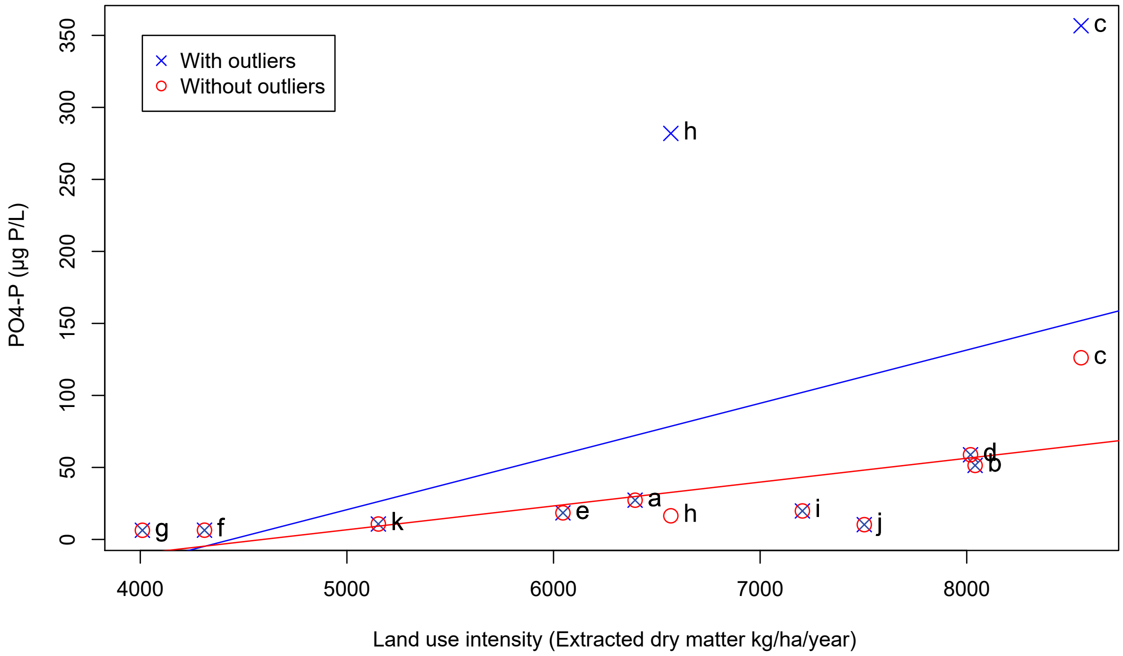


Figure 5.9: Relationship between orthophosphate (PO_4-P (µg P/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The crosses/circles are labelled according to catchment. The blue crosses represent the mean values of the data set containing the outliers and the blue line represents the least squared linear regression line for these data points. The red circles and line represent the same concept but for the data set where the outliers have been removed.

The results show that when removing the outliers there is still a significant correlation between the water quality and land use intensity. For nitrite and orthophosphate the significance of the correlation is marginally stronger while for nitrate there is almost no difference (with: r =0.76, without: r=0.74). Therefore it can be concluded that the outliers have no real impact on the strength and significance of the correlation. The following analysis will consequently use the data containing all data points.

5.4 Correlation according to height of water flow

All measurements were classed according to the height of the flow into low, medium or high. The categories low and medium contain three measurements each, while high contains one. In the following it is tested if the height of the flow affects the correlation between water quality and land use intensity. The section is structured so that the difference between the flow heights is first analysed for nitrate followed by nitrite and orthophosphate.

The data for nitrate were found to have a parametric distribution for low flow (W = 0.92, p= 0.32) and medium flow (W = 0.89, p= 0.13). However high flow data are not normally distributed (W= 0.84, p-value = 0.03). The mean value of the catchments for each flow height and water parameter can be found in appendix B table 1.

There is a significant strong positive correlation for all flow heights: low (r=0.70, t = 2.93, df = 9, p=1.66×10^{-2}) medium (r= 0.76, t = 3.47, df = 9, p= 7.00×10^{-3}) and high (Spearman’s rank rho=0.85, p= 8.36×10^{-4} and Kendall's rank correlation tau = 0.74, z = 3.07, p= 2.11×10^{-3}) (see figure 5.10).

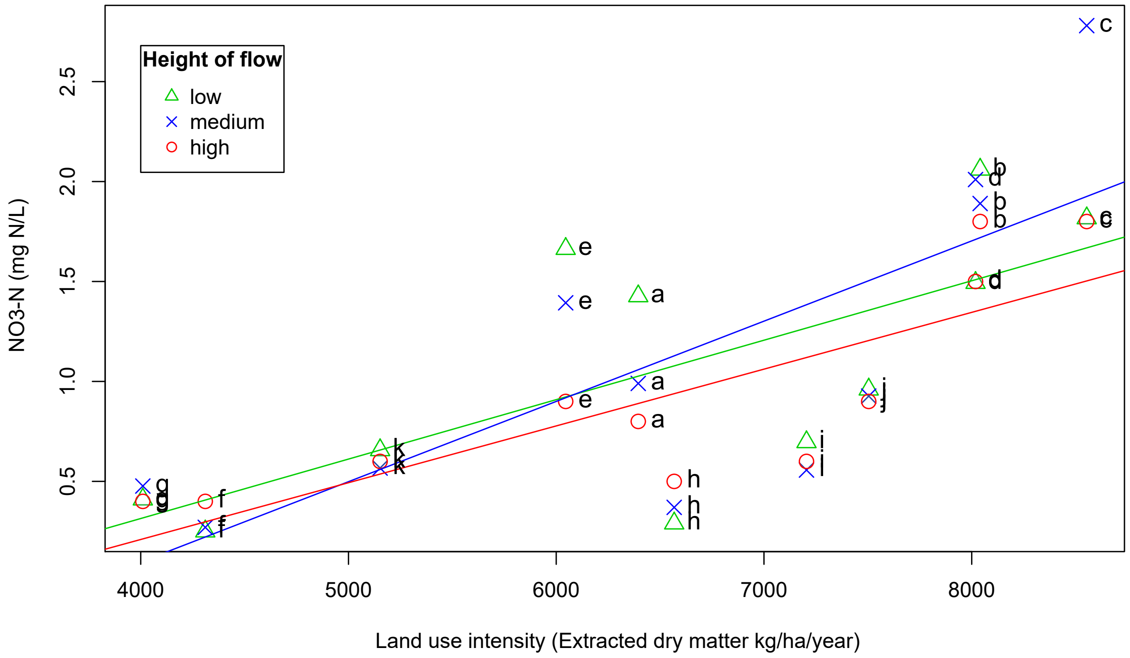


Figure 5.10: Relationship between nitrate (NO_3-N (mg N/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The points are labelled according to the catchment. The green triangles represent the mean value for a given catchment of the data classed as low flow, and the green line represents the least squared linear regression line for these data points. The same concept applies for medium flow (blue) and high flow (red).

The data for nitrite were found to have a non-parametric distribution for all the flow heights: low (W=0.60, p=2.78 x 10^{-5}), medium (W=0.65, p=1.17x 10^{-4}) and high (W=0.51, p=2.22 x 10^{-6}).

Using Kendall's rank correlation there appears to be a moderate positive significant correlation for nitrite at low water flow (Kendall's rank correlation tau=0.48, p=0.04). However Spearman's rank correlation test shows no significant correlation (Spearman's rank rho=0.57, p = 0.07). Kendall's tau is less sensitive to error and discrepancies in data compared to Spearman's rho, and is most accurate with smaller sample sizes (Statistics Solutions, 2016). Therefore it is assumed that for low water flow there is a moderate positive significant correlation. For medium flow there is also a moderate positive significant correlation (Spearman's rank rho=0.63, p= 0.04 and Kendall's rank correlation tau = 0.50, z = 2.05, p= 0.04) as well as for high flow (Spearman's rank rho=0.67, p= 0.03 and Kendall's rank correlation tau = 0.54, z=2.15, p=0.03) (see figure 5.11).

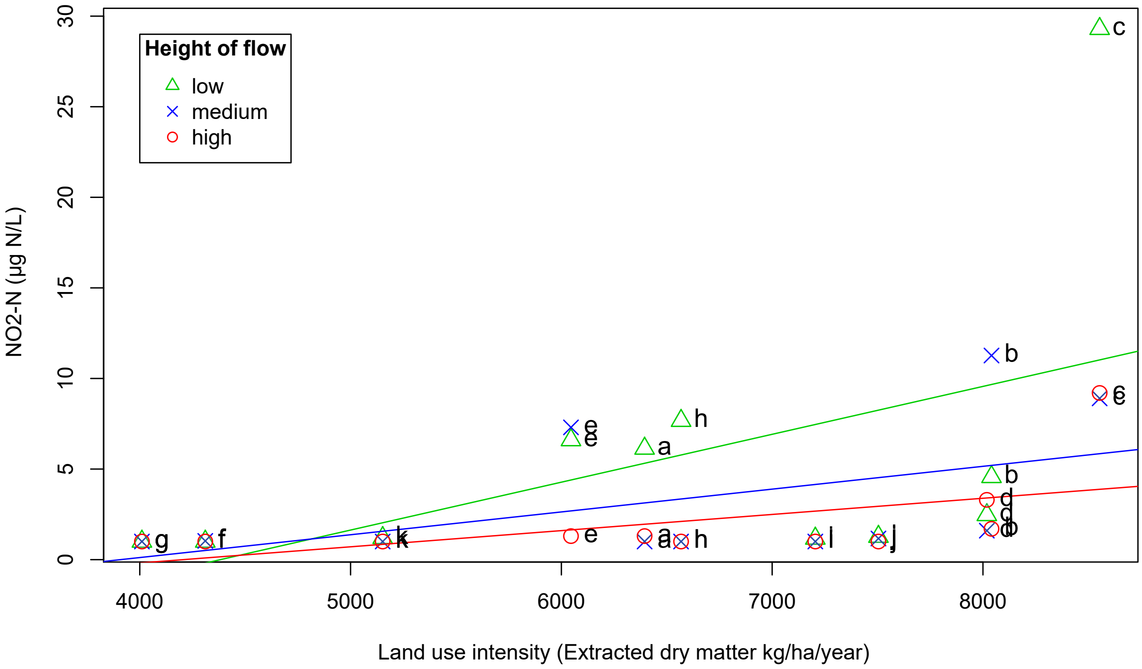


Figure 5.11: Relationship between nitrite (NO_2-N (mg N/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The points are labelled according to the catchment. The green triangles represent the mean value for a given catchment of the data classed as low flow and the green line represents the least squared linear regression line for these data points. The same concept applies for medium flow (blue) and high flow (red).

The orthophosphate data for all the flow heights are non-parametrically distributed: low (W=0.57, p= 5.62 x 10^{-6}), medium (W = 0.63, p= 6.10 x 10^{-5}) and high (W = 0.85, p= 0.04).

There is a moderate positive significant correlation for low flow (Spearman's rank rho=0.72, p=0.01 and Kendall's rank correlation tau = 0.60, z = 2.57, p= 0.01) as well as high flow (Spearman's rank rho = 0.80, p = 3.11x 10^{-3} and Kendall's rank correlation tau = 0.60, z = 2.57, p=0.01). For medium flow there is a strong positive significant correlation (Spearman's rank rho=0.83, p=1.68x 10^{-3} and Kendall's rank correlation tau = 0.67, z = 2.88, p= 3.97 x 10^{-3}) (see figure 5.12).

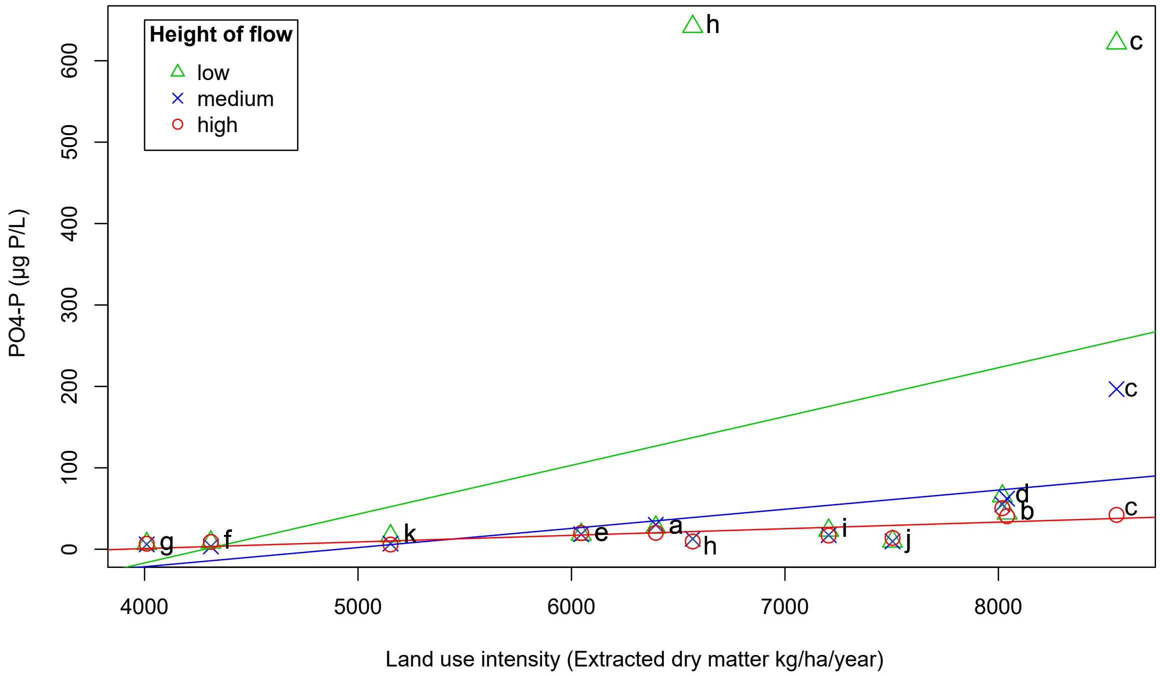


Figure 5.12: Relationship between orthophosphate (PO$_4$-P (µg P/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The points are labelled according to the catchment. The green triangles represent the mean value for a given catchment of the data classed as low flow and the green line represents the least squared linear regression line for these data points. The same concept applies for medium flow (blue) and high flow (red).

The results show that for all water quality parameters and heights of flow there is a moderate to strong positive significant correlation. The strengths of all correlations are summarised in table 5.7. The correlation slightly increases in strength with increasing flow, except for orthophosphate where the low and high flow are both 0.70.

Table 5.7 Strength of correlation for each water quality parameter according to height of flow. Strength of correlation is the mean value of the Spearman's rank rho and Kendall's rank correlation tau, except for nitrate at low and medium flow where it is the r value (Pearson's product-moment correlation)

Water quality parameter	low	medium	high
Nitrite (NO_2-N (mg N/L))	0.52	0.57	0.60
Nitrate (NO_3-N (mg N/L))	0.70	0.76	0.80
Orthophosphate (PO_4-P (µg P/L))	0.70	0.75	0.70

The scatterplots for nitrite and orthophosphate show that the concentration reduces with increasing flow, which can be seen by most individual values and by the regression lines. For nitrate this is also partly true. Although the steepest regression line is the medium flow, most individual values show decreasing concentration with increasing flow, or have very similar values for all flow heights. For the higher mean land use intensity catchments d and c the highest concentrations are for medium. This makes the regression line steeper and intersects with the other regression lines at around 6000 kg/ha/year, compared to 4000/5000 kg/ha/year. Additionally the lower intensity catchments seem to have less variation according to height of flow.

5.5 Correlation according to state of weather

5.5.1 Classification of the data

The data were categorised according to the state of weather. This is based on precipitation data from Schüpfheim. Since all the catchments lie in close proximity it is assumed that they experience the same weather conditions. Table 5.8 shows precipitation within a given time previous to the measurement and is based on hourly precipitation data. Figure 5.13 shows the daily total precipitation. Therefore depending on the time of day the sampling was undertaken, there might have been precipitation e.g. in the last 12 hours. However this might not show up on figure 5.13, since it occurred on the previous day. With the help of this precipitation information the data were categorised into three classes: dry, during rain and after a rainfall event.

Table 5.8: Total amount of precipitation (mm) within a given time previous to measurement and classification of the sampling day

Sampling day	6h	12h	24h	36h	48h	Classification
21/07/2015	0.00	0.00	0.00	1.35	1.35	dry
10/08/2015	0.00	2.28	5.82	8.35	8.90	rain
11/08/2015	0.00	0.27	3.32	5.51	9.14	after rain
16/08/2015	2.23	8.94	19.95	23.62	32.88	rain
25/08/2015	0.00	1.30	13.51	14.32	19.23	after rain
26/08/2015	0.00	0.00	0.00	0.00	13.03	dry
29/08/2015	0.00	0.00	0.00	0.00	0.00	dry

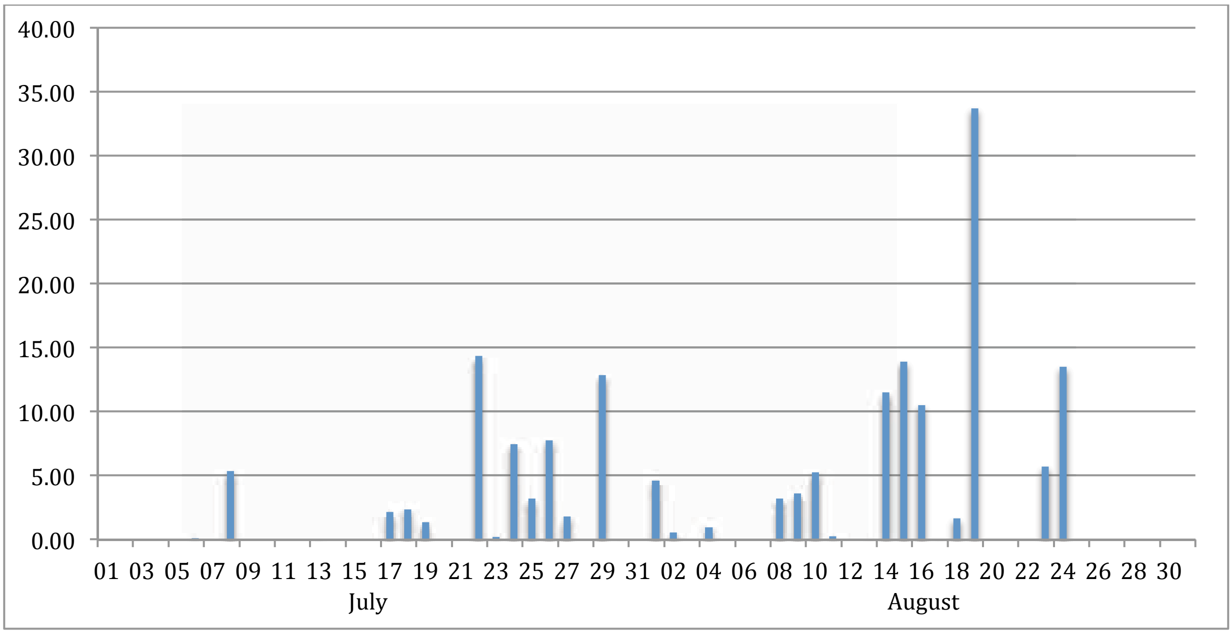


Figure 5.13: Daily precipitation (mm) in Schüpfheim in July and August 2015.

5.5.2 Correlation analysis

The data for nitrate have a parametric distribution for all states of weather: dry (W = 0.92, p= 0.35), rain (W = 0.93, p= 0.42) and after rain (W = 0.87, p= 0.08). The mean values of the catchments for each state of weather and water parameter can be found in appendix B table 2.

There is a significant strong positive correlation for all weather conditions: dry (r= 0.71, t= 3.02, df= 9, p= 1.45 x 10^{-2}), rain (r=0.76, t = 3.49, df= 9, p= 6.85 x 10^{-3}) and after rainfall (r=0.76, t=3.49, df= 9, p=6.81 x 10^{-3}) (see figure 5.14).

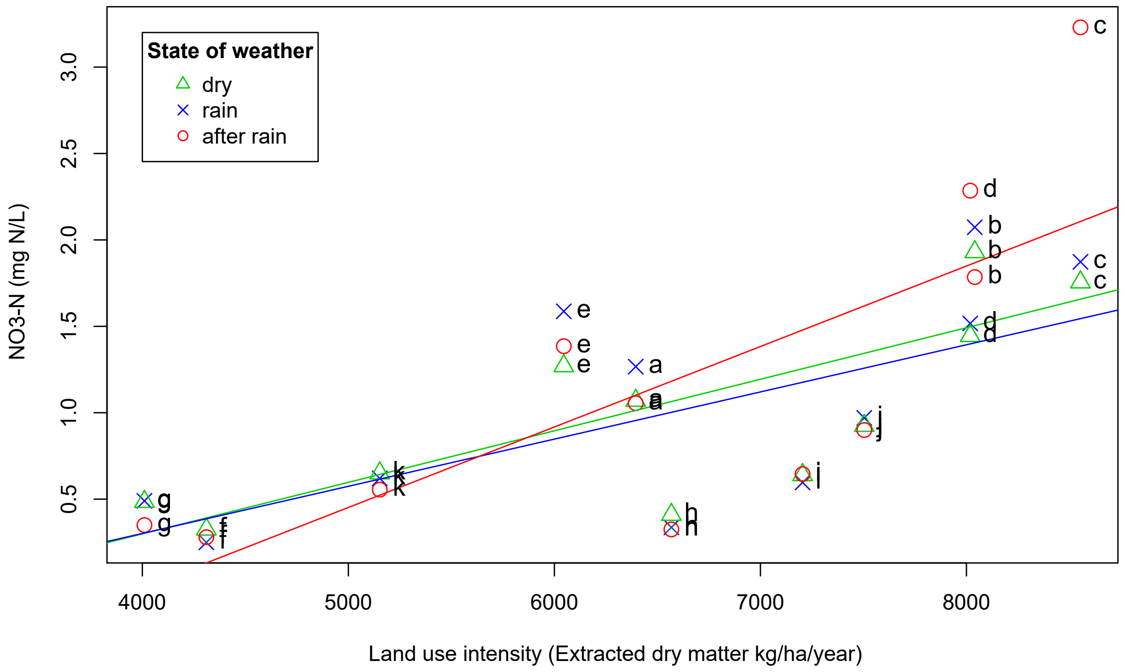


Figure 5.14: Relationship between nitrate (NO_3-N (mg N/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The points are labelled according to the catchment. The green triangles represent the mean value for each catchment of the data classed as dry state of weather and the green line represents the least squared linear regression line for these data points. The same concept applies for rain (blue) and after rain (red).

The data for nitrite were found to have a non-parametric distribution for all states of weather: dry (W=0.80, p= 0.01), rain (W=0.44, p=3.30 x 10^{-7}) and after rain (W=0.63, p=6.72 x 10^{-5}).

There is a moderate positive significant correlation for the dry weather condition (Spearman's rank rho=0.64, 3.47 x 10^{-2} and Kendall's rank correlation tau=0.55, z=2.34, p=1.92 x 10^{-2}), no significant correlation for rain (Spearman's rank rho=0.55, p=7.95 x 10^{-2} and Kendall's rank correlation tau=0.43, z=1.71, p=8.71 x 10^{-2}) and a significant strong positive correlation for after rain (Spearman's rank rho=0.73, p=1.01 x 10^{-2} and Kendall's rank correlation tau =0.64, z=2.68, p=7.43 x 10^{-3}) (See figure 5.15).

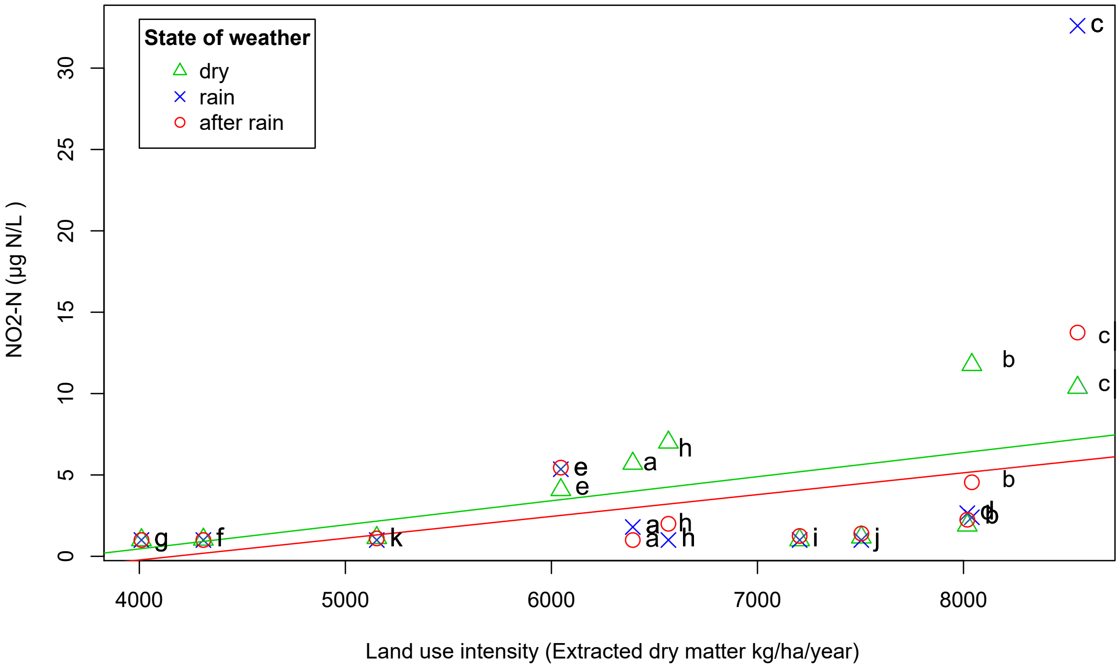


Figure 5.15: Relationship between nitrite (NO_2-N (mg N/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The points are labelled according to the catchment. The green triangles represent the mean value for each catchment of the data classed as dry state of weather and the green line represents the least squared linear regression line for these data points. The same concept applies for rain (blue) and after rain (red), although for rain there is no regression line since no significant correlation was found.

The data for orthophosphate were found to have a non-parametric distribution for all states of weather: dry (W = 0.51, p= 2.22 x 10^{-6}), rain (W = 0.39, p= 8.36 x 10^{-8}) and after rain (W=0.66, p= 1.28 x 10^{-4}).

For the dry weather state there is a moderate positive significant correlation (Spearman's rank rho=0.71, p= 1.46 x 10^{-2} and Kendall's rank correlation tau =0.56, z=2.41, p=1.58 x 10^{-2}). For rain and after rain there is a significant positive strong correlation: rain (Spearman's rank rho=0.82, p= 2.08 x 10^{-3} and Kendall's rank correlation tau =0.64, z = 2.72, p=6.43 x 10^{-3}) and after rain (Spearman's rank rho=0.85, p= 8.06 x 10^{-4} and Kendall's rank correlation tau =0.67, z = 2.88, p= 3.97 x 10^{-3}) (see figure 5.16).

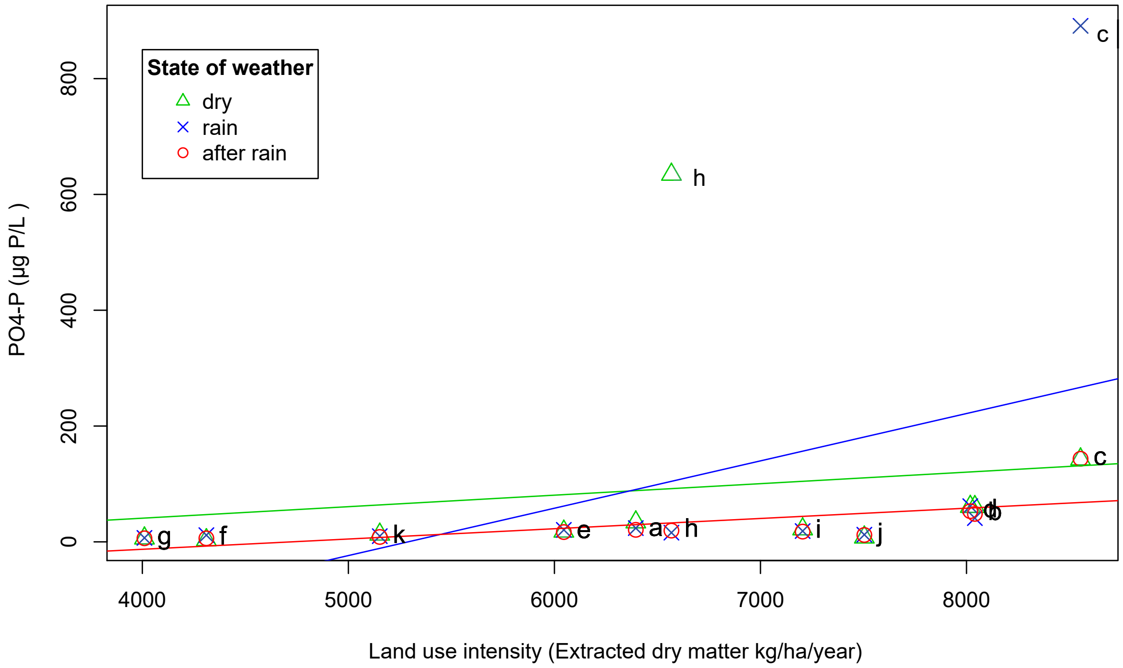


Figure 5.16: Relationship between orthophosphate (PO_4-P (µg P/L)) and mean land use intensity (Extracted dry matter kg/ha/year). The points are labelled according to the catchment. The green triangles represent the mean value for each catchment of the data classed as dry state of weather and the green line represents the least squared linear regression line for these data points. The same concept applies for rain (blue) and after rain (red).

The strength of the correlation is generally weaker for the dry state compared to rain and after rain (see table 5.9). The exception is nitrite, where there is no significant correlation for rain. However for after rain the correlation is stronger compared to dry, but the steepness of the regression lines is roughly the same. The steepest regression line for orthophosphate is during rain and for nitrate after rain.

Table 5.9: Strength of correlation for each water quality parameter according to state of weather. Nitrate is expressed in the r value (Pearson’s product-moment correlation test) while the mean value of Spearman’s rank rho and Kendall's rank correlation tau is used for nitrite and orthophosphate

Water quality parameter	Dry	Rain	after rain
Nitrite (NO_2-N (mg N/L))	0.59	0.43*	0.68
Nitrate (NO_3-N (mg N/L))	0.71	0.76	0.76
Orthophosphate (PO_4-P (µg P/L))	0.64	0.73	0.76

*Correlation is not significant $p>0.05$

6 Discussion

This chapter interprets the results presented in chapter 5 in relation to the aims and objectives of this dissertation. Firstly the impact of agriculture on water quality in UBE is discussed. Then the water quality status (according to classification of the Swiss Environmental Department) is described and possible explanations for very high nutrient values are given. Lastly the statistical methods are evaluated and limitations of the study are presented.

6.1 The impact of agriculture on water quality

This part looks at how far the results support the initial assumption that agriculture has a negative impact on water quality. The results support this statement since almost all correlation analysis found a significant moderate to strong positive correlation between water quality and mean land use intensity. The exception is nitrite for state of weather rain, where the p value is slightly above the significant threshold value of $p<0.05$.

Both the correlation analysis and the differences in correlation between states of weather support this assumption. These differences can be explained in the light of pathways and processes of nutrient delivery depending on the type of source (as described in literature review).

The strength of the correlation is generally slightly weaker for the dry weather state compared to rain and just after rain. Although nitrate during rain forms an exception (there is no significant correlation) after rain has a slightly stronger correlation than dry.

These results could indicate that in the lower intensity catchments the addition of water leads to dilution, while for the higher intensity catchments N and P are washed out of the ground leading to higher concentrations in streams. This should be visible as a steeper regression line. In the case of linear relationships the strength of correlation is represented in the steepness of the simple linear regression line as well as how widely the points are scattered around the line.

In the case of orthophosphate the steepest regression line is rain and for nitrate it is after rain. This could be an indicator of the different pathways nitrogen and phosphorus take, and the difference in delivery time of nutrients. As stated in chapter 3 P is predominantly transported via surface runoff, which leads to flashy responses to rainfall events. N is more often transported via subsurface flow leading to a time delay and less flashy response of delivery. Therefore for nitrate the steepest regression line is for after rain, since the impact of agriculture is felt the most at that time. The individual values mostly support this as well: while for g, f, and k after rain has the lowest concentration, for c and d it is the highest (b the highest is rain). The steepest regression line for orthophosphate is during rain, reflecting the fact that the response is quicker, so the impact of agriculture is felt most strongly during that weather state. Hence the steepness of the two regression lines confirm that diffuse agriculture is the main source. However compared to nitrate and nitrite the individual catchment values for orthophosphate show little variation between the states. Furthermore for nitrite during rain there is no correlation and the highest nutrient concentrations are during the dry state. These lower concentrations during rain and after rain could indicate the main source is a point source, due to the dilution effect.

This assumption is supported by the difference in nutrient concentration according to river height: the higher the flow the lower the nutrient concentration. The regression lines for nitrite and orthophosphate are the steepest for low flow. However they seem to be strongly influenced by the outlier(s). Nevertheless the strength of the correlation increases with height of flow. Hence if the main source were from a point source, there would probably be no significant correlation between land use intensity and nutrient concentration. It is possible that even when the main source is diffuse there is a dilution effect. The high flow is only from one measurement. Previously it had been exceptionally dry for a long period and after 3 days of rain the flow in some streams was substantially higher and contained many small particles. Therefore the nutrients were possibly in particle form, which was not measured. Another explanation could be that the input from agriculture is minimal in summer. As stated in the literature review, nutrient levels build up in the soil during summer and are washed out with increasing precipitation in autumn and winter. Furthermore this is the period after harvest, when the ground is often left bare. Therefore the nutrient concentration increases with increased erosion. Consequently the nutrient concentration in the stream is low, which makes desorption of P from the sediments more likely (Edwards and Withers, 2008; Palmer-Felgate, 2009).

All sampling was done during summer, which is according to the climate diagram presented in chapter 3, the time of highest mean monthly precipitation. However the summer the sampling was undertaken it was exceptionally dry for a long period. As no data was collected on how saturated the soil is, it can only be assumed that the soils were very dry. Therefore the contribution from agriculture is small during the sampling period. Hence although rainfall events mean an increase in nutrient concentration in the short run, at lower flows there is a dilution effect, since N and P are stored in the soil. Furthermore due to the lower nutrient concentration during summer compared to autumn and winter, there might be desorption of P from the steam bed. This would mean the source of P is more consistent, so that additional water leads to dilution.

These explanations are however just possible interpretations and it cannot be said with certainty why these patterns emerged and if they are really linked to the nutrient input from agriculture. Furthermore the difference in strength of correlation between the height of flow/state of weather is not very large. Nonetheless in conclusion it can be said that since there was a significant moderate to high correlation for 23 out 24 correlation tests, there is clear evidence that intensive agricultural land use has a negative impact on water quality.

6.2 Water quality status and possible explanations of outliers

The water quality status (according to classification of the Swiss Environmental Department) for all water parameters was high or good in all catchments except c and h. Therefore all the streams excluding c and h meet the EU water framework directive objective of good chemical status of surface waters. Catchment c had the highest values for all 3 parameters and P was exceptionally high and achieved bad water quality status. Nitrate ranked as good, while the value of nitrite was ranked as good, but a slightly higher value would classify as moderate. These higher nutrient concentrations could be due to the catchment having the highest mean land use intensity or to the location of the sample point. It was very near a dairy farm, so it is possible that these very high values were only in that location and do not represent the whole catchment. Further implications of these high values will be discussed in the next chapter.

The bad water quality status of h regarding P is linked to one outlier. The mean value for P without the outlier would achieve high water quality status. Catchment h contains another outlier (nitrite), which is from the same water sample. While orthophosphate and nitrite are exceptionally high, nitrate (<0.25 mg N/L) lies below the average of 0.35 mg N/L. Sampling was done during a dry period. The water when collected was cloudy and contained many small particles. On all other days the water was clear and contained no particles. A possible source could be a farm which lies very near the stream and around 200m upstream of the sampling point. A possible explanation is that the barnyard or cowshed was washed that morning supplying particles and water with high quantities of nutrients. Another explanation is that pipes which are used to apply manure and fertiliser were washed and the wastewater ran into the stream. According to local farmers, cleaning the pipes by laying them in the stream used to be common practice. However this is now illegal and appears to have been discontinued.

Although this seems a plausible explanation, it is also possible that the measurement is wrong. There are many possible sources of error, which were all mentioned in chapter 3. For example the sample was stored for more than 24h, so there might have been interaction between particles and the water.

Another outlier is in catchment a: nitrite at 15.60 µg N/L (mean value: 3.24 µg N/L). The value for nitrate of the same water sample is the highest measurement at that location, while orthophosphate is just slightly above average. The water however did not appear distinctly different from other sampling days. The flow was slightly lower than on other days, which could indicate a reduced dilution effect. Furthermore the stream runs through the village of Hasle and a machine construction company is a few meters from the sampling point. As stated in chapter 2, settlements contribute nitrate in various ways. A possible explanation could be runoff from a construction site in Hasle. Although no construction site was observed, it could lie somewhere else in the catchment. Throughout the sampling period, there were various major road works mainly along the main road running through the reserve, especially in Schüpfheim.

There are two outliers for catchment c, which are from the same water sample: Nitrite (56.00 µg N/L) and orthophosphate (1740 µg P/L). The nitrate value lies at 1.7 mg N/L below the average. On the day of sampling the water was cloudy and contained small particles. Catchment c has the highest mean land use intensity and percentage land use for cropland, hayfield or pasture (75.49%). Since this sample was taken during a rainfall event, it is possible that due to high agricultural land use, high quantities of P and N were washed into the stream.

Catchment c has another outlier: nitrate at 4.82 mg N/L. In this water sample both nitrite (8.3 µg N) and orthophosphate (216.4 µg P/L) were well above the mean values of the data without outliers (1.27 µg N and 27.26 µg P/L). Sampling took place after a rainfall event. Another outlier was observed on the same day, but for catchment d. d has the 3rd highest land use intensity, and the 2nd highest agricultural land cover (73.40 %).
Therefore both the c and d outliers could be linked to agricultural land use. While for catchment d nothing particular was observed that day, directly beside the sampling point for c cows were grazing and the field was full of manure. Additionally the water sample contained few and very small particles. It could therefore be possible that due to the animals being very near the stream N concentrations were higher.

Although all these outliers could be due to measurement errors and it cannot categorically be said why they occurred, the explanations seem plausible. They would also support the findings from the correlation test that agriculture has a negative impact on water quality.

6.3 Evaluation of methods and study limitations

Although correlation does not automatically imply causality, the correlation analysis has been proven to be successful in suggesting a link between agriculture and water quality. The chosen catchments provided a wide range of mean land use intensities allowing for an effective correlation analysis. Furthermore the data obtained is insensitive to outliers as they hardly have an impact on the strength and significance of the correlation.

Although some studies use the test of difference between high and low intensity land use catchments, correlation analysis is the best option for the UBE. Comparison would have been unfeasible, as accessing the very low intensity areas is so difficult that it would not have been possible to do all sampling during one day. This is important so that differences of nutrient concentration can be linked to land use and not to different states of weather/flow. Furthermore the UBE was more interested in obtaining water quality data in the valley, where the water quality is possibly not as desired.

However there are some limitations. The number of sampled catchments is not very large. Increasing the amount of catchments would have made the statistical results more reliable. More importantly the number of sampling days poses some limitations. When the data was put into categories according to the factor state of weather or height of flow, it meant that each category comprised either two or three measurements, for high flow only one. Just one measurement is not representative of all the high flow conditions, so it is unclear how reliable the results are. Furthermore in a few categories that contained three measurements two of them were outliers. Although all the data was insensitive to outliers, it is possible that when there are fewer data points the outliers have an impact on the correlation.

The categorising according to the weather condition itself was however useful in detecting differences in correlation. The data from the weather station in Schüpfheim, on which the categorisation is based, is reliable. However as seen in chapter 3, there is some variation in the annual precipitation within the sampling area ranging from 1400 to 1700 mm a year. Since the precipitation data was however only used as a guide to make the classification, this does not impact the results.

The categorisation according to height of flow has some limitations. The visual estimation of flow is very subjective. Furthermore using categories does not allow testing for correlation between flow and concentration. However measuring the flow each time in each stream would have meant considerable time investment. Although it would provide great understanding of the relationship between flow and nutrients, the main aim of the dissertation was not to examine influences of weather events and flows on nutrient concentration but the impacts of land use on water quality. Data on flow and state of weather are secondary variables that are helpful to understand nutrient processes and pathways in order to support the findings of the test of correlation.

Further limitations arise from what was not measured in this study such as instream processes. Only soluble nutrients were measured. The quantities of N and P in particles are unknown, which means we do not have a full picture of all nutrients in the stream. Nothing is known about desorption/absorption from sediment or uptake of nutrients by plants. Furthermore the study looks at very small catchments and streams. So what are the implications of the results on the wider area? This will be discussed in the next chapter.

Finally all sampling was done during summer. Since seasonality is important when studying impact of land use on water quality, sampling would ideally take place over a whole year. This however is beyond the scope of a dissertation.

In conclusion it must be said that although it is important to note that there are many limitations to the methods (some which arise from being beyond the scope of a dissertation), they do not appear to profoundly undermine the results.

7 Conclusion

The over-enrichment of nutrients (mainly nitrogen and phosphor) in oceans, lakes and rivers is a major environmental problem worldwide. Not only does it negatively impact aquatic species it also adversely affects industry, agriculture and human health. In Europe one of the major sources of nutrients is from agriculture as many studies show. This is also true in Switzerland, especially central Switzerland due to high livestock densities. The agriculture in the UNESCO biosphere Entlebuch (UBE) is known to be unsustainable, too intensive and it has a negative impact on the biodiversity. As no data is available on water quality in the UBE, the aim of this study was to analyse the water quality in different catchments and investigate the impact of agricultural land use on water quality. The results show that in most streams the water quality is classified as good or high, so the objective of the EU water framework directive of achieving good chemical status of surface waters is met. One catchment however does not achieve good chemical status and the implications of this will be discussed shortly. Although overall the water quality is good, the study shows that there is a relationship between the mean land use intensity and the water quality. With increasing intensive agricultural land use in the catchments the water quality decreases. This study therefore supports what previous research found, namely agriculture has a negative impact on water quality.

This study's research is however on a local scale since the sampled catchments are small. So how can the results of this study be scaled up; what are the wider implications? Since most tributary streams have a good water quality status, there are no negative impacts on the streams themselves or on Kleine Emme, the main river running through the UBE. However catchment c had higher nutrient concentrations, especially for orthophosphate. This possibly causes localised negative impacts on the stream ecosystem. Whether these extreme values are due to the sampling location or to high intensity land use within the catchment is unclear. However from the correlation analysis it is clear that higher mean land use intensity negatively influences the water quality. It is therefore likely that catchments in the UBE with same mean land use intensities will have similar nutrient concentrations in their streams. The input of nutrients from many tributaries into the main river might lead to high nutrient concentration due to accumulation. However it is also very likely that it will have little impact: Headwater streams and tributaries draining low-intensity land use catchments also run into the Kleine Emme. These streams are expected to have very low concentrations, probably leading to dilution of nutrients. This second scenario seems more likely. Although there is no water quality data available from Kleine Emme within the UBE, there is a measuring station around 20 km further downstream. There the annual mean water quality achieves good status (UWE, 2015).

Only assumptions can be made about further implications. Therefore further research would be needed to address this issue. A suggestion is to increase the number of sampled tributaries as well as analyse the water quality in Kleine Emme at various points in the UBE. Additional sampling should be carried out over a longer time period. This study took water samples during July and August 2015, and June and July were exceptionally dry. The impact of agriculture on water quality varies throughout the year. While in summer the impact is usually limited, after harvest the impact increases and is usually highest during autumn and winter. Ideally research should therefore take place over at least a year.

Although overall the water quality is good, the results clearly show the relationship between agricultural land use and water quality. Therefore the water quality could be improved and it is known intense agricultural land use also has negative impacts on biodiversity in the UBE

(Knaus, 2015). Possible solutions should target the intense agricultural land use and would therefore address both these issues. Decreasing the intensity of land use is however difficult to achieve. Farmers would have to decrease the manure applied, which can only be achieved by reducing livestock. This would mean a reduction in income due to reduced production output as well as direct subsidies received (Knaus, 2011). Another alternative is increasing the area of set-asides and the number of organic farms. Although there are many challenges associated with these two options, the area of set aside and number of organic farms is relatively low in the agricultural region of the UBE (Knaus, 2001). Therefore there is room for improvement.

References

Allan, J. (2007) *Stream Ecology: Structure and function of running waters*. Dordrecht, Netherlands: Springer.

Arshad, M., Lowery, B.and Grossman, B. (1996) Physical Tests for Monitoring Soil Quality. In: Doran J.W., Jones A.J., editors. *Methods for assessing soil quality*. Madison, WI., 123-41.

Atlas of Switzerland (2016) *precipitation: information*.Wabern: Swiss Federal Office of Topography.

Bartram, J. and Ballance, R. (1996) *Water quality monitoring: a practical guide to the design and implementation of freshwater quality studies and monitoring programmes*, 1st edition. London: New York: E & FN Spon.

Bu, H., Meng, W., Zhang, Y. and Wan, J. (2014) Relationships between land use patterns and water quality in the Taizi River basin, China. *Ecological Indicators*, 41, 187-197.

Bundesamt für Meteorologie und Klimatologie MeteoSchweiz (2014) *Klimanormwerte Langnau i.E.-Normperiode 1981−2010.*
Available at: http://www.meteoschweiz.admin.ch/product/output/climate-data/climate-diagrams-normal-values-station-processing/LAG/climsheet_LAG_np8110_d.pdf
[Last accessed: 25/03/16]

Bundesamt für Umwelt BAFU (2012) *Einzugsgebietgliederung Schweiz* EZGG-CH

Bundesamt für Wasser und Geologie (2005) *Berichte des BWG*, Serie Wasser Nr.7, Bern, Switzerland.

Carpenter, S., Caraco, N., Correll, D., Howarth, R., Sharpley, A. and Smith, V. (1998) Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen. *Ecological Applications*, 8(3), 559-568.

Chapman, D. (ed), (1996) *Water Quality Assessments - A Guide to Use of Biota, Sediments and Water in Environmental Monitoring*, 2nd edition. London: Chapman and Hall.

Clifford, N., French, S. and Valentine, G. (2010). *Key methods in geography (2nd ed.)* Los Angeles: Calif., London: SAGE.

Davie, T. (2008) *Fundamentals of hydrology*, 2nd edition. Abingdon, Oxon: Routledge.

Dodds, W. (2002) *Freshwater ecology: concepts and environmental applications*. San Diego: Academic Press.

Edwards, A. and Withers, P. (2008) Transport and delivery of suspended solids, nitrogen and phosphorus from various sources to freshwaters in the UK. *Journal of Hydrology*, 350(3), 144-153.

EU (2000) The Water Framework Directive. Establishing a framework for community action in the field of water policy. *Official Journal of the European Communities* L, 327 (1)
Available at: http://eur-lex.europa.eu/resource.html?uri=cellar:5c835afb-2ec6-4577-bdf8-756d3d694eeb.0004.02/DOC_1&format=PDF
[Last accessed: 28/03/16]

Gemeinde Verband Sempachersee (2015) *Phosphorprojekt am Sempachersee*
Available at: http://www.sempachersee.ch/phosphorprojekt.html
[Last accessed: 22/03/16]

Harmel, R., Cooper, R., Slade, R., Haney, R. and Arnold, J. (2006) Cumulative uncertainty in measured streamflow and water quality data for small watersheds. *American Society of Agricultural and Biological Engineers*, 49(3), 689-701.

Hem, J. (1985) *Study and interpretation of the chemical characteristics of natural water*, Reston, Va.: Dept. of the Interior, U.S. Geological Survey; Alexandria, VA: Dept. of the Interior, U.S. Geological Survey.

Jarvie, H., Withers, J. and Neal, C. (2002) Review of robust measurement of phosphorus in river water: sampling, storage, fractionation and sensitivity. *Hydrology and Earth System Sciences*, 6(1), 113.

Jarvie, H., Withers, P., Hodgkinson, R., Bates, A., Neal, M., Wickham, H. D., Harman, S. and Armstrong, L. (2008a) Influence of rural land use on streamwater nutrients and their ecological significance. *Journal of Hydrology*, 350(3-4), 166-186.

Jarvie, H., Haygarth, P., Neal, C., Butler, P., Smith, B., Naden, P. and Palmer-Felgate, E. (2008b) Stream water chemistry and quality along an upland–lowland rural land-use continuum, south west England. *Journal of Hydrology*, 350(3), 215-231.

Jarvie, H., Withers, P., Bowes, M., Palmer-Felgate, E., Harper, D., Wasiak, K., Wasiak, P., Hodgkinson, R., Bates, A., Stoate, C., Neal, M., Wickham, H., Harman, S. and Armstrong, L. (2010) Streamwater phosphorus and nitrogen across a gradient in rural–agricultural land use intensity. *Agriculture, Ecosystems and Environment*, 135(4), 238-252.

Jiang, R., Woli, K., Kuramochi, K., Hayakawa, A., Shimizu, M., and Hatano, R. (2010) Hydrological process controls on nitrogen export during storm events in an agricultural watershed. *Soil Science and Plant Nutrition*, 56(1), 72-85.

Knaus, F. (2011) *Monitoring der Natur und Landschaft in der UNESCO Biosphäre Entlebuch. Interner Bericht*, Regionalmanagement UBE, Schüpfheim. unpublished

Knaus, F. (2015) *Die räumliche Verteilung ökologischer, landschaftlicher und gesellschaftlicher Werte und Gefahren für diese Werte in der UNESCO Biosphäre Entlebuch*. Interal Report, Schüpfheim and Zürich: Biosphärenmanagement and ETH Zürich.

Lal, R. and Shukla, M. (2004) *Principles of Soil Physics*, New York: Marcel Dekker, Inc.

Langmeier, M. (2012) *Bestimmung von Nitrit mittels Photometrie*, eawag standard operating procedure 77-08-1

Langmeier, M. (2015) *Bestimmung von ortho-phophate mittels Photometrie mit wenig Probevolumen*, eawag standard operating procedure 77-0x-1

Langmeier, M. and Freudemann, D. (2014) *Bestimmung von Chlorid, Nitrate und Sulfat mittels Ionenchromatographie*, eawag standard operating procedure 77-02-1

Liechti, P. (2010) *Methoden zur Untersuchung und Beurteilung der Fliessgewässer. Chemisch-physikalische Erhebungen, Nährstoffe.* Umwelt-Vollzug Nr. 1005. Bern: Bundesamt für Umwelt.

Monaghan, R., Wilcock, R., Smith, L., Tikkisetty, B., Thorrold, B. and Costall, D. (2007) Linkages between land management activities and water quality in an intensively farmed catchment in southern New Zealand. *Agriculture, Ecosystems and Environment*, 118, 211–222.

Palmer-Felgate, E. J., Jarvie, H. P., Withers, P. J. A., Mortimer, R. J. G. and Krom, M. D. (2009) Stream-bed phosphorus in paired catchments with different agricultural land use intensity. *Agriculture, Ecosystems and Environment*, 134(1), 53-66.

Petry, J., Soulsby, C., Malcolm, I. and Youngson, A. (2002). Hydrological controls on nutrient concentrations and fluxes in agricultural catchments. *Science of the Total Environment*, 294(1), 95-110.

R Core Team (2014). *R: A language and environment for statistical computing*. R Foundation for Statistical Computing, Vienna, Austria. URL
http://www.R-project.org/

Reedyk, S. and Forsyth, A. (2006) *Using field chemistry kits for monitoring nutrients in surface water*. Agriculture and agri-food Canada- PFRA
Available at: http://www5.agr.gc.ca/resources/prod/doc/terr/pdf/FieldChemKits_e.pdf
[Last accessed: 19/02/16]

Rockström, J., Steffen, W., Noone, K., Persson, A., Chapin, F., Lambin, E. and Foley, J. (2009). A safe operating space for humanity. *Nature*, 461(7263), 472-5.
Schlunegger, F. (2006) *Geologie und Geomorphologie des Entlebuchs – eine kleine Landschaftsgeschichte*
Available at: http://www.geo.unibe.ch/news/presse/Brattig_06b.pdf
[Last accessed on: 25/03/16]

Statistics Solutions (2016) *Kendall's Tau and Spearman's Rank Correlation Coefficient*
Available at: http://www.statisticssolutions.com/kendalls-tau-and-spearmans-rank-correlation-coefficient/
[Last accessed on: 15/03/16]

UBE (2006) *Zonierung UNESCO Biosphäre Entlebuch*
Available at: http://files.pxlpartner.ch.s3-eu-west-1.amazonaws.com/66417?CFID=b8d4418c-186b-48fa-a127-68d26dc6cb71&CFTOKEN=0
[Last accessed on: 25/03/16]

UBE (2016) *Zonierung*
Available at: http://www.biosphaere.ch/de/natur-landschaft/zonierung
[Last accessed on: 25/03/16]

UNESCO (2016) *Biosphere Reserves – Learning Sites for Sustainable Development*
Available at: http://www.unesco.org/new/en/natural-sciences/environment/ecological-sciences/biosphere-reserves/
[Last accessed on: 25/03/16]

UWE (2015) *Chemische Wasserqualität - Standort: 307: Kleine Emme Werthenstein*. Kanton Luzern
Available at: https://uwe.lu.ch/-/media/UWE/Dokumente/Dienstleistungen/Umweltzustand/Wasserqualitaet/wasserqual_chem_307.pdf?la=de-CH
[Last accessed: 10/02/16]

WHO (1997) *Guidelines for Drinking-Water Quality: Volume 3 - Surveillance and control of community supplies*, 2nd edition, Geneva
Available at: http://www.who.int/water_sanitation_health/dwq/gdwq2v1/en/index2.html
[Last accessed: 19/02/16]

Withers, P. and Haygarth, P. (2007). Agriculture, phosphorus and eutrophication: A European perspective. *Soil Use and Management*, 23, 1-4.

Woli, K., Nagumo,T., Kuramochi, K., and Hatano, R. (2004) Evaluating river water quality through land use analysis and N budget approaches in livestock farming areas. *Science of the Total Environment*, 329(1), 61-74.

WPO (2015) *Waters Protection Ordinance*
Available at: https://www.admin.ch/opc/en/classified-compilation/19983281/index.html
[Last accessed: 29/03/16]

Zhang, B., Tang, J., Gao, C., and Zepp, H. (2011). Subsurface lateral flow from hillslope and its contribution to nitrate loading in streams through an agricultural catchment during subtropical rainstorm events. *Hydrology and Earth System Sciences*, 15(10), 3153-3170

Appendix A

Table 1: Land use intensity per catchment: percentage area per intensity class

	Catchment										
Intensity class	g	f	k	e	a	h	i	j	d	b	c
0	7.86	23.36	14.49	17.14	23.36	8.47	6.88	6.36	11.48	5.42	9.45
1400	0.89	12.52	16.70	0	12.52	4.17	0.00	0.32	0.00	0.00	0.00
2800	13.75	4.90	7.14	7.24	4.93	0.00	0.00	0.33	0.41	1.32	0.00
4200	22.44	26.72	11.31	19.25	26.72	18.7	15.80	10.46	6.13	12.46	3.80
5600	27.43	8.06	7.70	10.89	8.06	6.38	13.15	14.52	9.10	10.08	10.25
7000	5.73	0.93	15.56	13.56	0.93	17.28	15.71	4.18	2.73	9.68	7.70
8400	16.76	4.17	5.16	2.18	4.17	32.82	6.97	30.09	5.41	10.49	0.00
9800	5.24	10.84	11.42	4.22	10.84	5.80	39.28	24.84	47.60	21.99	28.50
11200	0.14	8.58	10.79	25.36	8.58	6.96	2.82	8.62	17.32	28.88	40.26

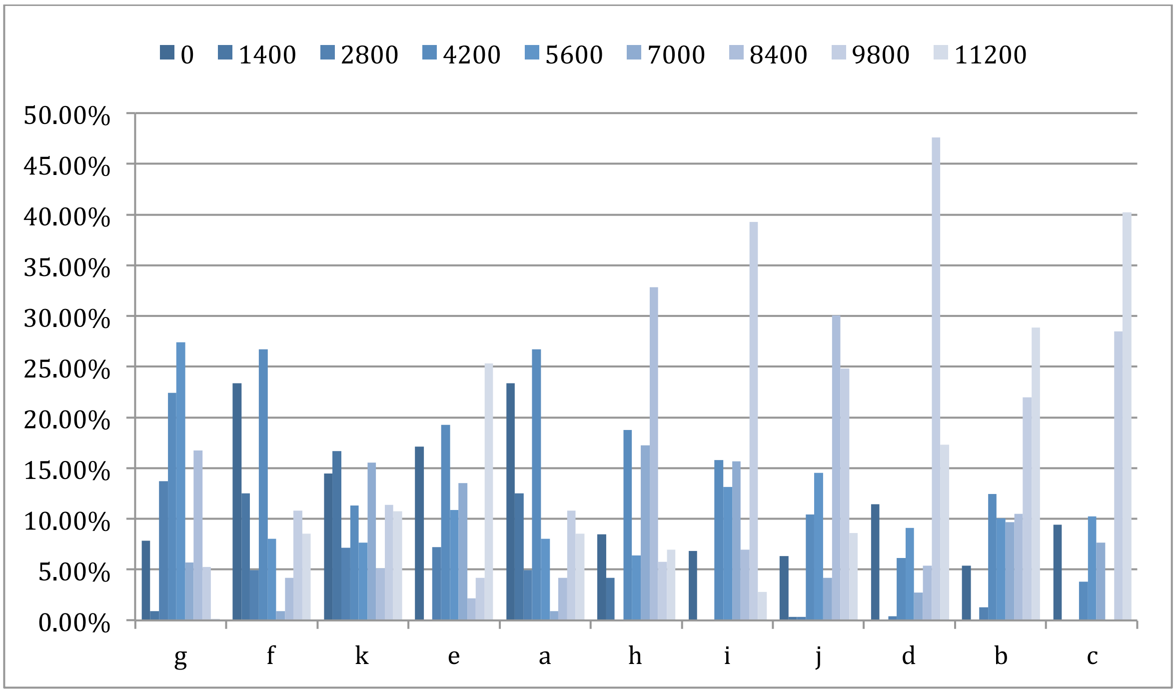


Figure 1: Land use intensity per catchment: percentage area per intensity class

Appendix B

Table 1: Mean water quality parameter for each catchment according to height of flow

Catchment	Nitrite (NO2-N (mg N/L))	Nitrate NO3-N (mg N/L))	Orthophosphate (PO4-P (µg P/L))	Height of flow
a	6.1	1.4	26.9	low
b	4.6	2.1	44.2	low
c	29.3	1.8	621.6	low
d	2.5	1.5	65.3	low
e	6.6	1.7	18.0	low
f	1.0	0.3	8.6	low
g	1.0	0.4	6.7	low
h	7.7	0.3	641.8	low
i	1.2	0.7	23.2	low
j	1.3	1.0	9.7	low
k	1.2	0.7	16.1	low
a	1.0	1.0	30.0	medium
b	11.3	1.9	62.2	medium
c	8.9	2.8	196.7	medium
d	1.6	2.0	55.1	medium
e	7.3	1.4	18.4	medium
f	1.0	0.3	3.4	medium
g	1.0	0.5	6.0	medium
h	1.0	0.4	12.8	medium
i	1.0	0.6	17.4	medium
j	1.2	0.9	9.6	medium
k	1.0	0.6	6.9	medium
a	1.3	0.8	20.2	high
b	1.7	1.8	40.6	high
c	9.2	1.8	42.2	high
d	3.3	1.5	50.5	high
e	1.3	0.9	19.9	high
f	1.0	0.4	9.0	high
g	1.0	0.4	6.8	high
h	1.0	0.5	9.6	high
i	1.0	0.6	16.9	high
j	1.0	0.9	13.8	high
k	1.0	0.6	5.8	high

Table 2: Mean water quality parameter for each catchment according to sate of weather

Catchment	Nitrite (NO2-N (mg N/L))	Nitrate NO3-N (mg N/L))	Orthophosphate (PO4-P (µg P/L))	State of weather
a	5.70	1.27	33.93	Dry
b	11.77	2.07	60.43	Dry
c	10.37	1.87	142.60	Dry
d	1.90	1.52	60.77	Dry
e	4.08	1.59	18.00	Dry
f	1.03	0.25	3.23	Dry
g	1.00	0.49	6.15	Dry
h	7.00	0.34	634.33	Dry
i	1.00	0.60	21.93	Dry
j	1.17	0.97	7.83	Dry
k	1.13	0.62	12.80	Dry
a	1.80	1.07	23.75	Rain
b	2.40	1.93	41.00	Rain
c	32.60	1.75	891.10	Rain
d	2.65	1.45	61.65	Rain
e	5.356	1.27	20.70	Rain
f	1.00	0.33	11.60	Rain
g	1.00	0.49	6.80	Rain
h	1.00	0.41	15.85	Rain
i	1.00	0.64	18.65	Rain
j	1.00	0.93	12.35	Rain
k	1.00	0.65	9.85	Rain
a	1.00	1.06	20.75	After rain
b	4.55	1.79	48.25	After rain
c	13.75	3.23	143.50	After rain
d	2.25	2.29	52.95	After rain
e	5.45	1.39	16.90	After rain
f	1.00	0.28	6.05	After rain
g	1.00	0.35	6.15	After rain
h	2.00	0.33	19.40	After rain
i	1.25	0.65	17.70	After rain
j	1.40	0.90	11.85	After rain
k	1.10	0.56	8.45	After rain