THESIS

URBANIZED NUTRIENT ENRICHMENT OF THE KLINA RIVER IN KOSOVO: IMPACT ON SURFACE WATER AND DRINKING WATER QUALITY IN A DEVELOPING COUNTRY

Submitted by

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ABSTRACT

URBANIZED NUTRIENT ENRICHMENT OF THE KLINA RIVER IN KOSOVO: IMPACT ON SURFACE WATER AND DRINKING WATER QUALITY IN A DEVELOPING COUNTRY

Urban development is a present and future challenge for water managers, with one of those challenges being nutrient enrichment. While the ecological and health impacts of nutrient enrichment are well documented and understood, the challenge still remains in helping developing countries initiate a sustainable water quality program that will address nutrient enrichment and other water quality problems. The Klina River in Kosovo has shown evidence of eutrophication in multiple locations. The goal of this research was to quantify the nutrient concentrations and loads of NH_4, NO_3, and PO_4; and determine what level influence urban development was having on the Klina River's water quality.

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1.1.1 Population and Urbanization Trends

We as a world population have quietly passed the 7 billion mark on October 31, 2011. While that date is merely symbolic to reflect the latest population estimates, the reality of roughly 7 billion people utilizing and sharing the earth's resources is felt , especially in cities, which are growing at a current annual rate of 1.5%. In 2008, for the first time in history more people (50.6% of the population) lived in cities rather than in rural areas. It is predicted that by the year 2050, approximately 70% of the world's population will live in an urban area (PRB 2011).

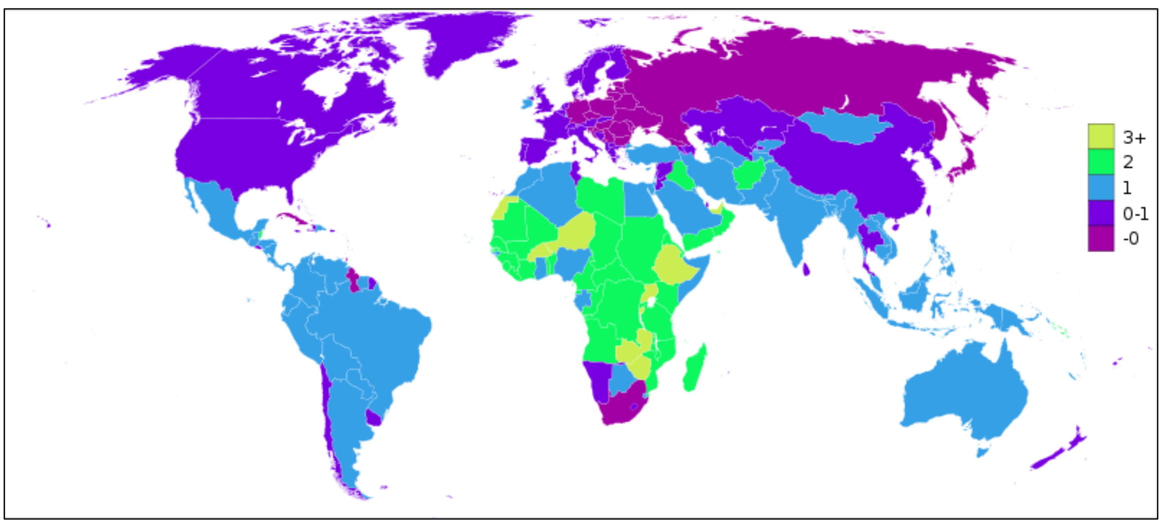


Figure 1.1. 2011 average population growth rate is approximately 1.2%. (CIA World Fact Book)

While the current population growth has decreased from the peak of over 2.2 % in 1963 to it's current growth rate of 1.2%, it is expected that the population will still to continue to grow by 83 million annually until the year 2050, with virtually all of that growth occurring in economically less developed countries

(Cohen 2011). Though the worldwide average has decreased, many regions like Africa continue to have significantly higher growth rates (Figure 1.1). With this rate and the immigration trend of people towards cities, by 2050, populations living in urban areas will have doubled from 2.5 billion in 2010 to approximately 5.3 billion (UN-Habitat 2008).

This growth is due in large part to urban growth being undeniably linked with economic development. The level of urbanization in a country is often an indicator of its wealth, with the nations with the highest per capita incomes being the most urbanized. Norway is a good example of this. With an average income of $ 52,000, approximately 84% of the nations population lives in urban areas. It is also true that nations that are experiencing the greatest economic growth also tend to have the quickest rate of urbanization (UN-HABITAT 2008). China for the past 2-3 decades have been experiencing approximately 10% annual economic growth. The majority of this growth has been centered in cities along China's eastern seaboard. Not only are these cities more economically successful than the rest of the country, but they are also the most urbanized areas in the country, with some cities growth rates in double digits.

In contrast, the nations with the lowest per capita incomes tend to be some of the least urbanized. The nation of Burundi, which has an average annual income of $412, currently has a total of 11% of its population living in urban areas. While this trend is generally true for underdeveloped countries, issues more specific to developing countries make the link between urban growth and economic development less substantial.

1.1.2 **Urban Growth in Developing Countries**

Currently 44% of the world's population (3.1 billion) live in cities in 'underdeveloped' countries. Those involved with international development have viewed urbanization in these countries with mixed views. On one hand, cities represent areas where there are generally better economic opportunities, health care, and rights for gender equality. However, urban areas in underdeveloped countries also present serious problems for governing and managing bodies. Slums, traffic jams, air pollution, lack of water and wastewater treatment, and crime are all serious problems facing cities in these area (Bazoglu 2011).

These problems are serious and will intensify as population growth in cities continues. Governing bodies are and will be limited in their ability to provide the needed infrastructure to meet the growing demands. However cities with good governing strategies are having better success in meeting the infrastructure needs despite their growing populations. Cities such as Delhi (India), Jakarta (Indonesia), Belo Horizonte (Brazil), though varying greatly in population all have a relatively high level of infrastructure provision. Each city certainly has inequality issues that arguably need to be dealt with, however each city has had certain levels of success in integrating their new populations. Characteristic of each is the governing bodies pro-urban development view, empowerment of local governing bodies, and sensible decentralization of infrastructure and services (Bazoglu 2011). While there are certainly good examples of successful management of growing urban areas in developing countries, the overall tendency is for developing countries to lack the resources and infrastructure needed to accommodate the demands of their cities surging populations.

Currently 75 % of developed nations population lives within urban areas (PRB 2011). While more people are moving to cities, many people are living in satellite cities and suburban neighborhoods that have lower population densities and a potentially better lifestyle. This trend of growing urban sprawl has long been seen as mostly unique to America, however the last 10-20 years has seen 'horizontal spreading' move to urban areas in developing countries like Beijing in China, Mexico City in Mexico, Cairo in Egypt, and Johannesburg in South Africa (UN-HABITAT 2008).

As urban sprawl continues growing in developing countries, so also do the problems associated with it. Growing urban sprawl generally leads to higher energy consumption, transportation management issues, and higher requirement of materials like concrete, asphalt, and metal. In many countries urban sprawl also leads to a reduction of available farmland and a degradation of ecosystems, particularly aquatic ecosystems.

Urban growth, as stated previously, is directly linked to economic development. While much of a country's ability to respond to urban growth problems depends on its governance, the countries gross domestic product (GDP) is also a strong indicator. In this way, developed countries have a strong economic advantage. Another noteworthy advantage is their ability to get useful information to the individual. While it could be argued that the ability to communicate is linked to it's economic development, it could also be argued that much depends on the men and women governing the population and their willingness to communicate openly and freely to the general population. In Denmark, their solution was to develop a political policy with free access to information, which was deemed necessary and beneficial to the promotion, efficiency, and rationalization of public institutions and enabling them to provide better services for the society (Friedman 1996).

1.2 Human & Environmental Impacts of Urbanization

While there are arguably many benefits to living in urban areas, particularly economic benefits, there are numerous health and environmental issues related to urban development especially in relation to its impact on water quality.

We are currently living in a period of time the United Nations has deemed "the decade of water." Together with natural forces, various anthropogenic actions have caused increased pressure surrounding the availability of freshwater. As the global population continues to grow and urbanize, the demand for this finite resource to meet the agricultural, industrial, and domestic needs of countries is intensifying. For example, China's steady population and economic growth for the last two decades have led to serious water related problems as officials have decided to shift water away from China's farmers to utilize it in their growing municipalities and industrial areas, leading to global food shortage problems as China looks internationally to meet it's food demands (Brown 1998, Jiang 2009).

While discussing water scarcity, traditionally focus is generally given to obstruction of water quantity, whether natural or anthropogenic. However, within the last ten years, a greater focus has been given to the effects of water quality on water scarcity (Brown 1998 & UNEP 2010). Degraded water quality has an impact on water quantity in a number of ways.

First, depending on pollution levels, water often cannot be utilized for agriculture, bathing, drinking, or even industrial usage. China, has 50,000km of rivers and according to the UN Food and Agriculture Organization, 80% of these rivers are unable to support fish life (Brown 1998). As a result of dangerous discharge from industries and municipalities, the Yellow River is loaded with toxins, nutrients, and heavy metals that make its water unfit for irrigation (Jiang 2009). In the Shanxi province, rice and cabbage grown with water from the Yellow River has been found with excessive levels of lead, cadmium, and chromium. As industrialization and urbanization in China outgrows efforts to control pollution, more and more of these waterways are becoming unusable for agriculture and domestic usage.

Second, as pollution levels in water increase so increases the difficulties in treating this water to useable standards. Treatment typically focuses on removal of pollutants, creating a waste sludge. The poorer the quality of the water, the greater the level of treatment, and the less the amount of safe water that is available that will be available for usage after treatment. In addition, more treatment means a greater cost for usable water, as more energy must be used to pump, purify, and filter the water. Greater energy use in turn has implications as water must be allocated for energy production and reduces water availability for domestic and agricultural consumption (UNEP 2010).

Lastly, as is the case with most urban development, the amount of water that infiltrates to the groundwater is reduced, leading to a increased volume of runoff. This in turn results in greater amounts of contaminants being released into the stream flow, reducing the quality of water often to the point of being unusable without significant treatment. However, as is often the case in developing countries water that we in the west would classify as polluted and would be deemed unsafe is used, leading to serious health related issues (Cairncross 2010).

1.2.1 Health Related Impacts of Urbanization

Many of the health related issues in urban (and rural) areas can be attributed to a lack of understanding and implementation of proper water supply, sanitation, and hygiene practices. It is estimated that 1.7 million deaths a year occur as a result of unsafe or inadequate water, sanitation, and hygiene (WHO 2002). The vast majority of health threats and ensuing diseases produced by poor water quality in developing countries is a product of microbial contamination. Water related diseases are one of the major causes of death among children under the age of five. Many of the disease causing pathogens are ingested through drinking water and lead to diarrhea and then death. The World Health Organization estimates that 39% of all cases of disease that lead to the 'water, sanitation, hygiene' disease burden are diarrheal diseases (Figure 1.2). The category "diarrhea" includes severe diseases like dysentery, cholera, and typhoid fever. Children from undeveloped nations share a disproportionate share of these deaths as children under the age of 14 accounts for over 20% of all deaths related to unsafe water, inadequate sanitation, or insufficient hygiene (WHO 2008).

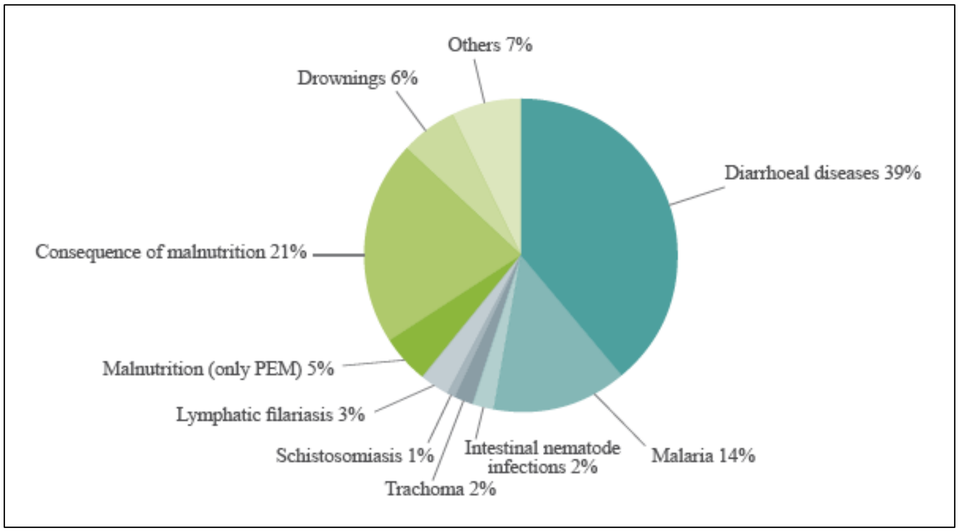


Figure 1.2. Diseases contributing to the water, sanitation, and hygiene-related disease burden (WHO 2008).

A certain level of responsibility for this problem belongs to urban areas. As expanding populations concentrate in one area, an increase of sewage and other forms of domestic waste overburdens streams and waste treatment systems. In fact, in many developing nations, wastewater treatment either does not exist or cannot meet the demands of the growing population; sewage remains untreated and is dumped directly into the local waterway. A study done by the United Nations Environmental Program gathered data from river monitoring sites near major cities from around the world (Figure 1.3). Results showed that fecal coliform concentrations, which are indicators for potential presence of water related pathogens, were concentrated in urban areas with the largest populations in countries that are generally considered 'underdeveloped'. Investment in wastewater treatment infrastructure in these countries is generally unable to keep pace with population growth, leaving most wastewater untreated (UNEP 2010).

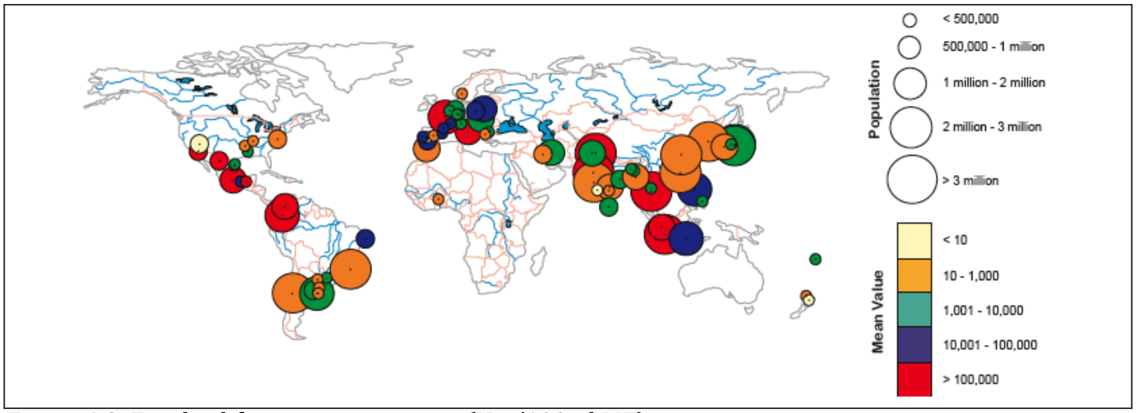


Figure 1.3. Fecal coliform concentrations (No./100ml MF) at river monitoring stations near major cities (UNEP 2010).

While the vast majority of water related disease is attributed to microbial pathogens, research has shed more light on the impact of anthropogenic nutrient enrichment on human health. It has been understood for some time now that ingestion of high nutrient levels in drinking water, most notably nitrate, has shown to have adverse affects on the health of people especially young children. Infants under the age of 4 months are the most susceptible to a condition known as methemoglobinemia (Wolfe 2002). Nitrates are reduced in the anaerobic environment of the digestive tract. This results in a blocking of hemoglobin's ability to carry oxygen to the tissues of the body. The World Health Organization (WHO) has reported approximately 3000 cases of methemoglobinemia worldwide since 1945 (WHO 1996; Wolfe 2002). While this number may appear statistically insignificant, it should be noted that water quality testing and primary healthcare throughout the developing world is highly under resourced, therefore having accurate data to this condition is difficult.

Ingestion of nitrates and nitrites has also been linked to the development of cancers of the digestive tract. Nitrates aid in the bacterial genesis of nitrosamines in the digestive tract. Nitrosamines are known carcinogens that form from a low pH reaction of nitrite and amine, forming dimethylnitrosamines. Carcinogenicity by dimethylnitrosamines can occur from either long-term exposure of small doses or a short-term exposure to a single large dose (Wolfe 2002). In addition, long-term ingestion of nitrates and nitrites has been linked to mutagenicity, teratogenicity, birth defects, increased risks for non-Hodgkin's lymphoma, and bladder and ovarian cancers (Camargo 2006).

Studies within the last decade have suggested that nutrient enrichment may also have an indirect negative impact on human (and animal) health by enhancing pathogen abundance (Johnson et al 2010). According to Johnson et al, anthropogenic inputs of nutrients often correlate to the increased pervasiveness, intensity, and dissemination of water related infectious diseases in nature. It is suggested that linkages exist between increased nutrient enrichment and changes in host profusion, and shifts in pathogen virulence.

Recent studies revolving around malaria have provided a convincing example of the relationship between disease and nutrient enrichment. Malaria is a vector borne pathogen, meaning that transmission requires a virulent parasite (Plasmodium spp.), a mosquito vector, and a primate host. Numerous ecological processes control abundance of mosquito larvae and the resulting adults in aquatic ecosystems (Johnson et al 2007 & Johnson et al 2010). Aquatic plants provide protection for larvae and detritus to the bacteria that mosquito larvae feed on. An increase in nutrient enrichment contributes to plant growth and potentially enabling the survival of species of mosquitos that are more proficient in the transmission of malaria.

A 2005 study in Belize (Pope et al 2005), found that wetlands with higher levels of phosphorus had a higher survival rate of mosquito larvae (Anopheles vestitipennis), thus increasing the malaria risk across a broad region. A 2004 study (Reiskind et al 2004) of *Culex restuans*, a vector for the West Nile virus, showed that control of the nutrient levels also controlled the growth and survival of the larvae (Figure 1.4).

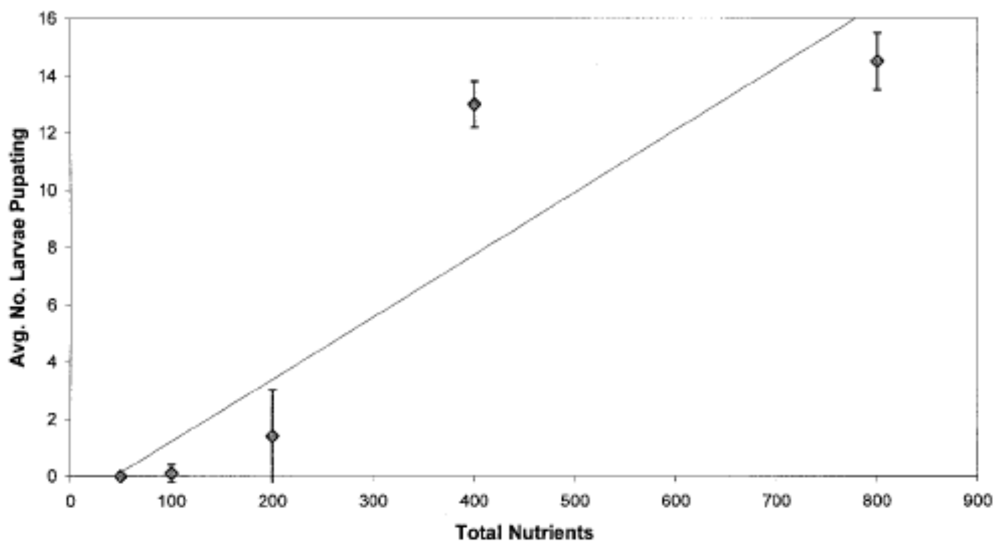


Figure 1.4. Total Nutrients (water volume multiplied by nutrient concentration) impact on larval mosquitoes survival (Reiskind et al. 2004).

Similar patterns have emerged in wildlife diseases as pathogens have responded positively to nutrient enriched waters and led to increased wildlife mortality. Examples include mycoplasmosis in birds, toxoplasmosis in sea otters, and chytridiomycosis in amphibians (Johnson et al. 2010). A 2004 study (Johnson 2004) suggested that eutrophication, as a result of anthropogenic disturbance, resulted in a number of changes to the aquatic food web and a proliferation of the parasitic flatworm *Ribeiroia ondatrae*. It has been found that infection of R. ondatrae is a strong predictor of amphibian malformation levels (Figure 1.5).

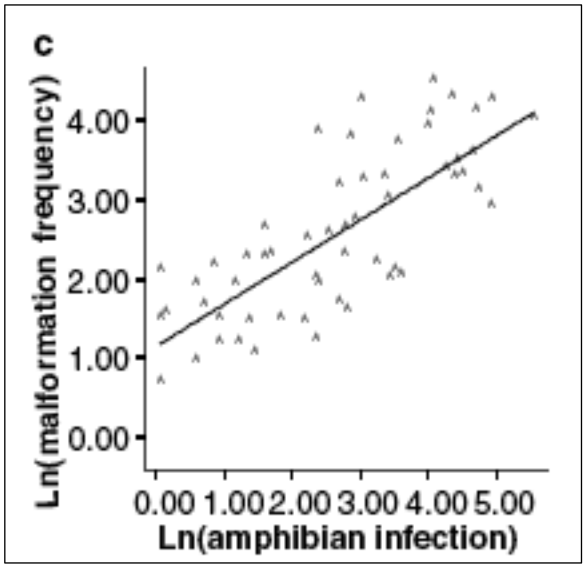


Figure 1.5. Relationship between infection of Ribeiroia ondatrae and the frequency of amphibian malformation (Johnson 2004).

As the global population continues to expand, and urbanize, the negative effects of urban growth and development will intensify. The challenge of mitigating the negative health (and environmental) impacts of urbanization is and will be at the forefront of problems facing governing officials.

1.2.2 Environmental Impacts of Urbanization

Despite increased environmental awareness and a greater effort to regulate contamination, urban development continues to increase pressure on aquatic ecosystems.

Hydrology

Arguably the most dominating aspect of urban development is the increase of impervious surfaces (any material that decreases the infiltration of precipitation into the soil), leading to a decrease in precipitation infiltration and an increase in surface runoff (Dunne & Leopold 1978). As the percentage of impervious surface cover (ISC) increases to 10–20%, runoff doubles; 35–50% ISC results in runoff tripling; and 75–100% ISC increases surface runoff more than five times over forested catchments (Figure 1.6) (Arnold & Gibbons 1996).

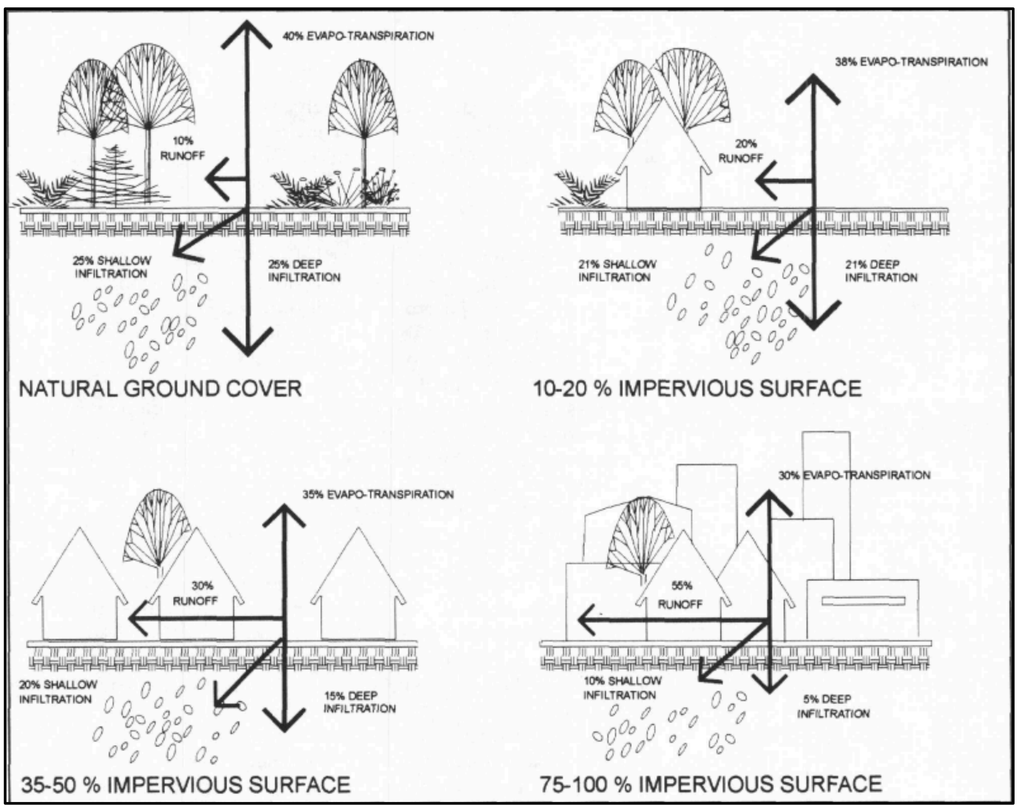


Figure 1.6. Changes in the water cycle associated with increased impervious surface cover as a result of increased urban development (Arnold & Gibbons 1996)

The increasing of impervious surfaces alters stream lag time (time difference between the center of precipitation volume to the center of runoff volume), resulting in floods that peak more quickly but have much higher discharges. Flooding discharges were found to be 250% higher in urban watersheds than forested watersheds after similar storms (Paul & Meyer 2001). Increased discharge has important environmental effects, leading to significant geomorphological, chemical, and ecological changes to riverine ecosystem.

Geomorphology

The biggest effect urbanization has on stream morphology is the transformation of drainage density, which is a measure of stream length per catchment area (km/km^2). Channel densities decrease sizably in urban watersheds as smaller streams are paved over or filled in (Dunne & Leopold 1978).

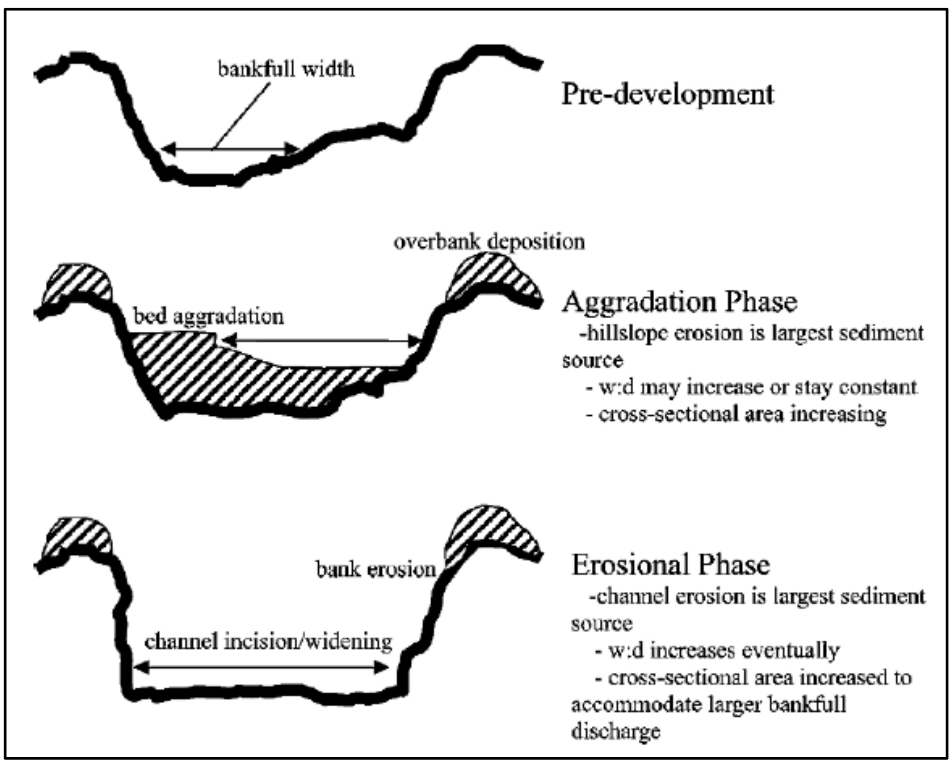


Figure 1.7. Geomorphological changes to streams as a result of urbanization (Paul & Meyer 2001)

A governing principle in stream geomorphology is that in response to consistent changes in sediment supply, streams adjust their channel dimensions. Urban development leads to both heavy sediment loading and stream discharge (Booth & Henshaw 2001).

For example, as an area begins development, and goes under construction, erosion of soils increases thus increasing sediment yields. Increased sediment yields to an aggradation phase where urban streams begin filling with sediment, and channel capacity. Decreased capacity leads to increased flooding, overbank deposits of sediment, and increased bank heights (Paul & Meyer 2001). After aggradation, sediment yield decreases and geomorphic readjustment occurs, leading to additional erosion and a deepening and widening of the stream channel (Figure 1.7). One of the results of the increased erosion and sedimentation is increased levels of nutrient enrichment.

Nutrient Enrichment

Urban development typically leads to greater levels of both phosphorus and nitrogen. Although concentrations of both are increased, increased concentrations of nitrogen have been found to be much higher. In some cases, cities have shown to raise both nitrate and ammonium levels for hundreds of kilometers downstream. A 1998 study showed that the Paris megalopolis elevated nutrient concentrations and has a distal impact up to 200 kilometers downstream (Meybeck 1998). Elevated nutrient levels depend largely on the level of wastewater treatment, degree of illegal discharging, and fertilizer usage. As is often the case in many developing countries, wastewater treatment is limited or non-existent and urban waste is deposited directly in the local stream channel. Though urban centers are significant contributors to nutrient enrichment, streams draining from agricultural watersheds tend to have greater nutrient loads (USGS 1999). Continued enrichment leads to eutrophication and a number of related ecological problems.

The first of these problems is nutrient cycling. Nutrients, upon entering a riverine ecosystem, go through a natural process called nutrient spiraling. Nutrient spiraling consists of two aspects: the distance moved by the dissolved element from point of release to point of benthic uptake, and the distance transported within the benthic uptake (Figure 1.8) (Newbold 1983). Uptake length of nitrogen and phosphorus varies depending on the ecosystem and variation in biotic status of the system, stream hydrology and channel morphology.

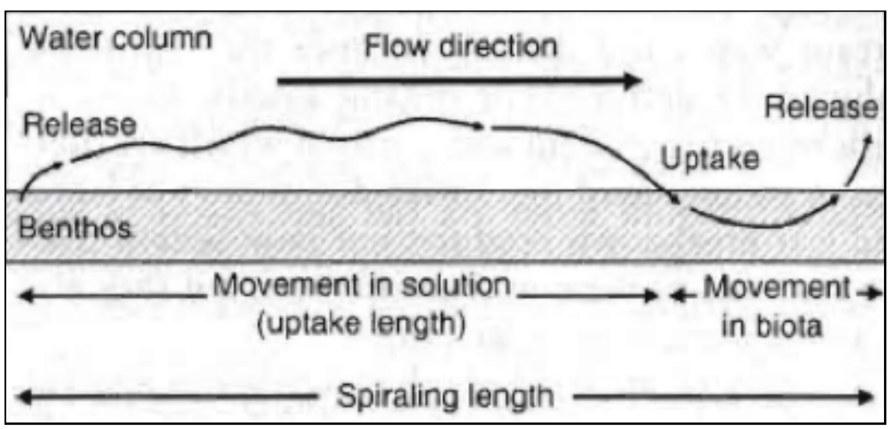


Figure 1.8. Nutrient spiraling length is based on how tightly nutrients are recycled and how retentive the stream is in regards to transporting elements. Shorter spiraling patters usually refer to higher biological activity. (Fisher 2009)

Studies have shown that excessive nutrient loading, contributed by wastewater effluent from urban centers increases the length in which nutrients travel before being removed from the water column. Uptake lengths in these rivers are considerably longer than in nonurban rivers of comparable size, indicating that nutrient loading is increased in urban streams, but the streams efficiency in removing nutrients is significantly reduced (Marti et al 2004, Pollock et al 2001).

The result of this is increased nutrient loading of downstream reservoirs and estuaries. This in turn has led to increased levels of eutrophication in marine ecosystems and sizeable areas (km^2), which are hypoxic and unable to sustain aquatic life. According to Diaz et al., a hypoxic event in the New York Bight during 1976 covered approximately $1000km^2$ and caused the death of masses of benthos and demersal fishes (Diaz et al 2008).

This leads to a second type of nutrient enrichment problem, reduced bio-diversity. Increases in nutrients predominately benefit primary producers. Producers, like algae, receive a surge of nutrients from anthropogenic sources and experience massive population growth called an algal bloom. Algal blooms tend to negatively impact benthos and other bottom dwelling organisms by limiting daylight and greatly reducing dissolved oxygen after dark during respiration.

As nutrient levels decline, algal blooms are unable to sustain growth and begin to die off. This allows microorganisms to feed off of and decompose the dead algae, adding to declining dissolved oxygen levels and increased hypoxic conditions. Hypoxia starves fish and other marine animals of oxygen leading to potential death depending on the species ability to tolerate low O_2 levels. A 2009 paper listed numerous fish species (*Trinectes maculates*. Leiostomus xanthurus, *Micropogonius undulates*, etc) avoid massive areas of the Gulf of Mexico because the oxygen concentrations were too low (between 0.5 – 2.0 mg L^{-1}) (Levin et al 2009). The shift of species composition and diversity yield in this area has changed the energy flow pathways and trophic structure as well as affecting other ecosystem functions like production, burial of organic C, and cycling of organic matter.

1.3 Nutrient Sources and Factors Controlling Enrichment

1.3.1 Point Source vs. Nonpoint Source Nutrient Pollution

One of the greatest challenges in managing water quality is understanding the source(s) of the nutrient enrichment and determining the factors that influence it's load and ultimate fate in an aquatic ecosystem, which change over spatial and temporal scales (Mouri et al 2011). Pollution emanating from one source is called point-source pollution. Pollution that does not emanate from one particular source is called nonpoint-source pollution.

Nutrient enrichment from point source pollution is a significant source, particularly from developing countries where two thirds of the urban wastewater in the world still receives no treatment before being deposited into streams and rivers (Marti et al 2010). Even when wastewater treatment facilities are in place, the certainty of enrichment is understood as many streams receive between 10-90% of their flow from wastewater effluent (Paul & Meyer 2001). Domestic wastewater effluent is a mixture of inorganic and organic forms nitrogen and phosphorus, though most consideration is given to the inorganic forms of both nutrients (Sawyer et al 2003). This is not to say however that organic forms of N & P are not significant. For example, most organic nitrogen in domestic wastewater is in the form of proteins, amino acids, and polypeptides. Destruction of the organic segment of the compound releases nitrogen as ammonia (NH_3) making it free for biological uptake, which leads to greater productivity (Kirchman 1994).

While the negative impact from point source pollution cannot be argued, it is generally agreed that nonpoint-source pollution (storm water runoff, agricultural runoff) is a larger contributor of nutrient pollution and is much more difficult to manage. This trend can be seen clearly in the European Union's (EU) attempt to limit the impact of nutrient enrichment and it's effects on European marine ecosystems (Artioli 2008). The EU has implemented several directives and policies (e.g. Urban Waste Water Treatment Directive, Water Framework Directive, Nitrates Directive) intended to negate the effects of eutrophication. A 2008 study of the most impacted European seas (Baltic Proper, coastal North Sea, Northern Adriatic, and North-Western Black Sea Shelf), studied water quality data and the policies governing these water bodies to determine the effectiveness of these policies to limit nutrient pollution. They concluded that effectiveness of these policies were successful because of their intervention on point source pollution, particularly phosphorus because of the outlawing of phosphorus in detergent. However, the results were mixed because they found that the EU policies were ineffectual in managing nonpoint-source pollution, particularly from agricultural dominated areas (Artioli 2008).

1.3.2 Factors influencing the load and fate of nutrients

The chemistry of river water changes continuously in a downstream direction. The chemical composition of river water is a result of precipitation input, sediment types, runoff, and the dissolution of inorganic matter as precipitation works its way through the soil into streams.

Water is changed further as it is affected within the channel by biological uptake and release, and concentration of salts through evaporation. At the same time phosphorus and nitrogen act as limiting factors for biological processes in streams. For example, leaf decomposition can be slowed by limiting the amount of available nitrogen to bacteria and fungi (Fisher 2009). Conversely, added nitrogen can increase leaf decomposition, making more nitrogen available to decomposers. This can lead to bacteria and fungi removing nitrogen from solution and limiting how much is transported downstream. Photosynthetic plants also can cause a downstream decline of N & P by taking up these nutrients. This action is the basis of the thought that streams purify water based on this process (Fisher 2009).

The essence of nutrient cycling is that organisms acquire elements they need from the environment around them and return those elements through metabolic processes and through decay at their death. Nutrient cycling in rivers is no different except they are affected by downstream transport of nutrients as a result of stream flow. Contrary to regular nutrient cycling, nutrients in rivers spiral and are stretched out over space (Figure 1.8).

Uptake length of nitrogen and phosphorus varies depending on the ecosystem and variation in biotic status of the system, stream hydrology and channel morphology. For example, the primary determinants of NH_4 uptake length were stream depth and current velocity (Peterson et al 2001). Their study of 15 different headwater streams showed that NH_4 was removed from the water column primarily through assimilation by heterotrophic and photosynthetic organisms and by sorption to sediments (Figure 1.9). Nitrification played a role in NH4 removal, but was considered secondary and varied widely (3-60% of removal). They concluded that 70-80% of NH4 removal could be attributed to uptake by the stream bottom and 20-30% to nitrification.

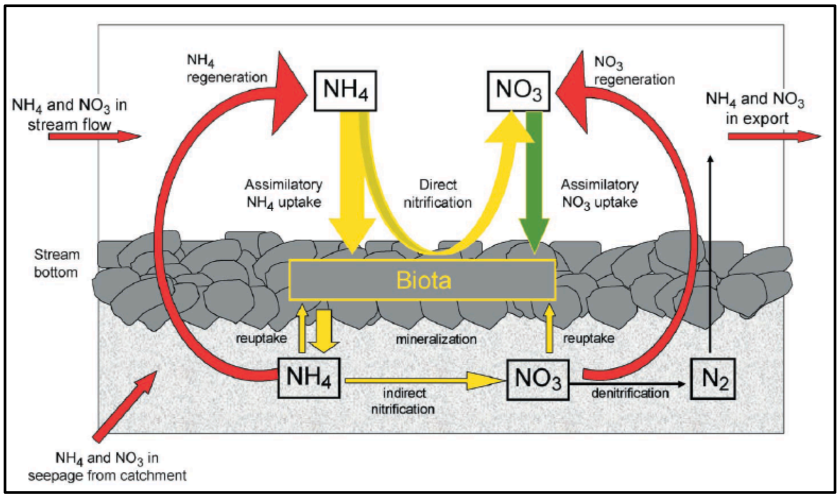


Figure 1.9 Model of dissolved inorganic nitrogen in headwater streams. NH_4 removal is due generally to uptake by bacteria, fungi, primary producers, and direct nitrification. NO_3 removal from the water is primarily via assimilation by biota and denitrification on the channel bottom. The release of NH_4 and NO_3 from the stream bottom back to the water column is the net result of several interacting processes, including denitrification, mineralization, indirect nitrification, and reuptake by biota. The remaining NH_4 and NO_3 are exported downstream (Peterson et al 2001).

Another example is phosphorus, which is a limiting element, would likely have a short uptake length in streams which have large amounts of seasonal algae growth due influx of nutrients in the spring, and a level of death during the late fall and winter months (Fig 1.10). Conversely seasonal flooding would lead to longer uptake lengths as greater flow would likely decrease how quickly nutrients are assimilated. Newbold et al found that the uptake length (travel in the dissolved form) accounted for nearly 90% of the total spiraling length. They suggest that factors that control phosphorus uptake from the water may be of more significance in controlling the overall rate of P utilization than factors controlling downstream transport and regeneration rates of P in particulates (Newbold 1983).

Figure 1.10. Seasonal algae growth of the Klina River. The greatest eutrophication of the Klina River occurs during the months of June through August when temperatures are highest, and flow rates are lowest. A) May 2009 B) August 2009

It is well documented that aquatic macrophytes, aufwuchs, and riparian vegetation uptake, store, and release large amounts of nutrients from their environment (Hill 1979; Tabacchi 2000; Newbold 1983). Primary producers in essence become a significant sink for nutrients, particularly nitrogen and phosphorus, excluding organic and mineral components. In addition, they also release organic matter and mineral components through decomposition. In both scenarios, the nutrient uptake and release influence water quality in streams (Figure 1.11).

It is suggested in a 1992 study that stream autotrophs may be an important mechanism for nutrient retention during periods where light levels are high. This would indicate that primary producers have a significant role in regulating nutrient concentrations in stream ecosystems. The 24-hour pattern for NO_2 & NO_3

concentrations (Figure 1.12) during this study suggested that producers helped account for the high rates of nutrient

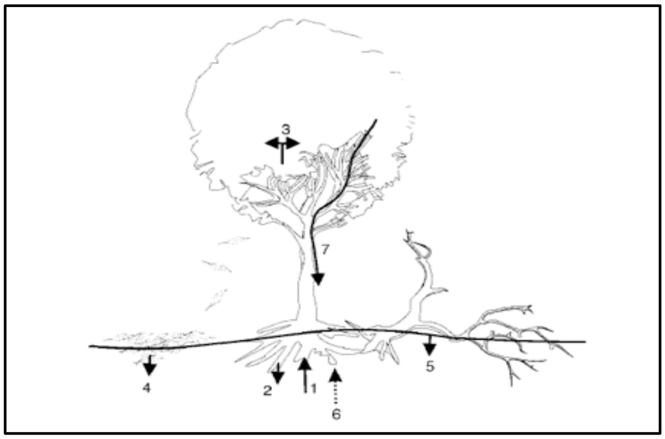


Figure 1.11. The main effects of primary producers on water quality: 1. Nutrient uptake; 2. Root excretions; 3. storage of mineral and organic components; 4. Fast decomposing matter from litter; 5. Slow decomposing matter from woody debris; 6. indirect uptake through symbiotic relationships; 7. leaching of pollutants at plant surface (Tabacchi 2000)

retention found in late winter and early spring when leaf detritus was in low supply (Mulholland 1992). Other studies supported this, suggesting that sediment organic matter may determine P uptake in streams with physiochemical buffering dominating when organic matter is low and biotic processes dominating in rivers where organic rich sediments could be found (Klotz 1991).

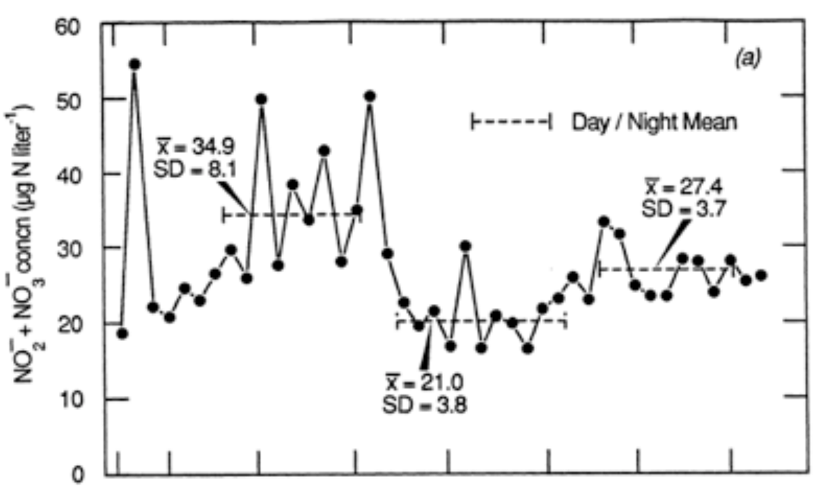


Figure 1.12. Twenty-four hour variation in NO_3 & NO_2 levels in stream water. N levels were lowest during the day and highest at night suggesting producers utilizing the nutrients for biological processes. (Mulholland 1992)

This suggests an important role producers play in creating nutrient rich organic matter that in turn helps in biological regulation of nutrients in streams. The findings from the Mulholland study also suggest that biological regulation may be due in part to the relative stability of stream-flow of that particular stream. Streams that tend to have high storm-flows that are flashy probably have less instream biological regulation, which varies depending on the season.

Uptake by Decomposers

It is well known that heterotrophs, especially heterotrophic bacteria, are responsible for a large portion of total uptake of inorganic nutrients in freshwater (Kirchman 1994). Studies of nutrient dynamics in rivers have mostly focused on uptake processes, leaving a quantitative gap on information on mineralization. Because of this, there is little understanding of the level of influence of instream nutrient processes on the relative availability of phosphorus and nitrogen and how this affects the function and structure of downstream systems.

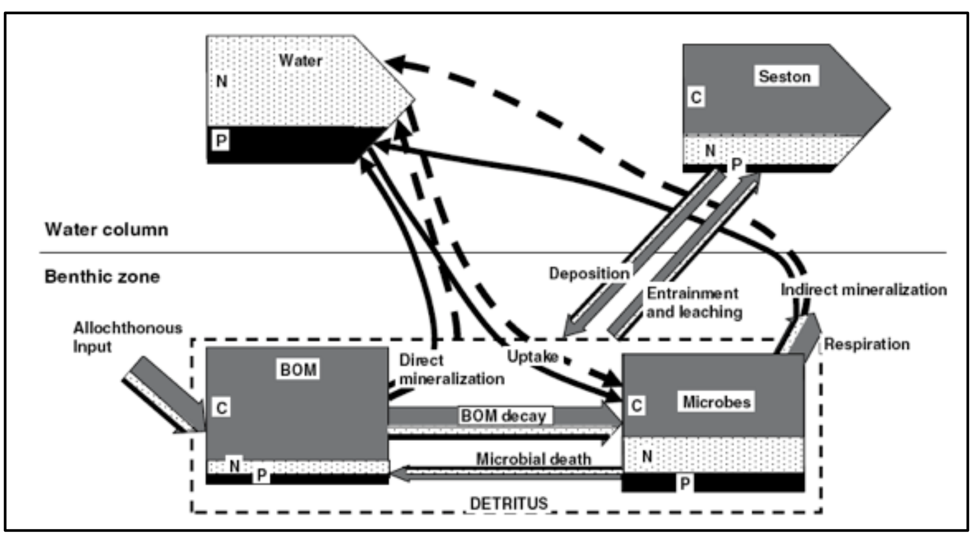


Figure 1.13. Model of nutrient dynamics in a stream dominated by allochthonous organic sources. Water and particles in transport are in the water column. The detritus, made of the decaying leaves and associated microbes, is stationary on the river bottom. Solid and dashed arrows represent inorganic nitrogen and phosphorus. Other arrows represent organic N, P, & C. (Webster 2009)

In 2009, a model study (Figure 1.13) was performed to determine how heterotrophic uptake of nutrients and microbial mineralization occurring during the decay of leaves in freshwater may be more important in modifying nutrient concentrations in streams (Webster et al 2009). Their model has four elements – dissolved inorganic nutrients in water column, transported particles in the water column, decaying leaves on the stream bottom, and microbes associated with decaying leaves.

For the purpose of the model, microbe parameters of the model were based almost exclusively on fungi, as they are the primary agents of leaf decay (especially in early stages) in stream ecosystems. Their model found that microbial processes on decaying leaves modified water column nutrient concentrations in large ways (Figure 1.14). However, leaf fall does not happen all at once and in a uniform manner.

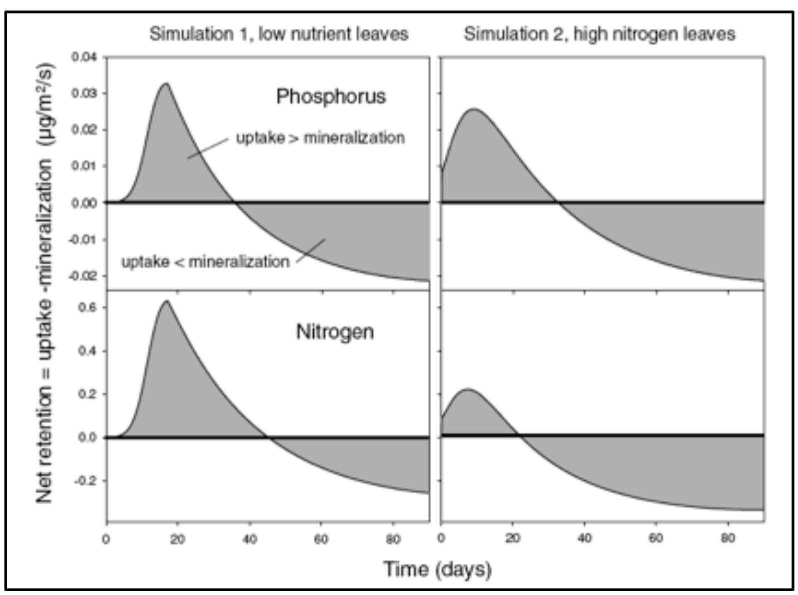


Figure 1.14. Simulations of phosphorus and nitrogen uptake. Points above the zero line represent times when uptake was greater than mineralization and conversely for points below the zero line (Webster 2009).

Therefore, the effect of microbial uptake and mineralization in streams is probably not as dramatic as their simulations showed. However, several studies (Gessner 1999, Gessner et al 2007, Newbold 2005, Webster 2009) have shown a direct correlation between nutrient uptake and leaf decay. One study showed steep declines in phosphate and nitrate concentrations during autumn leaf fall (Mulholland 2004). They attributed this to a high rate of uptake by microbes during colonization as leaf detritus provided new inputs. There are also questions to what extent microbes use nutrients from both the water column and from decaying leaf matter.

A number studies show that microbes that decompose leaf matter do in fact depend on nutrients from both the water column and from detritus. Gessner et al showed that fungal activity and leaf decay are correlated to the concentration of nutrients in the water column (Gessner et al 2007). In addition, direct experimentation has also shown microbial use of water column nutrients. An experiment by Findlay and Tenore (1982) showed how microbes growing on decaying *Spartina* grass utilized nitrogen mainly from the water column. Finally a stream experiment using ^{15}N or radiolabeled phosphorus in a fourth-order pristine tundra river in Canada have shown rapid immobilization of nutrients in the water column (Peterson et al 1997). The fourth-order Kuparuk River ecosystem retained 60% of the NH_4 within one hour and one kilometer of the point of tracer addition and measurable amounts of N-15 were found in stream biota for up to two years. Data suggests that storage of nutrients with the streams ecosystem influences the timing of nutrient release and influences downstream ecosystems.

Mineralization

As it is widely known, leaf litter breakdown is a vital ecosystem process in streams and rivers. Dissolved organic carbon (DOC) is generally accepted as the primary resource for biological decomposition in aquatic ecosystems and arguably could be considered a limiting factor of important ecosystem processes (Cook and Allan 1992). Traditionally this process is broken into three separate stages (leaching, conditioning, and fragmentation) (Fig 1.14).

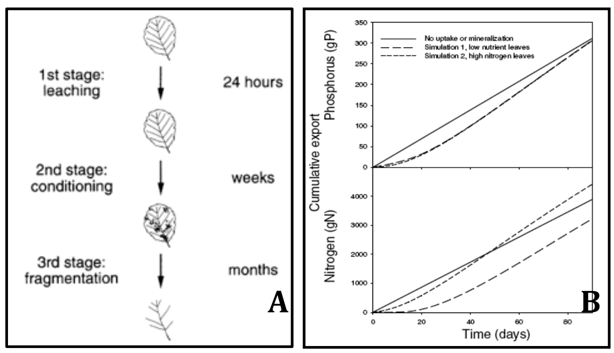


Figure 1.14. A) Conceptual model of leaf litter breakdown in streams (Petersen 1974). B) Cumulative export of dissolved inorganic nitrogen and phosphorus with high and low nutrient leaves. The solid line represents an export with no mineralization or uptake (Webster 2009).

Through leaching, a massive amount of soluble leaf components are lost within 24 hours. The conditioning or enhancement of leaf palatability by microbial colonization prepares litter for detritivores to consume. Physical fragmentation generally occurs from the wearing and stress applied by the flowing water (Gessner 1999).

While much is known about the processes of litter decomposition, questions still remain about the factors that determine whether there is going to be a net retention or net mineralization of nutrients in streams. Model studies by Webster et al suggest that initial net retention of both phosphorus and nitrogen, led to only a slight mineralization of phosphorus over a 190 day period, and a net retention of 8% of inorganic nitrogen (Figure 1.14) (2009).

If a section of stream is net retentive, nutrients are likely exported as dissolved organic matter and mineralization occurs further downstream. Some studies did suggest that breakdown of leaf litter occurs where they fall in the stream (Webster 2009), but still others show that nutrients in the form of dissolved organic matter and small particles can be transferred considerable distances before mineralization occurs (Newbold 2005). Conversely, quick uptake and mineralization of immobilized and detrital nutrients may simply delay the transfer of inorganic nutrients downstream to the ocean.

Denitrification

Surplus concentrations of nitrogen, in the form of nitrate, are a significant and growing water quality problem across the globe. While it is known that nitrate concentrations in rivers in developed countries have risen considerably from the use of synthetic N fertilizers (Turner 2003), little is known about water quality and nitrogen levels in streams in developing countries like Kosovo. It is estimated that up to 75% of nitrogen is removed before it is transferred to a marine ecosystem, primarily through denitrification (Howarth 1996). This is due mainly to biological processes, removing nitrate as water passes over or through sediments. However, current research points to alternative nitrate removal pathways other than denitrification and assimilation (Burgin 2007 & Weber etal 2006).

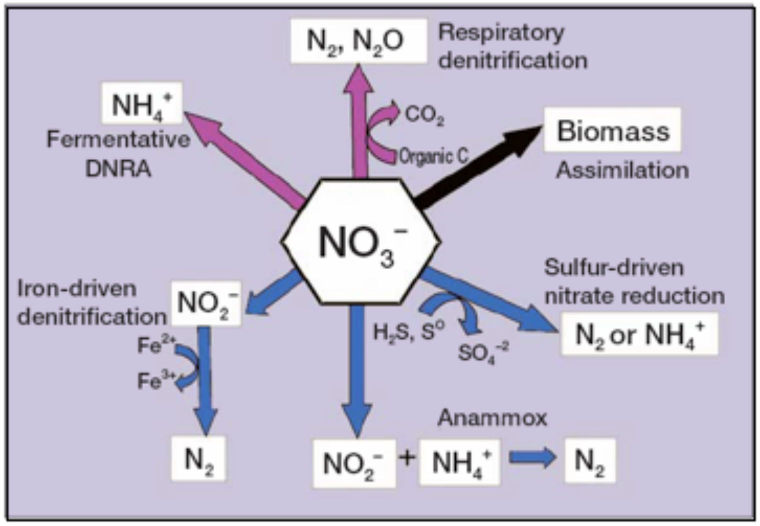


Figure 1.15. Potential pathways for nitrate removal. Purple arrows represent heterotrophic pathways while blue arrows designate autotrophic pathways. (Weber 2006)

These pathways (Figure 1.15) could rival denitrification in significance, but further research is needed to understand their role in comparison to the importance of respiratory denitrification in ecosystem nitrate removal. A number of the processes being studied include dissimilatory nitrate reduction to ammonium, anaerobic ammonium oxidation, denitrification coupled to sulfide oxidation (Burgin 2007). A process of particular interest is the reduction of nitrate coupled to abiotic or biotically mediated oxidation of iron (Weber 2006).

Reduction of nitrate via iron (Fe) cycling is believed to occur by abiotic and biotic pathways. One example of an abiotic pathway is the conversion of nitrate to nitrite (NO_2^-) by ferrous iron (Fe^{2+}). This is followed by a rapid reaction of the NO_2^- to N_2 by iron driven denitrification (Burgin 2007). While this abiotic process does occur in aquatic ecosystems, it's more likely that biotic reduction by microbes dominates surface waters. Biotic reduction of nitrate occurs at relatively low temperatures (compared to temperatures suited for abiotic reduction) and pH levels between 5.5-7.2 (Weber 2001). The majority of the current work has been on identifying and describing the microbes capable of this reaction, so the actual controls of this process are not well understood. The prevalence of these pathways could have important implications for water resource managers attempting to regulate nitrate loads as NO_3 removal via alternative pathways can lead to formation of noxious gases like N_2O.

The growing need for remediation of many of the world's major water bodies has forced science to better understand the various processes that control the loading and fate of nutrients. While much progress has been made, particularly in western countries, a serious gap exists between the scientific understanding in developed countries and the ability to implement it in developing nations.

1.4 Limitations of Water Quality Management in Developing Countries

It is a common precedent in developing countries, to develop a national policy in order to govern water resources, particularly in regards to water supply. However, very few of these countries include mandates to control water quality, instead leaving the role of identifying and managing pollution to local authorities. Very few national governments in developing countries have relevant information about the contaminants polluting their water bodies. Therefore they lack the ability to make informed decisions about what water policy will have the greatest economic or public health impact (Ongley 1993).

Central to this challenge is the establishment of data gathering programs (monitoring and data use) that use methods and technologies that are not relevant to the local location and are unsustainable due to logistical problems and lack of finances. Such programs tend to be ‘data driven’ rather than ‘needs driven’. This leads to programs that are not cost effective and rarely implemented (Ongley 2000). Ongley (2000) instead suggests establishing water quality programs based around the management issues, specific to the needs of the water stakeholders of the land. The technical aspects of data gathering would develop from these decisions, instead of driving them (Ongley 2000). The challenge is to create methods and solutions that provide relevant and useful water quality information, and can be implemented and sustained by developing countries.

The overall goal of this thesis is to do just that. In 2008, I as a part of the organization Water for Life Institute was invited to the village of Tushile in north central Kosovo to help them establish a plan to develop safe water for their community. Tushile is a village of 750 people, located in rural farmland approximately ten kilometers downstream from the city of Skenderaj (population circa 51,000). As villagers utilize the Klina River for a drinking water source, one of our objectives as a non-governmental organization was to understand the quality of water flowing in a stream in which eutrophication was evident. We decided to study this reach of the Klina River because of its direct impact on the village of Tushile and because it showed similar patterns of anthropogenic degradation that we saw in other areas of Kosovo.

Through much research, it became evident that there was little to no water quality data regarding this stream or any river in Kosovo. With this in mind, I have set out to determine if simple and relative inexpensive nutrient testing methods can provide the information necessary to identify major nutrient pollution sources and help guide the management process.

1.5 Research Objectives & Hypothesis

Hypothesis: The municipality of Skenderaj is the primary source of nutrient pollution of the Klina River before reaching the village of Tushile, and it significantly increases the load levels of NH_4, NO_3, & PO_4; negatively affecting drinking water quality for villages downstream.

Objective 1: Measure and calculate the load levels of NH_4, NO_3, & PO_4 entering and leaving the city of Skenderaj.

Objective 2: Track other potential sources of NH_4, NO_3, & PO_4 by measuring and calculating load levels at various points between Skenderaj and the village Tushile.

Objective 3: Determine seasonal factors that may potentially influence nutrient loads.

Objective 4: Use data from this study to help develop recommendations for how to improve the current water quality of the Klina River.

2.0 Methods & Materials

2.1 Study Area

The study area is located in the central region of Drenica, Kosovo, near the municipality Skenderaj. The area has a continental climate with Mediterranean and Alpine influences. This results in warm summers with temperatures +30 °C and winter temperatures as low as -10 °C. Average annual rainfall is 600 mm, with the maximum rainfall rate between the months of October - December, and March – May (Figure 2.1). Snowfall is common between the months of November and March (ICMM 2011).

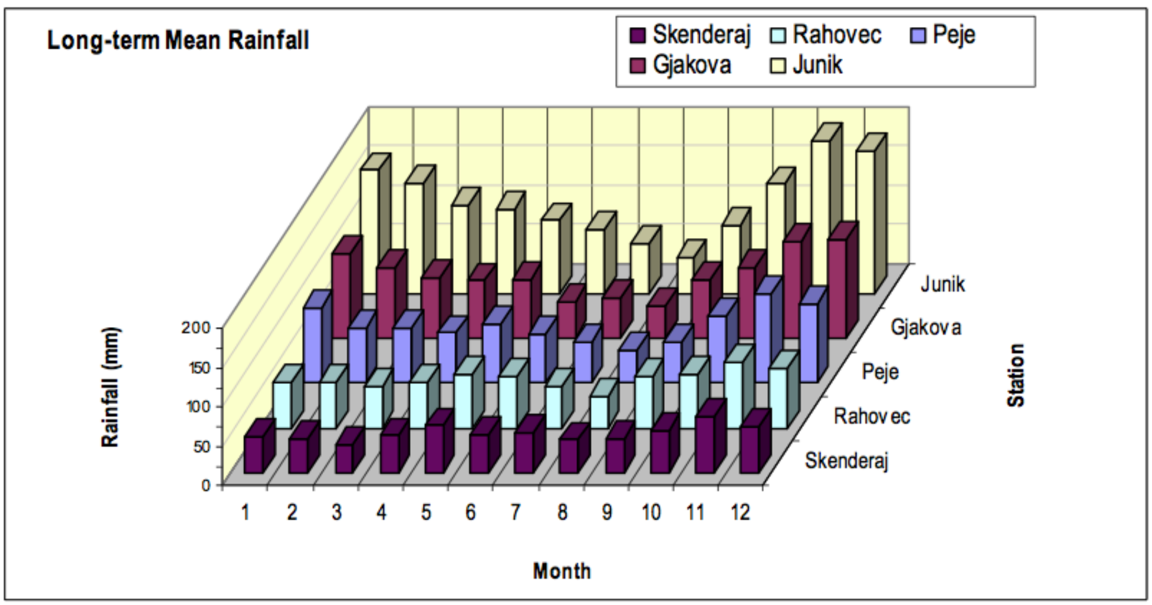


Figure 2.1 Rainfall data from stations feeding into the Drini I Bardhe River basin. Due to a loss of data from the war with Serbia, most precipitation data is lost, and Mean Rainfall is based on data from 2004-Present (ICMM 2011).

The Klina River (Figure 2.2) is a second order stream that originates from the northeastern slopes of the Suva Planina Mountain below the Rudopolje peak, which

Figure 2.2 The Klina River flowing southeast through the city of Skenderaj, and emptying into the White Drini River just past the city of Klina.

is approximately twenty kilometers northwest of Skenderaj. It is approximately 62 kilometers in length and has a basin area of 439km^2 (GFA 2009). The Klina River is a tributary of the Drini I Bardhë (White Drin) River, which is the second largest river in Kosovo with a basin area of 4289 km^2. There are four major river basins in Kosovo that drain into three different seas: the Aegean, the Adriatic, and the Black Sea, with the White Drin belonging to the Adriatic Sea drainage basin. Each river basin is considered relatively small with flow rates ranging from 6-65 m^3/s and an average of 28.25 m^3/s for all of them (Table 2.1).

Table 2.1 River Basins of Kosovo

River Basin	Catchment Area (km^2)	Flow (m^3/s)	Run-Off (l/s/km^2)
Drini I Bardhe	4289	65	33
Ibri	4369	33	7.6
Morava e Bincit	1564	6	5.9
Lepenci	685	9	15.5
TOTAL	10907	113	10.7

The geology of this area is fractured. The valley in which the city of Skenderaj lies, and the Klina River flows into, is part of the Upper Cretaceous layer and is a mixture of clastic sediments, clays, sand, and gravel. The Klina River continues to flow into a hill region consisting of a mixture of sandstone, siltstone, and marlstone (ICMM 2006). Soil characterization for the area is made up of a loamy alluvium in the river valley, with shallow to moderately deep brown soil on top of flysch. Land cover for the area is mixed with forested areas in surrounding mountains, developed urban area in the open valley, and rural farming in the proximity of most of this particular reach of the Klina River (Figure 2.2).

2.2 Site Selection

Sites for the spatial and temporal variation tests were selected by walking the 11 kilometers from upper boundary of Skenderaj downstream to the upper boundary entering the village of Tushile to determine suitable sites (Table 2.2). Each site selected was representative of the environment under study, was easily accessible for monitoring, and were approximately 400-600 meters apart to provide a consistent spatial coverage of the distance between the city of Skenderaj and the upstream of the municipality (Figure 2.3). It was selected as a control- monitoring site to compare nutrient concentrations going into Skenderaj to all measurements gathered downstream from the city. Measurements were also taken around any tributary feeding into the Klina River to determine its influence on nutrient concentrations and loads.

Table 2.2 Site Descriptions

Site	Distance from Skenderaj (km)	Description
S1	0	Upper border of Skenderaj. Noarrow and moderately deep channel. Moderate evidence of erosion
S2	N/A	In city limits. Deep channel with steep sides. Strong evidence of erosion.
S3	0	Lower border of Skenderaj. Deep channel with steep sides. Strong evidence of erosion.
S4	0.6	Moderate channel depth. Bordered by forest and farm. Evidence of erosion.
S5	1.2	Moderate channel depth. Bordered on both sides by farms. Evidence of erosion.
S6	1.7	Moderate channel depth bordered by forest and farm. Evidence of erosion.
S7	2.2 *	Moderate channel depth. Bordered on both sides by farms. Evidence of erosion.
S8	2.2 *	**Tributary**.Bordered on both sides by farms. Evidence of erosion.
S9	2.2 *	Moderate channel depth. Bordered on both sides by farms. Evidence of erosion.
S10	2.5 *	Moderate channel depth. Bordered on both sides by farms. Evidence of erosion.
S11	2.5 *	**Tributary**.Bordered on both sides by farms. Evidence of erosion.
S12	2.5 *	Moderate channel depth. Bordered on both sides by farms. Evidence of erosion.
S13	3.9	Moderate channel depth. Located near inactive WWTP. No evidence of erosion.
S14	4.5	Located near the highway. Narrow and moderately deep channel. Strong evidence of erosion.
S15	5.4	Located near the highway. Narrow and moderately deep channel. Strong evidence of erosion.
S16	6.5 *	Moderate channel depth. Bordered on both sides by farms. Evidence of erosion.
S17	6.5 *	**Tributary**.Bordered on both sides by farms. Evidence of erosion.
S18	6.5 *	Moderate channel depth. Bordered on both sides by farms. Evidence of erosion.
S19	6.9	Moderate channel depth bordered by forest and farm. Evidence of erosion.
T1	7.3	Upper border of Tushile. Narrow and deep channel. Strong evidence of erosion.

Figure 2.3 Study area and site selection for spatial and temporal tests.

Samples were taken 3-5 meters upstream from the tributary, 3-5 meters upstream in the tributary, and 3-5 meters downstream from the tributary. This procedure is represented in sites S7-9, S10-12, and S16-18 (Table 2.2).

2.3 Sampling Strategy

The first inquiry, a spatial variation analysis, consisted of a total of 80 measurements from twenty sites (S1 – T1), over a four-month period, using a multi-parameter probe to measure NH_4, NO_3, and temperature (Celsius); and a colorimeter to measure PO_4 concentrations. The second inquiry, a temporal variation analysis, was performed through two tests within a five-week period. In the first test, a total of sixty measurements were taken from three different sites (S1, S3, & T1) over twenty hours. Due to technical difficulties, the test ended at hour twenty. The second test consisted of 72 measurements, from the same three sites over twenty-four hours. The tests for this experiment were minimalistic by design, to pursue the goal of using simple and relatively inexpensive nutrient testing methods to provide the information necessary to identify major nutrient pollution sources and help guide future management decisions.

The instruments used were a YSI Professional Plus multi-parameter probe, a LaMotte SMART2 colorimeter to measure NH_4, NO_3, & PO_4 concentrations, and a Flowatch JDC flow meter to measure water velocity (km hr^{-1}). The YSI multi-parameter probe has an accuracy of ±10% of reading or 2 mg/L-N, whichever is greater and has a resolution of 0.01 mg L^{-1}. To calibrate the YSI device, a solution of 100 mg L^{-1} solution of either NH_4^+ or NO_3^- is made depending on the probe. The probe then recognizes the solution, and when reading has stabilized, a point has taken. A second calibration point was made to increase accuracy. The SMART2 colorimeter has an accuracy of 2% of Full Scale (FS), and a resolution of 1%FS. To calibrate the SMART2, the setting was set to Total Phosphorus (HR) and then a sample of distilled water is measured to set the scale. This was done before each sample of of PO_4 was measured. Sterile plastic sampling bags were used to collect PO_4 samples, which were measured within hours of collection.

2.4 Sampling Methodology

At each site, a 100 ml sample of river water was taken by submerging a sterile plastic sample bag approximately 25 centimeters underwater in the pathway of the stream flow. This sample was used for the measurement of PO_4 concentration (mg L^{-1}). Orthophosphate reacts in acidic conditions with ammonium vanadomolybdate, forming vanadomolybdophosphoric acid. The yellow color that forms is proportional to the orthophosphate concentration and is measured colorimetrically.

Next, a multi-parameter probe was lowered approximately 25 centimeters (or until the probe was completely submerged) into the center of the stream to measure concentrations (mg L^{-1}) of NH_4 and NO_3. Lastly, a flow meter probe was lowered 25 centimeters into the center of stream to measure the velocity of the stream (km/h). This measurement, combined with area estimates, was used to calculate stream flow.

To calculate the stream flow, the sampling area of the river was first estimated. This was don Flowatch JDC flow meter e by calculating the area of A1, A2, and A3 (m^2) and then multiplying each of these areas by the stream velocity (km h^{-1}) (Figure 2.4). Equations used for calculations are listed below(Eq. 2.1, 2.2, & 2.3).

Equation 2.1

$$A1 = \frac{1}{2}d1\frac{L}{3} = \frac{1}{6}d1 * L$$

Equation 2.2

$$A2 = \frac{1}{6}d2 * L$$

Equation 2.3

$$A3 = \frac{\frac{1}{2}(d1 + d2)L}{3} = \frac{1}{6}L(d1 + d2)$$

The average flow was calculated by adding the flow velocity estimates ($m3/h^{-1}$) for each section and converting to a common measurement (L s^{-1}) (Eq. 2.4). Flow velocity was measured using Flowatch JDC flow meter by placing the probe into the stream in approximately the center of the stream/flow and holding the probe approximately 25 cm in the water for 30-60 seconds to gain a stable velocity reading.

Equation 2.4

$$Q = V1A1 + V2A2 + V3A3$$
$$= \frac{1}{6}d1 * L * V1 + \frac{1}{6}d2 * L * V2 + \frac{1}{6}L(d1 + d2) * V3$$
$$= \frac{L}{6}[d1V1 + d2V2 + V3(d1 + d2)]$$

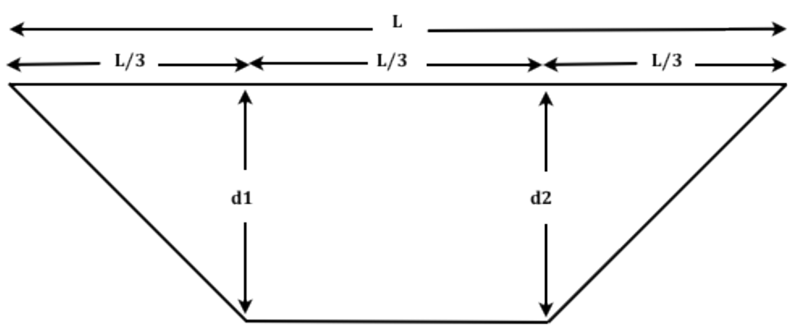


Figure 2.4 Schematic for estimating area of a sampling location on the Klina River.

2.5 Logistics

Based on the location of the study area, there were several key things necessary for completion of the study that were unique to Kosovo as a foreign and developing country. First, gaining permission and access to certain sections of the river was difficult and required the aid of a translator. Due to years of war and being forced off their property, local Albanians are distrustful of outsiders and most of their property is fenced off with barbed wire all the way to riverbank. Some areas of the river were off limits and we were forced to find alternative sampling sites.

Second, because the type of work that we were doing was unique in Kosovo, and because it was being done at odd hours, by necessity we were required to hire a local university student to communicate with skeptical residents to prevent incident. Next, it was necessary to locate a suitable vehicle that could transport our equipment and drive off-road, as some of our testing sites were not accessible from the highway. This required making a rental agreement with the local chapter of the Red Cross.

Finally, obtaining the reagent needed for the PO_4 measurements required vanadomolybdate, which is considered a hazardous chemical and is illegal to ship from the United States to Europe and is impossible to purchase in Kosovo. Therefore, we identified a source from the United Kingdom and had them shipped to a contact at the Peja Agricultural Institute to receive the chemicals, as having a permanent local address was required for receiving such shipments.

3.0 Results & Discussion

3.1 Spatial Variation of Nutrient Enrichment

Ammonium & Nitrate

A series of twenty different sites (Figure 2.2) were monitored over a four-month period, from April 2011 through July 2011, to determine potential point sources of nutrient enrichment. A four-month average showed that ammonium (NH_4) concentration increased by 780% from 0.10 mg L^{-1} at S1 to a peak of 0.88 mg L^{-1} at S3 (Figure 3.1). This was calculated by finding the four-month mean of each site and then calculating the percent increase (Eq. 3.1).

Equation 3.1 $$(S3-S1)/S1 * 100$$

Over the next approximately seven kilometers, average NH_4 concentration steadily decreased from 0.88 mg L^{-1} to 0.24 mg L^{-1} at T1 (Figure 3.1 A). The month

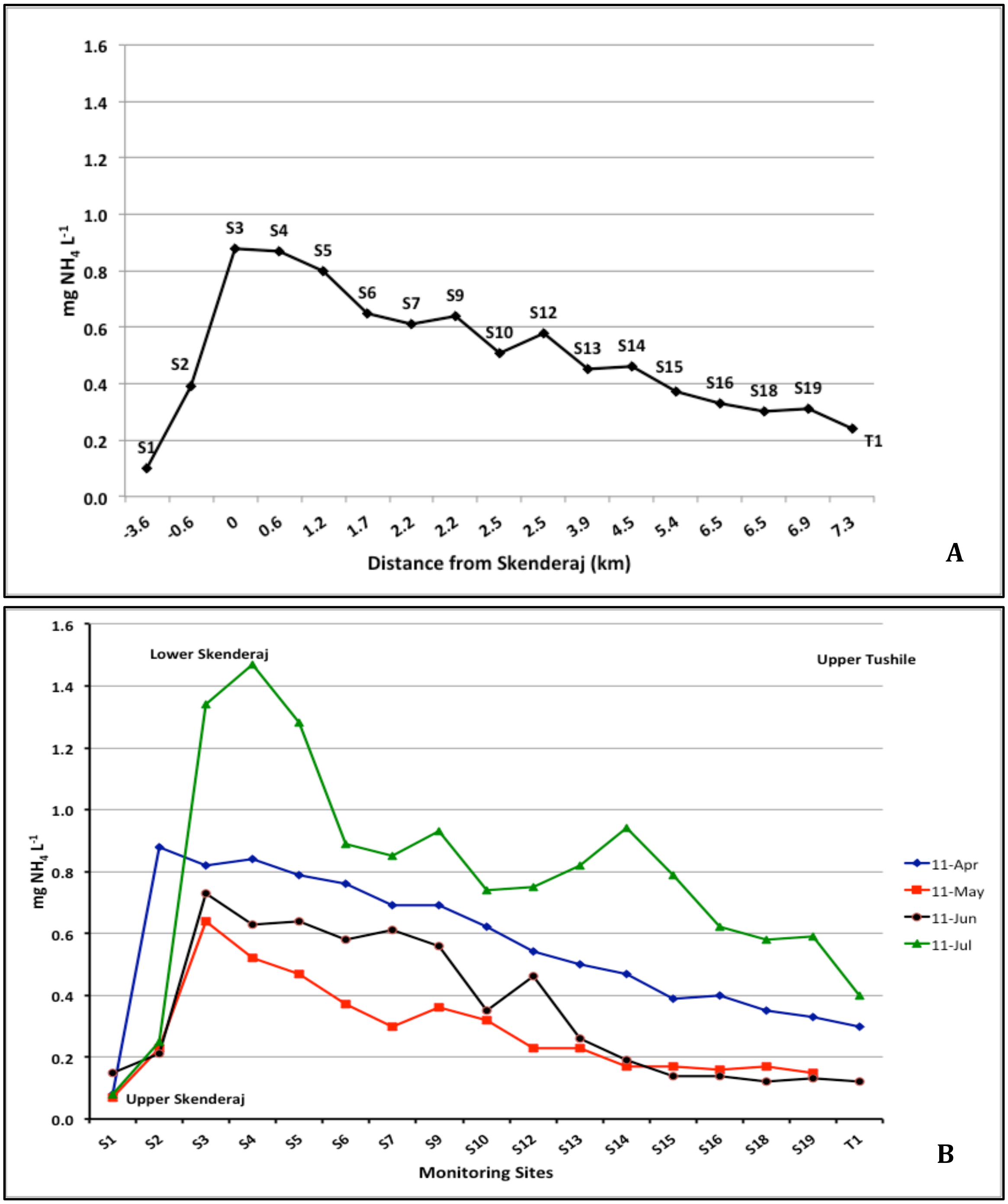


Figure 3.1 Average NH_4-N concentration in mg L^{-1} in mg L^{-1}. S1 and S3 mark the upper and lower boundaries of the city of Skenderaj while T1 marks the upper boundary of the village of Tushile (A) Monthly comparisons of NH_4-N concentration. (B)

of July saw the sharpest increase in concentration with a 1700% increase from 0.08 mg L^{-1} at S1 to 1.47 mg L^{-1} at S4 (Figure 3.1 B). Three tributaries (S8, S11, S17), fed

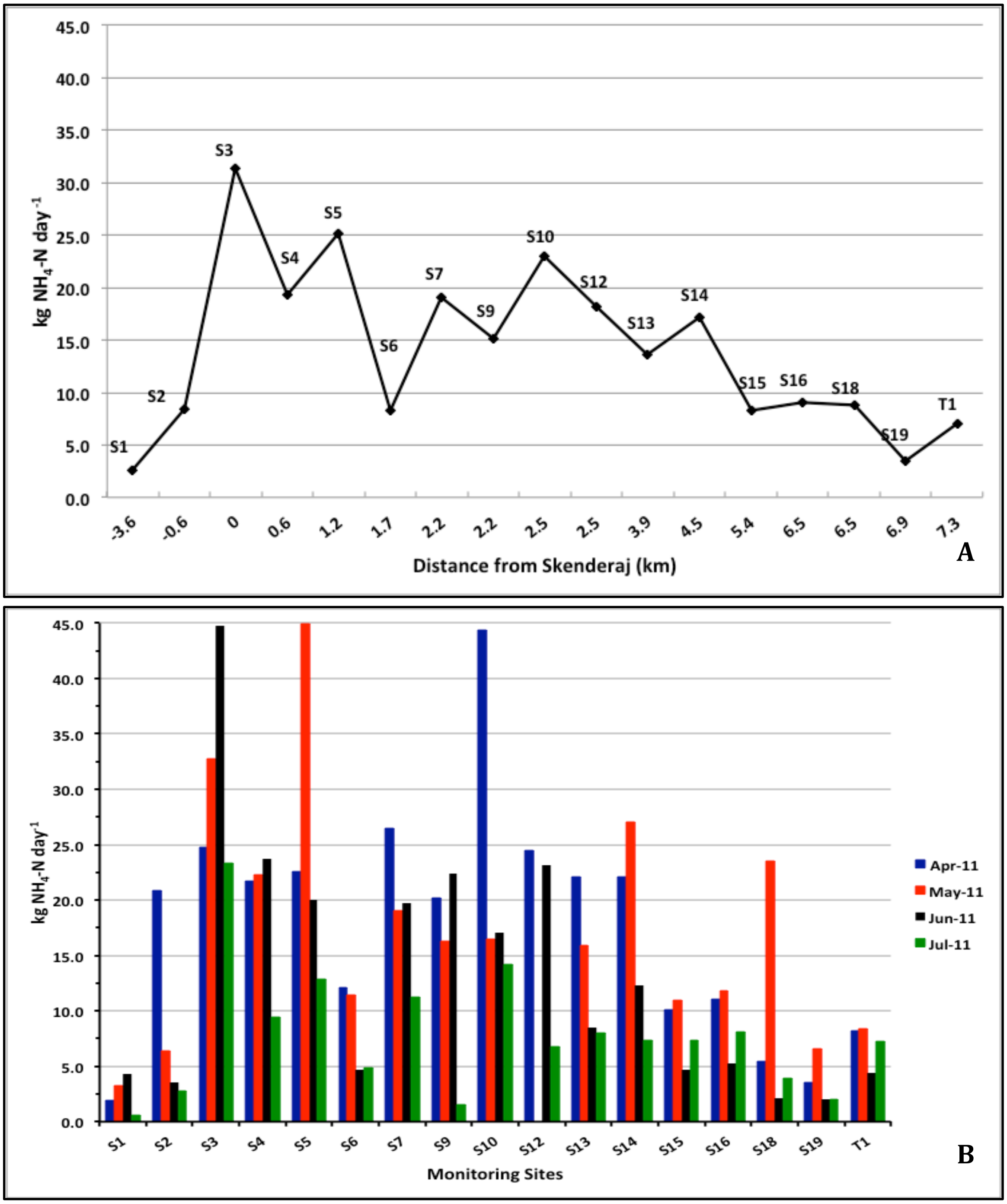


Figure 3.2 Average NH_4-N load kg day^{-1} (A) and monthly collations of NH_4-N load kg day^{-1} (B) show a similar pattern of increasing after leaving the city of Skenderaj and steadily decreasing over the next

seven kilometers. Load trends also appear to track closely with past and predicted precipitation inputs (Fig 2.1).

into this reach of the Klina River. NH_4 concentrations in each tributary decreased by 65-90 %, seeing nutrient levels similar to those found at S1.

Average ammonium nitrogen loads for this time saw a steeper rise, increasing over 1000% from 2.5 kg day^{-1} at S1 to 31.4 kg day^{-1} at S3. Like concentration levels, NH_4 load levels steadily decreased, reaching 7.1 kg day^{-1} entering the village of Tushile (Figure 3.2 A). A four-month comparison displays results with the months of April and May having highest overall nutrient loads (Figure 3.2 B). While load rates did decrease in NH_4 enrichment over the 11km stretch of river, load rates were decisively more variable than concentration levels. Despite the variability, nutrient loads decreased by an average of 77% over the four month period. Nitrate nitrogen (NO_3-N), was found to have a much different trend, with only a slight increase in concentration from S1 to S3. Average concentration levels then dipped slightly from S3 to S5, and then increased steadily to T1. Overall, there was a 111% increase from 0.92 mg L^{-1} at S1 to 1.94 mg L^{-1} at T1 (Figure 3.3 A). A monthly comparison of NO_3 concentrations showed similar trends each month, with increases each month, with July showing the highest concentrations levels S1 to T1 (Figure 3.3 B). Average NO_3 load patterns trended similarly, with a steady increase of 192% from 6.17 kg day^{-1} at S1 to 18.01 kg day^{-1} at T1 (Figure 3.4 A). However there was much stronger variation, especially in the month of May seeing a spike of 80 kg day^{-1} at S18. Where July showed the highest concentrations levels S1 to T1, load levels of NO_3 were the lowest in July (Figure 3.4 B). This would be a result of the Klina River losing much of it's volume and nearly drying up during the summer months.

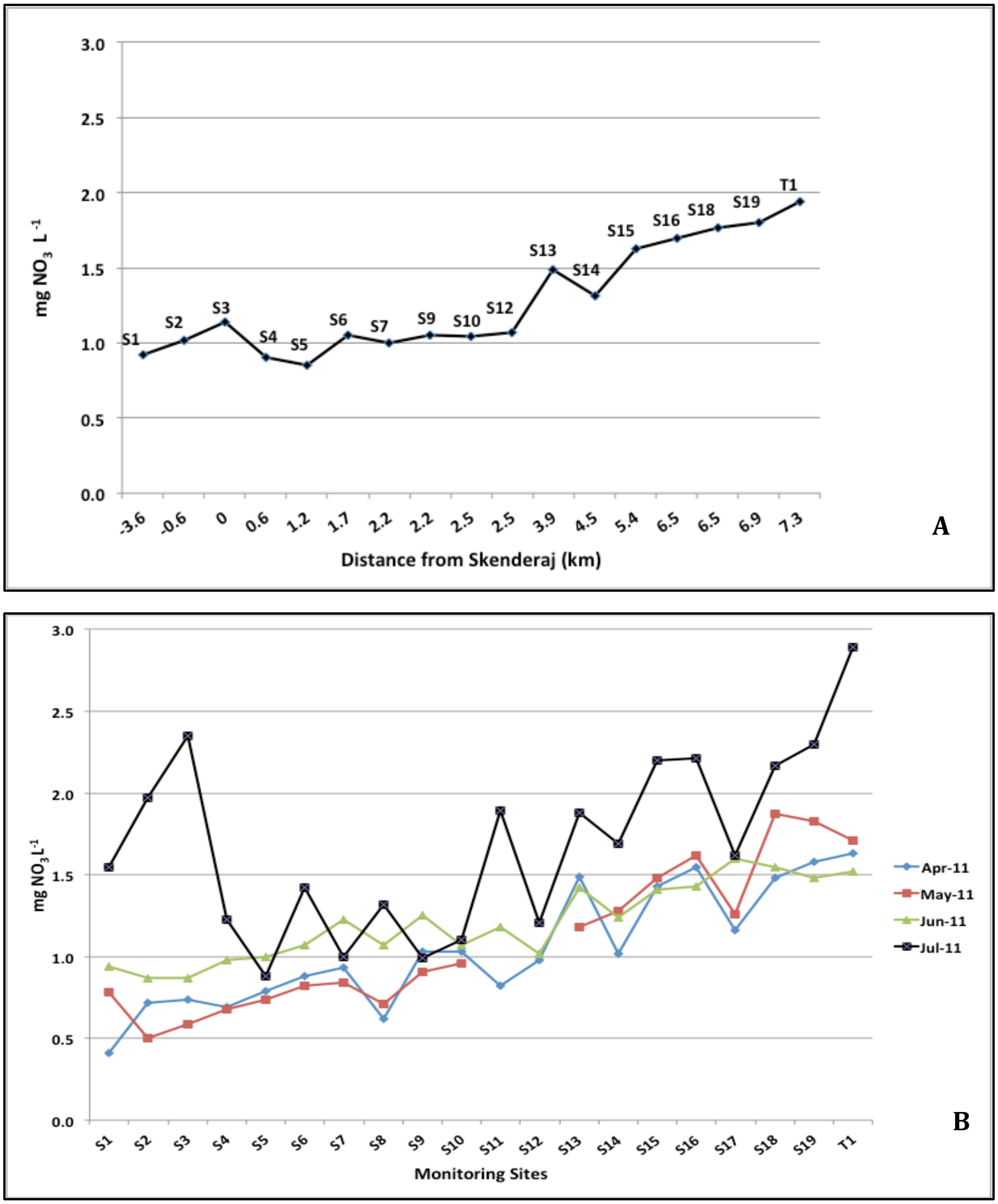
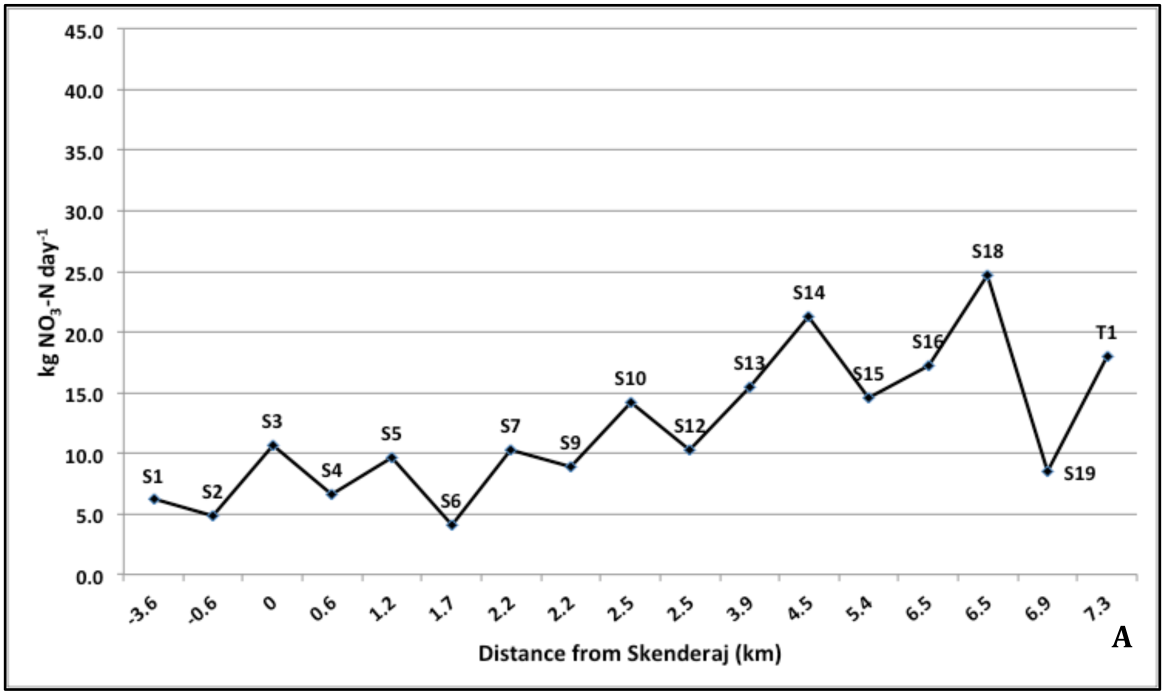
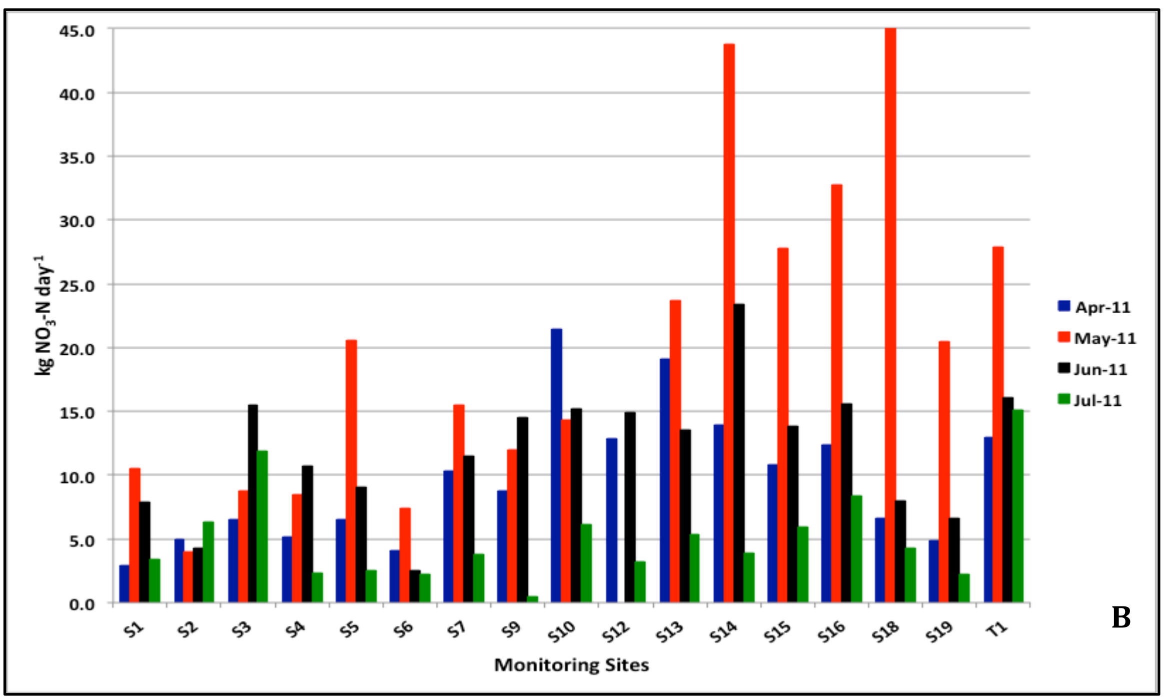


Figure 3.3 Average NO_3-N concentration mg L^{-1} April – July 2011 shows a steady increase of NO_3-N in this stretch of the Klina River (A) A four-month comparison (April – July 2011) of NO_3-N concentration (B) shows that concentration levels also increase in the summer months which is potentially linked to decreasing flow levels in the Klina River (Table 4.1).



45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
kg NO3-N day-1
S1
S2
S3
S4
S5
S6
S7
S9
S10
S12
S13
S14
S15
S16
S18
S19
T1
-3.6
-0.6
0
0.6
1.2
1.7
2.2
2.2
2.5
2.5
3.9
4.5
5.4
6.5
6.5
6.9
7.3
Distance from Skenderaj (km)
A

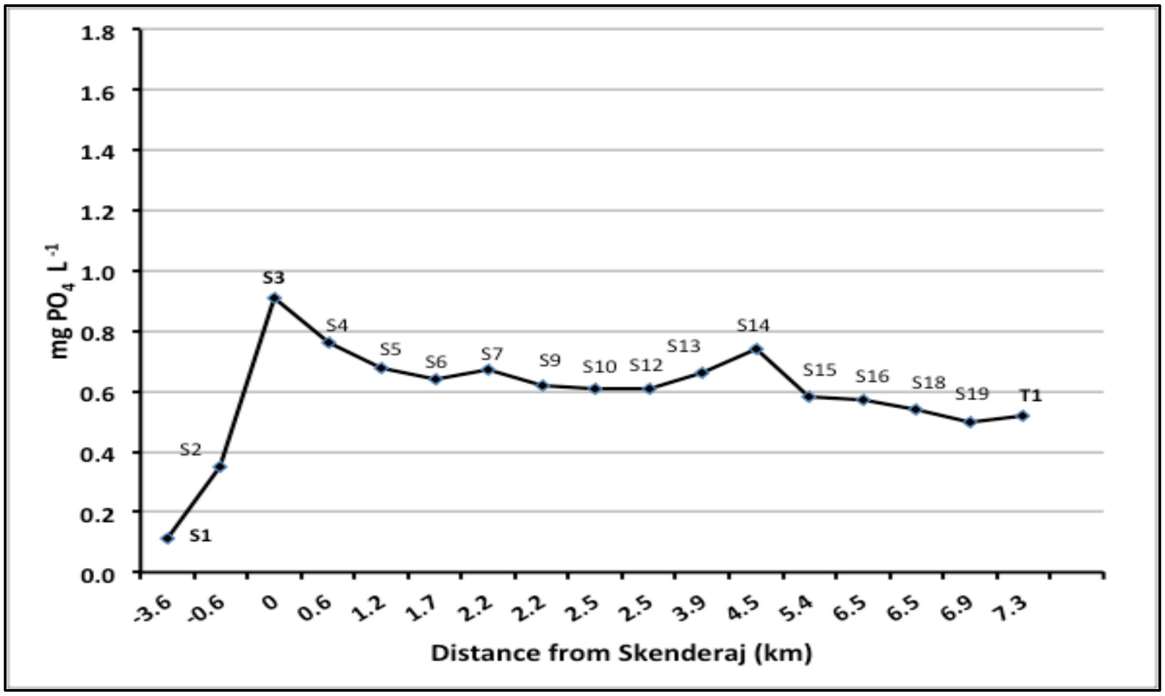


45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
kg NO3-N day-1
Apr-11
May-11
Jun-11
Jul-11
S1
S2
S3
S4
S5
S6
S7
S9
S10
S12
S13
S14
S15
S16
S18
S19
T1
Monitoring Sites
B

Figure 3.4 Average NO_3-N load kg day^{-1} shows a general pattern of increase over this 11km stretch of the Klina River (A) A four month comparison (April – July 2011) of NO_3-N load (B) shows that load rates are not only influence by flow rates (Table 4.1), but also potentially by environmental factors like temperature (Fig 3.8).

Phosphate

Measurements of average PO_4 concentrations showed a strong increase of 727% from 0.11 mg L^{-1} at S1 to 0.91 mg L^{-1} at S3. PO_4 concentrations then steadily



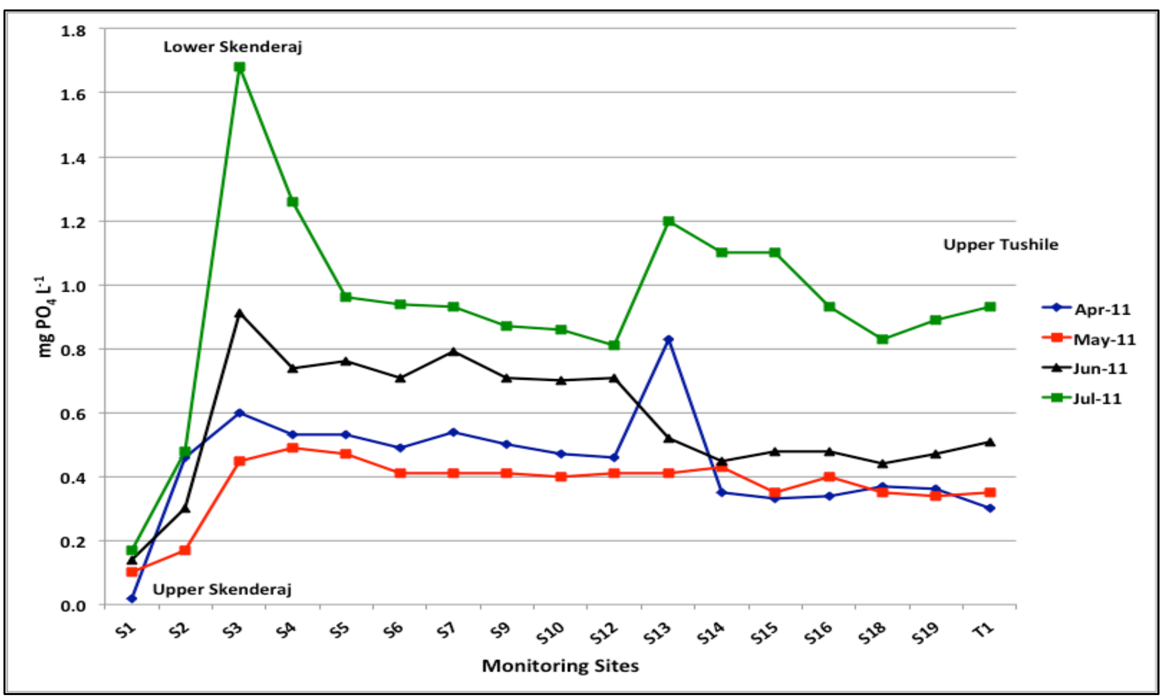


Figure 3.5 Average PO_4 concentration mg L^{-1} April – July 2011 show that PO_4 follows a similar pattern as NH_4-N (A) A four-month comparison (April – July 2011) of PO_4 concentration shows, like NH_4-N, that concentration levels increase during the summer months (B).

declined from S4 to T1, ending with a concentration of 0.52 mg L^{-1} (Figure 3.5 A). A monthly comparison of April – July 2011 showed similar patterns of enrichment from S1-T1, with July seeing the highest concentration levels (Figure 3.5 B).

Load rates of PO_4-P saw a very strong average increase of 1100% from 1.10 kg day^{-1} at S1 to 13.23 kg day^{-1} at S3 (Figure 3.6). Load rates continued to generally decrease despite spiking to 27.42 kg day^{-1} at S12 before ending at 6.63 kg day^{-1}, a 500% increase from S1. The months of May and July saw the highest and lowest overall load rates respectively (Figure 3.7).

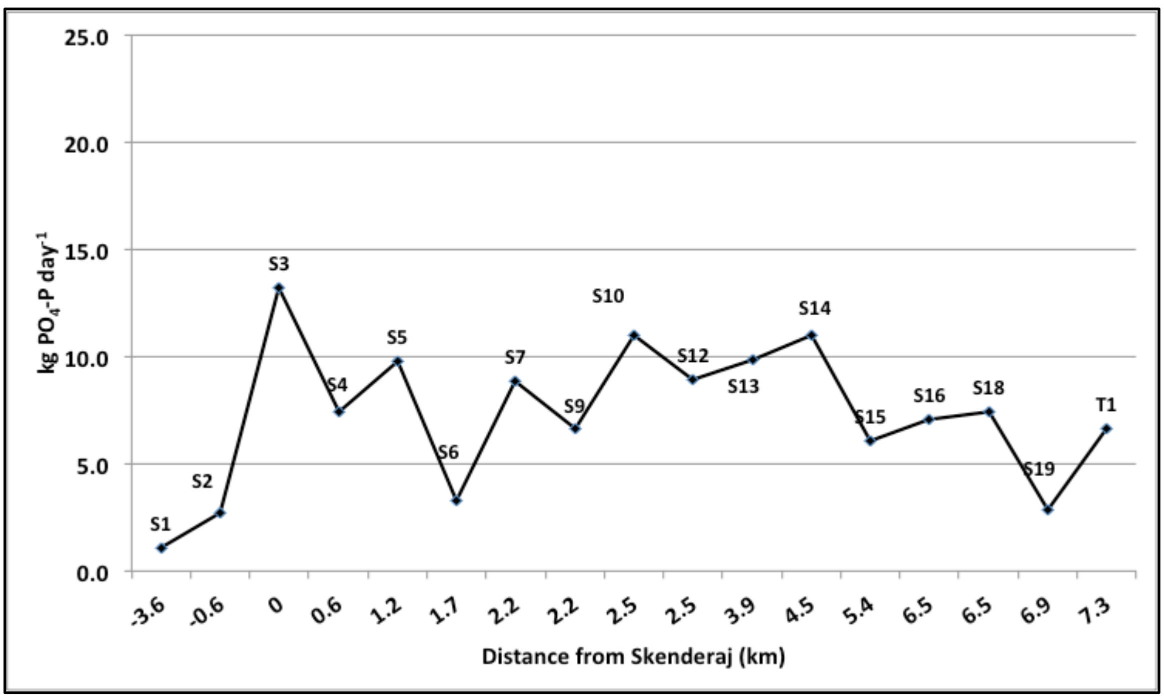


Figure 3.6 Average PO_4-P load kg day^{-1} April – July 2011 show that load rates that significantly increase in waters leaving Skenderaj (S3) and then steadily decrease over the next seven kilometers. Average load rates entering Tushile (T1) are approximately 500% higher than those entering Skenderaj (S1). A four-month comparison (April – July 2011) of PO_4-P load kg day^{-1} corresponding to distance in kilometers (D) Averages were not calculated for tributary sites (S8,11,&17).

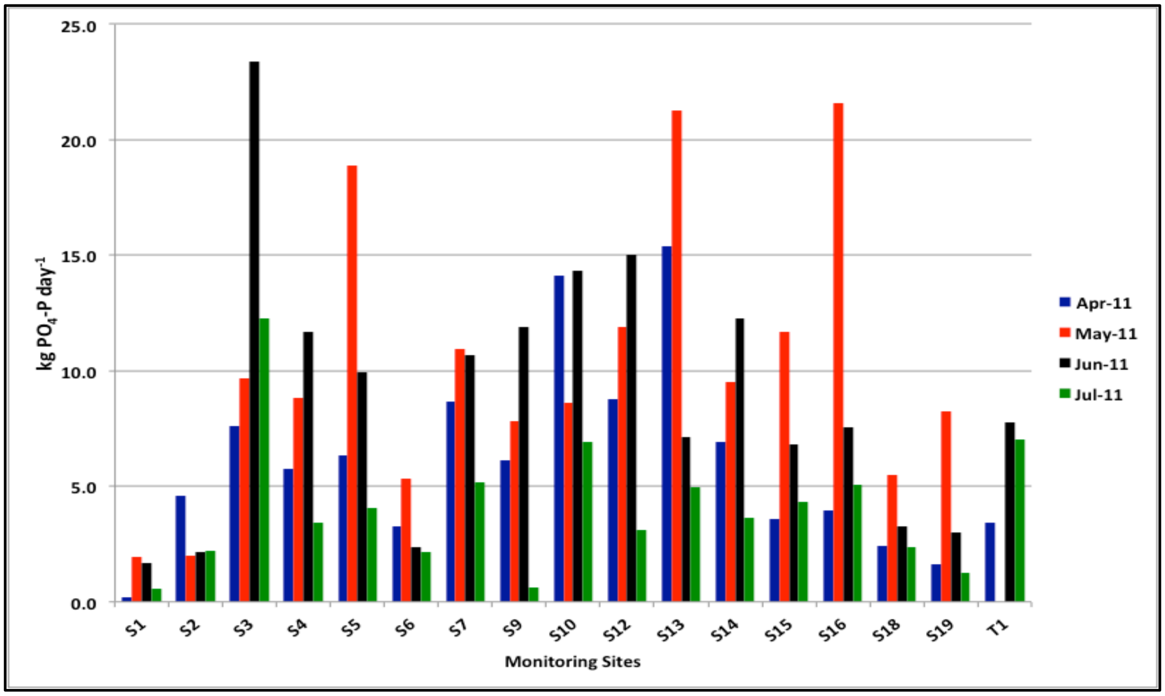


Figure 3.7 PO_4-P load kg day^{-1}. A four-month comparison (April – July 2011) of PO_4-P load rates shows that PO4-P loads were highest during months that had the highest flows (Fig. 3.7) potentially indicating that seasonal flow patterns are a controlling factor of nutrient loads.

Flows

Flow rates for the Klina River during the time period of April – July 2011 show the river flowing at an average rate of 15.3 cubic feet per second (cfs). However the flow of the Klina River varies greatly and is significantly influenced by seasonal precipitation in May and June, which was consistent with predicted seasonal patterns for this area of Kosovo (Figure 2.1). Average flow rates ranged from a low of 4.5 cfs in July to a high of 28.3 cfs in May, with a number of the monitoring sites peaking with flow rates above 50 cfs (Figure 3.8). This increase of flow can be partially attributed to the three tributaries **(S8, S11, S17)** that flow into

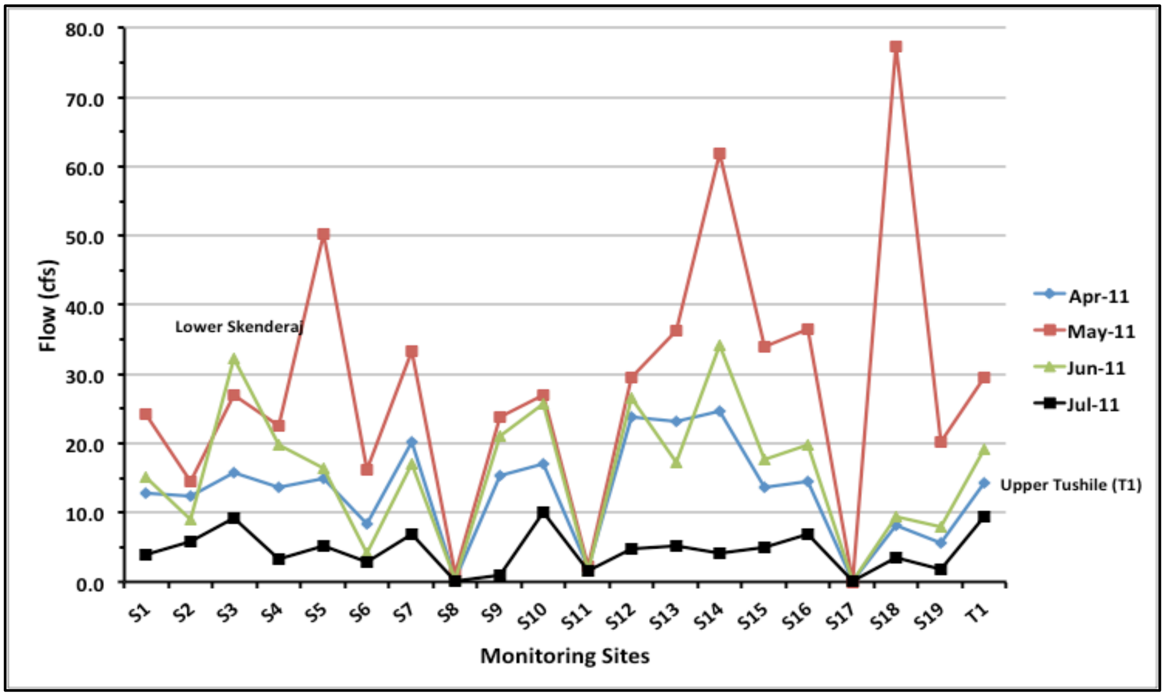


Figure 3.8 Flow rates cubic feet per second (cfs). A four-month comparison (April – July 2011) shows a strong decrease from May to July, likely as a result of the flow being strongly influenced by seasonal precipitation.

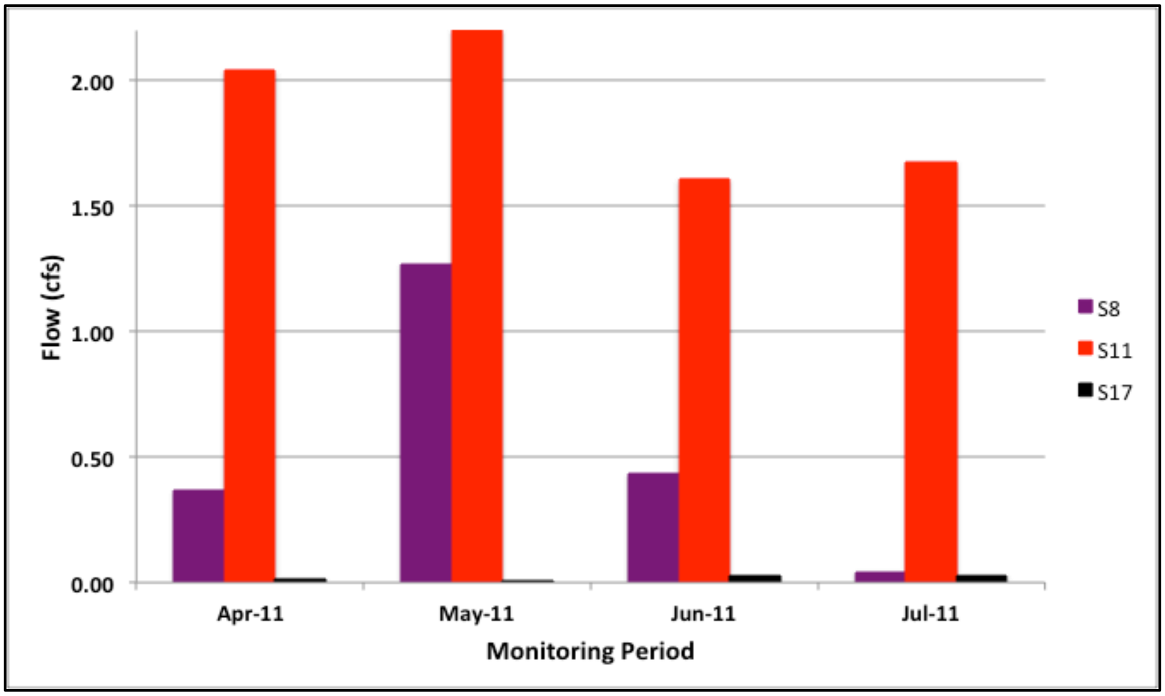


Figure 3.9 Monthly flow rate (cubic feet per second) from tributaries. Tributary S11 shows to be the most significant source of water (Avg. 1.9 cfs) entering this section of the Klina River during this four-month period.

the Klina River (Fig 3.9). The S11 tributary consistently (& significantly) contributed a greater flow into the Klina River than S8 or S17, averaging a rate of 1.9 cfs (Fig 3.8).

Tributaries

Contributions of previously mentioned nutrients by tributaries in this reach of the Klina River were rather insignificant during the given monitoring period. Load rates for PO_4-P were lowest with ranges of 0.1 – 0.7 kg day^{-1}. NH_4-N load rates were slightly higher and ranged from 0.1 – 1.2 kg day^{-1}. NO_3-N rates were highest and ranged from 0.02 – 1.75 kg day^{-1}. Of the three tributaries, S11 was the largest source of all three nutrients contributing 136% more NH_4-N and NO_3-N and 166% more PO_4-P than tributary S8 (Figure 3.10 & 3.11).

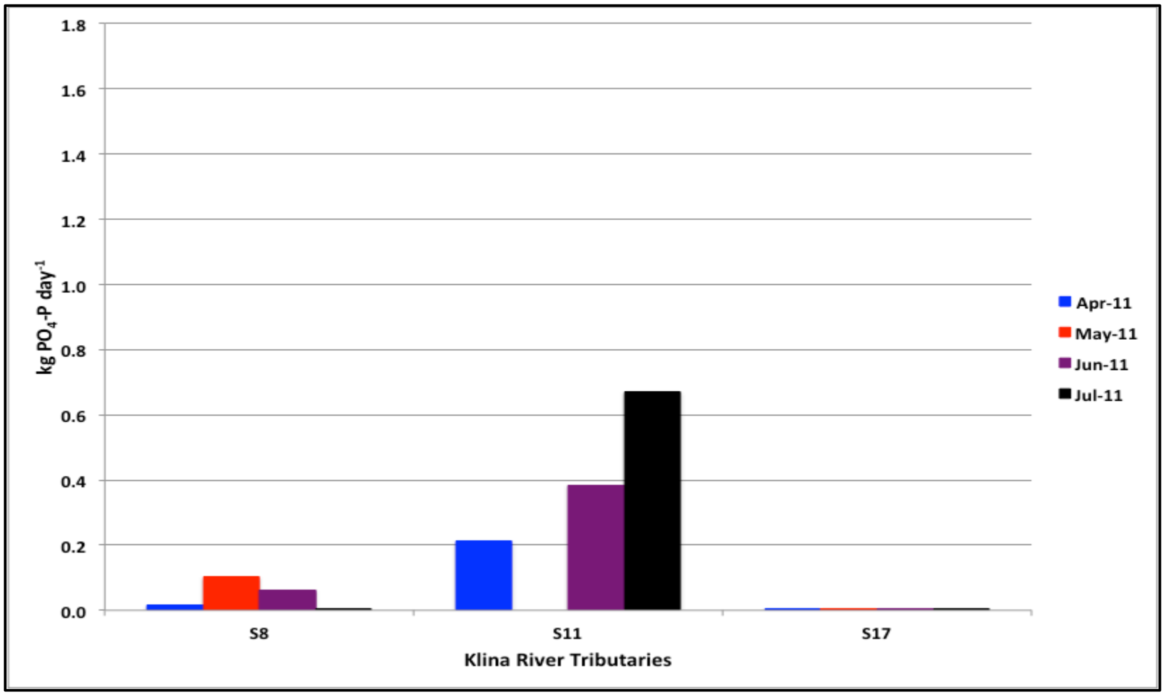
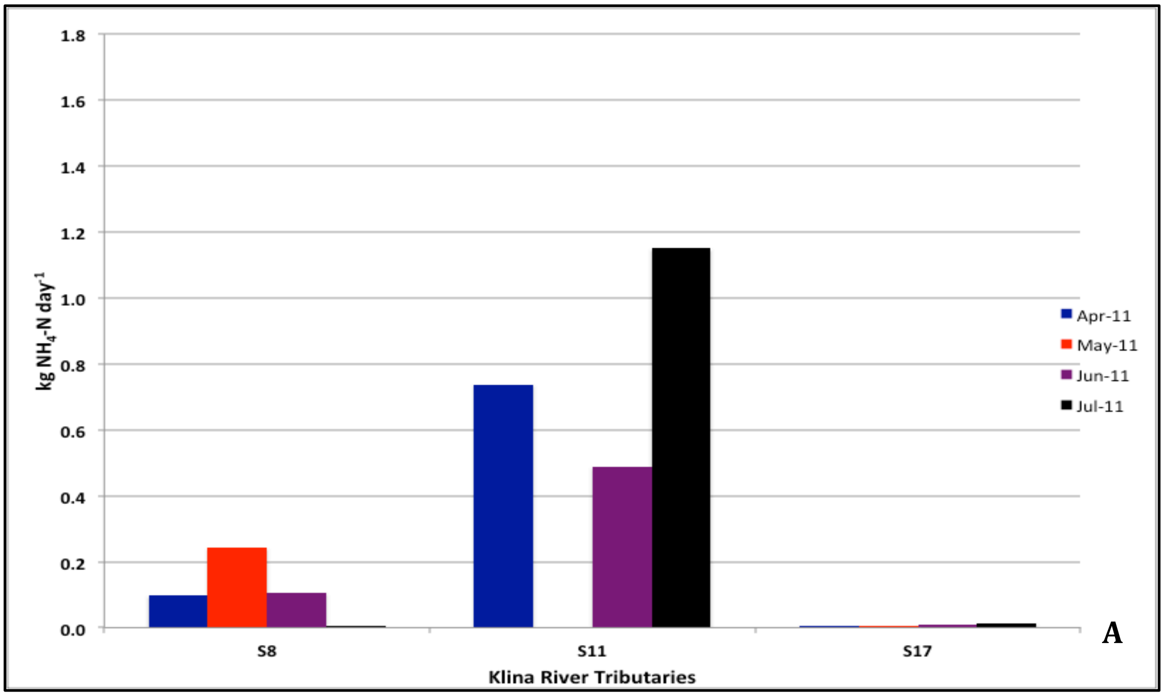


Figure 3.10 PO_4-P load rates (kg day^{-1}) in the Klina tributaries were relatively low in comparison to the actual stream. Tributary S11 was significantly higher than the other two tributaries likely in part from it running through the village of Llaushe before entering the Klina River (Fig 2.3).



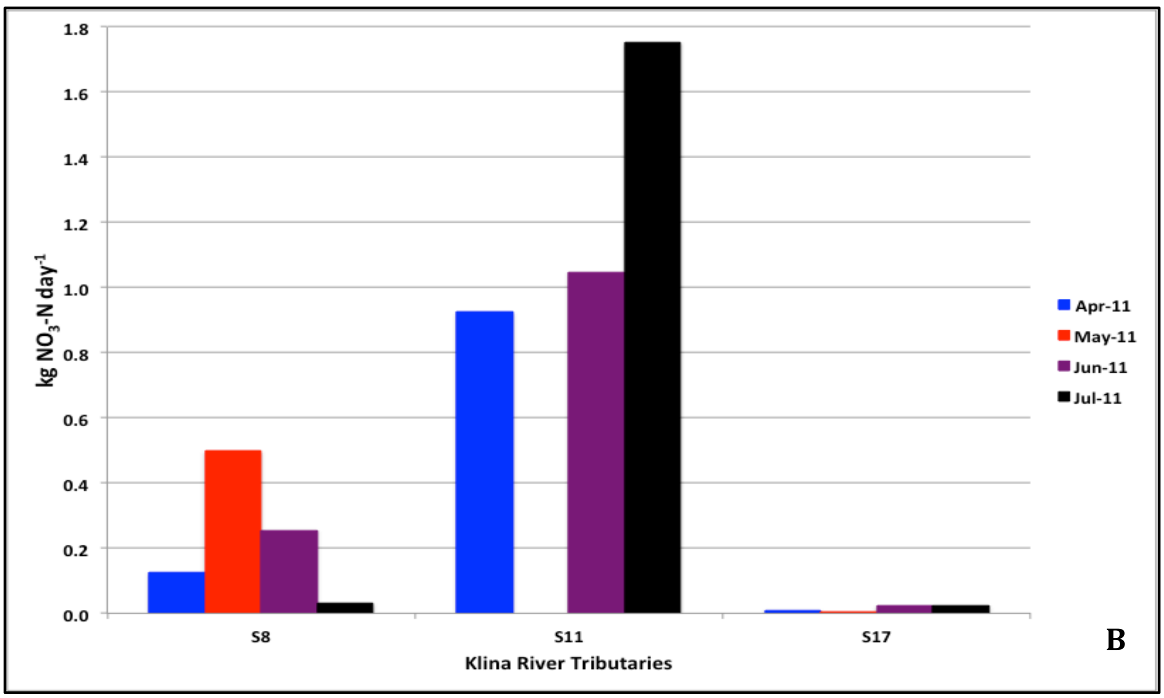


Figure 3.11 Nutrient load rates (kg day^{-1}) of NH_4-N(A) and NO_3-N(B). Tributaries S8 and S11 contributed an average of 98% of NH_4-N and 96% of NO_3-N delivered by all three tributaries. Due in part by steady flow from S11 (Fig. 3.8), nitrogen load rates stayed consistently high during the months in which precipitation usually decreases.

Temperature

Water temperature was monitored at each site (S1 to T1) for the four-month period (April – July 2011) to determine any significant seasonal change. Stream temperatures increased only moderately from S1 to T1 each month (April to July). However when comparing each month, increases of 2.6 – 8.3 °C were measured (Figure 3.12).

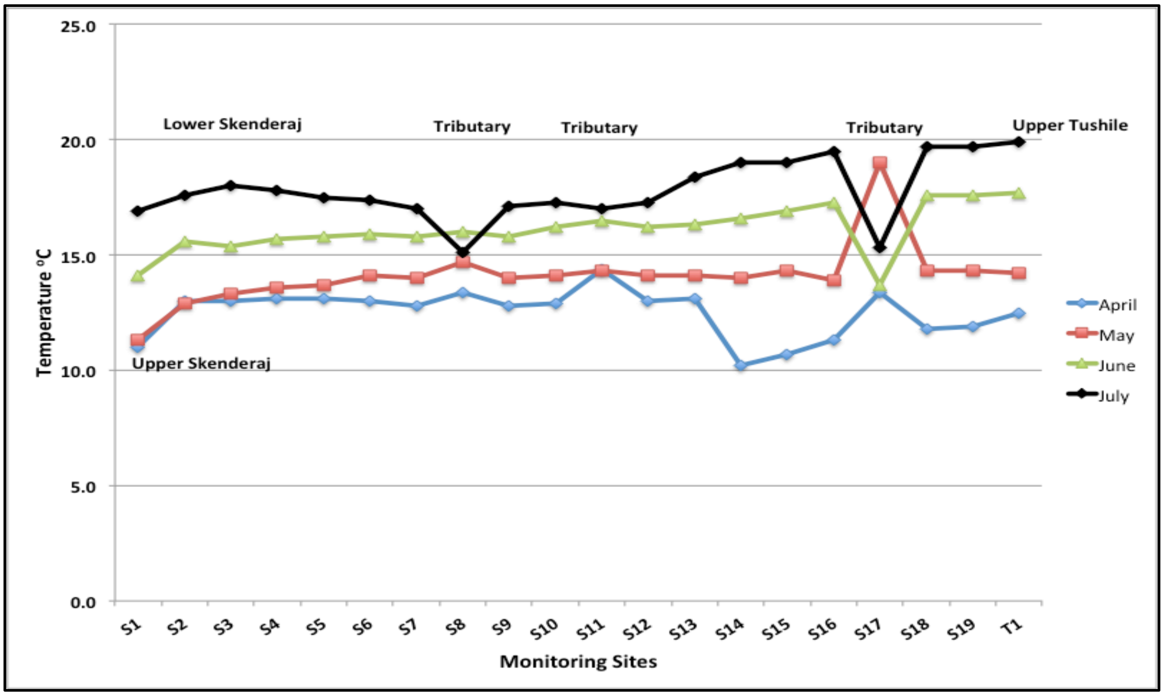


Figure 3.12 A four-month (April to July 2011) comparison of stream temperature °C. shows the steady increase of water temperature over each month. The Klina River increased by an average of 5.3°C during these four months.

3.2 Temporal Variation of Nutrient Enrichment (24h. Analysis)

A 24-hour monitoring of the Klina River was performed twice during a five-week period on April 27, 2011 and June 1, 2011. Stream waters entering and leaving Skenderaj were sampled and compared every hour, with waters entering the village of Tushile.

Nutrient Concentrations

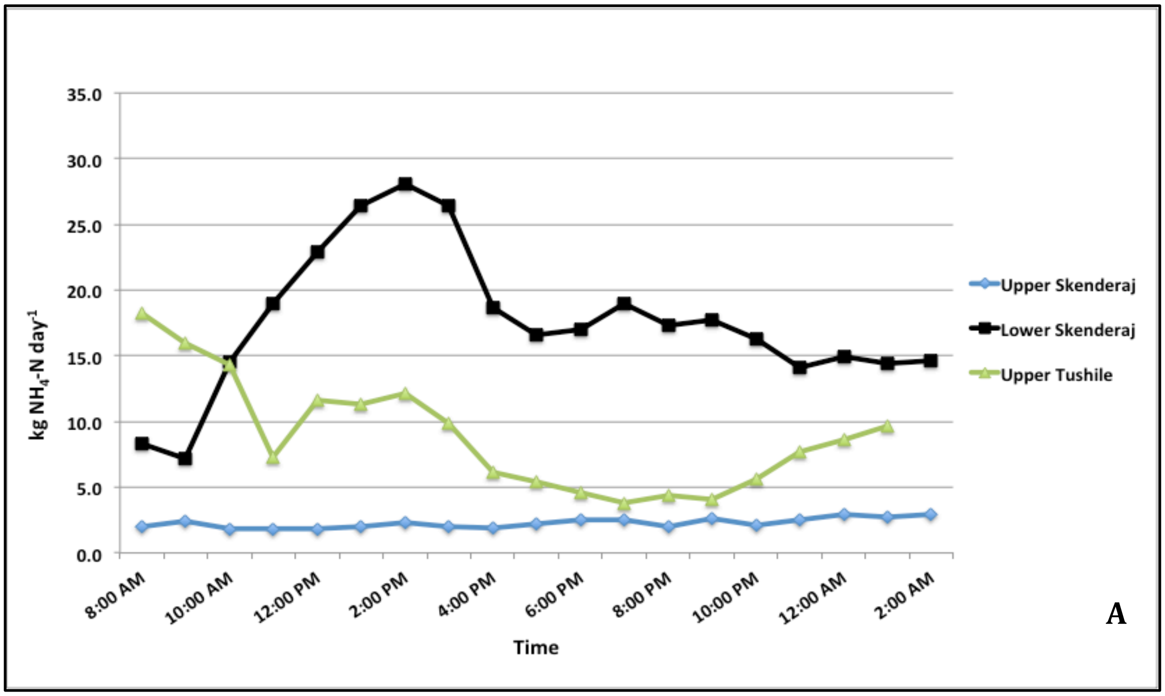
In the first test, average concentrations of NH_4 increased from 0.1 mg L^{-1} at S1 to 0.76 mg L^{-1} at S3. The second test saw NH_4 concentrations increase from 0.09 mg L^{-1} at S1 to 0.44 mg L^{-1} at S3, an average increase of 480%. At T1, which is approximately seven kilometers downstream from S3, average concentrations of NH_4 decreased to 0.32 mg L^{-1} and 0.18 mg L^{-1} for test 1 and 2 respectively. At the same time, NO_3 concentrations from test 1(April 2011) and 2(June 2011) increased slightly from 0.83 and 1.11 mg L^{-1} at S1 to 1.28 and 1.22 mg L^{-1} respectively at S3. NO_3 concentrations at T1 increased to 1.68 and 1.82 mg L^{-1} (Table 3.1). Increases of average PO_4 concentrations were higher, increasing by 467% from 0.04 and 0.13 mg L^{-1} at S1 to 0.48 and 0.53 mg L^{-1} at S3, and then finally decreasing to 0.32 and 0.33 mg L^{-1} at T1.

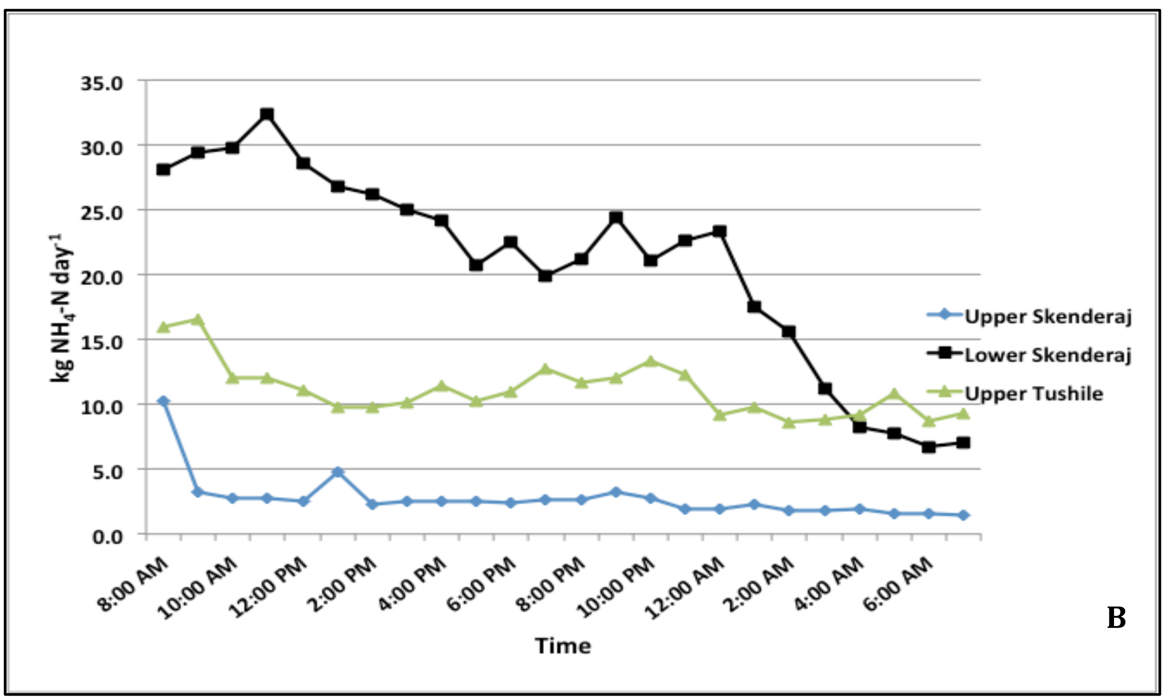
Table 3.1: 24-Hour Average Nutrient Concentrations (mg L^{-1}) with standard deviation.

	4/27/2011 (Test 1)			6/1/2011 (Test 2)		
	S1	**S3**	**T1**	**S1**	**S3**	**T1**
NH_4	0.10 (±0.01)	0.76 (±0.17)	0.31 (±0.11)	0.09 (±0.05)	0.44 (±0.13)	0.18 (±0.04)
NO_3	0.83 (±0.11)	1.28 (±0.68)	1.68 (±0.22)	1.11 (±0.11)	1.22 (±0.08)	1.82 (±0.19)
PO_4	0.04 (±0.02)	0.48 (±0.17)	0.32 (±0.05)	0.13 (±0.05)	0.53 (±0.11)	0.33 (±0.09)

Nutrient Loads

Nutrient loads for these two tests saw similar trends, with nutrient levels (kg day^{-1}) for all three nutrients increasing downstream of Skenderaj city limits (S3).





NH_4-N loads increased from 2.27 and 2.76 kg day^{-1} at S1 to 17.54 and 8.60 kg day^{-1} at S3. Averages for T1 were 8.93 and 11.13 kg day^{-1}, an average 300 % increase from load levels at S1 (Figure 3.13). NO_3-N load levels saw occasional spiking at S3,

Figure 3.13 Temporal variation of NH_4-N loads (kg day^{-1}) of the Klina River. Panel A represents a 20hr period of monitoring in April 2011 of NH_4-N loads upstream and leaving the city of Skenderaj (S1&S3) and entering the village of Tushile (T1). Panel B represents a 24hr monitoring of the same locations in June 2011.

but generally saw a slight increase from S1, and then saw significant increases at T1 (Figure 3.14 a & b). Results for PO_4-P loading showed similar trends as NH_4-N, seeing average loads of 0.41 and .160 kg day^{-1} at S1 increase to 4.79 and 10.42 kg day^{-1} at S3 and eventually decreasing to 3.68 and 8.13 kg day^{-1} at T1 (Fig 3.15 a & b).

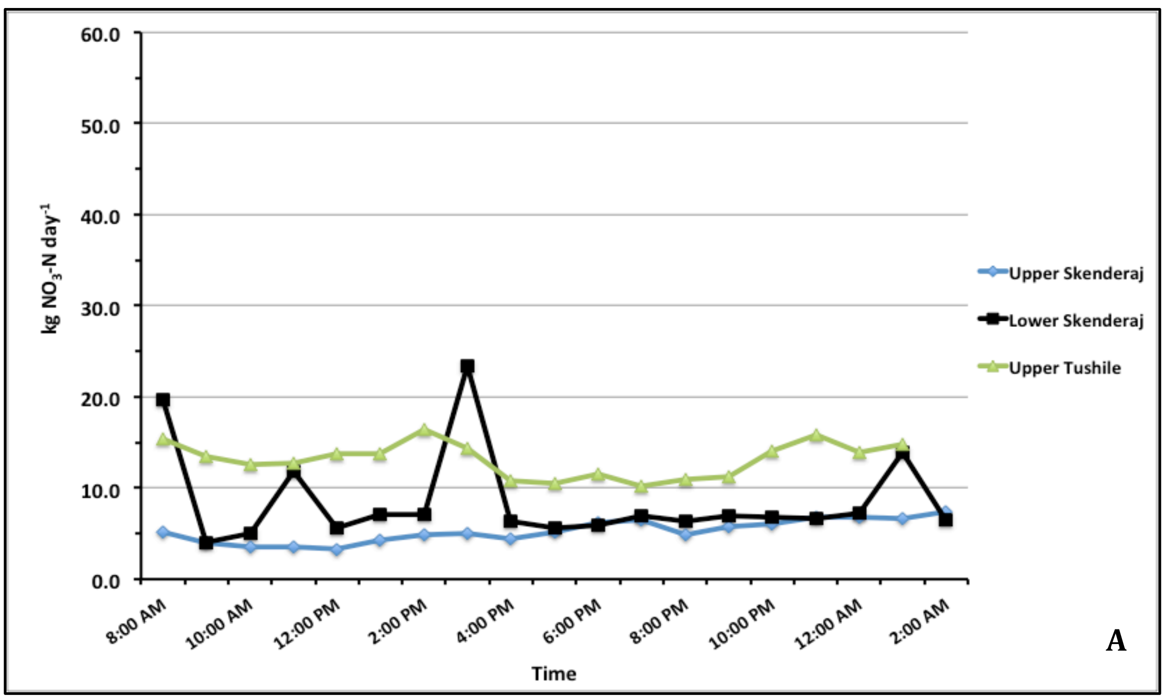


Figure 3.14a Temporal variation of NO_3-N loads (kg day^{-1}) of the Klina River. Panel A represents a 20hr period of monitoring in April 2011 of NO_3-N loads upstream and leaving the city of Skenderaj (S1&S3) and entering the village of Tushile (T1). This chart shows periodic peaking of NO_3-N loads leaving the city of Skenderaj and much greater levels 7km downstream entering the village of Tushile.

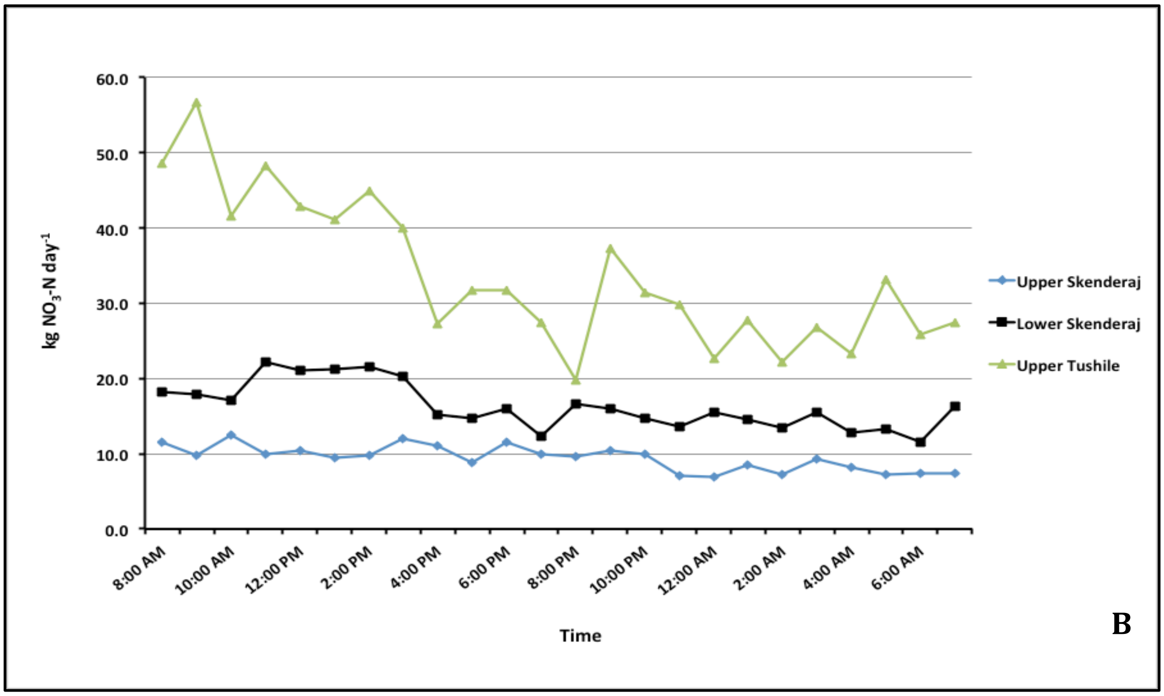


Figure 3.14b Panel B represents a 24hr monitoring of NO_3-N loads at the same locations in June 2011. In the time span between test 1 in April and test 2 in June, NO_3-N loads at each site more than doubled, though the trend of increasing downstream from Lower Skenderaj to Upper Tushile was consistent in both tests.

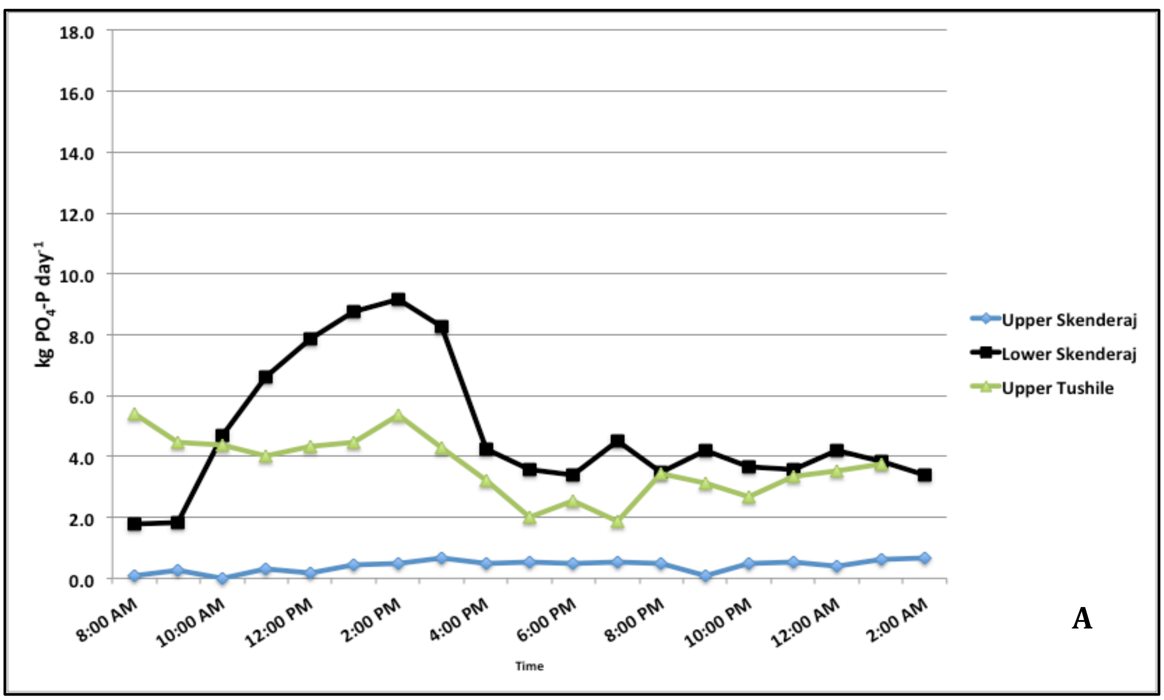


Figure 3.15a Temporal variation of PO_4-P loads (kg day^{-1}) of the Klina River. PO_4-P loads leaving Skenderaj increased throughout the day and peaked in the afternoon. This trend was consistent in both the April 2011 and June 2011 tests (Fig 3.14b).

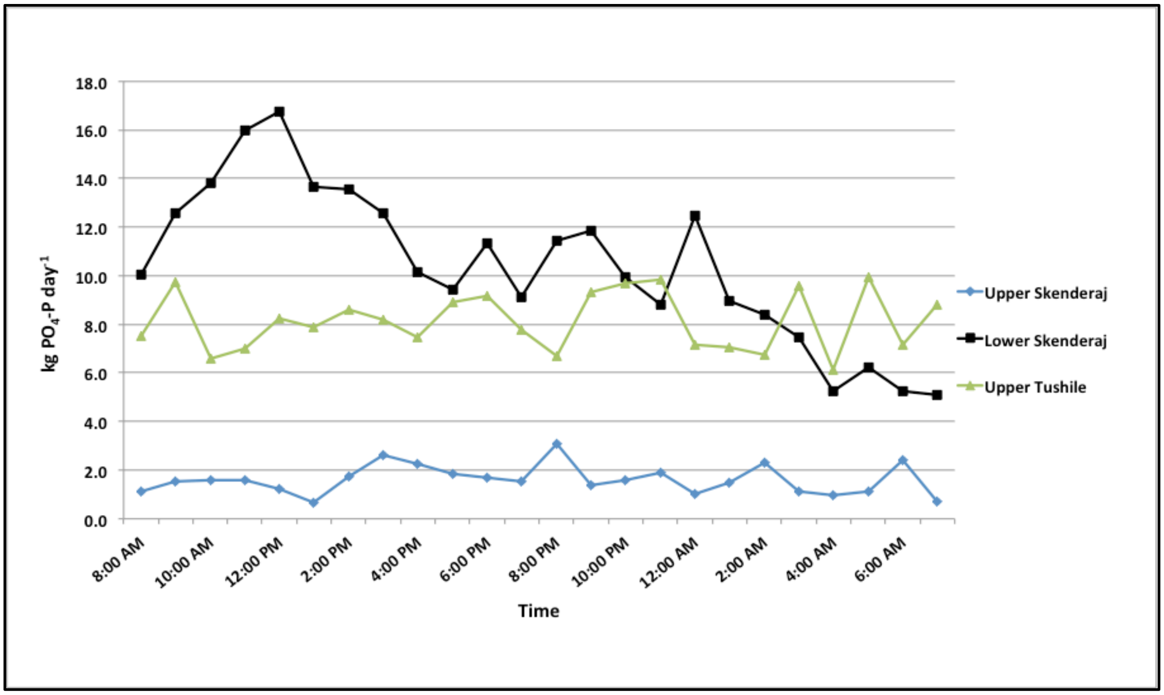


Figure 3.15b Panel B represents a 24-hour monitoring of PO_4-P load (kg day^{-1}) in June 2011. Overall load rates of PO_4-P almost doubled from load rates in April 2011 (Fig 3.14a).

4.0 Discussion

4.1 Spatial Variation of Nutrient Enrichment

Ammonium & Nitrate

It is clear that the municipality of Skenderaj is one of the largest contributors of nutrient enrichment to the Kline River. If Kosovo were part of the European Union, the Klina River would likely be ecologically classified category A3 by the council directive 75/440/EEC, which is the standard for ecologically classifying all streams within the EU. Category A3 indicates that biological quality elements for surface water deviate moderately from those under undisturbed conditions (ECE

2011). As a guide council directive 75/440/EEC states that waters used for drinking water must meet the following accepted nutrient concentrations (mg L^{-1}):

NH_4 - 2 mg L^{-1}; NO_3 - 10 mg L^{-1}; PO_4 - 0.7 mg L^{-1}.

Nutrient concentration and load levels upstream of Skenderaj were within these accepted European Union (EU) standards (ECE 2011). However, NH_4 and NO_3 measurements made directly downstream of Skenderaj, though still within EU standards, were 500-1000% higher than upstream concentrations. PO_4 concentrations exceeded EU standards at S3 during the months of June and the majority of the sites downstream from Skenderaj violated EU standards during the month of July. Such increases pose ecological and potential drinking water problems downstream as phosphates in drinking water increase the presence of protozoan, fungal, and bacterial microbes (CDPHE 2011). The European Union has developed aggressive water quality regulations (example: PO4 – 0.7mg L^{-}1) to reduce the ecological problems and potential health risks that have developed in European

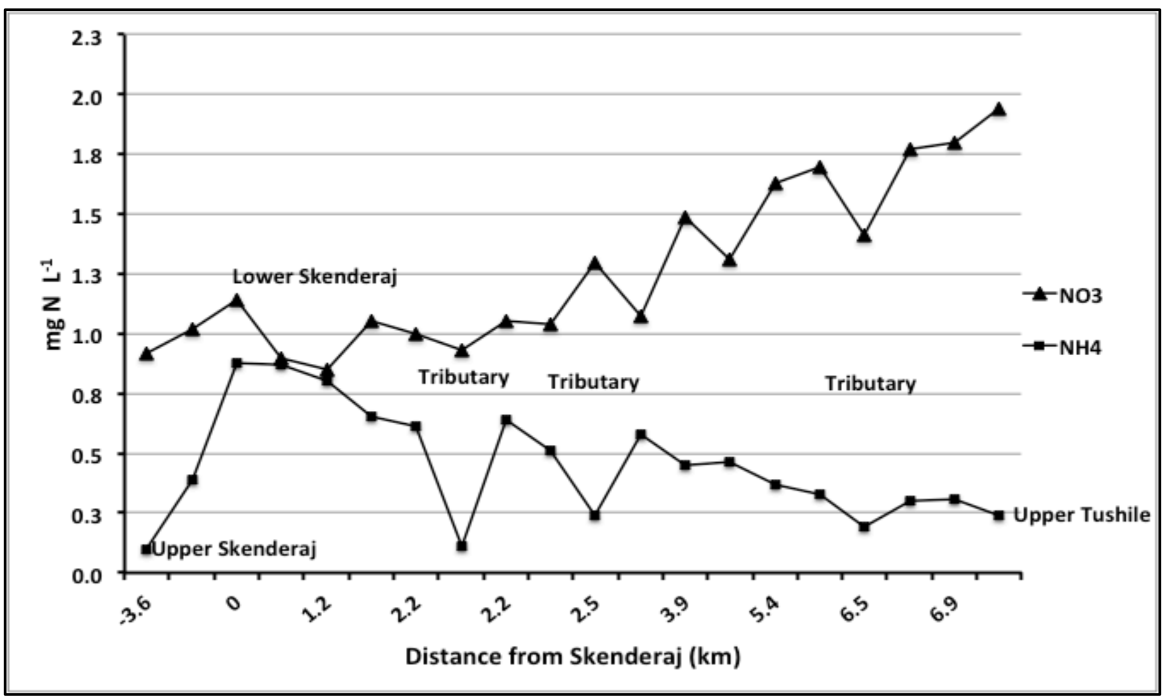


Figure 4.1 Average results of NH_4 and NO_3 concentrations (mg L^{-1}). The chart on the left shows the steady decline of NH_4 while the one on the right indicates the nitrification process and a transformation to NO_3.

waters (Artioli 2008). Those who live downstream from Skenderaj, utilize the stream as a drinking water source during the summer months when groundwater levels decrease causing hand-dug wells to go dry.

Figure 3.1shows a steady decrease of mean concentration levels for NH_4. It also shows three sharp decreases in nutrient levels where tributaries (S8,S11, S17) feed into the Klina River. This indicates that no significant point source of NH_4 exists downstream of Skenderaj. A comparison of mean NH_4 and NO_3 concentrations (Figure 4.1) shows a clear pattern of nitrification, with NH_4 being oxygenated through the nitrification process and converting eventually to NO_3. A 2002 study of the influence of ammonium on the nitrification process on a prairie stream showed similar trends when the concentration of NH_4 was purposefully increased. Kemp and Dodds found that when adding NH_4, depending on the strata type and oxygen levels, that the nitrification process increased as much as 300%, as did the concentration of NO_3 (Figure 4.2). NH_4 and NO_3 peaks did not always match indicating that nitrification was not the only process controlling NO3 concentrations (2002).

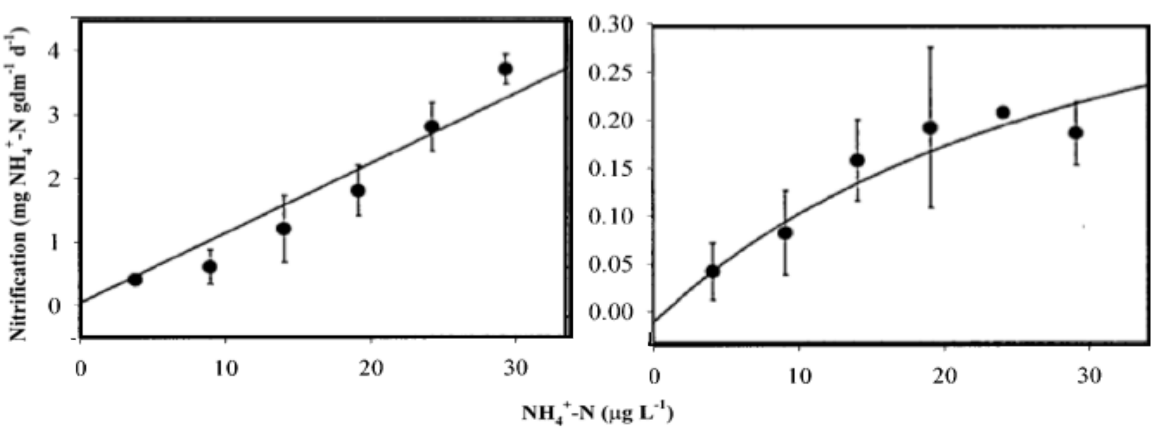
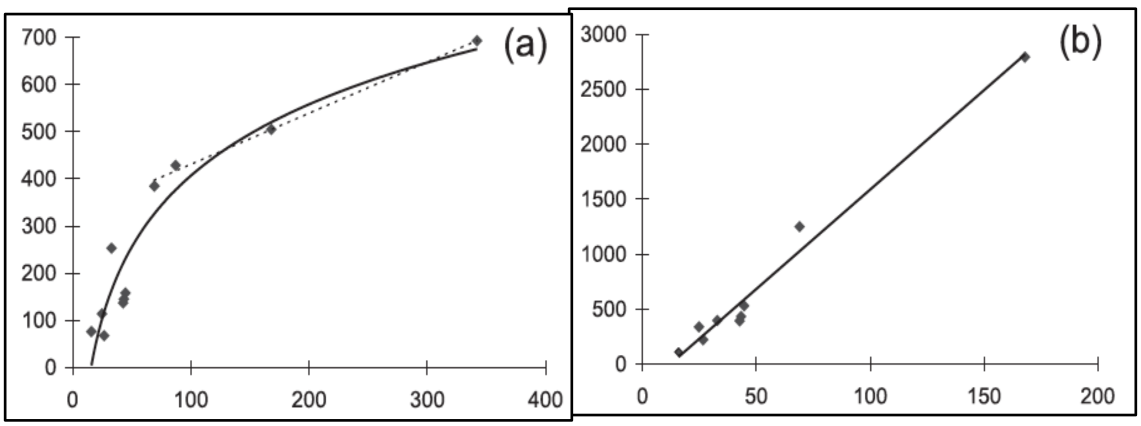


Figure 4.2 Mean nitrification (mg NH4–N gdm^{-1} d^{-1}) response to increasing NH_4-N μg L^{-1} concentration above ambient prairie stream substrata after three days incubation.

In addition, results from this analysis indicated significant seasonal variation in nutrient loads, particularly with NH_4. This is likely due to NH_4 being more sensitive to slight changes (physical, biological, and chemical) in the local environment than both NO_3 and PO_4 (Butturini and Sabater 1998, Gücker and Boëchat 2004). Spring and early summer (May and June) are generally the wettest times in Kosovo. The increase in runoff would likely lead to greater variability as short and intense rainfall increases runoff into the stream, leading to increased enrichment and spatial variability. This would suggest that the hydrological conditions (flow levels) were the main contributor of seasonal variation. A 2009 study of streams in Spain showed similar results when comparing the spatial variability between permanent and intermittent reaches of a tributary of the Segura River (Gomez et al 2009). Gomez et al found that nutrient variability of NH_4 and NO_3 concentrations was 5.7 times higher in the intermittent reach than the permanent stream. They attributed the strong variability to hydrological conditions (high-flow periods and drought), suggesting that the hydrological fluctuations influenced a variety of abiotic and biotic features in the fluvial ecosystem causing either a shrinking or elongating of the inorganic N cycle. They did acknowledge however that in permanent reaches where the hydrological habitat is more stable, seasonal variation had less influence on the variability in N concentrations.

Phosphate

Results show clearly that Skenderaj is a major contributor to PO_4 enrichment, and in this reach of the Klina River, is the largest contributor. Like NH_4, PO_4 shows a steady trend over eight kilometers of decreasing, as the nutrient is taken up through biotic and abiotic processes in the fluvial ecosystem (Fig 3.6). It is likely that the decades of nutrient loading by the municipality has altered nutrient uptake and elongated the P uptake length in the Klina River, as PO_4 concentrations downstream at Tushile never reach the same levels as those upriver from Skenderaj. A 2004 for study found that effluent from wastewater treatment facilities in Spain increased



PO_4 concentrations by at least 760%, which were similar to the increases found in this study. Nutrient uptake lengths increased by an order of magnitude for PO_4 and for NH_4 compared to streams considered pristine(Marti et al 2004). However, in other studies of

Figure 4.3 The mean nutrient uptake in meters for NH4 (a) and PO4 (b) in response to increased flow (L s^{-1}) (Butturini and Sabater 1998)

nonpolluted streams (Butturini and Sabater 1998, Peterson et al 2001), a positive relationship was shown to exist between nutrient uptake and stream flow. As flow increases, the nutrient uptake length also increases (Figure 4.3), indicating a decreased efficiency in retaining nutrients as the contact time between nutrients and stream sediment decreases.

4.2 Temporal Variation of Nutrient Enrichment

Results from this study showed clearly a pattern of increased enrichment for all three nutrients (NH_4, NO_3, and PO_4). However, Figures 3.14-15 indicates several differences between the April 27,2011 and June 1, 2011 tests. First, the load rates for all three nutrients are higher in the second test. This is possibly due to a change in flow rate ($m^3\ h^{-1}$) (Table 4.1) as nutrient loading and uptake in small streams is often controlled by the flow rate and surface area of the stream bed which potentially limit the amount and rate in which nutrients sorb to the stream sediment. (Peterson etal 2001). In panel A of Figure 3.14, NO_3 load rates from S3 spike several times. Though these rates are consistent with levels indicated in panel B, these measurements are outliers and lack statistical significance to verify accuracy.

Table 4.1 Average Flow Rate for 24hr. Analyses

Flow Rate $m^3\ h^{-1}$			
	S1	S3	T1
27-Apr-11	1172	1227	1453
1-Jun-11	1582	2460	3463

Secondly, the two tests showed a large difference in load rates for NO^3. One potential explanation of the increased NO^3 loads could be attributed to the increase in water temperature from April to June of 2011. Average water temperature increased by 5.5 to 6.5 degrees Celsius for each site (Table 4.2) (Appendix 1).

Table 4.2 Average Temperature for 24hr. Analyses

Temperature °C			
	S1	**S3**	**T1**
27-Apr-11	9.4	9.9	10.3
1-Jun-11	15.8	16.4	15.9

In some streams, seasonal changes in temperature may also affect biotic demand for inorganic nutrients from the stream (Hoellin et al 2007, Mulholland 2002,). Temperature activates cellular metabolism, thus any seasonal change in temperature would influence bacteria's to utilize inorganic nutrients in the water column (Fdz-Palanco 1994).

Next, it is important to surmise the potential sources of the nutrients that are being enriched by Skenderaj. It is estimated that humans, through urine and feces, excrete between 2.0-4.0 kg nitrogen and 0.5 – 1.0 kg phosphorus annually (Kirchman & Peterson 1995, Guyton 2000). The city of Skenderaj produces approximately 2.5 – 3.0 million liters of sewage daily (Appendix 3). With these conservative figures, it is estimated that approximately 46,000 kg of nitrogen and 9,000 kg of phosphorus are released into the stream untreated each year from human waste alone (Appendix 3). Often the largest urban nonpoint source of phosphorus is fertilizer (approximately 80%) as it is applied to lawns and ends up in the gutters as storm water and street dirt (Waschbusch et al 1999). However this is unlikely in Skenderaj as having a lawn is not common and the practice of fertilizing is even more infrequent. It is more likely that increased concentrations of PO_4 could be attributed to the soaps being used at the numerous carwashes. A 2009 study done by the city of Federal Way, Washington showed that residential car washes discharged an estimated 145 kilograms of phosphorus annually (Smith and Shilley 2009).

In addition, it was estimated that near equal amounts (30 and 27 kg) of nitrate and ammonia were discharged annually from residential carwashes. A thorough search of this reach of the Klina River showed no industrial sources for pollution, leading me to conclude that the municipalities discharging of wastewater was the major source of nutrient enrichment through a combination of detergents and human waste. However, in saying that, it is acknowledged that because the Klina River runs through agricultural farmland, the potential influence of agricultural nitrogen and phosphorus from non point sources cannot be disregarded. Throughout this region and other parts of Kosovo, the application of cow manure to cropland is conducted during the months of March and April.

It is also acknowledged here that any comparisons found in these results apply only to the temporal and spatial scales (4 months in time and 1-11 km in space) of this study. Changing the scale of comparison is cautioned until a fuller study is made to better understand the various factors controlling nutrient load and uptake along the Klina River. However, this data does have potentially far reaching implications for Kosovo.

4.3 Implications for Kosovo

The likely biggest implication this data could have for Kosovo is for the people who live directly downstream from Skenderaj, especially the village of Tushile. This village has for decades used the Klina River as a drinking water source during summer the summer months as their wells run dry. This data shows clearly the adverse affect the city of Skenderaj is having on water quality. The potential health concerns, particularly for children and the elderly, as a result of biological and nutrient contamination from this point source are real (UNEP 2010, WHO 2008 & 2009). This data has also provided a clearer picture of what future water and sanitation steps should be taken in Tushile. It is understood by Water for Life Institute that future development work in the Drenica area must include promoting water quality regulations on point source pollution and implementing wastewater treatment that is affordable and sustainable. As actual wastewater treatment does not exist in Kosovo, the scenario between Skenderaj and Tushile is likely indicative of urban centers throughout Kosovo and this issue will need to continue to be addressed by the national government (Norman 2009).

Another potential impact this data could have is helping water managers understand what effect the Klina River is having on the eutrophication of the Adriatic Sea. As stated previously, the Klina River flows (2.3m^3 s^{-1}) into the White

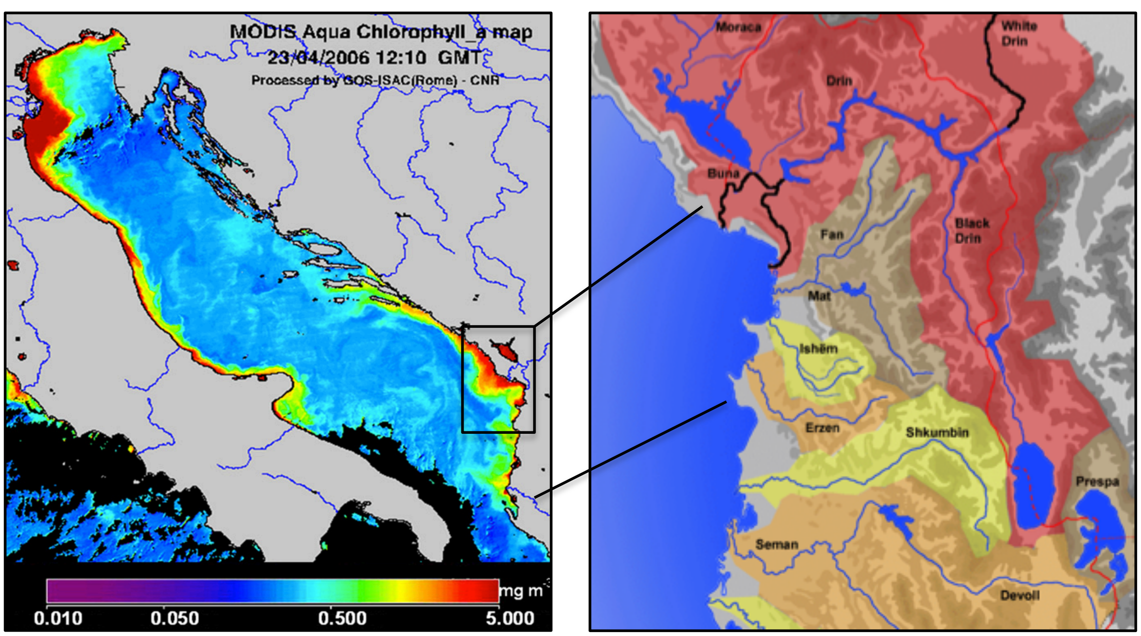


Figure 4.4 A MODIS image (Moderate Resolution Imaging Spectroradiometer) of chlorophyll concentrations on the Adriatic Sea. The White Drin River discharges flows into the Drin River. The Drin in turn discharges directly into the Adriatic Sea and the Bojana/Buna River and is partially responsible for the eutrophic state of the southeastern Adriatic costal region (Marini et al 2010).

Drin River (Kaqkini et al 2008) (Figure 2.1). The White Drin River flows (56.0 m^3 s^{-1}) into the Drin (350 m^3 s^{-1}), which discharges directly into the southeastern coastal Adriatic Sea and the Bojana/Buna River (Figure 4.4). Of the rivers flowing into the southeastern Adriatic, the Bojana/Buna River has the largest discharge rate at approximately 700 m^3 s^{-1} (Marini et al 2010). The total volume contribution from the Klina River to the Bojana/Buna River is quite small (0.3%) and calculating nutrient loading from the river and Skenderaj would be quite complex. However it would be safe to say that the trend of urbanized nutrient enrichment that is occurring along the Klina River is also likely occurring along the White Drin and Drin rivers, thus impacting the Bojana/Buna river as well.

In a multi year study, Marini et al studied the effects of the discharge from the Bojana/Buna River on the eutrophic status of the southeastern coastal area of the Adriatic Sea. They then compared these results with data from the Po River, which is the largest freshwater source that empties into the Northwestern Adriatic, which is a well-known coastal region that has had severe eutrophication problems (Figure 4.4) for decades (2010). Results from their study showed that despite the Po River having an average annual discharge rate of 1500 m^3 s^{-1} (Raicich 1996), Marini et al found that the maximum dissolved inorganic nitrogen concentrations (DIN) in the Bojana/Buna River plume was 50% higher than the Po plume (2010). This could potentially be a result of the restrictions imposed on point-sources of pollution within the EU (Artioli et al 2008) and the lack of any such restrictions throughout the Balkan region. As point-source restrictions have proven effective in improving water quality and in meeting water usage standards, it is likely that such restrictions in Skenderaj and Kosovo would significantly help to reduce nutrient and coliform pollution, and improving the health of people who use the Klina River for domestic purposes.

A second implication of this research would be in helping water managers meet water quality and environmental goals. Kosovo is working politically to become part of the European Union. Part of this process is to meet environmental goals set by the United Nations and European Environmental Agency. Kosovo has made a commitment to work towards meeting the Millennium Development Goals and using them as a tool for development (Norman, 2010). Part of these goals is to ensure environmental sustainability by decreasing by 50% the number of people without sustainable access to safe drinking water and sanitation. Yet without clear data of the physical, biological, and chemical makeup of their rivers authorities will be unable to make informed decisions regarding the programs and technology needed to manage their nations water resources.

Finally, as Kosovo continues to develop, and work towards meeting these goals, they will be forced to invest in wastewater infrastructure. As new countries become part of the European Union, they have been forced to increase the amount of money they spend on meeting wastewater standards. One country, that Kosovo has politically aligned itself with, is Austria. Between 1993 and 2006, Austria invested approximately $5 billion on water supplies and $12 billion on wastewater treatment facilities so that legal obligations can be met (Heidler, 2008). Paying for the new water infrastructure will require people paying more for their water and for wastewater. As the people in Kosovo pay almost nothing for this service now, it will be a dramatic increase in cost for them. In comparison, people in Kosovo pay approximately 2% of what Austrian citizens pay for wastewater services (Figure 4.5). Kosovo is currently ranked as the poorest nation of Europe with an annual per capita income of $2500 and an unemployment rate hovering around 50%. Of it's 2.1 million people, only 57% have access to treated drinking water, of that only 65% actually pay their water bills (WWRO 2009). The challenge for governing officials is to develop programs with technologies that are affordable and sustainable and help the people of Kosovo to understand their importance.

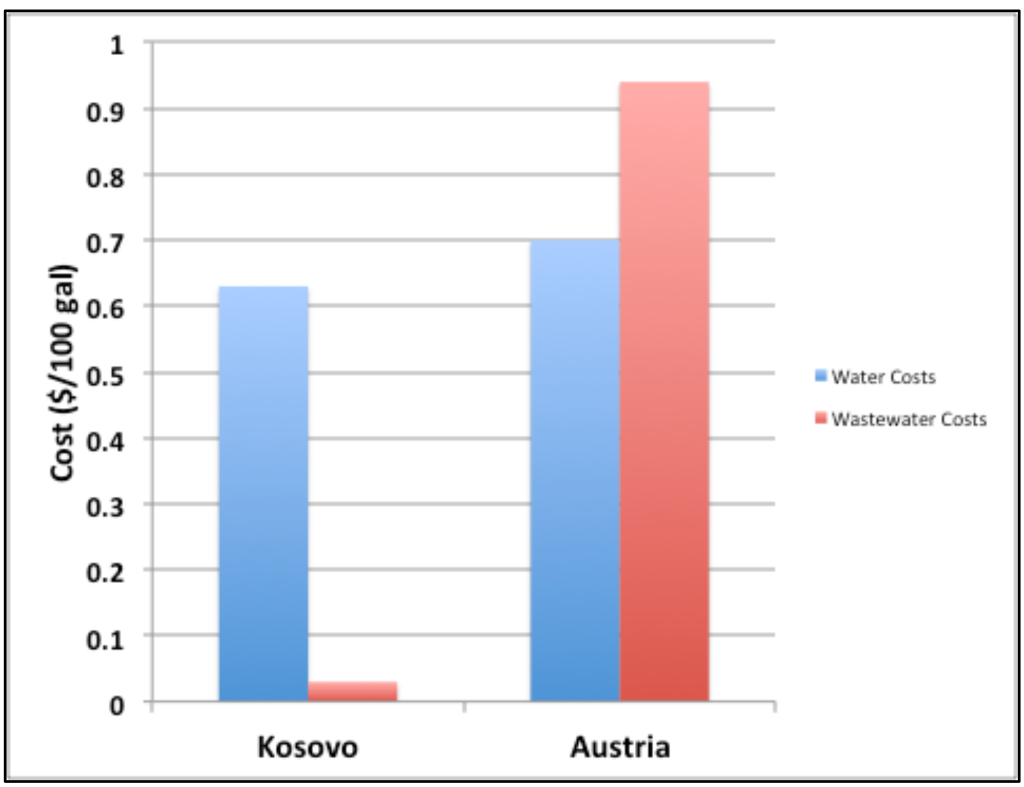


Figure 4.5 Comparison of average water and wastewater between Kosovo and Austria.

4.4 Solutions for Nutrient Enrichment in Kosovo

In a country of 2.1 million people, the city of Skenderaj represents only 2.5 % of the total population of Kosovo. As a nation, Kosovo lacks a number of things to adequately deal with nutrient enrichment; one of them being wastewater infrastructure. Ironically, the only wastewater treatment facility in Kosovo exists approximately 6 kilometers from the city of Skenderaj (S13 of Figure 2.1), and was constructed as a pilot project to promote and study wastewater treatment in Kosovo (ECLOK 2010) . Completion of the facility was made in February of 2008, yet because of property disputes the facility has yet to be put online. It is clear that its operation would significantly improve water quality, greatly impacting the village of Tushile, which is approximately 2-3 kilometers downstream.

However, it is doubtful on whether centralized wastewater treatment is an affordable and sustainable solution for Kosovo. A more likely affordable and sustainable solution would be the development and implementation of constructed wetlands. The practice of using constructed wetlands for water quality treatment has been occurring for decades and was first put into use in Germany in the 1960s (Vymazal 2011) and have been used throughout Europe and North American. Generally speaking, wetlands remove nutrients by promoting sedimentation, taking up nutrients in plant biomass, sorbing nutrients to sediment, and increasing denitrification (Fisher and Acreman 2004). Constructed wetlands are typically divided into two groups: subsurface-flow or surface-flow (Figure 4.6). Surface flow constructed wetlands contain zones of open water with submerged, emergent, and floating plants. They are designed with shallow depth and low velocity to increase aeration, promote sedimentation, and encourage chemical and biological uptake from the water column (Brix 1995). This style of constructed wetland is particularly effective in removing organic material and suspended solids through microbial degradation and sedimentation. Ammonia is most effectively removed in the aerobic zones through the nitrification process. Phosphorus is removed through adsorption and precipitation, but is limited in this style of wetland as it is limited by contact between the water column and soil (EPA 1988).

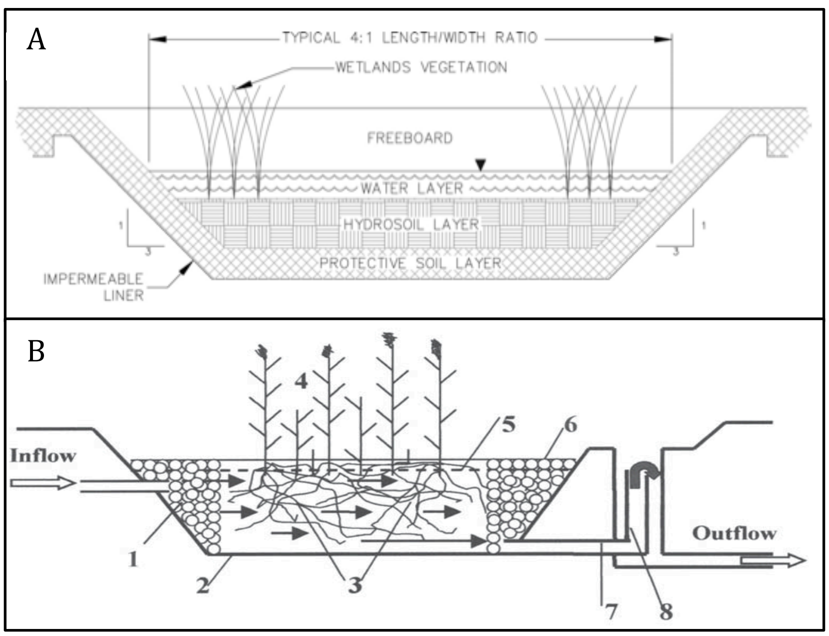


Figure 4.6 Design profile for constructed wetlands. A) surface –flow B) subsurface flow Elements of each system (sediment, vegetation, dimensions) are designed to increase biogeochemical process that will increase nutrient retention (GSW 2011).

Subsurface flow constructed wetlands on the other hand are generally quite effective at removing phosphorus as they are designed to allow effluent to discharge through rock media either vertically or horizontally. Emergent plants with substantial root systems aid in sorption and uptake of phosphorus and other nutrients. Uptake of phosphorus through wetlands is generally not as efficient as nitrogen unless special filtration material with high sorption capacity is added (Vymazal 2006). An Italian study of constructed wetlands (combination of subsurface and surface) in Morocco found removal rates of 86% for NH_4 and 94% for total phosphorus (Masi and Martinuzzi 2006). A study in Iran found that utilizing subsurface flow reed beds (150 m^2) for treatment of municipal wastewater had removal efficiencies of 56 and 99% for total nitrogen and total phosphorus (Badkoubi et al 1998).

While it is well understood such systems are more affordable and more easily operated and managed than conventional wastewater treatment facilities, they are not without potential drawbacks that would make implementation in Kosovo a challenge. First, acquiring enough land could be a limiting factor. The Iranian study found that 1-2 m^2 per person was needed to achieve the removal efficiencies previously sited. This could be a real challenge in Kosovo because land ownership is a heavily contested after the war and property rights are not well defined. Secondly, the availability of water during the summer months could be a limiting factor, as certain amounts of water are required to maintain wetland treatment. Kosovo experiences strong declines in surface water flows during the summer and fall months (WWRO 2009). As constructed wetlands in dry areas like this have seen high evapotranspiration rates (Kivaisi 2001) exceed water inflows. Therefore it is critical to design an appropriate system that accounts for the hydraulics of the wetland and watershed. Despite these potential challenges, the potential of constructed wetlands for nutrient removal from wastewater in Kosovo is promising and should be pursued. Successful projects implementing constructed wetlands have been found in other Mediterranean countries like Greece, Turkey, Croatia, Egypt, and Morocco (Masi and Martinuzzi 2007).

A second alternative solution to decreasing nutrient enrichment of streams in Kosovo is the reuse of wastewater for agriculture. On an international scale, the amount of wastewater reuse for agriculture is still relatively small (Ortiz et al 2010). However there is a growing trend, particularly in dry, arid, and water stressed countries, which Kosovo would fit. Kosovo is an area that, during the era of the Yugoslavian socialist democracy, was one of the leading agricultural exporters in Europe. In the 1980's, Kosovo utilized over 12,000 ha for production of fruit like apples, pear, and cherries. In 2006, the land being used for fruit production was 2600 ha (IPAK 2011). Wastewater effluent is higher in nitrogen and phosphates than regular irrigation water, making responsible use of it ideal for irrigation of fruit trees. In addition, reused water is often delivered by either drip irrigation, or sub-surface irrigation. This significantly reduces the amount of water that is lost through evaporation, potentially saving farmers significant money.

A 2010 study of water reuse for agriculture in Mexico found strong economic incentives for using wastewater for agriculture purposes. For decades, Mexico City has pumped their untreated wastewater to the Tula Valley to be used for agriculture. Savings were found in multiple areas. First, the farmers from Tula Valley received free untreated wastewater. The usage of this water was found to have increased their crop yields by at least 18% over fields with similar crops using regular irrigation water sources. Secondly, up until now the only costs related to wastewater that Mexico City has incurred has been the pumping of wastewater out of the valley in which the city is in. By using the wastewater in Tula Valley, they have avoided large infrastructure and treatment costs for enormous volumes of wastewater. Caution of course must be used in regards to utilizing wastewater for irrigation on food crops. The risk of spreading pathogens from fecal matter greatly increases and can lead to outbreaks of water related diseases if agriculture is not properly irrigated or cleaned (FAO 2010).

The challenge of implementing wastewater reuse in Kosovo is multi-faceted. First, there is an overall lack of understanding of the potential benefits regarding wastewater reuse. Despite living in an area of Europe that is considered 'highly water stressed' (EUWI, 2007) and the benefits wastewater reuse could have for farmers, no significant water reuse projects have been considered in Kosovo. Beyond this, Muslims are particularly skeptical of wastewater reuse on crops because of various religious and cultural concerns concerning 'uncleanliness". Lastly, Kosovo farmers for many decades have practiced dry farming and most do not irrigate their crops. The idea of having to pay for wastewater would likely not appeal to farmers and they would have to be convinced of the economic benefit for their farms before they would implement any such practice. Because of the costs of pumping wastewater, any economic benefit to be had would most benefit farmers closest to the municipalities (Brissaud 2009). Despite these potentially limiting factors, water reuse in Kosovo is a promising solution to the water challenges they currently face. In preliminary study for this thesis, greywater technology was analyzed as a potential water reuse option for decreasing the amount of nutrients delivered to the nations river systems, and was found to be an economically viable option for people of Kosovo (Appendix 1).

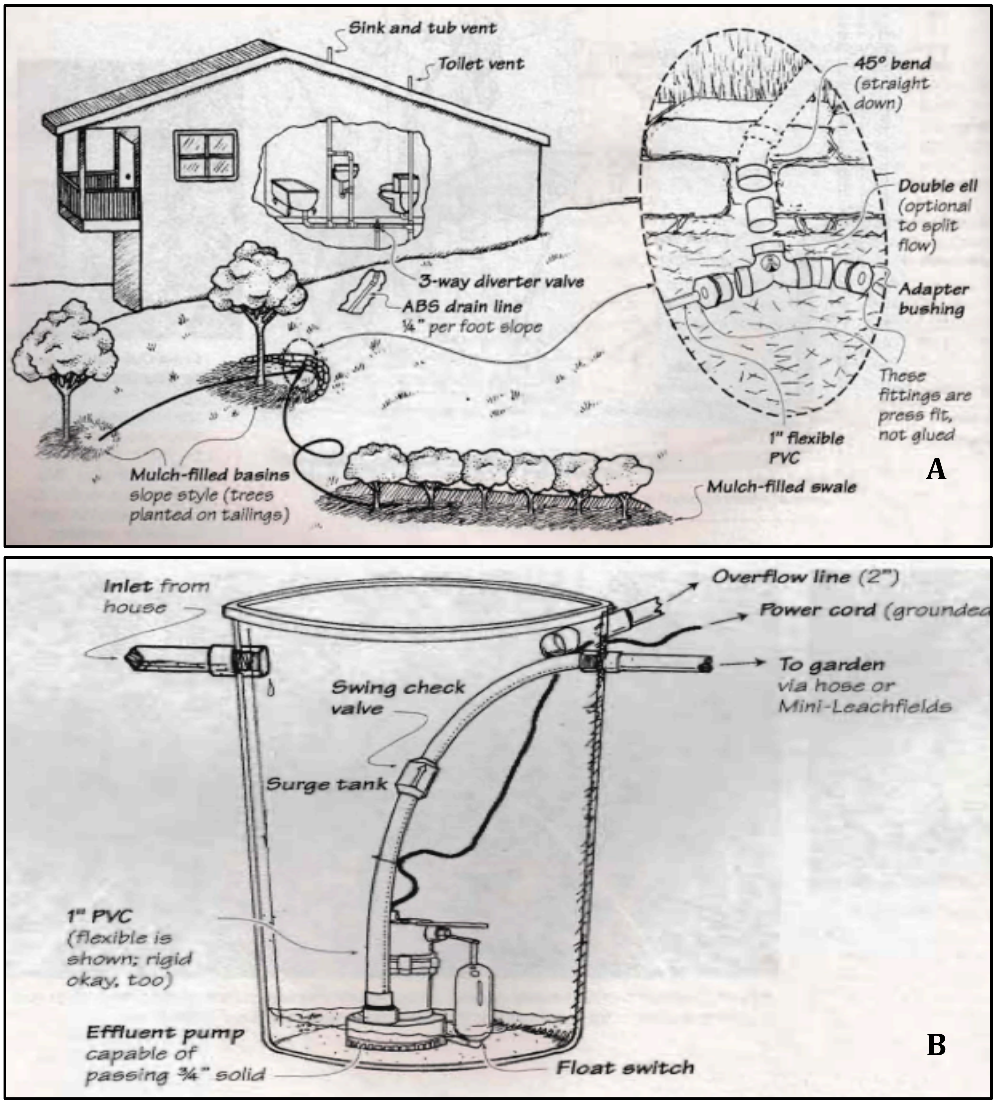


Figure 4.7 Greywater Systems. A) Movable Drain System – a non pressurized system that delivers greywater to mulched plants/trees. B) Drum with Effluent Pump System – a more expensive but affordable system that enables users to pump the greywater to where it is needed (Ludwig 2007)

Grey water by definition is all domestic water used except toilet water, which is defined as black water. This water has significantly less levels of fecal coliforms, and less potential for spread of pathogens (Ludwig 2007). Analysis of two proven greywater technologies (Figure 4.7) showed that utilization of these systems could help Kosovo meet many of its development goals, and save the average household approximately 5% of their annual GDP by reducing the amount of water that is consumed by 40% and decrease the amount of wastewater delivered by 50% (Appendix 2).

4.5 Recommendations for Future Development

Based on this study and research of the current political and economic situation of Kosovo, I recommend the following steps regarding future development of water and wastewater infrastructure in Kosovo:

- Study Ecoli and nutrient levels being released into streams by other municipalities.
- Conduct a cost/benefit analysis comparing costs of potential ecological and health risks from not treating wastewater versus benefits of treating it using affordable and sustainable technology
- Develop and implement an educational program to understand the ecological and health impacts that untreated wastewater has.
- Investment in a pilot project geared towards developing constructed wetlands infrastructure and wastewater reuse for agriculture.

5.0 Summary and Conclusions

Urban development is a present and future challenge for water managers. The complex interactions among urban development, rates of urban development, economic growth, and water resource and water quality management requires more investigation, particularly in developing countries. The disparities in education and economic growth in these nations compound the difficulties of identifying, isolating, and solving water quality problems in particular nutrient enrichment. While the ecological and health impacts of nutrient enrichment are well documented and understood, the challenge still remains in helping developing countries initiate a sustainable water quality program that will address nutrient enrichment and other water quality problems.

This was in part the motivation for developing this project in Kosovo. The evidence of nutrient enrichment was obvious in the Klina River as eutrophication could be seen in multiple areas of this river. Because of their need for safe water for domestic use and the implications that result from using contaminated water, I set out to identify the source(s) of the nutrient enrichment and develop a project that could provide relevant and useful data to those who manage water resources in Kosovo. Water quality data, particularly nutrient data, almost does not exist in Kosovo, as there is no program for monitoring the quality of their streams and rivers.

With the aid of local university students, and water monitoring equipment that was donated, I initiated two sets of tests over a four-month period to monitor levels of NH_4, NO_3, and PO_4 along an eleven kilometer stretch of the Klina River to identify potential point sources of contamination and determine what level of impact the city of Skenderaj has on nutrient enrichment. The first test was a spatial variation analysis to identify potential point sources of nutrient contamination. I monitored twenty different sites, starting upstream from Skenderaj at the city's upper border, once in the city limits, again at the lower city border, then approximately every 0.6 kilometers until reaching the upper border to the village of Tushile. Sampling occurred at each tributary feeding into the river. This test occurred over a four-month period. The second test was a temporal variation analysis designed to show the impact the city of Skenderaj has on nutrient enrichment by monitoring water quality as it enters and exits the city's borders every hour for twenty four hours. This test was performed twice over a five-week period.

Results from the spatial variation analysis showed a strong increase of both NH_4 and PO_4 concentrations (mg L^{-1}) from the upper city border to the lower city border. From there, both nutrients steadily decreased until reaching the upper border of Tushile. Concentration levels increased strongly from April to July while load levels (kg day^{-1}) generally decreased, which is indicative of hydrological influence. Nutrient concentrations entering Tushile were consistently higher than nutrient levels entering Skenderaj, indicating that the city was significantly changing the overall nutrient load in the Klina River. After calculating nutrient loads for NH_4 and PO_4, results showed the same steady declining trend. However at numerous points, nutrient loads would spike. As this reach of the Klina River is permanent, it is unlikely that the stream was being enriched from various contaminated groundwater sources as the geology in the area is fractured and a consistent water table does not exist. Past research and preliminary data has shown a strong contamination of ground water with increases in NH_4, NO_3, and PO_4 concentrations in Kosovo and the village of Tushile. Results for NO_3 concentrations were much different, showing only a moderate increase from the upper border to the lower border of Skenderaj. Instead of a steady of steady decline like the other two nutrients, NO_3 concentrations steadily increased over the eight-kilometer stretch between the lower border of Skenderaj and the upper border of Tushile. As no other potential point sources were identified, it is likely that this steady increase in concentration levels is a result of a combination of nonpoint sources (erosion and agricultural application of fertilizers) and the nitrification process as NH_4 is transformed to NO_3.

Results from temporal variation tests showed a similar pattern, with sharp increases in concentrations for both NH_4 and PO_4, but only moderate increases in NO_3. Nutrient concentration levels saw the sharpest increases while increases of nutrient loads were less pronounced. During the early afternoon time period, concentrations increased yet stream flow was consistent. This likely reflects the highest domestic water usage and the lag of time to deliver the water to the stream. Using dyes and measuring the time from release to output could test this.

While the complexity of calculating what affect urban areas are having on eutrophication downstream is high, and non-point source enrichment is generally a greater contributor of nutrients, it is clear that the city of Skenderaj is having a significant impact on the nutrient enrichment of the Klina River. Although concentration and load rates mostly stayed within accepted parameters for surface water within the European Union, the percentage of increased enrichment from Skenderaj should cause water managers concern. Skenderaj is approximately fourteen kilometers downstream from the source of the river. Such a heavy enrichment of the headwaters is likely having significant impact on the streams ability to retain nutrients, increasing the amount of nutrients that are flowing downstream and ending up in the Adriatic Sea and adding to the eutrophication problems facing that area.

Kosovo has several obstacles facing them that could prevent remediation of stream water quality. Arguably the greatest of these challenges is the economic obstacles facing Kosovo. With unemployment hovering at 50%, implementing a program for monitoring and remediation of water quality would be a large investment for the Kosovar government, and would likely be given a low priority.

Secondly, education and understanding regarding potentially affordable and sustainable solutions like constructed wetlands and water reuse is quite low. As economic development is arguably the highest priority for the Kosovar government, it is recommended that a benefit / cost analysis be made of these technologies. Such an analysis would provide the necessary economic and scientific information to the people who can implement change, yet in way that would help them better understand the implications (costs) of implementing or not implementing a water quality program.

Despite these challenges, solutions exist to deal with the water quality issues of Kosovo. The Kosovar government is currently working to become part of the European Union. To do this, certain environmental goals must be met to ensure this, so there is potential political will to work towards sustainable solutions for controlling water quality and limiting the effects urban development has on the streams and rivers of Kosovo.

In conclusion, this study has shown the following:

- Skenderaj is the largest contributor of nutrients in this reach of the Klina River. More study needs to be done on Ecoli and nutrients being released into streams by other municipalities.

- Nutrient levels downstream from Skenderaj are significantly increased when compared to nutrient levels entering Skenderaj. Development of a cost/benefit analysis comparing costs of potential ecological and health risks from not treating wastewater versus benefits of treating it using affordable and sustainable technology.

- The water leaving Skenderaj is nutrient rich and instead of having adverse ecological effects, could instead be utilized. Investment in a pilot project geared towards developing constructed wetlands infrastructure and wastewater reuse for agriculture should be pursued.

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Appendix 1: Temperature Analysis for 24hr. Tests

The purpose of this analysis was to determine if temperature was a factor that influenced the nitrification process on this reach of the Klina River. To do this, stream temperature was measured at S1,S3, and T1 during each hour of both 24hr tests.

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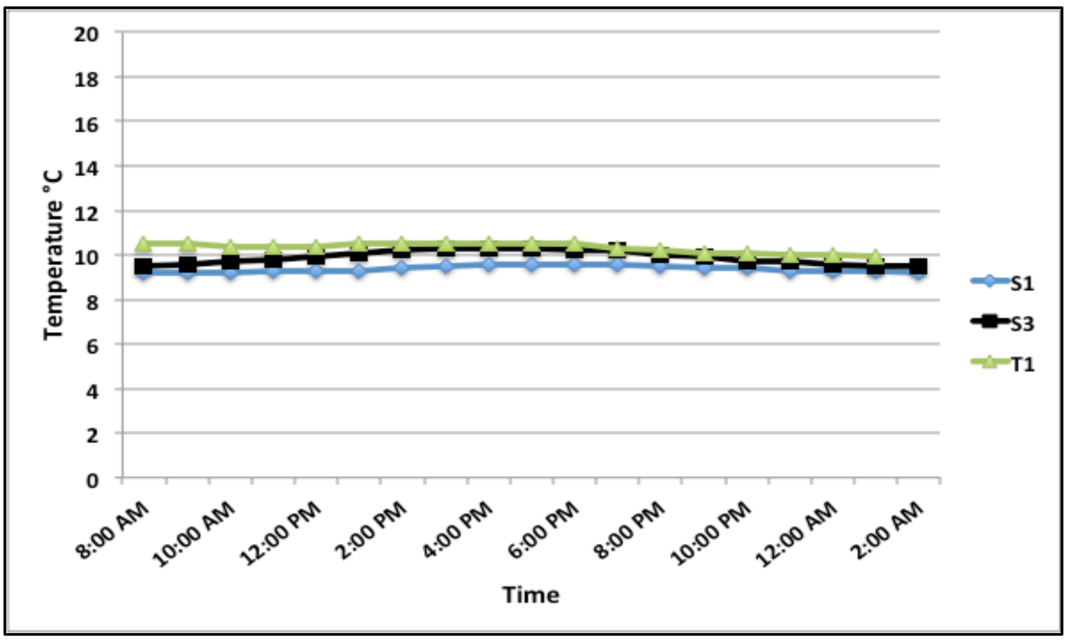

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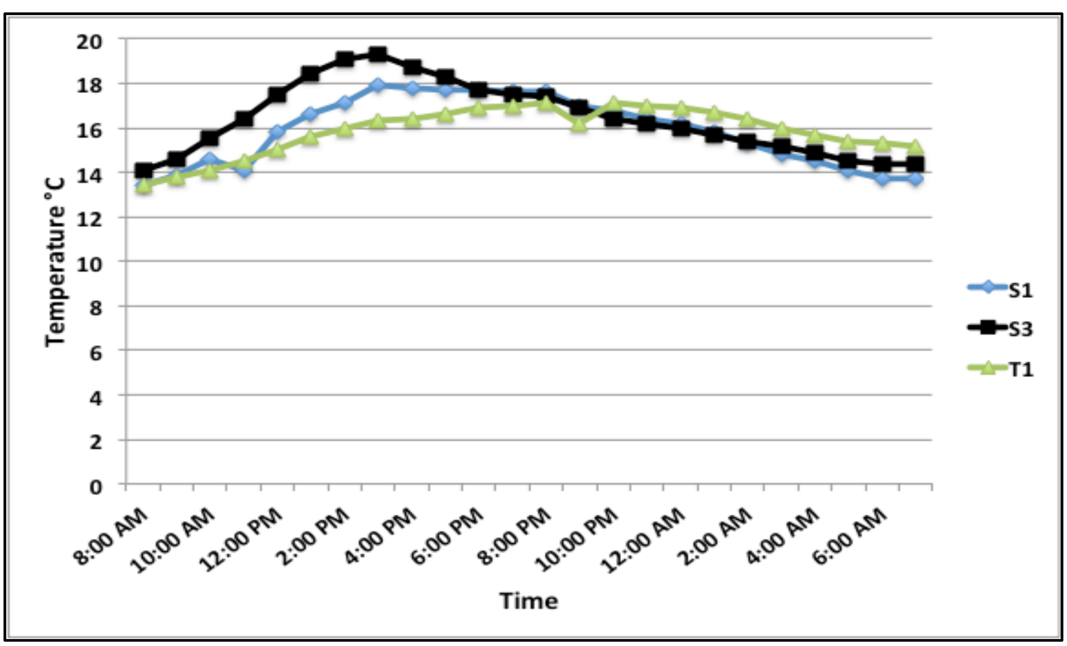


Appendix 2: Grey Water Savings

The purpose of this study was to determine if greywater technology was an affordable technology that could be implemented and sustained by the people of Kosovo. To do this, two well tested greywater technologies were analyzed for potential financial benefits by using the following criteria and assumptions:

1. All savings are based per household, with an average family being 6.4 people (ESI, 2006);
2. Average water consumption for Kosovo is 37.3 gallons per day (Norman, 2009);
3. Average water savings of 15 gallons per day per person for irrigation and toilet use;
4. All savings are based on 40% reduction in water consumption and 50% reduction in wastewater creation;
5. Assumed loan of 10%.

Basic Assumptions:
Remodel Construction
Family Size: 6.4 people
Average Water Consumption in Kosovo
Interest Rate of 10%

Annual Water Savings per Family					
Consumption Savings (gal/yr)		35,040			
Consumption Savings ($.67/100 gal)	$	234.77			
Sewage Savings ($.02/100 gal)	$	7.01			
Annual Water Savings per Family	**$**	**241.78**			
Annual Costs Movable Drain System			**Annual Costs Drum w/ Pump System**		
Repair	$	(5.00)	Repair	$	(10.00)
			Electricity	$	(20.00)
Total Annual Costs	$	(5.00)	**Total Annual Costs**	$	(30.00)
Capital Costs Movable Drain System			**Capital Costs Drum w/ Pump System**		
Pipe & Fittings	$	(60.00)	Pipe & Fittings	$	(60.00)
Hose	$	(40.00)	Hose	$	(40.00)
			Pump	$	(300.00)
			Surge Tank	$	(35.00)
Total Capital Costs	$	(100.00)	**Total Capital Costs**	$	(435.00)
Net Savings (year 1)	**$**	**141.78**	**Net Savings (year 1)**	$	(193.22)
Annual Net Savings	**$**	**236.78**	**Annual Net Savings**	**$**	**211.78**
Loan Payback Time	**4 months**		**Loan Payback Time**	**12 months**	

Appendix 3: Wastewater and Nutrient Production of Skenderaj

This calculation was done to approximate how much wastewater was being produced by the city of Skenderaj, and thus how much this municipality was contributing to the nutrient enrichment of the Klina River. The following table was created to show the amount of nutrients (kg $year^{-1}$) that were being released into the Klina River and to support the argument that cost effective infrastructure should be invested in to utilize these nutrients for agricultural purposes.

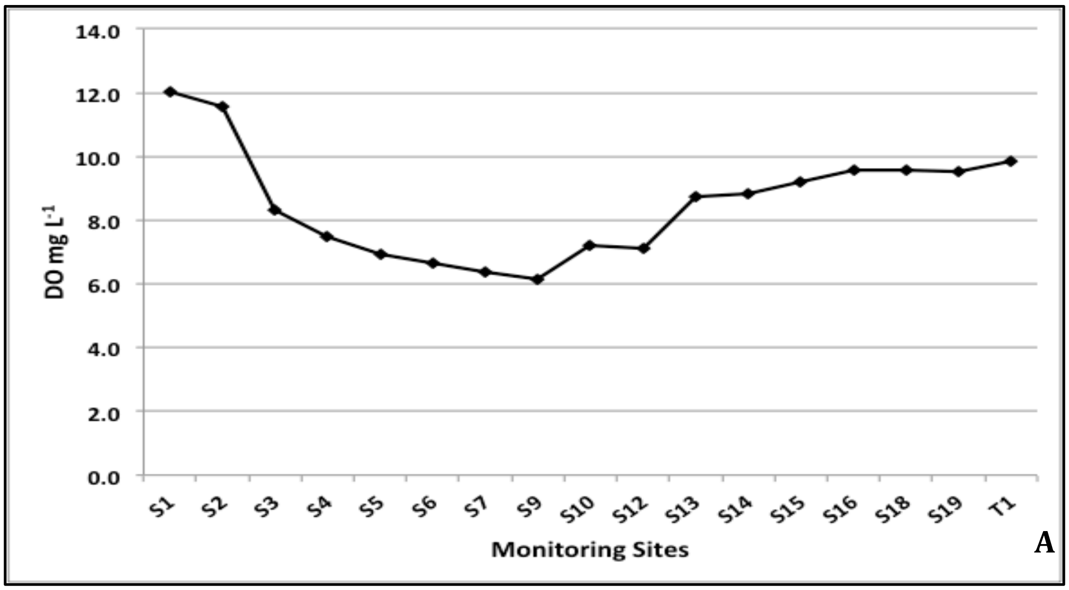
Skenderaj					
	Present	**2015**	**2020**	**2025**	**2030**
Population	20,000	20,386	21,047	21,729	22,434
Wastewater (m^3)	930,750	948,735	979,486	1,011,233	1,044,009
Human Feces (kg $year^{-1}$)	7,300,000	7,441,059	7,682,240	7,931,239	8,188,308
Nitrogen (kg $year^{-1}$)	46,538	47,437	48,974	50,562	52,200
Phosphorus (kg $year^{-1}$)	9,308	9,487	9,795	10,112	10,440

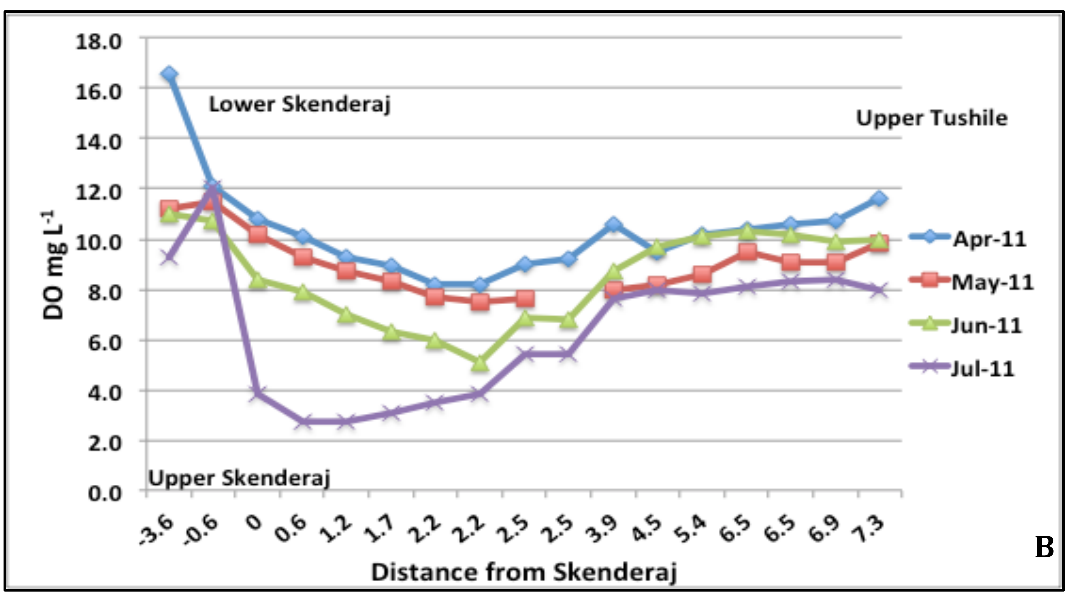
Numbers were based on the following calculations:

- Daily consumption of 150L day^{-1} $person^{-1}$
- 85% of water consumed is returned as wastewater (Ludwig 2007)
- Humans produce an average of 1000 – 1100 g feces day^{-1} (Marti etal 2004)
- Nitrogen concentration in wastewater of 50 mg L^{-1} (Marti etal 2004)
- Phosphorus concentration in wastewater of 10 mg L^{-1} (Marti etal 2004)
- An urban growth rate of 0.64% (Bazoglu 2007)

Appendix 4: Dissolved Oxygen of the Klina River

Dissolved oxygen (DO) analysis measures the concentration of oxygen (mg L^{-1}) in water. Understanding DO is critical in maintaining a healthy aquatic environment for fish and other aquatic animals. Wastewater from sewage contains organic materials that are decomposed by microorganisms, which use oxygen in the process. If too much organic material is present, it can reduce DO levels in streams to levels unsafe for aquatic life.





Appendix 5: Water Quality Data for Tushile Wells

The following data was collected over a six-month period from May – October 2010. This data is not all encompassing of the entire village of Tushile but is instead compiled from random wells from every area of the village. This data was intended to merely provide a snapshot of well water quality helping to determine a general direction for repair and remediation for villagers and Water for Life Institute.

Average Values for Tushile Well Data								
Tushile Water Quality Test Results								
	Temp (°C)	Bar. Pressure (mm Hg)	DO (mg/L)	Conductivity (µS/cm)	NH4 (mg/L)	NO3 (mg/L)	pH	Turbidity (FTU)
Mean	13.5	712.8	3.9	31.9	1.6	24.0	7.10	2.6
Median	12.4	714.6	3.8	32.4	1.4	18.6	7.09	2.0
Mode	12.0	714.8	6.1	41.2	1.0	#N/A	7.20	2.0
Well Volume Data, Tushile								
	Diameter	Ring Height	Depth to Top of Water	Depth to Bottom of Water	Depth of Water	Volume of Water (L)		
Mean	0.8	0.9	6.0	9.5	3.2	1219.1		
Median	0.8	1.0	5.5	7.4	1.7	768.9		
Mode	0.5	1.0	4.2	#N/A	0.0	0.0		