ASSESSING THE EFFECTIVENESS AND ENVIRONMENTAL IMPACTS OF USING NATURAL FLOCCULANTS TO MANAGE TURBIDITY

Final Report

SPR 615

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by

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16. Abstract

The objective of this research was to determine the feasibility of using chitosan as a natural flocculant to control turbidity during in-stream construction work. A series of field tests in Oak Creek, Corvallis, OR were conducted in order to test the effectiveness for turbidity control and the environmental impacts of applying chitosan directly into a stream environment. No significant removal was obtained with chitosan doses up to 0.5 mg/L under the conditions tested, mostly due to high pH of the creek and other unfavorable water quality parameters. Water quality analysis for total organic carbon, total phosphorus, total Kjeldahl nitrogen, and biochemical oxygen demand showed that chitosan does not adversely impact the aquatic environment at low doses.

Due to the inconclusiveness of the field test data, a series of bench-scale tests were conducted to evaluate the effectiveness of chitosan under controlled conditions, as well as its responses to different test conditions, e.g. pH, initial turbidity, chitosan dose and sediment type. The bench scale tests were conducted using water collected from Oak Creek and a standard jar tester. It was found that flocculation efficiency depends strongly on sediment type. However, the most critical factor that determines the effectiveness of chitosan seems to be an unidentified water quality parameter, which is likely related to the organic matter in the stream.

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		AREA		
in^2	square inches	645.2	millimeters squared	mm^2
ft^2	square feet	0.093	meters squared	m^2
yd^2	square yards	0.836	meters squared	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	kilometers squared	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	ml
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	meters cubed	m^3
yd^3	cubic yards	0.765	meters cubed	m^3
	NOTE: Volumes greater than 1000 L shall be shown in m^3.			
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg
		TEMPERATURE (exact)		
°F	Fahrenheit	(F-32)/1.8	Celsius	°C

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^2	millimeters squared	0.0016	square inches	in^2
m^2	meters squared	10.764	square feet	ft^2
m^2	meters squared	1.196	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	kilometers squared	0.386	square miles	mi^2
		VOLUME		
ml	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	meters cubed	35.315	cubic feet	ft^3
m^3	meters cubed	1.308	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams	1.102	short tons (2000 lb)	T
		TEMPERATURE (exact)		
°C	Celsius	1.8C+32	Fahrenheit	°F

*SI is the symbol for the International System of Measurement

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DISCLAIMER

ASSESSMENT THE EFFECTIVENESS AND ENVIRONMENTAL IMPACTS OF USING NATURAL FLOCCULANTS TO MANAGE TURBIDITY

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1.0 INTRODUCTION AND OBJECTIVES

Control of turbidity during in-stream work is a requirement of environmental permits, but it is difficult to achieve with conventional treatment methods. Without effective control on turbidity, the Oregon Department of Transportation (ODOT) is at risk of not meeting the required permit conditions and therefore, not being in compliance with the 1973 Endangered Species Act. Consequences of not meeting the required permit conditions would threaten projects with work shut-downs, and other enforcement actions.

The use of flocculants has been proven as a viable solution for controlling turbidity in waste water and drinking water treatment. However, some flocculants are not suitable for in-stream work due to their negative environmental impacts. A relatively new product, chitosan, shows great promise as an in-water flocculant treatment for controlling turbidity. Chitosan has been tested and accepted for use as a turbidity controlling method in the treatment of drinking water, wastewater, and construction run-off water collected in detention ponds. Because chitosan is derived from crustacean shells, it is anticipated to have a less damaging impact on the aquatic environment than other chemical flocculants.

In this study, the use of chitosan as a means of in-stream turbidity control was evaluated. There were two main objectives to this project. The primary objective was to determine the effects of chitosan when used in a natural stream. The effects to be determined were two fold: 1) to what degree does chitosan reduce turbidity from in-stream construction, and 2) what are the environmental impacts of introducing chitosan into the stream environment. The environmental effects that were investigated were the downstream water chemistry, and downstream turbidity. The secondary objective of the project was to determine whether and how chitosan should be used, and to establish guidelines for the use of chitosan during in-stream work.

2.0 LITERATURE REVIEW

2.1 REGULATIONS ON CONSTRUCTION WATER DAMAGE

Water pollution in the United States is regulated by the 1972 Clean Water Act (CWA). The original CWA primarily emphasized on the control of point source pollutants. Point source pollutants are defined as those pollutants that are discharged with water through a discrete conveyance, usually a pipe, from industrial or municipal facilities (*ODOT 1999*). In 1987, the CWA was amended to include the regulation of non-point source pollution; pollution that occurs when runoff from land carries pollutants into a stream. This amendment provides the basis for the National Pollutant Discharge Elimination System (NPDES) Stormwater Rule, also known as Phase I, which was adopted in 1990 (*DEQ 2001*). Phase I was in part implemented to regulate discharge from construction sites that disturbed at least five or more acres of land. In 1999, revisions to the NPDES permit were enacted in the Final Stormwater Phase II Rule (Phase II). According to Phase II, all construction sites that disturb a total of one acre or more must hold a general construction permit - the 1200-C permit for individual projects conducted by private firms, and the 1200-CA permit for governmental agencies. All permits in Oregon are issued by the Oregon Department of Environmental Quality (DEQ). Under these permits, construction sites are required to control and treat sediments, oil, gasoline, and solvents found on the site (*ODOT 1999*). The amount of sediment discharge is measured by the turbidity of the water discharged. Currently, Oregon Administrative Rule 340-041 allows no more than 10% increase in natural stream turbidity measured relative to a control point upstream (*DEQ 2004*).

2.1.1 Turbidity in Construction Run-Off Water

The major cause of turbidity in construction run-off water is erosion. Normally, erosion is a natural process by which soil and rock material is loosened over time and subsequently transported by wind, water, or ice. However, disturbance of the land has the ability to accelerate the erosion rate up to 1000 times the pre-construction rate (*ODOT 1999*).

In construction, erosion is often caused by the flow of water in various forms. ODOT defines five types of water erosion: splash, sheet, rill, gully, and channel. Each type is able to loosen exposed soil particles and wash them away with the water flow. Consequently, the water has a high content of soil particles and would result in an increased turbidity in the receiving water body if discharged without treatment.

A number of soil characteristics such as soil texture and organic matter influence erosion rates. Soil texture, a way of classifying the make up of the soil, is defined by the size and proportions of soil particles. Clay, for instance, has the ability to bind soil particles together and therefore is resistant to soil erosion, but once eroded is easily transported because of the small particle size. Sand on the other hand, which has a larger particle size, is easily eroded but requires higher flow velocities to stay in motion. The presence of organic matter can drastically reduce the erosion rate due to the improved structure of the soil matrix.

Erosion can have both environmental and economic negative impacts. Most eroded soils contain nutrients such as phosphorus and nitrogen, which increase the nutrient concentration in the receiving stream. Elevated nutrient levels in natural water bodies can cause algal blooms, which may result in the depletion of dissolved oxygen, decrease in water clarity, generate a foul odor, and finally kill fish. One of the properties of turbidity, or sediment in a stream, is its ability to absorb sunlight. This increased absorption of solar irradiation causes an increase in the stream temperature, resulting in degradation of a spawning area.

Increased turbidity leads to problems associated with the filtering, feeding, and respiratory functions of aquatic life forms. For example, fine sediments can cause gill abrasion affecting the respiratory system of fish. The sediments can also force behavioral changes related to mating and feeding within a fish species.

Increasing the fine sediment concentration in a stream can smother bottom plants and destroy spawning habitat for many fish species, such as salmon. Salmonids (salmon and trout) use river gravel beds as spawning and incubating habitat (*Wu 2000*). Accumulation of fine sediment within the gravel substrate is regarded as the most detrimental factor contributing to the degradation of spawning habitat (*Pitlick and Van Steeter 1998*). Once the fines have amassed in the gravel bed, it is impossible for them to be flushed without the movement of the bed material. This accumulation of sediment is believed to reduce substrate permeability and the water velocity through the gravels. The lower flow velocity leads to a reduction in the amount of oxygen available to fish embryos and a reduction in waste removal. In other words fine sediments suffocate the embryos (*Wu 2000*).

Economic impacts are another reason to control turbidity. Increased amounts of sediment into streams can reduce the storage capacity of reservoirs. As a result, sediment removal will have to occur more often. Accumulation of sediments decreases the flow capacity of the river, thereby harming the shipping industry that relies on natural water ways to deliver goods to consumers. In highly eroded areas, the top soil layer has been washed away, leading to decreased land productivity.

In-stream construction projects that cause movement of bed sediments are of particular concern because of the pollutants released from the disturbed sediment. Pollutants, as defined by ODOT, are substances that can render water harmful to fish, wildlife, and humans, and/or hinder recreation or impair any other beneficial use of the area. Included in the list of pollutants are heavy metals, petroleum products, nutrients, sediments, and oxygen demanding compounds. In-stream construction also increases the amount of pollutants in a stream by increasing the impervious area and traffic volume during construction work.

2.1.2 Current Practices for In-Stream Turbidity Control

The Hydraulic Manual for Erosion and Sediment Control (*ODOT 1999*) recommends various best management practices (BMP) for construction contractors to use in order to meet permit requirements. It also provides a method for contractors to choose, design, and size a best management practice for erosion and sediment control, based on the type of work being done and the type of erosion control needed. The choices are categorized by the types of control measures: erosion prevention application, run off control, and sediment control measures. Because this project addresses the turbidity control issue during in-stream construction, only the sediment control BMP options suitable for in-stream applications will be discussed - straw bales, biofilter bags, sand bags, sediment traps and flocculation.

Straw bales offer a temporary sediment barrier that consists of a row of anchored straw bales combined with other control measures. Straw bales create impoundments that trap small amounts of sediment by reducing sheet flow, or moderate channel flow velocities. Typically, to make this method more effective, an aggregate weir needs to be installed with a sediment fence in place after the weir. Water is channeled through the weir and sediments are trapped by the sediment fence. Straw bales are used on vertical slopes less than 1:2, below areas subject to rill or sheet erosion, and a maximum drainage area of 0.1 hectares per 305 m (0.25 acre per 100 ft) of straw bales (*ODOT 1999*). Straw bales are an inexpensive short term method of erosion control. However, there are a few disadvantages associated with their application. First, if the straw bales are not installed correctly or misused, there will actually be an increase in sediment loading due to flow between the joints or flow moving around the edges of the straw bales. Secondly, straw bales are not suitable for areas with high flow. Thirdly, they are heavy, difficult to move when wet and only have a three-month lifetime. Moreover, while straw bales are effective at reducing the turbidity level of the stream, they also reduce the amount of dissolved oxygen in the stream (*DEQ 2003*).

Biofilter bags can be used to capture and retain sediments on slopes and drain inlets. They are also effective at sediment capture, and flow velocity reduction in lined and unlined channels. The biofilter bags are manufactured from 100% recycled wood product waste that is placed in plastic mesh bags. They have several advantages over other recommended BMPs. Biofilter bags are inexpensive to use and they can be used in place of straw bales and sediment fences on slopes. The installation of biofilter bags is simple and the bags are easy to remove. The disadvantages of biofilter bags include: 1) they only last a few months; 2) the bags can be damaged by construction equipment; 3) if not properly installed, they can increase sediment loading on sloped areas; 4) they require frequent maintenance due to the low sediment retention capacity; and 5) they are only to be used for low flows.

Sand bags are an alternative to both straw bales and biofilter bags. Sand bags can be used to capture and retain sediment on sloped areas as well as reduce water flow velocities and capture sediment in unlined or lined channels. Sand bags are constructed from durable, weatherproof, woven material that prohibits leakage of filter material. Sand bags are low in cost, easy to install and move, and are effective in areas with concentrated flow. They can also be used to divert flow. However, like straw bales, sand bags are not effective in areas with high flow. They can be damaged by construction equipment and only last a few months. Sand bags also contribute to sediment loading if the bags are ruptured.

Sediment traps are effective erosion control measures used in areas with a drainage size of 2.0 hectares (5 acres) or more located in proximity of salmonid streams, wetlands, or phosphorus sensitive areas. The lifetime of sediment traps is approximately six months, depending on the amount of sediment captured. The sediment traps have the ability to protect downstream riparian areas from sediment deposits and to remove particles down to 0.02 mm (0.78 mil) in size. However, sediment traps and the above mentioned BMPs do not reduce turbidity caused by fine silts and clays. Maintenance of the sediment traps can also be a nuisance.

Currently, the Oregon DEQ recommends flocculation as a BMP option for construction water turbidity treatment. The recommended flocculant is chitosan. This BMP method is recommended to be used in conjunction with detention ponds, and in areas with small sized particles. Due to the small particle size, gravity settling alone is not capable of reducing the turbidity level of the discharge waters to meet permit requirements. According to the Oregon DEQ, the use of a coagulant, or flocculant, such as chitosan can decrease the settling time and improve the clarity of the water. It has been found that with the application of chitosan, settling of particles in wastewater is complete after five minutes (*DEQ 2003*). While the coagulants can be very effective, this method requires careful maintenance and contracting with a consultant to develop and implement the system.

2.2 HISTORY AND DEFINITION OF CHITOSAN

Chitosan is a derivative of chitin, the second most abundant natural polymer on earth, after cellulose. It is found in the shells of crustaceans, insect shells, and fungi cell walls. Therefore, one possible source for viable industrial chitin is the waste produced by fisheries. On average, fishery waste amounts to 1.44 million tons (1.3 million megagrams) per year, of which 250,000 tons (227,000 megagrams) per year are available for the production of chitin (*Peter 2002*). The primary producer of chitin is Japan. Japan yields approximately 20-30% of all dry crustacean matter created every year (*Peter 2002*). India has the largest amount of shell fish caught per year, which could be a major resource for chitin production. Other producing areas include Norway, the North Atlantic region of the United States, Ukraine, Poland, and Panama (*Peter 2002*). Due to the location of the large sources, most research on chitin and chitosan is done in these regions.

The earliest chitin compound was found in an insect fossil that was dated to the Oligocene period, 24.7 million years ago (*Peter 2002*). Research on chitin began in 1811 with a French professor of Natural History, H. Braconnot. Braconnot isolated chitin from higher fungi and called it fungine (*Roberts 1992*).

Research continued and in 1823, A. Odier isolated an insoluble resin from a beetle which he decided to call chitin (*Roberts 1992*). In 1824, J.G. Children published an English translated version of Odier's paper with additions of his own research. Children's research proved the presence of nitrogen in chitin (*Roberts 1992*).

In 1894, research began to appear showing that chitin could be obtained from heating crab, scorpion, or spider shells in a potassium hydroxide (KOH) solution at 180 °C (356°F), which produced a product that was soluble in acetic acid and would come out of solution with the addition of an alkali (*Roberts 1992*). This discovery was made by F. Hoppe-Seyler and it was he who named the compound chitosan (*Rogers 1992*). Research progressed and in 1939, E. Fischer and H. Leuchs used synthesis of D-glucosamine to prove the configuration of chitosan.

The first patents on chitin were obtained in 1935 by G.W. Rigby and in 1936 by DuPont. The first textbook on chitin was published in 1977 by Ricardo A. Muzzarelli titled, "Chitin" (*Peter 2002*). Research continued and led to the creation of such organizations as the Society for the Study of Chitin and Chitosan, and the Japanese Society for Chitin and Chitosan. There is also an international conference that is held annually in varying locations.

2.3 MOLECULAR STRUCTURE OF CHITOSAN

Through the years it has been determined that chitosan is a high molecular weight linear heteropolysaccharide (*Domard 1998*). The molecular structure of chitin and chitosan are the same. They are both linear copolymers of linked β-(1→4)-D-glucosamine and N-acetyl-D-glucosamine (*Domard 1998*). Figure 2.1 shows the chemical structure of chitosan with all the acetyl groups removed. The actual chemical composition of chitosan always contains some acetylamine groups. The amount of acetyle groups is often referred to as a degree of acetylation (DA) and is used to distinguish chitin and chitosan. Usually the definition of chitosan requires it to have a DA lower than 50%. As shown in Figure 2.1, the major functional groups of chitosan are the amino groups that protonate at solution pH ranging from acidic to slightly basic (*Domard 1998*). These amino groups are responsible for the positive charges that chitosan carries at natural water pH. The pH of 95% of all natural water ranges from 6.5 to 9.0 (*Snoeyink and Jenkins 198*). Chitosan, with a high content of free amino groups, i.e. low DA, are the most effective in coagulation (*No and Meyers 1997*).

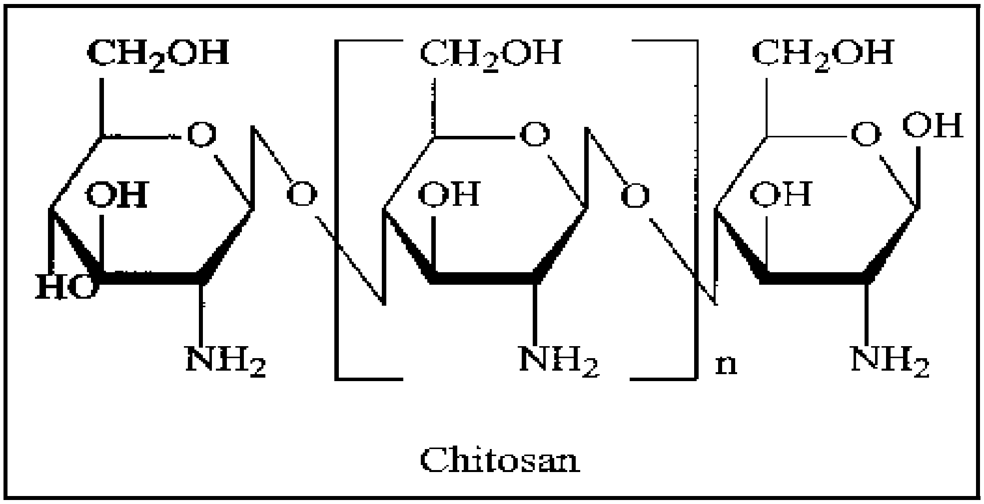

Figure 2.1: Chemical structure of completely deacetylated chitosan

2.4 PREPARATION OF CHITOSAN

Chitosan is the deacetylation product of chitin. The preparation of chitosan is a four step process: deproteinization, demineralization, decolorization, and deacetylation. Although the processing of chitin is done regularly, there is no standardized system for production (*Onsoyen and Skaugrud 1990*).

Deproteinization involves the removal of proteins. To remove the proteins from crustacean shell waste, the shells are ground and treated with a dilute alkaline solution (*Muzzarelli 1977*). While sodium hydroxide (NaOH) is usually preferred, a wide variety of reagents such as sodium carbonate (Na_2CO_3), potassium hydroxide (KOH), and sodium sulfide (Na_2S) can be used (*Roberts 1992*). Deproteinization is carried out at temperatures between 65-100 ºC (149 ºF-212 ºF), and the average reaction time is between 0.5 and 6 hours (*Muzzarelli 1977*). Enzymes can also be used to remove proteins, but this process takes longer than chemical treatments and offers no advantage over other methods (*Roberts 1992*).

After deproteinization is complete, the compound then goes through a demineralization process during which calcium carbonate in the raw material is dissolved under acidic conditions (*Muzzarelli 1977*). This process can be carried out with a number of acids such as hydrochloric acid (HCl), nitric acid (HNO_3), and acetic acid (CH_3COOH) (*Roberts 1992*). It has been reported that the process takes from 2 to3 hours with proper agitation (*Muzzarelli 1977*).

The third step in the production of chitosan is decolorization. Carotenoids are primarily responsible for the color of crustaceans. These are removed by treating the ground shells with ethanol or acetone (*Roberts 1992*).

Deacetylation is the final step in the conversion of chitin to chitosan. The degree of deacetylation is used to distinguish between the numerous forms of chitosan. Deacetylation is carried out by either alkali fusion or using an aqueous alkali. Alkali fusion is the most extreme method which involves using KOH at elevated temperatures around 180˚C (356 ºF). This method results in high degrees of deacetylation around 95% (*Roberts 1992*). Deacetylation using an aqueous alkali is the most commonly used method. Many alkalis can be used for this process, but the most commonly used is NaOH (*Roberts 1992*). Deacetylation is carried out at temperatures 100 ºC (212 ºF) or higher (*Muzzarellii 1997*). It is during this process that some or all of the acetyl groups are removed from chitin. There are several factors that affect deacetylation such as temperature, concentration of the alkali used, treatment conditions applied in chitin isolation, particle size of the raw material, and time of deacetylation. These factors must be controlled to produce a form of chitosan that is soluble in acetic acid (*Muzzarellii 1997*).

2.5 PHYSICOCHEMICAL PROPERTIES OF CHITOSAN

The physical properties of chitosan are varied. Chitosan in the liquid form is clear to pale yellow in color and has a pungent vinegar odor (*Vanson Halosource Inc. 2003*). According to the Material Safety Data Sheet from Vanson HaloSource Inc., Liqui-Floc, a liquid form of commercial chitosan that is used as a settling aid, is soluble in water, has a specific gravity of 1.0-1.1, a boiling point of 211˚F (99 ºC), and a pH of 3.9-4.1 (*Natural Site Solutions 2004*).

Chitosan is a linear polymer with a wide range of molecular weights. Its molecular weight varies with the type of biological material used to manufacture chitosan, and the degree of deacetylation (*Peter 2002*). The determination of the molecular weight is complicated by the presence of micro-gels that is caused by uneven treatment during deacetylation. The other complication is that chitosan tends to aggregate in standing solution (*Roberts 1992*). Despite the difficulties in measuring the molecular weight of chitosan, a range from 10,000 to 1,000,000 daltons has been reported (*Onsoyen and Skaugrud 1990*).

Although chitin is insoluble in most solvents, the solubility of chitosan varies widely. Usually, acid must be added in order to enable solubilization of chitosan in water. It is insoluble in water at pH levels above 6.5. Solubility of chitosan salts depends on the degree of acetylation, molecular weight, solution chemistry and the temperature.

Because some amino groups are acetylated, the acid dissociation constant, pKa, of chitosan is affected by the degree of deacetylation (*Domard 1998*). When the degree of deacetylation increases, the pKa increases, leading to an increase in solubility. Theoretically, when the degree of deacetylation approaches 50%, the compound becomes soluble at all pH levels. In practice, the degree of deacetylation necessary to obtain a soluble product should be 80 - 85% or higher (*National Toxicology Program 2004*). Chitosan solubility decreases as the molecular weight of the compound increases (*Domard 1998*). Solubility is inversely proportional to the ionic strength of the solution. As the ionic strength increases, the solubility decreases due to the charge screening effect (*Domard 1998*). The solubility of chitosan is also found to vary with the nature of the anions involved. It is soluble in mineral acids such as HCl, $HClO_4$, HNO_3, and HBr as well as in select organic acids. The chitosan salts of these anions are usually water soluble as well. However, it is insoluble in sulfuric acid because sulphate ions tend to form insoluble complexes with chitosan (*Domard 1998*). The pKa value of the alcohol groups of chitosan are unknown, but for different hexoses it has been found to vary between 12 and 12.5 (*Domard 1998*).

Another physicochemical property that has been investigated is viscosity. It has been found that the viscosity of chitosan is a function of its concentration. As the concentration of chitosan increases, the viscosity increases exponentially (*Onsoyen and Skaugrud 1990*). This is due to the high molecular weight of chitosan and its linear structure.

Of particular interest to the commercial value of chitosan is its affinity to heavy metals, which is utilized for heavy metal recovery. Chitosan has been found to be effective at removing heavy metals from water sources. In particular it has been used for metal ion adsorption in soil and waste water treatment. Research has been conducted to reveal the mechanisms of metal uptake by chitosan to determine the important factors that affect metal binding to chitosan and to test various types of metals that chitosan may adsorb effectively.

It has been shown that the mechanism of metal uptake by chitosan is a combination of adsorption, ion exchange and chelating (*Onsoyen and Skaugrud 1990*). The process is complicated and not yet fully understood. Chitosan is found to be most effective at forming complexes with transition and post transition metal ions, but it does not form complexes with alkali and alkaline earth metals (*Roberts 1992*).

Most of the research on the mechanisms of metal uptake by chitosan have been done using Cu(II) ions. A study conducted by Sag and Aktay (*2002*) found that Cu(II) ions were recovered by chitosan through chelation due to the presence of amino groups, specifically those from the glucosamine unit. The optimum pH for Cu(II) recovery was found to be pH 4. Metal uptake is less effective at a lower pH because it leads to an increased competition between Cu(II) ions and protons in solution and consequently lower Cu(II) adsorption efficiency. From this study it was also found that metal adsorption capacity is inversely proportional to chitosan particle size. The optimum particle size range of chitosan for maximum Cu(II) recovery was 250-450 μm.

The rate of metal ion adsorption by chitosan is controlled by both boundary layer resistance and intraparticle diffusion (*Onsoyen and Skaugrud 1990*). It has been found that the rate of metal ion uptake by chitosan is not significantly affected by the degree of deacetylation or the species origin of the raw material, while the manufacturing process of chitosan seems to play a more important role (*Onsoyen and Skaugrud 1990*). The complexation capacity of chitosan is comparable to that of chitin (*Onsoyen and Skaugrud 1990*).

Chitosan can be very effective at removing metal ions from wastewater and drinking water in the appropriate pH range. It is also being tested for arsenic removal. The United States Army Engineering Research and Development Center is currently testing chitosan coated ceramic plates to determine if they will be effective at removing arsenic compounds from drinking water. So far the experiment has been successful, but it is still in the testing phase (*Boddu and Smith 2002*). According to this study the adsorption capacities for As (III) is 56.5 mg/g of chitosan and 93.5 mg/g of chitosan for As(V). This could be a promising development in drinking water treatment.

One of the most appealing aspects of chitosan is its biodegradability. The compound is 100% biodegradable. In nature, for instance, when crustaceans decompose, chitin from the shells is quickly degraded by extracellular enzymes and microorganisms. This is the main reason why chitin does not accumulate in nature (*Peter 2002*). This degradation plays an essential role in the development of arthropods and vertebrates. The majority of the biodegradation information that exists on chitosan is for chitosan that is found in nature. There have not been many studies conducted on the biodegradation of commercial chitosan manufactured for water and wastewater treatment applications.

In an investigation in degradation of polymer films in marine environments, linked chitosan films was found to degrade in weeks. In a soil environment 10 $\mu g/mm^2$ were degraded per week (*Mayer, et al. 1996*). The rate of biodegradation was determined to be 11.6 $\mu g/mm^2$-week in natural marine sediments, and 7.5 $\mu g/mm^2$-week in marine water (*Mayer, et al. 1996*).

In another study using microcrystalline chitosan in an aqueous medium (*Ratajska, et al. 2003*), it was found that the rate of degradation increases with increasing temperature, with an optimum temperature of 40°C (104 °F). In a carbon starved environment, with microorganisms present in an active sludge from a cellulose plant, complete degradation of a 0.14 mm (5.5 mils) thick chitosan film occurred in four weeks at temperatures between 30-40°C (86-104 °F). It was also found that the degree of deacetylation decreases with the progression of decomposition. Unfortunately, few studies have been conducted to assess the impacts of chitosan degradation on dissolved oxygen concentration in water.

While the biodegradation of chitosan is appealing, the most compelling aspect of chitosan is that it is non-toxic at concentration levels commonly encountered. The main evidence of its low toxicity is that it is present in food that humans consume on a daily basis such as mushrooms and seafood (*Peter 2002*).

Toxicity studies have been carried out to assess the impact of chitosan on different species of fish. A study conducted by Natural Site Solutions (*2004*) found that the toxicity level of chitosan on fish is acceptable for its use in streams based on the EPA standards, which states that mortality has to be less than 20%. Water treated with chitosan was used in the tests. Values for pH, turbidity, and acute aquatic toxicity were also reported. Results of the study are shown in Table 2.1. Table 2.1 shows the LC50 values for chitosan. LC50 is the amount of material that will result in a 50% mortality rate of the population being tested. Both tables were published by Natural Site Solution and can be found at the website: http://www.naturalsitesolutions.com/AquaticSafety.html.

Table 2.1: Results of chitosan toxicity tests

Test#	Turbidity		pH		Aquatic Toxicity Tests	
	Before	After	Before	After	Trout	Daphnia
1	79	2.7	7.0	7.0	0% mortality	0% mortality
2	150	1	6.9	6.9	0% mortality	0% mortality
3	365	2	7.1	7.1	0% mortality	2% mortality
4	643	3.1	7.1	7.1	0% mortality	0% mortality

Table 2.2: LC_{50} levels of chitosan for three fish species tested

Test Species	Chitosan LC_{50} Values[3]
Fathead Minnow	1108 mg/L
Rainbow Trout	155 mg/L
Daphina Pulex	417 mg/L

In an exaggerated chitosan dose toxicity test, also conducted by Natural Site Solutions, a very high chitosan dose, 20.4 mg/L, 20 times the recommended dosage was tested. Chitosan at this concentration was found to cause no stress on either Rainbow Trout or Daphnia (*Natural Site Solutions 2004*).

2.6 CURRENT APPLICATIONS OF CHITOSAN

Chitosan has many practical applications. Because it is a long-chain polymer with positive charges at natural water pH, chitosan can effectively coagulate natural particulate and colloidal materials, which are negatively charged, through adsorption, charge neutralization, inter-particle bridging, as well as hydrophobic flocculation (*Weber 1972; Parazak, et al. 1988*). Therefore, it has been used as a natural coagulant/flocculant for treatment of drinking water and municipal wastewater, storm water and construction discharge water in detention ponds, pharmaceutical discharge water, and industrial wastes.

2.6.1 Chitosan in Water and Wastewater Treatment

In drinking water and wastewater treatment, chitosan is used as an effective coagulant/flocculant alternative to conventional inorganic coagulants such as alum and ferric chloride. Chitosan is desirable in these applications because it is a natural, non-toxic material, and is 100% biodegradable. Chitosan is unique in that it is capable of binding to negatively charged particles, heavy metals, and oils. It is commonly used as a filtration aid in commercial aquariums to produce high clarity water and is proven to be safe to fish at the dosage commonly used.

The effectiveness of conventional coagulants is highly dependent on solution pH, which often requires careful pH adjustment of the raw water. The use of alum or ferric chloride also results in significant residual concentration of Al or Fe ions in the treated water. In drinking water treatment, the high residual Al level poses a potential public health issue because of its possible connection with Alzheimer's disease. Both Al and Fe ions in the treated water may precipitate in the distribution system causing a reduction in pipe diameter and a loss of hydraulic power. The accumulation of these metal ions in natural water bodies is a concern because they are not easily taken up by microorganisms. Another problem related to the use of conventional iron or aluminum coagulants is the disposal of the sludge produced during the coagulation process because both aluminum and iron salts are not biodegradable. The application of chitosan as a coagulant/flocculant not only makes the treated water safer, but also avoids various problems related to disposal of the sludge from water or wastewater treatment facilities. The natural abundance of chitin makes the choice of chitosan economically more favorable than alum or ferric chloride.

Laboratory experiments have been conducted to evaluate the effectiveness and feasibility of using chitosan for coagulating colloidal particles in water and wastewater. Huang and Chen (*1996*) conducted a series of coagulation tests using chitosan prepared from crab shells to determine if it can be used as an alternative coagulant to aluminum sulfate or polyaluminum sulfate for use in water treatment systems in Taiwan. Both synthetic suspensions containing bentonite or kaolinite particles and a natural water sample taken from the water intake of a water treatment plant were tested. The turbidity of the suspensions tested ranged from 30 to 600 NTU (nephelometric turbidity unit).

An optimal chitosan dose was found for each of the initial turbidities tested. Below the optimal dose, turbidity removal increased with increasing chitosan dose. For chitosan doses above the optimal value, lower treatment efficiency was observed, indicating destruction of particle bridging which leads to particle restabilization (a stable clay suspension), and consequently higher residual turbidity. The optimal dose was found to increase with increasing initial turbidity almost linearly. The low dosage required when the initial turbidity level is low makes chitosan preferable to alum or ferric chloride for low turbidity water. The main mechanisms of coagulation by alum or ferric chloride at neutral pH are charge neutralization and enmeshment.

Under neutral pH conditions, excess Al or Fe coagulant is required in water of low turbidity to create probability of collision between the coagulant and the particles.

It was found in the same study that chitosan coagulation efficiency was affected by the properties of clay particles. Particle size, surface properties and surface structures are believed to attribute to the different coagulation efficiencies for kaolinite, bentonite, and colloidal materials in raw natural water. The best turbidity removal was achieved with bentonite, for which the turbidity of the suspension was lowered from 30 to 0.56 NTU with the addition of 1.0 mg/dm^3 (1.0 mg/L) chitosan. For all initial concentrations of kaolinite tested, the residual turbidity was above 15 NTU. Interestingly, the addition of bentonite was found to improve coagulation of kaolinite by chitosan. In the presence of bentonite, turbidity of 30 NTU from kaolin was able to be reduced to 0.6 NTU with the addition of approximately 2 mg/dm ^{3} (2.0 mg/L) of chitosan.

The effect of pH on chitosan coagulation was also studied in Huang and Chen's (*1996*) investigation. With the same chitosan dose, maximum turbidity removal was achieved at pH 6. However, only a small difference in residual turbidity was observed within the pH range from 4 to 8. At a pH lower than 4 or greater than 8, residual turbidities increased significantly. The optimal chitosan dosage for all initial turbidity levels was found to increase with increasing pH.

In another study pertaining to the flocculation of kaolinite suspensions in water, Divakaran and Pillai (*2001*) achieved successful kaolinite colloid removal for a wide initial turbidity range from 10 to 160 NTU using chitosan prepared from prawn shells. Within the pH range tested, from pH 5 to pH 9, the maximum turbidity removal occurred at a pH of 7.5. The optimal chitosan dose was found to be 1 mg/L regardless of the initial turbidity, although a higher initial concentration of suspended solids tends to produce larger flocculation in a shorter time. Kaolinite removal of up to 95% was achieved at this dosage level. Further increase of chitosan dosage had no effect on the residual turbidity. Restabilization of particles was not observed, presumably because the maximum dose used was not high enough to cause charge reversal. Divakaran and Pillai also found that the coagulation/flocculation process of kaolinite was enhanced by trace quantities of soil particles present in natural water. It was found in a later investigation by Divakaran and Pillai (*2004*) on flocculation of titanium dioxide particles that humic acids present in natural water and soil enhance the flocculation process.

To test the effectiveness of chitosan coagulation/flocculation for removal of colloidal materials in natural water, coagulation experiments were also conducted with river silts extracted from Periyar River, India, using the same chitosan material as in the kaolinite study previously discussed(*Divakaran and Pillai 2002*). The silt tested consisted mainly of silica particles with some adsorbed iron oxide. Experiments were conducted in the pH range of 4-9, with initial concentrations of suspended solids of 20-80 mg/L, corresponding to turbidity level of 10 to 160 NTU. The optimal pH was found to be at 7.0 and turbidity removal from 80 to 95% was achieved at this pH by coagulation alone, without filtration (*Divakarn and Pillai 2002*). Optimal turbidity removal was achieved at the chitosan dose of 0.5 mg/L, above which particle restabilization took place. The chitosan dosage required for restabilization increased with particle concentration. Similar results were obtained using turbid water from the Periyar River during flooding.

Chitosan has also been tested for flocculation of various bacteria. It was found that the settling rate of *E. Coli.* was greatly improved with the addition of chitosan (*Agerkvist, et al. 1990*). With 100% deacetylated chitosan, 98% of *E. Coli.* cell debris was removed by flocculation followed by sedimentation within 30 minutes, compared to 70% removal when no chitosan was added. Strand, et al. (*2002*) reported a large variation in chitosan flocculation efficiency of different types of bacteria suspensions. However, no clear correlation was found between flocculation efficiency and general bacterium surface characteristics, such as surface charge and hydrophobicity.

Chitosan has proven to be effective at treating vegetable canning wastes. Typically cannery wastes are high in organic material and therefore need to be treated before discharge. By using chitosan, turbidity can be reduced from 85 to 8.7 NTU (*Muzzerelli 1977*). Chitosan has also been used as an adsorbent for sorption of dyes, phenols and polychlorinated biphenyls (PCB) from industrial and food processing waste (*No and Meyers 2000*).

2.6.2 Chitosan for Turbidity Control During Construction

High turbidity is a major problem in storm water and construction discharge treatment. Currently, according to the Oregon Administrative Rule 340-041, there can be no more than a 10% cumulative increase in natural stream turbidity measured relative to a control point upstream (*DEQ 2004*). Due to the increasingly stringent standards on discharge into natural water bodies, conventional coagulants are not appropriate mainly because of their toxicity and persistence in the environment. Chitosan has been widely used for treatment of construction water discharge into receiving water bodies because it is non-toxic and 100% biodegradable. Most applications of chitosan for turbidity control involve the use of detention ponds. Construction discharge or storm water is collected in a detention pond where it is treated with chitosan. The clarified water with a lower turbidity level is then discharged to a receiving water body.

No studies have been conducted using chitosan for in-stream turbidity control, although chitosan has been used to treat turbidity caused by natural sediments. One such project reported was the Tahoe Key Marina access channel dredging project (*Macpherson, et al. 2002*). For this project approximately 7900 yd^3 (6040 m^3) of sediments were to be removed from the channel with the dredge water being discharged into a dry marsh nearby at a flow rate of approximately 4,500-5,000 gpm (17,035-18,927 lpm). The dredge water contained up to 20% solids, with a turbidity level higher than 1000 NTU. The turbidity had to be reduced to below 20 NTU before discharge, which was not possible by natural sedimentation. Due to increased concerns of environmental impacts of industrial water treatment chemicals, chitosan was chosen to treat the turbidity.

The chitosan product used in this project was Gel-Floc™, distributed by Natural Site Solutions. Gel-Floc™ is a gelatinous form of chitosan that is sewn into a segmented fabric sock. When water passes through the sock, the gel slowly dissolves into the water and acts as a natural settling aid. The sedimentation process consists of three settling ponds in series with a total capacity of 2 million gallons and a retention time of seven hours. The whole system was operated at a flow-through mode with intermittent recirculation when the influent turbidity was excessively high. Over the tested period, the system was able to maintain an average turbidity of 17 NTU.

Water quality was monitored immediately after the settling ponds, as well as upstream and downstream of the discharging marsh. The parameters monitored included pH, temperature, conductivity, total nitrogen, total Kjeldahl nitrogen, total phosphorous and turbidity. During the testing period, no significant changes in pH, conductivity, or temperature were caused by the use of chitosan. Good removal of phosphorous and nitrogen were also mentioned in the report.

Chitosan is also used as a filtration aid in construction water treatment. The US Department of Transportation Federal Highway Administration (FHWA) used Liqui-Floc™, a liquid form of chitosan, manufactured by Vanson HaloSource, for treatment of construction site run-off water while building an interchange along I-90 near Seattle, Washington (*FHWA 2002a*). The project used chitosan in conjunction with detention ponds, followed by sand and ground infiltration. Water was collected in the detention ponds, from which it is pumped to the sand filtration pods. The Liqui-Floc™ was added to the water as it entered the pipe between the detention ponds and the filtration pods. With the help of chitosan, the run-off water turbidity was reduced from 150 NTU to 1 NTU, more than 99% removal compared to the maximum 50% removal by filtration alone. In this project, chitosan was also proved effective at removing phosphorous, heavy metals and oils from the water. Because the pH of the water was between 6 and 8, within the working range of Liqui-Floc™, no pH adjustment was necessary.

In a road improvement project also sponsored by Natural Site Solutions, chitosan was used along with portable settling tanks. The project was conducted by the Federal Highway Administration in Prince of Wales Island, in 2002. The storm turbidity ranged from 900 to 4,500 NTU and the discharge standard was less than 10 NTU. Due to the narrowness of the project site, Gel-Floc™ was used in above ground settling tanks, followed by sand filtration enhanced by Liqui-Floc™ injection. It was found that the Gel-Floc™ helped to reduce the turbidity by 90% in the settling tank, while the Liqui-Floc™ enhanced the sand filtration system further reducing the residual turbidity to less than 5 NTU. The use of chitosan did not cause any change in the pH of the storm water (*FWHA 2002b*).

2.6.3 Other Applications

Chitosan has many applications outside of water treatment (*Muzzerelli 1977*). It has been demonstrated to be very useful in many industrial processes. Chitosan is used extensively in the paper making industry to make paper water proof. It is used in the textile industry to manufacture glass and plastic fabrics, polymeric dyes to keep dyes on fabric used in batiking, and to shrink proof wool. It is also used as a stain repellent for carpets and upholsteries. In the medical field chitosan has extensive applications; the most common is using chitosan as a dietary aid due to its ability to bind to fats and oils. Other medical applications of chitosan include: artificial kidney membranes, pharmaceutical carriers, wound healing accelerators and the manufacturing of artificial skin.

2.7 MECHANISM OF CHITOSAN FLOCCULATION

2.7.1 Flocculation Chemistry

In a stable colloid suspension, the individual particles carry an overall charge. A stable suspension is one in which all particles remain in suspension due to the repulsive forces caused by the charge, which in turn is related to the particle size, the ionic strength of the solution, and the surface potential. The addition of an oppositely charged polymer or polyelectrolyte destabilizes the suspension through charge neutralization followed by floc formation. Under the proper conditions the floc will settle, essentially sweeping through the water removing more suspended materials.

Flocculation is conventionally achieved by the addition of an electrolyte such as Alum (also a polymer) or Ferric Chloride. When added to water these substances undergo hydrolysis reactions which form precipitates and cationic complexes which destabilize the suspension by adsorbing to negatively charged colloids. Through this destabilization, the net negative charges on the colloid particles are reduced, allowing the particles to move closer together and form larger aggregates with the polyelectrolyte particles.

An alternative to flocculation by simple electrolytes is to use a high molecular weight polymer, such as chitosan. Inter-particle bridging is the major mechanism of polymer flocculation (*Sonntag 1993*). A high molecular weight polymer is often used because it has long protruding tails that can extend from one particle to another. First, the polymer adsorbs to the colloidal particles causing charge neutralization. This destabilization is known as coagulation (*USAE 2001*). In most waters, colloids and organic material are negatively charged. The adsorption of a cationic polymer on a negatively charged particle surface causes a reduction in the net electrostatic repulsive forces between particles, which allows the particles to move closer together and form inter-particle bridges through polymer chains. This process is known as flocculation (*USAE 2001*). The result of this process is the formation of large sized flocs that settle. Once the flocs are fully formed, they further remove suspended materials by a sweeping mechanism.

The kinetics of polymer bridging depends on the rates of particle collisions with polyelectrolyte macromolecules, reconfirmation of the adsorbed polymer molecules, collision rate and efficiency of destabilized particles, and the rate of deaggregation (*Sonntag 1993*). In general, the polymer adsorption rate is greater than the flocculation rate. Therefore, flocculation is often the limiting step of the process.

2.7.2 Mechanisms of Flocculation Induced by Chitosan

Although chitosan has been used as a flocculant in many applications, the mechanisms of flocculation induced by chitosan are not fully understood. A study conducted by Divakaran and Pillai (*2004*) to determine the mechanism of kaolinite and titanium dioxide flocculation using chitosan, proposed that dissolved humic particles, either negatively or positively charged, play a major role in the flocculation process. At low pH, there are more positively charged humic particles than negatively charged particles. The positively charged humic particles adsorb to the negatively charged kaolinite particles destabilizing the colloidal suspension. Since the positive portion of the humic particles, which exhibit multiple charges, adsorbs to the clay particles, the negatively charged outer edges of the humic substance are exposed causing a net negative charge which restabilizes the clay suspension (*Divakaran and Pillai 2004*). The addition of cationic chitosan acts to destabilize the humic coated kaolinite suspension and form bridges between particles which settle. This study found that this process is most efficient at a weakly acidic pH, due to the presence of NH_3^+. Higher than neutral pH causes the humic particles to be stripped off the clay particles because the humus is in the form of salt and therefore has no amine groups which results in the inefficiency of chitosan flocculation (*Divakaran and Pillai 2004*).

In another study of chitosan flocculation, it was found that inter-particle bridging was the main mechanism (*Chen, et al. 2003*). The molecular weight of chitosan was found to define the charge neutralization capacity, although charge neutralization is not the main mechanism for chitosan flocculation (*Chen, et al. 2003*). Roussy, et al (*2004*) arrived at a similar conclusion that charge neutralization efficiency is dependent on the molecular weight of chitosan, but flocculation occurs predominantly by the inter-particle bridging via polymer molecules that adsorb in a loop and tail conformation (*Roussy, et al. 2004*). It was proposed in this study that in acidic solutions, chitosan has positively charged amine groups which adsorb to the negatively charged colloidal particle surface (*Roussy, et al. 2004*).

2.8 CLAY PROERTIES AND FLOCCULATION

Clay particle, smaller than 0.002 mm (0.078 mil), dispersions are often used to study the mechanisms of flocculation because once suspended, the dispersions are stable in most neutral waters making it difficult to remove particles by settling alone. The most important types of clays are kaolins, smectites (montmorillonite clay whose main constituents are bentonite), illite, and mixed layered clays. Kaolin and bentonite were chosen for this study because of their abundance and the availability of research done using both of them.

Clays are formed from fluid, weathering, or hydro-thermal alteration of different types of parent materials (*Lagaly 1993*). The most useful clay in civil engineering practice is bentonite. Bentonite is considered pure clay because it does not require pretreatment to be used in a variety of construction applications. Kaolin on the other hand contains coarse particles of quartz, feldspar, micas, and unaltered granite. Kaolin clay has to be altered by size separation or refining before it is useful.

Since the 17th century in Western Europe, and earlier in China and Japan, kaolin has been used as the raw material for fine porcelain products (*Giese and van Oss 2002*). Kaolin is a 1:1 layered silicate clay with one tetrahedral sheet attached to one octahedral sheet. The layers are uncharged and are held together by hydrogen bonds and van der Waals forces. The general formula of kaolin is $Al_2(OH)_4Si_2O_5$.

Kaolin dispersions are more stable in the presence of salt, than without salt, because the particles have a plate like structure. The flat sides of the particles are negatively charged, while the edges of kaolin, which are thicker than most types of clay, are positively charged. This causes the clay particles to align in a house of cards flocculated structure, which breaks down when the particles become hydrated (*Giese and van Oss 2002*). The card house structure forms because the negatively charged faces of the plates repel each other, but the faces are attracted to the positively charged edges which causes the flocculation of kaolin in a house of cards structure (*Giese and van Oss 2002*).

Bentonite is commonly used to stabilize the walls of drilling operations. In 1982, 2.5 million tons (1.8 million megagrams) of bentonite were used in the preparation of drilling mud (*Lagaly 1993*). Bentonite is a 2:1 clay mineral with two tetrahedral sheets attached to one octahedral sheet. The chemical formula is $(Na, Ca)_{0.3}(Al, Mg)_2Si_4O_{10}(OH)_2 \bullet nH_2O$. The layers of bentonite carry an overall negative charge (*Lagaly 1993*). The interlayer space contains water molecules, the amount of which depends on the charge of the layers, the vapor pressure of the water surrounding the clay particles, and on the type and concentration of salt present (*Lagaly 1993*).

2.9 POTENTIAL OF AND IMPACTS OF USING CHITOSAN FOR IN-STREAM TURBIDITY CONTROL

As described above, chitosan has proven to have many useful applications from waste water treatment to medicine. Its effectiveness in all applications is dependent on the physicochemical properties and the raw material from which it was produced. While the use of chitosan has been well documented for medical, food, water and wastewater industries, the full potential of chitosan as a flocculant to be used in natural streams for turbidity control has yet to be studied.

3.0 TESTING METHODS AND MATERIALS

3.1 FIELD TEST

A total of six field tests were conducted in one day. Field tests were conducted in Oak Creek located in Corvallis, Oregon. During the tests, construction site run off was simulated using sediment from the banks of Oak Creek and the introduction of the liquid form of chitosan. One background test and two control tests with only sediment introduction were conducted. There were three tests done with the introduction of two different chitosan doses.

3.1.1 Stream Classification

The stream chosen for the field tests was Oak Creek in Corvallis, Oregon. The Oak Creek watershed located in Benton County Oregon is 8,229 acres (3,330 hectares) in size. The headwaters of Oak Creek are located in the McDonald-Dunn experimental forest located north of Corvallis. The stream flows through the forest, agricultural lands, and then through an urban section of Corvallis, until its conjunction with the Mary's River. Oregon State University manages 40% of all the land within the watershed.

There are three main reaches of Oak Creek - the forest section, the agricultural section, and an urban section (*Oregon State University 2002*). The field tests were carried out in the agricultural section. The land surrounding the test site is mainly pasture and farmland, with a riparian area that is comprised of Oak and Alder trees. The test site, see Figure 3.1, located along Campus Way, has an approximate width of 3.5 ft (1.07 m) and an average summer stream flow of 0.028 m^3/s (0.036 yd^3/s). The stream has had documented runs of cut throat trout, salmon, and other non-game fish. This stream was chosen because it has been heavily researched and there are no endangered species present during the low flow season.

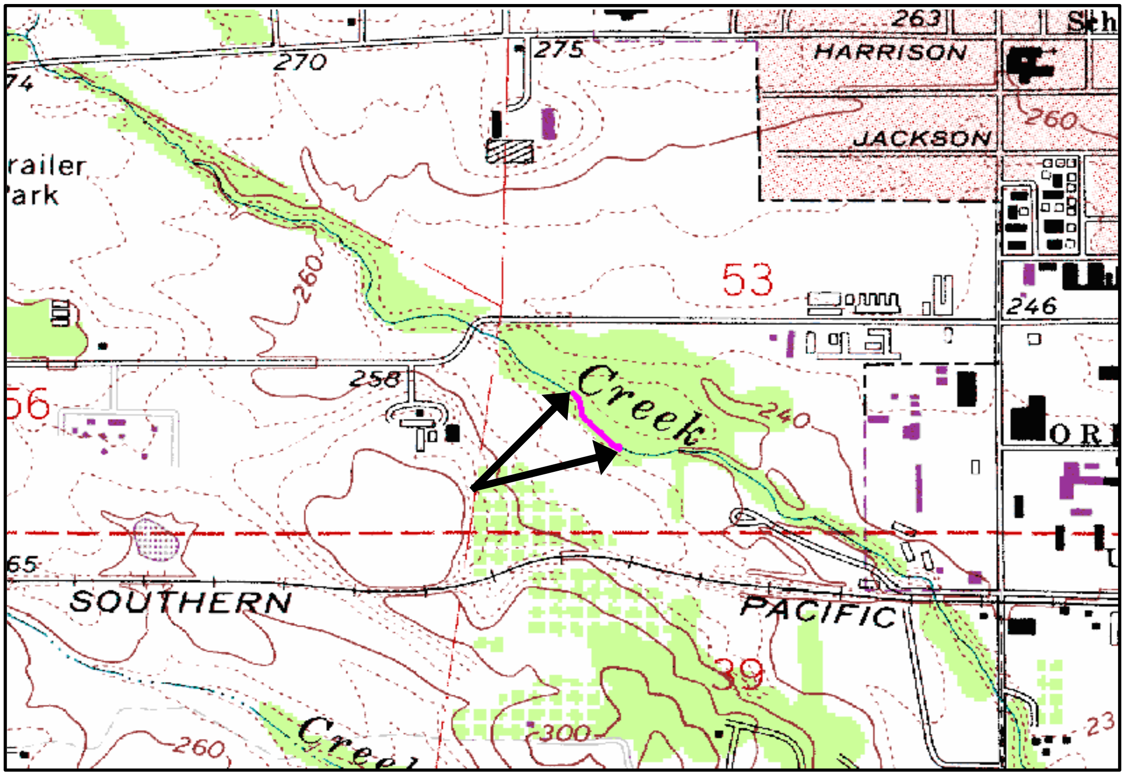

Figure 3.1: Chitosan test site, Oak Creek, Corvallis, Oregon. The arrows mark the approximate location of the test site along the creek.

A survey of the stream was conducted using a Leica TCRA 1105 Total Station. The survey was preformed following the guidelines outlined by Harrelson, et al. (*1994*). It consisted of six transverse cross sections and a longitudinal profile through the length of the study section. The slope and the sinuosity of the stream were determined from the survey results. However, because Oak Creek has been channelized and consequently is no longer a natural stream system, it could not be classified using the Rosgen Method. The slope was determined using Equation 3-1 below.

$$Slope = \frac{elevation\,between\,points}{distance\,between\,end\,points} \tag{3-1}$$

The sinuosity was determined using the following definition:

$$Sinuosity = \frac{Stream\,Length}{Valley\,Length} \tag{3-2}$$

On the same day as the stream survey, a pebble count was done following the random step-toe procedure outlined by Harrelson, et al. (*1994*). Once the stream reach was designated, cross-sectional transects were randomly chosen. With every step made by the surveyor along each transect, the first pebble encountered in the stream that was closest to the surveyor's right foot was picked up while the surveyor looked away. The diameter, corresponding to the widest part of the B (intermediate) axis, of the pebble was then measured and recorded on a tally sheet. This process was repeated 127 times to develop a size distribution of pebbles. The pebble count gives an approximate idea of the composition of the bed of the stream.

3.1.2 Timing and Permits

The project was conducted on Sept 21, 2005, within the time window defined by the Oregon Department of Fish and Wildlife's (ODFW) guidelines for timing of in-water work. The guidelines state that all in-stream work needs to be completed, for the Mary's River Watershed, by September 30 due to the possible presence of Cutthroat Trout and possible runs of Spring Chinook Salmon (*Oregon Department of Fish and Wildlife 2000*).

The lack of Spring Chinook during the low flow season allowed this project to be considered a no effect project and was therefore not subjected to Endangered Species Act compliance. The project did not require a US Army Corps of Engineers Section 404 removal/fill permit because the project disturbed less than 1 yd^3 (0.76 m^3) of material, and was conducted according to the ODFW's guidelines for in-stream work.

3.2 FIELD TESTING METHODS

The general approach of the field tests was to introduce sediment into the stream to simulate the turbidity caused by construction activities. The turbidity and other water quality parameters with and without chitosan treatment were then compared at different locations downstream of the sediment introduction site.

One preliminary test and six field tests were conducted. The purpose of the preliminary test was to evaluate the field test protocol and to obtain experimental parameters needed for the field tests. The experimental conditions and parameters that were tested included: 1) method of sediment introduction; 2) location of the monitoring; 3) performance of the water quality monitoring systems; 4) stream flow rate; and 5) stream water pH, conductivity, dissolved oxygen.

Six field tests were performed within one day. Table 3.1 summarizes the field tests, the order the tests were conducted, the length of each test, and the number of water quality samples collected during each test.

Table 3.1: Summary of test condition

Test#	Test Description	Length of Test, min	Chitosan Dose, ppm	# of Water Quality Samples per Test
1	Background Monitoring: no sediment and no treatment	10	0	1
2	Control test I: Sediment introduction	60	0	3
3	Low dosage treatment I: sediment introduction	30	0.25	3
4	Low dosage treatment II: sediment introduction (introduction site moved upstream)	30	0.25	3
5	High dosage treatment: sediment introduction	30	0.5	2
6	Control test II: sediment introduction	30	0	0

Stream water turbidity, pH, temperature, conductivity, and dissolved oxygen (DO) were monitored for the duration of each field test. To determine the environmental impacts of chitosan, water quality samples were taken under all test conditions. Samples were collected for analysis of biochemical oxygen demand (BOD), total phosphorous (TP), total Kjeldahl nitrogen (TKN), total organic carbon (TOC), and residual free chitosan. Sediment samples were collected for analysis of heavy metal concentrations and sediment particle size distribution. The water quality parameters and sediment properties determined from these analyses were used to determine the effects of chitosan on stream water quality.

3.2.1 Sediment Introduction

Local sediment was used to ensure that the sediment properties were representative of construction sediments introduced during in-stream work. Sediment was taken from the stream bank - above the two year flood level in order to remain within the limits of the US Army Corps of Engineers Section 404 removal/fill permit. Because of this permit, the sediment could not be collected from the stream. The sediment introduction site was located close to a down-stream pool of water, where the flow velocity is lower, so that a relatively stable turbidity level could be achieved at the site of introduction. Turbidity was monitored at five sites: one upstream and four downstream. The NPDES permit requires that introduced turbidity can not exceed 10% above background levels 100 feet (30.48 m)downstream of the construction site relative to an upstream monitoring site. Due to the lack of information about the possible Best Management Practices for in-stream construction projects, it was necessary to exceed the NPDES permit requirements. This was necessary due to the fact that introduced turbidity levels needed to be high enough to exceed the natural variation in the background turbidity levels.

It was desirable to create a stable introduced turbidity of 200 NTU to the stream by introducing sediment at a constant rate. However, sediment characterization and turbidity measurements made during the early stages of the project demonstrated that continuous introduction of sediment over the monitoring period would not be feasible, due to the large amount of sediment needed. Each of the five field tests involving sediment introduction were planned to last 60 minutes. This would have required approximately 704 kg (1,552 lb) of dried, fine sediment to create a constant turbidity of 200 NTU, with a stream flow rate of 0.11 m3/s (0.14 yd^3/s). Therefore, it was decided that short pulses of sediment would be introduced into the stream.

Approximately 0.4 yd^3 (0.3 m^3) of material was excavated from the stream bank to remain within the guidelines, which limits disturbance to less than 2 yd^3 (1.53 m^3) of material. The sediment was pulverized for approximately 1.5 hours, using a pulverizer to ensure the material was fine enough to stay in suspension. 0.5 kg (1.1 lb) of dried sediment was placed in each of the four 5 gal (18.9 L) buckets, suspended with stream water, and thoroughly mixed with a standard metal paint mixer attached to a battery operated drill. After the sediment was mixed, the suspension was poured into the stream, two buckets at a time, in succession. Results from the preliminary test showed that the introduction of two buckets of sediment suspension could create a reproducible average turbidity of 203 ± 12 NTU. However, the turbidity peak created using this method attenuated quickly. Therefore, four buckets of suspension were used instead.

The particle size analysis of the pulverized sediment was conducted following the American Society for Testing and Materials (ASTM) designation: D 422-63 (*ASTM 1987*). A mass of 250 g (0.55 lbs) of sediment was sieved for 10 minutes to determine the mass retained on each sieve. The percent of soil passing, or the percent finer than, was calculated using Equation 3-3 (*Das 2002*):

$$F = \frac{(\Sigma M - (M_1 + M_2 + \dots M_i))}{\Sigma M} \times 100 \tag{3-3}$$

Where F = % soil passing the ith sieve
M_i = mass retained on the ith sieve
ΣM = total mass of soil

The gradation was determined using the method outlined by Folk and Ward (*1957*). The particle size distribution using phi units was calculated using Equation 3-4 (*Krumbein 1934*):

$$\Phi = -\log_2 (d/d_0) \tag{3-4}$$

Φ = logarithmic transformation of the Wentworth grade scale
d = sieve opening size, mm
d_0 = 1 mm, standard grain size

After calculating the phi scale values, the cumulative mass versus phi value was plotted. The degree of sorting of the sediment was determined using the formula for the standard deviation of the sieve analysis, Equation 3-5 (*Folk and Ward 1957*).

$$\sigma_1 = \frac{(\Phi_{84} - \Phi_{16})}{4} + \frac{(\Phi_{95} - \Phi_5)}{6.6} \tag{3-5}$$

σ_1 = Inclusive graphic standard deviation
$\Phi_{84,\,16,\,95,\,5}$ = value of Φ that corresponds to 84%, 16%, 95%, and 5%, respectively, of the cumulative frequency curve, estimated from the particle size distribution graph.

The range of values corresponding to very well sorted, moderately well sorted, poorly sorted and extremely poorly sorted particle size distributions are: 0.35, 0.50-0.71, 0.71-1.00, 1.00-2.00, and > 4.00, respectively (*Folk and Ward 1957*).

3.2.2 Chitosan Introduction

Liquid chitosan was donated by Natural Site Solutions, Redmond, Washington. It is a mixture of chitin, water, and acetic acid to form a 2% solution of chitosan acetate. The solution was uniformly sprayed over the width of the stream using ¾ in flexible Tygon tubing. Holes were poked in the tubing using a 16 gauge needle, every 6 in (15.24 cm). The flow rate of the chitosan solution was controlled by a MasterFlex L/S peristaltic pump to obtain the target chitosan dosage in the stream - 0.25 ppm for field test #3 and test #4, and 0.50 ppm for field test #5. In test # 3, chitosan was introduced 15 ft (4.58 m) downstream of the sediment introduction site and then moved upstream starting from test # 4 to 5 ft (1.52 m) below the sediment introduction site (see Figure 3.2 for the location of the chitosan introduction sites). The chitosan introduction site was moved in order to obtain better mixing and longer retention time of chitosan. The dosing started approximately 10 seconds before the introduction of the sediment and after the sediment peak passed the chitosan introduction site.

3.2.3 Stream Water Quality Monitoring

A total of five monitoring sites were set up for the testing day. The first monitoring site, monitoring site 0, was located approximately 7 ft (2.14 m) upstream of the sediment/chitosan introduction site. The other four monitoring sites were located at 50, 105, and 125 ft respectively (15.25, 32, 38 m), downstream of the introduction site. Monitoring site number 3 was the site that corresponds to the downstream distance of 100 ft (32 m) within which turbidity must be reduced to within 10% above background during construction work. Monitoring site number 4 was located just downstream of site number 3 at 125 ft (38 m). The monitoring site locations are shown in the schematic in Figure 3.2.

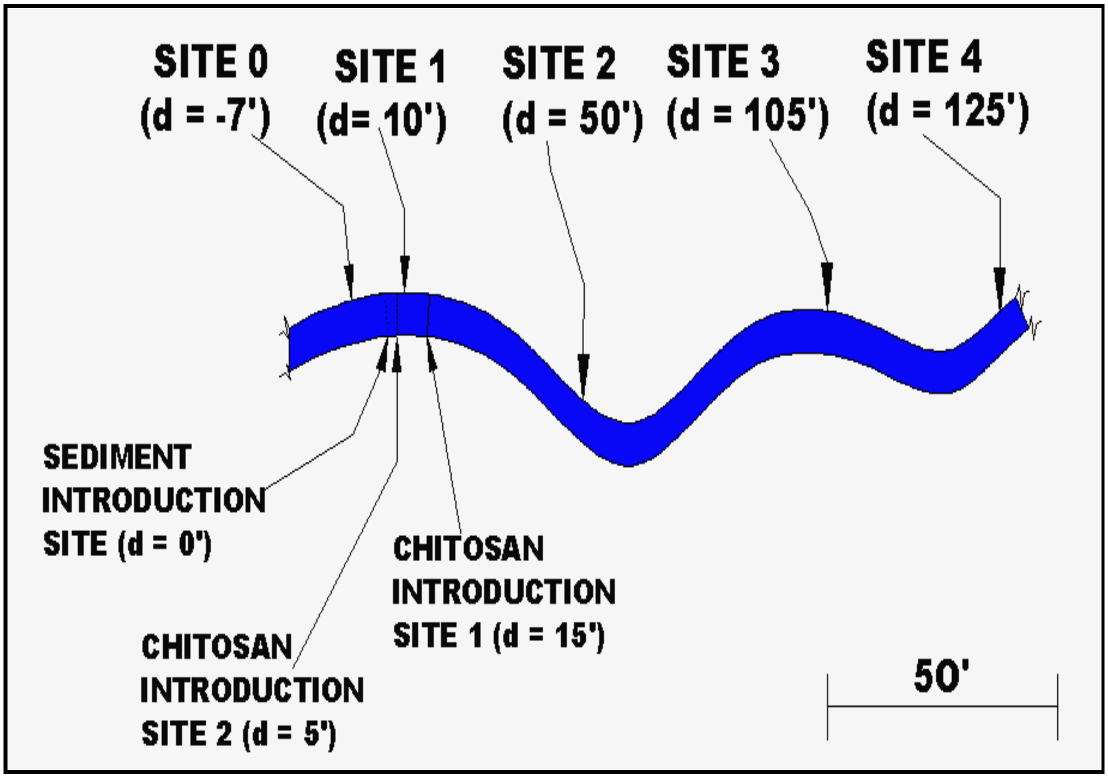

Figure 3.2: Schematic diagram of monitoring site locations

Each of the monitoring sites was set up with a water quality monitoring system, a Horiba U22-XD. The Horiba U22-XD is a multi-parameter probe that monitors turbidity, pH, temperature, conductivity, and dissolved oxygen (DO), simultaneously. It has a data logging device that can store up to 2880 data points and is capable of taking measurements as frequently as every 0.5 seconds. For this test, the data loggers were programmed to take measurements for the above mentioned parameters every 16 seconds. Site # 4 turbidity data was eliminated from analysis due to problems encountered with the probes.

The probes were positioned in the stream at locations with the highest velocity along the cross-section whenever possible. Otherwise, the probes were placed as close to the center of the stream as possible.

For every test that involved sediment introduction, water quality monitoring began 5 minutes prior to sediment introduction. In field test #1, the control test, monitoring continued for 10 minutes. Field test #2, sediment introduction without treatment, monitoring continued for 60 minutes. Monitoring during the rest of the field tests was shortened to 30 min because the sediment pulse cleared out of the test reach well within 30 minutes; much faster than had occurred during previous preliminary tests. This was most likely due to the unexpected rain which increased the flow rate of the stream.

3.2.4 Measurement of the Stream Flow Rate

A Marsh-McBirney Flowmeter was used to determine the velocity and average flow rate of the stream on the day of the field test at each monitoring site. The flow meter calculates the 20-sec-time-averaged velocity using the energy equation, assuming that the change in elevation and the head loss equal zero. At each of the five monitoring sites, a measuring tape was stretched across the stream. Velocity measurements were taken at ten points of equal distance across the stream, at 80% of the total depth. The calculated average flow rate of the stream, on the day of the field test, was 0.11 m^3/s (0.14 yd^3/s).

3.2.5 Water Sample Collection

Water quality samples were taken during all tests for analysis of biochemical oxygen demand (BOD), total organic carbon (TOC), total phosphorous (TP), and total Kjeldahl nitrogen (TKN) to determine the impact of chitosan treatment on stream water quality. The number of water quality samples collected during each test is summarized in Table 3.1.

The water quality samples were collected immediately downstream of the multi-parameter probes to minimize the disturbance to the probe measurement. BOD samples were collected in 2.0 L (0.26 gal) polypropylene sample bottles. TKN, TP, and TOC samples were collected in 250 mL (8.45 fl oz) amber colored glass bottles to avoid organic contamination from leaching of the container material. The samples were divided for TP, TKN, and TOC analysis in the Environmental Engineering Lab at Oregon State University.

Prior to every sample, the sampling bottle was rinsed three times with stream water. The bottle, with the lid on, was then lowered into the stream and the lid was removed to collect the sample. The water samples were taken at approximately half the depth of the stream. Once the samples were collected, they were placed in a cooler filled with ice packs in order to keep the samples cool until they were returned to the Environmental Engineering Lab at Oregon State University. The coolers used for BOD samples were filled with a mixture of ice and water to ensure quick cooling. Once the samples were back at the lab, they were stored in a 4˚C (39.2 °F), constant temperature room until analysis.

The day after the samples were collected, the samples for TKN, TP, and TOC were separated. 100 mL (3.4 fl oz) and 50 mL (1.7 fl oz) samples were needed for the TKN/TP and TOC analysis respectively. The TKN/TP samples were then transported to the Central Analytical Lab at Oregon State University, for analysis. TOC and BOD analysis began the day after the field testing.

3.2.6 Collection and Analysis of Sediment Samples

In all tests involving sediment introduction, sediment transport samples were collected to determine the sediment precipitation rate, the particle size distribution of the settled sediment particles and heavy metal contents of the sediment collected.

Solid walled sediment samplers were used for the sediment sample collection. The samplers were made using two gallon plastic paint buckets filled with washed pea gravel obtained from

Willamette Graystone in Corvallis, Oregon. A collar, made from stainless steel, was placed into the stream bed at each monitoring site before any of the tests started. Before each test, a sediment sampler was placed inside of each collar so that the sediment sampler is flush with the stream bed. A rubber gasket was made to go over the top of the sampler to keep it in place. At the end of each testing period, the sediment samplers were retrieved from the stream, by carefully pulling the samplers vertically out of the stream. The collars remained in place. After the field tests, the samples were transported back to the lab, dried at 103˚C (217 °F) overnight and then sieved. Due to the short sampling time, there was not enough sediment collected for analysis.

3.3 WATER QUALITY ANALYSIS METHODS

The TP and TKN concentrations of the water samples were analyzed at the OSU Central Analytical Laboratory. The BOD samples were analyzed following Standard Method 5210 B and the TOC samples were analyzed using a DC-190 High-Temperature TOC analyzer following Standard Method 5310 B. A BOD test of a background stream water sample was conducted one week before the field tests, to estimate its BOD level and to determine if dilution of the samples was needed.

3.3.1 TOC Analysis

TOC was analyzed following standard method number 5310 B, from the Standard Methods for the Examination of Water and Wastewater, 20th Ed (*Clesceri 1998*). Before analysis, the TOC samples were filtered using a Whatman 0.45μm-pore-diameter disposable syringe filter to remove particulate matter. The first 5.0 mL of filtrate was discarded to ensure that the filter membrane was saturated with the sample and no further adsorption of TOC to the membrane filter would occur. Two aliquots of the following sample filtrate were collected in TOC sample vials that could be used with the auto-sampler.

Standard method number 5310 B (*Clesceri 1998*) utilizes a combustion based total organic carbon analyzer. A DC-190 High Temperature TOC Analyzer was used. The basic principle of this method is to homogenize the sample, and then inject it into a heated reaction chamber within the analyzer. The sample is then oxidized to CO_2 and water. The CO_2 produced is then transported in a carrier gas stream and is then measured by infrared (IR) spectrometry and reported as total carbon (TC). Inorganic carbon (IC) is measured by acid digesting the sample and then purging the CO_2 produced to the IR detector. The acid digestion condition is controlled so that all of the inorganic carbon is converted to CO_2. TOC is obtained from the difference between the TC concentration and the IC concentration.

Calibration of total carbon concentrations were performed using potassium biphthalate, $C_8H_5KO_4$, as the standard at four concentrations covering the range of the field sample TOC concentrations. Due to the difficulty in keeping inorganic carbon in the aqueous phase when the samples were exposed to the atmosphere, inorganic carbon content was calibrated at only one concentration. Because the CO_2 concentration in TC and IC measurements is analyzed in the same way, the slope of the TC calibration curve was used for IC calibration.

3.3.2 TKN/TP Analysis

TP and TKN were measured at the Central Analytical Laboratory located at OSU. The laboratory uses a Perstorp Analytical 550 Auto-analyzer to measure TP and TKN after sample digestion. 100 mL (3.4 fl oz) TKN/TP samples were sent to the lab for analysis the day after the field testing. The samples were analyzed for TKN and TP. An automatic Nitrogen and Phosphorous analyzer was used to analyze the samples.

3.3.3 BOD Analysis

BOD samples were analyzed following Standard Method 5210 B, 5-Day BOD Test (*Clesceri 1998*). The 2 L (0.53 gal) water samples were collected during the field test. The samples were analyzed within 24 hours after collection. Since the background turbidity of Oak Creek was low, implying that the stream has little biological activity, the BOD samples were not diluted, but were seeded with 2.0 mL (0.068 fl oz) of wastewater collected from the Corvallis, Oregon Wastewater Treatment Plant. The seed was placed into a 300 mL (10.2 fl oz) BOD bottle, which was filled with sample water to over flowing. The DO of the sample was read using a Hach DO175 Dissolved Oxygen Probe (Hach, Loveland, CO, USA) fitted with a rubber stopper to minimize exposure to the atmosphere. All samples were run in triplicates. Once the initial DO had been read, the bottle was gently rotated to rid the bottle of small air bubbles. Once the air bubbles had been removed, the bottle was refilled to overflowing, with a ground glass stopper, a water seal, and aluminum foil wrapped around the top of the bottle to prevent evaporation during the five day incubation period. The BOD bottles were placed in a box and allowed to incubate in a 20˚C (68 °F) room for five days. At the end of five days, the samples were removed and the final DO was measured and recorded. The BOD_5 was then calculated following the methods in the standard methods.

3.3.4 Colorimetric Determination of Residual Chitosan

3.3.4.1 Analytical Methods

The analytical method followed for this test was provided by JW Macpherson, Natural Site Solutions LLC. The procedure was originally designed to be used during a field test, but was instead used in the laboratory with water samples collected during the field test because the test kit was not available until the field tests had been completed. The colorimetric determination of residual chitosan is a test to determine whether or not free chitosan is present. It is not a method to quantify the amount of chitosan present in the water sample.

The test method is based on the reaction between iodine, naturally rust colored, and polysaccharides. When a polysaccharide, such as chitosan, is present, the color of the iodine will change from rust to a deep blue-black color.

The water samples were filtered using a vacuum filtration apparatus, with a 47mm (1.8 in) diameter 1μm-pore-size glass fiber filter. This was necessary because the turbidity of the water samples were so high that it masked the color from the iodine-polysaccharide reaction. Once the water samples were filtered the pH was adjusted to above 8 by adding approximately 5 g (0.175 oz) of sodium bicarbonate to the 1000 mL (34 fl oz) filtered water sample and stirred using a magnetic stir plate and stir bar. After the sample was thoroughly mixed, it was allowed to stand for approximately five minutes.

A 200 mL (6.8 fl oz) sample of the pH adjusted, filtered, creek water was slowly filtered through a borosilicate micro-fiber disposable syringe filter of 25 mm (0.98 in) in diameter with a pore opening of 0.25 µm. The filter paper was removed and then dried in a microwave oven for 1 minute. Once the filter paper was dry, one drop of iodine was placed on the filter. After 15 minutes, the results were read and interpreted.

A light yellow-rust colored filter paper indicated that the concentration of free chitosan was lower than 0.1 mg/L, the detection limit of this method. Dark blue colored filter paper indicated that chitosan was present with a concentration greater than 0.1 mg/L.

3.3.4.2 Calibration

Calibration of the method was performed, following the procedure described above, using standard solutions with chitosan concentrations of 0, 0.05, 0.1, 0.125, 0.25, and 0.5 mg/L to verify the threshold concentration at which color change occurs. The standard solutions were prepared using 2% liquid chitosan and DI water.

3.4 JAR TESTING METHODS AND MATERIALS

3.4.1 Mixing and Flocculation Procedure

Jar tests were conducted following a modified method published by Phipps & Bird and can be found at the website: www.phippsbird.com. Six, 2000 mL (68 fl oz) beakers were used in conjunction with a Phipps and Bird Jar Testing apparatus. Once all six jars were prepared, sediment suspension in each jar was mixed at 100 RPM for one minute before dosing (rapid mixing). Chitosan was added to all jars simultaneously while the same rapid mixing rate was maintained. One minute after chitosan dosing, the paddle stirrers were slowed down to 25 RPM for 20 minutes (slow mixing). At the end of the 20 minute slow mixing time, the paddle stirrers were turned off and the suspension was allowed to settle. The procedure is summarized in Table 3.2.

Table 3.2: Summary of mixing conditions for jar tests

Initial Mixing Time (min)	Initial Mixing Speed (RPM)	Dose (mg/L)	Slow Mixing Time (min)	Slow Mixing Speed (RPM)
1	100	1	20	25

3.4.2 Sample Collecting Procedure

Samples were collected after 15, 30 and 60 minutes of settling time. Each sample was collected in the center of the jar at a depth of 5 cm (1.97 in), measured from the water surface. The turbidity of each sample was measured using a Hach Company 2100P Portable Turbidimeter.

3.4.3 Test Conditions and Materials

All jar tests were done using water collected from Oak Creek, Corvallis, OR. The effects of the following four parameters were investigated: sediment type, solution pH, initial turbidity and chitosan dose.

3.4.3.1 Sediment Type

Three different types of sediment were used to determine the effect of different sediment types on chitosan flocculation: 1) Kaolin or Aluminum Silicate Dihydrate (Al_2O_3•$2SiO_2$•$2H_20$),; 2) Bentonite (Montmorillonite) from Panther Creek, CO, USA; and 3) sediment from the banks of Oak Creek, collected for the field test. For each type of sediment a relationship between total suspended solids and turbidity was determined following the method described later in this section. This information was used to prepare the jars for each test to achieve the target turbidity.

3.4.3.2 Solution pH

Each type of sediment was tested at a pH from 4 to 9, (see Table 3.3) to determine the effect of pH on the effectiveness of chitosan. For these tests, the initial turbidity, which varied for each test and sediment type, was the same for all jars and a chitosan dose of 1.0 mg/L was used. These tests were used to determine a pH for subsequent tests that would yield significant turbidity removal and be similar to the pH of a natural stream system.

Table 3.3: Conditions for varying initial pH

Jar#	pH
1	4
2	5
3	6
4	7
5	8
6	9

3.4.3.3 Initial Turbidity

Each sediment type, kaolin, bentonite, and Oak Creek sediment, were tested at different initial turbidities. The first step was to determine the relationship between total suspended solids (TSS) and turbidity. Based on the relationship between TSS and turbidity, the initial turbidity of each jar was varied between 50 and 300 NTU, see Table 3.4. For this test, the pH was adjusted based on the pH value that obtained significant removal. The chitosan dose used was 1.0 mg/L.

Table 3.4: Initial Turbidity Tested

Jar #	Initial Turbidity (NTU)
1	300
2	250
3	200
4	150
5	100
6	50

3.4.3.4 Chitosan Dose

For each type of sediment, a test was conducted to determine the optimum chitosan dose. Chitosan doses tested ranged from 0.25 to 2.0 mg/L (seeTable 3.5). In each test, the pH and initial turbidity were kept the same for each jar so the difference in residual turbidity would only be attributed to the different chitosan doses.

Table 3.5: Chitosan Dose Tested

Jar #	Dose (mg/L)
1	0.25
2	0.5
3	0.75
4	1.0
5	1.5
6	2.0

3.5 DETERMINATION OF TSS/TURBIDITY CORRELATION COEFFICIANT

Laboratory tests were conducted to determine a coefficient relating turbidity to total suspended solids, or sediment mass concentration, for each sediment type. The principle of this test is that there is a non-linear relationship between TSS and turbidity related by a constant; i.e. turbidity is a power function of TSS (*Metcalf and Eddy 2003*). To determine the coefficient, turbidity of solutions with a range of TSS concentrations were measured using a 2100P Portable Turbidimeter.

The stock solution was prepared by suspending 20 g (0.7 oz) of dry sediment in 1000 mL (3.4 fl oz) DI water. It was then diluted to create turbidities ranging from 0 to 1000 NTU (the limits of the turbidimeter). Once a desired dilution was made, it was thoroughly mixed. A 15 mL (0.5 fl oz) sample was quickly poured into a sampling vial. The turbidity of the sample was then measured and recorded in triplicates. The relationship between turbidity and TSS was determined by fitting the data with a power function.

4.0 RESULTS AND DISCUSSION

4.1 FIELD TESTING RESULTS

4.1.1 Results from Stream Classification

Using Equations 3-3, 3-4 and 3-5, outlined in Chapter 3, the slope of the study reach was found to be approximately 0.0087 (ft/ft), and the sinuosity (a measure of the straightness of a channel) was 1.12. The surveying results are shown in Figure 4.1.

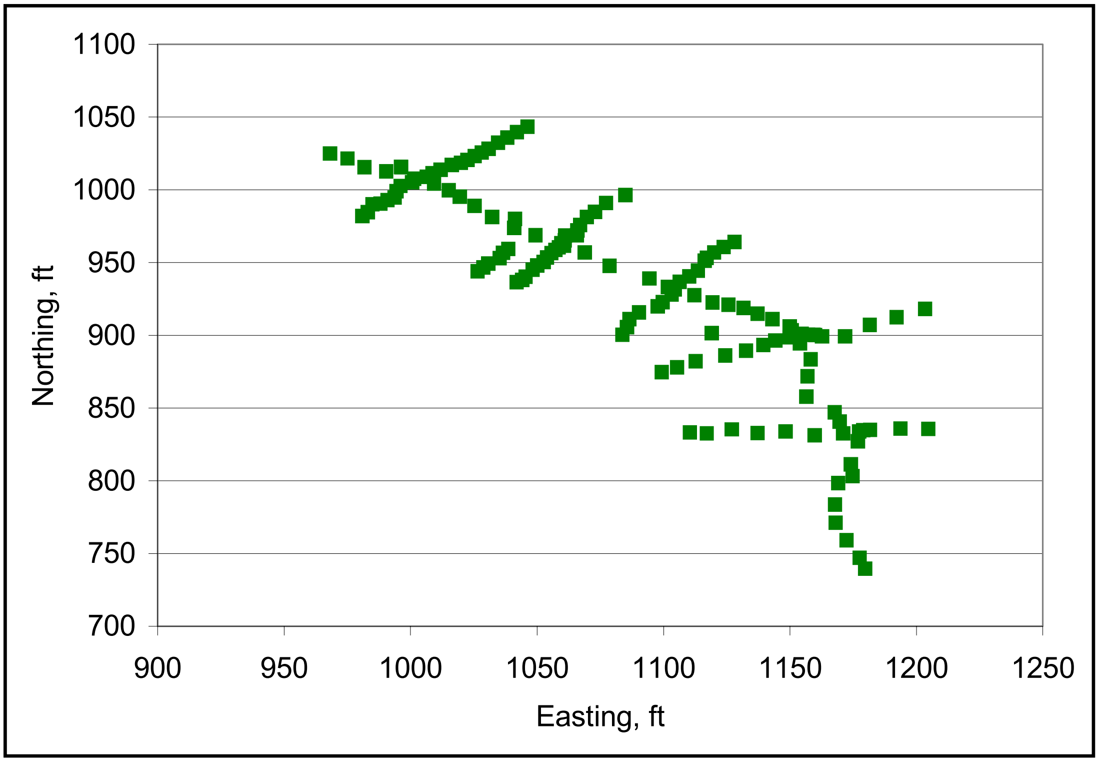

Figure 4.1: Results of Oak Creek Survey. The graph shows the longitudinal and cross-sectional profiles of the stream.

The particle size distribution created from the random step toe pebble count is shown in Figure 4.2. The results are based on 127 pebble diameters. The Oak Creek stream bed is well graded with a variety of particle sizes.

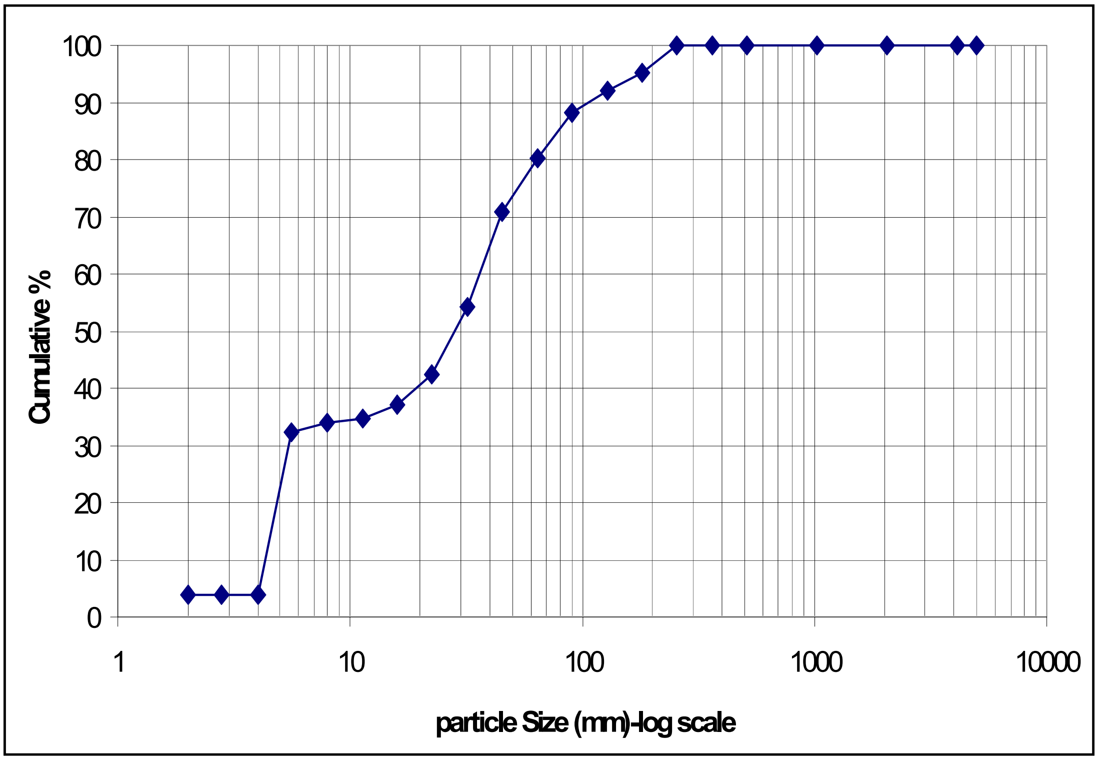

Figure 4.2: Combined results of random step-toe pebble counts, plotted as the cumulative % vs. the log of the particle size in mm

4.1.2 Oak Creek Sediment Particle Size Distribution

The results of the particle size analysis of the sediment used in the field tests can be found in Figure 4.3. The sediment was found to be moderately sorted, following the Folk and Ward (*1957*) method. The standard deviation of the sediment particle size was 0.89 Φ units, determined using the method outlined in Folk and Ward (*1957*). This standard deviation corresponds to a soil that is moderately sorted, or moderately well graded. After pulverizing, 43 % passed the number 200 (0.075 mm) sieve, meaning that pulverizing reduced the particle size of the sediment to such an extent that a large fraction of the pulverized sediment is in the size range of silts and clays, known as fines. This ensured that the majority of the sediment remained in suspension when added to the stream, instead of settling out before traveling downstream.

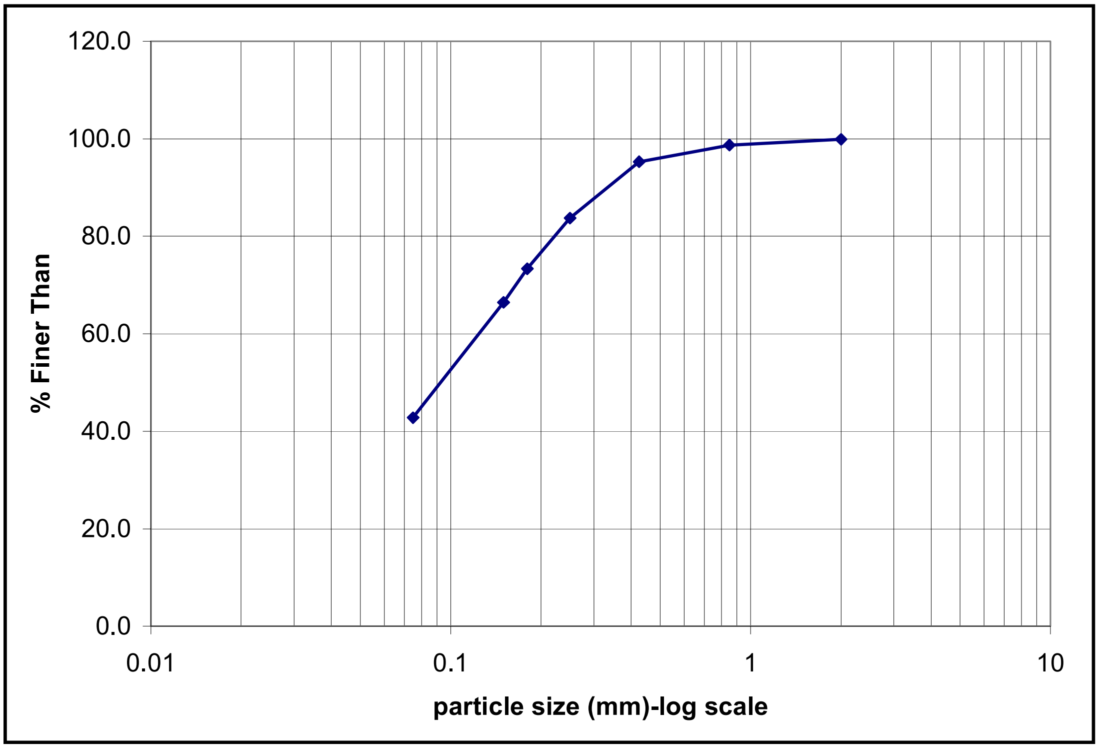

Figure 4.3: Particle size analysis results, pulverized sediment from the banks of Oak Creek

4.1.3 Stream Water Quality Monitoring

The Horiba probes were programmed to record measurements for pH, DO, temperature, conductivity, and turbidity. All results from the water quality probes are depicted graphically in Figures 4.4 through 4.10. The average temperature of Oak Creek the day of the field testing was 13 ˚C (55.4 ˚F).

4.1.3.1 Stream Water pH

The pH of the stream water was 8 at all monitoring sites throughout the entire testing period. An example of the measurement results are shown for site #1 in Figure 4.4. The addition of chitosan did not cause a detectable change in the stream water pH due to the low concentrations used.

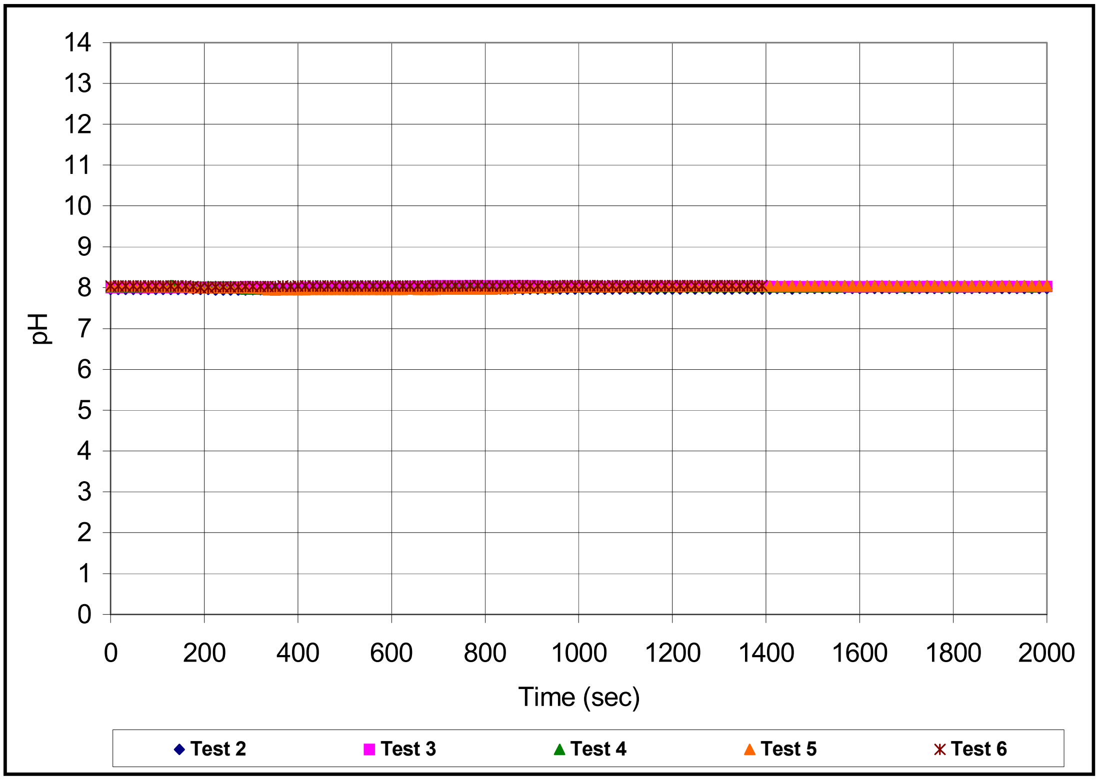

Figure 4.4: pH results for all tests at site 1, located 5 ft downstream from the sediment introduction site

The pH level measured was unusually high for a natural stream system in this geographic region. The recommended pH range for effective flocculation by chitosan is 6.5 - 8.5. A pH of 8 is at the high end of the effective pH range for chitosan induced flocculation. However, it will be shown later that the effective pH range depends on the sediment type.

4.1.3.2 Conductivity

The conductivity of the Oak Creek water ranged from approximately 0.23 to 0.26 mS/cm. In all tests that included treatment by chitosan there was no detectable change in the conductivity, implying that chitosan does not have an effect on the conductivity of the stream water.

4.1.3.3 Dissolved Oxygen (DO)

The DO at different monitoring sites ranged from 8 to 10 mg/L and remained constant throughout the day at each site. It can be concluded that chitosan has little to no effect on the DO of the stream water on a short time scale.

4.1.3.4 Stream Water Turbidity

The turbidity of the stream water during the field testing is represented graphically in Figures 4.9 through 4.12 for each site. Site #4 was excluded from the data analysis due to an unanticipated problem with the monitoring probe. The x axis is the duration of the tests in sec, and the y axis is the turbidity in NTU.

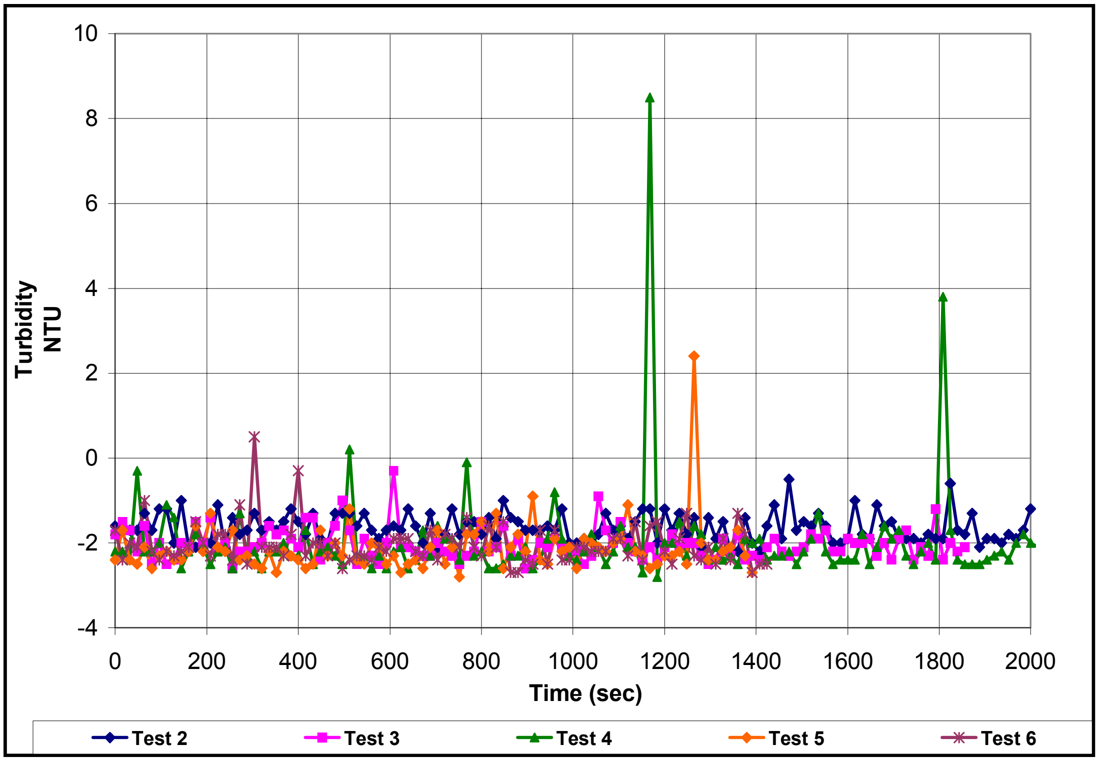

Figure 4.5: Background turbidity at site #0, located 7 ft upstream of the sediment introduction site

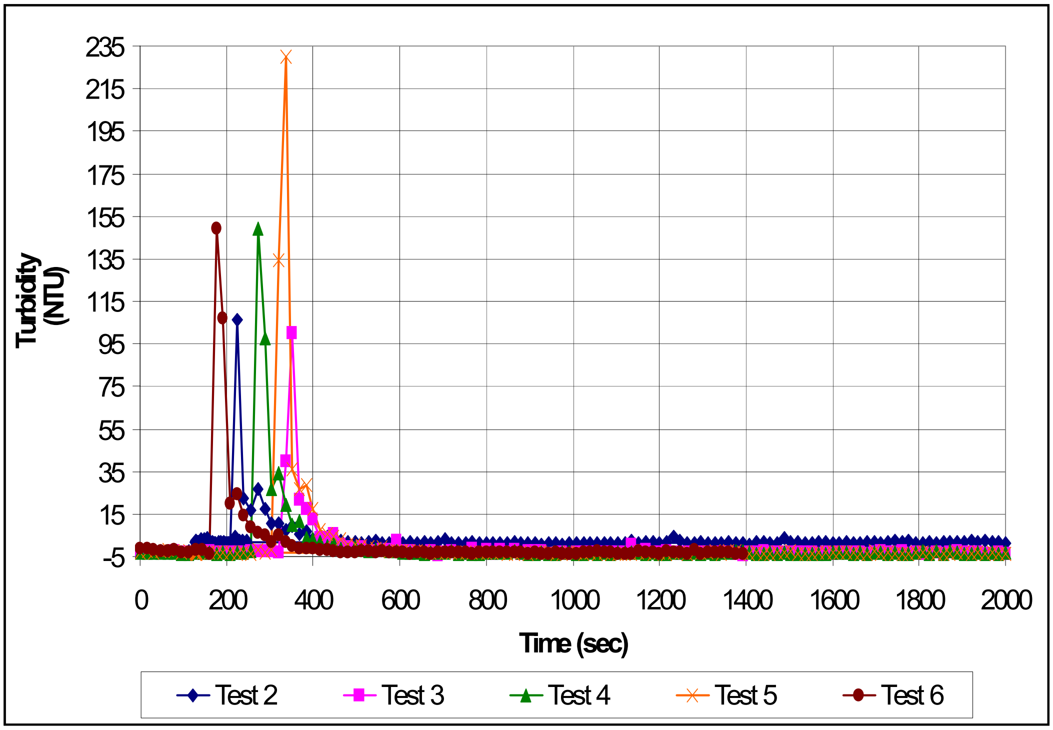

Figure 4.6: Turbidity at site #1, located 10 ft downstream of the sediment introduction site

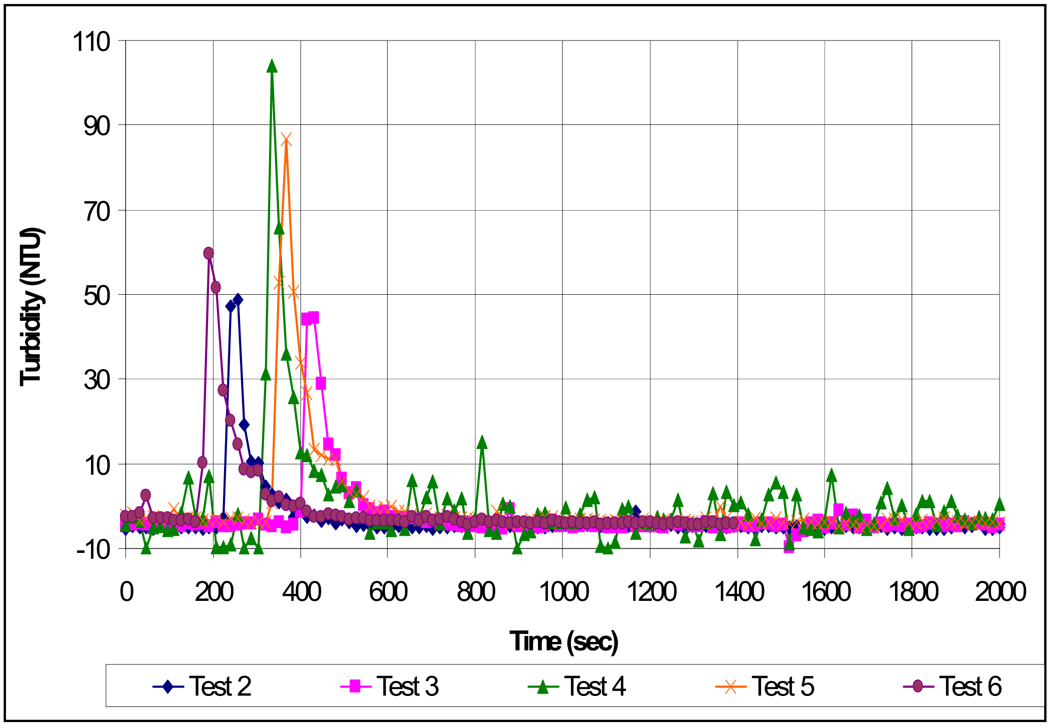

Figure 4.7: Turbidity at site #2, located 50 ft downstream of the sediment introduction site

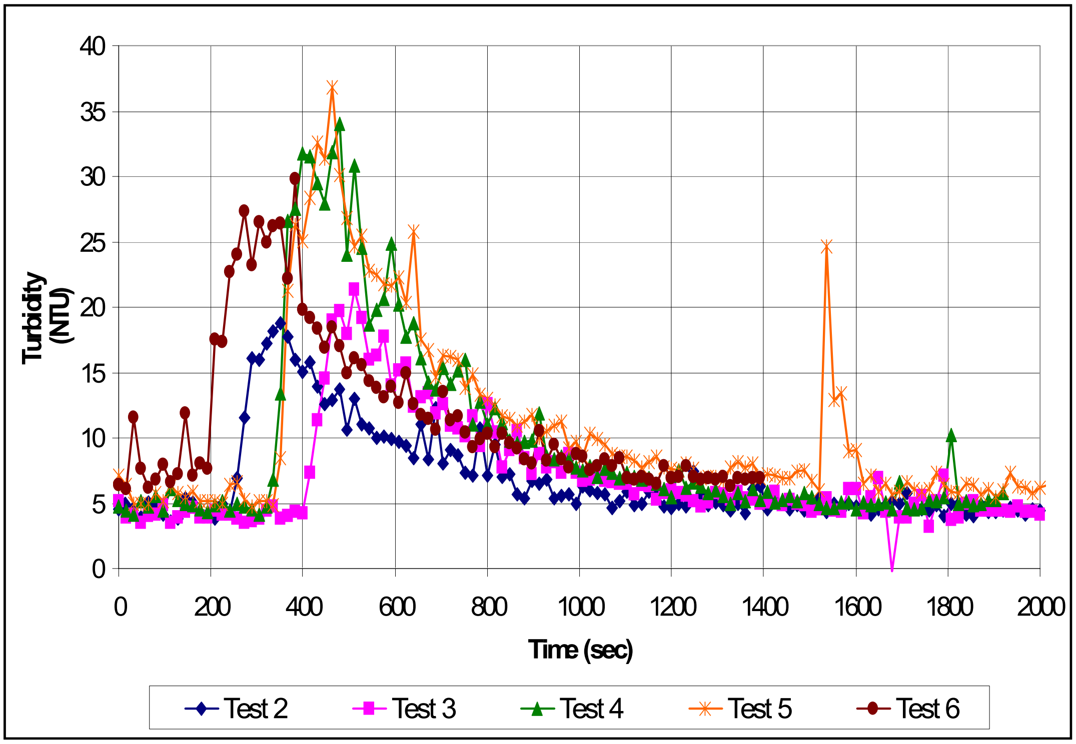

Figure 4.8: Turbidity at site #3, located 105 ft downstream of the sediment introduction site

Due to permitting restrictions on the amount of sediment that can be introduced to a stream, a sediment pulse was manually introduced at the beginning of every test. As a result, the introduced turbidity varied from one experiment to another, ranging from 106 to 230 NTU. Because of this variation, the turbidity data was normalized by the introduced turbidity, or the peak turbidity at site #1, which gave the percent remaining of the turbidity. The results of this analysis can be found in Figures 4.9 and 4.10 for site #2 and site #3, respectively.

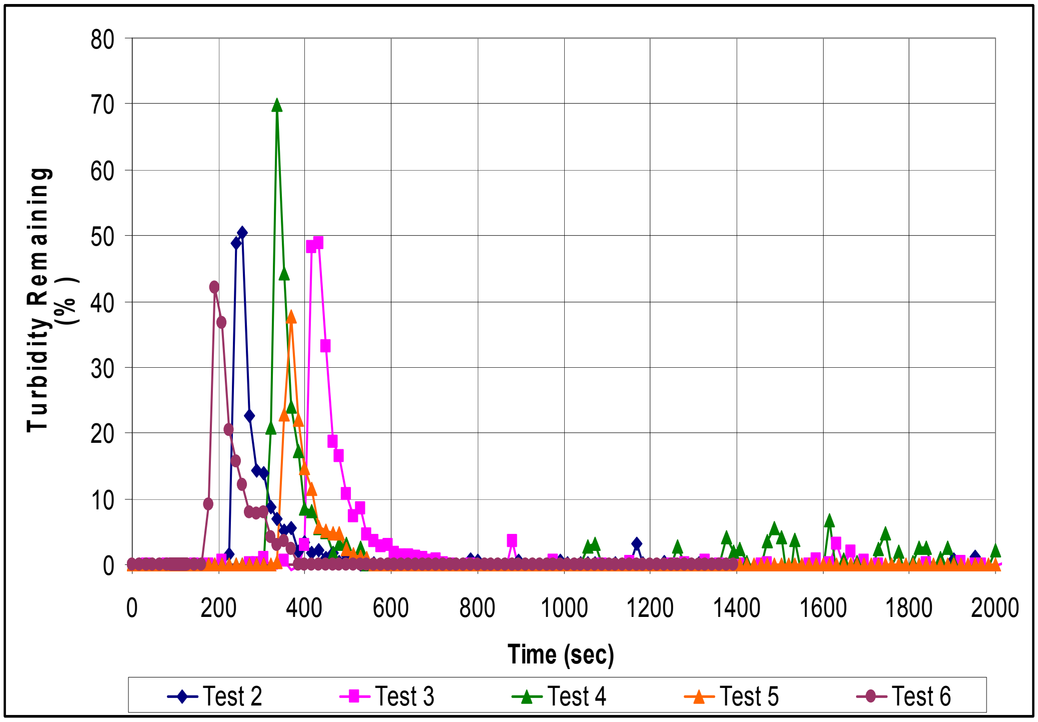

Figure 4.9: Percent turbidity remaining at site #2, 50 ft downstream from sediment introduction site

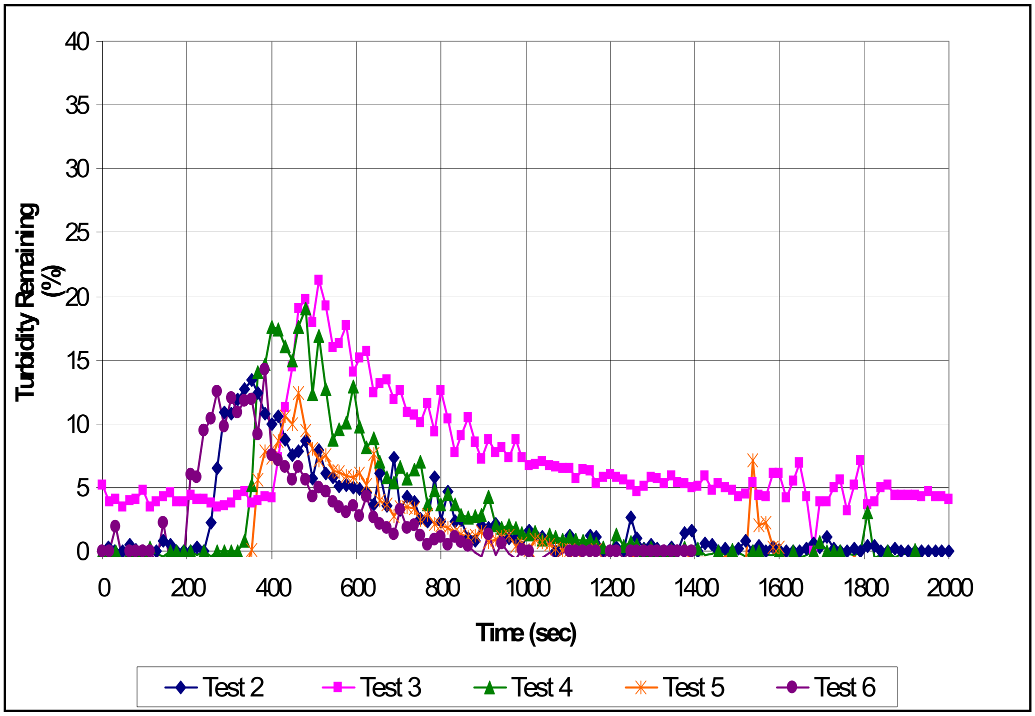

Figure 4.10: Percent turbidity remaining at site #3, 105 ft downstream from the sediment introduction site

During test # 5, the high dose test, with a chitosan dose of 0.5 mg/L, there was a reduction in turbidity levels at site #2 compared to test # 2 and # 6 with no chitosan dose. At site #2, the turbidity remaining (peak value) was approximately 38%, while at site #3 the remaining turbidity was 13% of the initial turbidity. As a comparison, the percent turbidity remaining during test # 2, sediment introduction alone, was 46% and 13% for sites number 2 and 3, respectively. The % turbidity remaining during test #6, control test II, was 42 % and 12 % for sites number 2 and 3 respectively. In tests number 3 and 4, in which a dose of 0.25 mg/L was used, no significant improvement of turbidity was observed. The poor treatment results in tests number 3 and 4 may be due to the combination of the low chitosan dose, high stream flow rate, high stream water pH, and other adverse water qualities.

Because of dispersion, the peak value of the stream water turbidity is not a good measurement of the suspended sediment. A better way of evaluating the effectiveness of chitosan flocculation is to calculate the amount of suspended solids remaining at different times based on the turbidity data. The amount of sediment that settled out can then be calculated and used to evaluate the effectiveness of the chitosan.

To obtain the amount of suspended solids present in the stream, a TSS versus turbidity plot was developed to obtain a coefficient to relate the two. The method followed is outlined in the Chapter 3. The relationship between the two can be found in Figure 4.11.

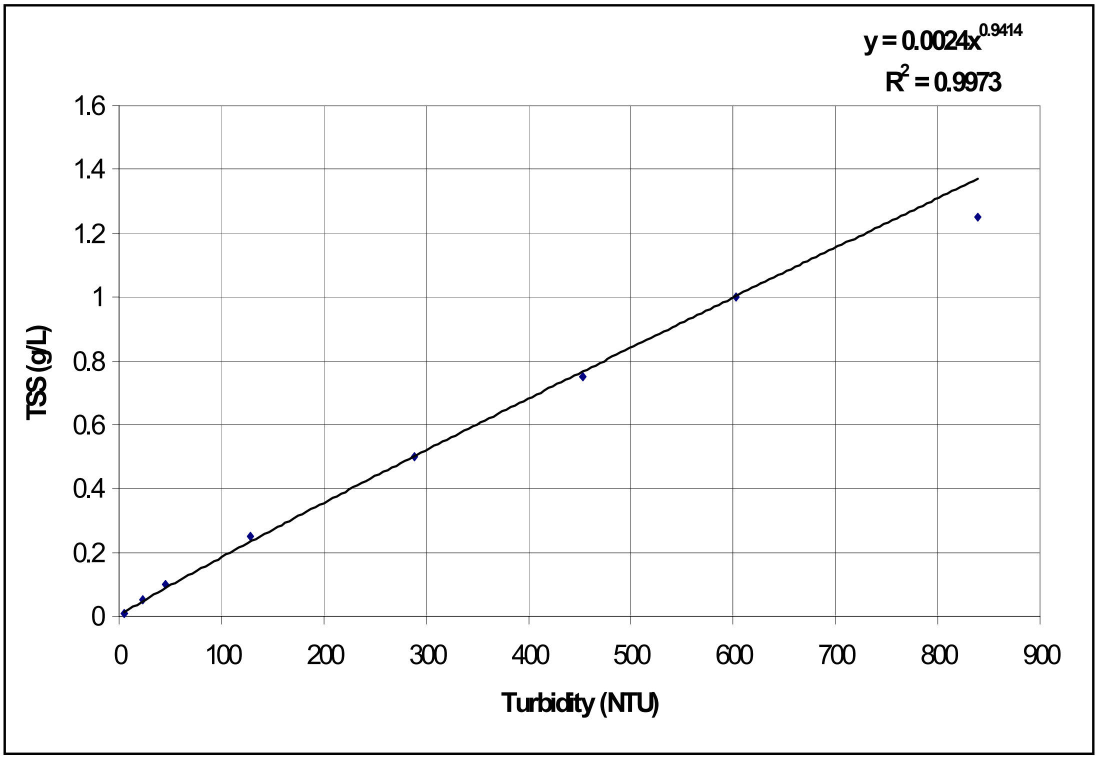

Figure 4.11: Relationship between TSS and Turbidity, Oak Creek Pulverized Sediment

From this relationship it was possible to determine the change in sediment mass concentration with time, as the sediment pulse moved downstream. The same data analysis procedure was followed for the sediment mass concentration as for the turbidity data. Figures 4.12 and 4.13 show the results of the analysis.

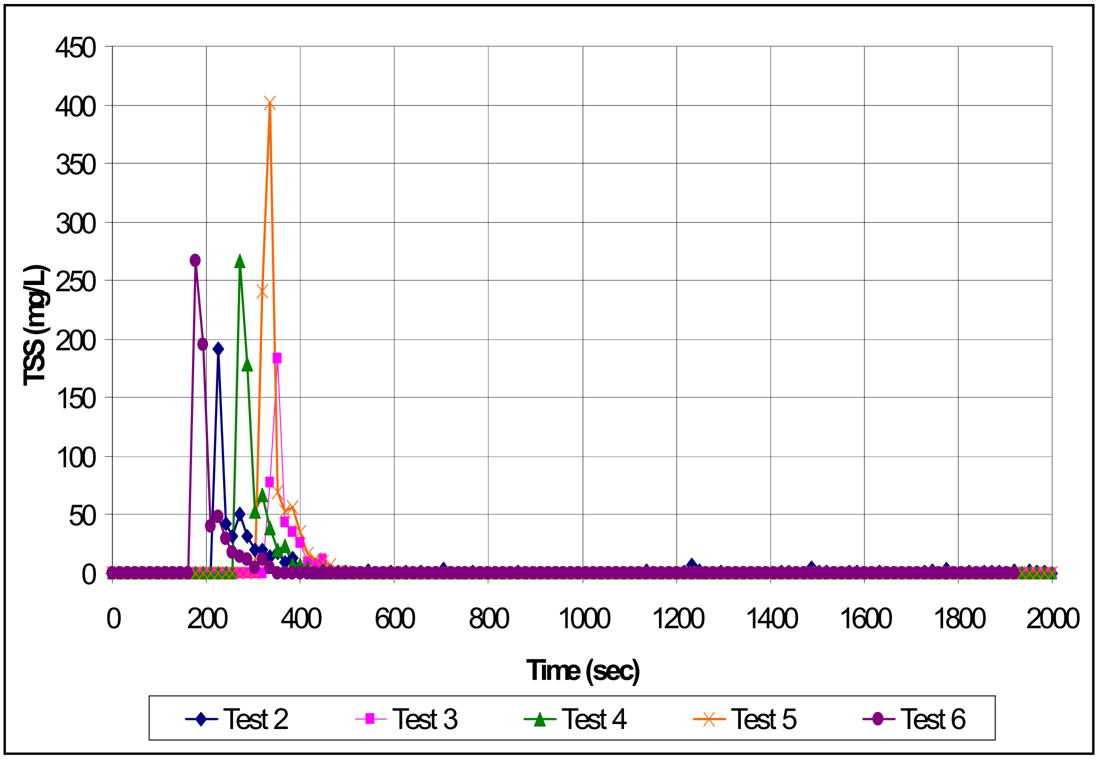

Figure 4.12: Concentration of TSS, site #1, 5 ft downstream of the sediment introduction site

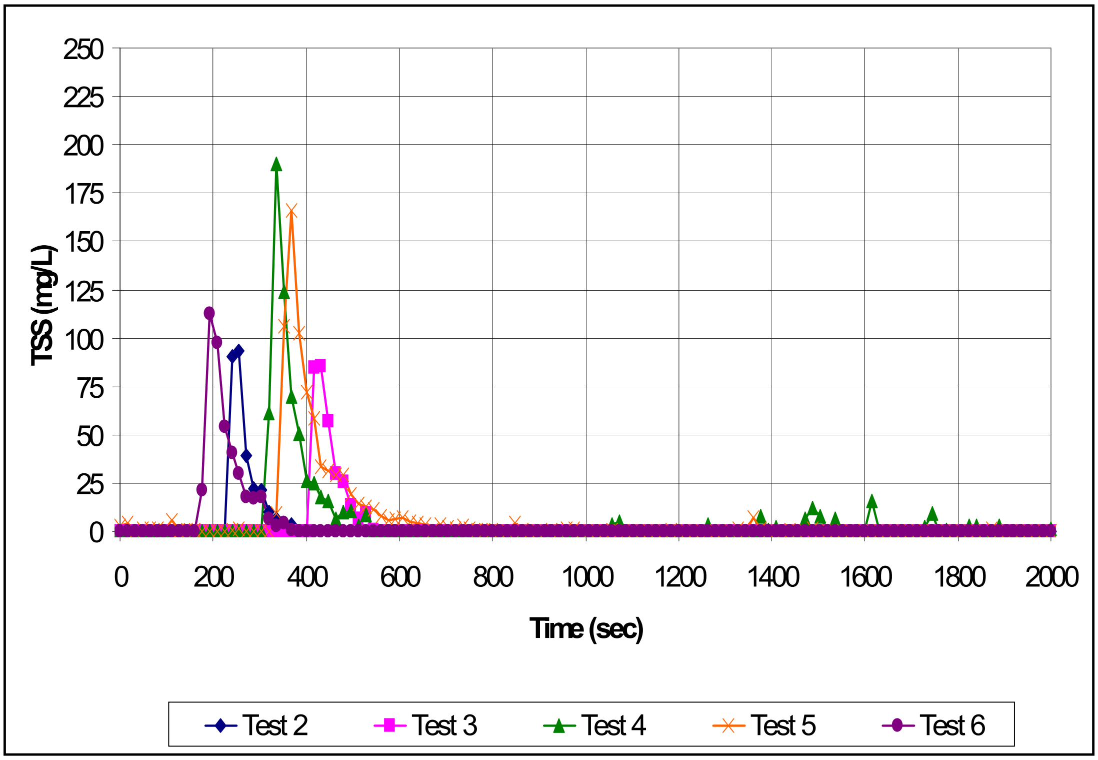

Figure 4.13: Concentration of TSS, site#2, 50 ft downstream of the sediment introduction site

Based on Figures 4.11 - 4.13 the sediment concentration in different tests at site #1 varied between 175 and 400 mg/L, and between 190 and 90 mg/L at site #2. Because of the wide variation in introduced turbidity, the TSS data was normalized by the introduced peak TSS value at site #1, which gave the percentage of concentration remaining (see Figures 4.14 and 4.15).

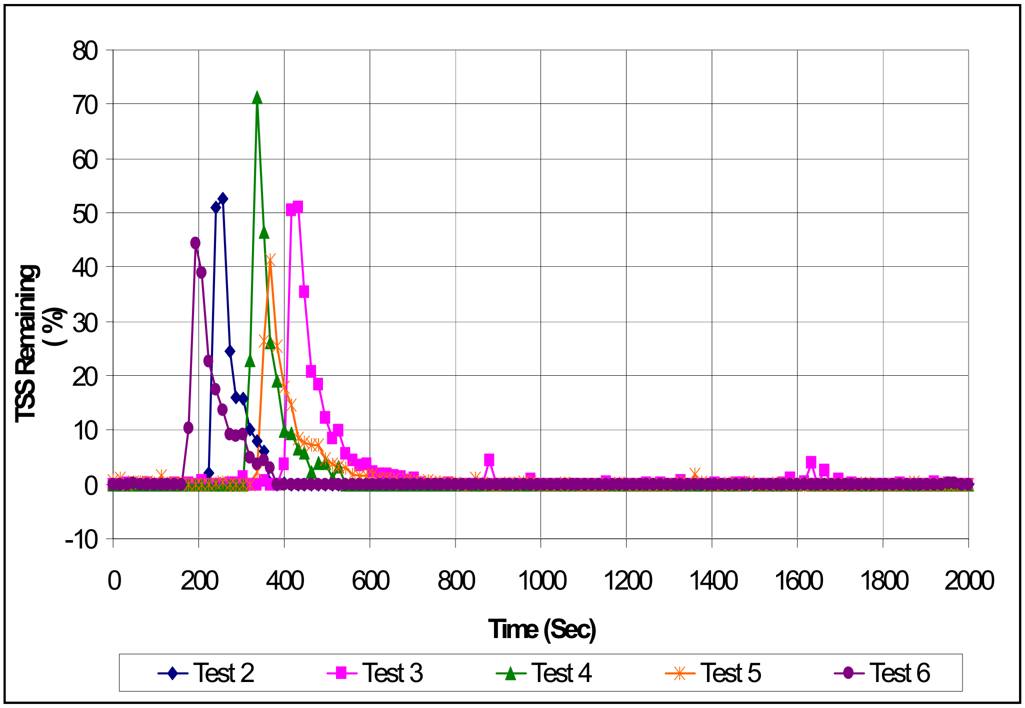

Figure 4.14: Percent TSS remaining, site #2, 50 ft downstream from the sediment introduction site

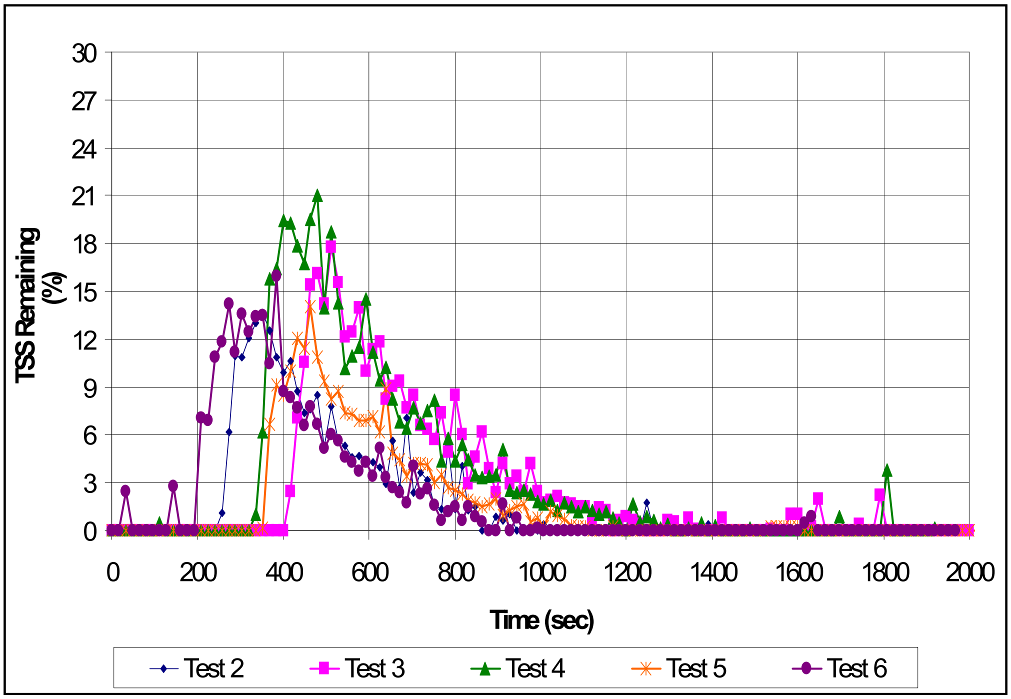

Figure 4.15: Percent TSS remaining, site #3, 105 ft downstream from the sediment introduction site

When compared to sediment removal by natural settling (test # 2 and test # 6), additional removal of TSS was observed during test #5, with a chitosan dose of 0.5 mg/L, at site #2. At site #2 and #3, the peak remaining concentration was 40% and 13 %, respectively, of the introduced TSS. However, in tests # 3 and #4, at a chitosan dose of 0.25 mg/L, the TSS percent remaining at sites #2 and #3 was higher than that measured in control tests I and II, tests #2 and #6.

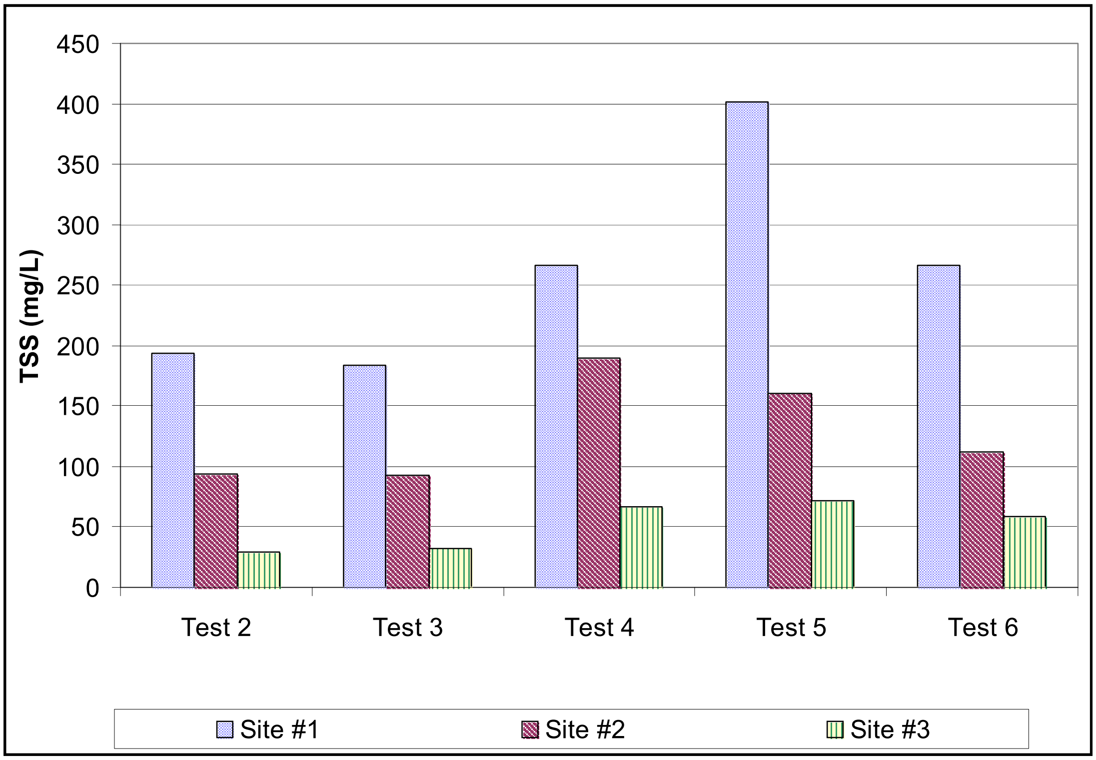

Figure 4.16: Sediment peak as it moves downstream for each test

Figure 4.16 shows the sediment concentration peak as it moves downstream. From this figure it is evident that test #5, the test with a chitosan dose of 0.5 ppm, had the highest peak concentration, 401 mg/L, at site #1. This test demonstrated the highest removal with 160 mg/L of the sediment peak remaining at site #2 a 60% reduction in concentration. For comparison, test #2, the test without treatment by chitosan, had a peak mass concentration of 194 mg/L at site #1. Due to natural attenuation, the sediment peak was reduced to 93 mg/L at site #2 located 50 ft downstream, a 52 % reduction. During test #6 the introduced TSS peak was reduced to 112 mg/L, a 60 % reduction.

In order to determine the amount of sediment that was reduced as the sediment peak moved downstream, the sediment pulse curve was integrated for each site and each test. The results are presented in Figure 4.17. This was possible due to the good correlation between turbidity and TSS that was determined from laboratory studies, see Figure 4.11.

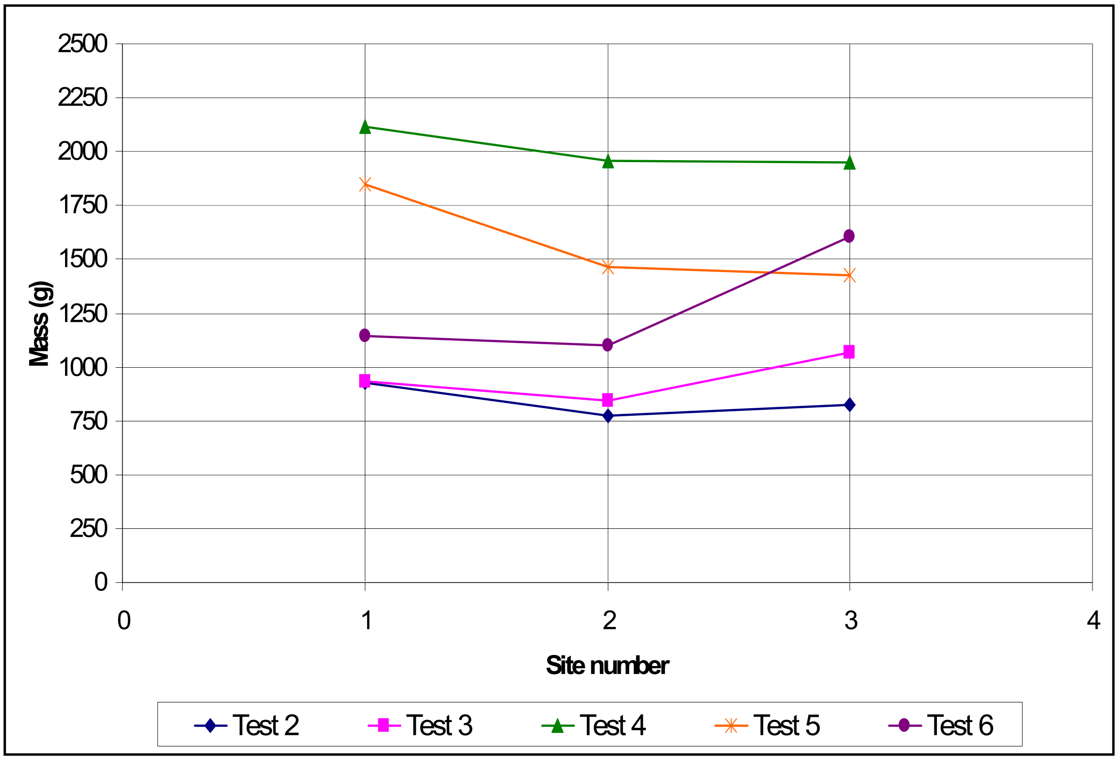

Figure 4.17: Mass integration results for all test and all sites

Figure 4.17 shows that the sediment mass decreased between sites #1 and #2, for all tests with sediment introduction. During tests #2, #3, #5, and #6, there is an increase in the mass at site #3. This increase could be due to sharp spikes in the turbidity data that may have been caused by large particles moving by the probe. The spikes are evident in Figure 4.8, turbidity for site #3. Without removing the spikes from the integration analysis, it is not possible to draw any conclusions from the data.

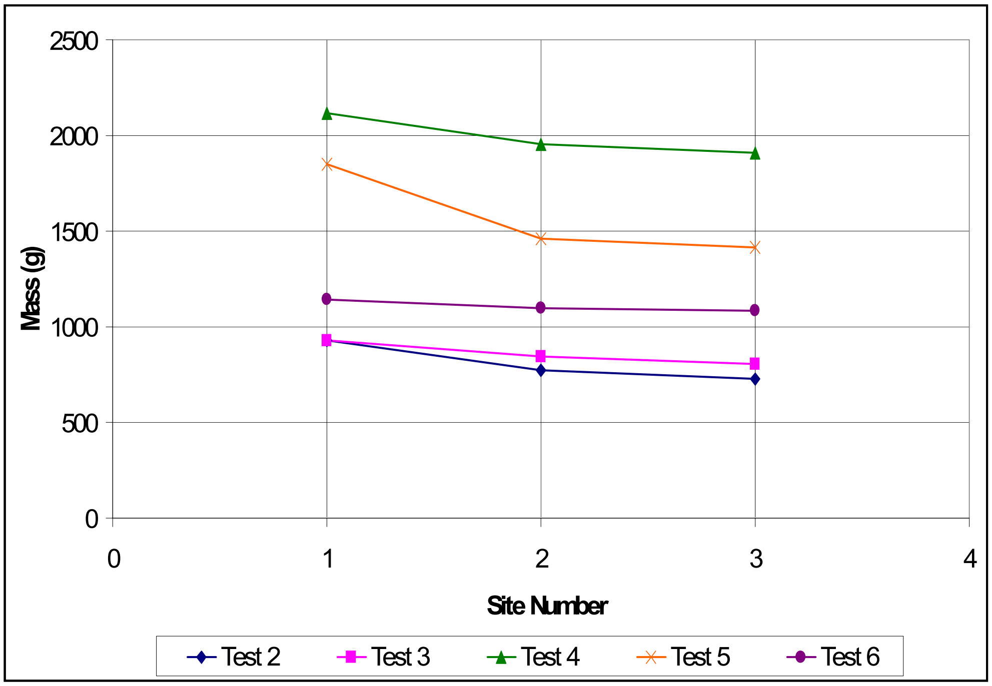

Figure 4.18: Mass integration results for all test and all sites with turbidity spikes removed

By removing the turbidity spikes, a slight reduction in mass between sites #2 and #3 is noticeable for all tests. Figure 4.18 shows the results of the integration with turbidity spikes at site #3 removed. During test #6, 1080 g passed the probe at site #3 compared with 1606 g before the removal of the spikes. Without the turbidity spikes, the greatest reduction in mass occurs during test #5 between sites #2 and #3. During test #5, 76 % of the mass is remaining at site #3, compared with 89 % remaining during test #2 and 95 % during test #6 at the same site.

4.2 WATER QUALITY ANALYSIS RESULTS

4.2.1 TOC Results

Figures 4.19 through 4.22 shows the TC, TOC, and IC concentrations for each site in all of the tests. Each data point represents the average of three measurements. The numbers on the figures were used to show the test number and the sampling time. One sample was collected during test #1 to determine the background TOC concentration. Three samples were collected every 20 minutes during test #2. Three samples were collected during tests #3 and #4 every 10 minutes. Two samples were collected during test #5 at 10 minute intervals. The data labels represent the sampling time during the test. The number refers to the test number and the letter refers to the sampling time: (a) was used for sample #1, (b) was used for sample #2, and (c) was used for sample #3. From these figures it is obvious that there was very little change in the carbon content between tests, or throughout the day.

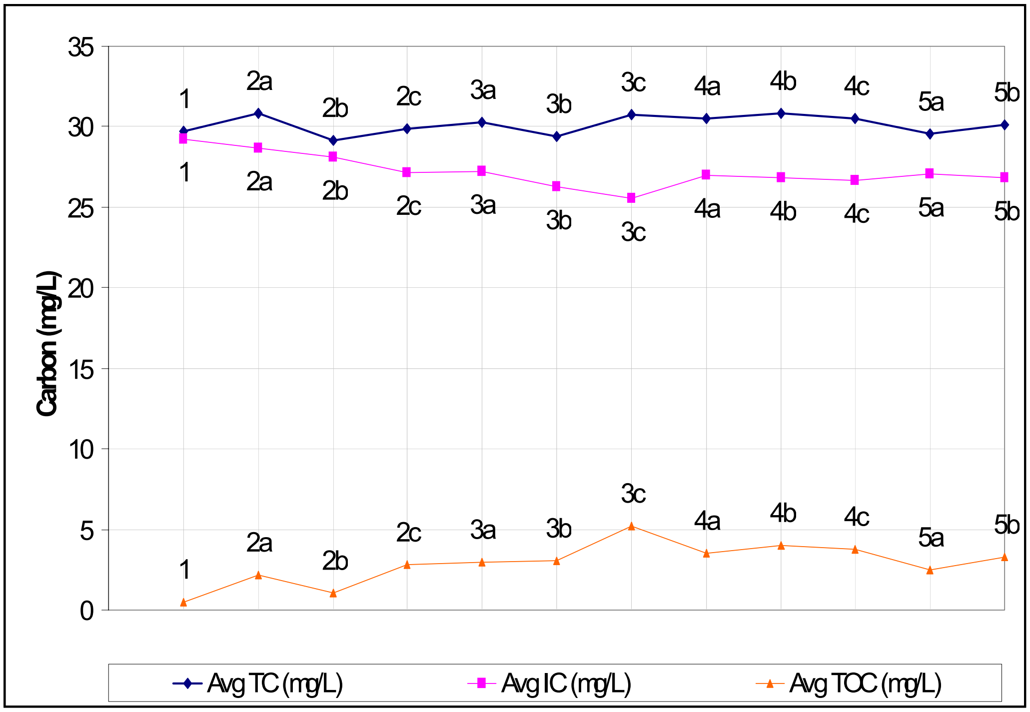

Figure 4.19: Site #1, average TC, IC, TOC

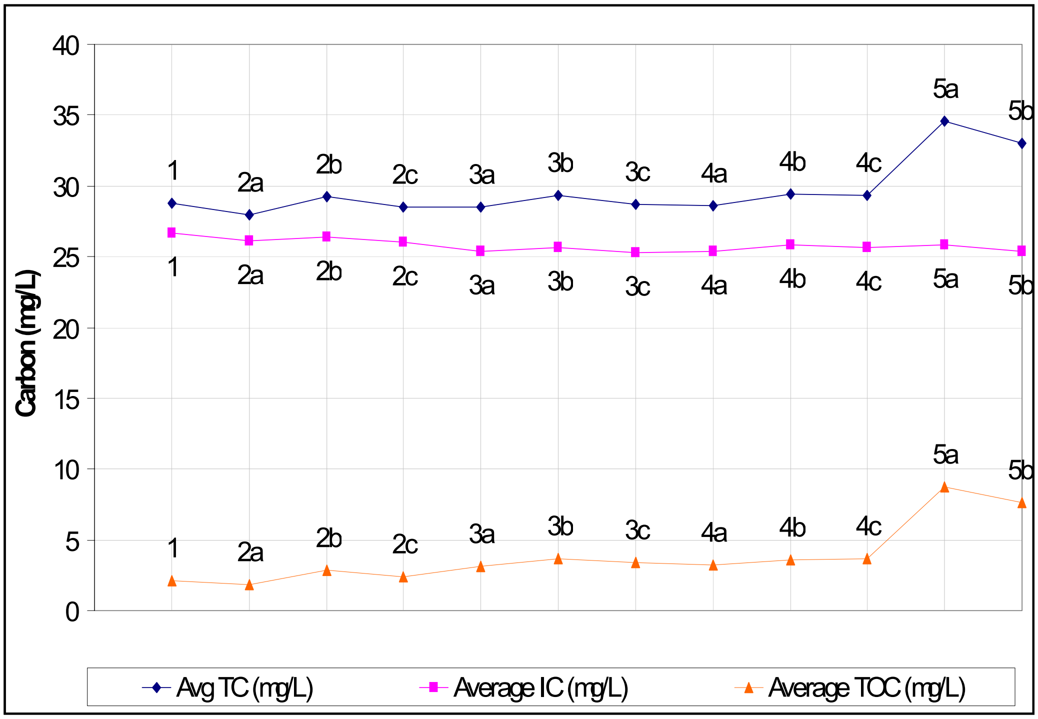

Figure 4.20: Site #2, average TC, IC, TOC

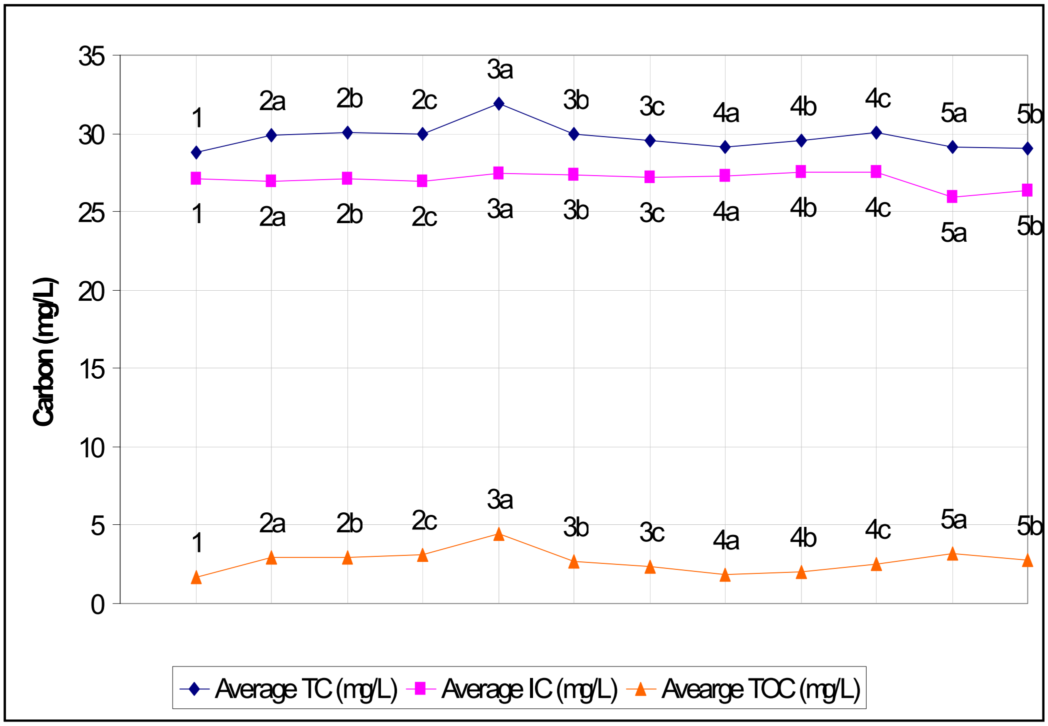

Figure 4.21: Site #3, average TC, IC, TOC

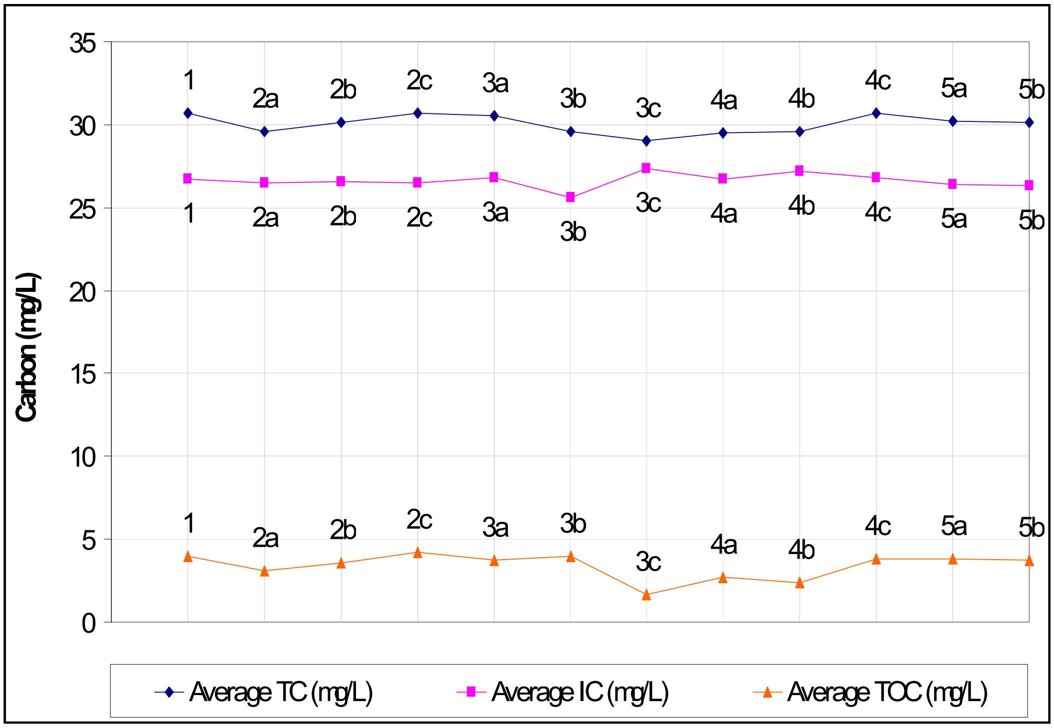

Figure 4.22: Site #4, average TC, IC, TOC

As shown in Figures 4.19 through 4.22, the TOC concentrations at all sites except site #4 during all tests were higher than the background TOC level (measured during test #1). The increase of TOC concentration above the background level was much higher than the chitosan dosage used (0.25 mg/L for tests #3 and #4, 0.5 mg/L for test #5). This may be attributed to two factors: 1) poor mixing of chitosan due to the problems of the simple spraying equipment resulted in a high chitosan concentration peak; and 2) part of the increased TOC may also be caused by organic compounds associated with the introduced sediment. The second factor was demonstrated by the higher TOC concentrations measured during test #2, when there was only sediment introduction, but no chitosan application. The temporal variation of the stream water quality upstream of the test site may also play a role in the change of TOC concentrations. Figures 4.19-4.22 demonstrate that during every test, and throughout the day, there was little change in TOC levels of the water with the introduction of the chitosan.

In any case, the change of TOC concentration in the stream was not significant enough to cause potential negative impacts on the stream ecosystem.

4.2.2 TKN/TP Results

Water samples of 100 mL (3.4 fl oz) were sent to the Central Analytical Lab at OSU the day after the field testing, for analysis of total Kjeldahl nitrogen (TKN) and total phosphorous (TP). An automatic nitrogen and phosphorous analyzer was used to analyze the samples. Results from the lab are represented in Figures 4.23 through 4.32.

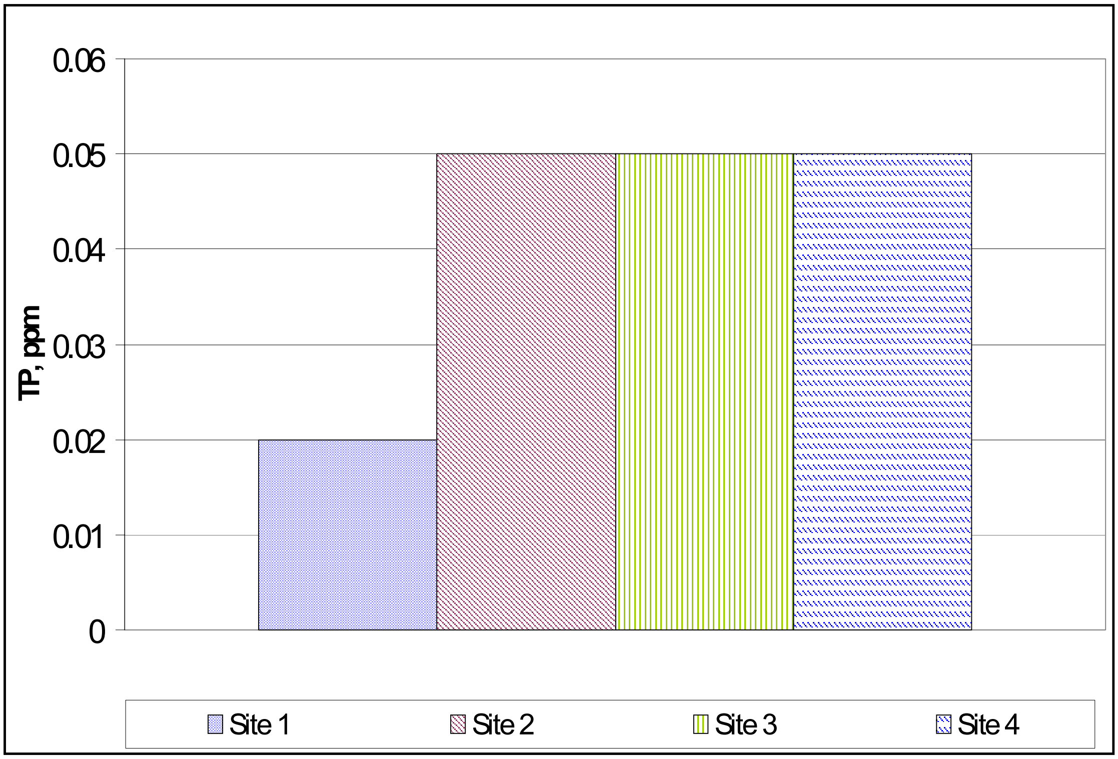

Figure 4.23: TP during test #1 at all sites

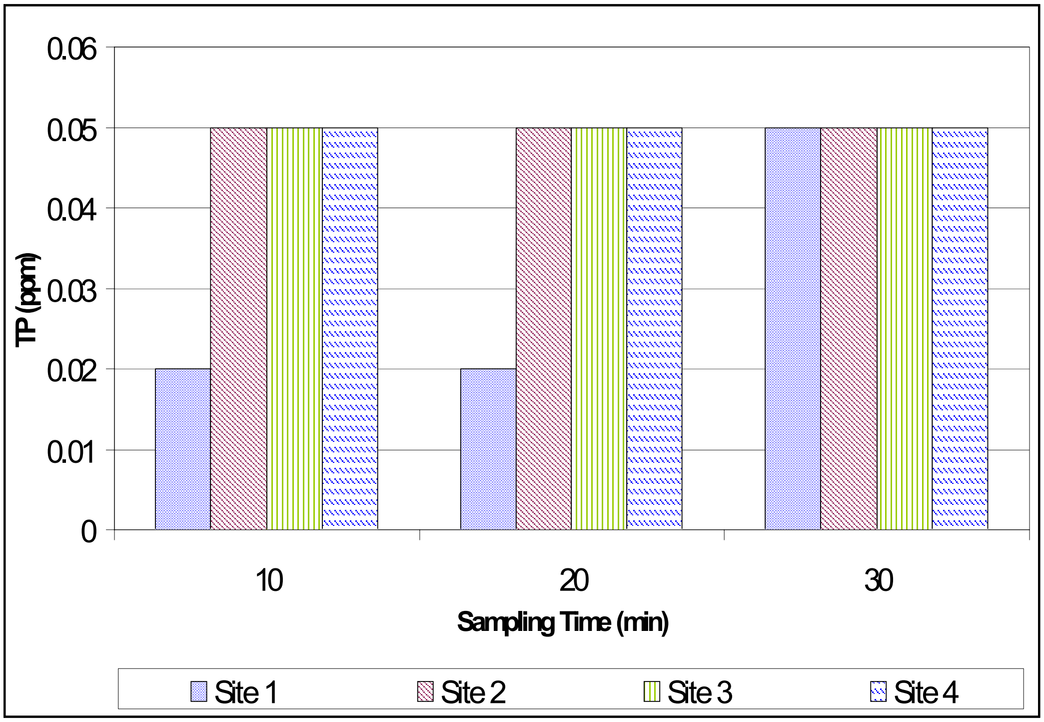

Figure 4.24: TP during test #2 at all sites

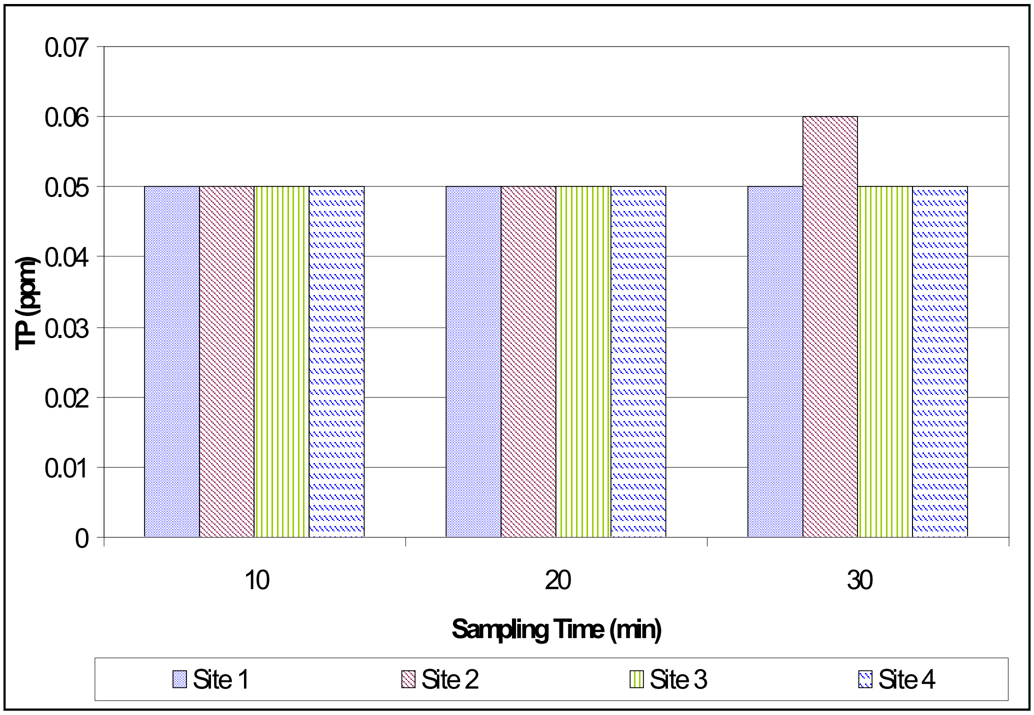

Figure 4.25: TP during test #3 at all sites

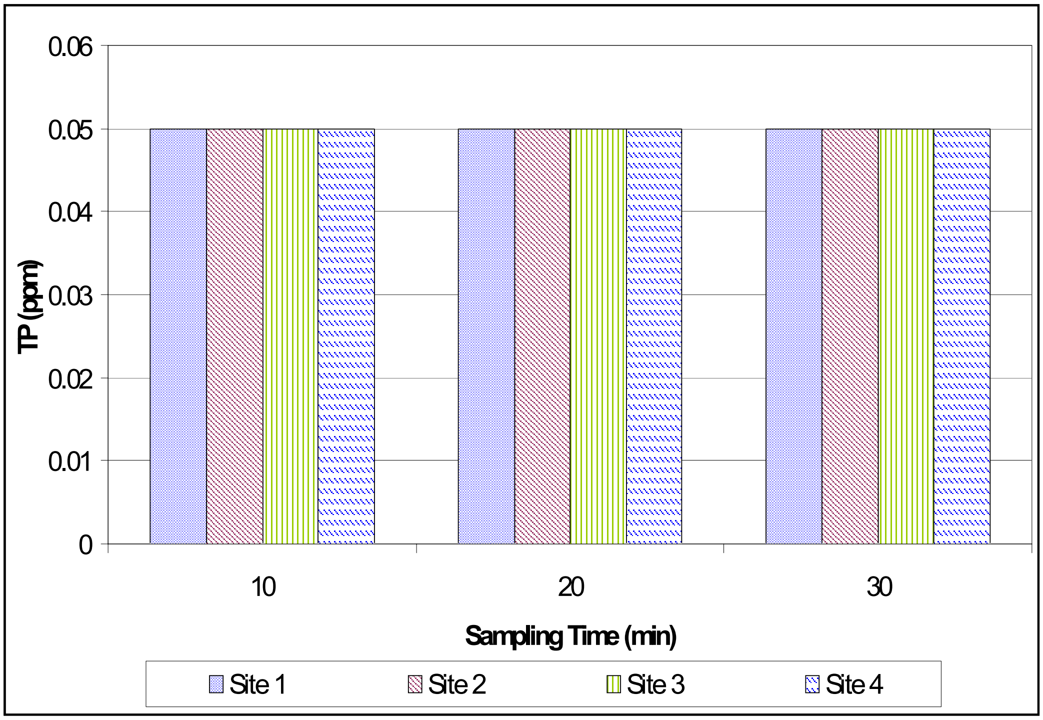

Figure 4.26: TP during test #4 at all sites

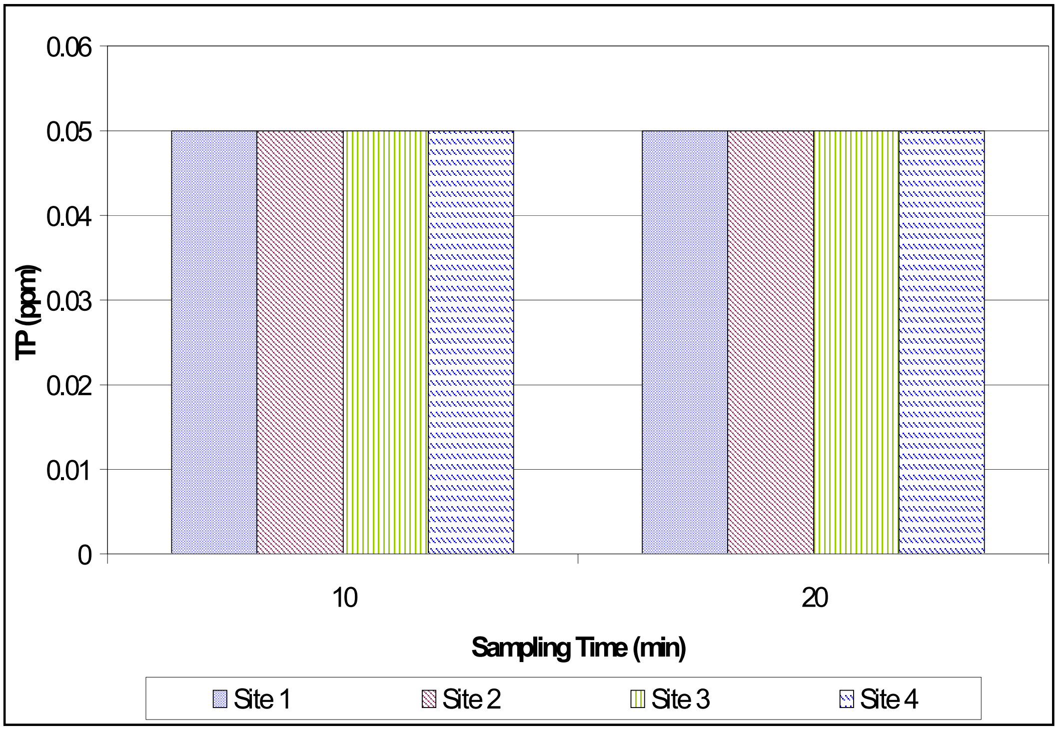

Figure 4.27: TP during test #5 at all sites

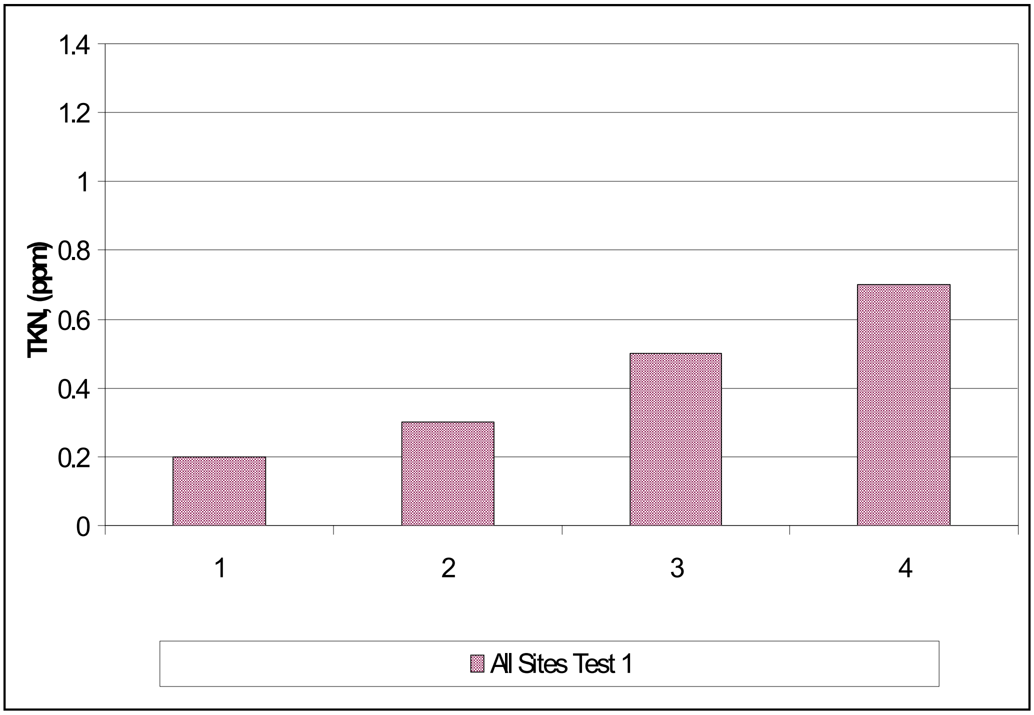

Figure 4.28: TKN during test #1 at all sites

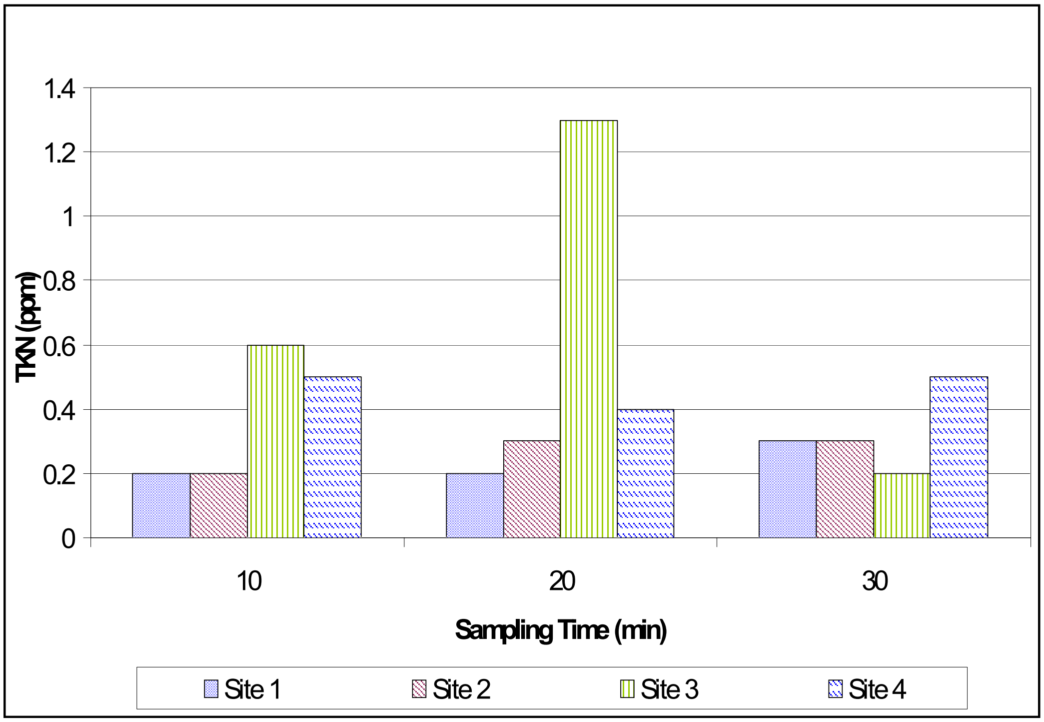

Figure 4.29: TKN during test #2 at all sites

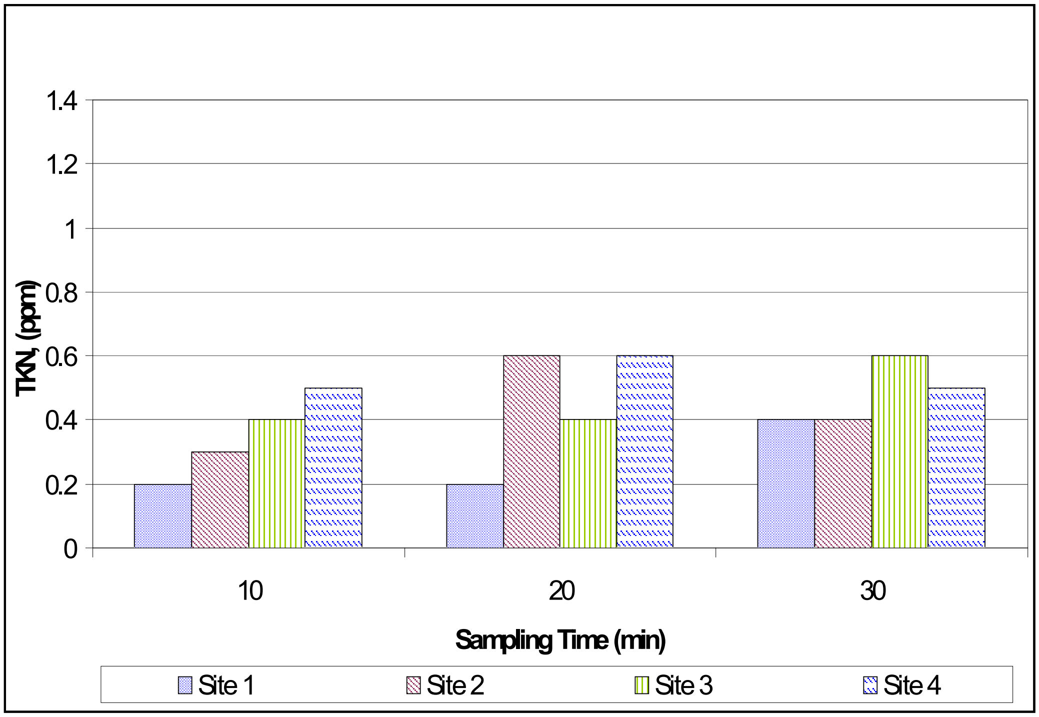

Figure 4.30: TKN during test #3 at all sites

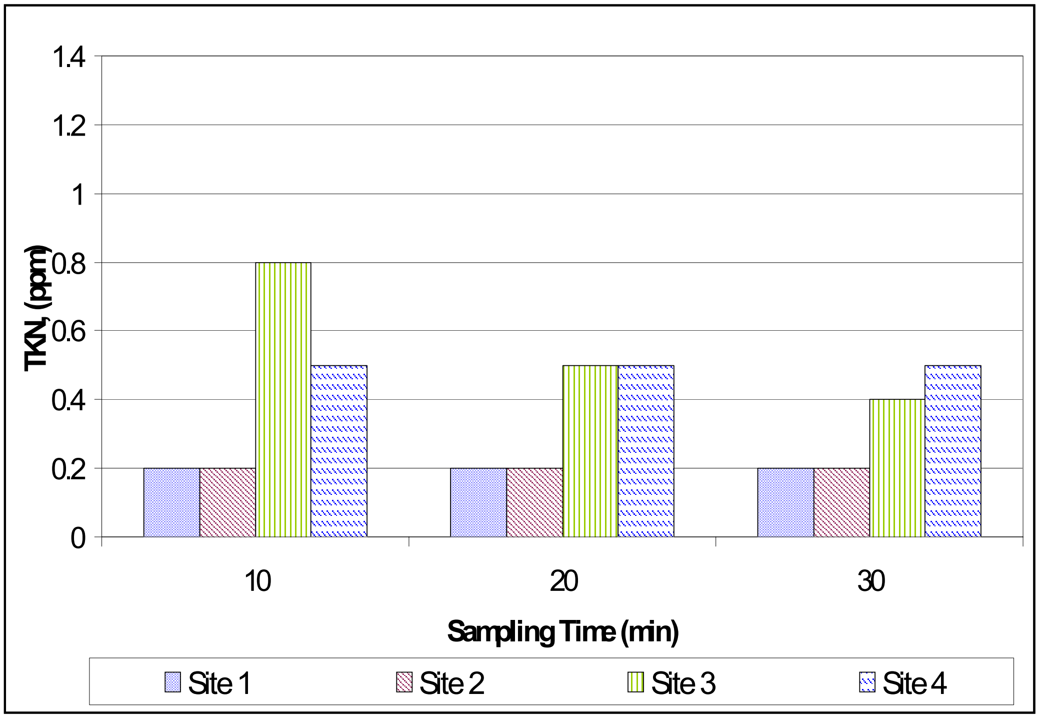

Figure 4.31: TKN during test #4 at all sites

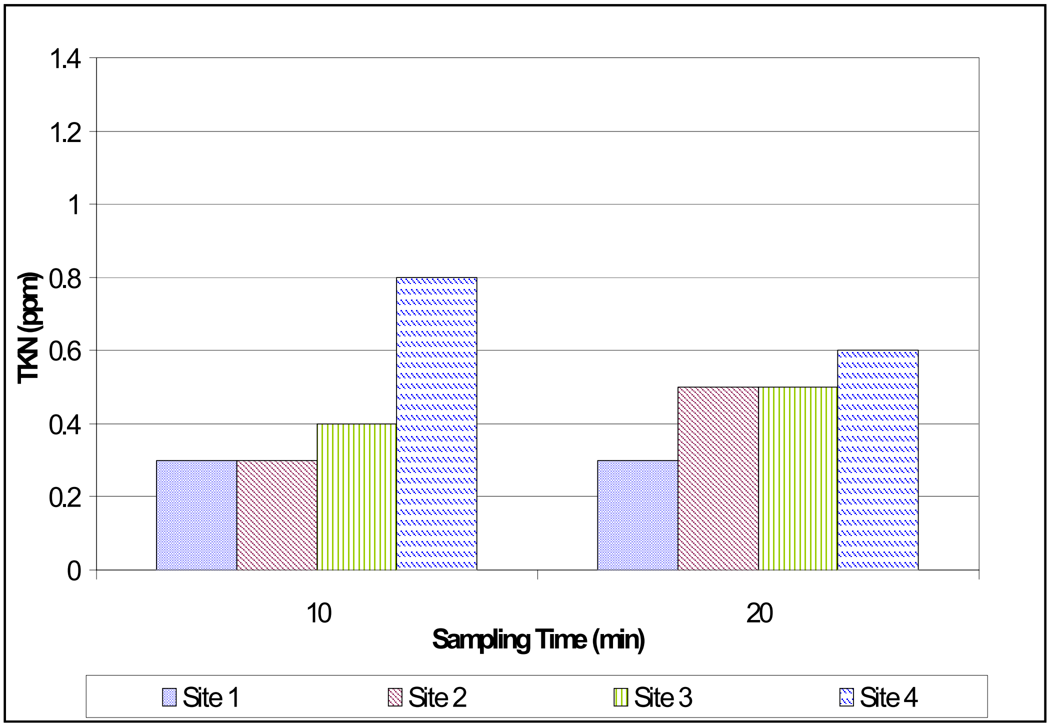

Figure 4.32: TKN during test #5 at all sites

The TP value remained fairly constant throughout the field testing day, implying that chitosan does not impact the phosphorous content of the stream. The detection limit for TP is 0.01 ppm.

Significant TKN was detected in stream water samples; the detection limit of the analyzer was 0.1 ppm. The nitrogen content of the stream varied more throughout the day than the TP. It generally varied between 0.2 and 0.8 ppm. During test #2, at site #3, there was a nitrogen peak of 1.3 ppm. This could be due to analytical error, or sampling techniques. Most likely this peak, since it was not evident further down stream at a later time, was not due to the introduction of chitosan. There is no conclusive evidence that the introduction of the chitosan increased the total nitrogen level of the stream.

4.2.3 BOD Results

There was little to no DO degradation of the BOD samples after the five day incubation period. This shows that Oak Creek has very little microbiological activity.

4.2.4 Residual Chitosan Analysis Results

The results of the free chitosan test are shown pictorially in Figures 4.33 through 4.35.

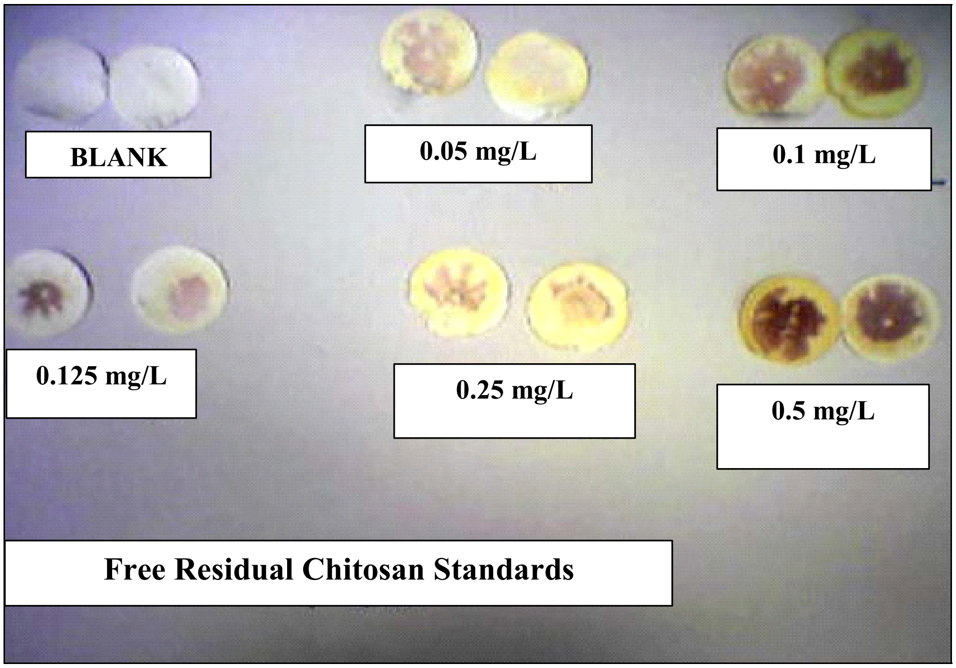

Figure 4.33: Results of free chitosan test standard calibration. Standards made using 2% liquid chitosan and DI water. All samples turned dark blue to brown in color.

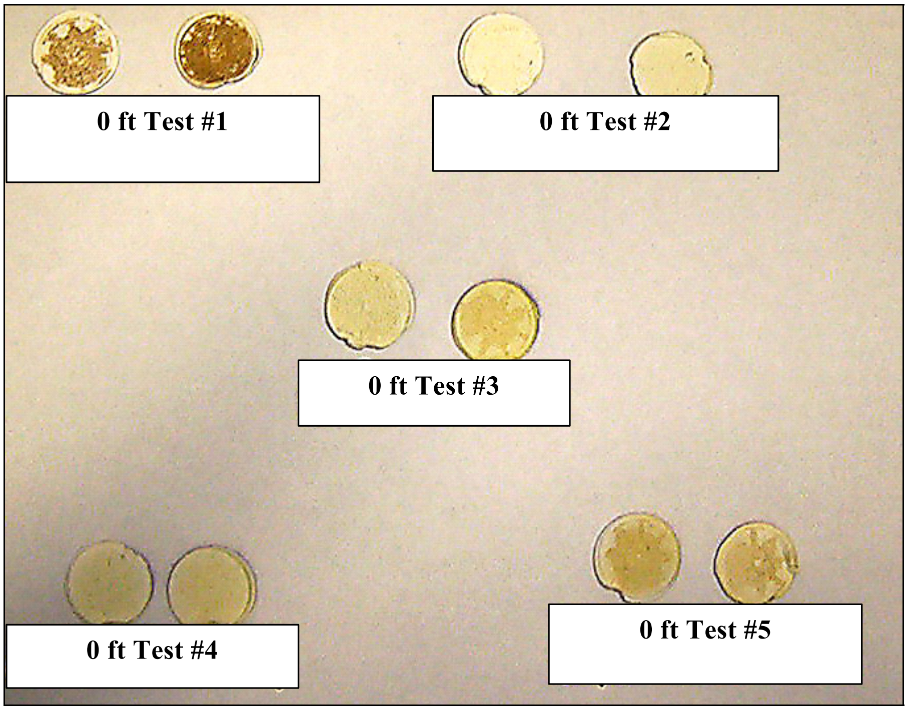

Figure 4.34: Results of free Chitosan test. Samples collected at site 0, -7 ft upstream of the sediment introduction site. No chitosan present.

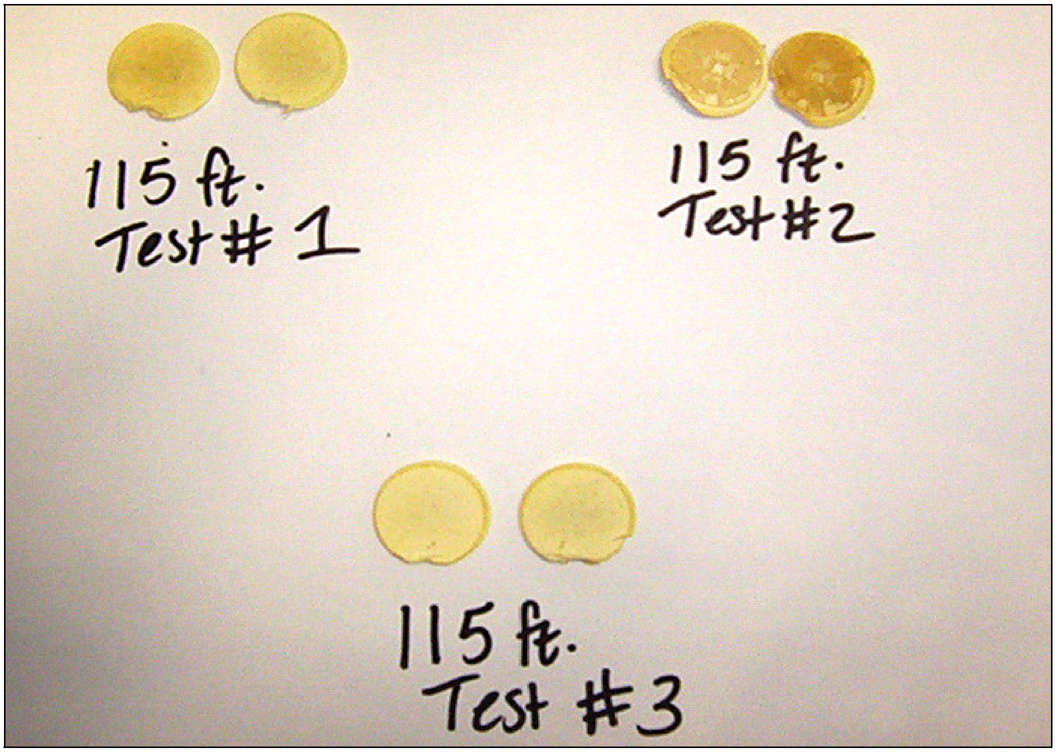

Figure 4.35: Results from free chitosan test. Samples collected near monitoring site number 3. No chitosan present at site #3.

As shown in Figure 4.35, free chitosan was not present at concentration above 0.1 mg/L in the samples taken near site #3, 115 ft (35 m) downstream of the sediment introduction site. Loss of chitosan during sample filtration may have contributed to the non-detectable free chitosan level.

4.3 JAR TEST RESULTS

Bench scale flocculation/sedimentation experiments, referred to as jar tests, were conducted to understand the effects of various water quality and experimental parameters on the effectiveness of chitosan in turbidity removal.

4.3.1 Effect of pH

Jar tests were conducted at pH values ranging from 4 to 9 with each sediment type to determine the effect of pH on the flocculation efficiency of chitosan. The experimental results are presented in Figures 4.36 to 4.38.

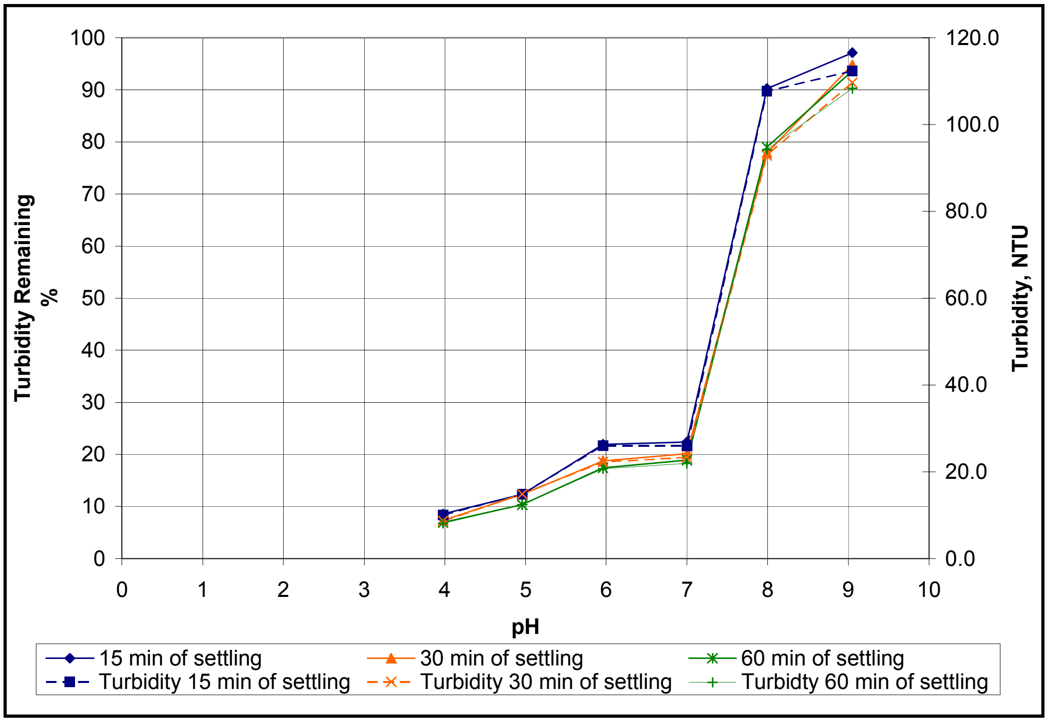

Figure 4.36: Effect of pH on turbidity removal by chitosan. Solid lines are % turbidity remaining and dotted lines are remaining turbidities in NTU. Sediment type: Kaolin; initial turbidity: 117 NTU; chitosan dose: 1 mg/L.

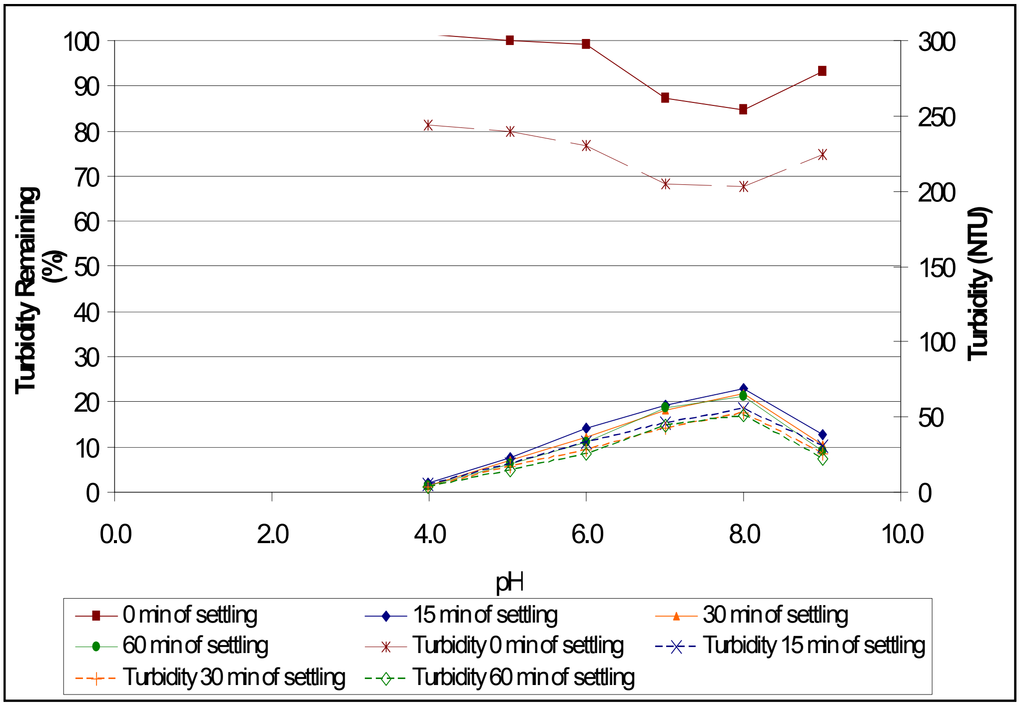

Figure 4.37: Effect of pH on turbidity removal by chitosan. Solid lines are % turbidity remaining and dotted lines are remaining turbidities in NTU. Sediment type: bentonite; initial turbidity: 164 NTU; and chitosan dose: 1mg/L

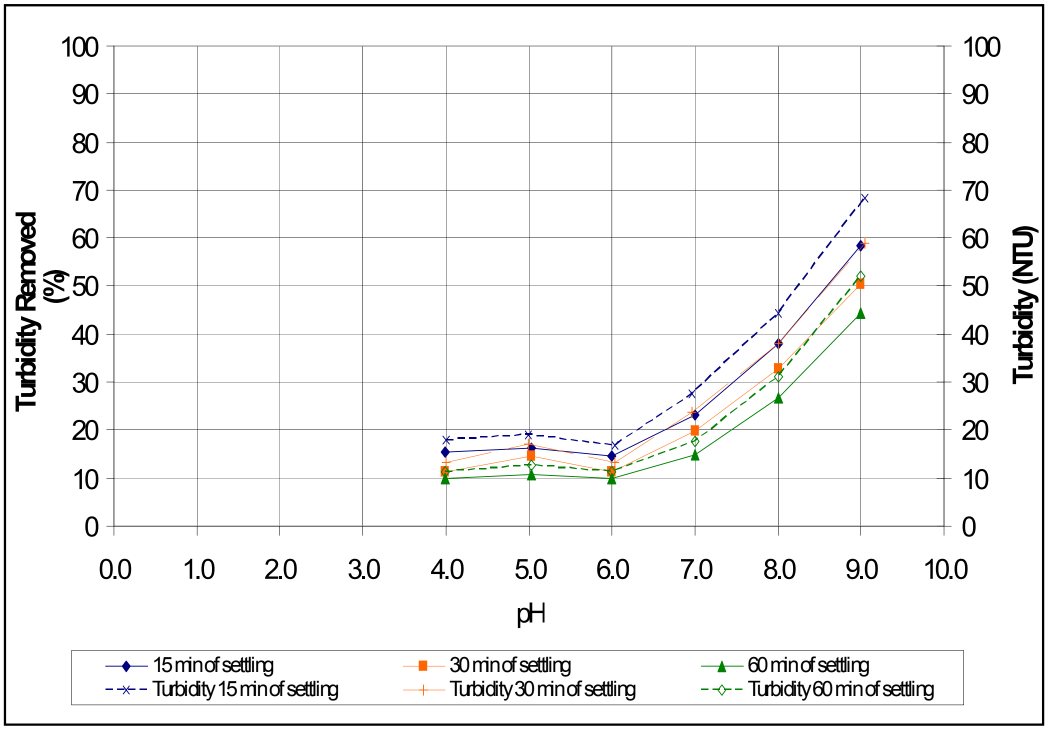

Figure 4.38: Effect of pH on turbidity removal by chitosan. Solid lines are % turbidity remaining and dotted lines are remaining turbidities in NTU. Sediment type: Oak Creek sediment; initial turbidity: 117 NTU; and chitosan dose: 1 mg/L.

Chitosan flocculation was found to be highly dependent on pH for both kaolin and the pulverized sediment from Oak Creek. In both cases, flocculation efficiency decreases with increasing pH. For kaolin, turbidity removal efficiency decreased from 92.6% (7.4% or 8.7 NTU remaining) at a pH of 4 to only 5% (95% or 110 NTU remaining) at a pH of 9 after 30 minutes of settling. With the pulverized Oak Creek sediment, the most efficient pH was also 4, which achieved 88.6% removal (11.4% or 13 NTU remaining) of the initial turbidity; while pH 9, the least effective pH, achieved 49.6 % removal (50.4% or 59 NTU remaining) of the initial turbidity after 30 minutes of settling.

Unlike kaolin, or the pulverized Oak Creek sediment, consistently good removal was achieved with bentonite over the pH range of 4 to 9. The most efficient turbidity removal was obtained at pH 4, with only 2.1% (5.0 NTU) of the initial turbidity remaining after 30 minutes of settling. The flocculation efficiency decreases when the pH increases above pH 4. The least effective removal was found at pH 8, which resulted in 23% (55 NTU) of the initial turbidity remaining. Further increase in pH seems to result in better turbidity removal. However, only one pH, pH 9, was tested in the high pH range.

4.3.2 Effect of Initial Turbidity

Jar tests were conducted to test the effectiveness of chitosan for differing levels of initial turbidity for each sediment type. Figures 4.39 to 4.41 present the results for kaolin, bentonite and the pulverized Oak Creek sediment, respectively.

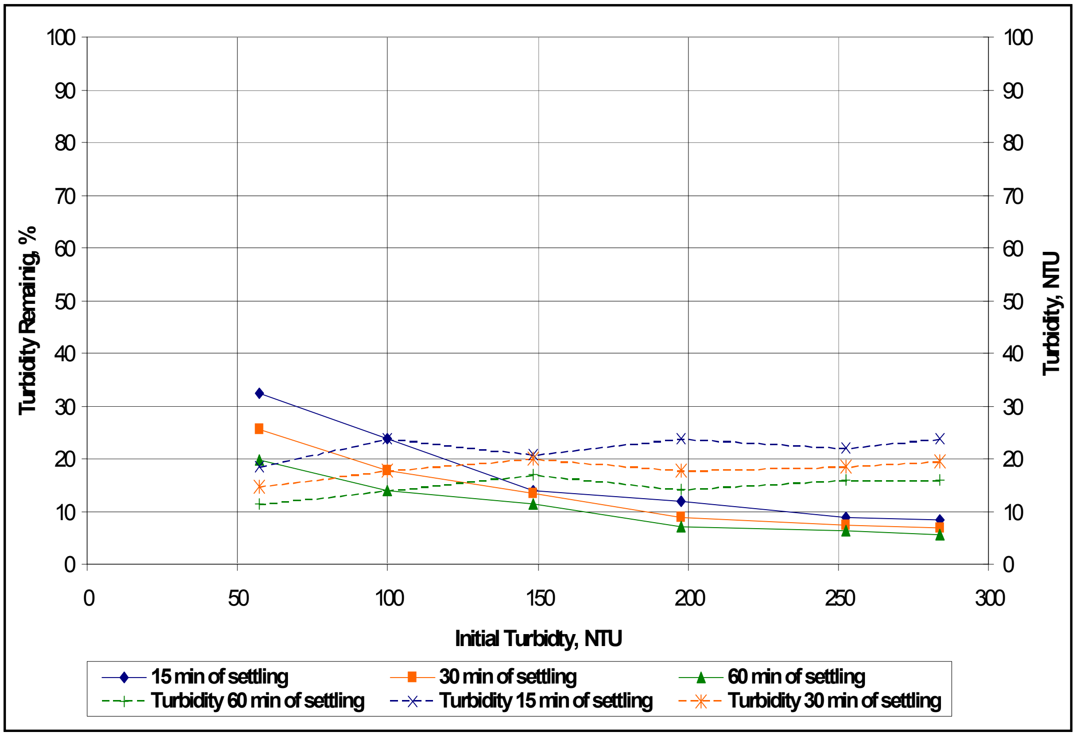

Figure 4.39: Effect of initial turbidity on turbidity removal by chitosan. Solid lines are % turbidity remaining and dotted lines are remaining turbidities in NTU. Sediment type: kaolin; initial pH (adjusted): 6.5; and chitosan dose: 1 mg/L.

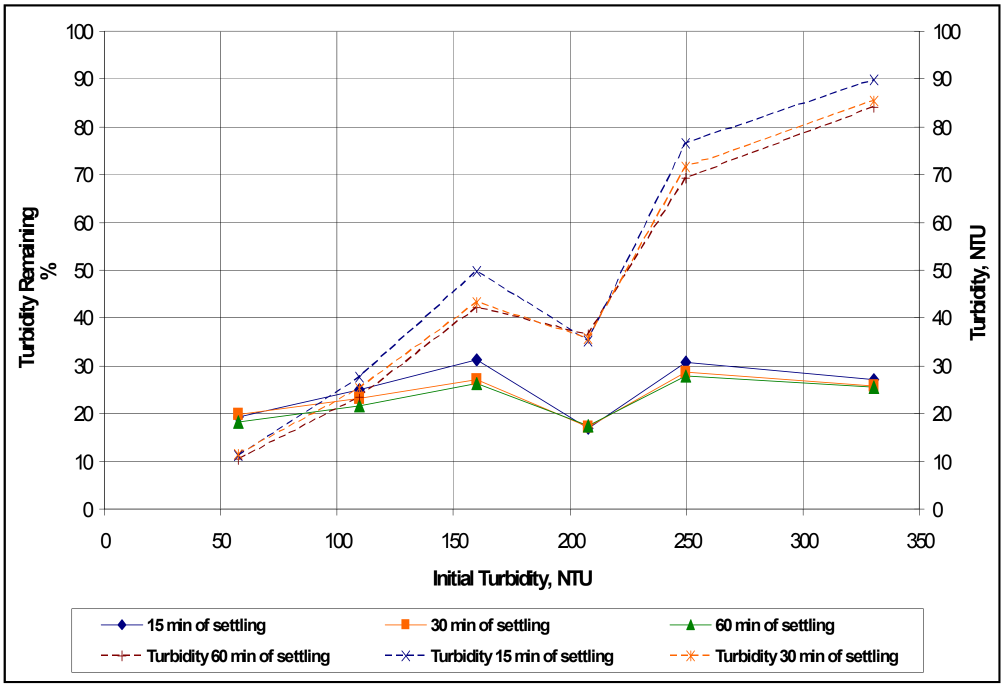

Figure 4.40: Effect of initial turbidity on turbidity removal by chitosan. Solid lines are % turbidity remaining and dotted lines are remaining turbidities in NTU. Sediment type: bentonite; initial pH: 7.8; and chitosan dose: 1 mg/L.

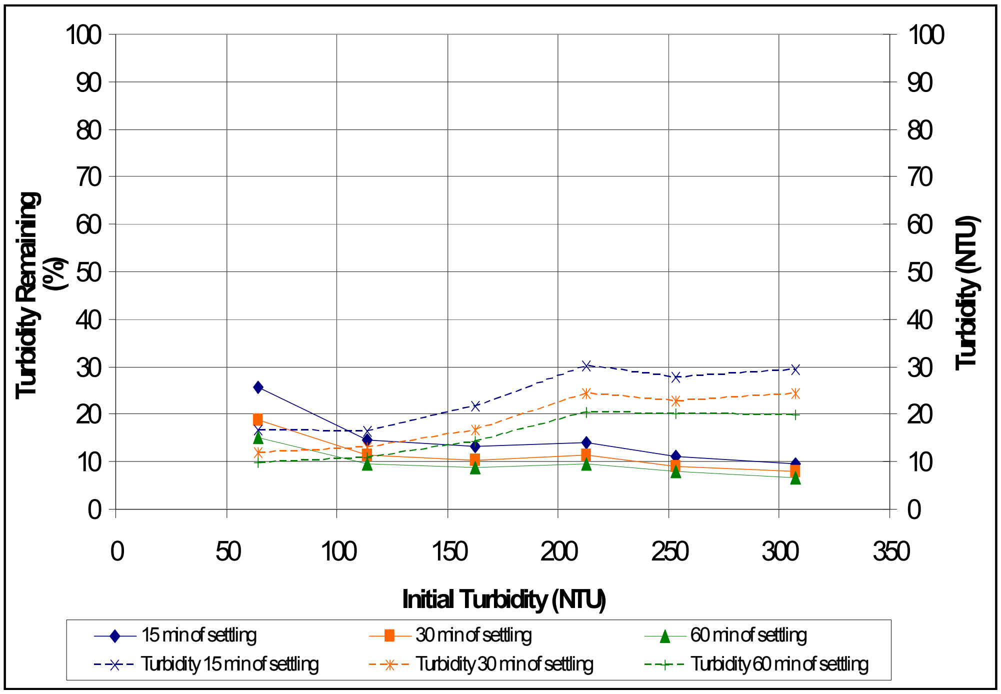

Figure 4.41: Effect of initial turbidity on turbidity removal by chitosan. Solid lines are % turbidity remaining and dotted lines are remaining turbidities in NTU. Sediment type: Pulverized Oak Creek sediment; initial pH 6.3; and Chitosan dose: 1 mg/L.

As shown in Figures 4.39 to 4.41, initial turbidity had less of an effect on chitosan flocculation efficiency than solution pH. For kaolin, the turbidity remaining after the tests was fairly similar for jars of different initial turbidity levels (Figure 4.39). As a result, the percentage of turbidity removed increases with increasing initial turbidity. For example, after 30 minutes of settling, there was 7% of the initial turbidity remaining in the jar that had an initial turbidity of 284 NTU, while the test jar with an initial turbidity of 58 NTU had 26% turbidity remaining, although the absolute turbidity level of both jars are similar: 15 NTU and 19.5 NTU, respectively.

Bentonite demonstrated different behavior than Kaolin. The percentage of turbidity removal was approximately the same regardless of the initial turbidity, while the absolute level of the remaining turbidity varied widely, as shown in Figure 4.40. The highest percentage removal, 83% after 30 minutes of settling, was observed with the initial turbidity of 208 NTU, and the lowest was 71% for the initial turbidity of 250 NTU. However, the absolute level of turbidity after 30 minutes of settling generally increases with increasing initial turbidity, except for the jar with an initial turbidity of 208 NTU.

The jar tests performed using Oak Creek pulverized sediment demonstrated increased percentage removal with increased initial turbidity, although the changes were small for an initial turbidity above 114 NTU. The remaining turbidity in NTU increased with increasing initial turbidity. The most effective for turbidity removal was obtained with the highest initial turbidity tested, 307 NTU, with 7.9% (24 NTU) turbidity remaining after 30 minutes of settling. The least effective removal was found with the lowest initial turbidity tested, 64 NTU, with 19 % (12 NTU) remaining after 30 minutes of settling.

4.3.3 Effect of Chitosan Dose

To determine the optimum chitosan dose, chitosan doses ranging from 0.25 mg/L to 2.0 mg/L were tested. The results are presented in Figures 4.42 to 4.44.

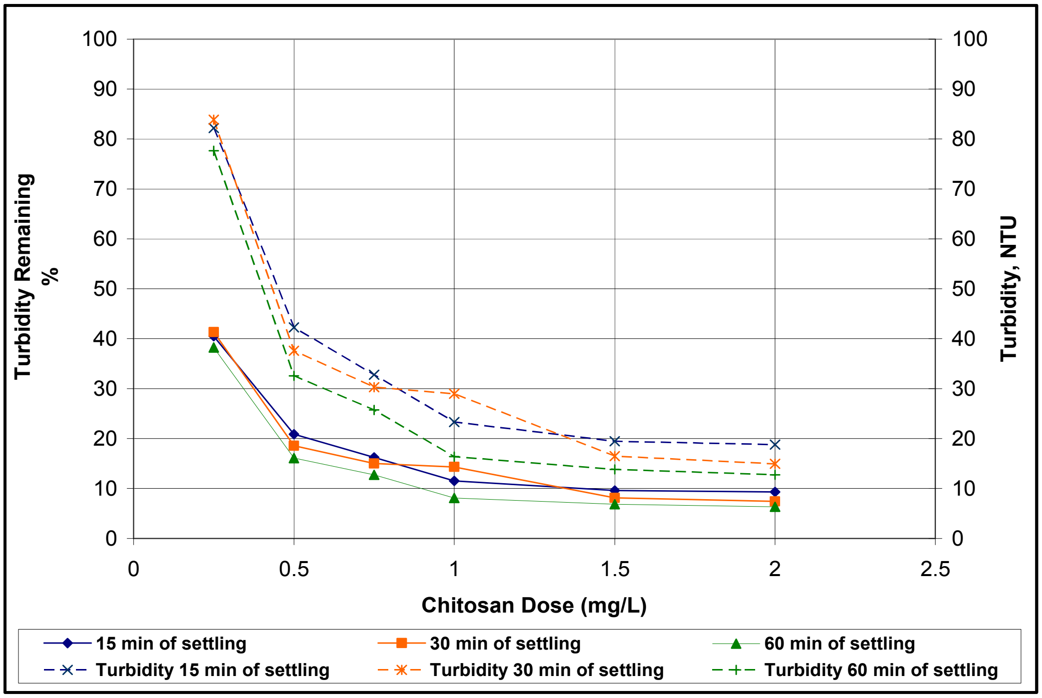

Figure 4.42: Effect of chitosan dose on turbidity removal. Solid lines are % turbidity remaining and dotted lines are remaining turbidities in NTU. Sediment type: Kaolin; initial pH (adjusted): 6.5; and initial turbidity: 203 NTU.

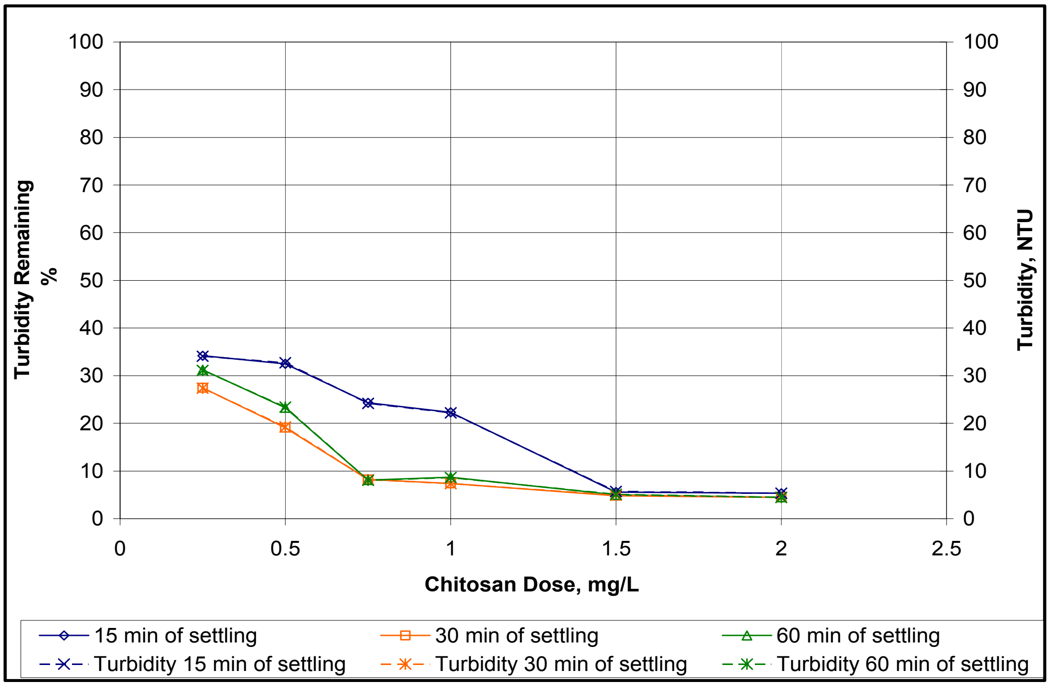

Figure 4.43: Effect of chitosan dose on turbidity removal. Sediment type: Solid lines are % turbidity remaining and dotted lines are remaining turbidities in NTU. Sediment type: bentonite; initial pH: 7.8; and initial turbidity: 100 NTU.

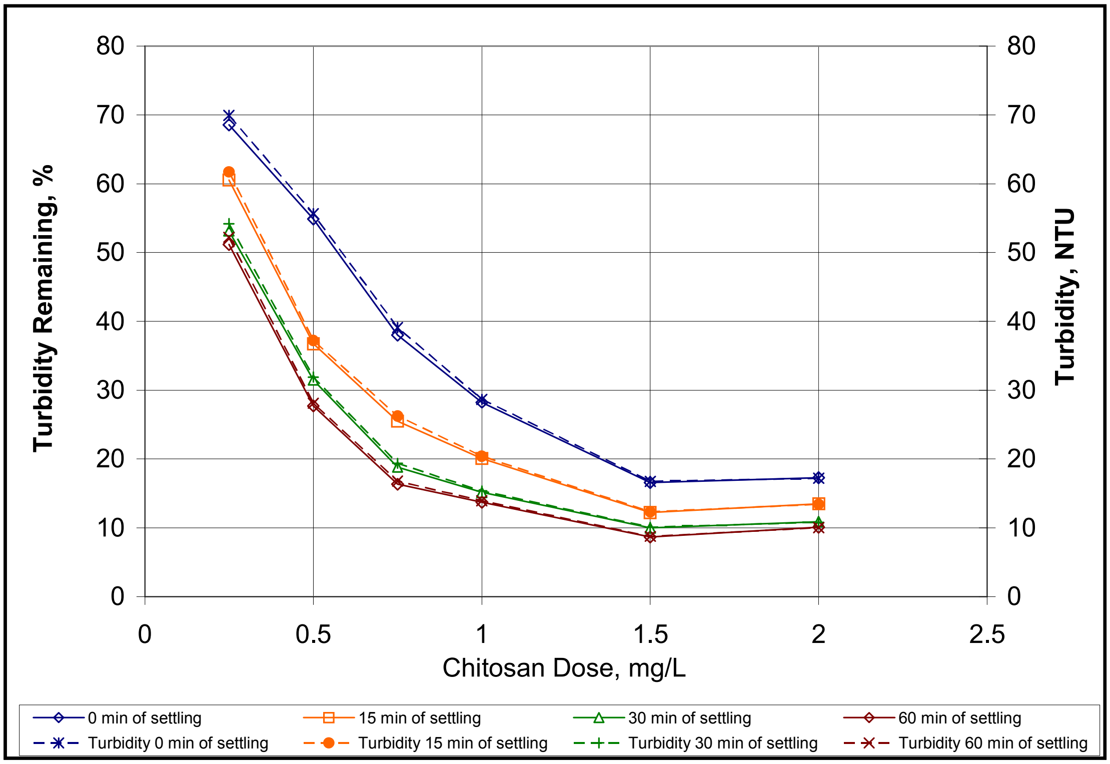

Figure 4.44: Effect of chitosan dose on turbidity removal. Solid lines are % turbidity remaining and dotted lines are remaining turbidities in NTU. Sediment type: Oak Creek sediment; initial pH 6.5; and initial turbidity: 100.

For all of the three sediment types, the turbidity removal efficiency increased as the chitosan dose increased. Bentonite showed the highest percentage of removal. In the test with bentonite suspension, all test jars had a pH of 7.8 and an initial turbidity of 100 NTU. With a chitosan dose of 1.5 mg/L or higher, there was 5.0% (5.0 NTU) of the initial turbidity remaining after 30 minutes of settling. The lowest removal was obtained with the lowest dose, 0.25 mg/L. With this dosage, there was 28 % (28 NTU) of the turbidity remaining after 30 minutes of settling.

In the test performed with a Kaolin suspension (Figure 4.42), the solution pH was 6.5 and the initial turbidity was 203 NTU. The remaining turbidity, after 30 minutes of settling, decreased 41.3 % (84 NTU) with a dose of 0.25 mg/L to 7.4 % (15 NTU) with a chitosan dose of 2.0 mg/L.

A suspension at pH of 6.3, with an initial turbidity of 100 NTU was used in the test with the pulverized Oak Creek sediment. After 30 minutes of settling, the remaining turbidity ranged from 13 % (13 NTU) of the initial turbidity at a chitosan dose of 2.0 mg/L, to 61% (61 NTU) of the initial turbidity when a chitosan dose of 0.25 mg/L was used. As shown in Figures 4.42 through 4.44, there was little to no advantage to using a chitosan dose above 1.0 mg/L - the maximum dose recommended by the manufacturer.

4.3.4 Effect of Settling Time

In all of the jar tests, for the three different sediment types, it was found that an increased settling time improved the turbidity removal, although there was an insignificant difference in the turbidity removal efficiency when the settling time was increased beyond 30 minutes.

4.3.5 Effect of Sediment Type

As shown in the jar test results, different types of sediment behaved differently in response to the change in pH, initial turbidity and chitosan dose; although Kaolin and the pulverized Oak Creek sediment in general demonstrated similar behavior with the exception that higher turbidity removal was achieved with the pulverized Oak Creek sediment. In all, the tests conducted using bentonite showed consistently efficient flocculation under all experimental conditions.

4.3.6 Effect of Water Quality

The jar tests were conducted using two different batches of water samples collected from Oak Creek. The first batch of water was collected on 3/28/05, after a period of heavy rains. Addition of 1 mg/L of chitosan to the sediment suspensions prepared with this water did not cause flocculation over the adjusted pH range of 4 to 9, indicating water quality parameters other than pH were controlling the flocculation process.

The second batch of water was collected on 04/05/05, after a period of dry weather. Jar tests conducted with this water showed reasonable results. All of the jar test results presented in Section 4.3 were obtained using the second batch of water.

Water quality analysis was performed to determine the key water quality parameters that caused the different flocculation behaviors of the two batches of water. Water quality parameters tested included: total hardness, alkalinity, conductivity, and common anions and cations. The anions tested were flouride (F^-), chloride (Cl^-), nitrate (NO_3^{2-}), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}). The cations tested were: magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), iron (Fe^{3+}), and sodium (Na^+). There was no change in the anion and cation concentrations between the water samples. The major anions that were present were, Cl^-, PO_4^{3-}, and NO_3^{2-}. The results of the water quality analysis are summarized in Table 4.1.

Table 4.1: Results of water quality analysis

Sample Date	pH	Turbidity (NTU)	Alkalinity (mg/L as $CaCO_3$)	Conductivity (mS/cm)	Hardness (mg/L as $CaCO_3$)
9/21/2005 (Field Test)	8.0	5.6	112.5	0.26	63.42
3/28/2005 (No Flocculation)	8.3	44	88.5	0.18	63.10
4/5/2005 (Flocculation)	8.0	9.5	54.6	0.41	73.70

As is evident from Table 4.1, the water collected during the field test, and on March 28, 2005, had higher alkalinity and lower conductivity than the water collected on April 5, 2005. In order to test whether or not these two parameters affected the flocculation efficiency of chitosan, jar tests were conducted raising the alkalinity of the water sample from 4/5/1005 to 85 mg/L as $CaCO_3$, and raising the conductivity of the water collected on 3/28/2005 to 0.5 mS/cm. The adjustment of these two parameters did not affect the results of the jar test. The water collected on March 28, 2005 still did not flocculate, while the water collected on April 5, 2005 did flocculate.

In order to determine if organic material was responsible for the different behavior of the water samples, TC, TOC, and IC were analyzed, Figure 4.45. However, no clear correlation was found between the TOC level of the water samples and their flocculation behavior.

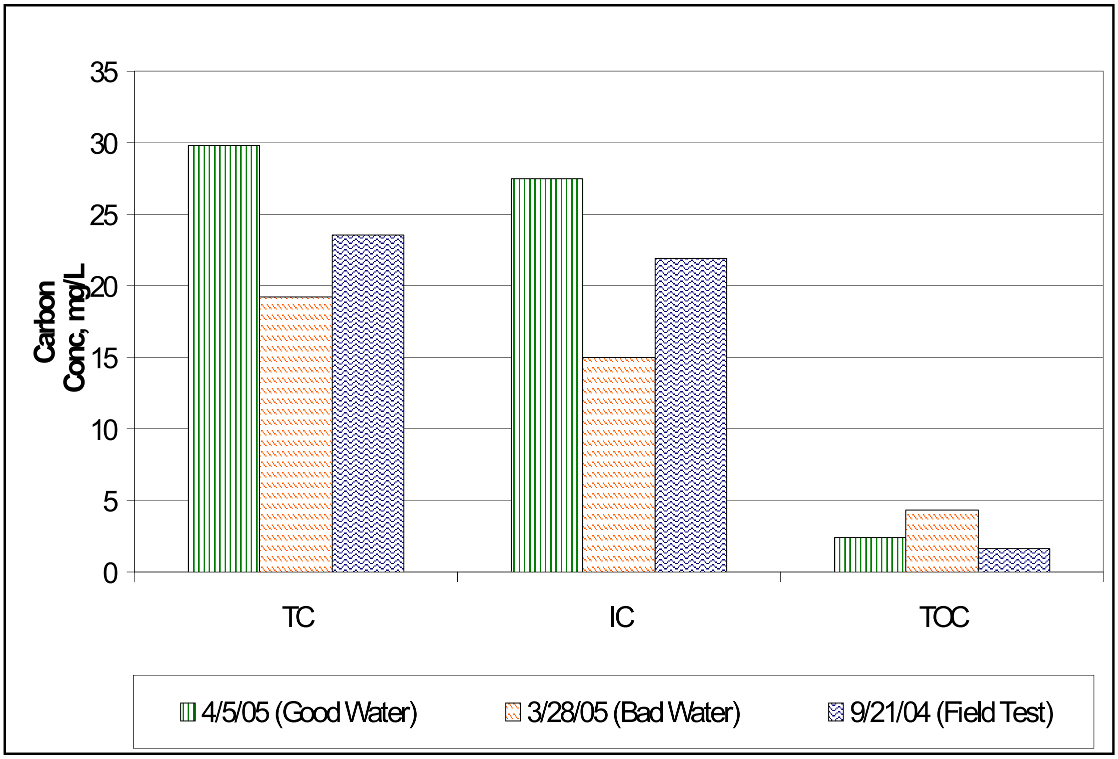

Figure 4.45: Results of carbon analysis for water samples collected on 4/5/2005, 3/28/2005 and 9/21/2004

The differences in water quality between the two water samples may have to do with run off from near by farms due to the heavy rains before collection of the first sample. It is worth mentioning that heavy rain was also experienced before the field tests. Water quality similar to that of the water collected on 3/28/2005 was expected.

It is evident that the efficiency of chitosan flocculation strongly depends on unknown water quality parameters, other than pH. The effect of which may far out weigh any of the parameters tested in this study. Therefore, it is very important to identify the key water quality parameters controlling chitosan flocculation efficiency in order to determine if chitosan treatment will be efficient for a particular stream.

5.0 CONCLUSIONS AND FUTURE RESEARCH

5.1 CONCLUSIONS

Field experiments were conducted to determine the feasibility of using chitosan as a natural flocculant during in-stream construction work. Through these field experiments it was found that with a chitosan dose of 0.5 mg/L there was a noticeable reduction in turbidity levels at different distances downstream from the simulated "construction site". With a lower chitosan dose of 0.25 mg/L, no significant improvement in turbidity removal was observed when compared to the natural settling. However, the variation in initial turbidity due to the sediment introduction methods was too high to make sound conclusions on chitosan treatment efficiency. The poor treatment observed in the field tests may be due to the combination of low chitosan doses, high water pH, and other inappropriate water quality parameters which may have resulted from the heavy rain fall before the field tests.

Water quality analysis was conducted to determine the concentration of TOC, TKN, TP and BOD before and after chitosan addition in the field tests. It was found that chitosan had little to no effect on the water quality of the stream, indicating it is safe for use in streams without adversely affecting the aquatic chemical environment.

Bench-scale jar tests were conducted to learn more about the effect of chitosan on different types of sediment and how it was affected by water quality. It was found that the effectiveness of chitosan was strongly dependent on the chemistry of the stream water that was used to prepare the sediment suspension. For all of the sediment types tested in this study, turbidity removal increased with decreasing pH, within the pH range of 4 to 9. Initial turbidity was not a major factor in determining the effectiveness of chitosan flocculation. Although the efficiency of turbidity removal increased with increasing chitosan dose, 1.0 mg/L seemed to be the optimal dosage because little or no benefit was found by a further increase in dose. The dose of 1.0 mg/L is the highest dose recommended by the manufacturer due to the potential toxicity to certain fish.

The most important factor seems to be the water quality. Jar tests conducted using water samples collected from Oak Creek on two different days showed completely different results, even at the same pH level. The sample collected after a period of heavy rain fall did not obtain any flocculation over the pH range of 4 to 9 at a chitosan dose of 1.0 mg/L. However, the water samples collected after a period of dry weather did demonstrate effective flocculation over the pH range of 4 to 9. This dramatic difference between water samples indicates that water quality parameters other than pH have a dominating effect on chitosan flocculation. Further analysis of the water quality revealed that the distinct behaviors of the two batches of water were not caused by commonly analyzed parameters such as ph, turbidity, hardness, conductivity, alkalinity, or TOC content.

5.2 FUTURE RESEARCH

During the field testing portion of this project, only one stream was tested,on one day during the low flow season. This did not allow for studies on the effects of stream type and temporal variation of water quality. In the future, streams with different water chemistries and sediment characteristics should be tested. Meanwhile, it is important to test available BMPs in conjunction with the chitosan. As demonstrated in the jar tests, floc formation can begin very soon after the addition of chitosan. However, significant settling time is required to achieve good turbidity removal. Various methods to slow down the water flow need to be tested to determine whether or not an increased residence time will increase the effectiveness of chitosan, as would be expected based on the jar tests results.

The jar test results obtained using three sediment types suspended in Oak Creek water are very different from data reported in the literature, especially the effect of pH. The most effective pH was found to be pH 4, not pH 6.5, which is commonly reported, and the initial turbidity did not have a significant impact on turbidity reduction. This is most likely due to the water chemistry of Oak Creek. Further studies should be conducted with different synthetic, as well as natural waters, to identify the key water quality parameters that control chitosan flocculation and their effects on turbidity removal. A careful examination on the effect of agricultural practices, waste discharge, and run off from surrounding land is needed to determine how these activities affect the stream water quality, and consequently the effectiveness of chitosan flocculation. Based on these studies, it will be possible to determine when and where it would be beneficial to use chitosan to control turbidity caused by in-stream construction work.

Due to the widely varied effectiveness of chitosan, when used under different conditions, it is important to develop an operation manual that provides guidelines for using chitosan in conjunction with in-stream con4struction work.

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