Fate of As, Se, and Hg in a Passive Integrated System for Treatment of Fossil Plant Wastewater

Final Report

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ABSTRACT

TVA is collaborating with EPRI and DOE to demonstrate a passive treatment system for removing SCR-derived ammonia and trace elements from a coal-fired power plant wastewater stream. The components of the integrated system consist of trickling filters for ammonia oxidation, reaction cells containing zero-valent iron (ZVI) for trace contaminant removal, a settling basin for storage of iron hydroxide floc, and anaerobic vertical-flow wetlands for biological denitrification. The passive integrated treatment system will treat up to 0.25 million gallons per day (gpd) of flue gas desulfurization (FGD) pond effluent, with a configuration requiring only gravity flow to obviate the need for pumps. The design of the system will enable a comparative evaluation of two parallel treatment trains, with and without the ZVI extraction trench and settling/oxidation basin components. One of the main objectives is to gain a better understanding of the chemical transformations that species of trace elements such as arsenic, selenium, and mercury undergo as they are treated in passive treatment system components with differing environmental conditions. This progress report details the design criteria for the passive integrated system for treating fossil power plant wastewater as well as performance results from the first several months of operation. Engineering work on the project has been completed, and construction took place during the summer of 2005. Monitoring of the passive treatment system was initiated in October 2005 and continued until May 18 2006. The results to date indicate that the treatment system is effective in reducing levels of nitrogen compounds and trace metals. Concentrations of both ammonia and trace metals were lower than expected in the influent FGD water, and additions to increase these concentrations will be done in the future to further test the removal efficiency of the treatment system. In May 2006, the wetland cells were drained of FGD water, refilled with less toxic ash pond water, and replanted due to low survival rates from the first planting the previous summer. The goals of the TVA-EPRI-DOE collaboration include building a better understanding of the chemical transformations that trace elements such as arsenic, selenium, and mercury undergo as they are treated in a passive treatment system, and to evaluate the performance of a large-scale replicated passive treatment system to provide additional design criteria and economic factors.

INTRODUCTION

Installation of air pollution control equipment at coal-fired power plants to reduce air pollutant emissions impacts the power plant wastewater stream. The primary impact to the power plant wastewater stream is the addition of ammonia from the selective catalytic reduction (SCR) process. Because ammonia is fed in stoichiometric excess in the SCR process, a slip occurs in which ammonia is captured on the coal fly ash and ultimately released to the power plant wastewater stream (EPRI, 1999, 2000). Another impact on wastewater results from the flue-gas desulfurization (FGD) process. This process utilizes crushed limestone which reacts with sulfur dioxide in flue gas to form calcium sulfate, or gypsum. The FGD process greatly reduces air emissions of sulfur dioxide at the expense of increased levels of mercury and selenium in the power plant wastewater stream (EPRI, 1998).

Coal combustion products are typically sluiced to a series of ponds where solids settle out of the sluice water. Dissolved metals and metalloids such as arsenic, selenium, mercury, antimony, aluminum, barium, boron, cadmium, copper, nickel, thallium, and zinc are present in ash pond and FGD pond effluent (EPRI, 1998). Each day millions of gallons of water are required to sluice fly ash and scrubber gypsum to the ponding areas at power plants. Combined ash pond and FGD pond effluents from a single power plant can range from 10 to over 30 million gallons per day (gpd).

FGD pond water typically contains higher concentrations of metal ions than does ash pond water. This is due primarily to pH effects, as many metal species form precipitates at higher pH. Ash pond water often has a higher pH than FGD pond water. The FGD process reduces emissions of airborne mercury and selenium; however, because many contaminants are retained in the FGD gypsum byproduct, levels in FGD water are elevated compared to ash pond water. Nickel is present in the limestone used in the FGD process, and as a result, nickel is also present in elevated levels in FGD water (EPRI, 1998).

Power plants equipped with both SCR and FGD produce a wastewater stream that contains nutrients such as ammonia, nitrate, and dissolved trace elements. Treating this mixed waste stream is a challenging task because several mechanisms are involved in removing the various contaminants in the wastewater stream. There is a tremendous need to develop an integrated treatment system for removing nutrients and metals from power plant wastewater.

Passive wastewater treatment technology includes systems and strategies that incorporate natural, self-maintaining engineering designs and processes that result in low- to no-maintenance facilities. Passive treatment systems do not require active introduction of treatment chemicals, continuous monitoring and adjustment, or intense operational management. Passive treatment systems are often based on constructed wetlands, are generally staged, and may include other passive components such as anoxic limestone drains, oxidation ponds, settling ponds, successive alkalinity producing systems (SAPS), algae ponds, vertical limestone drains and aeration basins (Brodie, et al., 2001).

When compared to conventional treatment technologies, passive treatment technologies require less costly chemical reagents, incur lower operational costs, and involve limited maintenance activities. Passive treatment is often an attractive alternative to a conventional wastewater treatment facility when available land is not a factor. Aerobic technologies used include mixed oxidation, hydrolysis, precipitation, and limestone dissolution reactions. These processes are most effective when the water being treated is net alkaline. Aerobic passive technologies include aerobic wetlands, oxidation ponds, open limestone drains, aeration structures, and alkaline recharge basins. Anaerobic passive treatment technologies promote anaerobic bacterial activity and limestone dissolution that result in the precipitation of metal sulfides and the generation of alkalinity. Anaerobic technologies include anoxic limestone drains, SAPS, and anaerobic constructed wetlands (Brodie, et al., 2001).

TVA is collaborating with EPRI and DOE to demonstrate a passive treatment system for removing SCR-derived ammonia and trace elements from a coal fired power plant wastewater stream. TVA in collaboration with EPRI and some of its member utilities is installing a passive treatment system to remove SCR-derived nitrogen from the FGD wastewater stream at Paradise Fossil Plant (PAF), Paradise, Kentucky. The name for the TVA-EPRI collaborative project is ATOXIC. TVA in collaboration with EPRI and DOE are integrating into ATOXIC a passive treatment component using zero-valent iron (ZVI) in an extraction trench to reduce the concentrations of trace elements such as arsenic, selenium, and mercury in the FGD wastewater stream. Furthermore, the TVA-EPRI-DOE collaborative effort will build a better understanding of the chemical transformations that pollutants such as arsenic, selenium, and mercury undergo as they are immobilized in the passive treatment system. Combining the resources of DOE, TVA, and EPRI offers scientists the opportunity to evaluate the performance of two passive treatment trains, with and without the use of ZVI to enhance the removal of trace elements from the FGD wastewater.

The components of the integrated system consist of trickling filters for ammonia oxidation (nitrification), a reaction cell containing ZVI for trace metal contaminant removal, a settling basin for storage of iron hydroxide floc, and anaerobic vertical-flow wetlands for biological denitrification (Figure 1). The passive integrated treatment system would optimize natural processes to treat up to 0.25 million gpd of FGD pond effluent, with a configuration requiring only gravity flow to obviate the need for pumps.

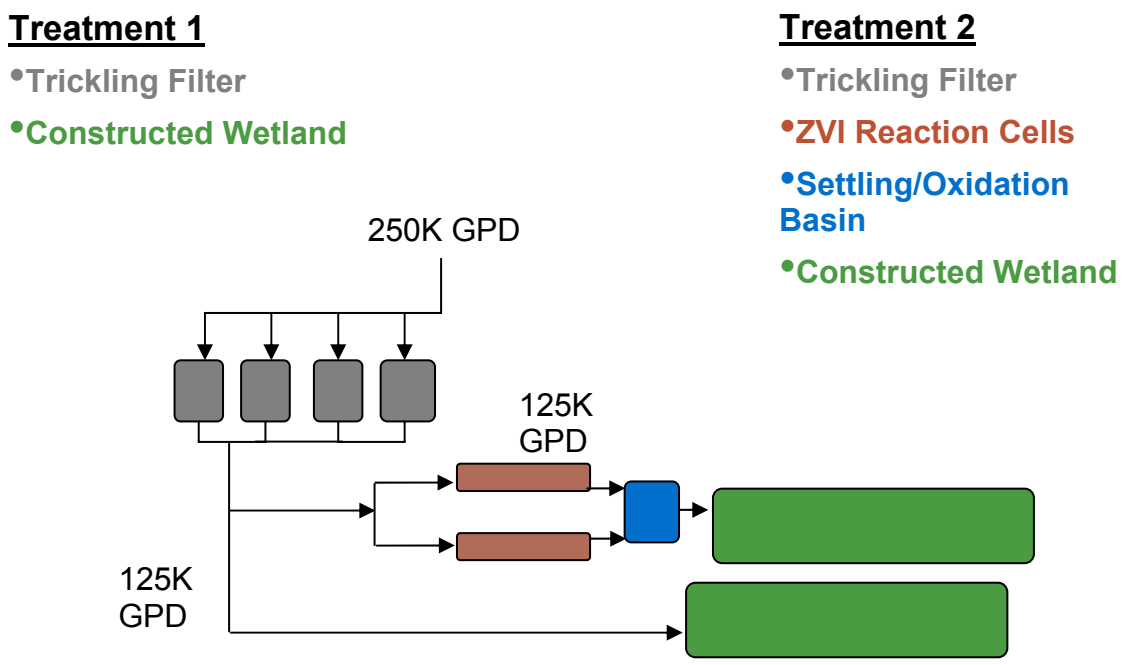


Figure 1 Flow Diagram ATOXIC/ASSET Passive Treatment System illustrating the two parallel treatment trains of the ATOXIC (treatment 1) and ASSET (treatment 2) passive treatment systems.

In a passive integrated system for treating power plant wastewater, the first step in the treatment process is removal of ammonia by the process of biological nitrification. Ammonia in FGD pond effluent is converted to nitrate in fixed film bioreactors (trickling filters) via nitrification reactions carried out by ammonium-oxidizing bacteria.

Effluent from the trickling filters is split into two streams of equal volume. One stream gravity flows to the reaction cells containing a mixture of ZVI and limestone while the other stream flows via gravity to one of two anaerobic vertical flow wetlands. The purpose of the reaction cell is two-fold. First, the reaction cell allows the wastewater to come in contact with iron surfaces where adsorption reactions take place. Secondly, the reaction cell introduces a slow release form of iron to the wastewater stream. ZVI readily oxidizes in the presence of water and oxygen. As the iron is oxidized, dissolved oxygen is scavenged from the water stream creating localized environments with anoxic conditions ideal for the reduction of anionic species such as nitrate and selenate.

As the ZVI rusts, iron oxides and hydroxides form and slowly settle out of solution. The design of the system includes a settling pond to allow the slowly released iron to precipitate from solution and settle in a storage area to minimize plugging in the downstream components. Because the iron oxyhydroxide floc particles have adsorptive properties, the floc generated is allowed to remain in the settling pond for long term storage. The collection of iron oxyhydroxide floc in the settling pond is vital to lasting

treatment efficiency of the integrated system. The work will provide the opportunity to study the sustainability of a slow-release form of iron such as ZVI. It is unknown how long the ZVI will remain active under the conditions of the FGD stream. The ZVI source in the reaction cell will be replenished if necessary in order to maximize the treatment efficacy. This practice will also allow for a thorough economic evaluation of using ZVI to treat power plant wastewater.

Effluent from the settling basin flows to the second of two vertical-flow constructed wetlands where biological denitrification takes place. The vertical-flow wetland consists of a limestone bed under a layer of organic substrate. The organic substrate provides a source of dissolved organic carbon necessary for denitrifying bacteria to thrive. Because the vertical-flow wetland is anaerobic, additional metals removal may occur due to the formation of insoluble sulfides. The vertical-flow wetland has been planted with several wetland species to aide in denitrification.

Paradise Fossil Plant

PAF is located in Muhlenberg County in western Kentucky approximately 35 miles northwest of Bowling Green and 95 miles southwest of Louisville. The plant is located on the south bank of the Green River at river mile 100.2 (upstream from the Green River's confluence with the Ohio River) and 8 miles downstream of the United States Army Corps of Engineers Lock and Dam No. 3, also on the Green River. The plant is located northeast of Drakesboro. A 2.2-mile-long railroad to the plant provides access from a spur of the CSX Railroad (Figure 2). The plant is on a large reservation of approximately 3,000 acres. Most nearby land adjoining the plant property is reclaimed coal mining land. There are no residences within 3 to 4 miles of the plant on the west side (plant side) of the Green River with the town of Drakesboro being the nearest community. On the east side of the Green River opposite the plant, the nearest residences are at a distance of approximately 2 miles. PAF is the eighth largest-capacity, coal-fired, steam electric plant built by TVA. Construction began in November 1959. The initial plant was operational in 1963 and has two generating units with a rated capacity of 704 MW each. At the time, these were the largest operating units in the world. A third unit was added in 1970 with a rated capacity of 1,150 MW. Currently, PAF produces over 7 million megawatt hours (MWh) of electricity per year. Each of the PAF boilers is of a cyclone design. PAF uses high-sulfur eastern coals primarily from nearby counties in western Kentucky and southern Illinois in Units 1 and 2. Unit 3 burns various blends of western Kentucky, Powder River Basin, and Utah bituminous coals. Coal is transported to the plant by truck, rail, and barge. In addition to its major role as a power producer for the region, PAF has demonstrated state-of-the-art pollution control technology. To reduce sulfur and ash content of the fuel, coal washing began in 1981 and as described above, wet limestone scrubbers were added to Units 1 and 2 in 1983. Electrostatic precipitators (ESPs) were installed on all three units to remove fly ash. However, ESPs are no longer operated on Units 1 and 2; particulate matter is controlled by the scrubbers.

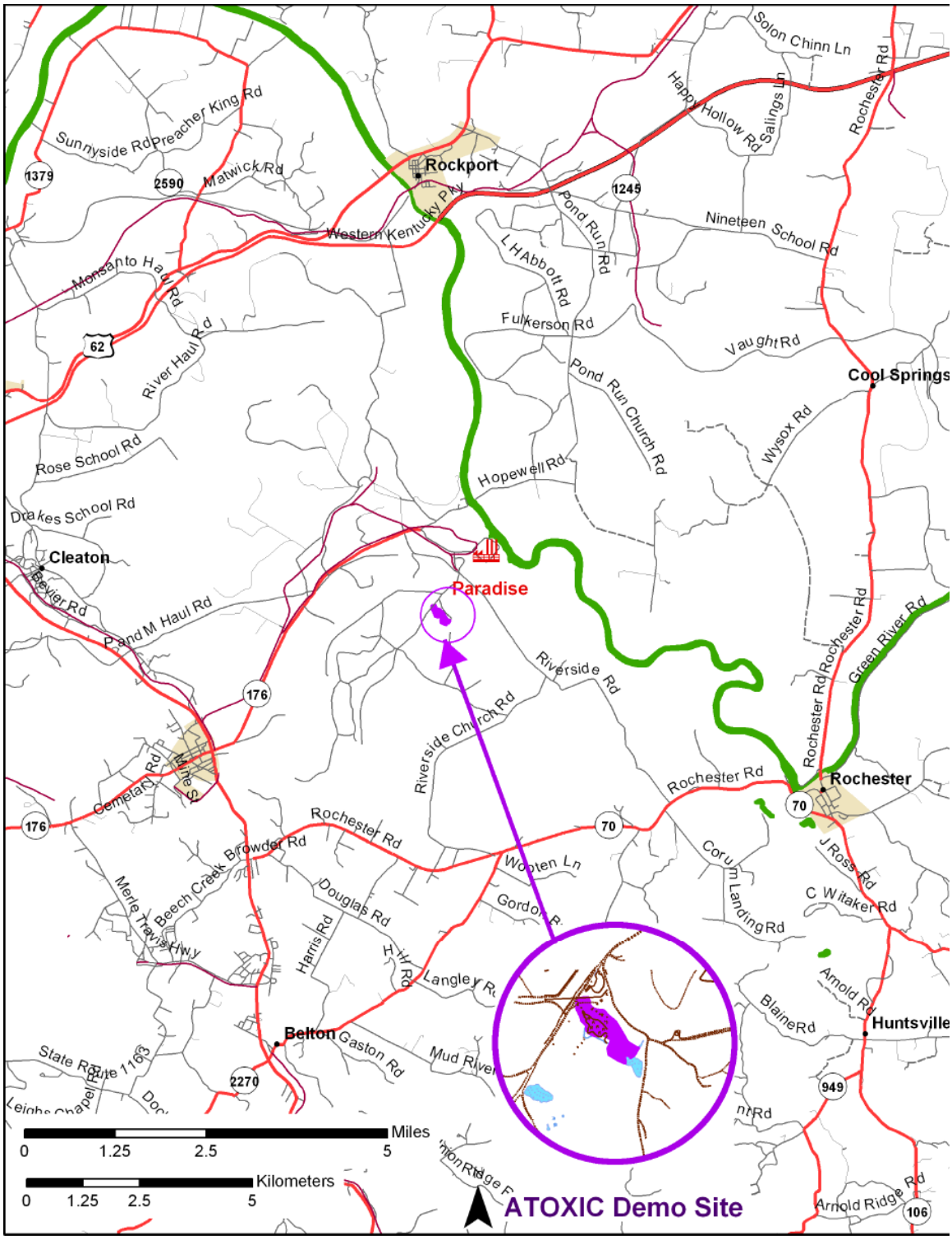


Figure 2 ATOXIC Demonstration Site Relative to Surrounding Area

Most recently, TVA has installed SCR equipment to reduce nitrogen oxide (NOx) emissions by approximately 90 percent from PAF. In all (excluding the currently proposed scrubber), TVA has spent $454 million since 1979 for modern pollution control equipment at PAF to accomplish a 70 percent reduction in SO_2 emissions.
River water from the Green River is used to sluice FGD scrubber gypsum to the designated rim-ditch gypsum stacking area at Paradise. Approximately 3 million gpd of river water are used to sluice the FGD scrubber gypsum. In the future it is expected that additional water withdrawals may be needed to sluice the increased quantity of scrubber gypsum that will be produced after the addition of another wet limestone scrubber. The anticipated FGD sluice stream is expected to be around 6 MGD. The FGD stream is added to another stream of water from the bottom ash pond, effectively diluting the FGD stream by a factor of 10 before the combined streams enter the ash pond. The total volume of water discharged from the plant including sluice water and plant process water is approximately 30 MGD.

For this project FGD water is withdrawn from a limestone trench upstream from the point at which the FGD stream is mixed with the bottom ash stream. By obtaining the FGD water from this point the likelihood of finding trace elements in measurable quantities is much better than if the water was withdrawn from further downstream beyond the point where the two streams are commingled.

The location of the ATOXICS demonstration is southeast of the road adjacent to the FGD channel, just east of the CQWESTERS project site, and north of the ash pond (Figure 3). The site geography slopes downhill toward the ash pond. This feature makes the site perfect for an experimental demonstration since the entire area drains to the ash pond.

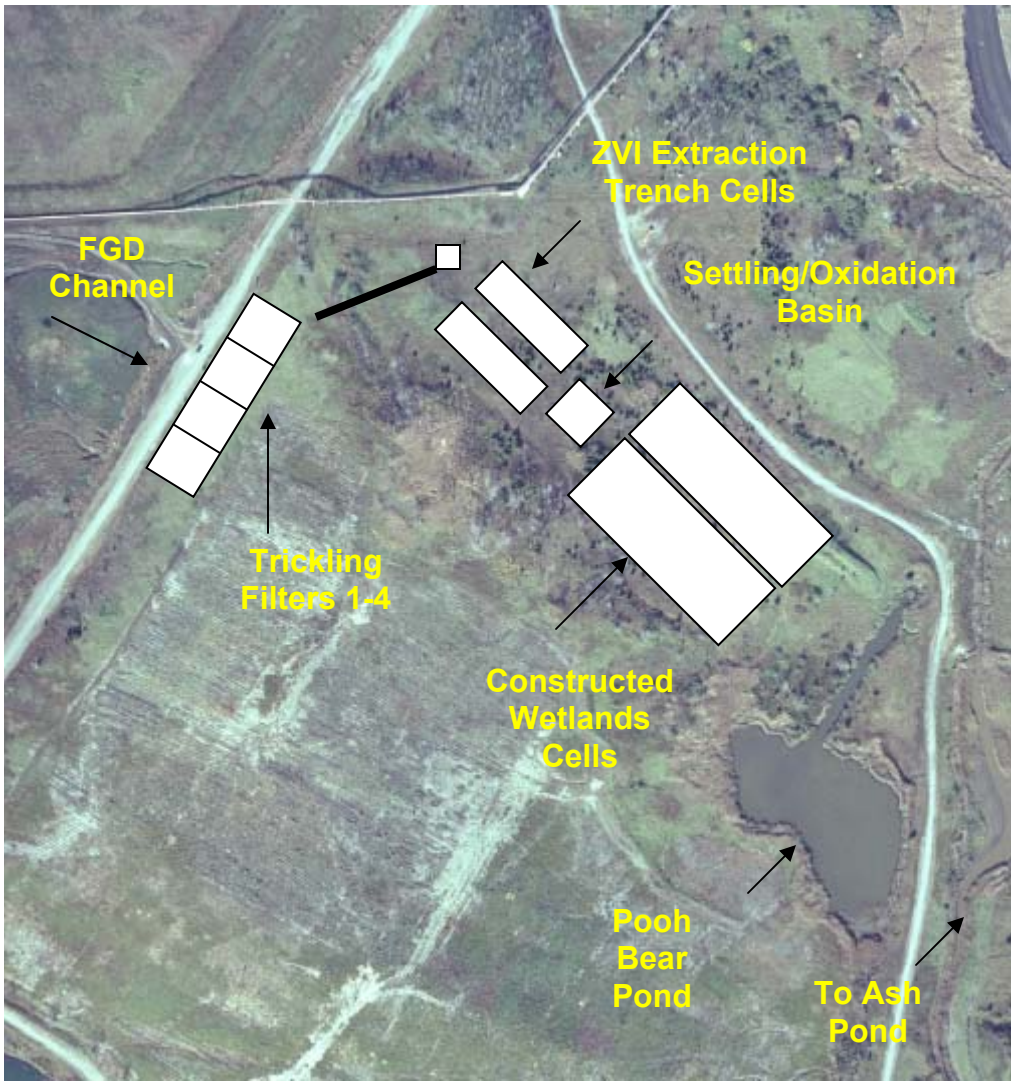


Figure 3 Aerial View ATOXIC/ASSET Demonstration Site. Water for the ATOXIC/ASSET demonstration is withdrawn from the FGD channel and distributed to four trickling filters. Following this treatment, water then flows via an aerial crossing to a splitter box which diverts the flow either to two ZVI extraction trench cells or directly to the ATOXIC constructed wetland. The water then flows to a settling/oxidation basin before treatment in the ASSET constructed wetland. Both constructed wetlands cells discharge to Pooh Bear Pond which ultimately flows into the ash pond. Drawings are not to scale.

Wetlands Issue

The initial site chosen for the location of the integrated passive treatment system was decided on due to its proximity to the source of FGD water and the available land suitable for construction. During the environmental review process conducted by TVA it was determined that much of the site was a wetlands. Several options were weighed including moving the entire project to another site and using a diesel powered pump to deliver the FGD water, and adjusting the size and location of the system components to keep the original site. It was decided to use the original site and place the system components on either side of the wetlands area. After relocating the components the

wetlands area that will be disturbed by the project is 15,854 sq. ft. or 0.36 acres (Figure 4). This solution satisfied the TVA environmental reviewer, and the US Army Corps of Engineers reviewed the proposed site. This series of events resulted in a delay of several months as well as increased costs of designing the system.

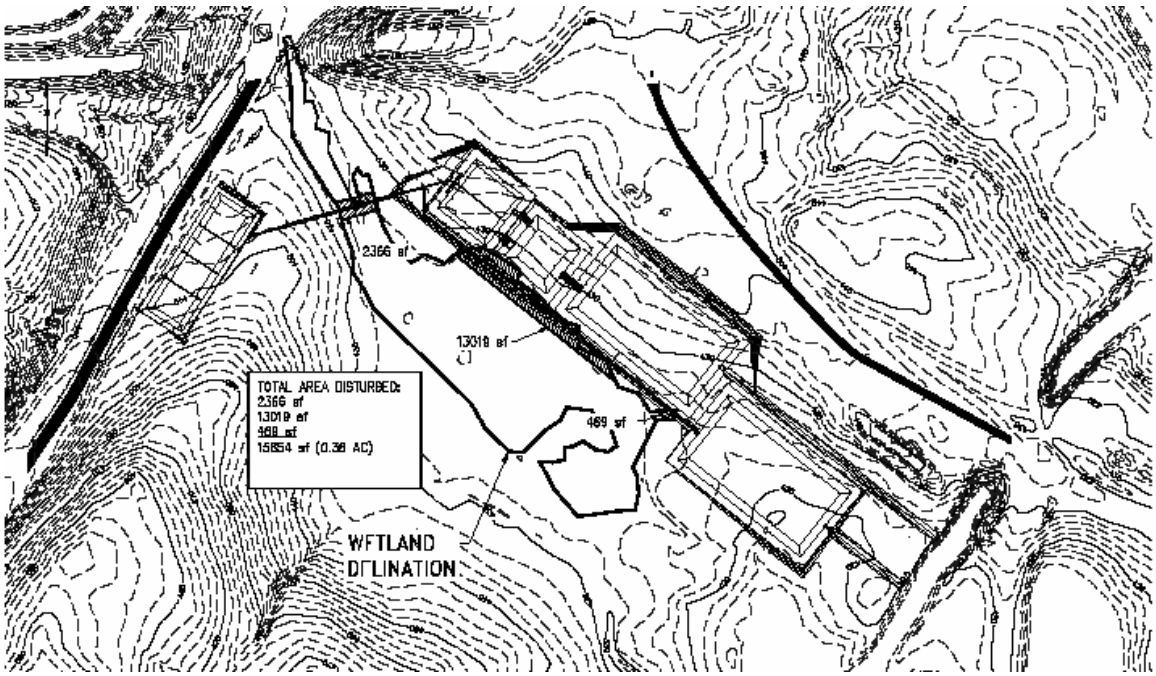


Figure 4 Site Layout Showing Wetlands Delineation.

Arsenic Chemistry

Arsenic occurs in surface waters due to natural weathering of mineral phases such as arsenopyrite (FeAsS) and orpiment (As_2S_3), the dissolution of arsenic-bearing iron minerals such as ironoxyhydroxides (FeOOH) and pyrite (FeS_2), and anthropogenic activities such as coal mining, coal combustion, agricultural practices, and wood treating.

Arsenic is a known human carcinogen and its toxicity has been well studied. An ingested dose of only 70-180 mg of arsenic trioxide (As_2O_3) was shown to be lethal to humans (Leonard, 1991). Chronic exposure to arsenic in drinking water has been linked to serious dermatological conditions, including blackfoot disease (Lu et al., 1991) as evidenced by the disaster in Bangladesh, India. Epidemiological studies have linked arsenic in drinking water with cancer of the skin, bladder, lung, liver, and kidney (Hindmarsh, 2000) and other ailments (Karim, 2000). Although both arsenite As(III) and arsenate As(V) are strongly adsorbed in the human body (Hindmarsh and McCurdy, 1986), the As(III) species are believed to be more toxic than the As(V) species because As(III) tends to accumulate in the tissues, whereas As(V) and organic arsenic are rapidly eliminated via the kidneys (Bertolero et al., 1987). The U.S. Environmental Protection Agency (USEPA) has recently lowered the maximum contaminant level (MCL) for arsenic in drinking water to 10 µg/L (ppb) from the previous standard of 50 µg/L. This move will

require many communities to install technologies for arsenic removal for municipal drinking water treatment facilities.

Arsenic is present in fly ash at variable concentrations. Ainsworth and Rai (1987), found that arsenic in fly ash ranged from 7.7 to 1,385 μg/g in 39 samples with a mean of 156.2 μg/g. Arsenic has been found in fly ash at values ranging from 2.3 to 279 μg/g in 48 samples with an average of 56.7 μg/g. Bottom ash contains much less arsenic ranging from <5 to 53.1 μg/g in 40 samples averaging 7.6 μg/g as reported by Ainsworth and Rai (1987). One reason for the variability of arsenic in fly ash is the sulfur content of the source coal. Arsenic in coal is commonly associated with iron sulfides such as pyrite, which can substitute arsenic for sulfur in the pyrite crystal lattice up to concentrations of 6000 μg/g (Boyle and Jonasson, 1973). High sulfur coal would predictably yield fly ash with higher arsenic content.

Arsenic becomes associated with the fine ash particles formed during coal combustion as volatile arsenic condenses on fly ash particles upon cooling. When wet sluicing is used to convey ash to the ash storage area, highly soluble arsenic species enter the sluice water stream via leaching from fly ash. Arsenic is typically found in concentrations ranging from 0 to 100 μg/L in ash pond and FGD pond discharges.

Arsenic is present in surface waters most often as arsenate, As(V), and arsenite, As(III). Arsenic is present predominantly in the As(V) form in aerobic waters and in the As(III) form under anaerobic conditions. Arsenate is found as the oxyanions arsenic acid $H_2AsO_4^{1-}$ between pH 2.2 and 7.0, and $HAsO_4^{2-}$ above pH 7 (Figure 5). Arsenite exists as arsenious acid H_3AsO_3 below pH 9.2. Arsenic can be methylated by bacteria to form organoarsenates; however these compounds are not known to bioaccumulate in biota.

Arsenic adsorbs onto many common aquifer and soil materials which is thought to limit the mobility of arsenic in most aquifer systems. Both As(III) and As(V) adsorb to particles of the hydrous oxides of iron (Pierce and Moore, 1982) and aluminum (Anderson et al., 1976). However, at circumneutral pH, arsenite exists as the uncharged arsenious acid H_3AsO_3 and is less strongly adsorbed onto the surfaces of iron oxyhydroxides than is arsenate.

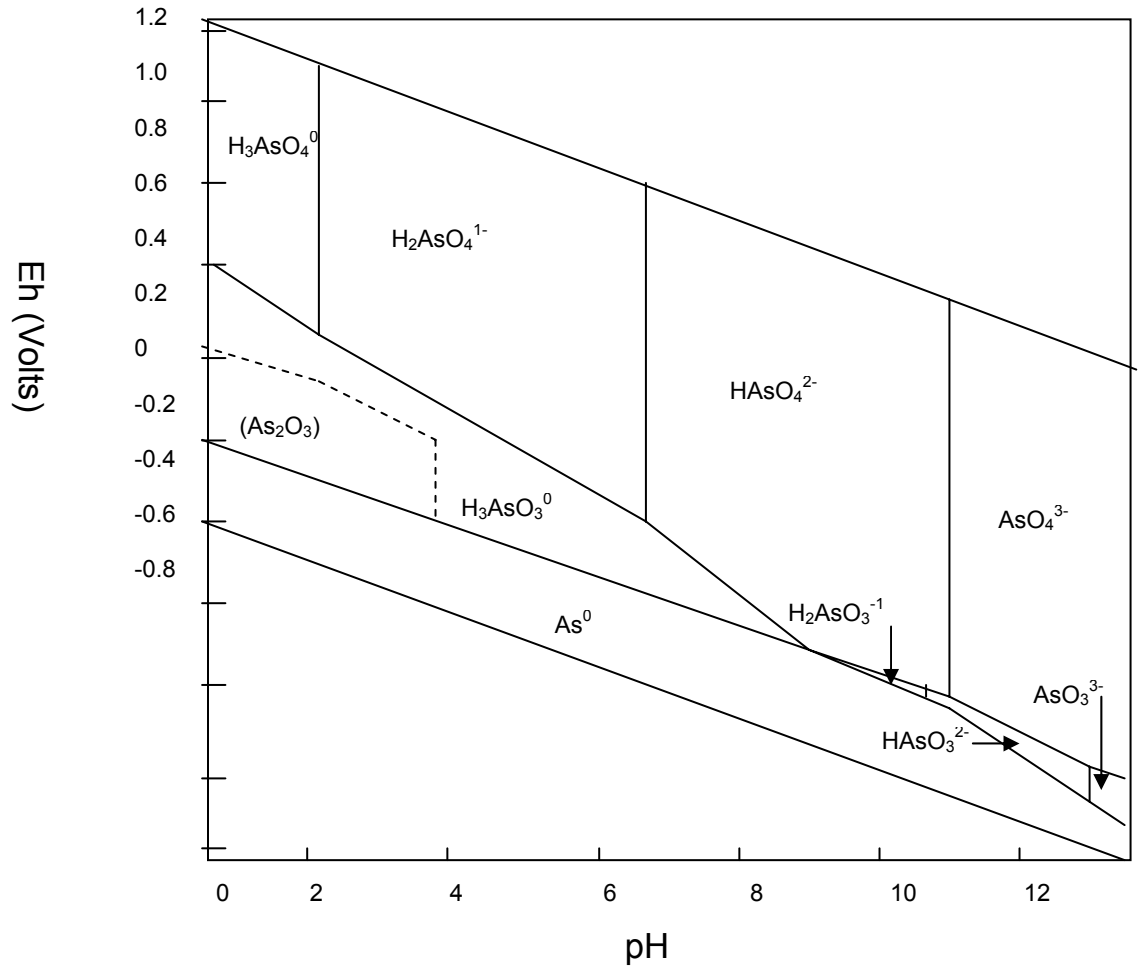


Figure 5 Arsenic Eh: pH Speciation Chart.

Aqueous carbonate, competing ions such as phosphate and silica, and organic matter in water can influence the adsorption of arsenic onto iron oxides and hydroxides. The presence of carbonate at common groundwater concentrations significantly reduces the tendency of arsenic to adsorb onto hydrated ferric oxide, and high concentrations of carbonate could cause the displacement of arsenic from the ferric oxide matrix (Appelo et al., 2002). Silica and phosphate may also interfere with arsenic sorption or promote arsenic desorption (Manning and Goldberg, 1996; Swendlund and Webster, 1999; Meng et al., 2000; Holm, 2002) through competitive binding interactions. Organic matter may influence arsenic adsorption to ferric oxides (Redman et al., 2002) as ferric iron is reduced to ferrous iron when reacted with organic matter, resulting in dissolution of iron oxides and an increase in arsenic mobility.

Selenium Chemistry

Selenium is an essential element for most plants and animals. Selenium occurs in elevated quantities only where seleniferous soils exist such as the Western United States. Anthropogenic sources of selenium include the mining, refinement, and combustion of

fossil fuels as well as irrigation of seleniferous soils for agriculture in regions with high rates of evapotranspiration (Lemly et al., 1993).

During microbial metabolism selenium is converted to organic forms such as seleno-amino acids, methyl selenides, and methyl selenones. When released from organisms, selenium can be converted to the volatile species dimethyl selenide (Masscheleyn and Patrick, 1993). Organic forms of selenium are known to bioaccumulate in aquatic organisms and bioconcentrate in the aquatic food chain (Lemly, 1999). Even levels as low as a few parts per billion of waterborne selenium can be detrimental to sensitive fish species. Because selenium targets the egg, which receives selenium from the female's diet and stores it until hatching, teratogenic deformity and death may occur. Adult fish may appear healthy while massive reproductive failure is occurring. Fish populations can decline or even disappear in a few years when exposed to slightly elevated levels of waterborne selenium (Lemly, 1999). Because of the toxicity of selenium to aquatic species, the USEPA is drafting revised aquatic life criteria to limit the whole fish tissue concentration of selenium to 7.91 ug/g dry weight.

Selenium is biomagnified in aquatic ecosystems, resulting in higher concentrations of the element in higher trophic levels. Biomagnification of selenium usually ranges from two to six times from the producers (algae and plants) to the lower level consumers (invertebrates and forage fish). Higher level consumers such as predatory fish, birds, and mammals may receive toxic quantities of selenium in their diet even if the water concentration is low. In ecosystems being ravaged by invasive bivalves such as San Francisco Bay and the Great Lakes Region, selenium bioaccumulation and toxicity is occurring in aquatic birds due to the invasive species disrupting natural food webs.

The burning of fossil fuels, most importantly coal, releases selenium to the environment as selenium is one of the more volatile trace elements present in coal. The concentration of selenium in coal is reported to be from 0.4-8 µg/g. Coal combustion wastes have been reported to contain up to 162 ug/g selenium (Ainsworth and Rai, 1987). During coal combustion, selenium is released mostly in the vapor phase; however, as flue gas is cooled selenium condenses onto fly ash particles and may be introduced to process water streams via wet-sluicing of coal combustion byproducts. At coal-fired utilities, coal combustion byproducts (CCBs) are either dry-stacked or sluiced to storage lagoons. Ash and/or FGD scrubber gypsum settles from the sluice water and is continuously dredged and stacked at the storage areas. The storage lagoons discharge water back to nearby surface waters from which the sluice water was withdrawn. Trace elements present in CCBs partition between the CCBs and the lagoon sluice water to varying degrees based on the solubility of the trace elements . Selenium is quite soluble in CCB sluice water and is released in significant quantities to surface waters due to CCB handling practices. Evidence of selenium negatively impacting aquatic life as a result of coal ash disposal practices are well documented (Lemly, 1999).

The chemistry of selenium is much like that of sulfur. Selenium is present in four oxidation states: selenide(-II), elemental selenium(0), selenite(IV) and selenate(VI) (Figure 6). Similar to arsenic, pH and redox control the valence state of selenium. Under

most environmental conditions selenium is present as one of the oxyanions. Selenite (SeO_3^{2-}) is favored under mildly oxidizing conditions. Selenate (SeO_4^{2-}) is stable in well oxidized environments and will be the predominant form of selenium under these conditions. Selenite species are reported to be more strongly adsorbed by iron oxides than selenate species (Benjamin and Bloom, 1981).

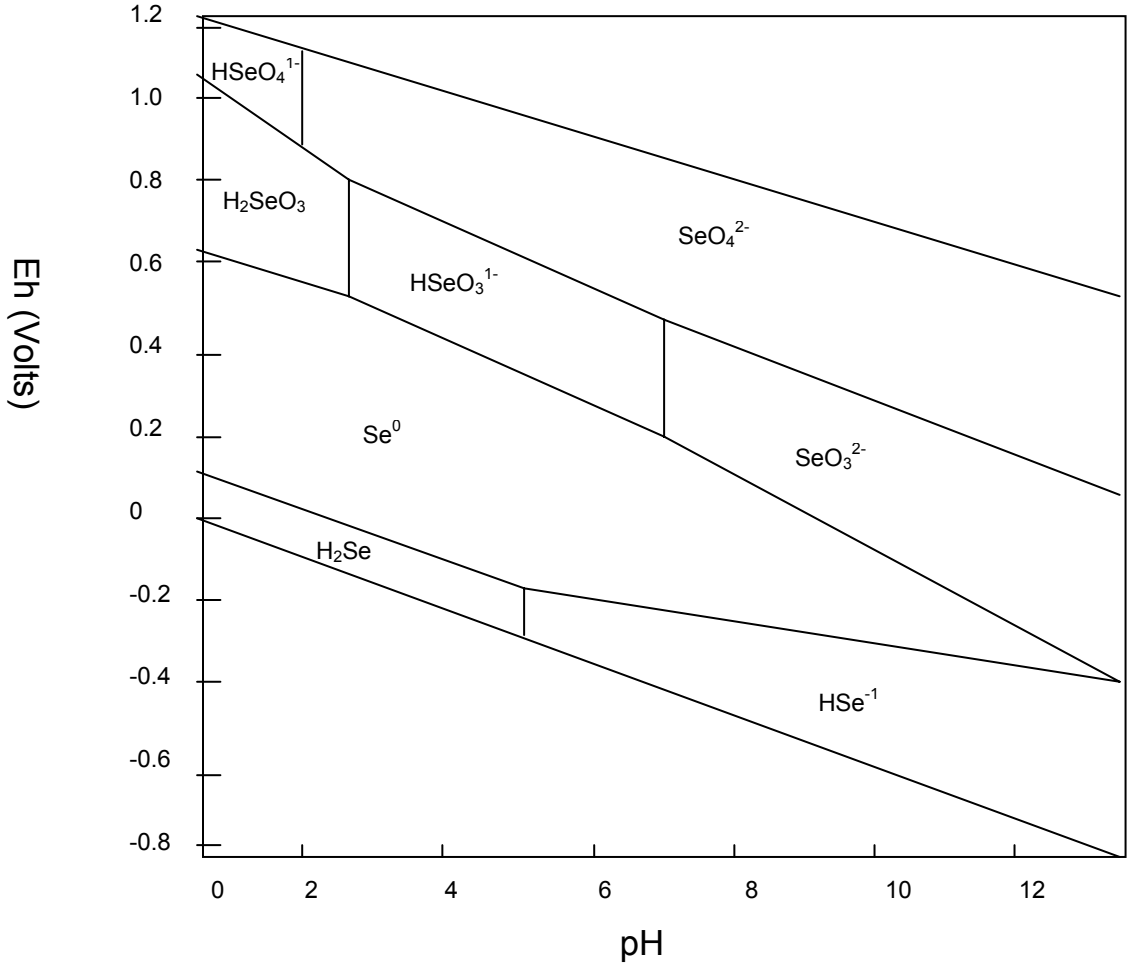


Figure 6 Selenium Eh: pH Speciation Chart.

In the extraction trench it is expected that selenium will be electrochemically reduced in the reaction cell containing ZVI to some degree. The highly reducing microenvironments present in the reaction cell will encourage the transformation of selenate to the less soluble selenite, or further reduction could yield elemental selenium or selenium sulfides. Another mechanism for selenium removal is the adsorption onto iron oxides and coprecipitation in the settling/oxidation pond.

Constructed wetlands have been shown to be quite effective at transforming selenium to insoluble species. The last treatment component in the passive integrated treatment system is a vertical flow constructed wetland containing a thick layer of organic material.

The long retention time and reducing conditions of the constructed wetland will remove much of the remaining water borne selenium.

It is well known that mercury reacts with sulfur to create stable complexes. Mercury has a high affinity for sulfur; similarly, mercury and selenium have a high affinity for one another and form stable complexes. In nature, and physiologically, sulfur is present in far greater quantities than selenium; yet mercury selectively binds to selenium due to the higher affinity of mercury selenium complexes. The compounds formed from reaction of mercury and selenium are ionic mercury selenides which have extremely low water solubility. The interaction between mercury and selenium has been considered a protective phenomenon, by which dietary selenium complexes mercury preventing the toxic effects associated with otherwise toxic exposure to mercury. The ability of selenium to decrease the toxic effects of mercury has been observed in species of mammals, birds, and fish.

Methylmercury has the ability to cross the blood-brain barrier and exhibits long-term retention once it gets across the barrier. Methylmercury's high affinity for selenium may enable it to sequester selenium in the brain and diminish selenoprotein synthesis. Mercury selenide precipitates have extremely low solubility rendering the complexes metabolically inert. It becomes apparent that the interaction between mercury and selenium affects the bioavailability of both substances. That is, mercury sequesters selenium and selenium sequesters mercury.

Several studies report on the role of selenium in the bioaccumulation of mercury in fish. Selenium amendments to Swedish lakes resulted in a 75%-85% reduction in mercury levels in fish measured over a three year period. Elimination of fly ash discharges rich in selenium to Rogers Quarry in Tennessee in 1989 resulted in a steady increase in mercury concentrations in fish. The aqueous selenium concentrations in the quarry decreased from 25 μg/L to < 2 μg/L. The mean selenium concentrations in bass declined from 3 mg/kg to 1 mg/kg over the first five years; then remained at 1-1.5 mg/kg for the remaining three years of study. During this time the mean mercury concentrations in bass rose from 0.02 mg/kg to 0.61 mg/kg.

Mercury Chemistry

Mercury is not known to be as essential element for any organism. The primary sources of mercury include the weathering of mercury ores, the manufacture of chlor-alkali, and the combustion of fossil fuels.

Mercury is present in coal combustion products at low concentrations ranging from 0 to 12 μg/g. The low concentrations found in ash pond and FGD pond effluents reflect the low mercury content of coal combustion products. Mercury concentrations of 4.8 and 18 ng/L have been reported for ash pond and FGD pond effluents, respectively.

Mercury occurs in the environment in three oxidation states: elemental mercury Hg(0), the relatively insoluble Hg(I), and the soluble Hg(II) (Figure 7). Elemental mercury is volatile and can be released to the atmosphere from reduced aquatic sediments. Mercury

in the solid and liquid phases exists primarily in the Hg(II) oxidation state under natural environmental conditions. In anaerobic sediments mercuric ions are biomethylated by microorganisms to some degree resulting in the formation of trace levels of monomethylmercury and dimethylmercury which are more toxic than the more prevalent mercuric compounds. Monomethyl mercury is bioaccumulated in aquatic ecosystems. Fish have been found to have mercury bioconcentration factors of 1,000,000 to 3,000,000 compared to aqueous concentrations of mercury (Zillioux et al., 1993).

Divalent mercury can be removed from water by adsorption onto manganese oxides (Lockwood and Chen, 1973) and iron oxides. Adsorption of mercury is dependent on the species present. $HgCl_2$ is the most predominant species in acidic solutions and chloride solutions, but is only weakly bound to most oxides and hydroxides. $Hg(OH)_2$ is readily adsorbed onto oxides of iron and manganese. In reducing environments, mercury solubility is controlled by the formation of insoluble cinnabar, HgS. However reducing conditions are optimum for the biological methylation of mercury to more toxic species.

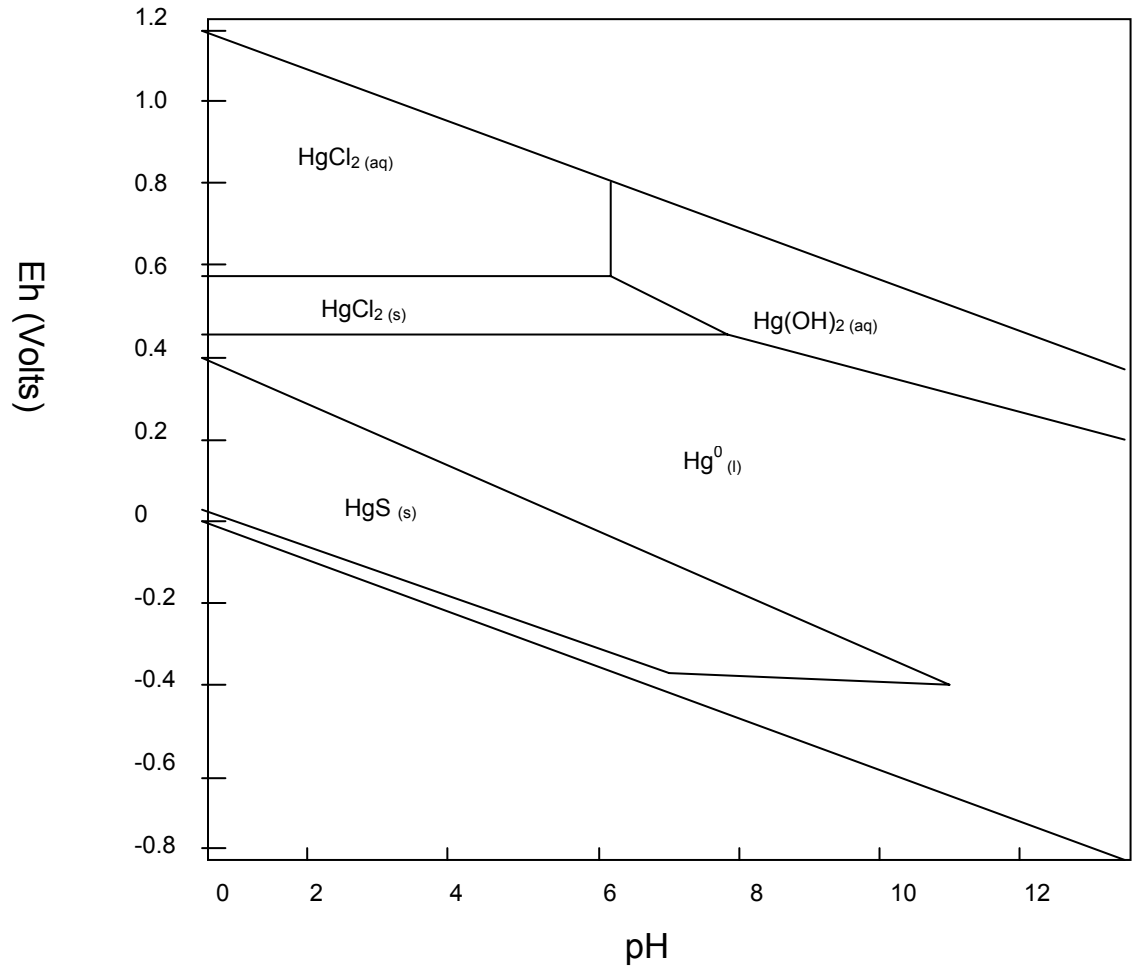


Figure 7 Mercury Eh: pH Speciation Chart.

In the passive integrated treatment system, it is believed that mercury could be transformed in the reaction cell containing ZVI to less soluble species or adsorbed onto the reactive iron surfaces of ZVI. Divalent mercury compounds reduced to elemental mercury could be volatilized. In the settling/oxidation basin, water-borne divalent mercury could adsorb onto iron oxides and be transferred to the solid phase. The reaction cell and settling/oxidation basin together act as a sink for mercury to lessen the mercury loading to the constructed wetland. Constructed wetlands create the necessary environmental conditions (i.e. high organic content, low dissolved oxygen, reducing conditions) for biological mercury methylation to occur.

Zero-Valent Iron Chemistry

ZVI is widely used in remediation projects because it is inexpensive, nontoxic, and it is a powerful reducing agent (Matheson and Tratnyek, 1994). ZVI has been used in permeable reactive barriers PRBs for the remediation of groundwater containing halogenated organic compounds (Gillham and O'Hannesin, 1994; Roberts et al., 1996; Johnson et al., 1996) and metals such as hexavalent chromium (Powell et al., 1995; Pratt et al., 1997; Astrup et al., 2000). Metals such as mercury (Namasivayam and Senthilkumar, 1997; Anacleto and Carvalho, 1996; Grau and Bisang, 1995) and metalloids such as arsenic (Su and Puls, 2001; Lackovic et al., 2000) and selenium (Yodnane et al., 1992; Merrill et al., 1986; Rast, 1998) have also been shown to adsorb onto iron and iron oxyhydroxides. ZVI is readily oxidized in the presence of water and oxygen resulting in the generation of iron oxides and hydroxides. A variety of metals and metalloids can be removed from water by coprecipitation with the insoluble iron oxides and hydroxides. Iron coprecipitation is often used for removing metals and metalloids such as arsenic, selenium, mercury, aluminum, cadmium, chromium, lead, nickel, thallium, and zinc from wastewater (Rast, 1998; Brewer and Passmore, 1994) Iron coprecipitation has also been used to remove arsenic and selenium from fly ash leachate (Yodnane et al., 1992), and ash pond effluent (Merrill et al., 1986).

ZVI has been shown to chemically reduce oxo-anions. Under near neutral pH (~7) and aerobic conditions, NO_3^-, BrO_3^-, and ClO_3^- were electrochemically reduced by ZVI in batch and continuous-flow packed column experiments. Mass balances provided strong evidence that ammonia is the primary reduction by-product from nitrate, chloride from chlorate, and bromide from bromate (Westerhoff, 2003). Similarly, oxo-anions of sulfur, arsenic, and selenium may be chemically reduced at the surface of ZVI, a consequence of reductive precipitation or coprecipitation reactions on the surfaces of the iron.

A number of secondary mineral formations have been shown to form on the surfaces of ZVI. The secondary phases formed on the surface of the ZVI have been characterized under several experimental conditions and by several different analytical methods (Kendelewicz et al., 2000; Satapauajaru et al., 2000; Sass et al.,1998; Blowes et al., 1997). These secondary phases include magnetite (Fe_3O_4), green rust [$FeII_4FeIII_2(OH)_{12}SO_4 \cdot H_2O$], goethite (FeOOH), and ferric hydroxide [$Fe(OH)_3$]. Minerals with Fe in a lower oxidation state, such as magnetite and green rust, are generally found near the ZVI, whereas minerals with Fe in a higher oxidation state, such as goethite, are generally found closer to the water interface (Pratt et al. 1997). A number

of carbonate minerals, including calcite ($CaCO_3$), aragonite ($CaCO_3$), and siderite ($FeCO_3$) are also commonly reported on the surfaces of ZVI.

The reactivity of ZVI varies greatly as its surface becomes coated with secondary mineral coatings formed when ZVI is oxidized (Sass et al., 1998; Scherer et al., 1998; Johnson et al., 1998; Pratt et al., 1997). As the ZVI surfaces become increasingly covered with secondary precipitates the removal rates change. For instance, Sass et al. (1998) reported that the half life of TCE degradation in a ZVI column increased from 2.0 to 2.6 hr after 35 pore volumes had been passed through the column. Satapanajaru et al. (2000) reported that although the reaction rates may initially decrease, they eventually increase again over extended durations. They attributed this chemical behavior to the semiconductor nature and the increased adsorptive capacity of the solid phase as magnetite and green rust are formed (Scherer et al., 1998). In the extraction trench design, it is believed that flow fluctuations due to weather events will help to physically remove loose iron oxyhydroxide particles from ZVI surfaces in the reaction cell and convey those particles to the settling/oxidation basin for long-term storage. Air or pressurized water can also be used to break up any build-up of iron oxides in the reaction cell as a part of routine maintenance of the system.

The purpose of the ZVI in the extraction trench design is two-fold. First, ZVI acts as a reactive surface for electrochemical reduction of targeted chemical species. Some chemical species will be reduced to less soluble forms at the iron surface or become permanently incorporated into various mineral phases that form on the surface of ZVI. Secondly, the ZVI acts as a slow release form of iron oxides. The FGD water stream is high in oxygen which will encourage the ZVI to rust (Figure 8). These iron oxides will be conveyed to the settling/oxidation basin over time for long term storage.

Figure 8 Partially Oxidized ZVI in Limestone Substrate

EXPERIMENTAL

Mechanisms of Pollutant Removal

Passive water treatment systems such as the ATOXIC and ASSET systems rely on physical, chemical, and biological mechanisms to trap, store, and transform pollutants in different environments.

Biological Nitrification

Nitrification is the bioprocess of oxidizing ammonium ion (NH_4^+) to nitrate with nitrite as an intermediate product. The microorganisms responsible are the autotrophic species *Nitrosomonas* and *Nitrobacter*. The two reaction steps are:

Step I: by *Nitrosomonas* $2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2\,H_2O$

Step II: by *Nitrobacter* $2NO_2^- + O_2 \rightarrow 2NO_3^-$

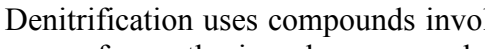
The biochemical reaction rate of *Nitrobacter* is greater than the *Nitrosomonas* reaction, and since no accumulation of nitrite occurs in the process, the reaction rate of *Nitromonas* will control the overall speed of the process. The alkalinity is a very important factor for nitrification. The pH sensitivity of nitrification is very acute, and the optimal pH range is shown to be a fairly narrow window from 7.2 to 8.6. Also, the nitrification reaction has an almost linear temperature dependence.

In the integrated passive treatment system, trickling filters are used to provide a matrix for fixed-film growth of nitrifying bacteria. Water distributed on the top of the limestone gravel matrix moves passively via gravity downward through the gravel, and ammonia is converted to nitrate by contact with the biofilm coating the gravel. Laboratory-scale studies were initially conducted to assess the applicability of trickling filters for FGD wastewater treatment, and to determine the design parameters for the field-scale trickling filters in the integrated passive treatment system. Experimental results showed that FGD water from the Paradise Fossil Plant, which can be toxic to biological organisms, did not inhibit the nitrifying bacteria in trickling filters. FGD water augmented with 20 mg/L NH_4-N required a trickling filter 4 feet deep and filled with ¼ inch diameter limestone gravel to reduce the NH_4-N concentration to zero, which was the performance target for the trickling filters. Trickling filter depths less than 4 feet deep did not provide sufficient contact time with nitrifying bacteria to meet the target reduction of 20 mg/L NH_4-N to 0 mg/L at flow rates that simulated the expected rates for the field-scale demonstration. Gravel larger than ¼ inch diameter limestone and several types of plastic crossflow modular matrixes did not have sufficient surface area for adequate nitrifying biofilm growth. Boron concentrations of 50-70 mg/L in the FGD wastewater were not reduced by the trickling filters.

Iron Coprecipitation

Iron coprecipitation is widely used as an industrial process for removing solids and metals from water streams. In the iron coprecipitation process, ferric salts are added to

the water stream and an iron oxyhydroxide precipitate is formed which then settles from solution.



$$FeCl_3 + 3\ H_2O \leftrightarrow Fe(OH)_3 \downarrow + 3\ H^+ + 3\ Cl^-$$

Metals and oxyanions are trapped within the oxyhydroxide floc and coprecipitated, or are adsorbed onto the precipitate and removed from the water matrix. Adjusting the pH and the iron dose can make it possible to remove a variety of metals using iron coprecipitation.

Iron coprecipitation often includes a coagulation step in which a chemical polymer is added to the water stream to aid in particle building. Chemical polymers allow individual iron oxide particles to stick together. Flocculation involves mixing so as to maximize interactions between particles, allowing the formation of larger particles that settle rapidly.

In the passive integrated treatment system, iron coprecipitation occurs passively as ZVI rusts in the reaction cell. Iron hydroxide forms on the surfaces of ZVI grains in the substrate. Occasionally, during periods of increased flow, loose iron hydroxide particles slough off and are conveyed to the settling/oxidation basin for storage.

Biological Denitrification

Denitrification uses compounds involving BOD (biological oxygen demand) as a carbon source for synthesis and energy, and nitrate as an oxygen source.

$$NO_3^- + BOD \rightarrow N_2 + CO_2 + H_2O + OH^- + \text{new cells}$$

The denitrification process consumes about 3.7 g COD (carbonaceous oxygen demand) per g NO_3-N reduced, and produces 3.57 g alkalinity that is used during the nitrification, although some of the alkalinity is lost by reacting with CO_2 generated by the microbial respiration.

Anaerobic vertical-flow wetlands are being used as the final component in the field-scale demonstration for denitrification of the FGD wastewater. The gravel matrix of the constructed wetlands provides the necessary surface area for growth of the denitrifying bacterial biofilm. Laboratory-scale studies indicated that, similar to the trickling filter laboratory studies, FGD water did not inhibit bacterial activity in the constructed wetlands. Compost and hay were both a good source of carbon for denitrification. Compost supplies a readily available source of carbon, but long-term use can exhaust the available carbon and lead to decreased rates of denitrification. Hay maintained dentrification for a longer period, but carbon is released more slowly. For these reasons, both compost and hay are being used in the field-scale demonstration, as described below in the Design Criteria section, until plant growth and biomass accumulation can provide a continuous source of carbon to the wetlands. Laboratory-scale studies were also used to determine the retention time needed to remove NO_3^- from the FGD wastewater.

Sulfate Reduction

In anaerobic wetlands sediments, oxidized forms of sulfur are reduced to hydrogen sulfide by bacteria such as *Desulfovibrio desulphuricans* which use sulfate as a hydrogen acceptor (Kadlec and Knight, 1996). Several metals form insoluble sulfides under these conditions including iron, zinc, cadmium, lead, nickel, mercury and selenium. High concentrations of free sulfide due to sulfate reduction reactions may cause precipitation of sulfide minerals with metalloids such as arsenic and selenium, including As_2S_3 , FeAsS, and SeS, removing these environmental pollutants from solution (Rittle et al., 1995; EPRI, 1987; Smedley and Kinniburgh, 2002).

In the passive integrated treatment system, sulfate reduction primarily takes place in the constructed wetland treatment component.

Design Criteria

Two parallel treatment trains exist in the passive treatment system. Treatment 1 consists of trickling filters for biological nitrification and vertical flow constructed wetlands for biological denitrification and removal of metals (Figure 9). Treatment 2 consists of trickling filters for biological nitrification, ZVI extraction trench cells for enhanced removal of arsenic and mercury, settling/oxidation basin for collection of iron oxides, and constructed wetlands for biological denitrification and removal of metals.

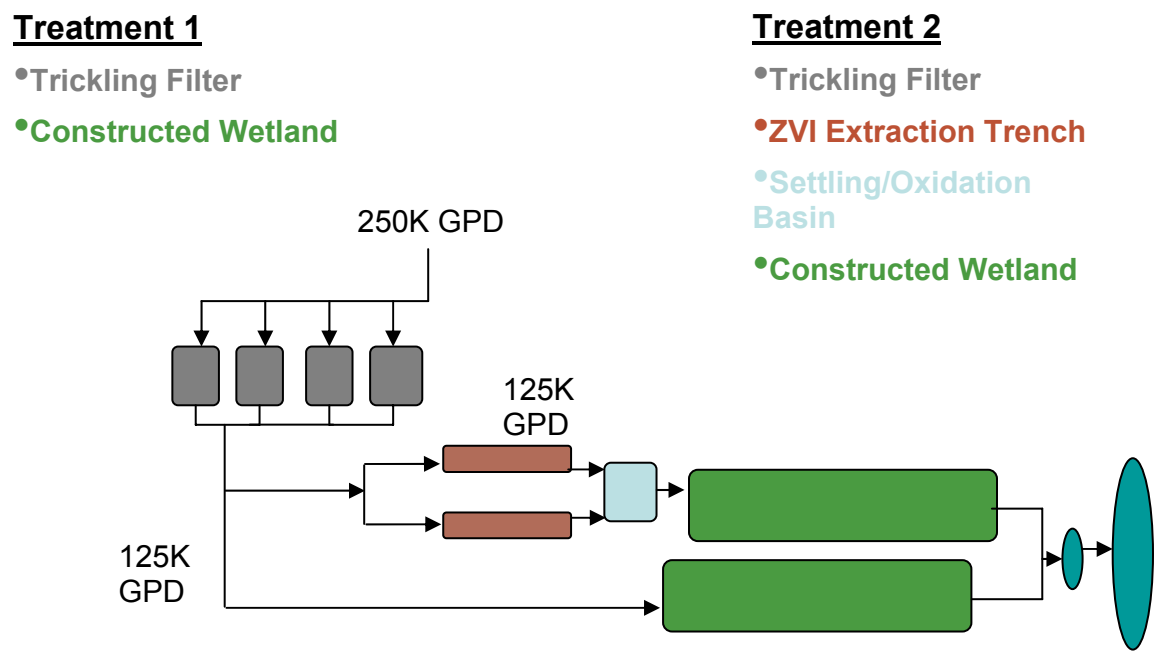


Figure 9 ATOXIC (Treatment 1) and ASSET (Treatment 2) Experimental Treatments

The target flow rate is 250,000 gallons of FGD water per day into the system measured at the FGD influent. The flow is split into four equal streams at the trickling filters. The trickling filter effluents are recombined and conveyed to the splitter box via an aerial pipeline. At the splitter box the FGD stream is divided into two equal flows of approximately 125,000 gpd. One stream flows directly to the ATOXIC wetland (CW 1) while the other stream is further divided and flows into two ZVI extraction trench cells. This stream then flows into the settling/oxidation basin through open channel flow and into the ASSET wetland (CW 2) through open channel flow.

Trickling Filters

The removal of ammonia from the wastewater stream is accomplished through biological oxidation of ammonia to nitrate (nitrification) in the trickling filters (Figure 10). The influent wastewater stream is split into four streams of equal volume, with each stream going to one of four trickling filters.

Figure 10 Trickling Filters

Four trickling filters provide replication of the wastewater treatment, and also allow different operating parameters and treatments to be applied to individual trickling filters. Each trickling filter consists of a gravel bed 4 feet deep, 60 feet long, and 30 feet wide, with 2:1 sloped berms. The beds were backfilled with 0.25 inch diameter crushed

limestone chips and lined with a 60 mil HDPE smooth liner, which was covered with geotextile fabric to prevent puncture of the liner by the gravel. Initially, perforated 4-inch diameter polyethylene drain pipe laid on the surface of the gravel bed was used to distribute water at a rate of 35 gal/ft^2/day. Water distribution across the area of the trickling filters was uneven, and the pipes became clogged with solids. The 4-inch drain pipe was replaced with 6-inch polyethylene pipe which was then drilled with a predetermined number of 1/8" diameter holes to distribute the water more evenly across the surface of the trickling filters. This modification was successful; however some maintenance is necessary as the small diameter holes become slightly plugged with scale over time and must be gently tapped with a hammer or other device to remove the plugging periodically.

Water moves downward through the gravel in each trickling filter and is collected in 8-inch diameter perforated underdrain pipes at the bottom of the trickling filter bed, and then moves to a concrete collection box at the end of the trickling filter. Effluent from all of the trickling filters is collected in a common outflow drain pipe and is conveyed across the natural wetland area via an aerial pipeline to a concrete splitter box (Figue 11). The stream is then split into two equal volumes of 125,000 gpd each, with one stream going to the ZVI reaction cells, and the other stream going to one of the vertical flow constructed wetlands.

Figure 11 Aerial Crossing from Trickling Filter Effluent

Zero-Valent Iron Reaction Cells

The wastewater stream diverted in the concrete splitter box to the ZVI reaction cells is further split into two equal streams and is distributed across the front section of two zero valent ion extraction trench cells (Figure 12). An H-shaped header constructed from 6" diameter PVC and polyethylene pipe predrilled with ¼" diameter holes is used to distribute water.

Figure 12 ZVI Extraction Trench Cells

The design features two reaction cells each 25' x 100' with 2:1 sloped berms. The depth of the cells is five feet with three feet of substrate, leaving two feet of freeboard. The cells were formed using cut and fill from the site and lined with a 60 mil polyethylene liner and overlying geotextile mat.

The substrate materials consist from the bottom up of: limestone rip-rap (clean, 6-10" diameter, 12" depth), limestone (2-4" diameter, 12" depth), medium limestone (3/4" diameter, 10" depth), and limestone chips (1/4-1/2" diameter, 2" depth).

Zero-Valent Iron (ZVI) from Peerless Metals (Detriot, MI) was applied at an average rate of 2.4 lb/ft^2 (60 tons/acre) to the surface of the cells. ZVI was applied at 3.6 lb/ft^2 over the front 1/3 of the cell, 2.4 lb/ft^2 for the middle 1/3 of the cell, and 1.2 lb/ft^2 for the back 1/3 of the cell. The ZVI media was granular and was shipped on pallets in 50 lb bags for easy handling. One hundred bags were placed on the front 1/3 of the cell, sixty-seven bags were placed on the middle section of the cell, and thirty-three bags of ZVI were placed on the back 1/3 of each extraction trench cell (Figure 13). Once the bags were placed in the cells, they were opened and spread evenly. Then, the ZVI was worked down into the upper layers of the limestone using a rake.

Figure 13 Installation of Zero-Valent Iron in Extraction Trench Cells

Water level control structures regulate flow out of the reaction cells. The water level is maintained at the surface of the iron filings so as to keep the ZVI wet at all times. This is imperative in order to prevent the ZVI from cementing. The water control structure is adjustable so that the entire cell can be drained rapidly for flushing if necessary. The reaction cells feature overflow pipes to accommodate heavy rain events. The theoretical hydraulic retention time of the reaction cells assuming a porosity of 35% and an average flow rate of 62,500 gpd is 7.5 hours.

At the influent end of each ZVI extraction trench cell where the ZVI loading rate is highest, aeration headers were installed in the gravel substrate so that pressurized air could be used to periodically free up void spaces in the gravel:iron substrate (Figure 14). A total of four star-shaped aeration headers each with 80 feet of ½" diameter PVC are buried in the ZVI extraction trench cells.

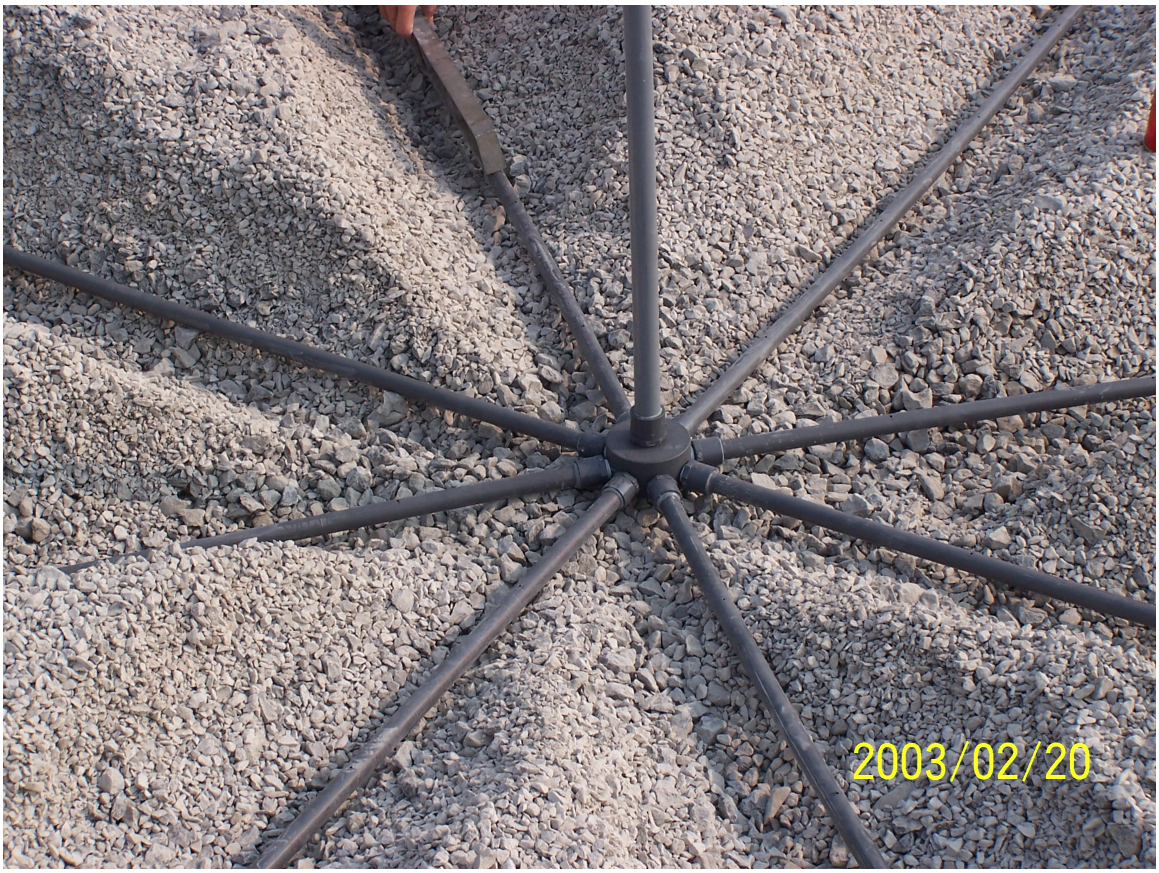


Figure 14 Installation of Aeration Headers (1 of 4) in ZVI Extraction Trench Cells

A windmill aerator was installed at the site to deliver pressurized air to the four aeration headers that were previously installed in the ZVI extraction trench cells and to provide aeration for the settling/oxidation basin (Figure 15). This proved to be a low-cost solution for "passively" using pressurized air to open channels within the gravel:iron substrate to prevent plugging of the substrate without having to use electricity at the site. Solar panels were utilized to charge a 12 V battery. This powers the electronics that control the system of solenoid valves which direct the flow of pressurized air through the different zones on timed intervals. If the wind is not blowing at optimum speeds a pressure tank builds up air pressure and releases it suddenly to create a burst of pressurized air to scour the gravel:iron substrate.

Figure 15 Windmill Powered Aeration System

The purpose of the reaction cell is two-fold. First, the reaction cell allows the wastewater to come in contact with iron surfaces where adsorption reactions take place. Also, the reaction cell introduces a slow release form of iron to the wastewater stream as ZVI readily oxidizes in the presence of water and oxygen. Iron oxides have tremendous surface area for binding trace elements such as arsenic, mercury, and to a lesser extent selenium.

Installation of ZVI and ZVI Loading Study

Immediately following installation of the ZVI in the extraction trench cells, water samples were collected from the ZVI extraction trench weirs after 1 hour, 2 hours, 4 hours, 8 hours, and 24 hours and analyzed for iron and manganese. After 8 hours and 24 hours, water samples were collected from the FGD influent water and the settling/oxidation basin and analyzed for iron and manganese. Field measurements were taken for the parameters pH and dissolved oxygen (DO) as well.

Iron concentrations spiked soon after water came into contact with the ZVI in the extraction trench cells (Figure 16). Twenty-four hours after addition of the ZVI, iron concentrations in the ZVI extraction trench effluents averaged over 1 mg/L while the FGD influent water contained about 0.3 mg/L iron.

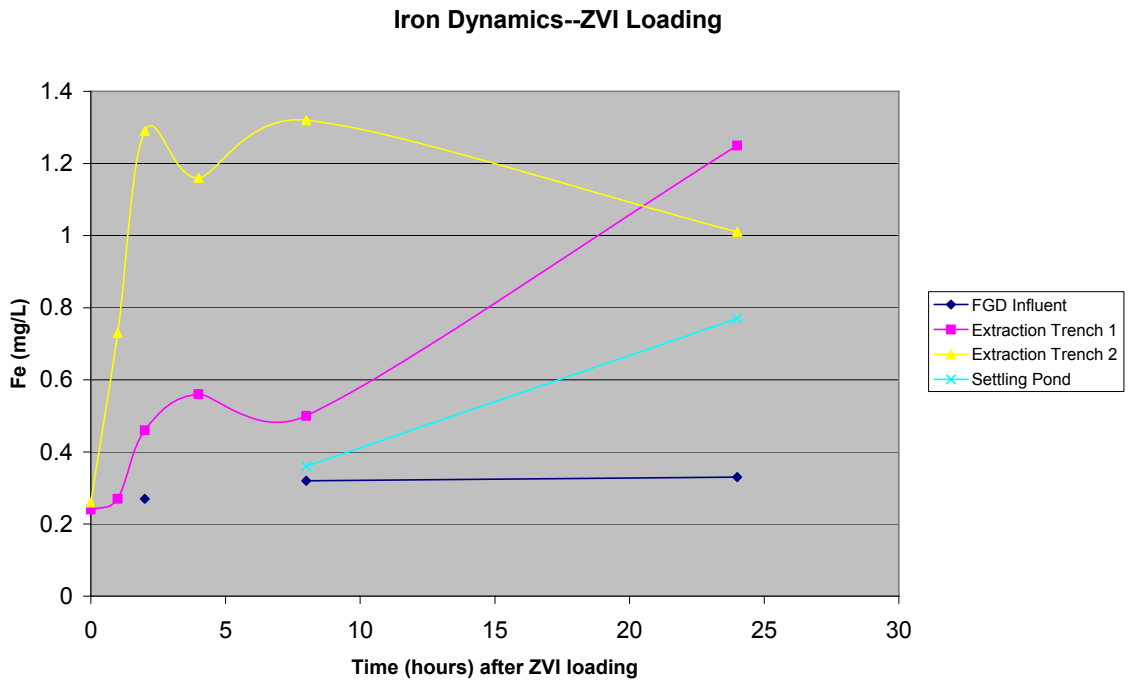


Figure 16 ZVI Loading Study—Iron Dynamics

Manganese trends were similar to the observed trends in iron dynamics soon after the installation of the ZVI in the extraction trench cells (Figure 17). FGD influent water contained an average concentration of 0.02 mg/L manganese while ZVI extraction trench effluents contained an average of 0.15 mg/L manganese 24 hours after the installation of the ZVI.

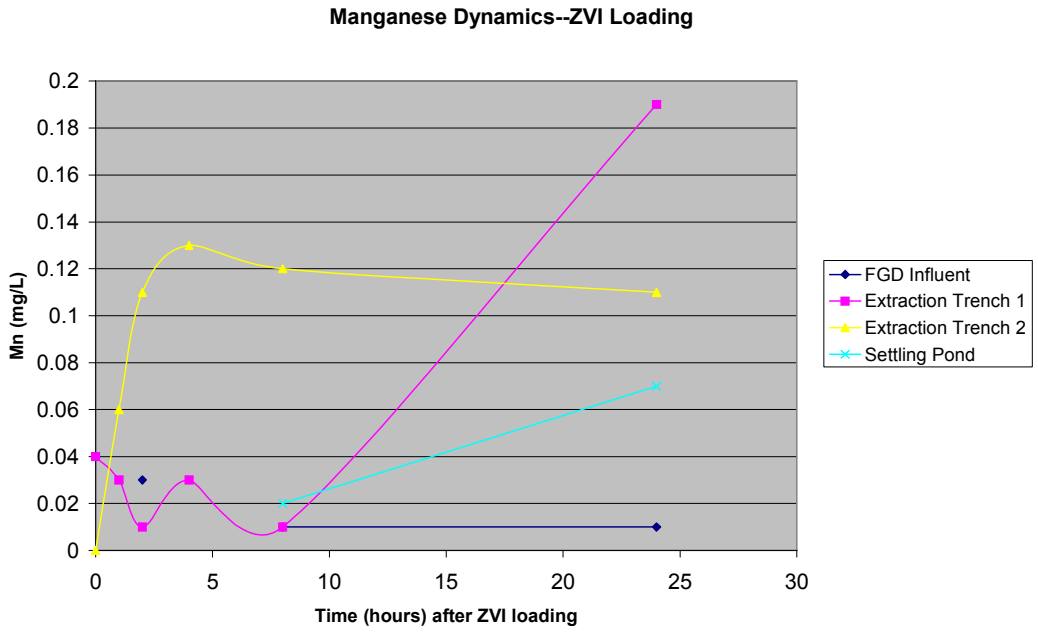


Figure 17 ZVI Loading Study—Manganese Dynamics

Oxygen is required to oxidize ZVI to iron oxides and iron hydroxides; as a result a decrease in the dissolved oxygen was observed in the ZVI extraction trenches immediately following installation of the ZVI (Figure 18). As water flowed through the aerobic environment of the settling/oxidation basin it became resaturated with oxygen.

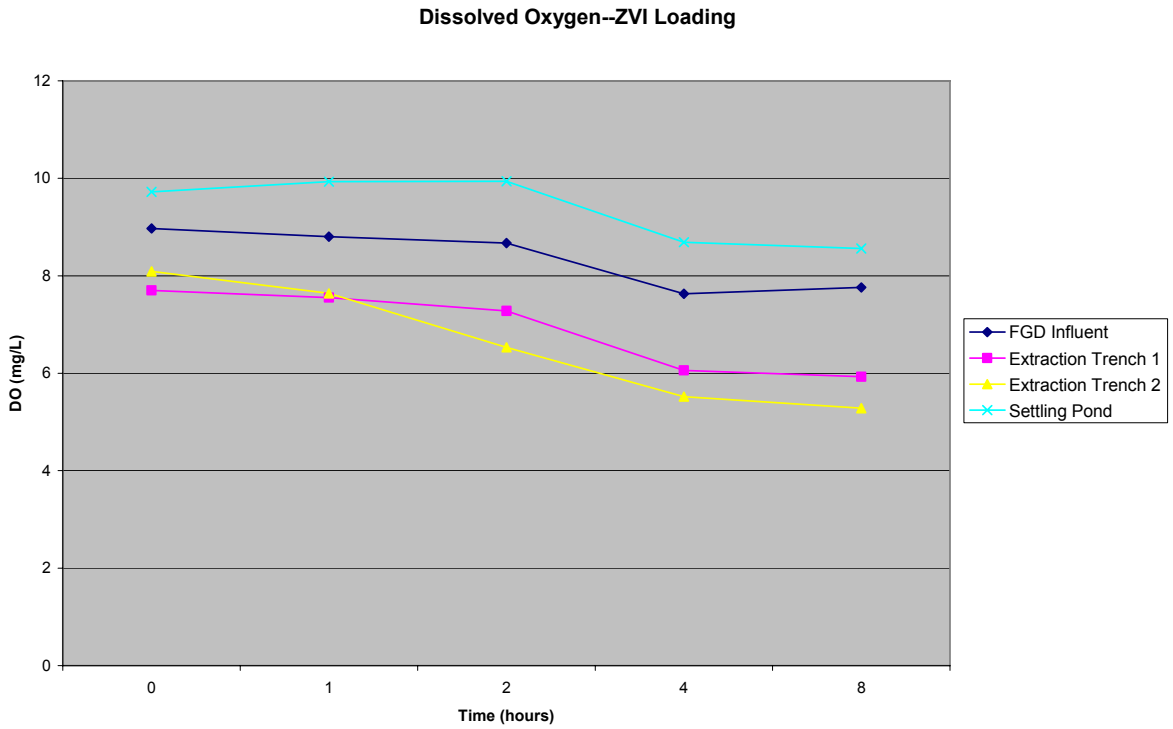


Figure 18 ZVI Loading Study—Dissolved Oxygen Dynamics

Slight increases were observed in pH for field measurements made in the ZVI reaction cells immediately after addition of ZVI to the ZVI extraction trench cells (Figure 19).

Settling/Oxidation Basin

Effluent from both extractions trenches discharges to the settling/oxidation basin through open channel flow. The basin is 35' x 35' and 10' deep, with a 2:1 sloped berm. The water depth is maintained at approximately 8', providing a hydraulic retention time of 24-36 hours at the design flow rate of 125,000 gpd (Figure 20). The design of the system allows for slowly released iron to precipitate from solution and settle in a storage area to minimize plugging in the downstream components. Because the iron oxyhydroxide floc particles have adsorptive properties, the floc generated is allowed to remain in the settling pond for long term storage. The collection of iron oxyhydroxide floc in the settling pond is vital to lasting treatment efficiency of the integrated system. The settling/oxidation basin acts as a long-term sink for the storage of pollutants trapped on iron oxides. As long as the oxidation basin remains an oxidizing environment, iron oxides will be produced and collected in the basin.

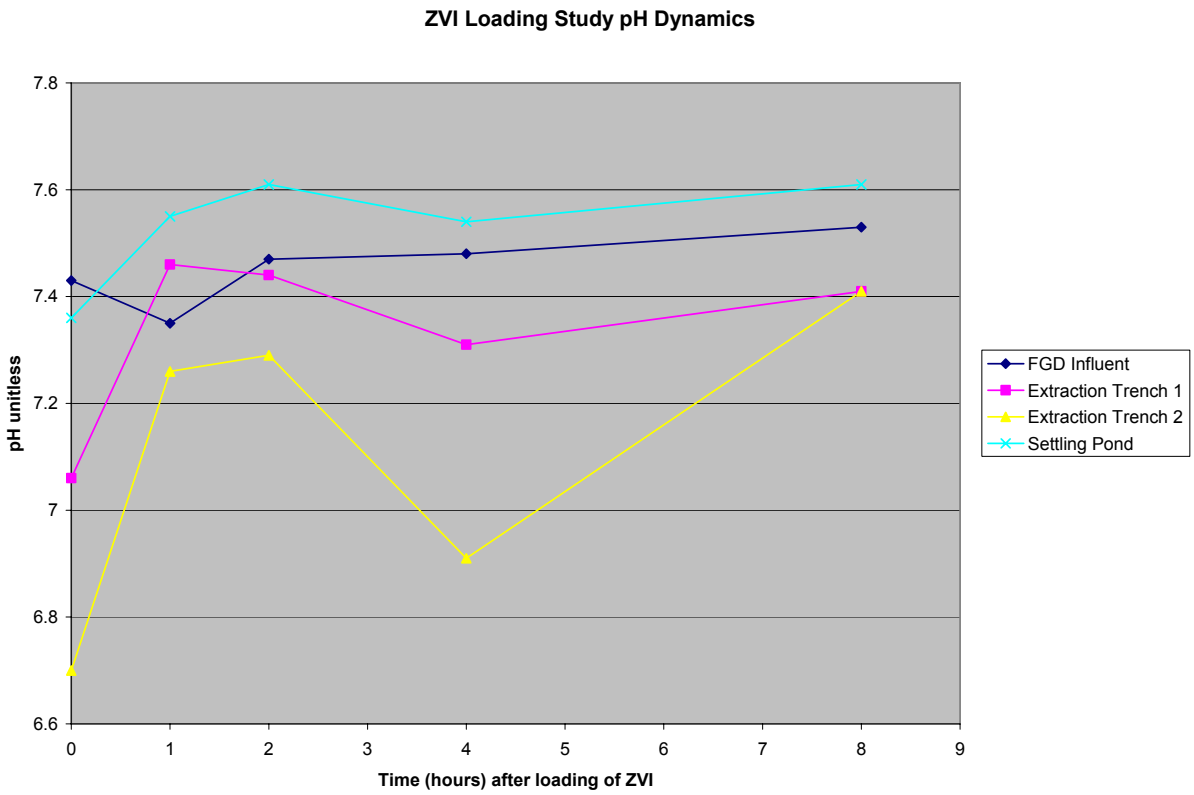


Figure 19 ZVI Loading Study—pH Dynamics

Figure 20 Settling/Oxidation Basin

Vertical Flow Constructed Wetlands

Two vertical flow constructed wetlands provide a reducing environment for biological denitrification and additional metals removal. As described above, the ATOXIC wetlands receive the effluent directly from the trickling filters, and the ASSET wetlands receive effluent from the ZVI extraction trenches. Each wetlands cell is 200 feet long, 65 feet wide, and 8 feet deep, with 2:1 sloped berms (Figure 21). The wetlands cells are side by side, and are divided lengthwise with a block wall. The cells are lined with a 60 mil HDPE smooth liner, which is covered with geotextile fabric. Each vertical-flow wetlands consists of a 2.5 foot deep limestone bed (1-2 inch diameter limestone) under a one-foot layer of organic substrate. During operations a layer of water 1-1.5 feet deep is maintained above the organic layer. Influent water enters into this water layer though a channel or pipe at one end of the bed. Baffles constructed from hay bales extend alternately from each side of the bed on top of the organic layer, and provide dispersion of the incoming water across the width of bed to reduce hydraulic short-circuiting in the wetlands. The water moves vertically down through the organic and gravel layers and horizontally through the length of the cell, and is discharged through an underdrain header at the bottom of the cell at the other end, opposite from the influent. Effluent water from the wetlands is discharged to "Pooh Bear Pond", and ultimately to the main ash pond at Paradise. Inflow to each wetlands is 125,000 gpd and the volume of each cell is 230,000-270,000 gallons, depending on the depth of the water layer on top of the wetlands, resulting in a hydraulic retention time of approximately two days in each vertical flow wetlands. The vertical flow wetlands were planted to aid in denitrification. Soon after construction was completed in the summer of 2005, the constructed wetlands were planted with bulrush, cattails, iris, pickerelweed, and burreed, all of which died shortly after planting. The cells were replanted in April 2006 with bulrush, cattails, iris, pickerelweed, and arrowhead. In mid-May of 2006, FGD water in the cells was drained and the cells were refilled with ash pond water, which is less toxic, until the plants become established. Currently the plants are alive and plant biomass is increasing.

Sampling and Monitoring Plan

The goal of the project is to build a better understanding of the transformations that pollutants such as arsenic, selenium, and mercury undergo as they travel through changing environments such as those provided by a passive treatment system. Water samples will periodically be collected and analyzed for the various chemical species of arsenic, selenium, and mercury to understand these transformations. Two oxidation states of inorganic arsenic will be quantified, as well as two oxidation states of selenium. Mercury analyses will include total mercury as well as methyl mercury. The design of the passive treatment system allows sampling at each treatment component. Replicates of treatment components are included if possible. The sampling plan is designed to delineate the treatment contributions from each component, and allows the comparison of two distinct treatment trains, with and without the extraction trench ZVI component.

Figure 21 Constructed Wetlands ASSET (Left) and ATOXIC (Right)

For the arsenic, selenium, and mercury speciation work, grab samples will be collected monthly from the FGD influent, trickling filter effluent, extraction trench effluent, settling/oxidation basin effluent, and both constructed wetlands effluents for a total of six sampling locations. Samples will be collected by the "clean hands, dirty hands" technique, preserved in the field, chilled, and shipped on the day of collection to a qualified lab for arsenic (III), arsenic (V), selenium(IV), selenium(VI), total mercury, and methyl mercury analyses. Strict QA/QC protocols will be adhered to.

More frequently, water samples will be collected from the FGD liquor and influent, each of the trickling filters, each extraction trench effluent, the settling/oxidation basin effluent, each constructed wetland effluent, a nearby pond that the entire system will discharge to (which ultimately leads to the ash pond), and the ash pond for a total of 13 sampling locations. These water samples will be preserved, chilled, and transported to TVA's laboratories for analyses. Water samples will be analyzed for COD, NH_4-N, NO_3-N, TKN, a suite of metals and trace elements including arsenic and selenium, alkalinity, suspended solids, and dissolved solids.

Water quality sondes will be deployed in each treatment component to continuously monitor pH, dissolved oxygen, conductivity, redox potential (Eh), and temperature.

RESULTS TO DATE

Flow Conditions

FGD water flow through the ATOXIC/ASSET passive treatment system was initiated in October 2005 and continued to the end of April 2006, when the wetland cells were drained and filled with ash pond water to enhance growth of planted wetland species, as discussed above in the *Vertical Flow Constructed Wetlands* section. The target flow rate is 250,000 gallons of FGD water per day into the system measured at the FGD influent. Flows were measured on 11 occasions and averaged 279,000 gpd as measured at the FGD influent diverter box at the FGD channel (Figure 22). Flow was measured at this location as the volume of water flowing over an adjustable V-notch weir gate. Most of the time 0.5 feet of head pressure was observed on the weir, which corresponds to a flow of 286,000 gpd through the system., and is the maximum flow recorded (Figure 23). The minimum flow measured at the FGD diverter box was on 2/23/2006 when a flow of 219,000 gpd was recorded.

Figure 22 FGD Influent Structure

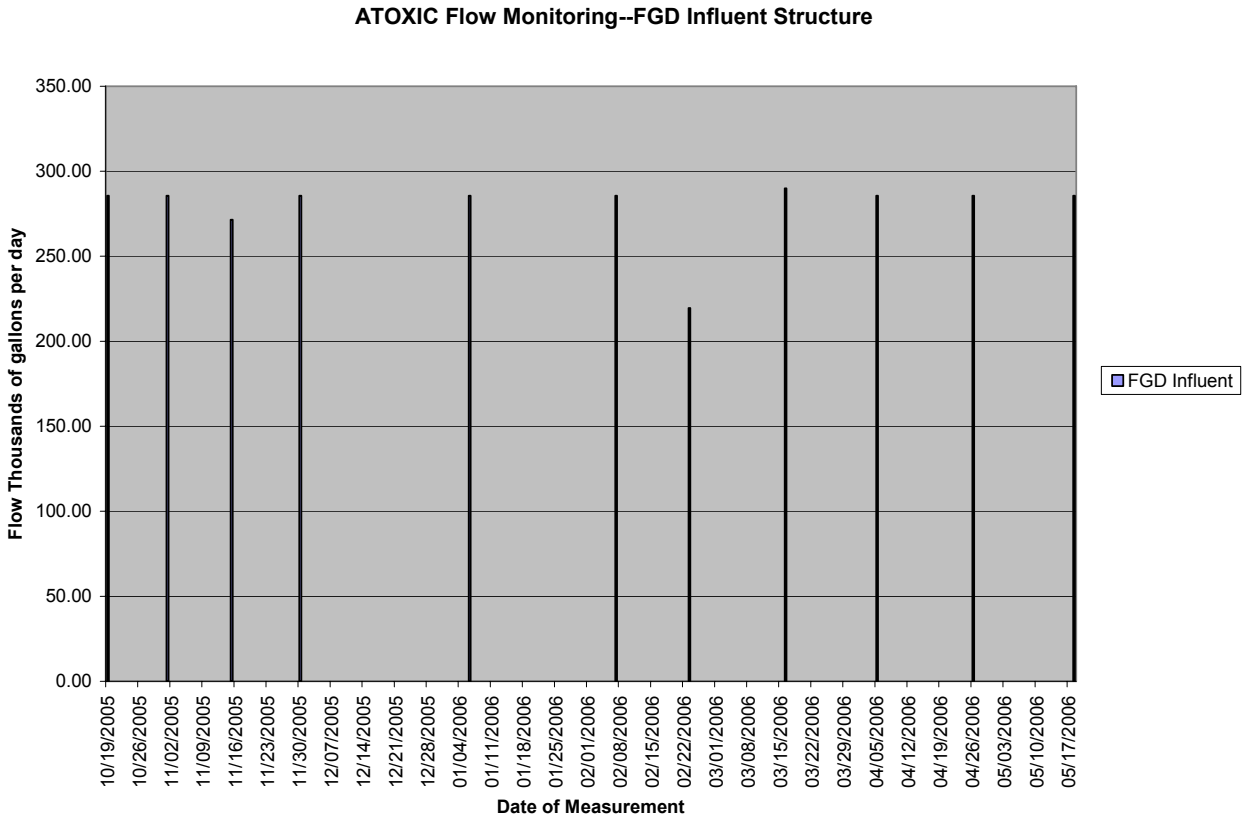


Figure 23 ATOXIC/ASSET Flow Data at FGD Influent Diverter Box

Total influent flow is also measured as the sum of the flows through the four trickling filters. The influent flow from the FGD channel is split into four equal streams, and the flow of each stream is measured in a plume immediately before the stream goes into the trickling filter (Figure 24). This measurement is quite likely more accurate than the FGD influent measurement, since the FGD influent measurement is dependent on an adjustable weir and the trickling filter plumes are fixed. Also, the trickling filter plumes are easy to read compared to the staff plates in the FGD diverter box. Flow averaged 300,000 gpd measured as the sum of the four trickling filter plumes. The minimum flow recorded at the trickling filter plumes was 195,000 gpd on 2/23/2006 (Figure 25). The maximum flow through the system measured at the trickling filter plumes was on 4/26/2006 and was 364,000 gpd.

Figure 24 Trickling Filter Plume (1 of 4)

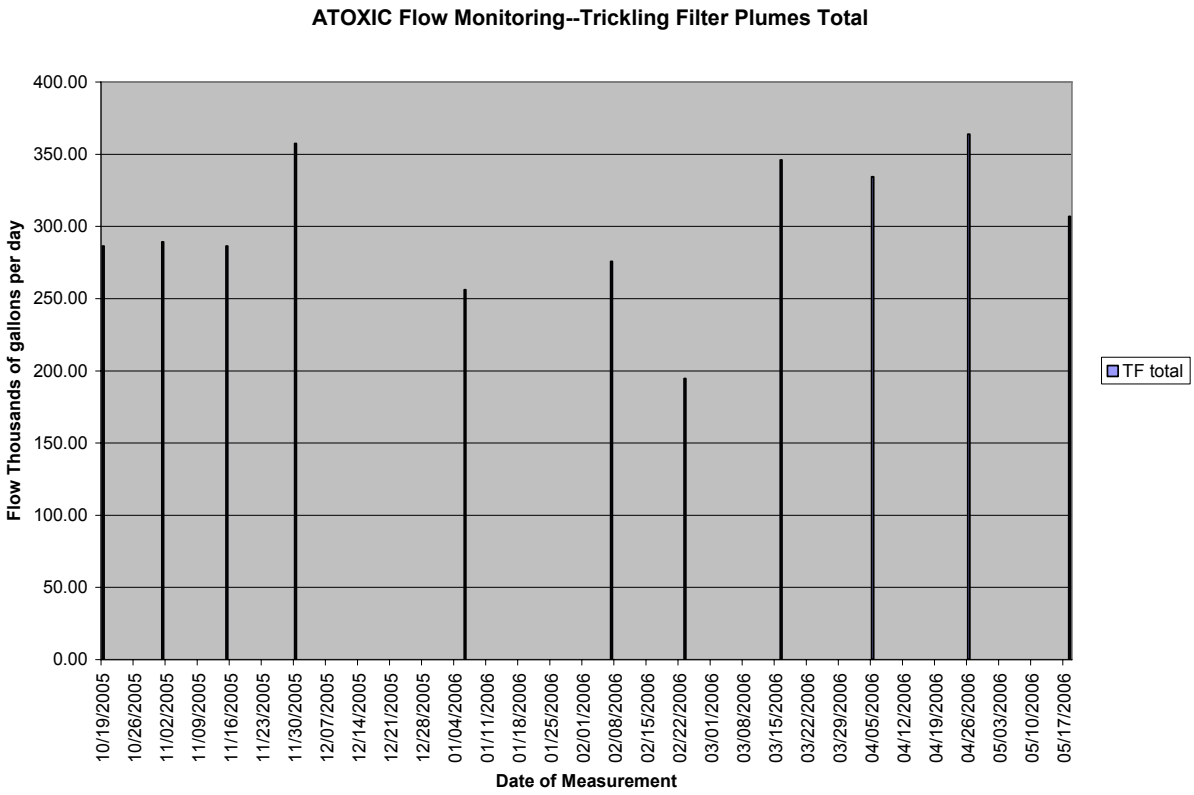


Figure 25 ATOXIC Flow Monitoring Trickling Filter Plumes Total

The difference in the measured flow at the FGD influent diverter box and the measured flow at the trickling filter plumes was monitored as a measure of the accuracy of the influent flow monitoring (Figure 26). The percentage delta averaged -7.1 % for the monitoring periods reported. The FGD influent measurement underestimated the flow through the passive treatment system or the trickling filter plumes overestimated the flow through the system. The percentage delta was greatest on 11/30/2005 and 4/26/2006 when very high flows were observed.

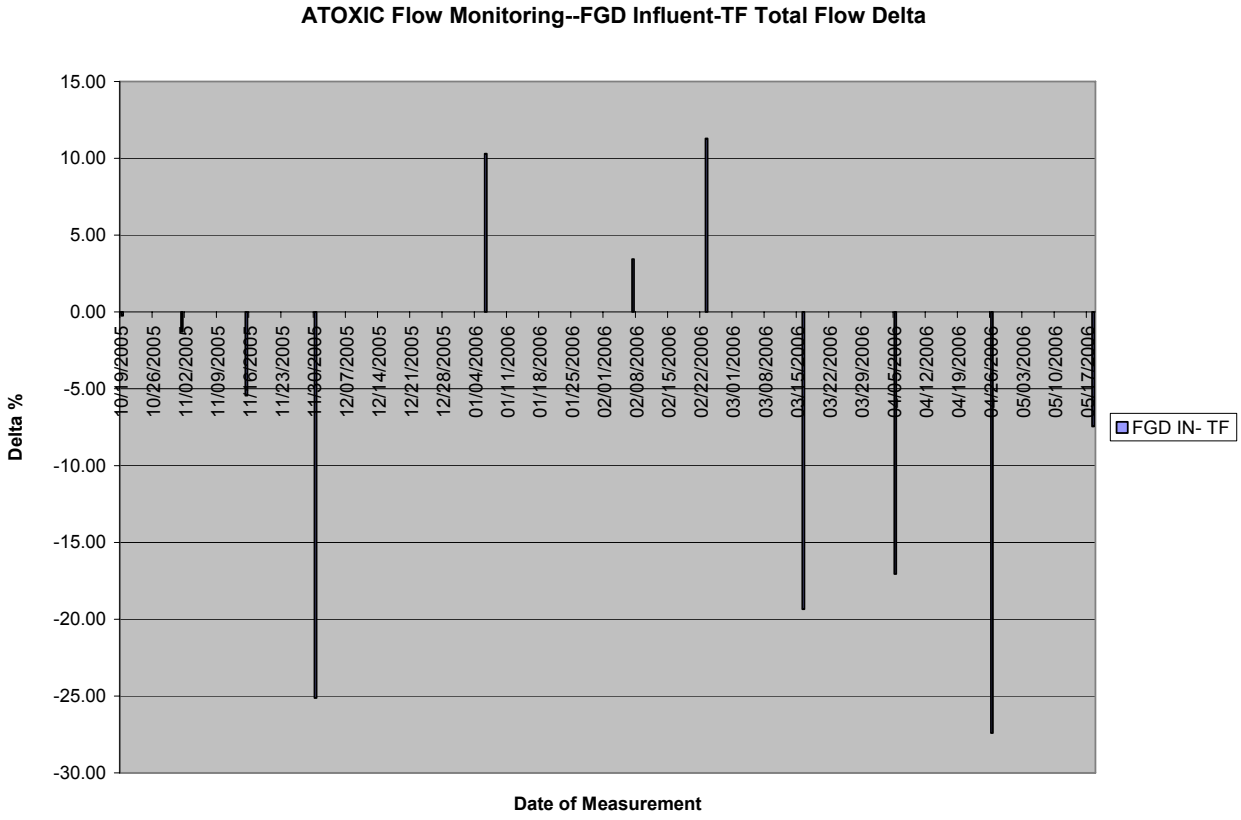


Figure 26 ATOXIC Flow Monitoring FGD Influent-TF Plumes Total Delta %

Flow for the ASSET components of the passive treatment system is measured at the splitter box (Figure 27). The splitter box is a concrete structure that receives the stream of water from the aerial pipeline delivering the combined effluent of the four trickling filters. This stream is split into two equal streams in the splitter box, with one stream providing flow to the two extraction trenches and the other stream going to the ATOXIC wetlands. The average flow measured at the splitter box was 142,000 gpd. The minimum flow measured at the splitter box was 126,000 gpd on 1/6/2006, and the maximum flow was 196,000 gpd on 11/30/2005 (Figure 27).

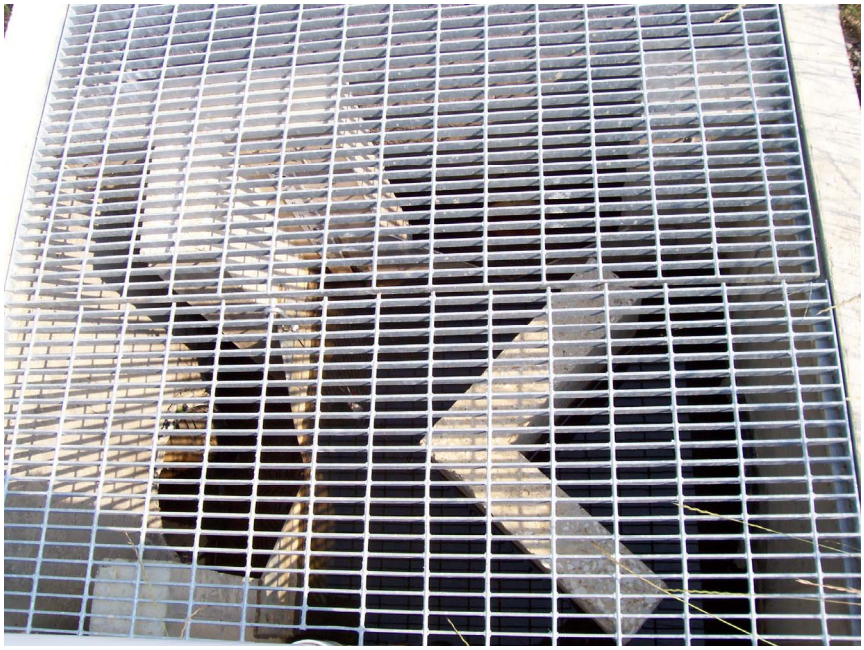


Figure 27 Splitter Box Structure

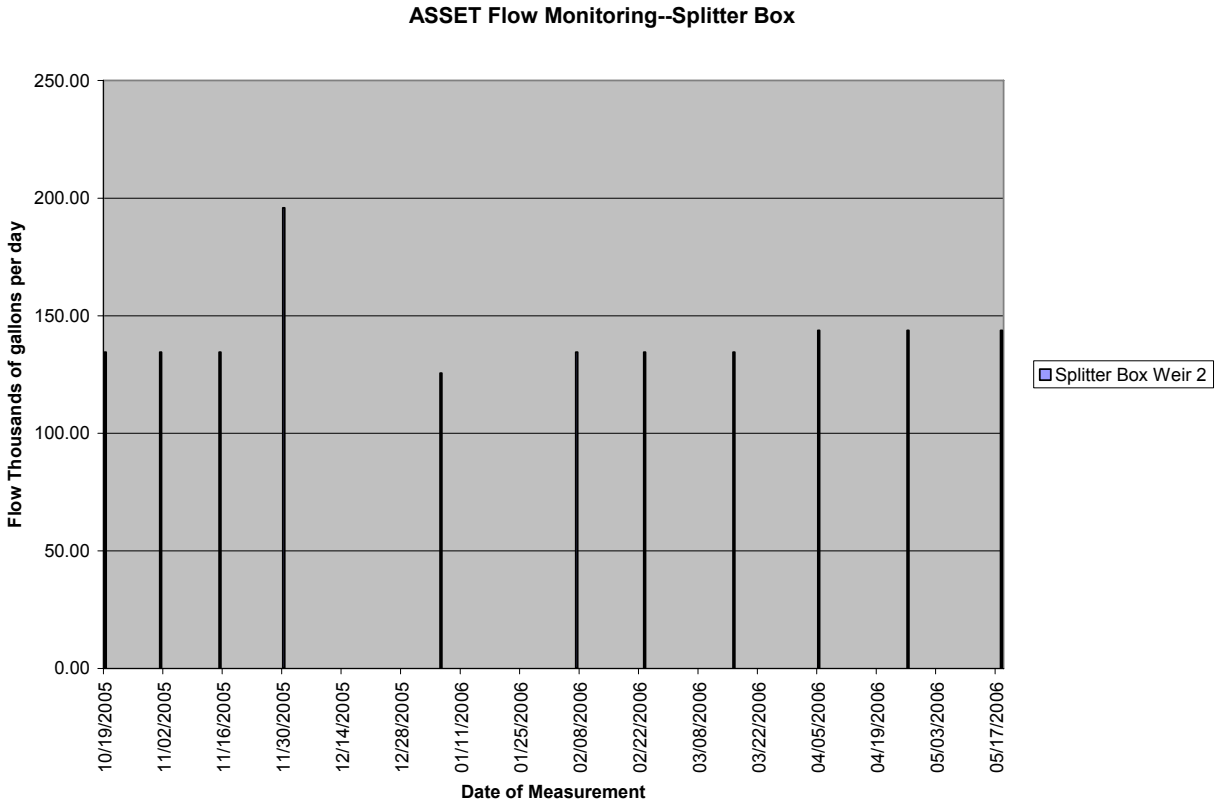


Figure 28 ASSET Flow Monitoring--Splitter Box

The stream for the two extraction trenches coming from the splitter box is again split into two approximately equal streams, with each stream going to an extraction trench. Flow through the ZVI extraction trench cells is measured as water spilling over a rectangular notch in a weir at the outflow of each cell (Figure 29). ZVI extraction trench 1 averaged 74,000 gpd of flow while ZVI extraction trench 2 averaged 71,000 gpd of flow. Minimum flows occurred on 2/23/2006 when flows of 67,000 and 57,000 gpd were measured for ZVI extraction trenches 1 and 2, respectively (Figure 30). Maximum flows occurred on 11/30/2005 when flows of 110,000 and 87,000 gpd were measured for ZVI extraction trenches 1 and 2, respectively.

Figure 29 ZVI Extraction Trench Rectangular Weir Structure

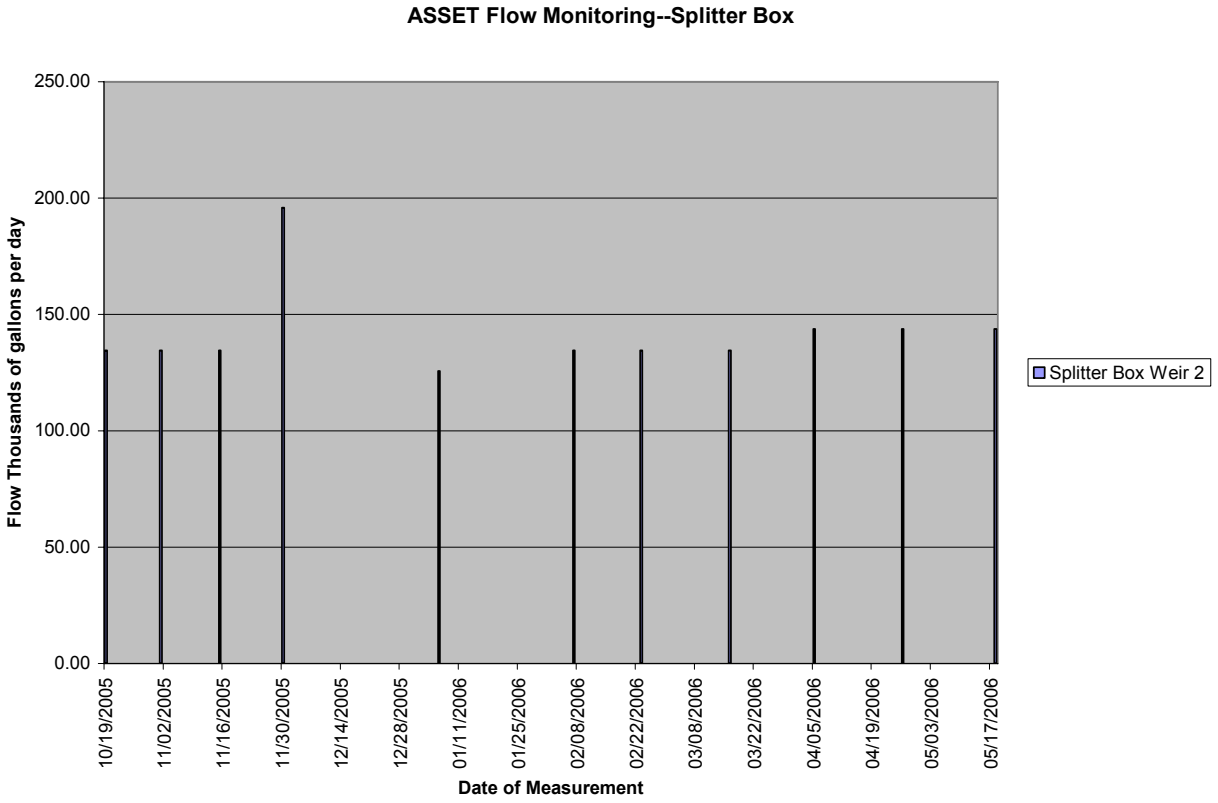


Figure 30 ASSET Flow Monitoring ZVI Extraction Trench Cells

Flow was measured at the outfall of each constructed wetlands cell as water poured over a V-notch weir. The average flow for the ATOXIC Wetland was 154,000 gpd, and the average flow through the ASSET wetland was 153,000 gpd. The minimum flow through the constructed wetlands was 135,000 gpd which occurred on 11/15/2005 (Figure 31). The maximum flow through the constructed wetlands was 185,000 gpd which occurred on 3/16/2006.

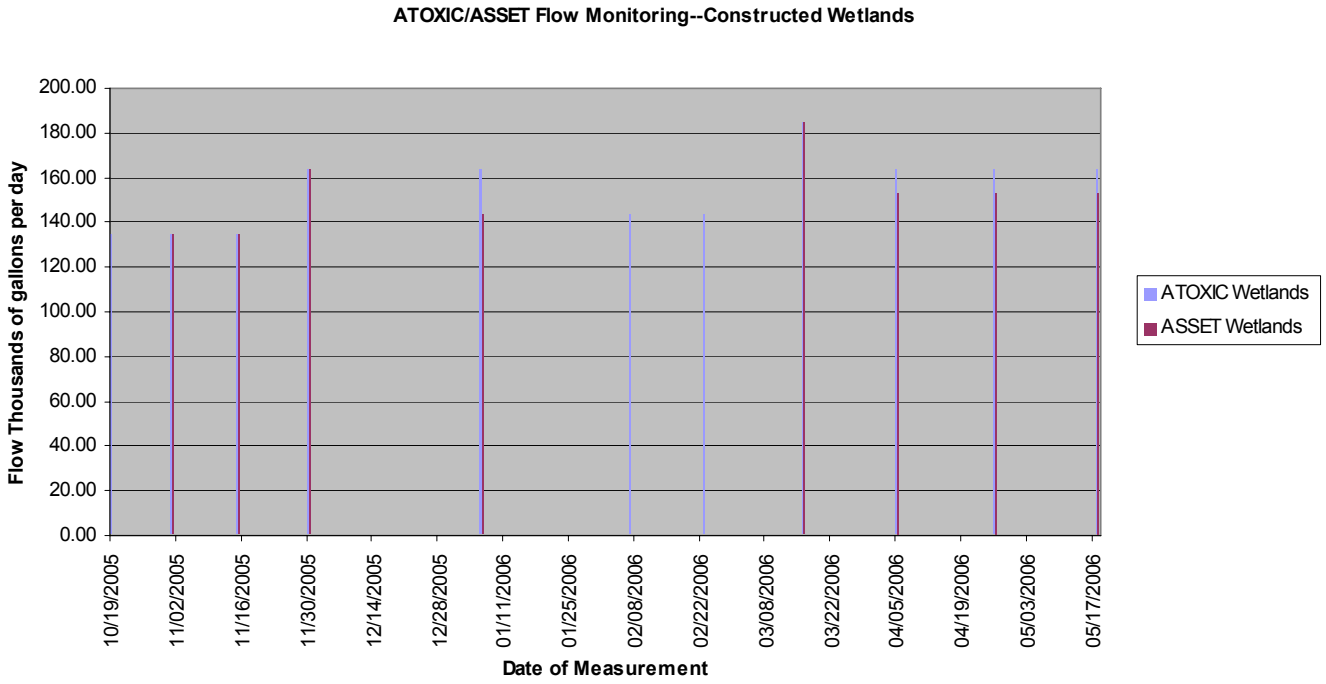


Figure 31 ATOXIC/ASSET Flow Monitoring

ATOXIC constructed wetlands evaporation rate was measured as the difference between the splitter box flow and the constructed wetlands flow (Figure 32). It was observed that the constructed wetlands was more of a water collector than a water evaporator. The data from 11/30/2005 could be misleading. It suggests that over 15 % of the water is being evaporated. In fact, a rain event caused the flow into the system to suddenly increase to around 375,000 gpd at the head of the system. The flow measured at the constructed wetlands outfall weir was 164,000 gpd. We were observing watershed effects of the system; as the wetlands outfall discharge was increasing throughout the day the evaporation rate decreased and ultimately became negative.

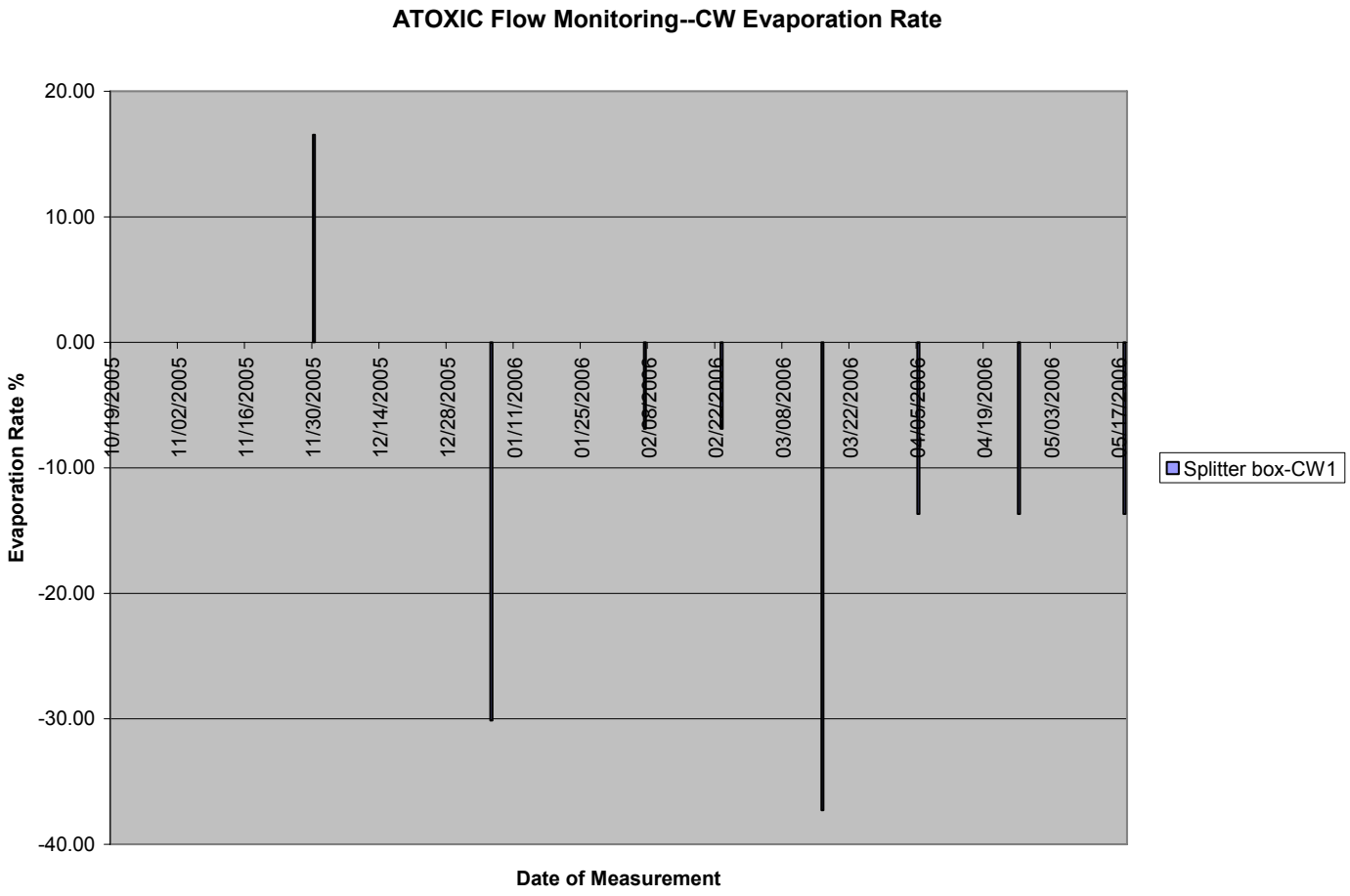


Figure 32 ATOXIC Constructed Wetlands Evaporation Rate

Continuous flow monitoring was performed at five locations throughout the ATOXIC/ASSET passive treatment system using Thalimedes water level monitoring equipment to measure the surface water level every fifteen minutes. The water level data was routinely downloaded during water sampling sessions using a notebook computer. Water level values were then translated into flow values from flow ratings tables for the different types of weir structures (i.e. V-notch, rectangular) at each location.

Water levels for the FGD influent measured with the Thalimedes system and the corresponding flows are shown in Figure 33. Initially, there was good agreement between these flows and the flows measured periodically at the FGD diverter box weir gate (Figure 23). However, with heavy rains in the spring the adjustable weir in the FGD influent diverter box needed to be raised to adjust flow into the system, and the flow monitoring system began to underestimate flow into the system at the FGD influent point.

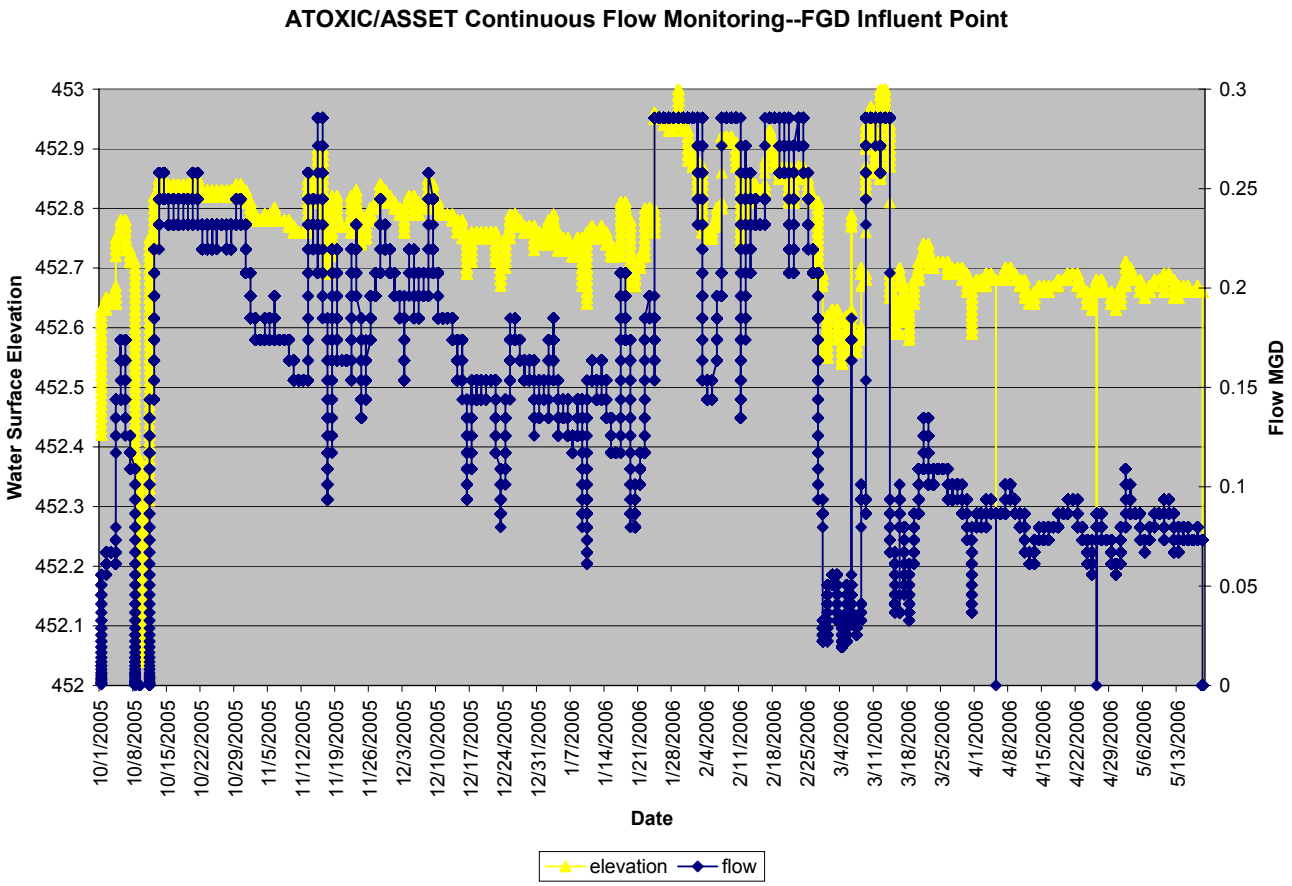


Figure 33 ATOXIC/ASSET Continuous Flow Monitoring—FGD Influent

Continuous flow monitoring at the splitter box has been very successful to date. This location has a fixed weir, so there is no question regarding the accuracy of the measurements of the water level at this location. Continuous flow monitoring results were in good agreement with results of measured flow monitoring (Figures 28 and 34). During February a large rain event caused flow to be measured at over 600,000 gpd at the splitter box, equivalent to a system flow of 1.2 MGD.

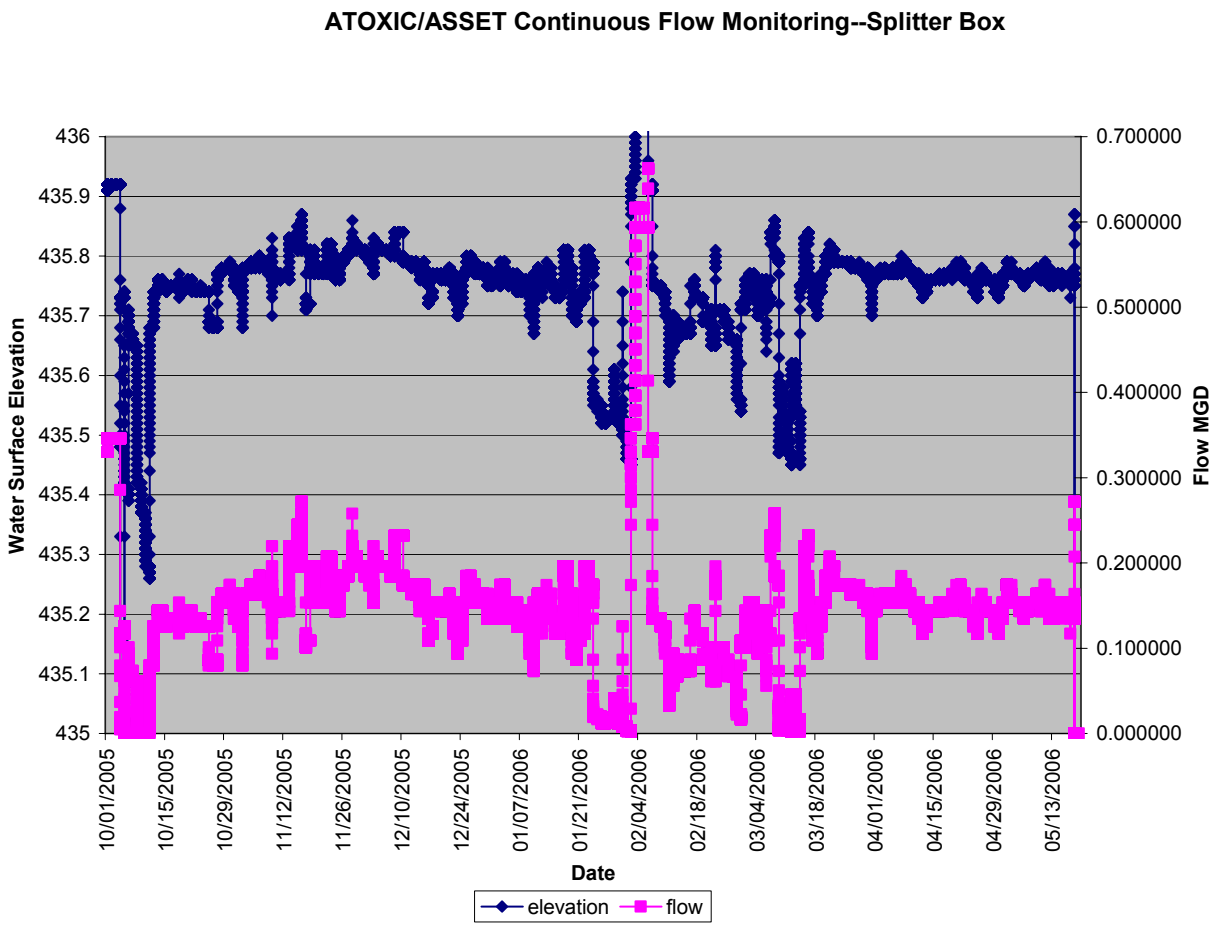


Figure 34 ATOXIC/ASSET Continuous Flow Monitoring—Splitter Box

Since rain events have a significant impact on the volume of water that flows through the ATOXIC/ASSET passive treatment system, rainfall data were collected at the site throughout the monitoring period to assess the impacts of rain events on the flow through the system (Figure 35). The 600,000 gpd flow rate at the splitter box corresponding to a total system flow of approximately 1.2 MGD due to a rain event definitely is pushing the upward limits of the system design specifications. During the spring months, flows were so erratic that the adjustable weir gate at the FGD influent point was raised so as to minimize the fluctuations in system flow.

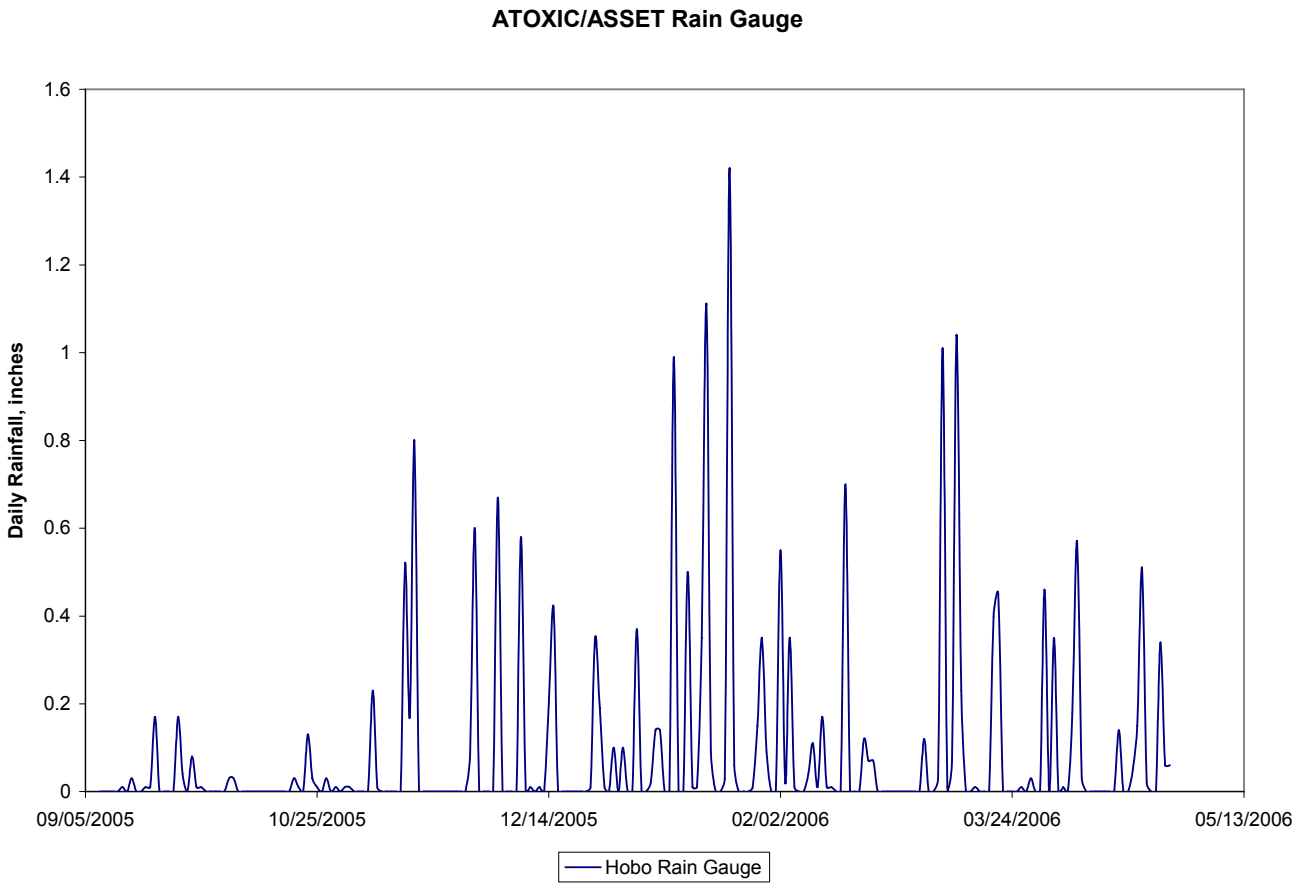


Figure 35 Daily Rainfall Data

Data from two rain events have been processed to assess the impacts on the flow to the ATOXIC/ASSET passive treatment system (Table 1). The first rain event occurred on November 13. This event totaled 0.51 inches and was a gentle rain. Prior to rain event 1, flow was measured at 144,000 gpd at the splitter box (Table 1; Figure 36). Immediately following rain event 1 peak flow was 220,000 gpd corresponding to a 34.5 % increase in flow. Average flow was 203,000 gpd following rain event 1.

Table 1. Rainfall Effects on ATOXIC/ASSET System Flows

	Event 1 11/13/2005	Event 2 11/17/2005
Baseline flow (MGD)	0.144	0.196
Peak flow (MGD)	0.22	0.272
Average flow (MGD)	0.203	0.225
Rainfall total (inches)	0.51	0.79
Flow increase %	34.5	27.9

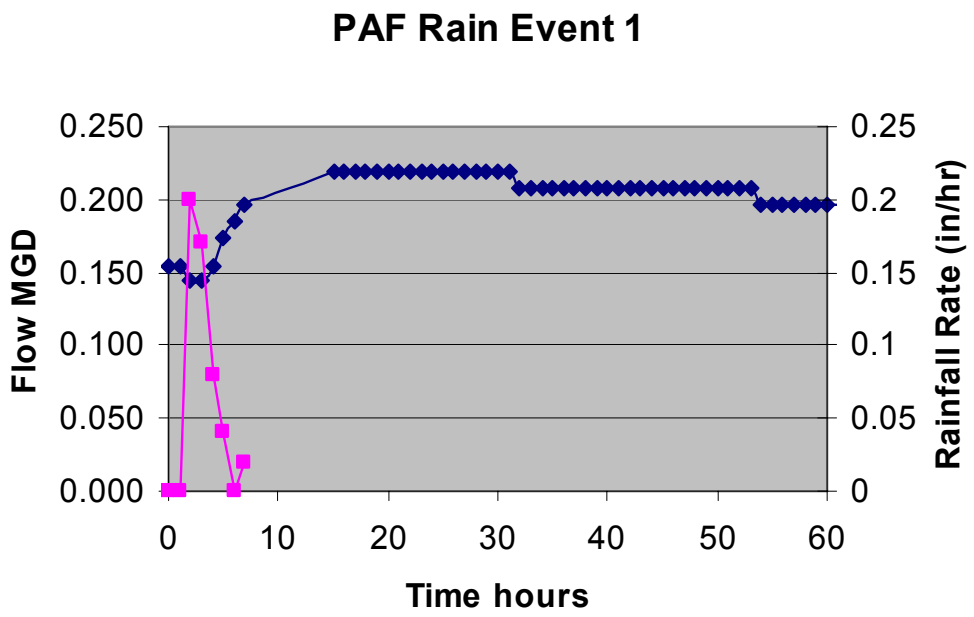


Figure 36 Rain Event 1 November 13, 2005.

Blue line depicts flow at splitter box; pink line is rainfall rate.

Rain event 2 occurred on November 17. This event totaled 0.79 inches in four hours (Table 1). Baseline flow through the system was measured at 196,000 gpd at the splitter box prior to rain event 2 (Figure 37). Peak flow was measured at 272,000 gpd 12 hours after the start of the rain event--an increase of 28 %. Average flow was 225,000 gpd following rain event 2.

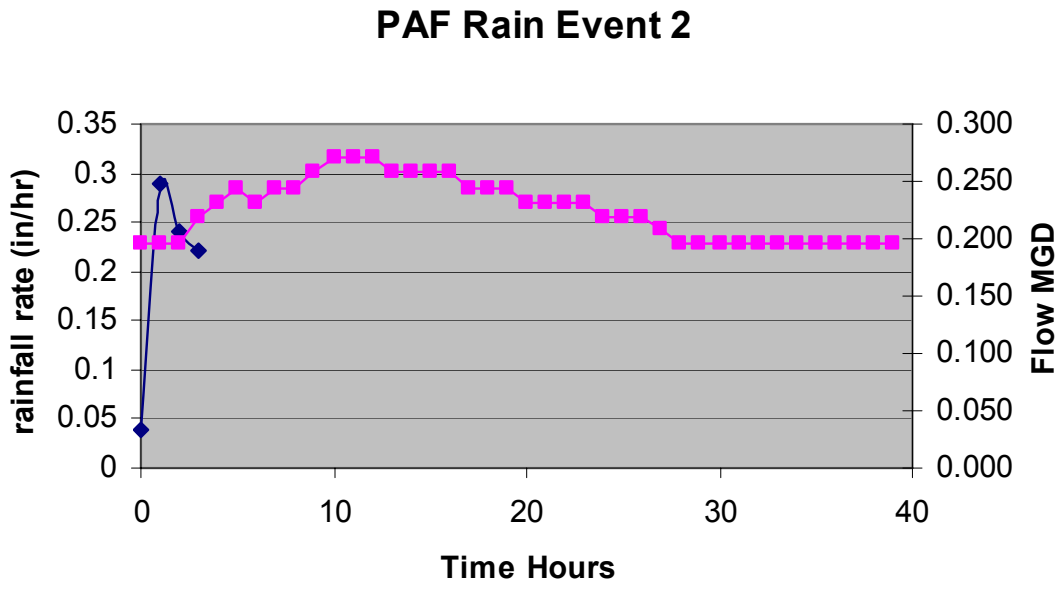


Figure 37 Rain Event 2 November 17, 2005.

Pink line depicts flow at splitter box; blue line is rainfall rate.

Water Quality Monitoring

Water quality sondes were placed throughout the ATOXIC/ASSET passive treatment system to continuously monitor water quality parameters during the study. Temperatures were 2-10 degrees C in the winter months and 11-25 degrees C in the spring and summer months (Figure 38).

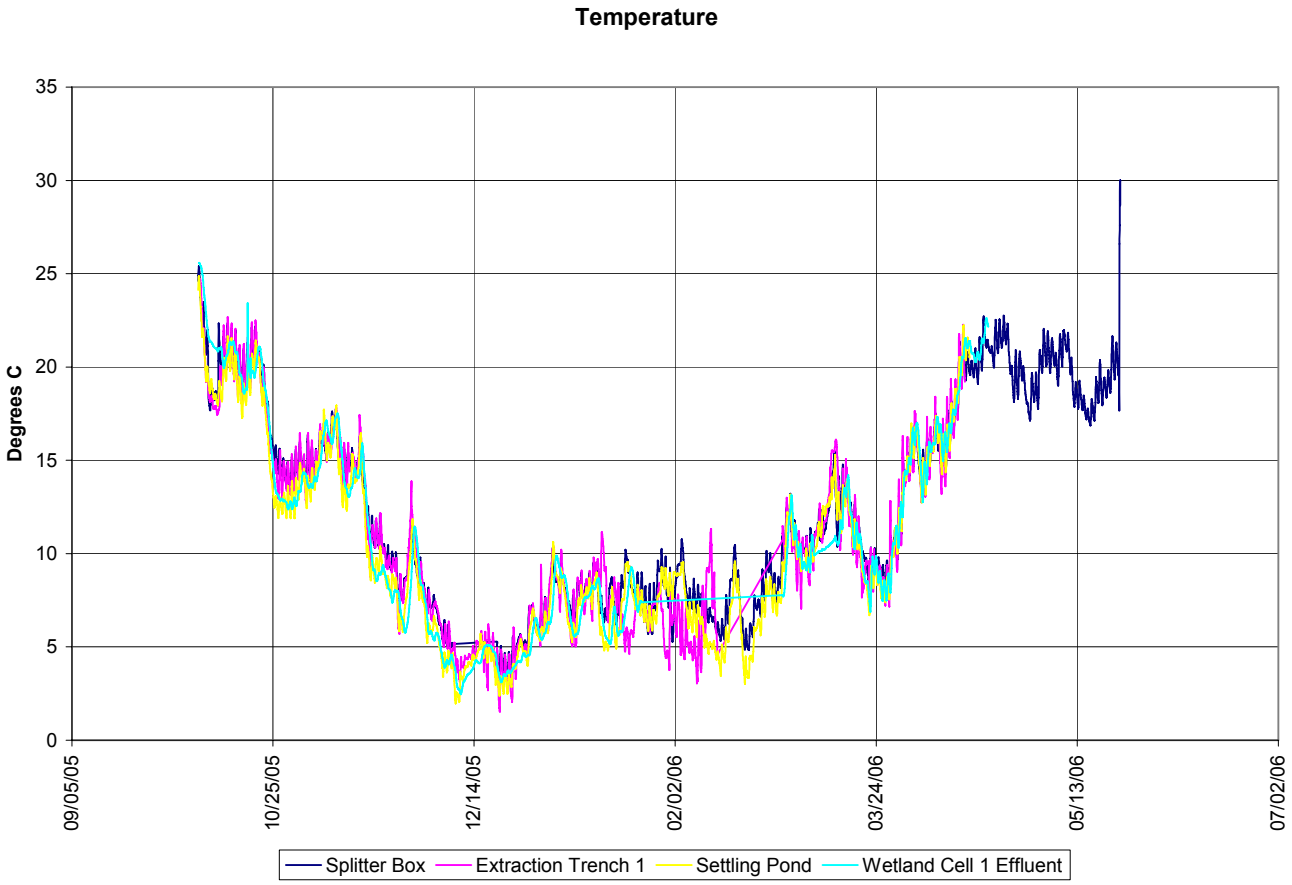


Figure 38 ATOXIC/ASSET Temperature Data

Changes in pH were evident upon addition of the ZVI in the extraction trench cells (Figure 39). A slight decrease in pH was observed in the ZVI extraction trench cells relative to the pH measured in the splitter box. In the settling/oxidation basin pH slowly increased and in the spring large fluctuations in pH were evident due to the growth of algae. The pH of the wetlands cell effluent remained lower than that of the other sites, possibly due to residual organic acids in the compost layer.

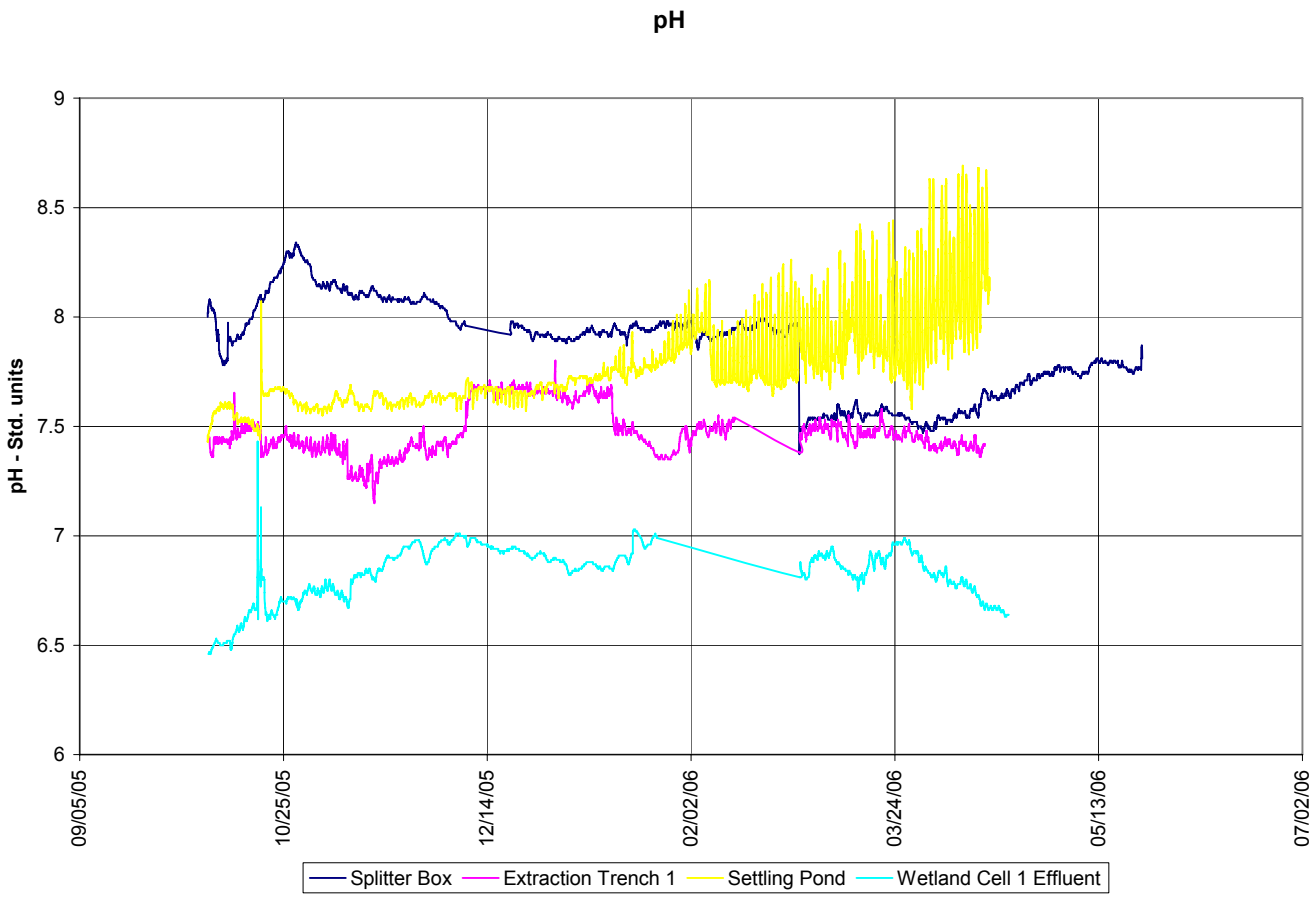


Figure 39 ATOXIC/ASSET pH Monitoring Data

Dissolved oxygen levels dropped in the ZVI extraction trench cells relative to the incoming water (splitter box) as oxygen was utilized in the oxidation of the ZVI to iron oxides (Figure 40). In the settling/oxidation basin, dissolved oxygen levels again increased slightly in the more aerobic environment, but did not return to concentrations observed in the splitter box, which most likely is oxygen-saturated water, until spring. During spring as the days became longer and algae growth proliferated, dissolved oxygen levels in the settling/oxidation basin began to fluctuate greatly between day and night. In the constructed wetlands cells, dissolved oxygen levels remained very low throughout the monitoring period, as expected for a wetlands designed for anaerobic conditions.

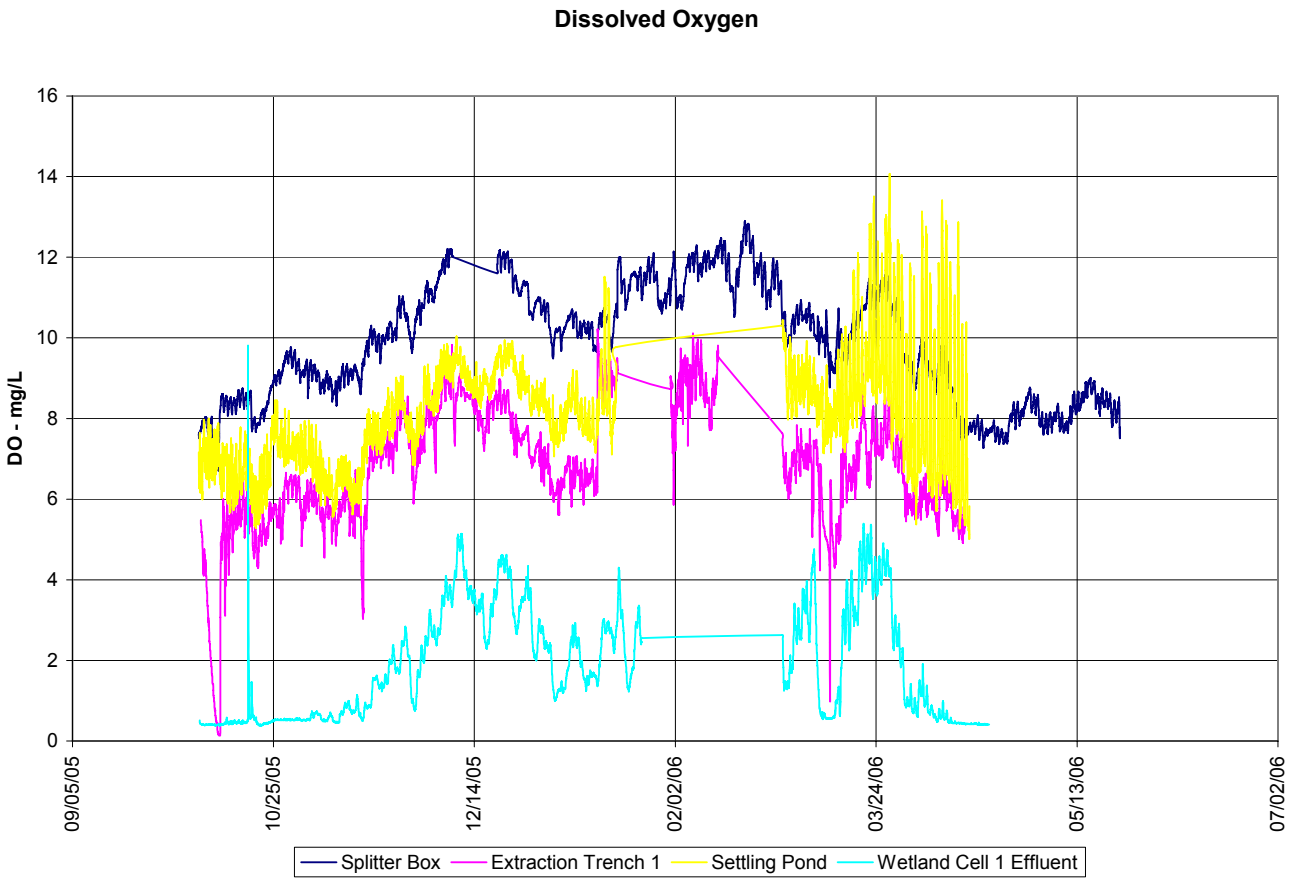


Figure 40 ATOXIC/ASSET Dissolved Oxygen Monitoring

No trends were observed for specific conductivity in the ATOXIC/ASSET passive treatment system (Figure 41). Specific conductivity levels fluctuated but remained very high throughout the monitoring period.

Water Quality Sampling

Water samples have been collected on 11 occasions and analytical results reported on seven sampling events at the time of the preparation of this report. During sampling events, water samples are collected as grab samples from the following 13 locations: FGD pipe (FGD liquor), FGD influent, trickling filters 1-4 (TF1-4) effluent collection boxes, ZVI extraction trenches 1 and 2 (ZVI ET1 and 2) discharge weirs, settling pond (SP), constructed wetland 1 and 2 (CW 1- and 2), Pooh Bear Pond (PB), Ash Pond (AP). Water quality values measured at the sampling sites is shown in Table 2. Data shown in bar charts in this report is the average of values taken from all measurements at each sampling location. The line charts show the dynamics of each parameter studied in each component of both the ATOXIC and ASSET experimental treatments over time.

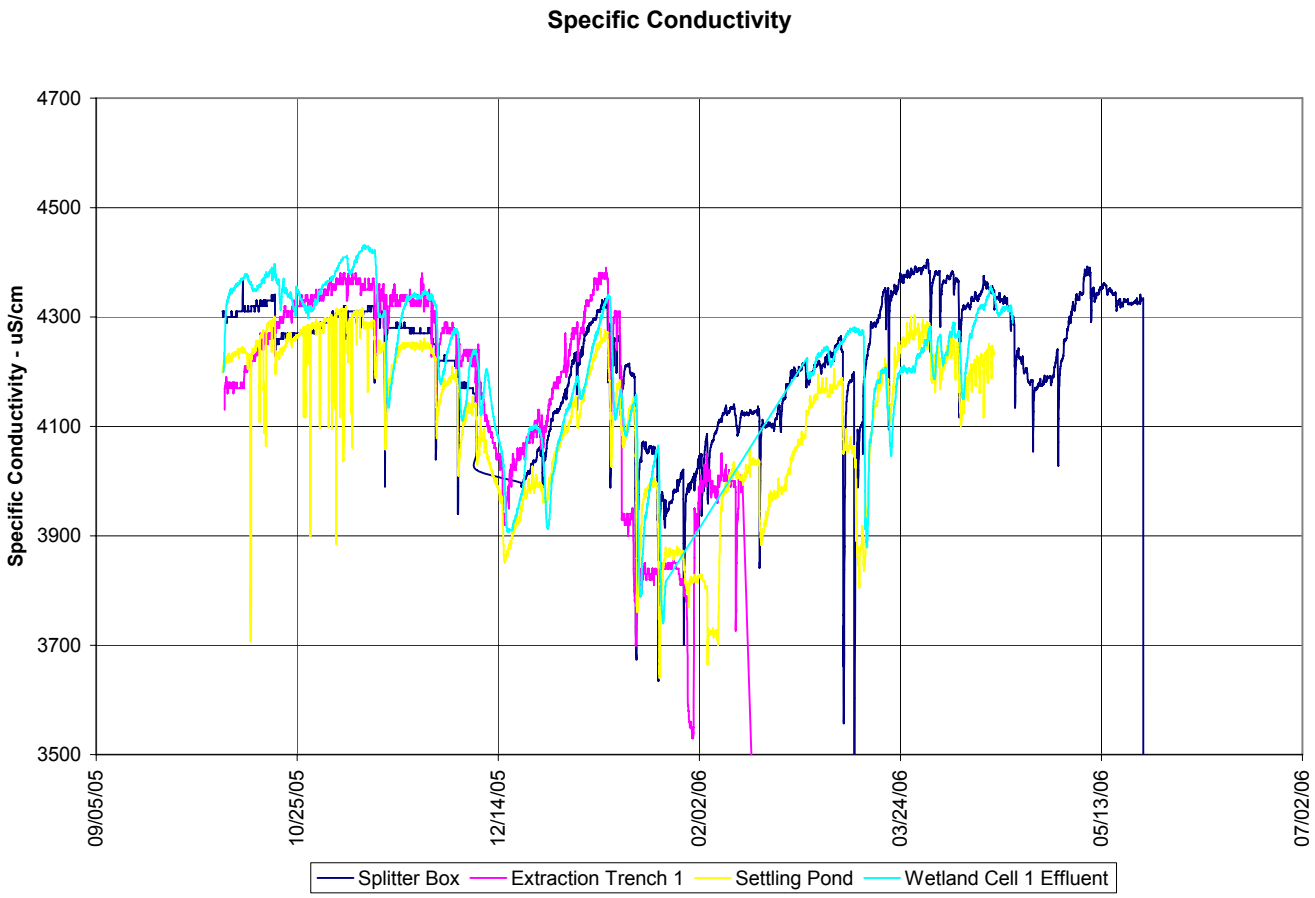


Figure 41 ATOXIC/ASSET Specific Conductivity Monitoring

Table 2 ATOXIC/ASSET Water Quality Summary

Location	ALKALN ave	TDS ave	TSS ave	Al (mg/L) ave	B (mg/L) ave	Ca (mg/L) ave	Fe (mg/L) ave	Si (mg/L) ave
FGD Pipe	69	3.85	40.349	80.36	47.7	3,290	123	58.2
FGD Influent	61	3.97	0.003	0.28	45.3	861	0.24	10.3
TF 1	60	3.98	0.001	0.19	45.1	857	0.18	9.8
TF 2	59	3.97	0.001	0.22	46.6	851	0.20	9.6
TF 3	59	3.99	0.002	0.16	45.1	869	0.18	9.8
TF 4	58	4.04	0.001	0.18	48.2	830	0.17	10.3
ET 1	58	4.02	0.001	0.17	44.6	875	0.26	8.8
ET 2	59	4.02	0.001	0.16	43.2	865	0.34	9.1
SP	57	4.01	0.002	0.18	43.5	852	0.25	9.1
CW 1	89	4.09	0.003	0.16	42.0	852	0.75	8.6
CW 2	75	4.04	0.004	0.18	40.9	848	0.45	7.7
PB	291	3.47	0.011	0.20	22.5	660	1.00	5.4
Ash pond	114	0.87	0.007	0.53	6.8	196	0.39	3.8

[1]values are the average of all measurements taken at each sampling location.

Nitrogen Dynamics

Ammonia nitrogen was present in PAF FGD liquor at an average concentration of 0.35 mg/L as NH_4-N (n=11 measurements) (Figure 42). The FGD influent water had ammonium nitrogen present at an average concentration of 0.21 mg/L as NH_4-N (n=11). This corresponds to an average NH_4-N removal rate of 40 % in the FGD rim ditch stacking area. Trickling filter effluents had ammonium nitrogen present at an average concentration of 0.13 mg/L as NH_4-N (n=39 measurements). This was a further reduction of 38 % of NH_4-N from the FGD influent water. Constructed wetlands cells 1 and 2 showed elevated levels of ammonium nitrogen in their effluents, most likely due to flushing of nutrients from the compost layer in the wetland cells. Ash pond ammonium nitrogen measurements were somewhat elevated due to another study in which ammonium was added to the ash pond; ammonium additions were made during January and February 2006 to study cold weather nitrification in ash ponds.

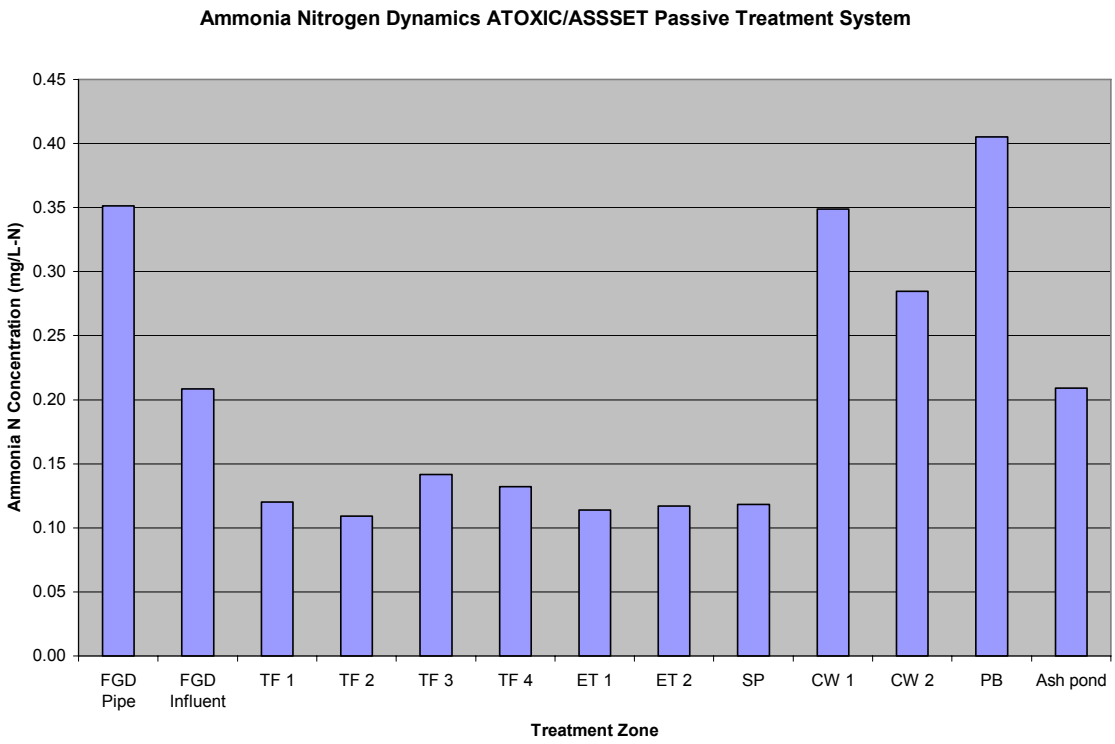


Figure 42 Ammonium Nitrogen Dynamics

Trickling filter effluent samples were consistently lower in ammonium concentration than samples of FGD liquor and FGD influent, which is evidence of biological nitrification taking place (Figure 43). The ATOXIC constructed wetlands effluent samples were high in ammonium initially as nutrients were flushed from the organic hydrosoils used as wetlands substrates. Ammonium concentrations also began to increase over the cold winter months of January and February in the ATOXIC constructed wetlands effluent.

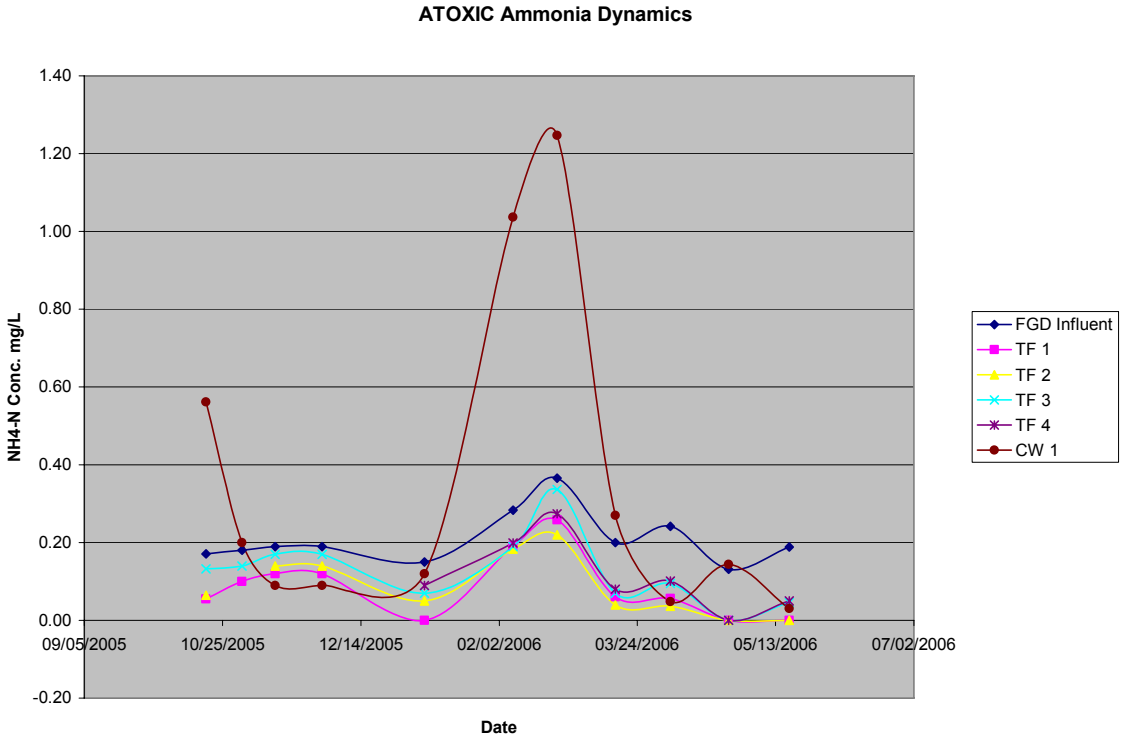


Figure 43 ATOXIC Ammonium Dynamics

The ASSET ammonium dynamics are similar to the ATOXIC ammonium dynamics. The FGD liquor and FGD influent contained higher levels of ammonium, while little difference was observed between the trickling filter effluent, ZVI extraction trench effluents, and settling pond effluent (Figure 44). The ASSET constructed wetland effluent samples were initially high in ammonium, and ammonium concentrations also began to increase over the cold winter months of January and February in the ASSET constructed wetlands effluent samples. The spike in ash pond ammonium during January and February reflect additions of ammonium that were made to the ash pond sluice channel during another study to better understand cold weather nitrification in ash ponds.

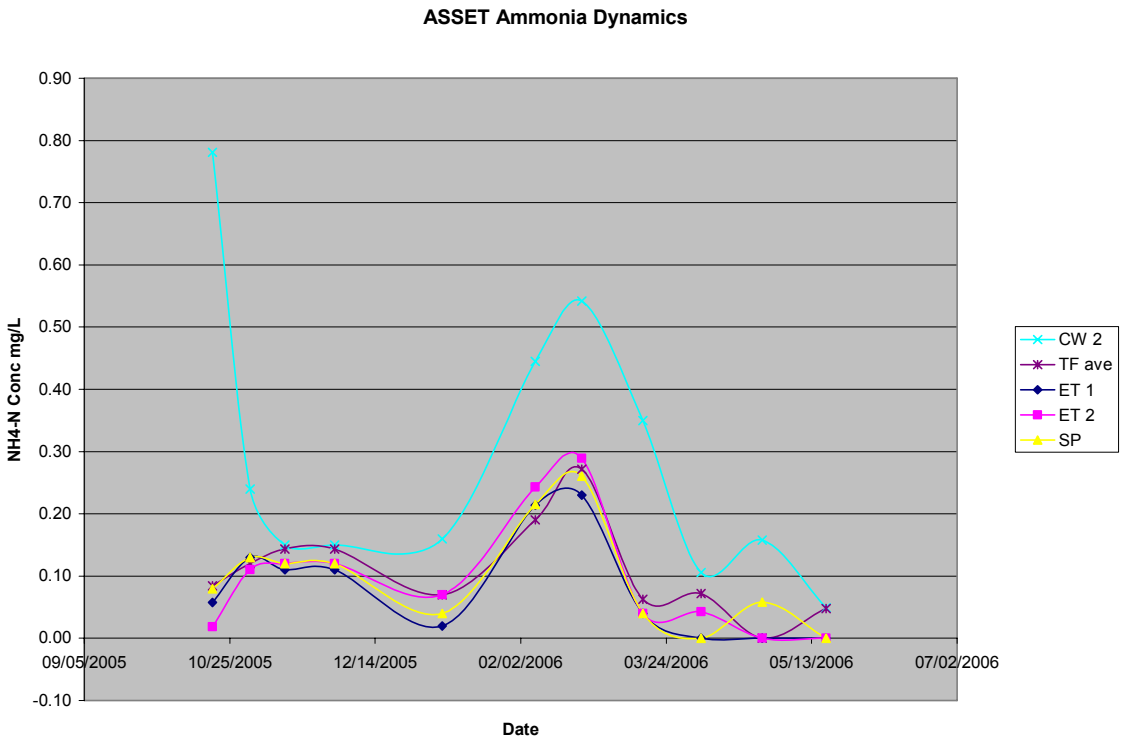


Figure 44 ASSET Ammonium Nitrogen Dynamics

Nitrate nitrogen was present at an average concentration of 11.7 mg/L NO_3-N in FGD liquor (n=11 measurements), and the FGD influent water had an average concentration of 10.9 mg/L NO_3-N, corresponding to a nitrate removal rate of 6.8 % in the FGD rim ditch stacking area (Figure 45). The trickling filter effluent had an average concentration of 11.4 mg/L (n=39 measurements). Constructed wetlands effluents had an average NO_3-N concentration of 6.24 mg/L (n=22 measurements); this reduction in the concentration (46 %) of nitrate-nitrogen was most likely due to biological denitrification. Pooh Bear Pond effluent average NO_3-N concentration is 2.06 mg/L (n=11), evidence of a further reduction of 64 % via biological denitrification and dilution effects.

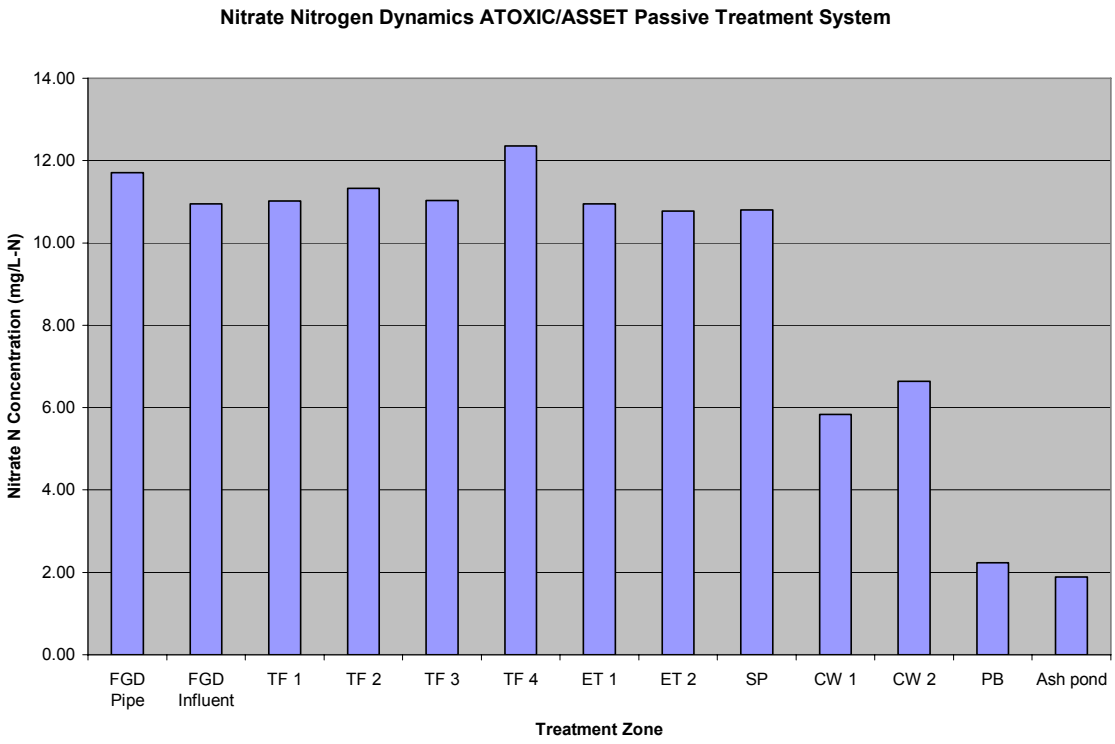


Figure 45 Nitrate Nitrogen Dynamics

Nitrate removal by biological denitrification was nearly 100 % initially in the ATOXIC constructed wetlands, but with colder temperatures in the winter months, denitrification rates decreased (Figure 46). Nitrate levels increased in the ATOXIC constructed wetlands effluents until 2/7/2006, when springtime temperatures occurred. This sampling event seemed to reflect a turning point when biological denitrification once again was initiated.

Nitrate removal was also nearly 100% initially in the ASSET constructed wetlands (Figure 47). During cold temperatures in the winter months, biological denitrification was hindered in the ASSET wetlands and nitrate levels escalated but always remained lower than levels in FGD influent water. Unlike the ATOXIC constructed wetlands, the ASSET wetlands did not respond immediately to springtime temperatures. One reason for the slow recovery is that the ASSET wetlands was not operational during part of February while the adjustable weir structure was reconfigured. Further denitrification occurred in Pooh Bear Pond (the pond that both the ATOXIC and ASSET wetlands discharge to, and that ultimately discharges to the ash pond sluice channel); this pond provides a favorable environment for biological denitrification because it provides alkalinity and soluble organic carbon. Denitrification also occurred to a lesser extent in the ash pond. The same seasonal fluctuations in denitrification observed in the constructed wetlands components were also observed in Pooh Bear Pond.

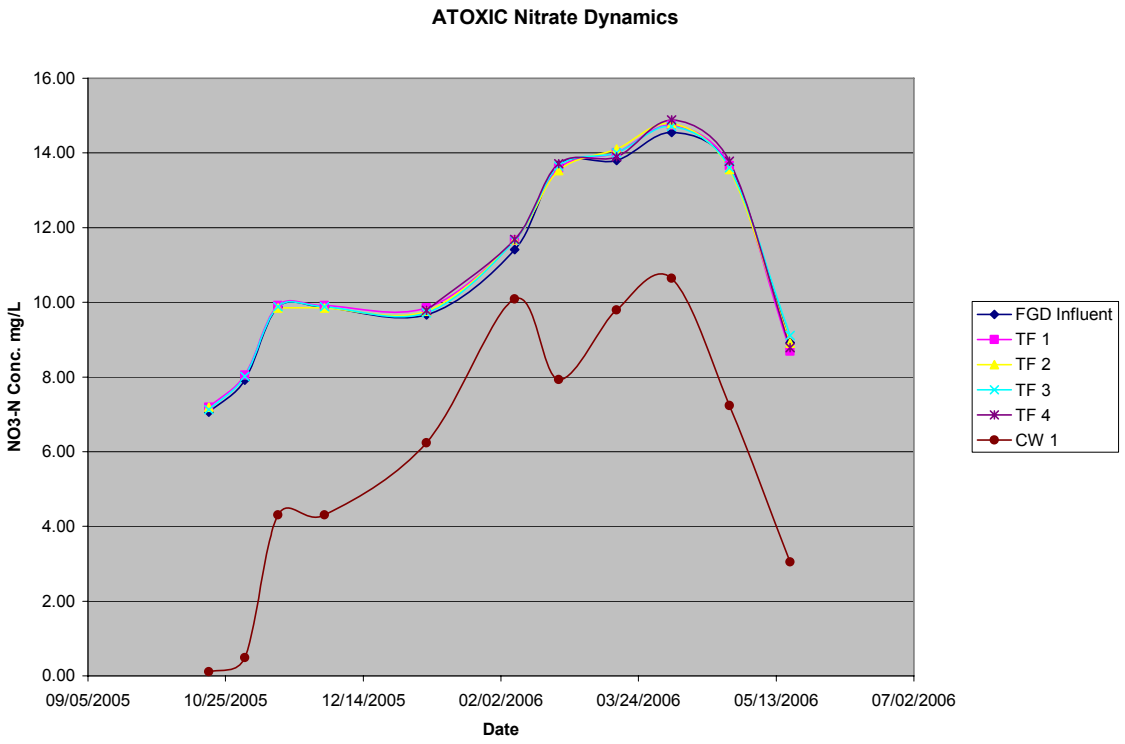


Figure 46 ATOXIC Nitrate Nitrogen Dynamics

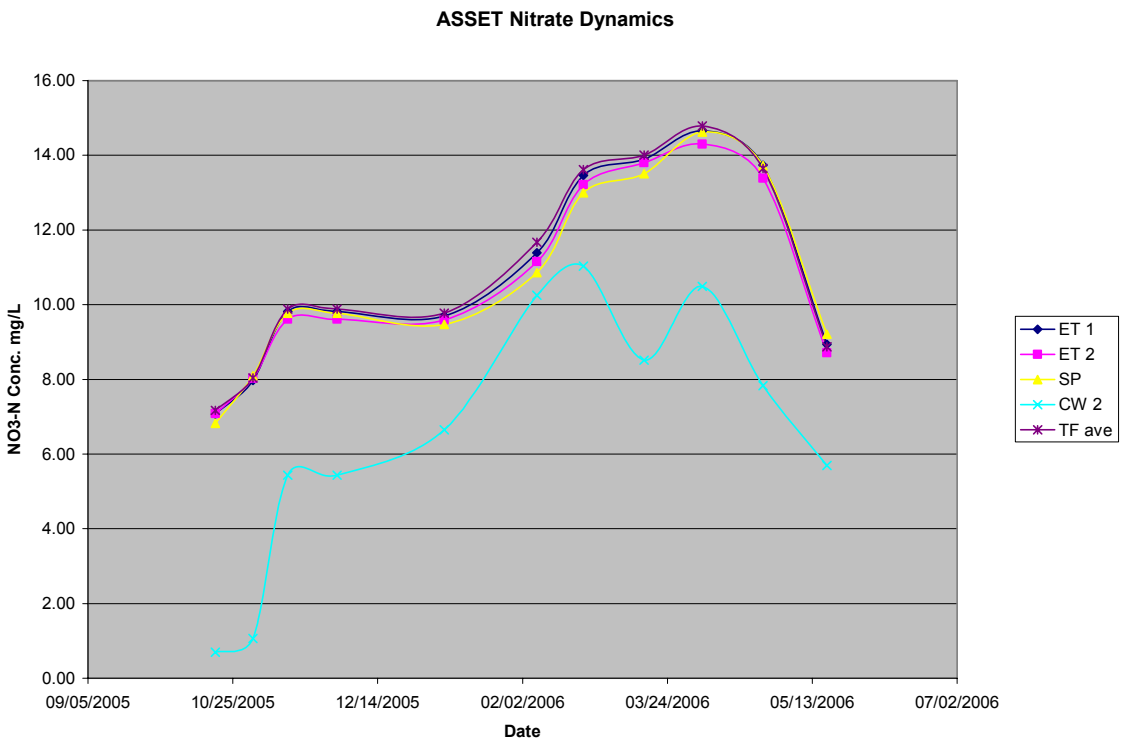


Figure 47 ASSET Nitrate Dynamics

TKN is the sum of NH_4-N and organic nitrogen in a water sample. All organic nitrogen is converted to NH_4-N and analyzed as NH_4-N during the TKN digestion procedure. FGD liquor contained an average of 3.38 mg/L TKN (n=11), and of that an average of 3.03 mg/L was organic nitrogen (Figure 48). FGD influent water contained 0.51 mg/L TKN (n=11). This corresponds to an average removal rate of 85 % of TKN in the FGD rim ditch stacking area. Trickling filter effluents contained an average of 0.56 mg/L TKN (n=39). Constructed wetlands effluents contained an average of 1.33 mg/L TKN (n=22). Pooh Bear Pond effluent averaged 0.82 mg/L TKN (n=11).

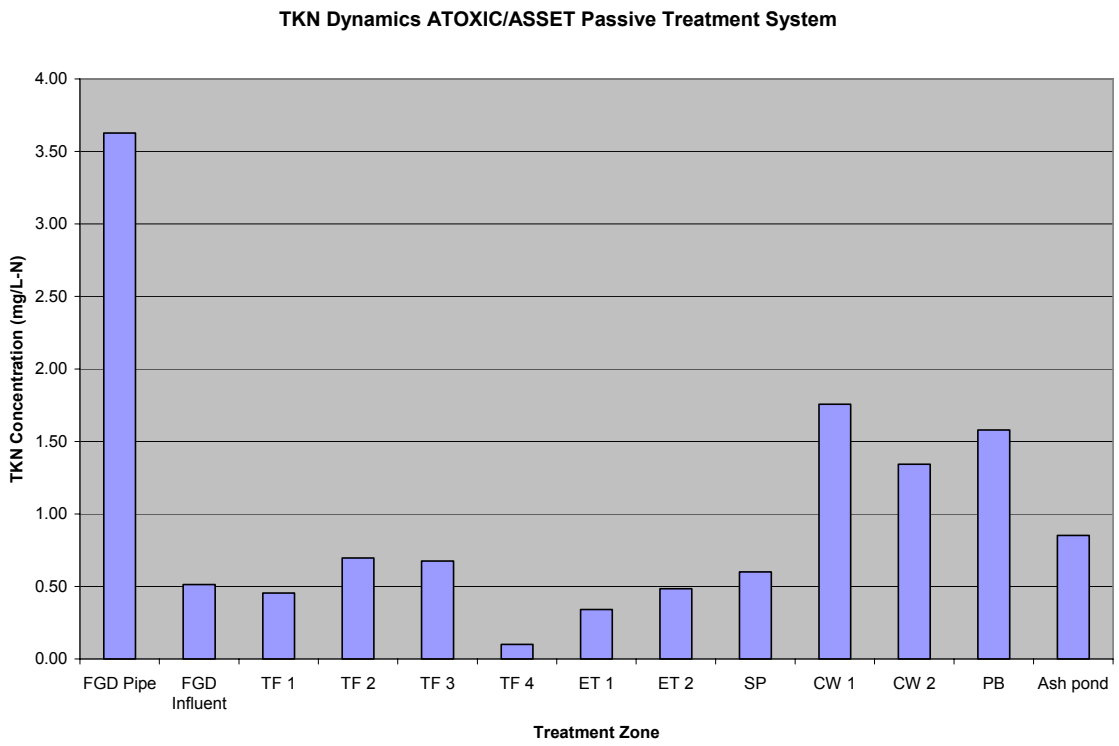
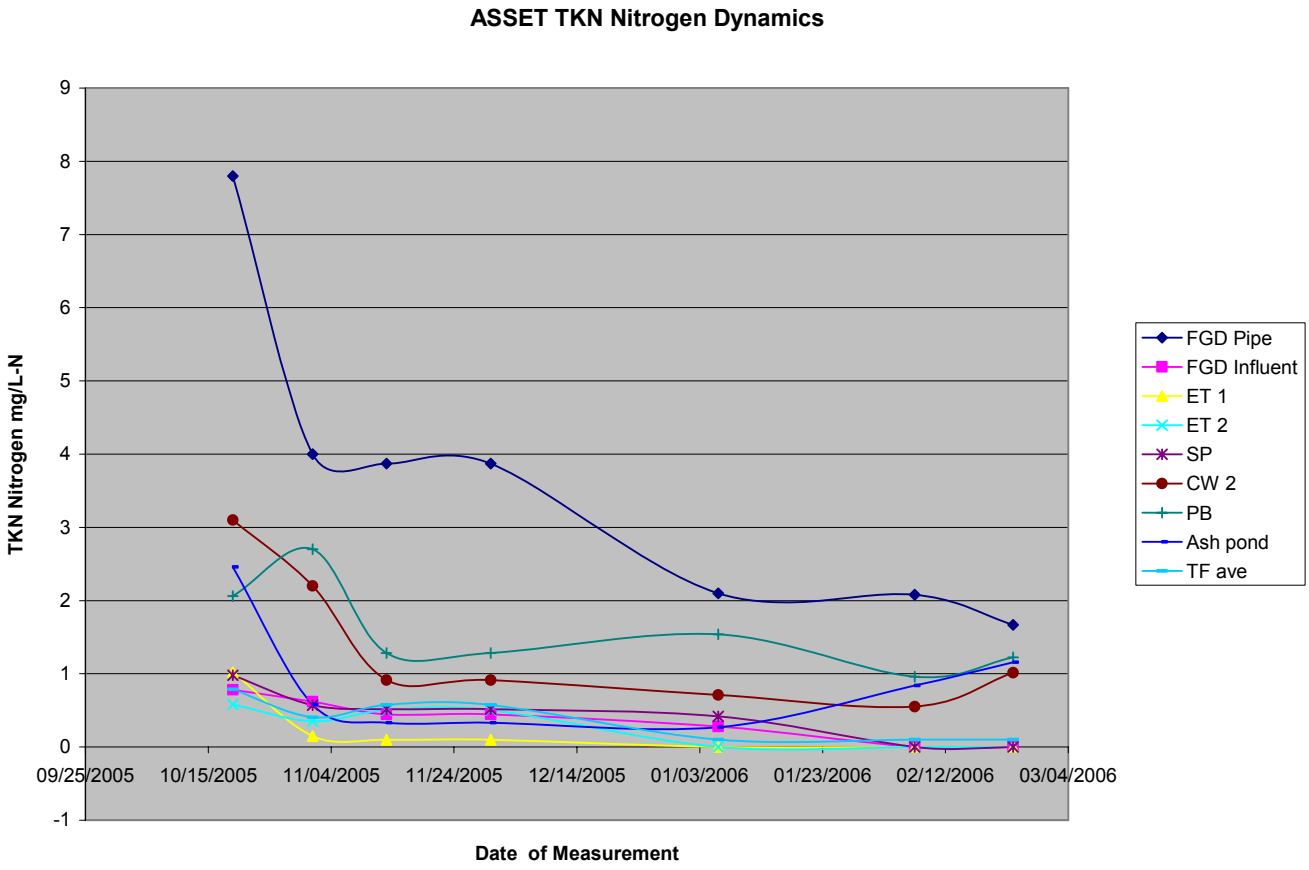


Figure 48 TKN Dynamics

TKN in the ATOXIC experimental treatment component samples was usually quite low with the exception of the FGD liquor samples (Figure 49). FGD influent and trickling filter samples were all very low in TKN, and eventually approached analytical detection limits. The ATOXIC constructed wetland samples were high in TKN initially as a result of flushing of nutrients from the wetlands hydrosoils. Over the winter months, TKN values decreased in ATOXIC wetlands samples and gradually increased again during the springtime warming.

Figure 49 ATOXIC TKN Nitrogen Dynamics

ASSET TKN dynamics are similar to those of the ATOXIC experimental treatment system (Figure 50). Most samples were low in TKN other than the FGD liquor. The FGD influent water, trickling filter average, and ZVI extraction trench effluents were all very low in TKN and approached analytical detection limits with time. The ASSET constructed wetlands samples were high in TKN initially as a result of flushing of nutrients from the wetlands hydrosoils. Over the winter months, TKN values decreased in ASSET wetlands samples and gradually increased again during the springtime warming. TKN levels were consistently higher in Pooh Bear Pond than other sampling locations, and a spike in TKN was observed in the Pooh Bear pond after the initial startup of the passive treatment system, most likely due to flushing of nutrients from the constructed wetlands cells. TKN in the ash pond samples began to escalate during January and February of 2006 due to additions of ammonium nitrogen to the ash pond sluice channel for the cold weather nitrification study being conducted at that time.



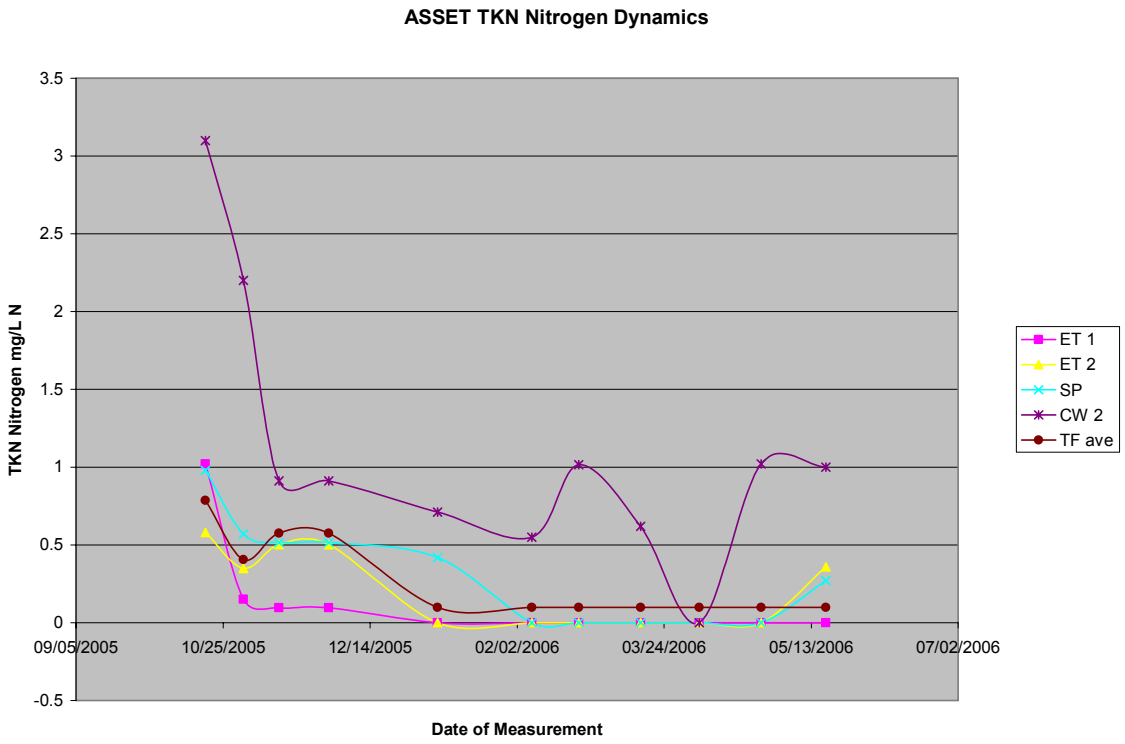


Figure 50 ASSET TKN Nitrogen Dynamics

Total nitrogen is reported as the sum of the TKN and the nitrate nitrogen concentrations. Total nitrogen in FGD liquor averaged 15.09 mg/L as N (n=11) (Figure 51). The FGD influent water had an average total nitrogen concentration of 11.46 mg/L (n=11). Trickling filter effluent total nitrogen concentration averaged 11.61 mg/L (n=39). ZVI extraction trench effluent average total nitrogen concentration was 11.26 mg/L (n=22). Constructed wetlands effluents averaged total nitrogen concentrations of 7.60 mg/L (n=22). Pooh Bear Pond total nitrogen concentration averaged 3.70 mg/L (n=11).

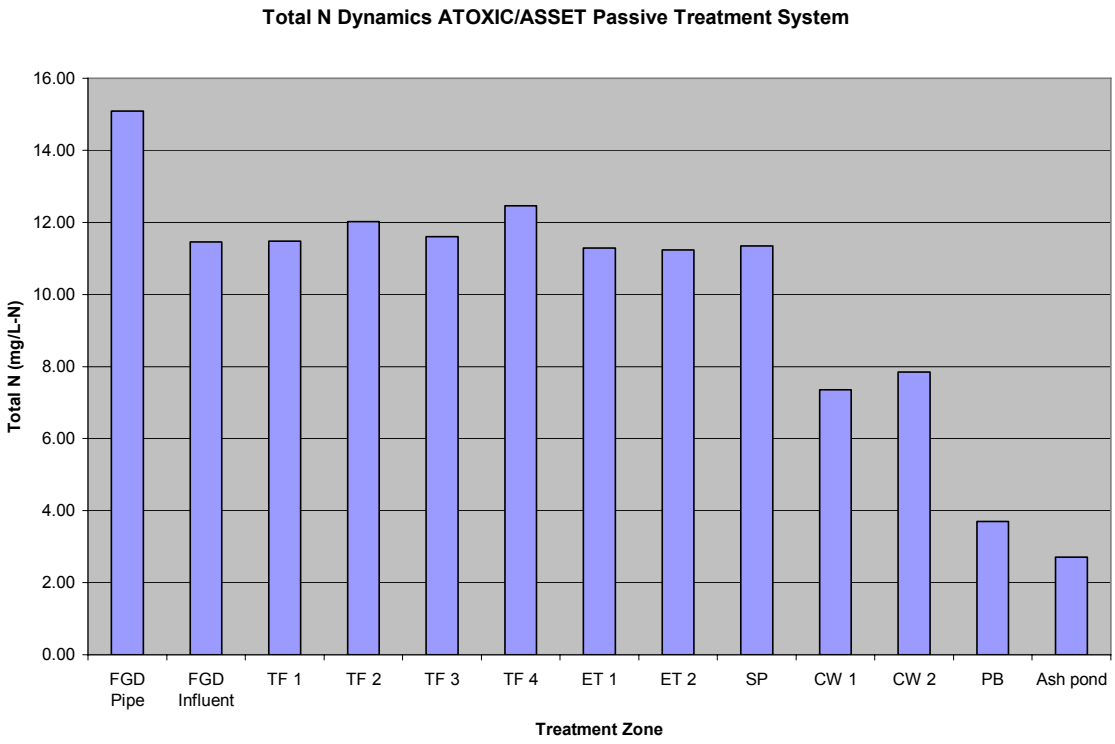


Figure 51 Total Nitrogen Dynamics

Arsenic Dynamics

Arsenic was present at an average concentration of 1099 µg/L in FGD liquor (n=11 measurements) (Figure 52). However, at the FGD influent point, the average concentration of arsenic in FGD water was only 6.5 µg/L (n=11). The mechanism for removal in the rim ditch stacking area is believed to be adsorption onto metal oxides and coprecipitation. Average arsenic concentrations for the trickling filter effluent, the extraction trench effluent, and the settling pond effluent were 3.7 (n=39), 2.9 (n=11), and 2.8 (n=11) µg/L, respectively. The ATOXIC wetland effluent average arsenic concentration was 2.6 (n=11) µg/L, and the ASSET wetland effluent average arsenic concentration was 2.9 µg/L (n=11). Because the concentrations of arsenic are so low in the FGD influent water, a spike study is planned to evaluate the performance of the passive treatment system with regard to arsenic removal.

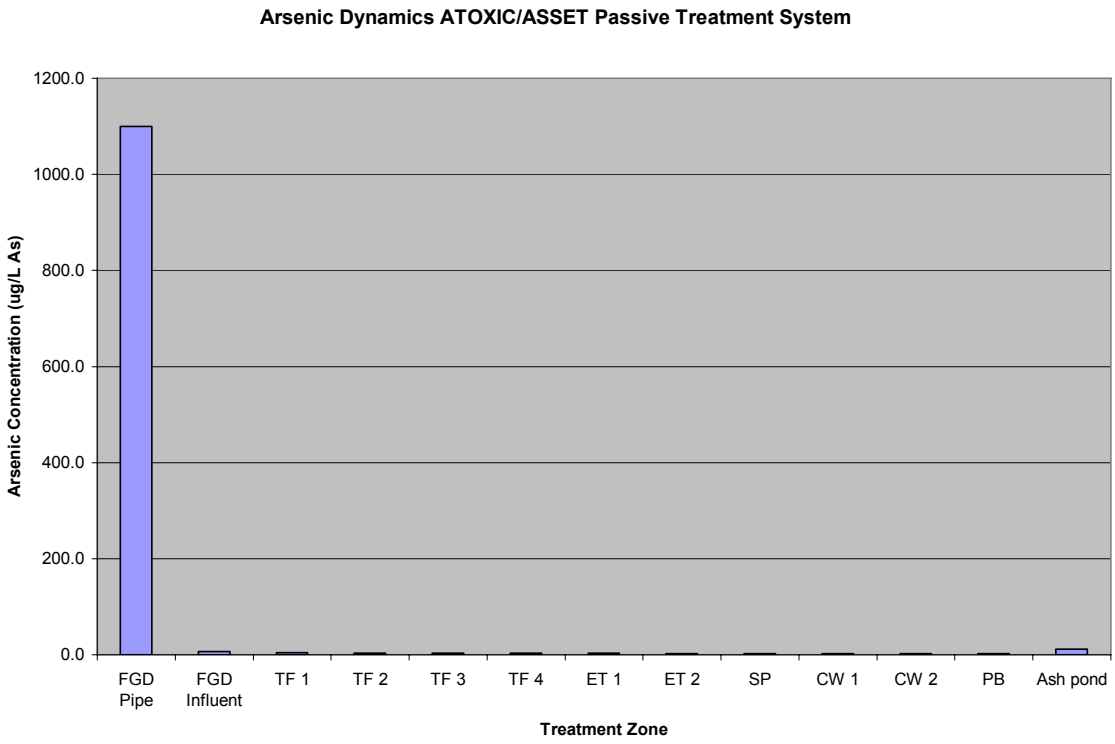


Figure 52 Arsenic Dynamics

Arsenic concentrations were very low in all water samples collected in the ATOXIC treatment components of the passive treatment system (Figure 53). FGD influent samples were always the highest in arsenic concentration. Trickling filter effluent arsenic concentrations were lower than FGD influent samples and tended to track the concentration profile of the FGD influent curve. This indicates that removal of arsenic was occurring in the trickling filters, most likely due to adsorption onto the gravel matrix. The ATOXIC constructed wetlands provided additional removal of arsenic as samples from this location consistently contained lower levels of arsenic than the trickling filter samples.

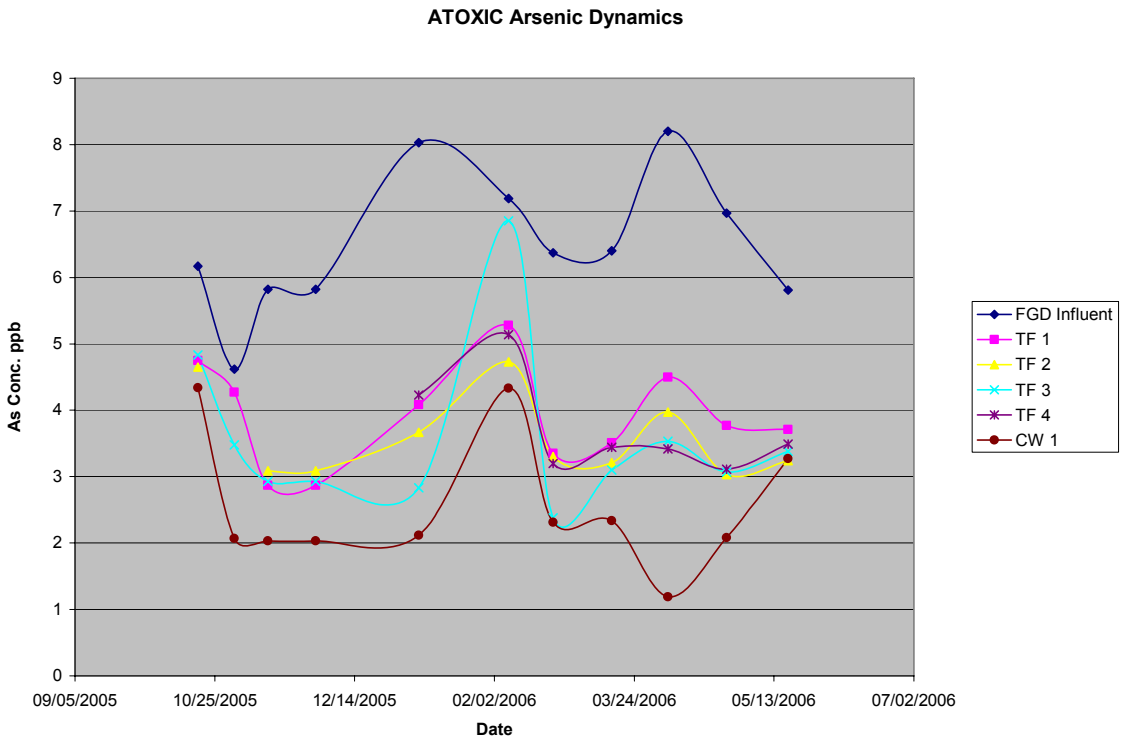


Figure 53 ATOXIC Arsenic Dynamics

Arsenic in the ASSET experimental treatment components was also very low in all samples collected (Figure 54). FGD influent water samples consistently contained higher concentrations of arsenic than did the downstream ASSET components such as the ZVI extraction trenches and settling/oxidation basin. The ASSET constructed wetlands provided arsenic removal in addition to the ZVI extraction trenches. The ash pond sample increased in arsenic significantly during January and February which coincides with the time period of the previously mentioned cold weather nitrification study in the ash pond in which ammonium was added to the ash pond sluice channel.

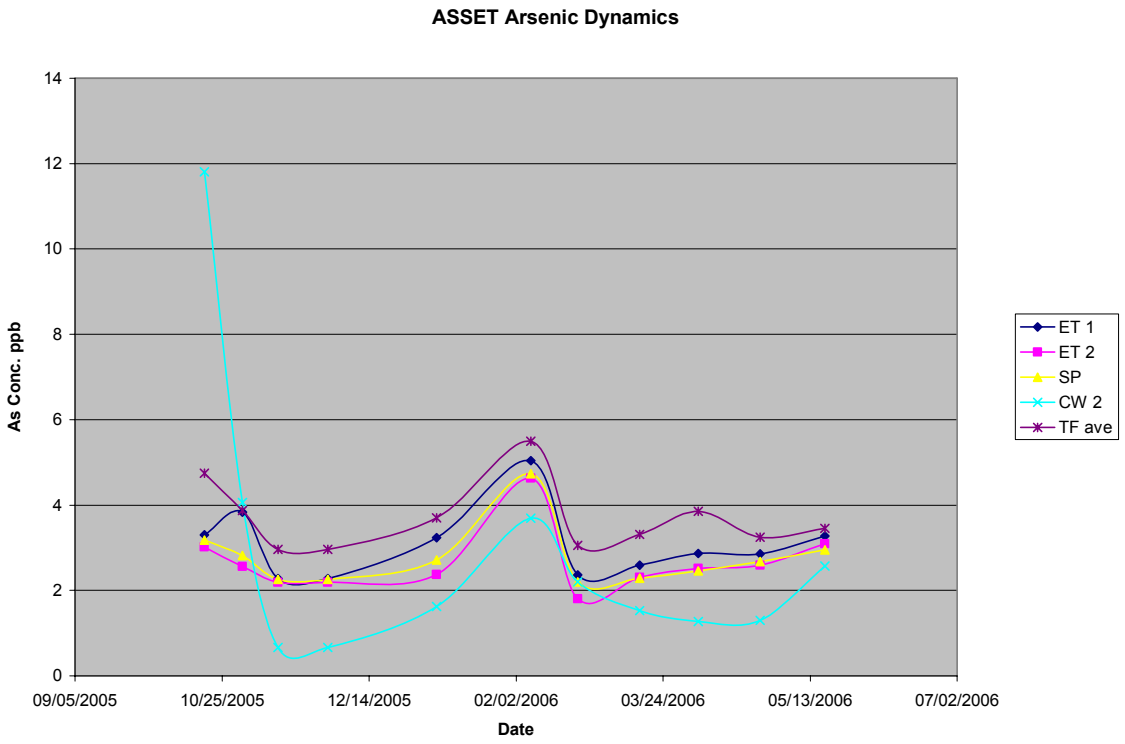


Figure 54 ASSET Arsenic Dynamics

Selenium Dynamics

Selenium concentrations averaged 173 µg/L in FGD liquor (n=6 measurements) (Figure 55). The FGD influent water had an average concentration of 56 µg/L selenium (n=6), corresponding to a removal of 68 % in the FGD rim ditch stacking area. The mechanism of removal was most likely iron coprecipitation and settling of metal oxides in the rim ditch stacking area. Trickling filter effluent concentrations averaged 34.2 µg/L (n=24) and 39% additional removal, ZVI extraction trench effluents averaged 28 µg/L (n=14) and 18 % additional removal, and constructed wetlands effluents averaged 24 µg/L (n=14) and 14 % additional removal.

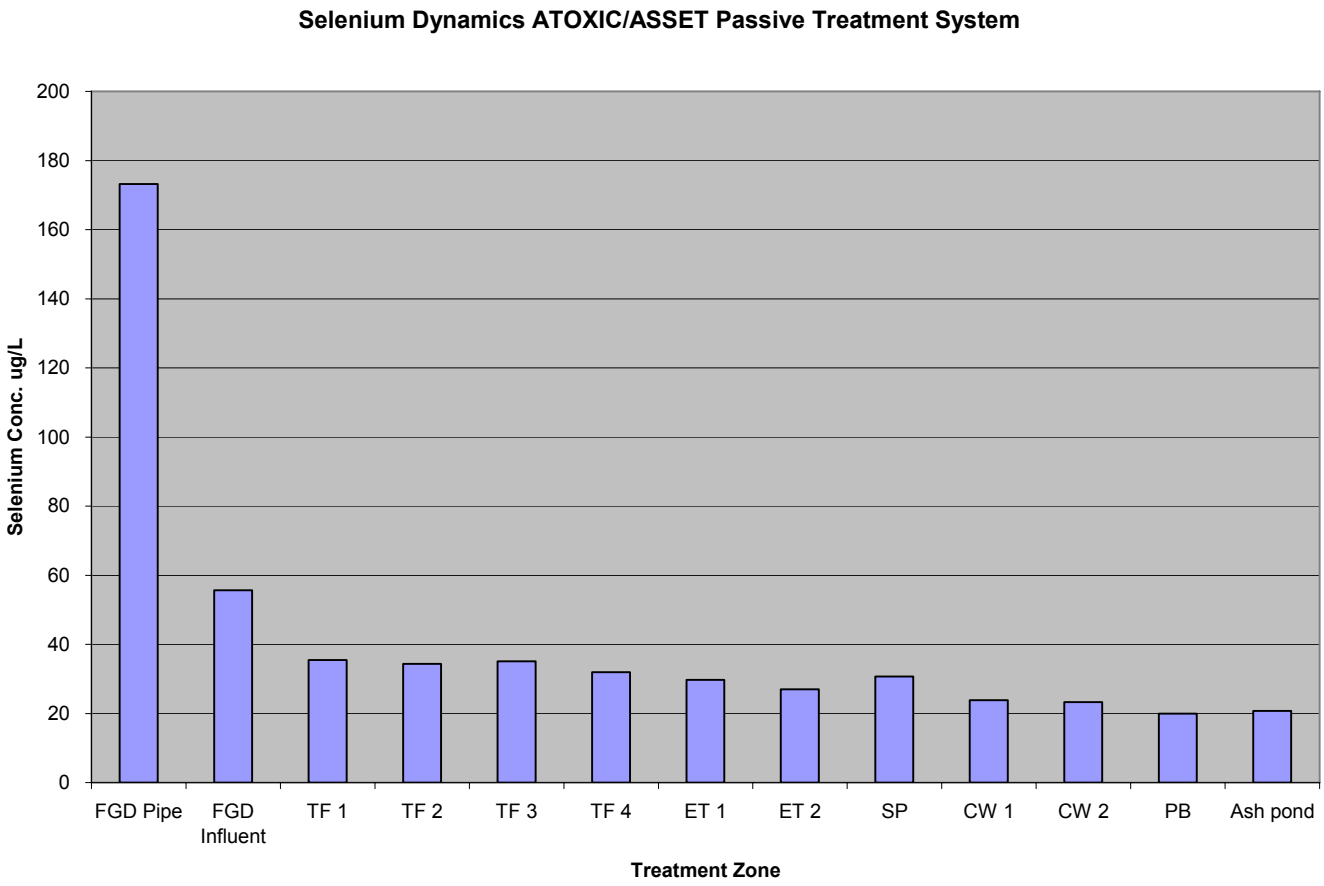


Figure 55 Selenium Dynamics

Selenium concentrations varied considerably, from 20 to 80 µg/L, over the measurement period (Figure 56). Trickling filter effluents consistently contained lower levels of selenium than the FGD influent samples, although the removal efficiency of the trickling filters was also quite variable. Selenium concentrations in the ATOXIC constructed wetlands samples were similar to that in the trickling filter effluent, indicating that little or no selenium removal was occurring in the constructed wetlands.

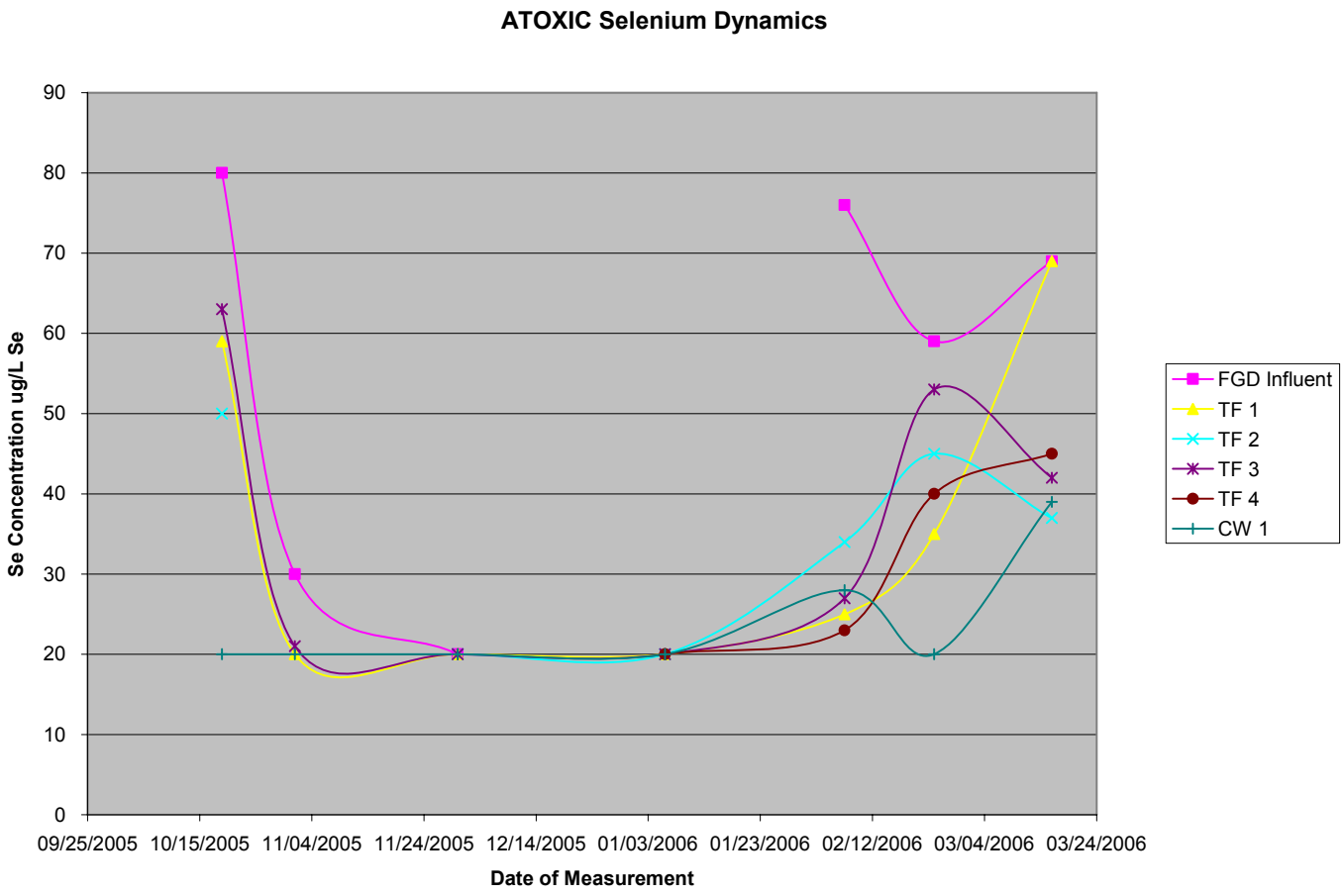


Figure 56 ATOXIC Selenium Dynamics

In the ASSET system, selenium concentrations were the same or only slightly lower in the effluents from the treatment components of the system compared to selenium concentrations in the FGD influent for the first half of the monitoring period (Figure 57). In the remaining portion of the monitoring period, selenium concentrations were significantly lower in the trickling filter effluent than in the FGD influent, and concentrations in the ZVI extraction trench effluents were lower still than in the trickling filter. In the more localized reducing conditions present in the extraction trenches selenium may have been reduced to less soluble forms. The ASSET wetlands removed little or no selenium except for the final sampling date.

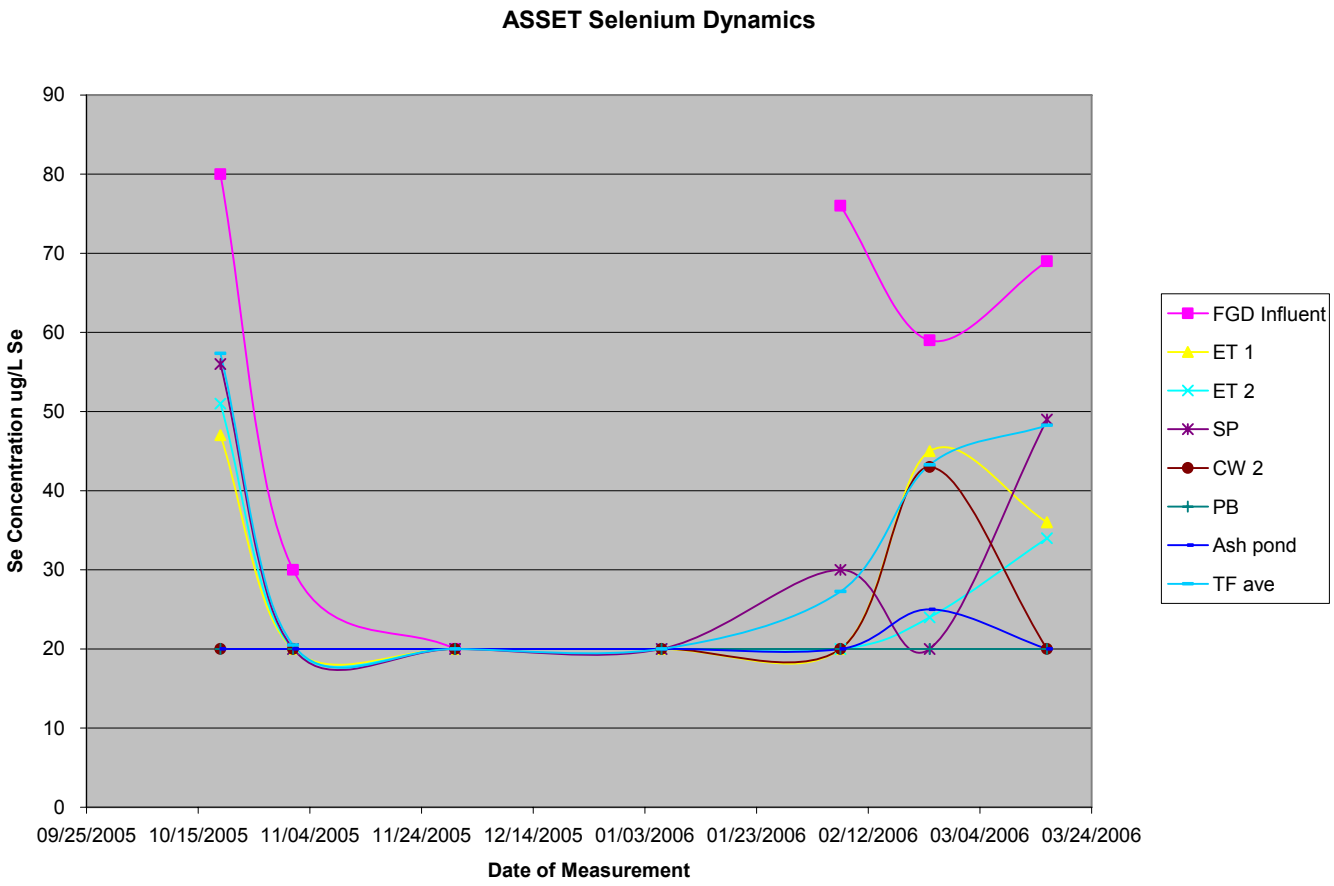


Figure 57 ASSET Selenium Dynamics

Iron Dynamics

Iron concentrations averaged 123 mg/L in FGD liquor (n=11 measurements), and the FGD influent water had an average concentration of 0.24 mg/L iron (n=11) (Figure 58). This corresponds to a removal of 99.8 % in the FGD rim ditch stacking area. Trickling filter effluents averaged 0.18 mg/L (n=39), which was an additional removal of 25% of the iron. Passage of the water through the ZVI extraction trench effluents increased the average iron concentration to 0.30 mg/L (n=22). The ATOXIC wetlands (CW 1) effluent of 0.75 mg/L iron was considerably higher than the iron effluent concentration of 0.45 mg/L for the ASSET wetlands (CW 2), and these were the highest iron concentrations of all the treatment components in passive treatment system.

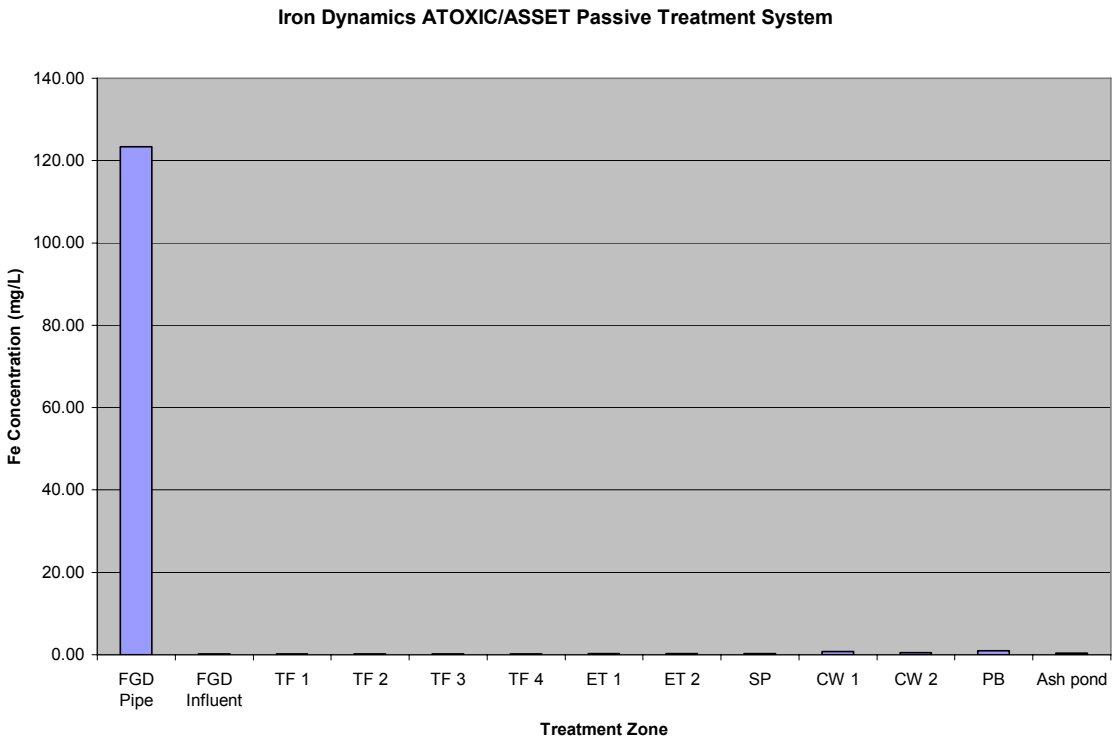


Figure 58 Iron Dynamics

Iron dynamics in the ATOXIC treatment components suggest that iron oxides were precipitating out in the trickling filters (Figure 59). The ATOXIC constructed wetlands samples have variable iron concentrations which could be due to seasonal fluctuations. Very low iron levels were observed during the coldest winter sampling events during which iron reducing bacteria would be expected to be less active.

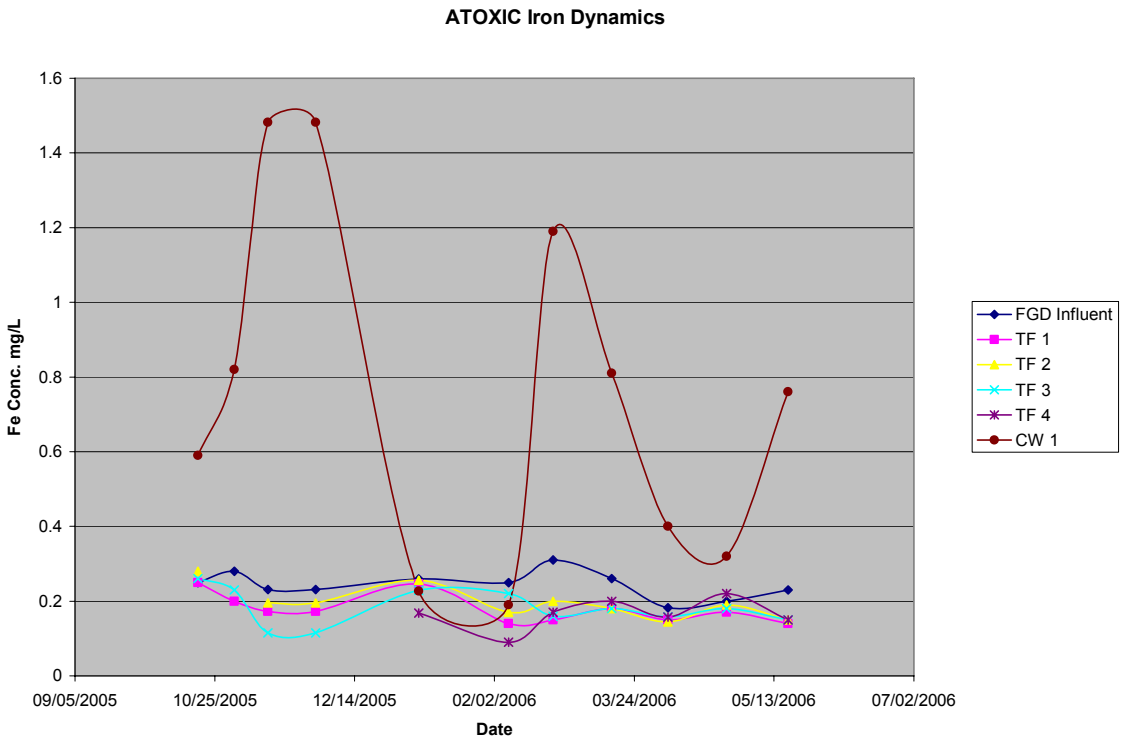


Figure 59 ATOXIC Iron Dynamics

In the ASSET treatment components, iron is added to the water stream by the slow oxidation of ZVI in the extraction trench cells. Iron concentrations were lowest in the trickling filter effluent (Figure 60). This effluent then goes to ZVI extraction trench 1 and 2, which act as a source of iron for the system. The iron is allowed to settle out in the settling/oxidation pond for long term storage. Unlike in the ATOXIC constructed wetlands in which high and variable iron levels were observed, the ASSET wetlands was observed to have lower levels of iron in effluent samples. Both of the constructed wetlands did show signs of increasing iron with the warming springtime temperatures. Pooh Bear Pond contains consistently high levels of iron, possibly due to the long retention time in the pond relative to that in the treatment system, which would result in accumulation of iron in the pond.

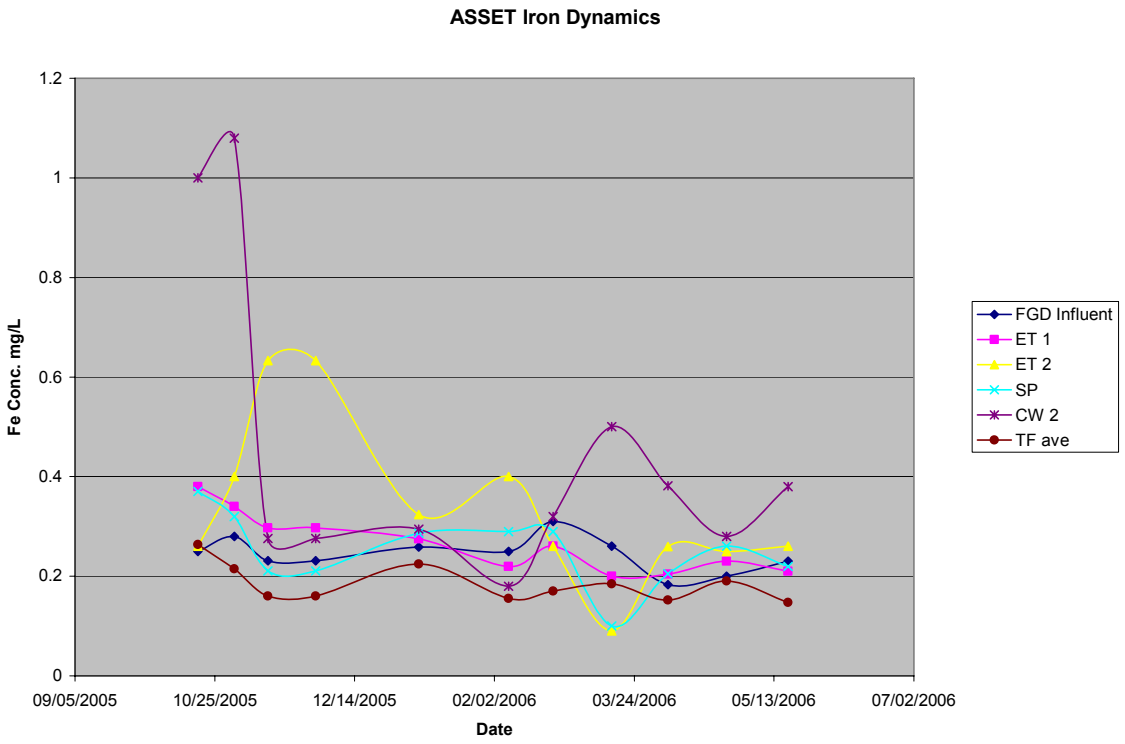


Figure 60 ASSET Iron Dynamics

Manganese Dynamics

Manganese concentrations averaged 2.44 mg/L in FGD liquor (n=11 measurements), with a decrease to an average concentration of 1.07 mg/L manganese (n=11) in the FGD influent (Figure 61). This corresponds to a removal of 56 % in the FGD rim ditch stacking area. Average manganese concentrations were reduced slightly in the trickling filter effluents and the ZVI extraction trench effluents, to 0.89 mg/L (n=39) and 0.82 mg/L (n=22), respectively. The average manganese concentration of 1.27 mg/L was the highest in the ATOXIC wetlands (CW 1) effluent out of all the treatment components in the passive system, and the concentration of 1.02 mg/L for the ASSET wetlands (CW 2) was the same or slightly higher than the other treatment components.

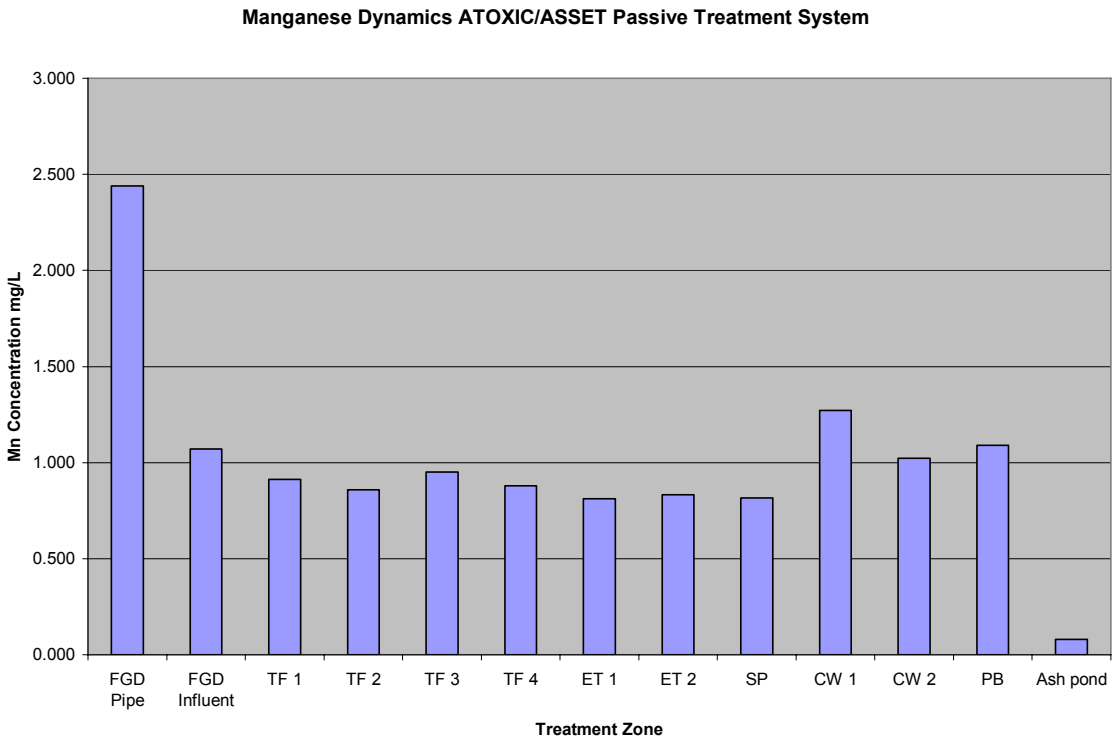


Figure 61 Manganese Dynamics

In the ATOXIC treatment components, manganese concentration trends were higher in FGD influent water and tended to be lower in the trickling filter effluents (Figure 62). This suggests that some manganese was being immobilized on the trickling filter gravel matrix, most likely as MnO_2 or MnO. The ATOXIC constructed wetland effluent samples tended to track the concentration profiles of the FGD influent samples but were elevated in concentration relative to the FGD influent.

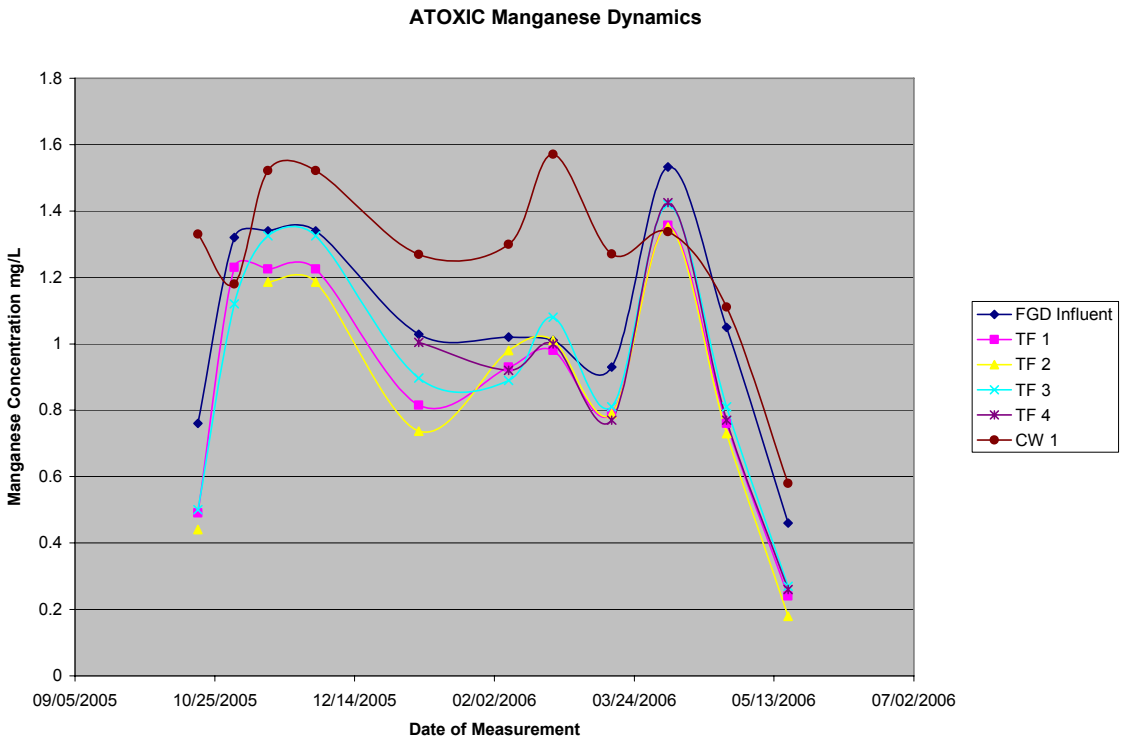


Figure 62 ATOXIC Manganese Dynamics

In the ASSET treatment components, manganese concentrations were consistently lower in the trickling filter effluent than in the FGD influent, and concentrations were lower still in the ZVI extraction trench and settling pond effluents, suggesting that manganese removal was occurring in these components of the ASSET system (Figure 63). The ASSET constructed wetlands effluent samples began to show increased levels of manganese as the temperatures warmed in the springtime. Pooh Bear Pond consistently showed high levels of manganese relative to the other sampling locations.

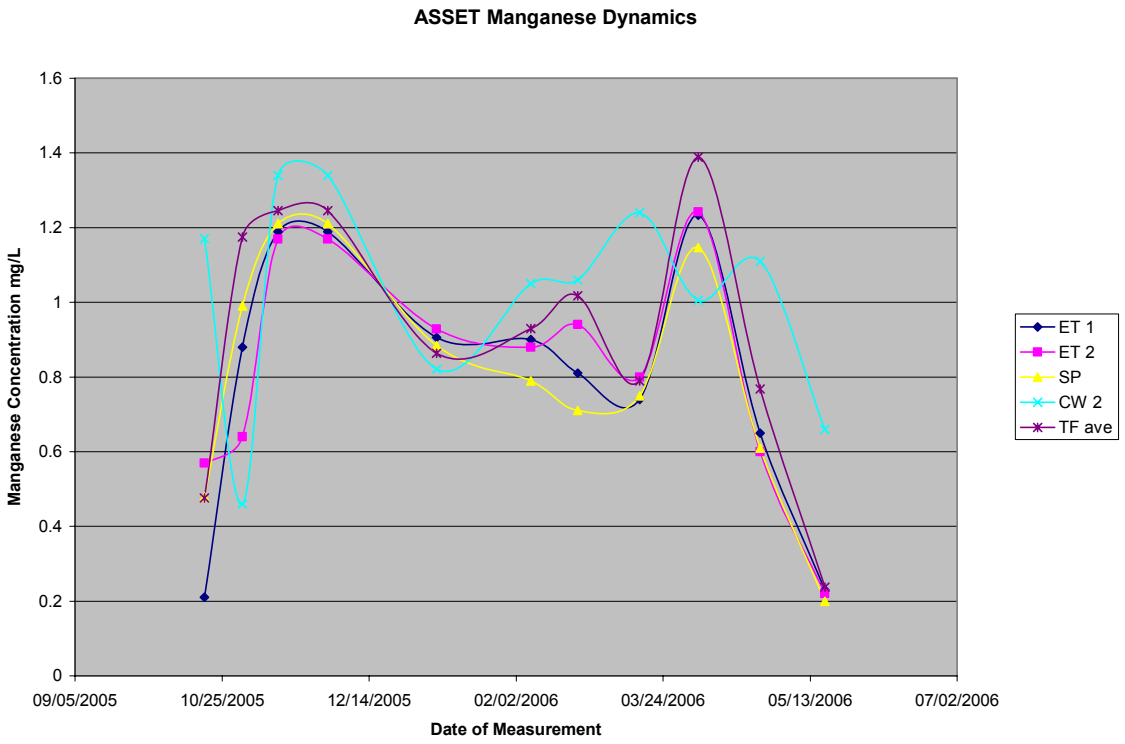


Figure 63 ASSET Manganese Dynamics

Chemical Oxygen Demand Dynamics

Chemical Oxygen Demand (COD) concentrations averaged 1680 mg/L in FGD liquor (n=11 measurements) (Figure 64). The high oxygen demand of the FGD liquor is most likely due to the high metal content of the FGD liquor. As the metals are oxidized, a tremendous amount of oxygen is required to form metal oxides. The FGD influent water has an average concentration of 27 mg/L COD (n=11), corresponding to a removal of 98 % of the COD in the FGD rim ditch stacking area. The mechanism of removal was most likely coprecipitation and settling of metal oxides in the rim ditch stacking area followed by saturation of the surface water with atmospheric oxygen. Trickling filter effluents averaged 29 mg/L (n=39), and ZVI extraction trench effluents averaged 22 mg/L (n=22). The COD average concentration increased to 33 mg/L (n=22) in the constructed wetlands effluents, most likely due to the addition of organic matter to the water stream from the compost layer and hay bales present in the wetlands.

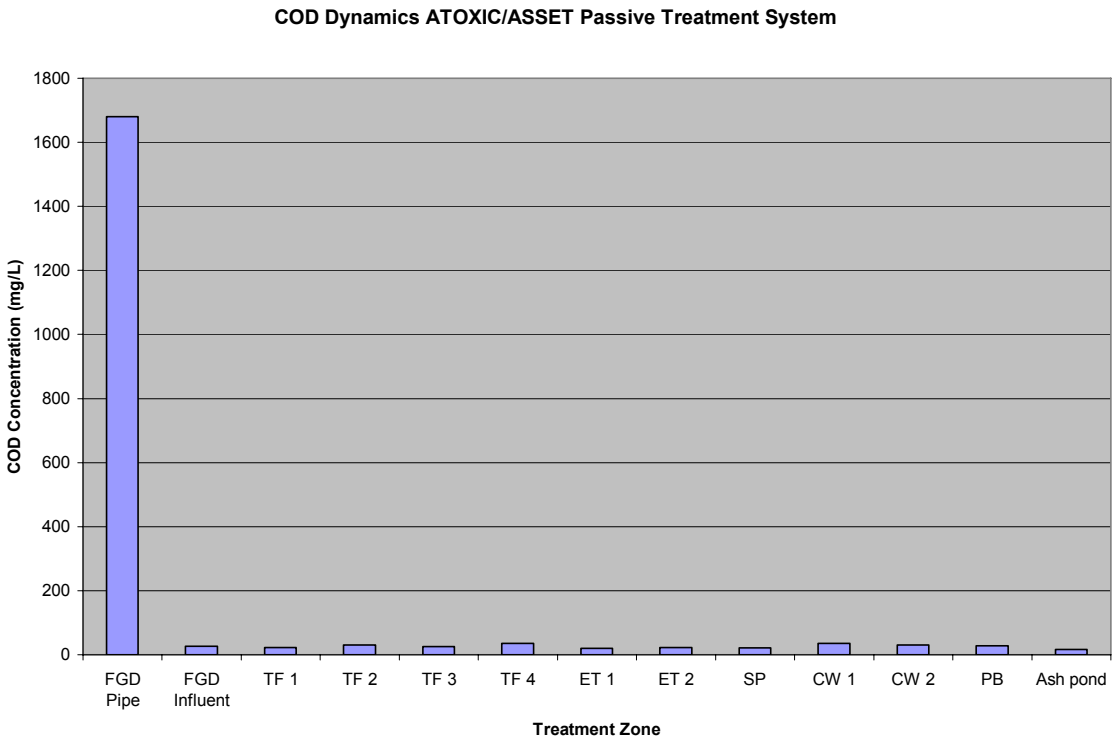


Figure 64 COD Dynamics

COD in the ATOXIC treatment components was generally low in the FGD influent and trickling tilter components with the exception of trickling filter 4, which experienced high levels of COD initially (Figure 65). The ATOXIC constructed wetlands contained variable levels of COD in the effluent samples. During the coldest part of the winter COD levels were actually lower in the ATOXIC constructed wetlands effluent than in the FGD influent water. Soon thereafter, springtime temperatures initiated biological activity and COD levels began to increase.

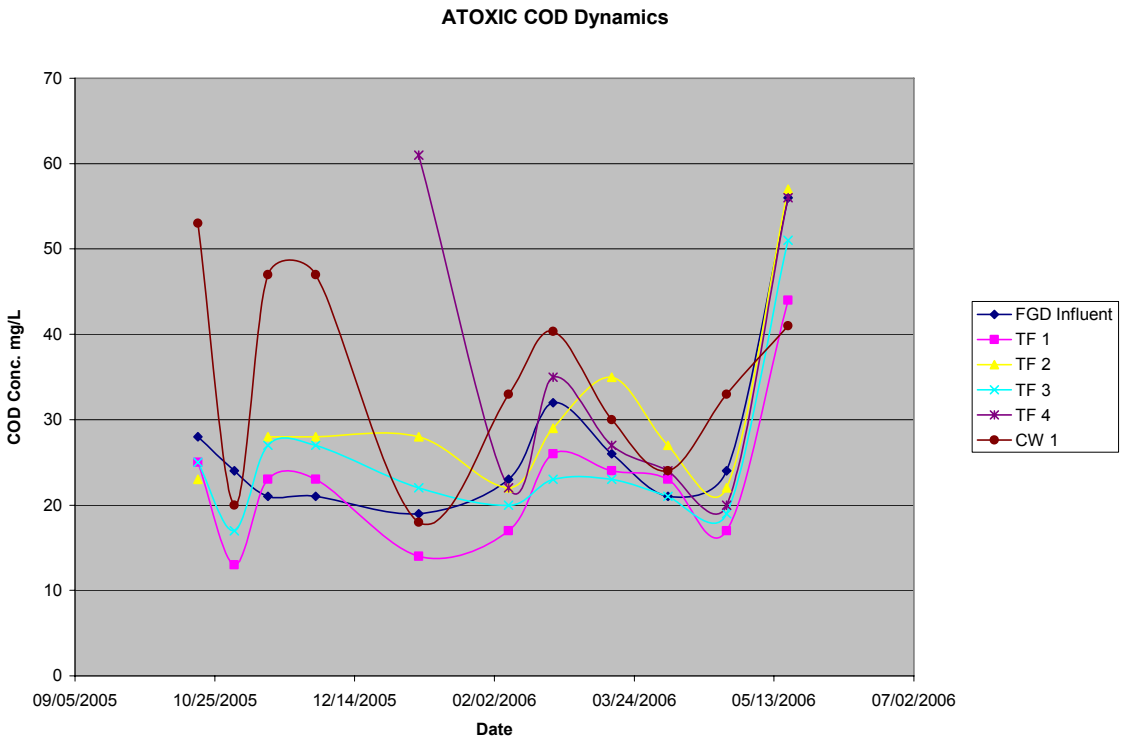


Figure 65 ATOXIC Constructed Wetlands COD Dynamics

In the ASSET treatment components, COD was in general low in the FGD influent and ZVI extraction trenches (Figure 66). Interestingly, as COD levels dropped in the ASSET constructed wetlands over the cold winter months, COD levels escalated in the settling pond quite possibly due to growth of algal biomass. In the springtime this trend reversed as the COD in the settling pond dropped steadily and the COD levels in the ASSET constructed wetlands increased with the warming temperatures. Also noteworthy, Pooh Bear Pond had only moderate levels of COD, which is required for denitrification, but this was sufficient for biological denitrification to a large degree due to its supply of alkalinity.

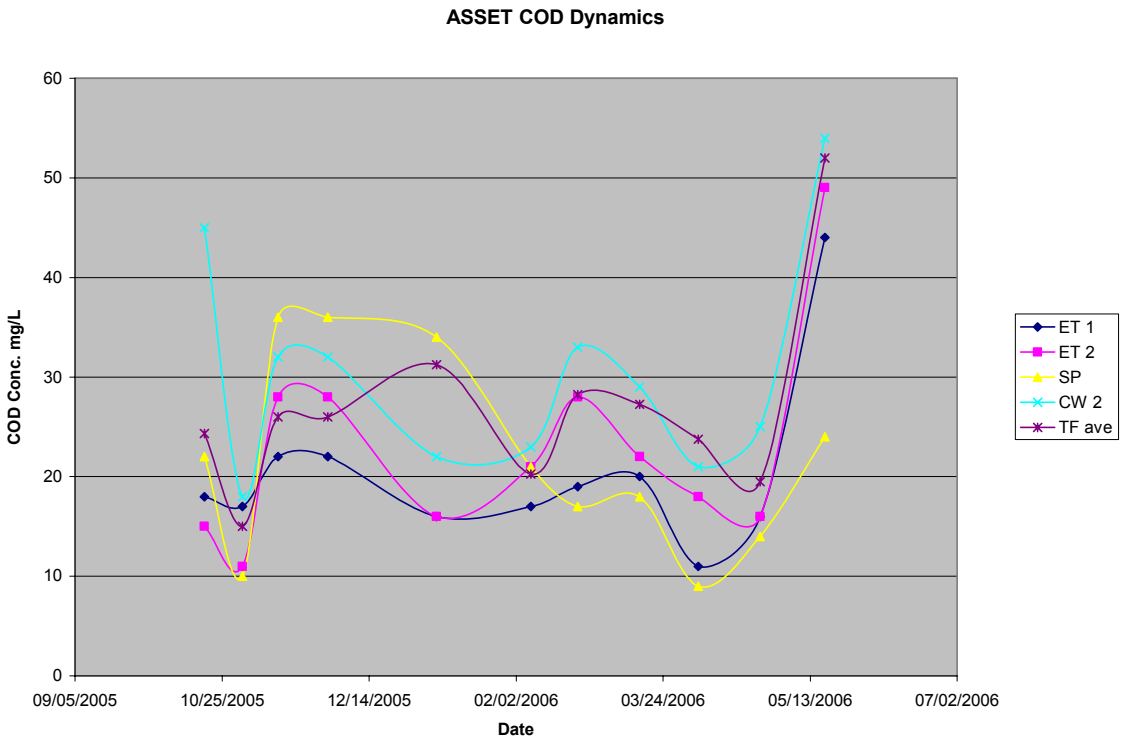


Figure 66 ASSET COD Dynamics

Alkalinity in the form of carbonate alkalinity was maintained at consistent levels throughout the passive treatment system (Figure 67). The ATOXIC and ASSET constructed wetlands added alkalinity to the system from the denitrification process and the slow decomposition of limestone substrate. Pooh Bear Pond provided a tremendous source of alkalinity, and has proven to be a great environment for promoting biological denitrification.

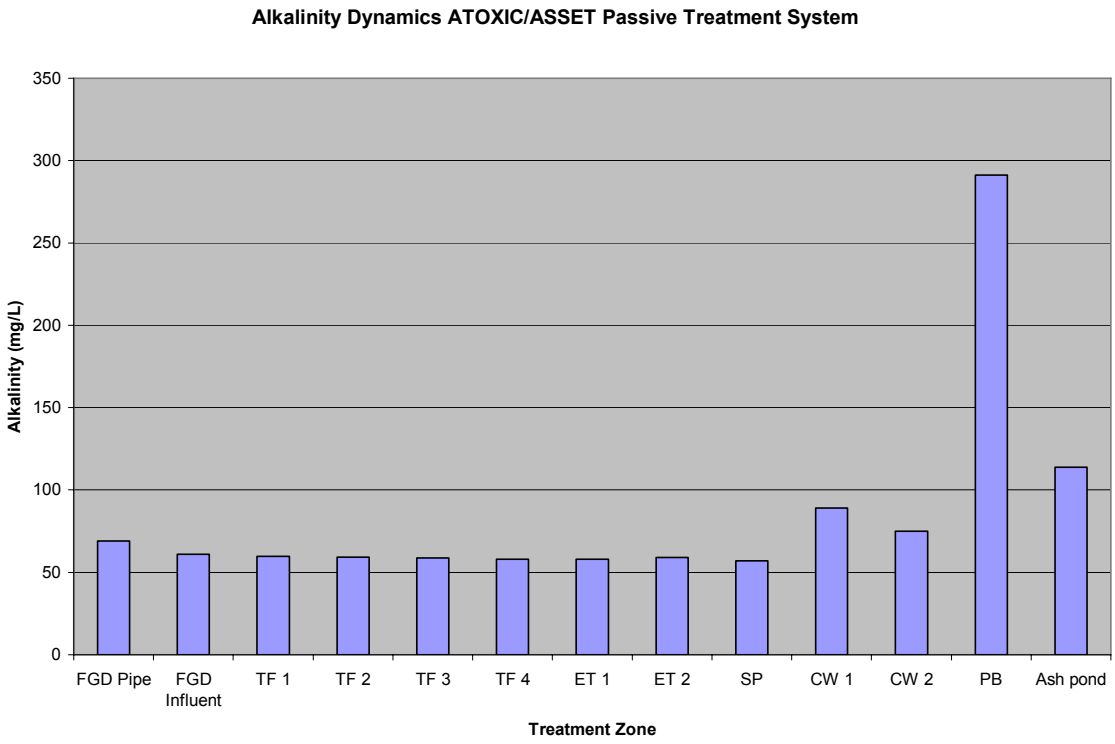


Figure 67 Alkalinity Dynamics

ATOXIC/ASSET Metals Dynamics

A thorough metals analysis was performed on samples in order to watch for interesting trends in metals dynamics as water was treated in different passive treatment environments such as the ATOXIC and ASSET systems. The bulk of metals removal occurs at the FGD rim ditch stacking area where metal oxides precipitate from the FGD liquor and settle into the FGD scrubber gypsum (Table 3).

Table 3 ATOXIC/ASSET Summary of Metals Dynamics

Location	V (mg/L) ave	Zn (mg/L) ave	Mo (mg/L) ave	Mn (mg/L) ave	Cu (mg/L) ave	Cr (mg/L) ave	Al (mg/L) ave
FGD Pipe	2.50	3.11	0.81	2.44	0.50	0.73	80.4
FGD Influent	0.02	0.17	1.04	1.07	0.01	0.02	0.28
TF 1	0.02	0.13	1.02	0.91	0.01	0.02	0.19
TF 2	0.02	0.13	0.99	0.86	0.01	0.02	0.22
TF 3	0.02	0.14	1.02	0.95	0.01	0.02	0.16
TF 4	0.02	0.15	1.01	0.88	0.01	0.01	0.18
ET 1	0.02	0.11	0.94	0.81	0.01	0.01	0.17
ET 2	0.01	0.10	0.97	0.83	0.01	0.02	0.16
SP	0.02	0.11	0.97	0.82	0.01	0.03	0.18
CW 1	0.01	0.15	0.88	1.27	0.00	0.01	0.16
CW 2	0.01	0.11	0.93	1.02	0.02	0.03	0.18
PB	0.01	0.24	0.37	1.09	0.01	0.01	0.20
Ash pond	0.06	0.24	0.19	0.08	0.00	0.01	0.53
TF Ave	0.02	0.14	1.01	0.90	0.01	0.02	0.19
ET Ave	0.01	0.10	0.96	0.82	0.00	0.02	0.17

[1]values are the average of all measurements taken at each sampling location.

Most of the vanadium, zinc, copper, and chromium were removed at the FGD stacking area and FGD stilling pond (Table 3). From there, the FGD influent containing mostly dissolved metals enters the ATOXIC system into the trickling filters. Slight decreases in most of the metals concentrations occurred due to the treatment of the water stream by the trickling filters (Figure 68). Very little change was observed for the effluent from the ATOXIC wetlands, except for a slight increase in zinc and manganese concentrations.

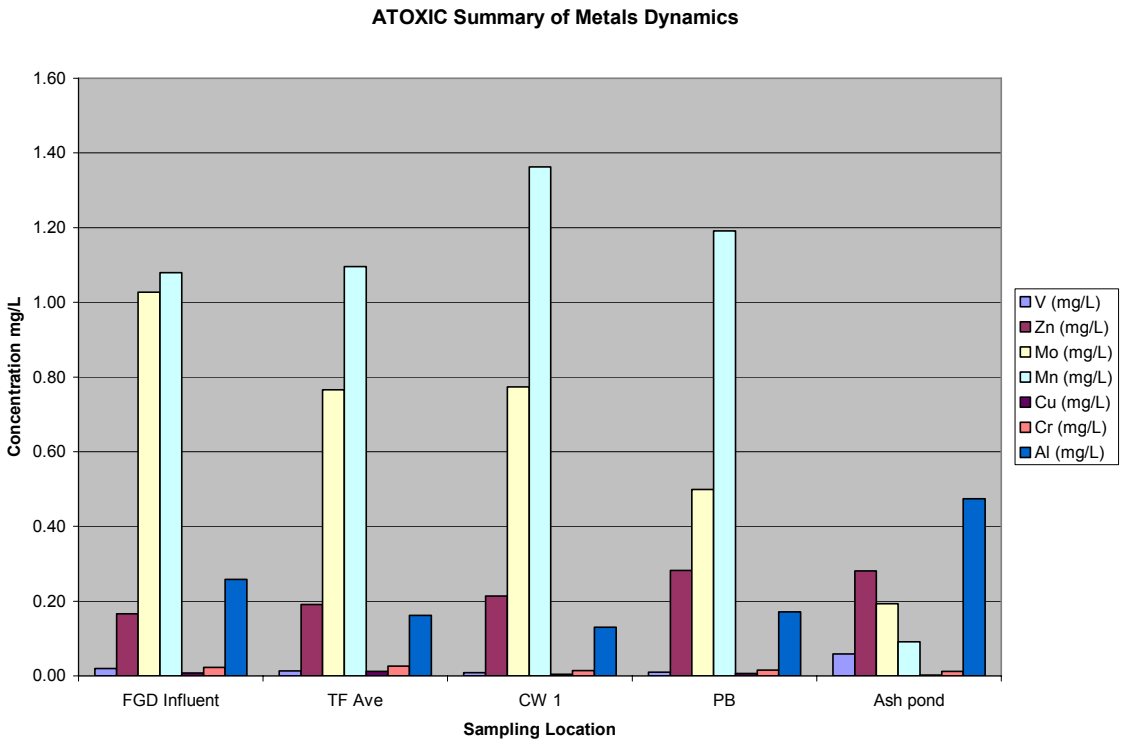


Figure 68 ATOXIC Summary of Metals Dynamics

In the ASSET experimental treatment, FGD influent water first flowed through the trickling filters, then to the ZVI extraction trenches. Decreased concentrations of zinc, molybdenum, and manganese were observed in the ZVI extraction trench effluent (Figure 69). The most significant decreases were for manganese for which an 11 % decrease in concentration were observed in the ZVI extraction trench effluent samples relative to the trickling filter effluent average. From the extraction trenches water flowed via open-channel flow to a settling/oxidation basin where slightly elevated vanadium, molybdenum, and chromium concentrations were observed relative to the extraction trench effluents. The ASSET constructed wetlands effluent samples had slightly elevated concentrations of zinc and manganese. Low levels of vanadium, zinc, molybdenum and chromium were ubiquitous throughout the ASSET passive treatment system.

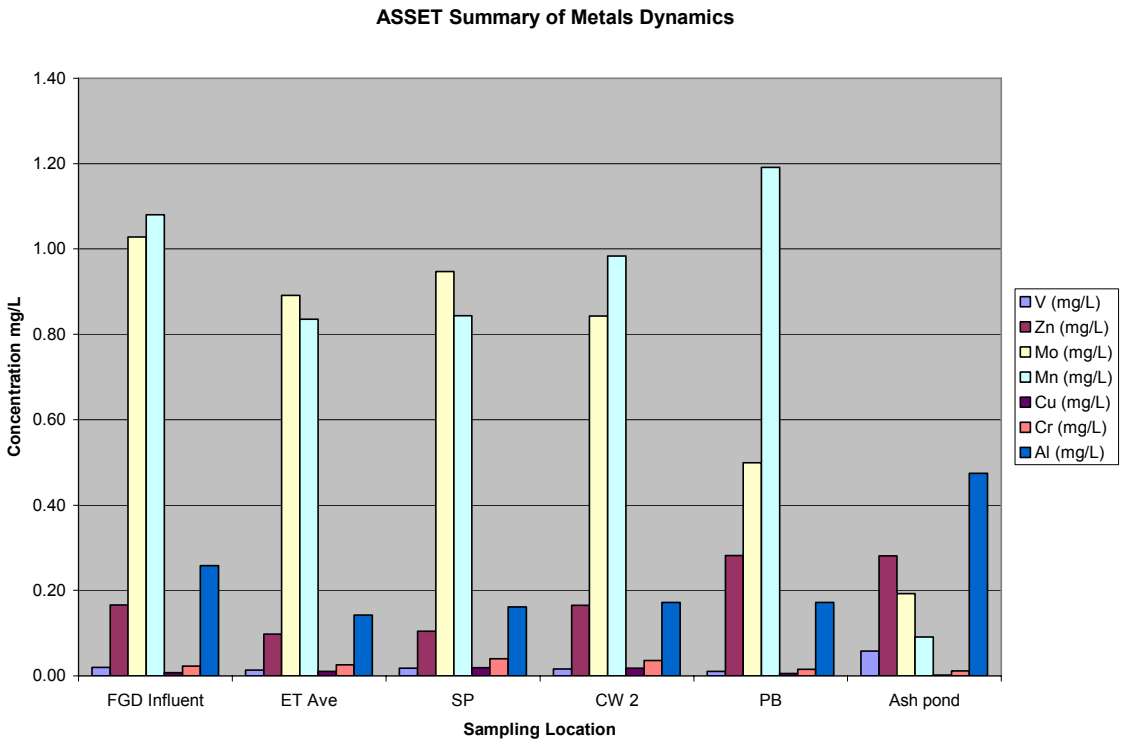


Figure 69 ASSET Summary of Metals Dynamics

The FGD influent water was very high in silicon, averaging 10.3 mg/L (n=11). Silicon concentrations in the trickling filter effluents were consistently lower than in the FGD influent and averaged 9.9 mg/L silicon (n=39) (Figure 70). The ATOXIC constructed wetlands effluent averaged 8.6 mg/L silicon (n=11), although at several sampling points the trickling filter concentrations were the same or lower than for the constructed wetlands.

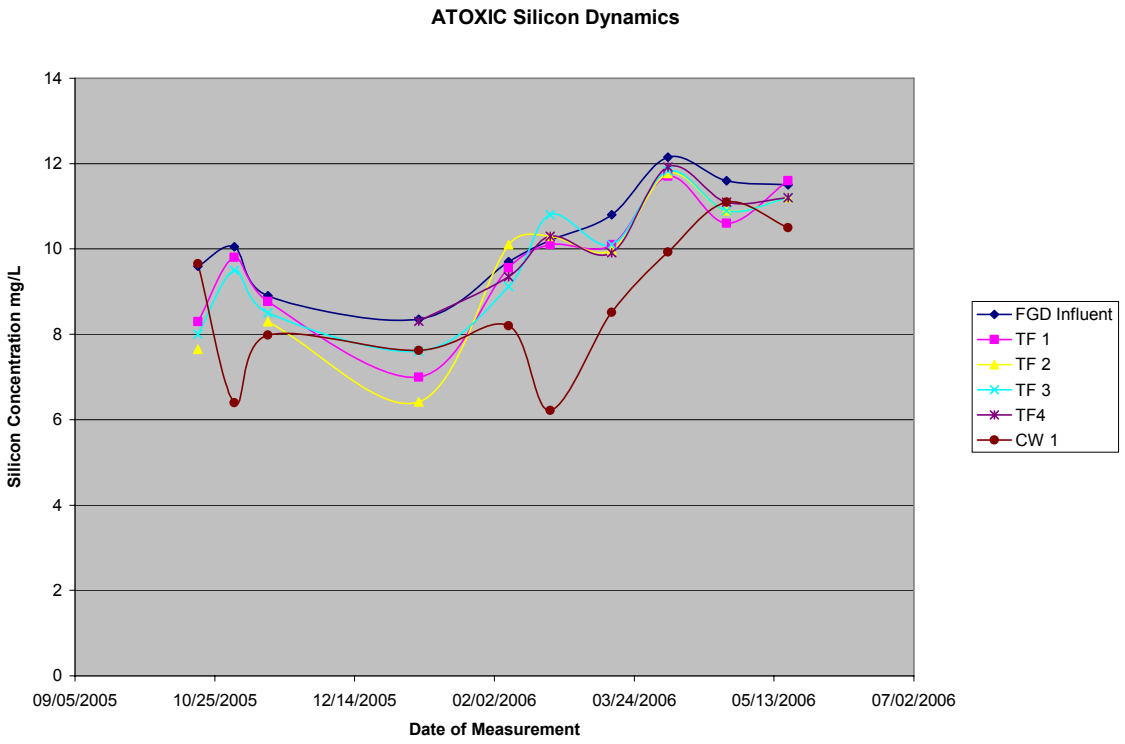


Figure 70 ATOXIC Silicon Dynamics

In the ASSET passive treatment system the ZVI in the extraction trench cells reacted with silicon in the FGD stream to initially lower the silicon concentrations (Figure 71). An average of 9.4 % of the silicon was removed in the ZVI extraction trench effluents relative to the trickling filter average. Most of this removal occurred soon after the installation of the ZVI as silicon reacted with the highly reactive iron surfaces of the ZVI. Over time as the ZVI surfaces become coated with oxides and other mineral phases, this reaction slowed.

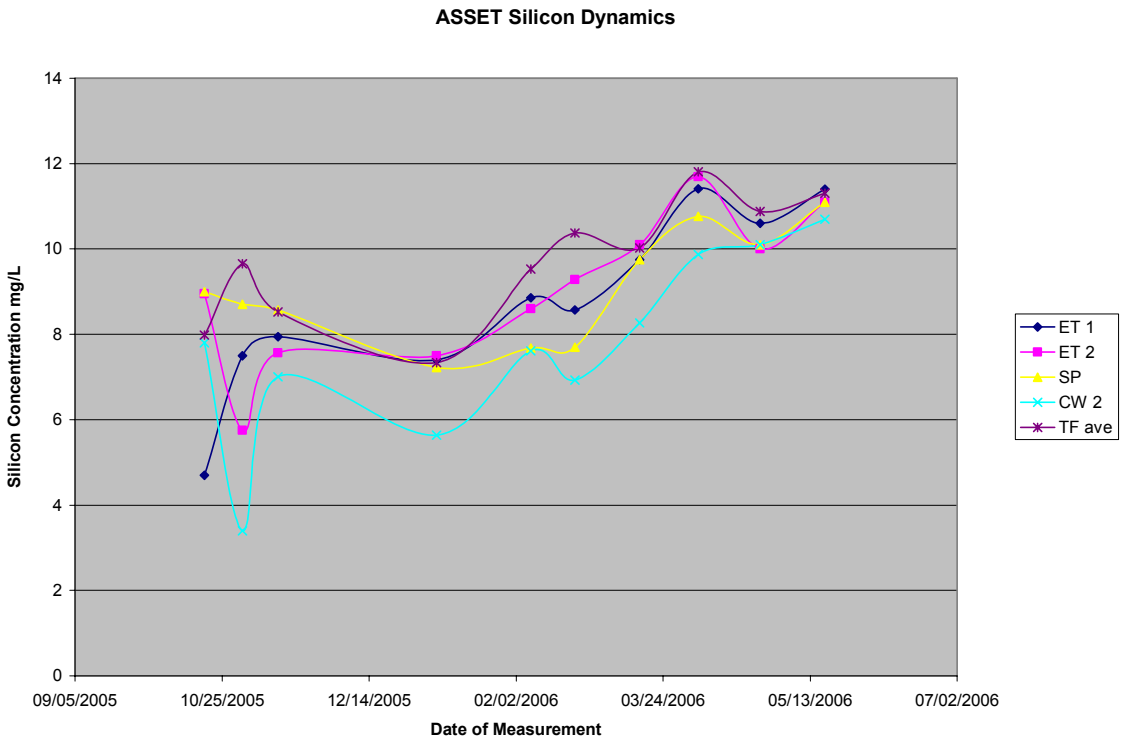


Figure 71 ASSET Silicon Dynamics

Boron concentrations were elevated throughout the ATOXIC passive treatment system (Figure 72). FGD liquor samples average 47.7 mg/L while FGD influent samples average 45.3 mg/L, so most of the boron in the FGD stream is very soluble. Little or no boron was removed by the trickling filters. A slight decrease in boron concentration was observed in the ATOXIC constructed wetlands. This is assumed to be due to adsorption onto the gravel matrix and compost layer in the wetlands; the concern is that once all the adsorption sites have been saturated, boron removal may slow or stop. At this time the treatment system has not been operational long enough to determine if this will occur.

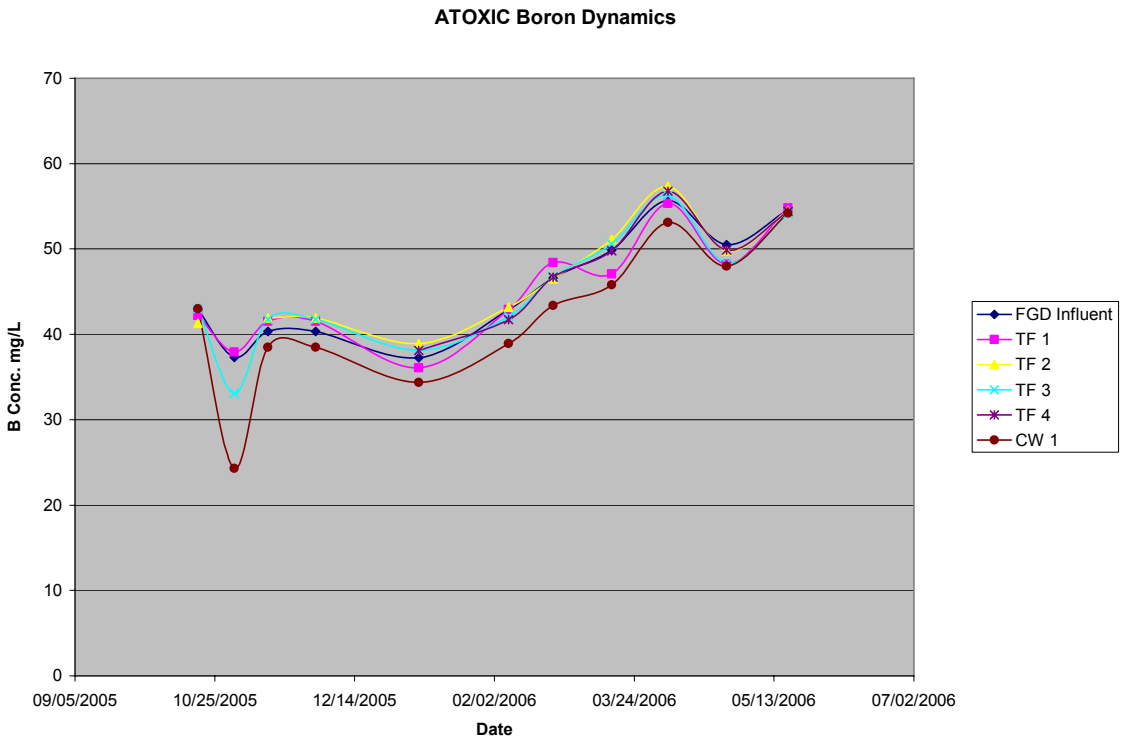


Figure 72 ATOXIC Boron Dynamics

In the ASSET passive treatment system, much like the ATOXIC system, boron is ubiquitous. Of note is that upon the installation of the ZVI in the extraction trenches, there was an initial drop in boron concentrations in the ZVI extraction trench effluents (Figure 73). This decrease in boron concentrations in the ZVI extraction trench effluents was short-lived but was a 30 % decrease shortly after installation of the ZVI.

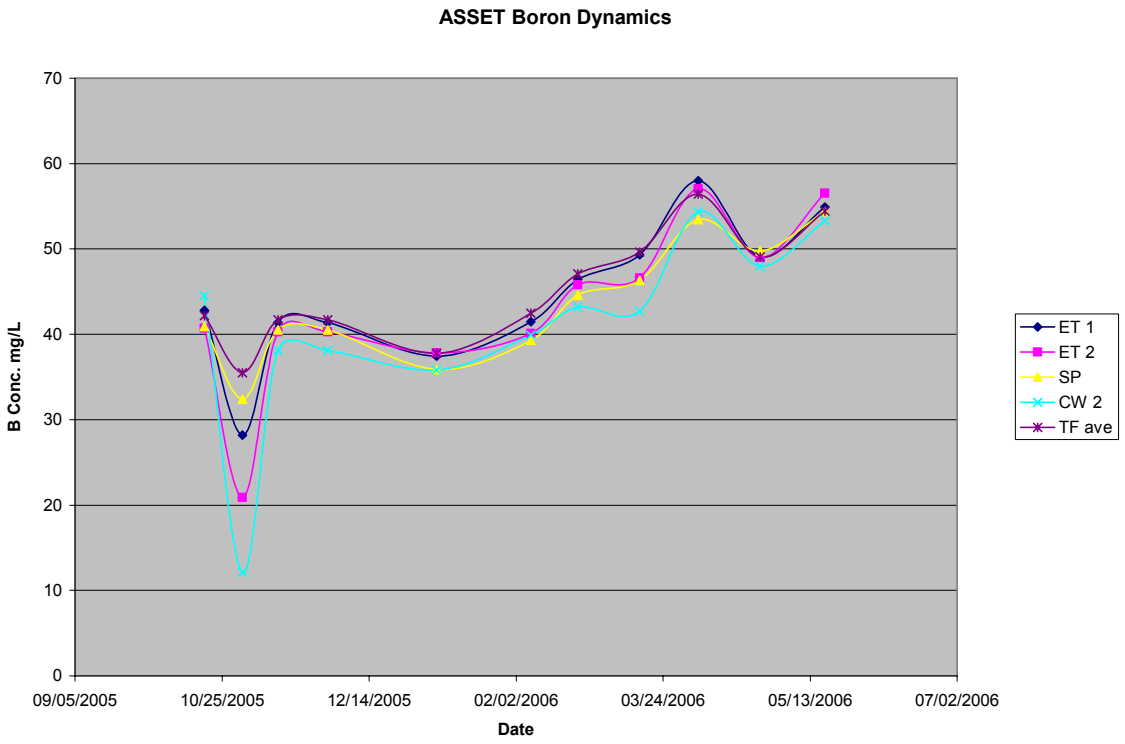


Figure 73 ASSET Boron Dynamics

SUMMARY AND CONCLUSIONS

The construction of the ATOXIC/ASSET passive treatment system was completed at the TVA Paradise fossil plant in the summer of 2005. Water quality sampling of the system with FGD water flow through the system was initiated in October 2005 and continued until May 18 2006, when FGD flow was discontinued to allow growth in the wetland cells of replanted wetland species. At this time, FGD water was drained from the wetland cells and replaced with less toxic water from the facility's ash pond to allow the replanted species to become established. At the time of this report, the wetland cells were still filled with ash pond water, and FGD water flow through the system has not been restarted. Plant growth under these conditions is excellent.

The design of this system allows the evaluation of two treatment trains, one with the ZVI extraction trench and one without, and their effect on the removal and transformation of trace metal species in the FGD water. The ZVI provides metals removal through adsorption and reduction to less soluble forms at the iron surface, and by formation of iron oxides and hydroxides which provide additional surfaces for metals adsorption. Water sampling from October 2005 to May 18, 2006 included analysis for total trace metals, along with analysis of nitrogen species (NH_4-N, NO_3-N, TKN) to track the ability of the system to remove nitrogen from FGD water. Analysis for speciation of the main trace metals of concern - arsenic, mercury, and selenium - was not conducted for these samplings.

The trickling filters component of the system, designed to remove ammonia in the FGD water by conversion of ammonia to nitrate via nitrification, reduced ammonia concentrations on average from 0.22 mg/L NH_4-N in the trickling filter influent to 0.15 mg/L in the effluent. This reduction of NH_4-N was not as efficient as that observed in laboratory-scale studies conducted before the construction of the treatment system at the Paradise Fossil Plant, in which trickling filters reduced 20 mg/L NH_4-N to concentrations close to zero. However, the low concentrations of NH_4-N in the influent and the low temperatures in the fall and winter most likely limited the growth of nitrifying bacteria in the trickling filters. Nitrate removal in the anaerobic constructed wetlands was more effective, but removal rates also decreased with lower temperatures in the winter. A study is planned in which the FGD water will be amended with ammonia to bring the concentration to 5 mg/l NH_4-N to test the efficiency of the trickling filters. Ammonia concentrations will be increased above 5 mg/L if the trickling filters are effective in removing ammonia at this concentration.

All components of the treatment system showed some removal of arsenic and selenium from the FGD water, with the trickling filters and the extraction trench more effective than the constructed wetlands, which reduced these concentrations only slightly. Mercury analysis data was not available at the time of this report. However, arsenic and selenium concentrations were also low, and along with amending the influent FGD water with ammonia, concentrations of arsenic, selenium, and mercury will be increased with amendments. The other trace metals sampled (Al, Fe, Si, V, Zn, Mo, Mn, Cu, and Cr) in general showed the same pattern of removal as did arsenic, selenium, and mercury, with removal occurring mostly in the trickling filters and the extraction trenches. The

exception was boron, which was present in high concentrations (average of 45 mg/L in the FGD influent), with no removal in the trickling filters and only slight reductions in concentrations in the extraction trenches and constructed wetlands.

The operation of the ATOXIC/ASSET passive treatment system and the results for water sample analyses provided in this report demonstrate that this system has been successfully designed and implemented to remediate the target volume of 250,000 gpd of FGD water. Continued operation of the system will provide results to further test and refine the efficiency of the system for removal of contaminants from FGD water.

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