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# Low-Level Pharmaceuticals and Personal Care Products in the Waters of Michigan

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# LOW-LEVEL PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN THE WATERS OF MICHIGAN

by

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Lisa M. Anderson

TABLE OF CONTENTS

Table of Contents—continued

Table of Contents—continued

LIST OF TABLES

LIST OF FIGURES

# INTRODUCTION

Pharmaceuticals and/or personal care products are used by most of us every day. Few of us think about where these compounds go after we have used them. One may not consider the fate of the chemical compounds contained in our shampoo, sun screen, laundry detergent, and hand soap as they are washed down the drain. Many citizens may not worry about the residual pharmaceuticals in our wastes after they have taken them for certain medical conditions or a simple headache. Pharmaceuticals are designed to be persistent so that they can be maintained long enough in the body to have the desired therapeutic effect. Therefore, it makes sense that a portion of the pharmaceuticals that we take will be excreted in our urine or feces. In the recent past, it was also conventional wisdom to flush unused or out of date pharmaceuticals down the toilet. This was to protect others from accidental use or intentional use without a prescription. Now, it is better to take unused prescriptions to drop off sites or to landfill the drugs with household garbage in order to slow their introduction to surface waters.

In many ways, pharmaceuticals and personal care products become a part of our waste stream; many are not completely removed by most conventional waste water treatment processes and are discharged into the environment. Recently, some of these compounds have been identified as a cause for concern, as endocrine disruptors in wildlife, even at very low levels (Mimeault et al., 2005; Ishibashi et al., 2006; Soares et al., 2008). The endocrine system in an organism regulates growth and sex hormones, so its disruption can cause negative consequences to a species. Scientists in European countries had been studying

these compounds in the environment for many years before researchers in the U.S. began looking for them (Ternes, 1998). The United States Geological Survey (USGS) spearheaded this research in the U.S. and developed analytical techniques to detect these compounds in the part per billion (ppb) range. In 2002, the USGS published the paper titled *Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance* (Kolpin et al., 2002). Streams that were likely impacted were sampled and many compounds were detected. Since then, research into pharmaceuticals and personal care products in the environment in the U.S. has greatly increased; ranging in emphasis from occurrence to toxicity and from fate in soils to groundwater. In fact, these studies are now occurring all over the world, as the research highlighted in the following paragraphs will illustrate.

As mentioned above, the USGS national reconnaissance article (Kolpin et al., 2002) was the premier pharmaceutical and personal care product occurrence study for the United States. During 1999 and 2000, the USGS sampled 139 streams in 30 states. The study results are not considered representative of all streams, because the stream selection was biased toward streams that were likely to be impacted. The streams chosen for study were downstream of urban areas or large livestock production areas (Kolpin et al., 2002). Analysis was conducted for 95 chemicals, chosen because of their high use, for which five new analytical techniques were developed. These analytical methods used either filtered water solid-phase extraction with liquid chromatography and mass spectrometry positive-ion electrospray analysis or whole water continuous liquid-liquid extraction and capillary gas chromatography and mass spectrometry analysis (Kolpin et al., 2002). The results show 80 percent of the streams sampled had one or more chemicals

detected. Furthermore, 82 of the 95 chemicals were detected at least once during the study. The most common chemicals detected were coprostanol (fecal steroid), cholesterol (plant and animal steroid), DEET (insect repellant), caffeine (stimulant), triclosan (antimicrobial disinfectant), tri(2-chloroethyl) phosphate (fire retardant), and 4-nonlyphenol (detergent metabolite). Most of the analytical results fell below 1 part per billion and mixtures of compounds were common. These concentrations rarely exceeded drinking water or ecological standards or criteria; however, these criteria only existed for 14 of the compounds studied. The paper called for further study of the effects of compound mixtures, metabolite fate and transport, and other compounds not analyzed in the study (Kolpin et al., 2002).

Another occurrence study by a group of German researchers investigated the River Elbe and its tributaries for the presence of pharmaceuticals (Wiegel et al., 2004a). The Elbe follows a course from the Czech Republic to its mouth at the North Sea in Germany. The River Saale, the third largest tributary of the Elbe, and the Elbe River were sampled in 1998, 1999, 2000, and 2002. The goal of the study was to investigate the distribution of different pharmaceuticals, presumably from municipal sewage treatment works discharge, along the entire Elbe River from its source to the City of Hamburg. The River Saale was studied to verify the results from the Elbe in regards to the distribution and sources of the pharmaceuticals (Wiegel et al., 2004a). The compounds chosen for analysis were based on consumption figures and on the nationally coordinated monitoring concept drafted by the Joint Federal and State Committee for Chemical Safety Standards created in 1999. Diclofenac, ibuprofen, carbamazepine, antibiotics, and lipid regulators were the main pharmaceuticals detected during the 1998 sampling. The analytical results from 1999 and 2000 show not only the presence of the drugs phenazone, isopropyl-

phenazone, and paracetamol, which are all analgesics, but also the presence of metabolites that contribute significantly to the overall pharmaceutical concentration of the river. It was also determined that the River Saale is a major contributor of pharmaceuticals to the River Elbe. Finally, the carbamazepine sampling of Saxony during 2002, showed that this compound is quite ubiquitous in surface waters. Carbamazepine is an antiepileptic drug and because it is highly persistent, it is an excellent tracer for pharmaceuticals in the environment (Wiegel et al., 2004a). This study verified that the pharmaceutical concentrations within the River Elbe and its tributaries can be attributed to the discharge of treated waste water into the rivers. Therefore, pharmaceuticals and their metabolites can be used as fecal indicators in surface waters impacted by human activity. The authors also stress the necessity to establish priority lists for pharmaceuticals in order to perform risk assessment studies. These are needed in order to understand the ecotoxicological effects of these compounds and then to determine their threat to the health of surface waters (Wiegel et al., 2004a).

A similar study was performed in France on the Arc River basin in the southeast portion of the Aix en Provence between March 2003 and April 2004 (Comoretto and Chiron, 2005). The presence of pharmaceuticals and how urban centers (i.e. waste water treatment plant discharges) contribute to the pharmaceutical concentration of the Arc River were investigated. Additional objectives of this study were to determine pharmaceutical seasonal variation and how they compared to the pesticide loads to the river from surrounding vineyards. The study confirmed that the discharge of treated waste water from urban centers is the major source of pharmaceuticals in the Arc River. The highest concentrations of pharmaceuticals were for carbamazepine and bezafibrate (lipid regulator). The

results also indicated the pesticide pollution had peaks in the spring months, as this is usually the time of application, whereas the pharmaceuticals were found to be regular additions to the river due to waste water discharge. There were higher concentrations of pharmaceuticals in the summer months, when river flow is low and a large portion of the river flow consists of waste water discharge (Comoretto and Chiron, 2005).

The occurrence studies cited above have one thing in common: they all had some focus on waste water discharge into rivers and streams because waste water treatment plant effluent is the largest point source for pharmaceuticals and personal care products into surface waters. It is no surprise that further study has been conducted on waste water effluent itself and some of the very unique compounds contained within it. For example, in 2002 a study was conducted by the U.S. Environmental Protection Agency and the USGS where effluent samples from 10 waste water treatment plants (WWTP) from across the U.S. were analyzed for 110 pharmaceuticals and waste water constituents (Glassmeyer et al., 2005). Samples were also obtained upstream of each WWTP and for two sample sites downstream of the plant. The goal was to determine if some of the chemicals occurring in human waste water could be used to assess the quality and/or safety of drinking and recreational waters instead of the indicator bacteria test currently used. The advantages of using the chemicals for this purpose are that the analysis time could potentially be more rapid than waiting for bacterial culture tests and that the chemicals are specific to human waste water. The bacterial tests (total coliform, fecal coliform, E. coli, and enterococci) do not discriminate between human or other animal sources. This is important, as it is the human sources that have a much greater potential to cause sickness in humans if they come into contact with or

consume the contaminated water (Glassmeyer et al., 2005). The results show that 78 of the 110 chemical analytes for were detected in at least one sample. Many of the same compounds were detected in the USGS national reconnaissance study cited above (Kolpin et al, 2002). The results of the study prove 35 of the waste water chemicals may be useful to indicate contamination by human fecal material. These compounds were selected as they show increased frequency of detection and concentration in the waste water treatment plant effluent when compared to the upstream sample location. These chemicals also decreased in occurrence and concentration the further downstream from the WWTP (Glassmeyer et al., 2005). The waste water chemicals ethyl citrate, galaxolide, and tonalide are good candidates for human fecal contamination indicators. Compounds such as carbamazepine, diphenhydramine, and caffeine are also potential indicators, because they are usually only used by humans. Coprostanol has the best potential as a human waste indicator as it shows the most change in concentration between sample sites and also has a human source. This study was designed to determine the relationship between the presence of waste water chemicals and human waste sources, and not to directly relate the presence of the chemicals to the presence of bacteria and other pathogens that are probably also present in the waste water. Further study would be needed to link the later two (Glassmeyer et al., 2005).

In another study by the USGS in Colorado, sewage treatment plant effluent and the Boulder Creek receiving water were sampled to investigate whether gadolinium (Gd) could be used as a tracer for waste water discharge. Previous studies from Italy, Japan, France, and the Czech Republic have shown there is a positive anomaly for gadolinium in the rare earth pattern in surface waters that received waste water effluent (Verplanck et al., 2005). This study is the first to

document this same anomaly in the United States. The enrichment of Gd has been attributed to the use of gadopentetic acid as a contrasting agent in magnetic resonance imaging or MRI. The Gd has a high magnetic moment which makes it ideal for use in MRI. It is also inert and passes through the kidneys with a half-life of 2 hours. The organic Gd compounds are very stable and may pass through most sewage treatment plants. As part of the study in Colorado, 4 effluent samples from sewage treatment plants that serve different populations were analyzed. They all showed a positive Gd anomaly except for the plant that serves a small population (1200 people) and contains no medical facilities (Verplanck et al., 2005). To evaluate the fate of Gd once it enters a surface water body and leaves the treatment plant, a 14 km section of Boulder Creek was sampled during low flow conditions. The results showed that the Gd anomaly decreased the further downstream from the treatment plant. This may be due to the loss of dissolved Gd or dilution of the effluent with distance downstream. This study has shown that Gd is an ideal tracer for sewage treatment plant effluent for communities that have MRI facilities. Using the Gd anomaly instead of pharmaceuticals or personal care products to evaluate sewage discharge impact has an advantage; Gd is easier to determine and the analytical difficulties with low concentrations of pharmaceuticals and personal care products are avoided (Verplanck et al., 2005).

A study conducted in Tromsø, Norway was the first survey to determine the presence of selected pharmaceuticals and other waste water compounds in Norwegian sewage and the receiving seawater (Wiegel et al., 2004b). The selected compounds include analgesics, β-blockers, anti-depressants, caffeine, triclosan, and DEET. The sewage produced in Tromsø is collected in sewers and either discharged directly into the sea or processed by mechanical filtration, with no

biological treatment, before being discharged into the sea. The analytical results indicate that caffeine, ibuprofen, ibuprofen metabolites, and triclosan were detected in all of the sewage samples. The sewage effluent from hospitals also contained additional pharmaceuticals such as anti-depressants and carbamazepine. With regard to the sea water samples from Tromsø-Sound, caffeine and DEET were present in all of the samples and ibuprofen and/or its metabolites were detected in most of the sea water samples (Wiegel et al., 2004b). Caffeine was distributed throughout the Sound, even at the reference locations in the open North Atlantic/Arctic Ocean near the coastline where a small village of about 500 inhabitants is located. This aspect of caffeine makes it a good candidate for a qualitative waste water tracer in a marine environment. The presence of ibuprofen and its metabolites in the sound is interesting, as they have been shown to be easily removed by sewage treatment and in limnic conditions. The researchers postulate that the low temperatures and low biological activity of the sound decrease the rapid transformation of these compounds (Wiegel et al., 2004b). The fact the sewage undergoes no biological pre-treatment before discharge into the sound may also help to explain the concentrations of ibuprofen and its metabolites in the sea water.

The studies above focused on effluent from waste water treatment plants, but they also begin to investigate the fate and transport of pharmaceuticals and personal care products during treatment and in the environment. Now, studies that investigate fate and transport of these compounds even further will be discussed. A review article from 2005 looked at the current research to summarize the fate of human pharmaceuticals in the waste water treatment process (Jones et al., 2005). The article makes the point that there are thousands of compounds taken for medicinal purposes all over the world. There are over 3000 individual

pharmaceutical substances licensed for use just in the United Kingdom (Jones et al., 2005). It is not feasible to study all of the compounds; therefore selection processes have been used to focus on those chemicals that may cause harm due to the volume of use or their toxicity. Most sewage treatment plants were not designed to deal with pharmaceutical compounds. These compounds vary in their physical and chemical properties, which causes differences in their removal efficiencies (Jones et al., 2005). The properties of pharmaceuticals that control their fate during waste water treatment and in the environment include their chemical structure, aqueous solubility, octanol/water partition coefficient, and Henry's law constant. For example, using the octanol/water coefficient ($K_{ow}$), the more hydrophilic a compound is, the likelier it will partition to the aqueous phase. So, the more hydrophobic a compound is, the greater the likelihood it will accumulate in the solid phase or sludge. The following guidelines for $K_{ow}$ have been used: Log $K_{ow}$ < 2.5: low sorption potential, Log $K_{ow}$ > 2.5 but < 4.0: medium sorption potential, Log $K_{ow}$ > 4.0: high sorption potential (Jones et al., 2005). The mechanism by which a compound partitions between water and organic carbon ($K_{oc}$) can also be useful to determine fate of a compound. As with $K_{ow}$ the higher the $K_{oc}$ the more likely the compound will sorb to organic matter in suspended solids, nonpolar fats and lipids, greases, surfactants, soils, and aquifer sediments. So, therefore, the lower the $K_{oc}$, the more likely the compound will remain with the liquid phase. Most pharmaceuticals are polar and soluble with low log $K_{ow}$ and $K_{oc}$ values, so most will remain in the aqueous phase. Their sorption to sludge is probably minor for most compounds (Jones et al., 2005). The fate of the pharmaceutical also greatly depends on the treatment processes used at the waste water treatment plant. The primary sedimentation stage, used at most sewage treatment plants, is unlikely to remove any of the polar

pharmaceuticals. There is potential to remove or degrade pharmaceuticals in the secondary phase, which commonly consists of activated sludge or trickling filters. Here, losses may be due to removal in sludge and/or degradation by resident bacteria. Some compounds are removed more efficiently if the sludge loading rate is reduced or if the hydraulic retention time is increased or both. This allows for slower growing bacteria to form which in turn allows for the pharmaceuticals to be exposed to a more diverse fauna of bacteria for potential degradation. This also allows for a greater acclimatization of the bacteria to the compounds so, in time, the degradation is more efficient (Jones et al., 2005). Sewage treatment plants that utilize nitrification and denitrification show lower concentrations of pharmaceuticals such as ibuprofen and naproxen. This is also probably due to a wider array of aerobic and anaerobic bacteria capable of degrading the drugs. The use of sewage lagoons during the secondary treatment phase has also been shown to remove some pharmaceuticals that are susceptible to photodegradation (Jones et al., 2005). For those waste water treatment facilities that have tertiary treatment, the remaining pharmaceuticals may be removed. It has been shown at water treatment plants with ozonation or membrane treatment that pharmaceuticals can be removed below detection limits. These treatments are costly however and not always required by regulation (Jones et al., 2005). Any remaining pharmaceuticals are then discharged into the environment via the effluent. The risks to humans, if exposed to these pharmaceuticals in the water, are often regarded as minor. However, there will only be an increase in the demand for the world's freshwater supplies and little is known about the effects of chronic, subtherapeutic exposure to pharmaceuticals. Consequences to aquatic ecosystems are also a major concern. With the pharmaceuticals that may partition to the sludge, such as fluoroquinolone antibiotics,

their release to the environment is possible if the sludge is land applied and the compounds leach into the groundwater or surface water. This impact can be minimized if the sludge is treated by digestion, which can be anerobic or aerobic, where the temperatures are elevated enough to degrade the pharmaceutical (Jones et al., 2005). The fate of pharmaceuticals in waste water treatment plants and beyond is quite important, as it is unlikely these compounds will be restricted due to their beneficial health effects to humans. It is also very likely their use and variety will only increase as our populations increase and age (Jones et al., 2005).

A study from Finland that was published in 2007 investigated the elimination of pharmaceuticals in sewage treatment plants in that country. Some of their results differ from those discussed in the article above (Jones et al., 2005). The sampling of 12 sewage treatment plants occurred in 2004 and 2005. A total of 21 samples were collected and include both influent and effluent samples. Eight pharmaceuticals were analyzed and include the β-blockers: acebutolol, atenolol, metoprolol, and sotalol, the antiepileptic carbamazepine, fluoroquinolone antibiotics: ciprofloxacin, norfloxacin, and ofloxacin (Vieno et al., 2007). All of the influent samples showed the presence of all of the β-blockers and carbamazepine. The antibiotics ciprofloxacin and ofloxacin were found in 20 of the influent samples, whereas norfloxacin was found in 13 of the samples. The pharmaceuticals were not completely eliminated by the sewage treatment processes and the β-blockers and carbamazepine were found to be ubiquitous in the effluent. The antibiotic ciprofloxacin was found in 18 of the effluent samples. The other antibiotics, ofloxacin and norfloxacin, were found in 17 and 1 effluent samples respectively (Vieno et al., 2007). The sewage treatment plants all have mechanical, chemical, and biological treatment processes. All of the plants use ferric salts for phosphorous coagulation. Most of the plants also use

activated sludge treatment for the removal of organic matter that is susceptible to bacterial degradation. Three of the plants used oxidation ditches and two of the plants used denitrification to improve nitrogen removal. Few of the plants use a tertiary treatment such as disinfection, biological filter, or chemical coagulation. The results from this study show that during the rainy period, the elimination of the β-blockers, except for sotalol, was reduced dramatically as higher concentrations were detected. This could be due to a decrease in the hydraulic retention times during high flow periods which allows for less bacterial degradation. The study found no correlation between the solids retention time and the elimination of pharmaceuticals (Vieno et al., 2007). This is contrary to the studies cited above (Jones et al., 2005). Differences in the treatment processes allowed for differences in the elimination rates for the pharmaceuticals. The use of nitrogen removal and/or a nitrifying biofilter did not increase the removal of pharmaceuticals. This is also contrary to previously published works. The results from this study place the studied pharmaceuticals into 4 different categories of elimination: Carbamazepine – no elimination, metoprolol – poor elimination (<40%), acebutolol, atenolol, sotalol – moderate elimination (40-80%), and ciprofloxacin, norfloxacin, ofloxacin – efficient elimination (>80%) (Vieno et al., 2007). This research emphasizes how complex the fate of pharmaceuticals can be in sewage treatment works.

A study from Germany sought to determine the fate of certain pharmaceuticals in water/sediment systems (Löffler et al., 2005). Six human and veterinary pharmaceuticals were chosen for study based on their use and environmental occurrence. Their pharmacological and physiochemical properties were also considered. Four major metabolites were also included in the study to determine fate of both metabolite and parent compound. The goal of the study was

to show the (bio)degradability of the pharmaceuticals in water/sediment systems using liquid chromatography in tandem with mass spectrometry and radiotracers as well (Löffler et al., 2005). Sediment and water samples were taken from Wickerbach Creek in Flörsheim, southwest Germany. The sediment had a low, but still environmentally relevant, organic carbon content of 2.4% dry weight in order to minimize the influence of sorption in this experiment. The water and sediment were placed in 500 ml amber glass flasks and spiked with the various pharmaceuticals. Samples of water and sediment were processed immediately after the addition of the pharmaceuticals and at 0.25, 1, 2, 7, 14, 28, 56, and 100 days (Löffler et al., 2005). The results showed that ibuprofen, its metabolite 2-hydroxyibuprofen, and paracetamol (or acetaminophen, an analgesic) had a low persistence in the water/sediment system. Ivermectin (parasiticide), oxazepam (diazepam metabolite), and iopromide (contrast medium) had a moderate persistence in the water/sediment system. Finally, carbamazepine, its metabolite 10,11,-dihydro-10,11dihydroxy-carbamazepine, clofibric acid (lipid regulator), and diazepam (tranquilizer) exhibited high persistence. The results from this study are laboratory based, so it should be expected that field conditions might give different results, including more efficient elimination of the pharmaceuticals due to photodegradation or nutrient replacement for bacterial degradation (Löffler et al., 2005).

As a sub-topic of the fate of pharmaceuticals and personal care products in the environment, more needs to be mentioned regarding the photodegradation potential of these compounds. Canadian researchers investigated the photochemical behavior of atorvastatin (lipid regulator), carbamazepine, levofloxacin (fluoroquinolone antibiotic), and sulfamethoxazole (antibiotic) in surface waters (Lam and Mabury, 2005). Two types of photodegradation may occur, including direct and

indirect photodegradation. Direct photodegradation occurs when organic compounds absorb radiation, become unstable, and then decompose. Indirect photodegradation occurs when intermediate compounds are created from other ultraviolet absorbing materials that break down. These intermediate compounds then react with the pharmaceutical to facilitate its decomposition. The intermediate compounds are usually hydroxyl, carbonate, alkyl peroxy radicals, singlet oxygen, and aqueous electrons. The absorption of radiation by nitrate and dissolved organic matter (DOM) leads to the production of most of the intermediates (Lam and Mabury, 2005). For all of the direct photolysis experiments, the solutions were prepared using deionized water. For all of the indirect photolysis experiments, natural water was simulated by adding DOM, nitrate, and bicarbonate to the solutions. Target pharmaceuticals were also added to both experimental solutions and then all were exposed to radiation from a Xenon lamp photosimulator. Water samples were analyzed after receiving radiation to look for the parent compound and also to monitor for photodegradation products (Lam and Mabury, 2005). This study showed direct photolysis is important to the elimination of levofloxacin and sulfamethoxazole. Indirect photolysis did not increase their degradation. In contrast, atorvastatin and carbamazepine were more susceptible to indirect photodegradation. The photodegradation products were less persistent than the parent compound in natural waters (Lam and Mabury, 2005).

Another study by researchers at the University of Minnesota studied the photodegradation of mefenamic acid (a non-steroidal anti-inflammatory drug (NSAID)) in the environment. Previous studies have shown that mefenamic acid is not removed during waste water treatment processes and has been shown to exist in both effluent and downstream of treatment plants (Werner et al., 2005). Another

structurally similar NSAID, diclofenac, has been shown to undergo direct photodegradation, so it is expected that this may also be the case for mefenamic acid. The photolysis experiments for mefenamic acid were conducted using natural sunlight and solutions made from ultra pure water. For the indirect photolysis experiments, Suwanee River fulvic acids were added to the solutions. Mefenamic acid was then added to the solutions and analysis was conducted at various time points. This study revealed that with direct photolysis, mefenamic acid has a half-life of 33 hours under direct sunlight, which corresponds to a half-life of 66 hours in surface water, after correcting for the lens effect of the test vessel. Indirect photolysis data, solutions containing the fulvic acids, showed that the presence of DOM contributed significantly to the photodegradation of the drug. Therefore, the loss of mefenamic acid in surface waters is dependent on both direct and indirect photodegradation (Werner et al., 2005). Because the photodegradation of mefenamic acid depends on both processes, it may be more persistent in the environment than diclofenac, which is much more dependent on direct photodegradation (Werner et al., 2005).

From the sections above, it is quite clear that pharmaceuticals and personal care products are present in surface waters around the world. Their origins, fate, and transport have been explored. Toxicity and endocrine disrupting actions of these chemicals on organisms living in ecosystems will be discussed in the following sections.

A study from Germany looked at the toxicity of a group of NSAIDS including; diclofenac, ibuprofen, naproxen, and acetylsalicylic acid. Worldwide, it is estimated that this group of drugs has an annual production of several kilotons. Because of this high use potential, NSAIDS can reach the environment in detectable

concentrations (Cleuvers, 2004). In this study, acute toxicity tests were performed using green algae and the water flea daphnia for single drugs and for mixtures. The mixture tests are particularly important, because mixtures are more likely in surface waters. For single compound tests, six concentrations were used (1, 3.2, 10, 32, 100, and 320 mg/L). For the mixture tests, concentrations of the drugs should add up to total effect of 5%, 10%, 20%, 50%, and 80%. Effect concentrations are the concentrations at which a percentage of the population shows an effect from the test substance. For example, an effect concentration of 50% ($EC_{50}$) indicates the concentration at which 50% of the population shows an effect from the drug. For the daphnia tests, the endpoint for the effect calculation is immobility. For the alga tests, results were in terms of chlorophyll fluorescence which indicates cell numbers. According to a European Union directive, different risk classes for chemicals are based on their lowest measured $EC_{50}$ value (Cleuvers, 2004). An $EC_{50}$ value of 1 mg/L or less would be classified as very toxic to aquatic organisms. An $EC_{50}$ value from 1 to 10 mg/L would be considered toxic to aquatic organisms and a value from 11 to 100 mg/L would be classified as harmful to aquatic organisms. Chemicals with an $EC_{50}$ value over 100 mg/L would not be classified. Using this scheme, the acute toxicity of all of the tested NSAID drugs is relatively low. Diclofenac, with an $EC_{50}$ value of 68.0 mg/L, and acetylsalicylic acid, with an $EC_{50}$ value of 88.1 mg/L, were the only drugs shown to be potentially harmful to aquatic organisms using the daphnia test. Diclofenac was also shown to be potentially harmful in the algae test with an $EC_{50}$ value of 71.9 mg/L (Cleuvers, 2004). Mixture toxicity, however, was more substantial. Toxicity was shown at concentrations for which a single compound showed little or no effect, except for some deviations in the daphnia tests. This study showed that because drug mixtures in the natural environment are more

likely, the acute mixture toxicity is important in environmental risk assessment. This study also makes the point that chronic effects may be important to aquatic organisms and that more toxicity tests, acute and chronic, should be performed on other organisms such as fish and macroinvertebrates (Cleuvers, 2004).

A research study by Flaherty and Dodson studied the effects of seven pharmaceuticals on the survival, growth, and reproduction of daphnia. Both acute (6-day) and chronic (30-day) toxicity tests were conducted using individual and mixtures of pharmaceuticals. The pharmaceuticals chosen for this study include: clofibric acid, fluoxetine, triclosan, and the antibiotics erythromycin, lincomycin, sulfamethoxazole, and trimethoprim. Not only immobility was evaluated for the daphnia after exposure to the chemicals, but also morphology, adult length, egg production, brood size, and sex ratio. Test concentrations of the pharmaceuticals ranged from 1 to 100 µg/L (Flaherty and Dodson, 2005). The results show that acute exposure to clofibric acid increased the amount of male offspring or affected the sex ratio. However, chronic exposure to clofibric acid did not show a significant effect. This shows the ability of the daphnia to acclimate to the environment stressed by the addition of a chemical. Fluoxetine is an antidepressant that may interfere with invertebrate endocrine systems by increasing serotonin. Serotonin is known to control oogenesis and molting in invertebrates. Chronic exposure to fluoxetine in this study did affect the brood size by increasing the number of daphnia produced. Chronic exposure to triclosan increased the sex ratio of the daphnia, but only in the first brood. Acute and chronic effects from the antibiotics were not detectable. Acute exposure to the mixture of fluoxetine (36 µg/L) and clofibric acid (100 µg/L) caused "significant mortality". An acute exposure to fluoxetine (36 µg/L) and only 10 µg/L of clofibric acid showed morphological abnormalities. Also,

mixtures of 3 or more antibiotics caused changes in the sex ratio of the daphnia (Flaherty and Dodson, 2005). This study has shown that acute and chronic exposure to pharmaceuticals can affect the daphnia differently. Also, compared to the individual effects of pharmaceuticals, the toxicity of mixtures was complex and unpredictable.

In another study by Hoeger et al. the effects of diclofenac on brown trout, which are native to German rivers, were studied. In Germany, it is estimated that the usage of this drug is 75 tons annually. Diclofenac has been shown to persist in German rivers at a median concentration of 0.15 µg/L with peak concentrations of 1.2 µg/L. In this study brown trout were exposed to diclofenac concentrations of 0.5, 5, and 50 µg/L for 7, 14, and 21 days. After sampling the water in which the fish were exposed, it was determined the actual concentrations of diclofenac were 1.15, 6.63, and 63.05 µg/L respectively (Hoeger et al., 2005). The results of investigations of organ sections after exposure to diclofenac showed adverse effects in the kidneys, gills, and livers of the fish (Hoeger et al., 2005). This study showed that vertebrates can have serious adverse effects from diclofenac at concentrations well below those indicated by acute or chronic toxicity tests with invertebrates. So therefore, diclofenac concentrations in surface waters at current levels should be regarded as potentially harmful to aquatic vertebrates (Hoeger et al., 2005).

There are certain pharmaceuticals and personal care products that are known to cause endocrine disruption to wildlife. A few research projects regarding endocrine disruption in fish will be discussed. The first is a study by Canadian researchers who investigated the effects of gemfibrozil, a lipid regulator, on goldfish (Mimeault et al., 2005). Gemfibrozil has been reported in treated waste waters at concentrations as high as 2.1 µg/L and 0.5 µg/L in surface waters. The goals of this

study were to determine if goldfish can take up gemfibrozil from the water and to determine if gemfibrozil can cause reproductive effects at environmentally relevant concentrations. Only male goldfish were used for this experiment and they were exposed to gemfibrozil either through the water or through injection (Mimeault et al., 2005). Both the acute and chronic experiments show a decrease in blood plasma testosterone levels. A five-fold decrease in testosterone was found after 96 hours of exposure to gemfibrozil and a 50% decrease after 14 days. Concentrations of gemfibrozil in goldfish blood plasma also indicated the drug can be taken up through the gills and bioconcentrated. This study shows that gemfibrozil can cause endocrine disruption in goldfish and probably other fish. Also, because the fish were shown to bioconcentrate the drug, risk assessment based on exposure concentrations alone may not be protective enough (Mimeault et al., 2005).

The endocrine disrupting effects of nonylphenol have also been studied. Nonylphenol is used as an industrial surfactant and also has household applications in detergents and emulsifiers. Nonylphenol has been shown to cause feminization and a decrease in male fertility in aquatic organisms. This chemical has also been shown to mimic the natural hormone 17β-oestradiol (Soares et al., 2008). The U. S. Environmental Protection Agency has acknowledged the risks of nonylphenol persistence in the environment and has prepared guidelines for its concentrations in freshwater at below 6.6 µg/L and below 1.7 µg/L for saltwater. In Europe, Canada, and Japan these surfactants are being replaced with other compounds that are considered to be more environmentally friendly (Soares et al., 2008). Nonylphenol is hydrophobic and has a low solubility in water with a log $K_{OW}$ value of 4.48. Due to these chemical characteristics, nonylphenol partitions to the soil and sediment phase, favoring association with organic matter (Soares et al., 2008). The endocrine

disruption effects to fish by nonylphenol are well known. In a study by Japanese researchers, the reproductive effects and bioconcentration of 4-nonylphenol on medaka fish were investigated (Ishibashi et al., 2006). Five mating pairs of medaka fish were exposed to concentrations of 4-nonylphenol of 0, 10, 50, and 100 µg/L for 21 days. There were no effects to the fish regarding total body length or body weight of either sex after the test period. However, 2 male fish died after their abdomens began to swell in the group exposed to 100 µg/L of 4-nonylphenol. In the third week, the total number of eggs collected from the 100 µg/L group was "significantly reduced". The fertility of these eggs was also greatly reduced as compared to the control groups over the 3 week period. No effects were observed regarding egg production or fertility for the groups exposed to lower levels of 4-nonylphenol (Ishibashi et al., 2006). Again, for the fish exposed to 100 µg/L of 4-nonlyphenol, the hatchability and the time to hatching of the embryos were adversely affected. The levels of 4-nonlyphenol were measured in the eggs produced for the 100 µg/L group and found to be between 2-7 µg/L of egg material. This indicates that the mother can transfer this chemical to the next generation and the chemical can be bioconcentrated (Ishibashi et al., 2006). The effects listed above occur at concentrations not usually environmentally relevant; however, it has been demonstrated that 4-nonylphenol can cause estrogenic activity in male fish at concentrations greater than or equal to 10 µg/L (Ishibashi et al., 2006).

Surface water and waste water have been studied extensively for the presence of pharmaceuticals and personal care products, as well as the potential effects to the ecosystem from these contaminants. Groundwater and drinking water, both surface water and groundwater sources, have also been studied for the presence of these compounds. The USGS performed a national reconnaissance

study to determine the impact to the nation's groundwater from pharmaceuticals, personal care products, and other organic waste water contaminants (Barnes et al., 2008). In 2000, 47 groundwater sites in 18 states were sampled. The sites selected were not necessarily representative of groundwater across the county, as sites were chosen because they were susceptible to contamination. The sample locations were near sources of human or animal wastewater, such as animal feedlots, unsewered residential areas, or downgradient of landfills (Barnes et al., 2008). Forty two wells, 3 springs, and 2 sumps were sampled. The wells chosen were used for various purposes; including observation, drinking water supply, and agriculture. The median depth of the wells was 19.2 meters with a range from 2.4 to 310.9 meters (Barnes et al., 2008). The results showed that one or more contaminants were detected at 81% of the sample locations. Thirty five of the 65 target compounds were detected at least once. The most common compounds detected were DEET (35%), bisphenol A (30%), tri(2-chloroethyl) phosphate (30%), sulfamethoxazole (23%), and 4-octylphenol monoethoxylate (19%). Mixtures were commonly reported, with a maximum of 14 compounds detected at a site, with a median of 2 for the entire sample set. Twenty five of the 47 sample sites had mixtures detected (Barnes et al., 2008). The majority (87%) of the compound concentrations were below 1 µg/L. Also, as well depths increased, the number of compounds detected decreased. This may indicate that many of the contaminants enter near or at the wellhead through inadequate seals or gravel packs. It is also possible that contaminants originate from well materials and well construction practices (Barnes et al., 2008). This study confirms impact to groundwater from organic waste water constituents.

In the summer of 2001, the USGS performed another national reconnaissance study in an effort to detect pharmaceuticals, personal care products,

and other organic waste water contaminants specifically in raw, untreated drinking water sources (Focazio et al., 2008). Twenty five groundwater and 49 surface water sources were sampled in 25 states and Puerto Rico. The number of people served by these sources ranged from one family to more than 8 million people. The sites selected for analysis were susceptible to contamination by a known upstream or upgradient source of human or animal waste water (Focazio et al., 2008). The analytical results show that of the 100 target compounds, 63 were detected at least once. The five compounds detected most frequently in surface water sources include; cholesterol (59%), metolachlor (53%), cotinine (51%), β-sitosterol (37%), and 1,7-dimethylxanthine (27%). In groundwater sources, the five most commonly detected compounds include; tetrachloroethylene (24%), carbamazepine (20%), bisphenol A (20%), 1,7-dimethlxanthine (16%), and tri(2-chloroethyl) phosphate (12%) (Focazio et al., 2008). The median number of compounds detected for the data set was 4, with a maximum number of 31; so mixtures were also common. The concentrations of the compounds detected were typically below 1 µg/L. In general, the frequency of detections was lower for the groundwater sources than for the surface water sources. This is probably due to the more direct pathway (i.e. waste water discharge) for these compounds to enter surface waters and/or greater attenuation in the subsurface (Focazio et al., 2008).

Knowing that pharmaceuticals and personal care products exist at low levels in some water supply sources, the efficiency of drinking water treatment to remove these compounds has been investigated (Stackelberg et al., 2007). The treatment plant chosen for study served about 850,000 people and received raw water from a highly urbanized surface water source. The raw water was analyzed for 113 compounds, of which 45 were detected at least once. At least 25% of the source

water samples contained 32 compounds. Most compound concentrations were below 1 µg/L (Stackelberg et al., 2007). The effectiveness of each step of the water treatment process was evaluated for removal of the organic waste water constituents. Clarification accounted for 15% of the removal. Disinfection accounted for 32% of the contaminant removal. Granular-activated-carbon filtration accounted for 53% of the removal (Stackelberg et al., 2007). Of course the effectiveness of any drinking water treatment plant to remove these compounds would depend upon the quality of the source water, the chemical characteristics of the compounds contained within the water, specific treatment process, and even the age of the activated carbon. This study determined that complete removal or degradation of the compounds detected did not occur during drinking water treatment, although the concentrations generally decreased. Carbamazepine and DEET were detected in all finished water samples. Cotinine was detected in 75% of the finished water samples and AHTN in 50% of the samples. Three to thirteen compounds were detected in every finished water sample (Stackelberg et al., 2007).

The risk of human exposure to low-level pharmaceuticals and personal care products contained in drinking water has been evaluated (Webb et al., 2003). Comparing the daily exposure through drinking water to a daily therapeutic dose, a difference of at least 3 orders of magnitude was determined. Typically, the margin of difference was much higher. This study concluded that there are no "substantial concerns" regarding exposure to these compounds via drinking water (Webb et al., 2003). However, the need for such assessments should not be disregarded, especially when low-level, long-term exposure to humans is considered (Webb et al., 2003). Also, much remains to be learned regarding mixture effects, indirect or unexpected effects of certain compounds, and chronic exposure to sensitive

populations (Servos et al., 2007).

As alluded to in groundwater discussion above, treated waste water can be a source of pharmaceuticals and personal care products in groundwater. Waste water is often discharged to surface ponds or spreading basins in an effort to reuse the water, especially in arid regions. Waste water is also used for irrigation purposes. The waste water is further treated by filtration and degradation as it percolates through sediments in the aquifer and ultimately recharges the groundwater. The subsurface fate and transport of pharmaceuticals and personal care products contained in the waste water used for artificial groundwater recharge has undergone further study. Two waste water reuse sites in the southwestern U.S. were investigated by sampling the treated waste water entering spreading basins and groundwater monitoring wells in the vicinity (Drewes et al., 2003). The samples were analyzed for selected pharmaceuticals. The results of the study showed that caffeine, anti-inflammatory drugs such as diclofenac, naproxen, and ibuprofen, and lipid regulating drugs such as gemfibrozil are effectively removed during groundwater recharge. The concentrations of these drugs were reduced to near or below the detection limits in the groundwater (Drewes et al., 2003). However, the anti-epileptic drugs carbamazepine and primidone are persistent in groundwater, under both anoxic and aerobic conditions. Artificial groundwater recharge by waste water reuse affects groundwater quality (Drews et al., 2003). A soil column study was conducted to determine if 131 pharmaceuticals and other organic waste water compounds could reach the groundwater under recharge conditions (Cordy et al., 2004). The 2.4 meter soil column was packed with a sandy loam from the Phoenix, Arizona region. Treated sewage effluent was passed through the column and samples were collected for analysis at the beginning and end of the experiment. Thirty three

organic waste water constituents were detected in the treated sewage effluent at the beginning of the column study. By the end of the experiment, 27 compounds were detected before the effluent was added to the column, which indicates that some of the compounds degraded or were adsorbed to material inside the storage tank (Cordy et al., 2004). Water samples collected after the effluent passed through the column indicate fourteen compounds were detected. This experiment also shows that organic waste water chemicals have the potential to reach groundwater when waste water is used for recharge purposes. Carbamazepine, sulfamethoxazole, benzophenone, 5-methyl-1H-benzotriazole, DEET, tributylphosphate, tri(2-chloroethyl) phosphate, and cholesterol were detected in all three water samples indicating that these compounds have a higher persistence and greater potential to reach the groundwater (Cordy et al., 2004).

Groundwater contaminated with waste water constituents has been shown to discharge to surface waters and therefore provide another source of these compounds (Standley et al., 2008). Six glacial kettle ponds were studied in Cape Cod Massachusetts, three in low residential density areas and three in high residential density areas, for the presence of 29 organic waste water constituents from on-site septic systems. These ponds are primarily fed by discharging groundwater as they generally do not have streams flowing into them. Ten of the compounds were detected at least once in the ponds (Standley et al., 2008). The ponds located in higher residential density areas had a higher mean (3.5 compounds) of detection than the ponds located within lower residential density areas (0.7 compounds). This study showed that surface waters can be impacted by waste water compounds contained in discharging groundwater. There are also human health implications in Cape Cod where aquifers are the sole source of

drinking water (Standley et al., 2008).

Surface waters contaminated with pharmaceuticals and personal care products can also contaminate groundwater through bank infiltration or induced recharge. Surface water and groundwater are known to interact and are considered one resource along the groundwater/surface water interface. Bank filtration or induced recharge has been used in Berlin, Germany for more than a century as a way to purify surface water through aquifer sediments to produce drinking water (Heberer et al., 2004). The drinking water supply wells are closely located to rivers or lakes, some as little as 600 meters. The pumping of the wells has been shown to introduce waste water compounds contained in the neighboring surface water bodies into the groundwater (Heberer et al., 2004). Two bank filtration sites, Lake Wannsee and Lake Tegel in Berlin, were studied further to determine the fate and transport of pharmaceuticals in the subsurface. Surface water and groundwater samples were obtained monthly and analyzed for more than 60 organic waste water compounds (Heberer et al., 2004). Six compounds; diclofenac, propyphenazone, carbamazepine, primidone, clofibric acid, and 1-acetyl-1-methyl-2-dimethyl-oxamoyl-2-phenylhydrazide, were found to enter the groundwater through induced recharge from the contaminated lakes. Bank filtration decreased the concentrations of the compounds detected either through dilution, partial removal, or total removal (Heberer et al., 2004). To investigate the transport behavior of clofibric acid, propyphenazone, and diclofenac further, a soil column experiment was completed using a medium grained sand from the Berlin area (Scheytt et al., 2004). Clofibric acid proved to be highly mobile and no degradation occurred. Diclofenac and propyphenazone sorbed to the column and were less mobile, although this sorbtion was reversible (Scheytt et al., 2004). The occurrence of these pharmaceuticals in

the groundwater is controlled not by degradation, but by sorption, desorption, and input variation (Scheytt et al., 2004).

Not only human pharmaceuticals have been studied for environmental occurrence and effects, but also veterinary pharmaceuticals. From 2000 to 2003 a population decline of 35% to 95% for the Oriental white-backed vulture was documented in Pakistan (Oaks et al., 2004). The main source of food for these birds is dead livestock. The study showed that birds that ate livestock treated with veterinary diclofenac, an anti-inflammatory drug, died from renal failure and visceral gout (Oaks et al., 2004). Laboratory tests confirmed that the cause of the deaths was due to diclofenac exposure. This is the first time pharmaceutical residues have been shown to trigger major ecological damage (Oaks et al., 2004). Veterinary pharmaceuticals are also released to the environment via livestock production and the disposal of the subsequent wastes. The occurrence of a widely used veterinary antibiotic, oxytetracycline, was studied in a watershed in Japan known to have a high density of livestock farms (Matsui et al., 2008). The concentrations of oxytetracycline ranged from 2 ng/L to 68 µg/L in the streams sampled. The daily loads of the antibiotic decreased downstream as a result of decomposition, adsorption to sediments, or both (Matsui et al., 2008). The concentration of oxytetracycline in the streams also increased during the winter. This is attributed to increased antibiotic use in the winter to prevent disease (Matsui et al., 2008).

Much of the previously cited studies concentrate on point sources for pharmaceuticals and personal care products, such as livestock production or waste water treatment plant effluent. Non-point sources of these compounds have also been investigated. Storm water canals in New Orleans were sampled and analyzed for a range of pharmaceuticals and personal care products (Boyd et al., 2004).

Naproxen, ibuprofen, triclosan, and bisphenol A were detected in the storm water canals. The source of these compounds is attributed to non-point source contamination from the New Orleans sewage system (Boyd et al., 2004). The storm water canals do not have waste water discharged to them. The sewage enters the storm canals through illicit cross connections and broken sewer pipes due to subsidence. The study also showed that during rainfall, the concentrations of the detected compounds increase due to a flushing effect from the aging sewer system (Boyd et al., 2004).

The occurrence and behavior of pharmaceuticals and personal care products in the environment is not limited to water analysis. Research regarding these chemicals also includes sediment and soil studies. Although beyond the scope of this research paper, a review article addressing the current research on pharmaceuticals and personal care products in sediments and soils is available (Pan et al., 2009). Sediments within surface water bodies are exposed to these compounds via waste water discharges and soils are exposed via land application of treated waste water and/or sludge. Research is also ongoing to determine the presence of pharmaceuticals and personal care products in sewage sludge (Eriksson et al., 2008). A review of the current research shows the presence of 192 compounds in sewage sludge, with the potential for many more to be detected with further study. A hazard assessment was completed for the compounds detected in sludge based on exposure levels and effects of specific chemicals (Eriksson et al., 2008). The result was to identify 23 priority pollutants to be used to indicate sludge quality, to target for removal from sludge, or to replace with less hazardous compounds (Eriksson et al., 2008).

The studies cited above are by no means an exhaustive list of research

regarding pharmaceuticals and personal care products in the environment, but a sample. The surface water occurrence and induced recharge groundwater studies are similar to the study completed for this dissertation. All of the studies above were discussed in detail to show how extensive the current research truly is on this topic. It is clear these compounds are released into the environment due to human activities around the world. Researchers everywhere are in a race to determine where the chemicals reside in the environment, how they degrade, how they can be removed, and what effects they may cause to the ecosystem and humans. In summary, from the research listed above, it is important to carefully test new chemicals before use, in order to avoid problems in the environment before they occur. Risk assessment should include other factors, such as other physical effects to an organism, not just mortality, and the effects of mixtures. Also, it is important to realize that mixture effects of these compounds are complex, difficult to predict, and are often more damaging to aquatic organisms than one single compound. Mixtures of these chemicals in the environment are very probable. The European Union has set lower discharge requirements than the U.S. for some of these compounds or started to phase them out if deemed necessary. It is important to realize that upgrading waste water treatment plants with more effective removal technologies, such as carbon filters, ozonation, or reverse osmosis, is costly. Due to the endocrine disrupting attributes of some of these compounds, it looks as though society might have to take on these costs and/or prevent more of these compounds from entering the waste stream. This may include replacing some household or industrial products with more environmentally friendly versions or increasing pharmaceutical collection sites or frequency of collections.

The results of this dissertation are the product of a 2 year study funded by the

Michigan Department of Environmental Quality (MDEQ) with monies from the Clean Michigan Initiative. The goals of the study include verifying that these chemicals exist in the waters of the State, looking for seasonal and occurrence trends, and identifying known or suspected endocrine disrupting compounds. It is my hope that this research can be considered a starting point for future research into pharmaceuticals and personal care products in the waters of Michigan. More research is needed to fully understand the occurrence and trends of these compounds in each of the rivers and water wells sampled.

# STUDY DESIGN

## Funding

Funding for this research project was provided by the Water Bureau of the Michigan Department of Environmental Quality (MDEQ). The monies, which were a portion of the Clean Water Fund of the Clean Michigan Initiative, were awarded as a Water Quality Monitoring for Emerging Issues Grant.

The grant agreement required quarterly reporting to the MDEQ, which included the progress of the river and groundwater sampling, data obtained to date, and financial status reports. At the completion of the data acquisition and the depletion of funds, six fact sheets regarding the research results, a fact sheet regarding the status of Polybrominated Diphenyl Ethers (PBDEs) research and analysis, and a literature review, satisfied with a copy of the dissertation introduction, were provided to the MDEQ per the grant agreement. PBDEs are a class of fire retardant compounds. The initial grant proposal provided for the inclusion of PBDE analysis for the rivers in this study. However, lab analysis was not possible at the time, so the PBDEs analysis was removed from the study and a fact sheet required. The seven fact sheets are located in Appendix A.

## USGS Partnership

This project would not have been possible without the assistance of the Michigan Office of the U.S. Geological Survey (USGS). Because the USGS was interested in the results of the sampling, their personnel agreed to collect the river

samples and allow the use of their filtering equipment and lab space. They also provided financial support to supplement the MDEQ funding. The USGS lab in Colorado also analyzed all of the water samples for this project.

## Sample Locations

Five rivers within the State of Michigan were chosen for study including the Clinton, Grand, Kalamazoo, Muskegon, and Saginaw Rivers. These rivers were selected based on population density and high USGS sampling frequency. A large portion of the State's population lives within the watersheds of these rivers, therefore the likelihood of compound detections was thought to be high. As shown on Figure 1, the sample location on each river is near the river mouth. These locations were chosen in order to obtain a cumulative effect from various sources of pharmaceuticals and personal care products along each river. There was a trade-off however; because sample locations were at the river mouth, dilution was a concern. In fact, as will be discussed in the results and discussion section, concentrations were quite low. Water samples were taken and analyzed for pharmaceuticals and personal care products at each river. The river sample locations are listed below in detail.

- Clinton River, Macomb County, Clinton Township, Shadyside Park, Gratiot Avenue, City of Mt. Clemens, Latitude 42.58417° N, Longitude -82.88278° W.
- Grand River, Ottawa County, Robinson Township, Riverside Park in the vicinity of Ottawa Center, Latitude 43.02667° N, Longitude -86.03389° W.
- Kalamazoo River, Allegan County, Manlius Township, 57$^{th}$ Street in the vicinity of New Richmond, Latitude 42.6511° N, Longitude -86.10611° W.
- Muskegon River, Muskegon County, Cedar Creek Township, Maple Island Road, Latitude 43.31778° N, Longitude -86.03889° W.

- Saginaw River, Bay County, Bangor Township, Main Street, City of Essexville, Latitude 43.61751° N, Longitude -83.84278° W.

Two municipal ground water supply wells were also selected for study. The City of Parchment, located on the Kalamazoo River, and the city of Portland, located on the Grand River, were gracious enough to allow the sampling of their wells. These shallow (approximately 50-80 feet in depth) municipal wells are located close to their respective rivers. The wells were sampled to determine if any pharmaceuticals and personal care products that were in the river water were being drawn in by these high capacity wells. The exact locations of these municipal wells will not be listed here due to security issues and drinking water safety.

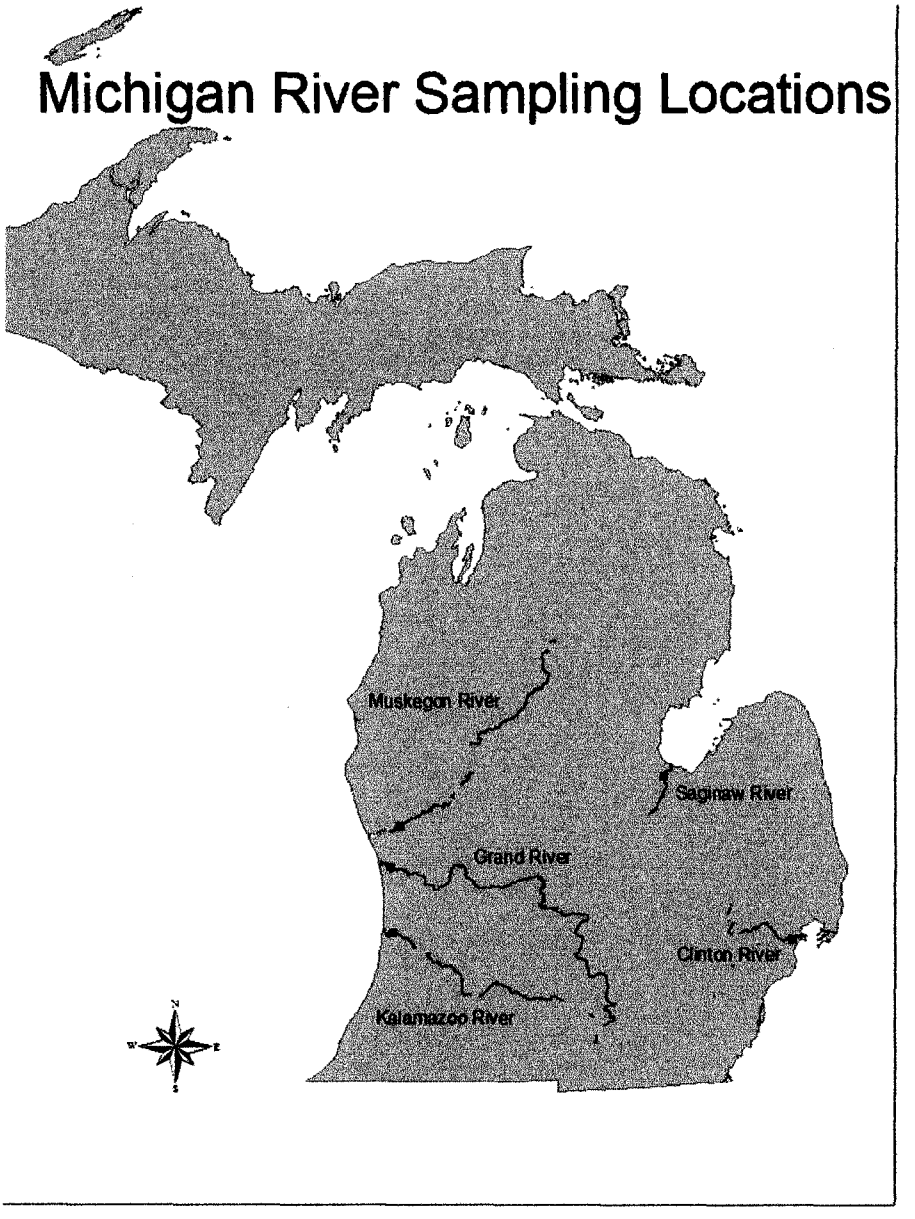



Figure 1: River sampling locations in Michigan (denoted by a square on each river).

## Sample Dates

All sample locations were sampled quarterly for two years, for a total of eight sample results per location. The sample dates for each sample location are listed

below.

- Clinton River: June 24, 2004, August 24, 2004, November 3, 2004, March 14, 2005, June 14, 2005, August 15, 2005, November 22, 2005, March 14, 2006.

- Grand River: June 15, 2004, August 18, 2004, November 17, 2004, March 22, 2005, June 27, 2005, August 23, 2005, November 21, 2005, March 13, 2006.

- Kalamazoo River: June 15, 2004, August 18, 2004, November 17, 2004, March 21, 2005, June 28, 2005, August 24, 2005, November 22, 2005, March 13, 2006.

- Muskegon River: June 16, 2004, August 19, 2004, October 27, 2004, March 22, 2005, June 27, 2005, August 23, 2005, November 21, 2005, March 13, 2006.

- Saginaw River: June 23, 2004, August 24, 2004, November 4, 2004, March 14, 2005, June 15, 2005, August 16, 2005, November 29, 2005, March 14, 2006.

- Parchment Well: June 28, 2004, August 31, 2004, November 9, 2004, March 29, 2005, June 29, 2005, August 25, 2005, November 23, 2005, March 22, 2006.

- Portland Well: June 28, 2004, August 31, 2004, November 9, 2004, March 29, 2005, June 16, 2005, August 18, 2005, November 23, 2005, March 23, 2006.

## River Control Sample

A one time river control sample was taken on August 17, 2005 at the South Branch of the Kalamazoo River in rural Hillsdale County, Moscow Township near Moscow, Michigan. The sample was taken where the first order stream crosses Moreland Road and is just east of Moscow Road. The latitude and longitude coordinates are: 42.0294° N, -84.5003° W. The object was to obtain a background sample before the waters of the river interact with urban and wastewater inputs. The river was approximately 10 feet across at the sample point and surrounded by

agricultural land and wooded areas. The area is sparsely populated with two houses, which are probably on well and septic, near the sample location. Interestingly, both the Grand and the Kalamazoo Rivers originate in Hillsdale and Jackson County just to the north.

## Analytical Scans

A waste water scan (schedule 1433) and a pharmaceutical scan (lab code 9003) were performed by the USGS lab in Colorado. The waste water scan consisted of 62-67 compounds. Four hormones were removed from the scan after the first sample round and dichlorvos was removed the last sample round. The scan included such compounds as diazinon, 4-nonlyphenol, camphor, naphthalene, bisphenol A, triclosan, and caffeine. See Table 1 for a full list of compounds contained within the waste water scan. The pharmaceutical scan included either 15 or 24 compounds. The number of compounds analyzed was reduced from 24 to 15 during the last two sample rounds. This scan included pharmaceuticals such as cotinine, acetaminophen, carbamazepine, fluoxetine, and codeine. Refer to Table 2 for a complete list of pharmaceuticals analyzed for in this study. The analytical scans changed over time because these were newly developed research methods. For example, some compounds were removed from the analytical scans if they did not perform well. Even with some uncertainty that was introduced when using new analytical methods, the importance of these data outweighed this issue.

Tables 1 and 2 also contain the minimum reporting level and sources and/or uses for each compound. The waste water scan table (Table 1) also indicates which compounds are currently known or suspected endocrine disrupting compounds. The waste water scan was performed on all rivers sampled and the two municipal

wells. The pharmaceutical scan was performed on the Kalamazoo and Grand Rivers only due to funding constraints.

## Octanol/Water Partition Coefficient

As discussed in the introduction, the octanol/water partition coefficient ($K_{OW}$) is used to predict whether a compound will preferentially partition to the water or sediment phase. In general the detergent metabolites, flame retardants, plasticizers, plant and animal sterols, pesticides, polycyclic aromatic hydrocarbons, and fragrances in the analytical scans are hydrophobic (Stackelberg et al., 2007). The pharmaceuticals, as a group, are generally hydrophilic (Stackelberg et al., 2007). There are outliers in these groups that do not follow this rule, such as the pharmaceutical fluoxetine which is hydrophobic.

In the drinking water treatment process, it was shown that the hydrophilic compounds were more frequently detected in the water samples and less so in the solids. Whereas, the hydrophobic compounds were more commonly detected in the solid phase of the treatment process (Stackelberg et al., 2007). However, this may not always be the case, as there are other chemical interactions that can occur within the treatment process and the $K_{OW}$ values assume the water and solids are in equilibrium, which may not always be true (Stackelberg et al, 2007). Scientists have also been urged to use the $D_{OW}$ of a compound instead of the $K_{OW}$ to help explain its behavior in the environment and treatment processes (Wells, 2006). The $D_{OW}$ is the pH dependent $K_{OW}$ of a compound. It is suggested that the pH range of 7-8 be used as this is the range at which most waste water treatment processes occur. The $D_{OW}$ may be a better predictor of whether these compounds will be present in surface waters (Wells, 2006).

Therefore, using the $K_{OW}$ of a compound to predict whether a compound is more likely to be detected in the aqueous or sediment phase is a good starting point, however, may not be a firm rule. Especially since this research and other listed in the introduction section show that hydrophobic compounds are commonly detected in water samples.

## Reporting Error Notification

The USGS notified the author in June of 2007 that for the duration of this project the compounds AHTN and HHCB had been transposed in the analytical data received. Therefore, if the compound was reported as AHTN, it was HHCB instead and vice versa. This should not have affected the data interpretation as both of these compounds are widely used musk fragrances.

The corrections have been made in the data tables within this document. If the raw data are inspected, these changes should be noted.

## Blank and Replicate Samples

Equipment blank samples were taken using organic free blank water provided by the USGS lab in Colorado. Sample replicates were also taken. The study was designed to allow for at least 10% blank and 10% replicate samples. As the results from the lab were received, however, it became necessary to increase the number of blanks. This issue will be discussed further in the Water Sampling Details section under Sample Containers and the Results section.

**Table 1**
**Waste Water Analytical Scan**
**Schedule 1433**

| Compound | MRL | Uses and Sources | EDP |
|---|---|---|---|
| 1,4 Dichlorobenzene | 0.5 | Moth repellant, fumigant, deodorant | S |
| **17beta-Estradiol** | 5 | Estrogen replacement therapy, estrogen metabolite | K |
| 1-Methylnaphthalene | 0.5 | 2-5% of gasoline, diesel fuel, or crude oil | |
| 2,6 Dimethylnaphthalene | 0.5 | Diesel and kerosene, trace in gasoline | |
| 2-Methylnaphthalene | 0.5 | 2-5% of gasoline, diesel fuel, or crude oil | |
| 3-beta-Coprostanol | 2 | Carnivore fecal indicator | |
| 3-Butyl-4-Hydroxyanisole | 5 | Antioxidant, general preservative | K |
| 3-Methyl-1H-Indole | 1 | Fragrance, stench in feces and coal tar (skatol) | |
| 4-Cumylphenol | 1 | Nonionic detergent metabolite | K |
| 4-Nonylphenol | 5 | Nonionic detergent metabolite | K |
| 4-Octylphenol | 1 | Nonionic detergent metabolite | K |
| 4-tert-Octylphenol | 1 | Nonionic detergent metabolite | K |
| 9,10 Anthraquinone | 0.5 | Manufacture of dye/textiles, seed treatment, bird repellant | |
| Acetophenone | 0.5 | Fragrance in detergent and tobacco, flavor in beverages | |
| AHTN | 0.5 | Musk fragrance (widespread usage) | |
| Anthracene | 0.5 | Wood preservative, component of tar, diesel, or crude oil | |
| Benzo(a)pyrene | 0.5 | Regulated polycyclicaromatic hydrocarbon, used in cancer research | K |
| Benzophenone | 0.5 | Fixative for perfumes and soaps | S |
| beta-Sitosterol | 2 | Plant sterol | |
| beta-Stigmastanol | 2 | Plant sterol | |
| Bisphenol A | 1 | Manufacture of polycarbonate resins, antioxidant, flame retardant | K |
| Bromacil | 0.5 | Herbicide, general use pesticide, noncrop usage on grass/brush | |
| Caffeine | 0.5 | Stimulant, food and beverage component, diuretic | |

**Table 1 - Continued**

| Compound | MRL | Uses and Sources | EDP |
|---|---|---|---|
| Camphor | 0.5 | Flavor, odorant, ointments | |
| Carbaryl | 1 | Insecticide, crop and garden use | K |
| Carbazole | 0.5 | Insecticide, manufacture of dyes, explosives, and lubricants | |
| Chlorpyrifos | 0.5 | Insecticide, domestic pest and termite control (restricted as of 2001) | K |
| Cholesterol | 2 | Used as a fecal indicator, also a plant sterol | |
| Cotinine | 1 | Metabolite of nicotine | |
| DEET | 0.5 | Insecticide, urban uses, mosquito repellent | |
| Diazinon | 0.5 | Insecticide, nonagricultural uses, ants, flies | K |
| ***Dichlorvos*** | 1 | Insecticide, pet collars, flies | S |
| Diethoxynonylphenol | 5 | Nonionic detergent metabolite | K |
| Diethoxyoctylphenol | 1 | Nonionic detergent metabolite | K |
| d-Limonene | 0.5 | Fungicide, antimicrobial, antiviral, fragrance in aerosols | |
| **Equilenin** | 5 | Hormone replacement drug therapy | |
| **Estrone** | 5 | Biogenic hormone | |
| Ethoxyoctylphenol | 1 | Nonionic detergent metabolite | |
| **Ethynyl estradiol** | 5 | Oral contraceptive | K |
| Fluoranthene | 0.5 | Component of coal tar and asphalt | |
| FYROL CEF | 0.5 | Flame retardant | |
| FYROL PCF | 0.5 | Flame retardant | |
| HHCB | 0.5 | Musk fragrance (widespread usage) | |
| Indole | 0.5 | Pesticide inert ingredient, fragrance in coffee | |
| Isoborneol | 0.5 | Fragrance in perfumes and disinfectants | |
| Isophorone | 0.5 | Solvent for lacquer, plastic, oil, silicon, resin | |
| Isopropylbenzene | 0.5 | Manufacture of phenol/acetone, fuels and paint thinner | |
| Isoquinoline | 0.5 | Flavors and fragrances | |
| Menthol | 0.5 | Cigarettes, cough drops, liniment, mouthwash | |

**Table 1 - Continued**

| Compound | MRL | Uses and Sources | EDP |
|---|---|---|---|
| Metalaxyl | 0.5 | Herbicide, fungicide, gen. use pesticide, mildew, blight, pathogens, golf/turf | |
| Methyl Salicylate | 0.5 | Liniment, food, beverages, ultra-violet absorbing lotion (sunscreen) | |
| Methylbenzotriazole | 2 | Antioxidant in antifreeze and deicers | |
| Metolachlor | 0.5 | Herbicide, general use pesticide, indicates agricultural drainage | |
| Naphthalene | 0.5 | Fumigant, moth repellant, component of gasoline | |
| p-Cresol | 1 | Wood preservative | S |
| Pentachlorophenol | 2 | Herbicide, fungicide, wood preservative, termite control | S |
| Phenanthrene | 0.5 | Manufacture of explosives, component of tar, diesel fuel, or crude oil | |
| Phenol | 0.5 | Disinfectant, manufacture of several products | |
| Prometon | 0.5 | Herbicide (noncrop only), applied prior to blacktop | |
| Pyrene | 0.5 | Component of coal tar and asphalt, traces in gasoline | |
| Tetrachloroethene | 0.5 | Solvent, degreaser, veterinary antihelmintic | |
| Tribromomethane | 0.5 | Waste water ozination byproduct, military/explosives | |
| Tributyl phosphate | 0.5 | Antifoaming agent, flame retardant | |
| Triclosan | 1 | Disinfectant, antimicrobial | S |
| Triethyl citrate | 0.5 | Cosmetics, pharmaceuticals | |
| Triphenyl phosphate | 0.5 | Plasticizer, resin, wax, finish, roofing paper, flame retardant | |
| Tris(butoxyethyl)phosphate | 0.5 | Flame retardant | |

**Key:**

Those compounds in **bold** indicate they were removed from the scan after the first sample round

Those chemicals in ***bold italic*** indicate they were removed from the scan for the last sample round

MRL = Minimum reporting level (µg/L)

EDP = Endocrine disrupting potential (S=suspected, K=known)

Table adapted from USGS table

**Table 2**
**Pharmaceutical Analytical Scan**
**Lab Code 9003**

| Compound | MRL | Indications/Use |
|---|---|---|
| 1,7-dimethylxanthine or p-Xanthine | 0.0208 | Caffeine metabolite |
| Acetaminophen | 0.0239 | Analgesic |
| **Azithromycin** | 0.0022 | Antibiotic |
| **Caffeine** | 0.008 | Stimulant and food component |
| Carbamazapine | 0.0179 | Anticonvulsant/antiepileptic |
| **Cimetidine** | 0.0061 | Stomach acid reducer |
| Codeine | 0.0223 | Analgesic |
| Cotinine | 0.0284 | Degradation product of Nicotine |
| Dehydronifedipine | 0.022 | Metabolite of Procardia (nifedipine), a vasodilator |
| Diltiazem | 0.0178 | Angina medication |
| Diphenhydramine | 0.0229 | Antihistamine |
| **Erythromycin** | 0.0046 | Antibiotic |
| Fluoxetine | 0.0156 | Antidepressant |
| **Furosemide** | NA | Edema associated with congestive heart failure |
| **Gemfibrozil** | 0.0064 | Lipid/cholesterol regulator |
| **Ibuprofen** | 0.0208 | Analgesic |
| **Metformin** | NA | Glycemic Control |
| **Miconazole** | 0.0088 | Antifungal medication |
| Ranitidine | 0.0252 | Stomach acid reducer |
| Salbutamol | 0.0139 | Bronchiodilator |
| Sulfamethoxazole | 0.0237 | Antibiotic |
| Thiabendazole | 0.025 | Antifungal/antiparasitic |
| Trimethoprim | 0.0203 | Antibiotic |
| Warfarin | 0.0188 | Anticoagulant |

**Key:**
Those compounds in **bold** indicate they were removed from the scan for the last two sample rounds
MRL = Minimum reporting level (µg/L)
NA = Not available
Table adapted from USGS table

## WATER SAMPLING DETAILS

### Sampling Methods

The USGS collected most of the river water samples for this project. The author personally accompanied them for some of the sample rounds to observe sample techniques and assist. These samples were taken in conjunction with their own sampling needs for the USGS statewide Water Chemistry Trend Monitoring Project (low level mercury, trace metals, polychlorinated biphenyls). The river water samples were taken by boat or by wading into the river; depending on river depth. If the samples were taken by boat, USGS personnel were careful to point the boat motor downstream and sample at the bow of the boat to avoid any petroleum products emitted from the motor. If the sample was taken by wading into the river, the person taking the sample would face upstream and take the sample in order to minimize any influence on the water sample from contact with their person. Sampling protocols also included the use of powder free nitrile gloves and for the sampler to limit personal care product and pharmaceutical use as best they could. This included avoiding the consumption of caffeinated beverages such as coffee and not using antibacterial soaps. The river water samples are similar to grab samples rather than composite samples from different depths. The USGS indicated, in their experience, the grab sampling method shows little analytical difference to the composite sampling method. To obtain the water sample, the container is held under water, with gloved hands, within a few feet of the waters surface.

The water well samples were taken from the sample tap located at each well

head. The samples were taken after allowing the well to pump for a time period sufficient to ensure the sample was from the aquifer and not from stagnant water in the well itself or its associated piping. Ideally, the well would have been in production for hours prior to sampling as it provided drinking water. This did occur a few times during sampling. The samples were taken prior to any addition of chlorine or other additives.

## Sample Containers

For the first two sample rounds, a high density polyethylene (HDPE) churn was used to obtain the river samples. This sample device had proven to provide quality samples with no problems in the blank samples for the USGS in the past. However, after the blank samples came back from the lab for this project and a few others the USGS was working on for pharmaceuticals and personal care products, it was evident there were sample contamination issues. Certain chemicals showed up consistently in the blanks even after proper sample container washing between samples. These chemicals include: naphthalene, phenol, 1,4 dichlorobenzene, 1-methylnaphthalene, 2-methylnaphthalene, benzophenone, DEET, and triphenyl phosphate. The USGS performed various tests to determine that these compounds could not be washed off of the HDPE churn effectively. The washing method includes washing with soap and water, rinsing with deionized water, rinsing with methanol, and finally rinsing with pesticide- or organic-free blank water numerous times. The sample containers were switched to Teflon bottles, with much greater success with the blank samples.

The water well samples were taken with an amber glass bottle obtained from Fisher Scientific. The same bottle washing technique described above was used

between samples for this sample container also. This sample method proved successful until some inconclusive results were received from the water wells; i.e. the same compounds in both well samples being detected in November 2005. Quality blanks were obtained from the glass bottle sample container, however. To be cautious, the sample container was switched to the baked amber glass bottles used to send the final filtered samples to the lab. The samples were collected in these bottles, and then filtered into another baked amber glass bottle for shipment to the lab. This was done for the last two sample rounds.

## Filtering the Samples

All water samples were filtered using a 0.7 µm glass fiber filter. A peristaltic pump was used to draw the water sample from the sample container and then force the water through the filter and into a baked amber glass bottle. The bottle was filled to the neck and headspace was allowed. The filter apparatus (see Figure 2) was placed inside a plastic bag when filtering samples to avoid contact with the ambient air in order to minimize outside contamination. During several of the initial sample rounds, the filtering was completed in the field at each sample location. There are many variables beyond the control of those sampling, such as cars going by and stirring up dust, mowing crews, wind, people in the area, etc., that could contribute to sample contamination. For this reason, later samples were filtered in the USGS lab in the Lansing office after sampling. This gave better control and consistency as to what the samples were or were not exposed to. Filtering in the lab also saved time, as the filter was no longer being set up and torn down at each sample site. After filtering, the bottles were carefully packed using foam sleeves and then sealed in an

individual zip top plastic bag. All of the bottles were then placed in a cooler with ice and shipped overnight to the USGS lab in Colorado for processing.

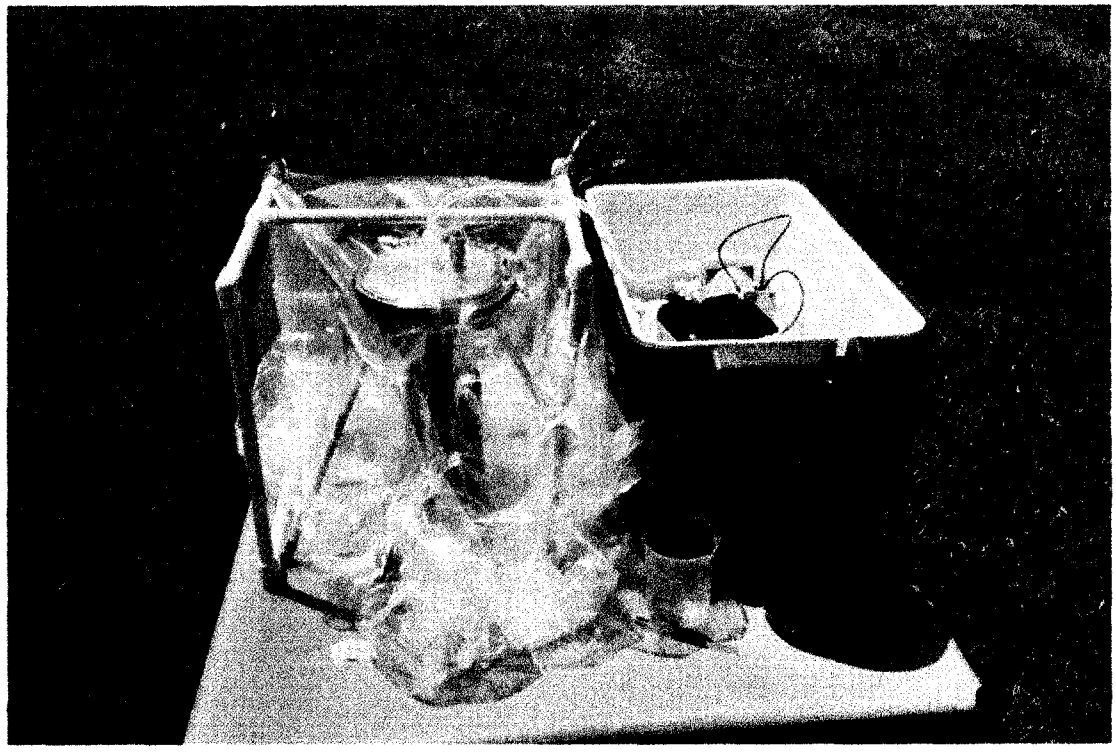


Figure 2: Sample filtration apparatus.

# RESULTS AND DISCUSSION

## River Data

### River Control Sample Results

Both the waste water scan and pharmaceutical scan were performed for the control sample taken in rural Hillsdale County on the Kalamazoo River. As is shown in Table 3, the only compounds detected in the control sample, other than what was also in the blank sample and disregarded, were indole and 3-methyl-1H-indole. Both of these compounds are known to be components of the odor of fecal material. At lower concentrations, however, they are used as fragrances and can have a flower-like aroma. Indole and 3-methyl-1H-indole, also known as skatol, are also components of coal tar. Indole and its derivatives are also used in pesticides as inert ingredients. These compounds could be present in the sample location for various reasons, including residential septic system inputs or more likely from agricultural pesticide application and the fact that road resurfacing with asphalt was being completed in the area the day the sample was collected.

The results of the control sample illustrate the difficulty in obtaining a pristine river sample that has not been impacted by human activity. The waste water scan is also quite inclusive and it is difficult to obtain a sample that does not contain one or more of its constituents. Overall, the control sample was a success, as the compounds that were detected can be explained by the human and agricultural presence in the area.

**Table 3**
**Analytical Results**
**Control Sample**
**South Branch Kalamazoo River**
**near Moscow, MI**
**August 17, 2005**

| **Compound** | **Concentration (µg/L)** |
|---|---|
| 3-Methyl-1H-indole | .0230 E |
| Indole | .0120 E |

**Key:**

E = Estimated value

River Sample Results

One hundred percent (100%) of all river samples had 1 or more compounds detected. This is important to note, when it is considered that each of the 5 rivers were sampled quarterly for two years yielding 40 total water samples. See Tables 4-8 for a compilation of the data, which includes all compounds detected for each sample event per river. The analytical data tables are arranged alphabetically by river name. Therefore, the data for the Clinton River is shown on Table 4 and the Grand River data are contained in Table 5. The analytical results for the Kalamazoo River are located in Table 6, whereas Table 7 contains the analytical data for the Muskegon River. Finally, Table 8 holds the data for the Saginaw River. Please note that any compound listed in Tables 4-8 that is in a different color other than black was detected in the blank for that sample round. Therefore, that compound was

disregarded in the data analysis in the following sections, including statistics, occurrence, seasonal trends, etc.

**Table 4**
**Analytical Results**
**Clinton River**

| June 24, 2004 | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .1200 E |
| 1-Methylnaphthalene | .0320 E |
| 2,6 Dimethlnaphthalene | .0360 E |
| 2-Methylnaphthalene | .0640 E |
| 4-t-Octylphenol | .0900 E |
| AHTN | .0820 E |
| Benzophenone | .0880 E |
| Bisphenol A | .2000 E |
| Caffeine | .1400 E |
| Camphor | .0300 E |
| Carbaryl | .1300 E |
| DEET | .1600 E |
| Diethoxynonylphenol | 3.9000 E |
| Fluoranthene | .0700 E |
| FYROL CEF | .2700 E |
| FYROL PCF | .1200 E |
| HHCB | .1200 E |
| Metolachlor | .1400 E |
| Naphthalene | .0510 E |
| Phenanthrene | .0340 E |
| Phenol | .1900 E |

| June 24, 2004 continued | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| Pyrene | .0620 E |
| Tribromomethane | .0120 E |
| Triethyl citrate | .1000 E |
| Triphenyl phosphate | .0860 E |
| Tris(butoxyethyl)PO4 | 1.1 |

| August 24, 2004 | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 9,10 Anthraquinone | .0087 E |
| AHTN | .0430 E |
| Caffeine | .1400 E |
| Cotinine | .1600 E |
| DEET | .0870 E |
| Fluoranthene | .0420 E |
| FYROL CEF | .1300 E |
| FYROL PCF | .1100 E |
| HHCB | .1200 E |
| Pyrene | .0270 E |
| Triethyl citrate | .0560 E |

**Table 4 - Continued**

| November 3, 2004 | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 3-beta-Coprostanol | 1.3000 E |
| 9,10 Anthraquinone | .1700 E |
| Caffeine | .2000 E |
| Cholesterol | 1.4000 E |
| Diethoxynonylphenol | 5.0000 E |
| Diethoxyoctylphenol | .2500 E |
| Fluoranthene | .0370 E |
| HHCB | .1100 E |
| Methyl salicylate | .0920 E |
| Pyrene | .0240 E |

| March 14, 2005 | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0630 E |
| 1-Methylnaphthalene | .0068 E |
| 2-Methylnaphthalene | .0076 E |
| 4-t-Octylphenol | .0380 E |
| 9,10 Anthraquinone | .1300 E |
| AHTN | .0560 E |
| Benzophenone | .0310 E |
| beta-Sitosterol | .2100 E |
| Bisphenol | .6100 E |
| Caffeine | .1700 E |
| Camphor | .0140 E |
| Carbazole | .0160 E |
| Cholesterol | .4300 E |
| Cotinine | .2000 E |
| DEET | .0730 E |
| Diethoxynonylphenol | 1.000 E |
| Ethoxyoctylphenol | .1100 E |
| Fluoranthene | .0500 E |
| FYROL CEF | .0510 E |
| FYROL PCF | .0610 E |
| HHCB | .1800 E |
| Indole | .0090 E |
| Isophorone | .0130 E |
| Menthol | .0330 E |
| Naphthalene | .0140 E |
| p-Cresol | .0340 E |

| March 14, 2005 continued | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| Phenanthrene | .0260 E |
| Pyrene | .0270 E |
| Tetrachloroethene | .0074 E |
| Tribromomethane | .0250 E |
| Tributyl phosphate | .1200 E |
| Triethyl citrate | .1000 E |
| Triphenyl phosphate | .0430 E |
| Tris (butoxyethyl) PO4 | 0.52 |

**Table 4 - Continued**

| Replicate (March 14, 2005) | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0820 E |
| 1-Methylnaphthalene | .0078 E |
| 2-Methylnaphthalene | .0091 E |
| 3-beta-Coprostanol | .2900 E |
| 4-t-Octylphenol | .0560 E |
| 9,10 Anthraquinone | .1200 E |
| AHTN | .0550 E |
| beta-Sitosterol | .4100 E |
| beta-Stigmastanol | .3800 E |
| Bisphenol | .6300 E |
| Caffeine | .1600 E |
| Camphor | .0140 E |
| Carbazole | .0150 E |
| Cholesterol | .5800 E |
| Cotinine | .2000 E |
| DEET | .0670 E |
| Diethoxynonylphenol | 1.100 E |
| Diethoxyoctylphenol | .1300 E |
| Ethoxyoctylphenol | .1000 E |
| Fluoranthene | .0520 E |
| FYROL CEF | .0530 E |
| FYROL PCF | .0760 E |
| HHCB | .2000 E |
| Indole | .0072 E |
| Isophorone | .0140 E |

| Replicate (March 14, 2005) continued | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| Menthol | .0280 E |
| Metolachlor | .0430 E |
| Naphthalene | .0140 E |
| p-Cresol | .0300 E |
| Phenanthrene | .0270 E |
| Pyrene | .0300 E |
| Tetrachloroethene | .0072 E |
| Tribromomethane | .0200 E |
| Tributyl phosphate | .0930 E |
| Triethyl citrate | .0980 E |
| Triphenyl phosphate | .0310 E |
| Tris (butoxyethyl) PO4 | 0.52 |

| Blank (March 14, 2005) | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0360 E |
| DEET | .0190 E |
| Menthol | .0200 E |
| Tributyl phosphate | .0530 E |

**Table 4 - Continued**

| June 14, 2005 | | June 14, 2005 (cont.) | |
|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0570 E | FRYOL PCF | .1300 E |
| 1-Methylnaphthalene | .0100 E | FYROL CEF | .2700 E |
| 2-Methylnaphthalene | .0130 E | HHCB | .1200 E |
| 3-beta-Coprostanol | 1.1000 E | Isoborneol | .0110 E |
| 4-Nonylphenol | .6800 E | Isophorone | .0390 E |
| 4-t-Octylphenol | .0620 E | Menthol | .1000 E |
| 9,10 Anthraquinone | .3100 E | Methylbenzotriazole | .5800 E |
| Acetophenone | .1200 E | Metolachlor | .0340 E |
| AHTN | .0260 E | Naphthalene | .0085 E |
| Anthracene | .0220 E | p-Cresol | .0210 E |
| Benzophenone | .0860 E | Phenanthrene | .0340 E |
| Beta-Sitosterol | 1.2000 E | Phenol | .3300 E |
| beta-Stigmastanol | 1.5000 E | Prometon | .1200 E |
| Bisphenol A | .2600 E | Pyrene | .0590 E |
| Caffeine | .4000 E | Tetrachloroethene | .0140 E |
| Camphor | .0330 E | Tribromomethane | .0200 E |
| Carbaryl | .2300 E | Tributyl phosphate | .0830 E |
| Carbazole | .0720 E | Triclosan | .0480 E |
| Cholesterol | 1.9000 E | Triethyl citrate | .0560 E |
| Cotinine | .1100 E | Triphenyl phosphate | .0340 E |
| DEET | .2500 E | Tris(butoxyethyl) PO4 | .8900 E |
| Diethoxynonylphenol | 8.0000 E | | |
| Diethoxyoctylphenol | .3600 E | | |
| Ethoxyoctylphenol | .7000 E | | |
| Fluoranthene | .0920 E | | |

**Table 4 - Continued**

| August 15, 2005 Compound | Conc. (µg/L) | August 15, 2005 continued Compound | Conc. (µg/L) | November 22, 2005 Compound | Conc. (µg/L) |
|---|---|---|---|---|---|
| | | | | 1,4 Dichlorobenzene | .0440 E |
| 3-beta-Coprostanol | .5300 E | Menthol | .1100 E | 2-Methylnaphthalene | .0052 E |
| 4-Nonylphenol | .6400 E | Metolachlor | .0750 E | AHTN | .0190 E |
| 4-t-Octylphenol | .1300 E | Naphthalene | .0120 E | Caffeine | .0490 E |
| 9,10 Anthraquinone | .3200 E | Phenanthrene | .0210 E | DEET | .0480 E |
| Acetophenone | .2400 E | | | Fluoranthene | .0140 E |
| Benzophenone | .0640 E | Prometon | .1200 E | HHCB | .1300 E |
| Beta-Sitosterol | 1.3000 E | Pyrene | .0440 E | | |
| Beta-Stigmastanol | 1.4000 E | Tributyl phosphate | .1200 E | | |
| Bisphenol A | .2000 E | Triethyl citrate | .1600 E | | |
| Caffeine | 0.72 | Triphenyl phosphate | .0660 E | | |
| Camphor | .0260 E | Tris(butoxyethyl)PO4 | 1.8 | | |
| Carbaryl | .1900 E | | | | |
| Carbazole | .0740 E | | | | |
| Cholesterol | 1.4000 E | | | | |
| Cotinine | .1900 E | | | | |
| DEET | .3200 E | | | | |
| Diazinon | .0600 E | | | | |
| Dichlorvos | .0730 E | | | | |
| Diethoxynonylphenol | 3.0000 E | | | | |
| Diethoxyoctylphenol | .1900 E | | | | |
| Fluoranthene | .0610 E | | | | |
| FYROL CEF | .1700 E | | | | |
| FYROL PCF | .1600 E | | | | |
| HHCB | .0980 E | | | | |

**Table 4 - Continued**

| March 14, 2006 | | Replicate (March 14, 2006) | | Blank (March 14, 2006) | |
|---|---|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0250 E | 1,4 Dichlorobenzene | .0260 E | 1,4 Dichlorobenzene | .0120 E |
| 1-Methylnaphthalene | .0083 E | 1-Methylnaphthalene | .0079 E | Isophorone | .0070 E |
| 2-Methylnaphthalene | .0110 E | 2-Methylnaphthalene | .0100 E | | |
| 3-Methyl-1H-Indole | .0110 E | 3-Methyl-1H-Indole | .0097 E | | |
| 9,10 Anthraquinone | .0960 E | 9,10 Anthraquinone | .0880 E | | |
| Acetophenone | .1100 E | Benzophenone | .0180 E | | |
| Benzophenone | .0160 E | Bisphenol A | .0900 E | | |
| Caffeine | .2800 E | Caffeine | .2900 E | | |
| Camphor | .0280 E | Carbazole | .0200 E | | |
| Carbazole | .0210 E | DEET | .0200 E | | |
| DEET | .0240 E | Diethyoxyoctylphenol | .1500 E | | |
| Fluoranthene | .0230 E | Fluoranthene | .0270 E | | |
| HHCB | .0500 E | HHCB | .0490 E | | |
| Isophorone | .0220 E | Isophorone | .0180 E | | |
| Menthol | .1100 E | Menthol | .1100 E | | |
| Methyl salicylate | .0082 E | Metolachlor | .0190 E | | |
| Metolachlor | .0180 E | Naphthalene | .0210 E | | |
| Naphthalene | .0180 E | Phenathrene | .0160 E | | |
| p-Cresol | .0490 E | Pyrene | .0160 E | | |
| Phenathrene | .0150 E | Tributyl phosphate | .0220 E | | |
| Pyrene | .0120 E | Triethyl citrate | .0140 E | | |
| Triphenyl phosphate | .0140 E | Triphenyl phosphate | .0160 E | | |
| Tris(butoxyethyl) PO4 | .2800 E | Tris(butoxyethyl) PO4 | .2800 E | | |

**Table 4 - Continued**

**Key:**

Conc. (µg/L) = concentration of compound in micrograms per liter

E = Estimated value

Name of compound with no underline – waste water scan – Schedule 1433

Name of compound with underline – pharmaceutical scan – Lab Code 9003

Name of compound in pink – compound found in June 2004 blank

Name of compound in turquoise – compound found in November 2004 blank (Pharm. Scan)

Name of compound in blue – compound found in March 2005 blank

Name of compound in green – compound found in June 2005 blank

Name of compound in purple – compound found in November 2005 blank

Name of compound in red – compound found in March 2006 blank

**Table 5**
**Analytical Results**
**Grand River**

| June 15, 2004 | | Replicate (June 15, 2004) | | Blank (June 15, 2004) | |
|---|---|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0820 E | 1,4 Dichlorobenzene | .0800 E | 1,4 Dichlorobenzene | .1200 E |
| 1-Methylnaphthalene | .0320 E | 1-Methylnaphthalene | .0280 E | 1-Methylnaphthalene | .0260 E |
| 2-Methylnaphthalene | .0860 E | 2-Methylnaphthalene | .0810 E | 2-Methylnaphthalene | .0760 E |
| 9,10 Anthraquinone | .1100 E | 9,10 Anthraquinone | .1100 E | Acetaminophen | 0.057 |
| Acetaminophen | 0.023 | Acetaminophen | 0.06 | Benzophenone | .1000 E |
| AHTN | .0860 E | AHTN | .0870 E | DEET | .1200 E |
| Benzophenone | .1000 E | Benzophenone | .0990 E | FYROL CEF | .1200 E |
| Caffeine | .1100 E | Caffeine | .1200 E | Naphthalene | .0530 E |
| Caffeine | 0.018 | Caffeine | 0.025 | Phenol | 1.2 |
| Camphor | .0310 E | Camphor | .0320 E | Triphenyl phosphate | .0980 E |
| DEET | .3300 E | DEET | .3300 E | | |
| Fluoranthene | .0600 E | Fluoranthene | .0600 E | | |
| FYROL CEF | .1200 E | FYROL CEF | .1300 E | | |
| FYROL PCF | .1300 E | FYROL PCF | .1300 E | | |
| HHCB | .1100 E | HHCB | .1200 E | | |
| Metolachlor | .3800 E | Metolachlor | .3900 E | | |
| Prometon | .1400 E | Phenol | .2500 E | | |
| Pyrene | .0640 E | Prometon | .1400 E | | |
| Tetrachloroethene | .0170 E | Pyrene | .0650 E | | |
| Tributyl phosphate | .1700 E | Tributyl phosphate | .1800 E | | |
| Triethyl citrate | .1500 E | Triethyl citrate | .1500 E | | |
| Triphenyl phosphate | .1000 E | Triphenyl phosphate | .1000 E | | |
| Tris(butoxyethyl) PO4 | 1.1000 E | Tris(butoxyethyl)PO4 | 1.1000 E | | |

**Table 5 - Continued**

| August 18, 2004 | | November 17, 2004 | |
|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0800 E | 1,4 Dichlorobenzene | .2400 E |
| 4-Nonylphenol | .8200 E | Carbamazepine | 0.018 |
| Benzophenone | .0840 E | Cotinine | 0.018 |
| Caffeine | .0470 E | Diltiazem | 0.012 |
| Caffeine | 0.011 | Diphenhydramine | 0.015 |
| Camphor | .0060 E | HHCB | .1500 E |
| Carbamazepine | 0.017 | Trimethoprim | 0.02 |
| Carbazole | .0062 E | | |
| Cholesterol | .6200 E | | |
| Codeine | .0043 E | | |
| Cotinine | 0.013 | | |
| DEET | .1000 E | | |
| Diphenhydramine | 0.0086 | | |
| Fluoranthene | .0060 E | | |
| FYROL CEF | .0710 E | | |
| FYROL PCF | .0670 E | | |
| HHCB | .0560 E | | |
| Isophorone | .0110 E | | |
| Metolachlor | .0660 E | | |
| Phenanthrene | .0086 E | | |
| Prometon | .0560 E | | |
| Pyrene | .0043 E | | |
| Tributyl phosphate | .0860 E | | |
| Triclosan | .0530 E | | |
| Triphenyl phosphate | .0440 E | | |
| Tris(butoxyethyl) PO4 | .4300 E | | |

**Table 5 - Continued**

| March 22, 2005 | | March 22, 2005 continued | |
|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0790 E | Menthol | .0490 E |
| 1,7 dimethylxanthine | 0.031 | Metolachlor | .0520 E |
| 1-Methylnaphthalene | .0061 E | Naphthalene | .0160 E |
| 2-Methylnaphthalene | .0098 E | Phenanthrene | .0054 E |
| 4-Nonylphenol | .7000 E | Pyrene | .0079 E |
| 4-t-Octylphenol | .0500 E | Tributyl phosphate | .0690 E |
| Acetaminophen | 0.018 | Triclosan | .0540 E |
| AHTN | .0520 E | Triethyl citrate | .0500 E |
| Benzophenone | .0400 E | Trimethoprim | 0.011 |
| Caffeine | .1900 E | Triphenyl phosphate | .0280 E |
| Caffeine | 0.083 | Tris (butoxyethyl) PO4 | 0.68 |
| Camphor | .0100 E | | |
| Carbamazepine | 0.0097 | | |
| Cholesterol | .3200 E | | |
| Cotinine | .2000 E | | |
| DEET | .0440 E | | |
| Diethoxynonylphenol | 2.300 E | | |
| Diethoxyoctylphenol | .1700 E | | |
| Diltiazem | 0.0086 | | |
| Diphenhydramine | 0.0098 | | |
| Ethoxyotcylphenol | .1000 E | | |
| Fluoranthene | .0086 E | | |
| FYROL CEF | .0380 E | | |
| FYROL PCF | .0430 E | | |
| HHCB | .1900 E | | |
| Isophorone | .0210 E | | |

**Table 5 - Continued**

| June 27, 2005 | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0640 E |
| 1-Methylnaphthalene | .0068 E |
| 2-Methylnaphthalene | .0110 E |
| AHTN | .0220 E |
| Benzophenone | .1300 E |
| Caffeine | .0450 E |
| Caffeine | 0.0177 |
| Camphor | .0160 E |
| Carbamazepine | 0.0116 |
| Cholesterol | .4500 E |
| Cotinine | 0.0064 |
| DEET | .0600 E |
| Diphenhydramine | 0.01 |
| Fluoranthene | .0059 E |
| FYROL CEF | .0440 E |
| FYROL PCF | .0500 E |
| HHCB | .0890 E |
| Isophorone | .0320 E |
| Menthol | .0740 E |
| Metolachlor | .1900 E |
| Naphthalene | .0120 E |
| Phenol | 0.58 |
| Prometon | .0480 E |
| Pyrene | .0047 E |
| Tetrachloroethene | .0088 E |
| Tributyl phosphate | .0530 E |

| June 27, 2005 continued | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| Triethyl citrate | .0200 E |
| Tris(butoxyethyl) PO4 | .3200 E |
| | |
| **Lab Blank Pharm. scan** | |
| **June 27, 2005** | |
| **Compound** | **Conc. (µg/L)** |
| Cotinine | 0.0136 |
| Diphenhydramine | 0.0191 |
| Trimethoprim | 0.0021 |

| August 23, 2005 | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| AHTN | .0100 E |
| Benzophenone | .0400 E |
| beta-Sitosterol | .5100 E |
| Caffeine | .0440 E |
| Camphor | .0100 E |
| Carbamazepine | 0.0361 |
| Cholesterol | .5000 E |
| Cimetidine | 0.009 |
| Cotinine | .0500 E |
| Cotinine | 0.0199 |
| DEET | .0920 E |
| Diltiazem | .0064 E |
| Fluoranthene | .0084 E |
| FYROL CEF | .0600 E |
| FYROL PCF | .0440 E |
| HHCB | .1100 E |
| | |
| Metolachlor | .0140 E |
| | |
| Pyrene | .0072 E |
| Ranitidine | .0036 E |
| Tributyl phosphate | .0450 E |
| Trimethoprim | 0.0168 |
| Tris(butoxyethyl) PO4 | .2100 E |

**Table 5 - Continued**

| November 21, 2005 | | March 13, 2006 | |
|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0490 E | 1,4 Dichlorobenzene | .0460 E |
| 1-Methylnaphthalene | .0200 E | 2-Methylnaphthalene | .0073 E |
| 2-Methylnaphthalene | .0320 E | 9,10 Anthraquinone | .0460 E |
| Acetaminophen | .0174 E | Acetaminophen | 0.0564 |
| AHTN | .0150 E | Benzophenone | .0170 E |
| Caffeine | .0620 E | Bisphenol A | .1200 E |
| Carbamazepine | .0140 E | Caffeine | .0420 E |
| Codeine | .0066 E | Cotinine | .0075 E |
| Cotinine | .0079 E | DEET | .0140 E |
| DEET | .0200 E | Diethoxyoctylphenol | .0330 E |
| Diphenhydramine | .0077 E | Fluoranthene | .0078 E |
| HHCB | .1200 E | HHCB | .0550 E |
| Isophorone | .0120 E | Isophorone | .0220 E |
| Naphthalene | .0400 E | Metolachlor | .0450 E |
| Phenol | .3300 E | Phenanthrene | .0069 E |
| Tributyl phosphate | .0700 E | Phenol | .1600 E |
| Triethyl citrate | .0240 E | Pyrene | .0052 E |
| Trimethoprim | .0098 E | Tetrachloroethene | .0160 E |
| Tris(butoxyethyl) PO4 | .2800 E | Triethyl citrate | .0240 E |
| | | Triphenyl phosphate | .0078 E |
| | | Tris(butoxyethyl) PO4 | .2400 E |

**Table 5 - Continued**

**Key:**

Conc. (µg/L) = concentration of compound in micrograms per liter

E = Estimated value

Name of compound with no underline – waste water scan – Schedule 1433

Name of compound with underline – pharmaceutical scan – Lab Code 9003

Name of compound in pink – compound found in June 2004 blank

Name of compound in turquoise – compound found in November 2004 blank (Pharm. Scan)

Name of compound in blue – compound found in March 2005 blank

Name of compound in green – compound found in June 2005 blank

Name of compound in purple – compound found in November 2005 blank

Name of compound in red – compound found in March 2006 blank

**Table 6**
**Analytical Results**
**Kalamazoo River**

| June 15, 2004 | | August 18, 2004 | |
|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .1500 E | 1,4 Dichlorobenzene | .0660 E |
| 1-Methylnaphthalene | .0390 E | 1-Methylnaphthalene | .0230 E |
| 2-Methylnaphthalene | .0980 E | 2-Methylnaphthalene | .0360 E |
| Acetaminophen | 0.0990 | 4-Nonylphenol | .9100 E |
| Benzophenone | .1200 E | Acetaminophen | 0.54 |
| Camphor | .0340 E | Benzophenone | .0880 E |
| DEET | .1800 E | Caffeine | .0410 E |
| Fluoranthene | .0560 E | Caffeine | 1.1 |
| FYROL CEF | .1400 E | Camphor | .0085 E |
| FYROL PCF | .1300 E | Cotinine | 0.014 |
| Metolachlor | .3000 E | DEET | .1100 E |
| Naphthalene | .0700 E | FYROL CEF | .0780 E |
| Pyrene | .0600 E | Isophorone | .0120 E |
| Tributyl phosphate | .1800 E | Methyl salicylate | .0200 E |
| Triphenyl phosphate | .1000 E | Metolachlor | .0540 E |
| Tris (butoxyethyl) PO4 | .3400 E | Naphthalene | .0280 E |
| | | Phenanthrene | .0085 E |
| | | Tribromomethane | .0110 E |
| | | Tributyl phosphate | .0760 E |
| | | Triphenyl phosphate | .0460 E |

**Table 6 - Continued**

| **November 17, 2004** | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .2200 E |
| Carbamazepine | 0.008 |
| Cotinine | 0.015 |

| **Replicate (November 17, 2004)** | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .1600 E |
| Carbamazepine | 0.008 |
| Cotinine | 0.015 |

**Blank (not used) (October 28, 2004)**

Blank broken in shipment, but analyzed

| **Compound** | **Conc. (µg/L)** |
|---|---|
| 1,4 Dichlorobenzene | .1400 E |
| 4-Nonylphenol | .6800 E |
| Acetophenone | .3900 E |
| Benzophenone | .1100 E |
| Bisphenol | .1400 E |
| DEET | .0950 E |
| FYROL CEF | .0640 E |
| FYROL PCF | .1400 E |
| Menthol | .0150 E |
| Naphthalene | .4100 E |
| Tributyl phosphate | .0300 E |

**Blank (November 17, 2004) Pharm. scan**

No detections

**Lab Blank Pharm. scan**

| **Compound** | **Conc. (µg/L)** |
|---|---|
| Dehydronifedipine | 0.007 |
| Diltiazem | 0.008 |
| Diphenhydramine | 0.012 |
| Fluoxetine | 0.016 |

**Table 6 – Continued**

| March 21, 2005 | | June 28, 2005 | | August 24, 2005 | |
|---|---|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0790 E | 1,4 Dichlorobenzene | .0530 E | | |
| 2-Methylnaphthalene | .0058 E | Benzophenone | .1100 E | Caffeine | .0340 E |
| 4-Nonylphenol | .5300 E | Caffeine | .0270 E | Camphor | .0130 E |
| Acetaminophen | 0.02 | Camphor | .0210 E | Carbamazepine | 0.0147 |
| Benzophenone | .0360 E | DEET | .0360 E | DEET | .0430 E |
| Caffeine | .0490 E | FYROL CEF | .0320 E | | |
| Camphor | .0095 E | HHCB | .0230 E | | |
| Carbamazepine | 0.0072 | Isoborneol | .0370 E | Tribromomethane | .0130 E |
| DEET | .0200 E | Isophorone | .0340 E | Tributyl phosphate | .0350 E |
| Fluoranthene | .0038 E | Menthol | .1200 E | Tris(butoxyethyl) PO4 | 1.1 |
| FYROL CEF | .0320 E | Metolachlor | .0490 E | | |
| HHCB | .0390 E | Phenol | .3000 E | | |
| Isophorone | .0220 E | Tributyl phosphate | .0440 E | | |
| Menthol | .0520 E | | | | |
| Metolachlor | .0470 E | | | | |
| Naphthalene | .0110 E | | | | |
| Phenanthrene | .0053 E | | | | |
| Pyrene | .0049 E | | | | |
| Tributyl phosphate | .0450 E | | | | |
| Triethyl citrate | .1600 E | | | | |

**Table 6 - Continued**

| **November 22, 2005** | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0290 E |
| 1-Methylnaphthalene | .0160 E |
| 2-Methylnaphthalene | .0270 E |
| Acetaminophen | .0954 E |
| Caffeine | .0380 E |
| Carbamazepine | .0091 E |
| Cotinine | .0056 E |
| Isophorone | .0120 E |
| Naphthalene | .0240 E |
| Phenanthrene | .0056 E |

| **Blank (November 22, 2005)** | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0160 E |
| Phenol | .1600 E |

| **March 13, 2006** | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0370 E |
| 2-Methylnaphthalene | .0067 E |
| Acetaminophen | .0248 E |
| Benzophenone | .0280 E |
| Caffeine | .0430 E |
| Carbamazepine | .0032 E |
| Cotinine | .0030 E |
| D-Limonene | .0120 E |
| Fluoranthene | .0030 E |
| Isophorone | .0120 E |
| Metolachlor | .0190 E |
| Phenanthrene | .0041 E |
| Phenol | .2900 E |
| Tributyl phosphate | .0450 E |
| Triethyl citrate | .0110 E |

**Table 6 - Continued**

**Key:**

Conc. (µg/L) = concentration of compound in micrograms per liter

E = Estimated value

Name of compound with no underline – waste water scan – Schedule 1433

Name of compound with underline – pharmaceutical scan – Lab Code 9003

Name of compound in pink – compound found in June 2004 blank

Name of compound in turquoise – compound found in November 2004 blank (Pharm. Scan)

**Name of compound in blue – compound found in March 2005 blank**

**Name of compound in green – compound found in June 2005 blank**

Name of compound in purple – compound found in November 2005 blank

Name of compound in red – compound found in March 2006 blank

**Table 7**
**Analytical Results**
**Muskegon River**

| June 16, 2004 | | August 19, 2004 | | October 27, 2004 | |
|---|---|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0990 E | 4-Nonylphenol | .7800 E | 1,4 Dichlorobenzene | .0470 E |
| 1-Methylnaphthalene | .0320 E | DEET | .0700 E | 4-Nonylphenol | .7200 E |
| 2-Methylnaphthalene | .0880 E | Tributyl phosphate | .0530 E | Camphor | .0059 E |
| Benzophenone | .1100 E | | | DEET | .0350 E |
| Camphor | .0300 E | | | Tribromomethane | .0100 E |
| DEET | .1300 E | | | Tributyl phosphate | .0330 E |
| Fluoranthene | .0540 E | | | | |
| Methyl salicylate | .0230 E | | | | |
| Metolachlor | .0800 E | | | | |
| Naphthalene | .0620 E | | | | |
| Pyrene | .0580 E | | | | |
| Tributyl phosphate | .1700 E | | | | |
| Triphenyl phosphate | .1000 E | | | | |

**Table 7 - Continued**

| **March 22, 2005** | | **June 27, 2005** | |
|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0680 E | 1,4 Dichlorobenzene | .0440 E |
| 1-Methylnaphthalene | .0049 E | AHTN | .0120 E |
| 2-Methylnaphthalene | .0073 E | Benzophenone | .1800 E |
| Benzophenone | .0340 E | Caffeine | .0300 E |
| Caffeine | .0400 E | Camphor | .0170 E |
| Camphor | .0090 E | DEET | .0380 E |
| DEET | .0250 E | HHCB | .0290 E |
| HHCB | .0290 E | Isoborneol | .0240 E |
| Isophorone | .0190 E | Isophorone | .0400 E |
| Menthol | .0470 E | Menthol | .1100 E |
| Naphthalene | .0140 E | Methyl salicylate | .0120 E |
| Tributyl phosphate | .0530 E | Metolachlor | .0097 E |
| | | Phenol | .2000 E |
| | | Tribromomethane | .0240 E |

| **August 23, 2005** | | **Replicate (Aug. 23, 2005)** | | **Blank (Aug. 23, 2005)** | |
|---|---|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| | | 1,4 Dichlorobenzene | .0480 E | | |
| DEET | .0320 E | Caffeine | .0300 E | | |
| | | DEET | .0320 E | | |
| Tribromomethane | .0280 E | Phenol | .1500 E | | |
| | | Tribromomethane | .0240 E | | |

**Table 7 - Continued**

| November 21, 2005 | | March 13, 2006 | |
|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0380 E | 1,4 Dichlorobenzene | .0380 E |
| 2-Methylnaphthalene | .0120 E | Caffeine | .0230 E |
| DEET | .0250 E | Camphor | .0220 E |
| Menthol | .0570 E | Isophorone | .0160 E |
| | | Metolachlor | .0120 E |
| | | p-Cresol | .1100 E |
| | | Phenol | .3900 E |

**Key:**

Conc. (µg/L) = concentration of compound in micrograms per liter
E = Estimated value
Name of compound with no underline – waste water scan – Schedule 1433
Name of compound with underline – pharmaceutical scan – Lab Code 9003
Name of compound in pink – compound found in June 2004 blank
Name of compound in turquoise – compound found in November 2004 blank (Pharm. Scan)
Name of compound in blue – compound found in March 2005 blank
Name of compound in green – compound found in June 2005 blank

Name of compound in purple – compound found in November 2005 blank
Name of compound in red – compound found in March 2006 blank

**Table 8**
**Analytical Results**
**Saginaw River**

| June 23, 2004 | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .3300 E |
| 1-Methylnaphthalene | .0790 E |
| 2-Methylnaphthalene | .1400 E |
| 2,6 Dimethlnaphthalene | .0420 E |
| 4-t-Octylphenol | .0980 E |
| AHTN | .0800 E |
| Benzophenone | .1400 E |
| Bisphenol A | .1800 E |
| Caffeine | .1500 E |
| DEET | .2800 E |
| Diethoxynonylphenol | 3.500 E |
| Fluoranthene | .0410 E |
| FYROL CEF | .0900 E |
| FYROL PCF | .1100 E |
| HHCB | .0940 E |
| Menthol | .0750 E |
| Methyl salicylate | .0670 E |
| Metolachlor | .3000 E |
| Naphthalene | .1100 E |
| p-Cresol | .0570 E |
| Phenanthrene | .0360 E |
| Phenol | .1800 E |

| June 23, 2004 continued | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| Pyrene | .0480 E |
| Triclosan | .0920 E |
| Triphenyl phosphate | .1100 E |
| Tris(butoxyethyl)PO4 | .8100 E |

| August 24, 2004 | |
|---|---|
| **Compound** | **Conc. (µg/L)** |
| Benzophenone | .0700 E |
| Caffeine | .0760 E |
| DEET | .1100 E |
| Fluoranthene | .0560 E |
| FYROL CEF | .0860 E |
| HHCB | .0720 E |
| Metolachlor | .0760 E |
| Pyrene | .0580 E |
| Tributyl phosphate | .0880 E |

**Table 8 - Continued**

| November 4, 2004 | | March 14, 2005 | | March 14, 2005 continued | |
|---|---|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0580 E | 1,4 Dichlorobenzene | .0740 E | Phenanthrene | .0073 E |
| Diethoxynonylphenol | 2.3000 E | 1-Methylnaphthalene | .0180 E | Pyrene | .0072 E |
| | | 2-Methylnaphthalene | .0290 E | Tributyl phosphate | .0650 E |
| | | 4-Nonylphenol | .9400 E | Triclosan | .0520 E |
| | | 4-t-Octylphenol | .0410 E | Triethyl citrate | .0310 E |
| | | AHTN | .0470 E | Triphenyl phosphate | .0180 E |
| | | Benzophenone | .0360 E | Tris (butoxyethyl) PO4 | .4400 E |
| | | Beta-Sitosterol | .3200 E | | |
| | | beta-Stigmastanol | .3300 E | | |
| | | Bisphenol | .5700 E | | |
| | | Caffeine | .1600 E | | |
| | | Camphor | .0140 E | | |
| | | Cholesterol | .5400 E | | |
| | | Cotinine | .1900 E | | |
| | | DEET | .0600 E | | |
| | | Diethoxynonylphenol | 1.100 E | | |
| | | Diethoxyoctylphenol | .1100 E | | |
| | | Ethoxyoctylphenol | .0910 E | | |
| | | Fluoranthene | .0086 E | | |
| | | FYROL CEF | .0230 E | | |
| | | FYROL PCF | .0450 E | | |
| | | HHCB | .1300 E | | |
| | | Isophorone | .0220 E | | |
| | | Menthol | .0360 E | | |
| | | Metolachlor | .0670 E | | |
| | | Naphthalene | .0420 E | | |

**Table 8 - Continued**

| June 15, 2005 | | Replicate (June 15, 2005) | | Blank (June 15, 2005) | |
|---|---|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** | 1,4 Dichlorobenzene | .0420 E |
| 1,4 Dichlorobenzene | .0730 E | 1,4 Dichlorobenzene | .0740 E | | |
| 9,10 Anthraquinone | .0880 E | 4-t-Octylphenol | .0210 E | | |
| Acetophenone | .0870 E | 9,10 Anthraquinone | .0660 E | | |
| AHTN | .0200 E | AHTN | .0140 E | | |
| Benzophenone | .3000 E | Benzophenone | .0440 E | | |
| Caffeine | .0930 E | Caffeine | .0800 E | | |
| Camphor | .0220 E | Camphor | .0150 E | | |
| Carbazole | .0100 E | Carbazole | .0100 E | | |
| DEET | .0850 E | DEET | .0760 E | | |
| Fluoranthene | .0140 E | Fluoranthene | .0150 E | | |
| FYROL CEF | .0320 E | FYROL CEF | .0250 E | | |
| FYROL PCF | .0480 E | FYROL PCF | .0450 E | | |
| HHCB | .0820 E | HHCB | .0640 E | | |
| Isoborneol | .0160 E | Isophorone | .0210 E | | |
| Isophorone | .0460 E | Menthol | .0500 E | | |
| Menthol | .1400 E | Metolachlor | .4400 E | | |
| Metolachlor | .4800 E | Pyrene | .0110 E | | |
| Phenol | .2200 E | Tributyl phosphate | .0210 E | | |
| Pyrene | .0120 E | Triethyl citrate | .0200 E | | |
| Tributyl phosphate | .0320 E | Triphenyl phosphate | .0160 E | | |
| Triclosan | .0280 E | Tris(butoxylethyl) PO4 | .3200 E | | |
| Triethyl citrate | .0200 E | | | | |
| Triphenyl phosphate | .0160 E | | | | |
| Tris(butoxyethyl) PO4 | .3300 E | | | | |

**Table 8 - Continued**

| August 16, 2005 | | November 29, 2005 | | March 14, 2006 | |
|---|---|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| | | 1,4 Dichlorobenzene | .0480 E | 1,4 Dichlorobenzene | .0530 E |
| 3-Beta-Coprostanol | .3100 E | 1-Methylnaphthalene | .0150 E | 1-Methylnaphthalene | .0064 E |
| Acetophenone | .1000 E | 2-Methylnaphthalene | .0220 E | 2-Methylnaphthalene | .0086 E |
| Benzophenone | .0380 E | Caffeine | .0880 E | 3-Methyl-1H-Indole | .0041 E |
| Beta-Sitosterol | .9800 E | DEET | .0480 E | Acetophenone | .1200 E |
| Beta-Stigmastanol | 1.0000 E | FYROL PCF | .2500 E | AHTN | .0076 E |
| Caffeine | .0480 E | HHCB | .1800 E | Caffeine | .0770 E |
| Camphor | .0130 E | Naphthalene | .0380 E | Camphor | .0290 E |
| Cholesterol | .9300 E | p-Cresol | .0440 E | Fluoranthene | .0095 E |
| DEET | .1200 E | Phenol | .1700 E | HHCB | .0340 E |
| Diethoxynonylphenol | 2.1000 E | Tributyl phosphate | .0700 E | Isophorone | .0230 E |
| Diethoxyoctylphenol | .0960 E | Tris(butoxyethyl) PO4 | .4600 E | Metolachlor | .0310 E |
| FYROL CEF | .0990 E | | | Naphthalene | .0180 E |
| FYROL PCF | .0710 E | | | p-Cresol | .4400 E |
| HHCB | .0460 E | | | Phenanthrene | .0120 E |
| | | | | Phenol | .1500 E |
| Metolachlor | .0800 E | | | Pyrene | .0067 E |
| | | | | Triphenyl phosphate | .0140 E |
| Tributyl phosphate | .1100 E | | | | |
| Triclosan | .0330 E | | | | |
| Tris(butoxyethyl)PO4 | .2800 E | | | | |

**Table 8 - Continued**

**Key:**

Conc. (µg/L) = concentration of compound in micrograms per liter

E = Estimated value

Name of compound with no underline – waste water scan – Schedule 1433

Name of compound with underline – pharmaceutical scan – Lab Code 9003

Name of compound in pink – compound found in June 2004 blank

Name of compound in turquoise – compound found in November 2004 blank (Pharm. Scan)

Name of compound in blue – compound found in March 2005 blank

Name of compound in green – compound found in June 2005 blank

Name of compound in purple – compound found in November 2005 blank

Name of compound in red – compound found in March 2006 blank

Statistics

Table 9 is a compilation of the minimum, mean, and maximum number of compounds detected for the rivers overall, i.e. taken as a whole, and for each river individually.

Table 9
Compound Detection Statistics for the Rivers Sampled

| | Overall | Clinton | Grand | Saginaw | Kalamazoo | Muskegon |
|---|---|---|---|---|---|---|
| Minimum | 1 | 6 | 4 | 1 | 2 | 2 |
| Mean | 14 | 22 | 20 | 15 | 10 | 5 |
| Maximum | 45 | 45 | 33 | 29 | 16 | 13 |

The table shows that the mean number of compounds detected overall is 14; with a minimum of 1 compound and a maximum of 45 compounds in a single river water sample. The order of the river names within the table is not random. They are in order of, what would appear to be, highest impact from pharmaceuticals and personal care products to lowest impact. This is evident, as the Clinton River has the highest mean number of compounds found throughout the study, followed by the Grand River with a mean of 20 compounds. The Saginaw and Kalamazoo Rivers have means of 15 and 10 compounds, respectively. Finally, the Muskegon River has a mean of 5 compounds detected and would appear to have the least impact from these compounds when compared to the other 4 rivers sampled. The table also shows that the maximum number of compounds detected per river follows this same trend.

These trends are to be expected, considering that the Clinton River is located in the suburban areas of the Detroit Metropolitan area and receives waste water inputs and urban runoff. The Lansing office of the USGS has also indicated that,

from its findings, the majority of the flow during dry periods of the year is from waste water discharge. The Grand River also has large cities along its course as it flows through Lansing and Grand Rapids. Grand Rapids is also still known to experience combined sewer overflows during large rain events. The city has been working for a number of years to separate its storm and sanitary sewers in an effort to stop these discharges of untreated sewage and storm water during large rainfalls. The Saginaw River is also expected to have moderate impacts as the City of Saginaw lies on its banks. It was a little surprising that the statistics for the Kalamazoo River place it near the moderate to low impact in comparison to the other 4 rivers, because the river flows through the cities of Battle Creek and Kalamazoo. However, the sample site is near the mouth of the river after it flows through a large expanse of rural area and a large reservoir (Lake Allegan). Therefore, perhaps dilution along the flow path has masked some of the large city impacts. The Muskegon River is the least impacted among the 5 rivers sampled. This is not too surprising as the sample location is upstream from the City of Muskegon and most of the river's flow path is through rural and agricultural areas.

When the statistical results from this study are compared to the national stream reconnaissance study (Kolpin et al., 2002), the mean (14) and the maximum number of compounds detected (45) are higher in Michigan. The mean number of compounds detected nationwide was 7 compounds, with a maximum number of 38 compounds detected in a single sample (Kolpin et al., 2002). This is unexpected, especially since the streams sampled in the national study were closer to sources of waste water discharge. These statistical differences may be explained by study design. The national reconnaissance study sampled 139 streams only once, whereas the five streams sampled in this study were sampled quarterly for two

years. As expected, the concentrations detected in the national survey were higher than the detections in this Michigan study. Estimated concentration values were reported in the national study as well, but 5% of the detections were over 1 µg/L (Kolpin et al., 2002). The Detection Issues and Low Concentrations section below contains a full discussion of the concentrations found in this study. The vast majority of concentrations in this study were estimated values and below 1µg/L. Table 10 lists the concentration ranges for each river.

Occurrence

In an effort to understand occurrence trends of the pharmaceuticals and personal care products, the data were examined as a whole and the number of different compounds detected at least once per river was determined. This can also be used as another indicator of impact to these rivers by the compounds studied. Again, as evident on Figure 3, the Clinton River shows the most impact, with a total of 51 individual compounds detected out of 67 analyzed during the two-year study. The Grand, Saginaw, and Kalamazoo Rivers follow with 45, 42, and 28 compounds detected, respectively. Finally, the Muskegon River shows the least amount of impact with 21 compounds detected at least once.

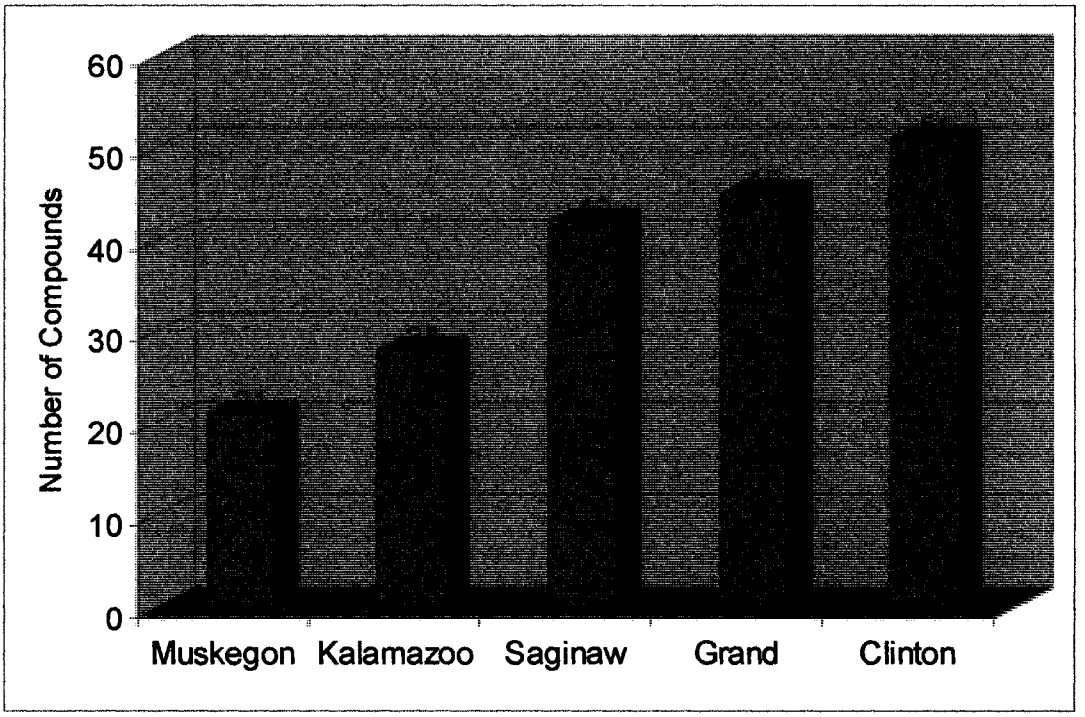



Figure 3 : The number of different compounds detected at least once per river.

Also, a list of compounds was determined to occur quite frequently in all the rivers. These compounds include the following classes: flame retardants, gasoline constituents, dyes, solvents, plasticizers, fragrances, detergent metabolites, pesticides, and pharmaceuticals (Kalamazoo and Grand Rivers analyzed only).

Seasonal Trends

Seasonal trends were investigated by comparing the number of compounds detected per sample event to river discharge data. The river discharge data were obtained from the United States Geological Survey website (http://water.usgs.gov/waterwatch/?m=real&r=mi). Two of the river sample sites, the Clinton and Kalamazoo Rivers, had river gages on site, so the discharge data could be used directly from the website. However, the Grand and Muskegon River sample

sites did not have river gages directly on site. For these two cases, different gages on the rivers were used and the discharge data were multiplied by a ratio to account for the differences in drainage area. The river gage used to obtain discharge data for the Grand River is located in Grand Rapids. This gage location is upstream from the Eastmanville Grand River sample site in this study. Therefore, the Grand Rapids gage can be used if the discharge data are multiplied by the ratio 1.06. The ratio accounts for the difference in drainage area and therefore flow between the two sites. The discharge data from the river gage located on the Muskegon River in Croton are therefore used for the study sample site located in Bridgeton if multiplied by a ratio of 1.05. These corrections to the discharge data for the Grand and Muskegon Rivers were completed before the data were used and analyzed in this dissertation. The ratios were provided by USGS field staff from the Lansing, Michigan office. There is a gage on site at the Saginaw River sample site located in Essexville, but this is a special case. No discharge data are provided for this site as the gage is so closely located to Lake Huron. At this gage location, river water flows into the lake at times and at other intervals flow is reversed and moves upstream, making discharge data impossible to interpret. Due to this issue, a different gage on the same river was used outright for the Saginaw River site. The gage is located on the Saginaw River upstream in the city of Saginaw.

The initial hypothesis was that as the river discharge increases, dilution will cause the number of detections to decrease and vice versa. However, none of the five rivers exhibited a consistent inverse relationship between river discharge and the number of compounds detected. This may indicate that other mechanisms, other than just dilution, are a factor; such as non-point source contributions from storm runoff. Please see Figures 4 – 8 for a graphical representation for each river. The

river figures are in alphabetical order, starting with the Clinton River in Figure 4 and concluding with the Saginaw River in Figure 8.

The figures show each river had its own character with regard to discharge and the number of compounds detected. There is no correlation between seasons or the different rivers when comparing this relationship. The figures also show the more urban rivers, the Clinton, Grand, and Saginaw, were much flashier than the Kalamazoo and Muskegon Rivers. The June 2004 discharge values were much higher than the June 2005 discharge values for the Clinton, Grand, Kalamazoo, and Muskegon Rivers. Whereas, the June 2004 discharge value was much lower than the June 2005 discharge value for the Saginaw River. These differences in discharge values would have caused more dilution in June of 2004 than in June of 2005 for the Clinton, Grand, Kalamazoo, and Muskegon Rivers. This may explain the lower number of detections in June 2004 as opposed to the number of detections in June 2005 for these rivers. Even though the Saginaw River would have had less dilution in June 2004 than in June 2005, fewer detections were observed in June of 2004. The censoring of the data during the first two sample rounds, including June 2004, due to blank issues, may have affected these relationships. The maximum number of compounds censored in June 2004 was 9 as compared to a maximum of 1 compound censored in June 2005. The March 2005 discharge values were much lower than the March 2006 discharge values for the Clinton, Grand, Muskegon, and Saginaw Rivers. This would have caused less dilution in March 2005 and may explain the higher number of detections for these rivers in March 2005 as opposed to the number of detections for March 2006. The spring discharge peaks occurred before the samples were taken in March 2005 for the Clinton, Grand, and Saginaw Rivers and after sampling for the Muskegon River.

The spring 2005 discharge peak also took place before the Kalamazoo River sample was taken, but no great difference in discharge rates or number of detections were observed between March 2005 and 2006. This may be due to the presence of Lake Allegan along the flow path of the river and its water storage capability. Due to seasonal discharge differences, a longer period of sampling may be needed to fully understand the trends.

The censoring of the data due to blank issues during the first two sample rounds caused the seasonal comparisons between both the number of detections and the compound types for each river to be very difficult if not impossible. The data censoring also made it very difficult to assess seasonal source differences. The compounds detected indicated a diverse set of sources for all of the rivers. The chemicals originated from waste water treatment, runoff (gasoline constituents, agricultural chemicals), and industrial (solvents) sources to varying degrees. The censoring of the data, however, did not affect the inverse relationship comparison between discharge and the number of compounds detected.

The inconsistent inverse relationship between discharge and the number of compounds detected could also be explained by some interesting information that was obtained from a waste water operator during a presentation of this data at a Michigan Water Environment Association meeting in early 2006. He indicated that in the winter, they store a portion of their treated waste water in lagoons and then in the spring when the ice is off the rivers, they release the waste water. They certainly cannot be the only municipality that does so. So, in the spring, when a large dilution would be expected due to spring rains and snow melt, there may also be a large influx of waste water constituents into the river systems. This type of waste water discharge was verified with Water Bureau, MDEQ staff of the Grand Rapids and

Kalamazoo District Offices. In fact, there are waste water lagoon systems that have a general permit to discharge seasonally. The lagoon treatment systems are located in smaller communities, mobile home parks, camps, and schools for example, that generally are designed to produce less than 1 million gallons per day of waste water. The lagoon systems are permitted to discharge waste water to the receiving stream during high flow conditions in the spring (March 1 to May 31) and fall (October 1 to December 31). No discharge is allowed from June 1 to September 30 and again from January 1 to February 28. Also, no discharge is allowed if ice is covering the receiving stream. Therefore, just as the waste water operator stated above, in March, when the ice is off from the rivers, there is a release of waste water from utilities with seasonal discharge permits. This discharge may explain, in part, the reason there is no consistent seasonal relationship between river discharge and the number of compounds detected; however, the large municipal waste water discharges (those over 1 million gallons per day) are ongoing throughout the year and are much larger point sources for these compounds. To test the effects of the waste water additions from seasonal discharge to the receiving streams, specific study of the effluents and streams would need to be completed.

The most probable cause of the inconsistent inverse relationship between discharge and the number of chemical compounds detected is the result of the sample location. The river samples were taken close to or at the mouth of each river. These locations integrate many sources of the compounds, maximize discharge, and allow for mixing. If the sample sites were closer to a major source of municipal waste water discharge, for example, seasonal trends would probably be clearer, as they were in the study by Kolpin et al., 2004. The researchers sampled upstream and downstream of selected cities in Iowa during different stream flow

conditions in 2001. They found that as stream flow increased, the number of contaminants decreased (Kolpin et al., 2004).

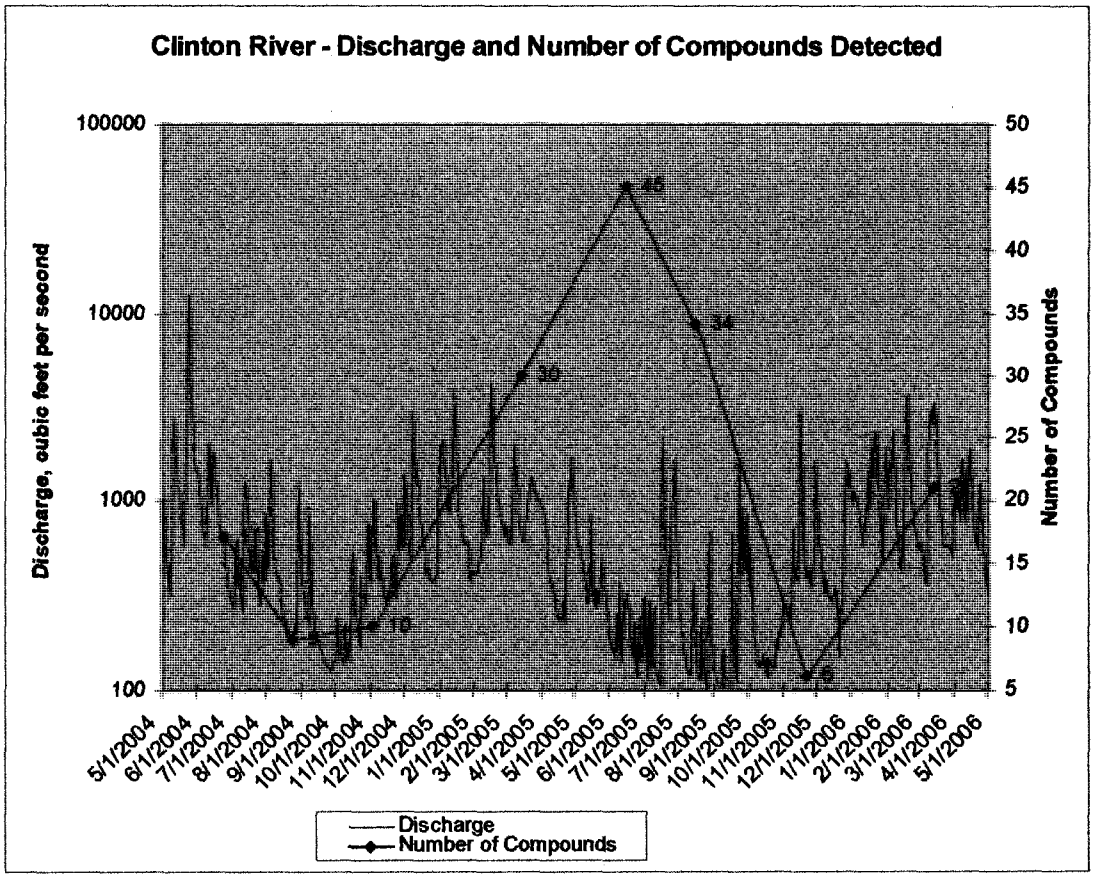



Figure 4: River discharge and the number of compounds detected versus time for the Clinton River. The river discharge data were obtained from the USGS.

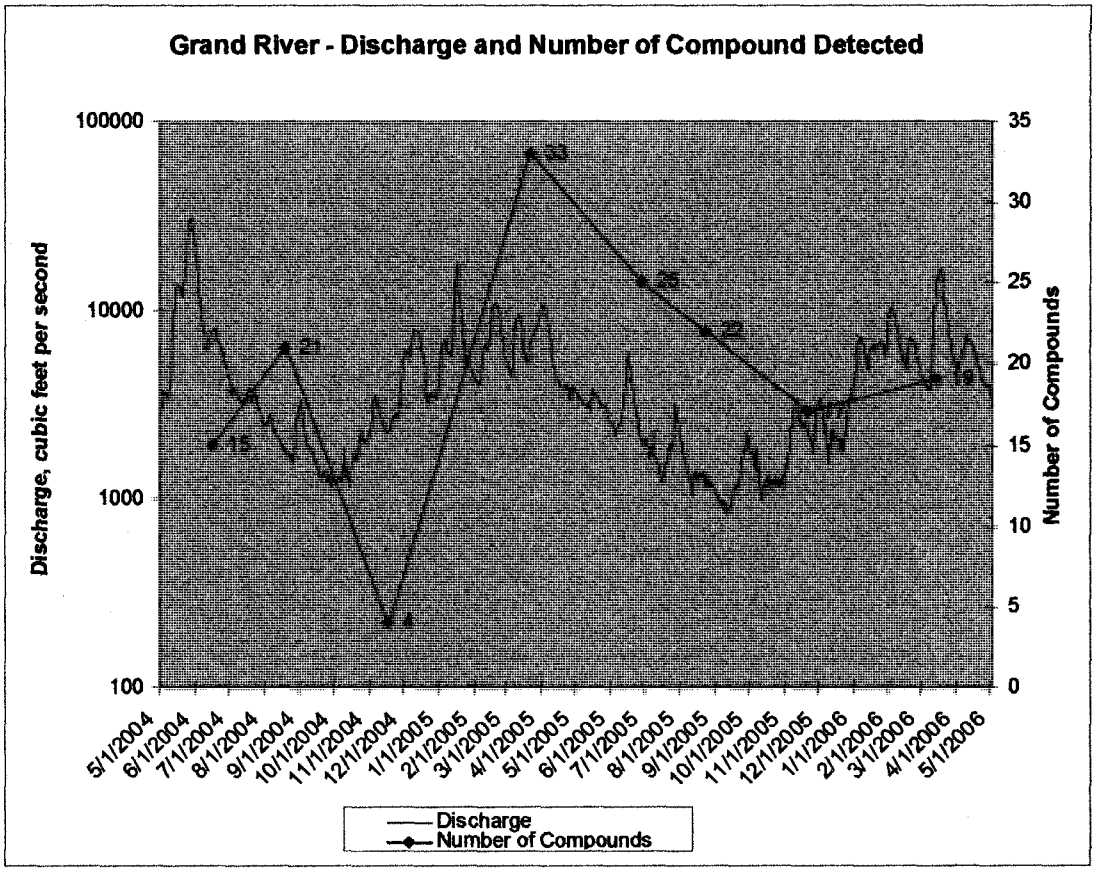



Figure 5: River discharge and the number of compounds detected versus time for the Grand River. The river discharge data were obtained from the USGS.

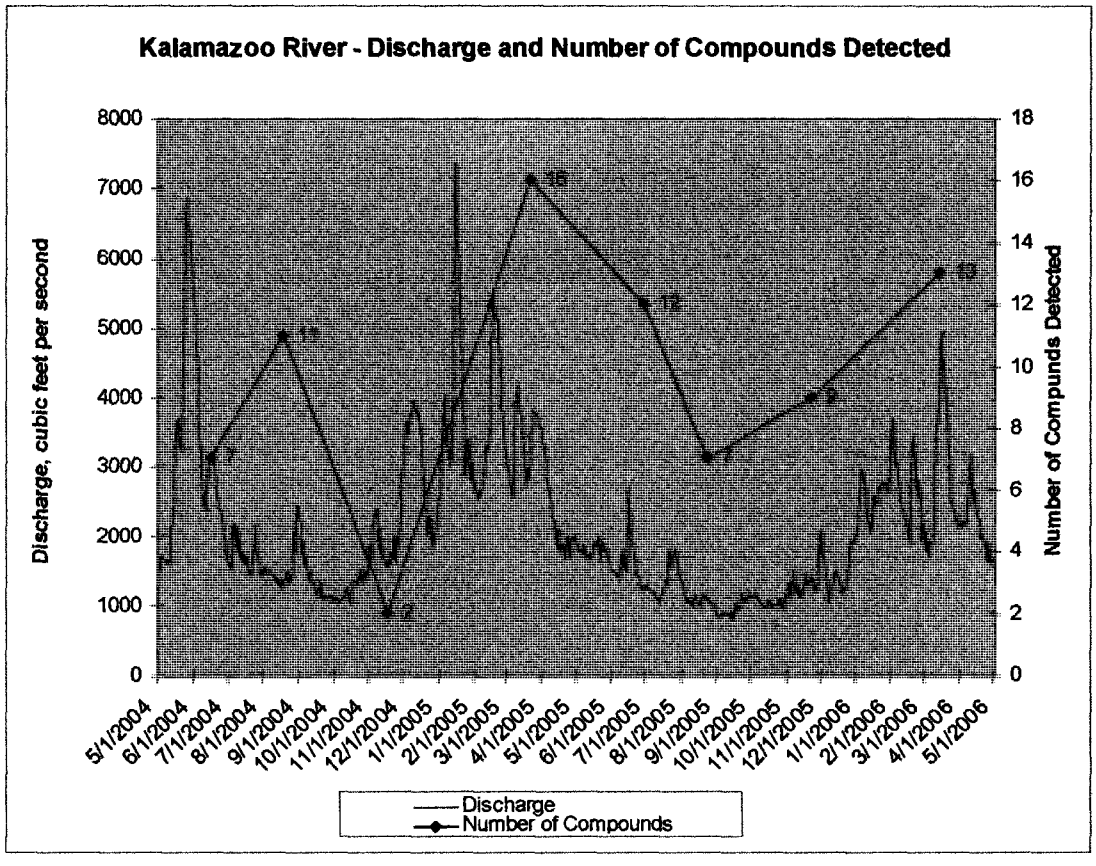



Figure 6: River discharge and the number of compounds detected versus time for the Kalamazoo River. The river discharge data were obtained from the USGS.

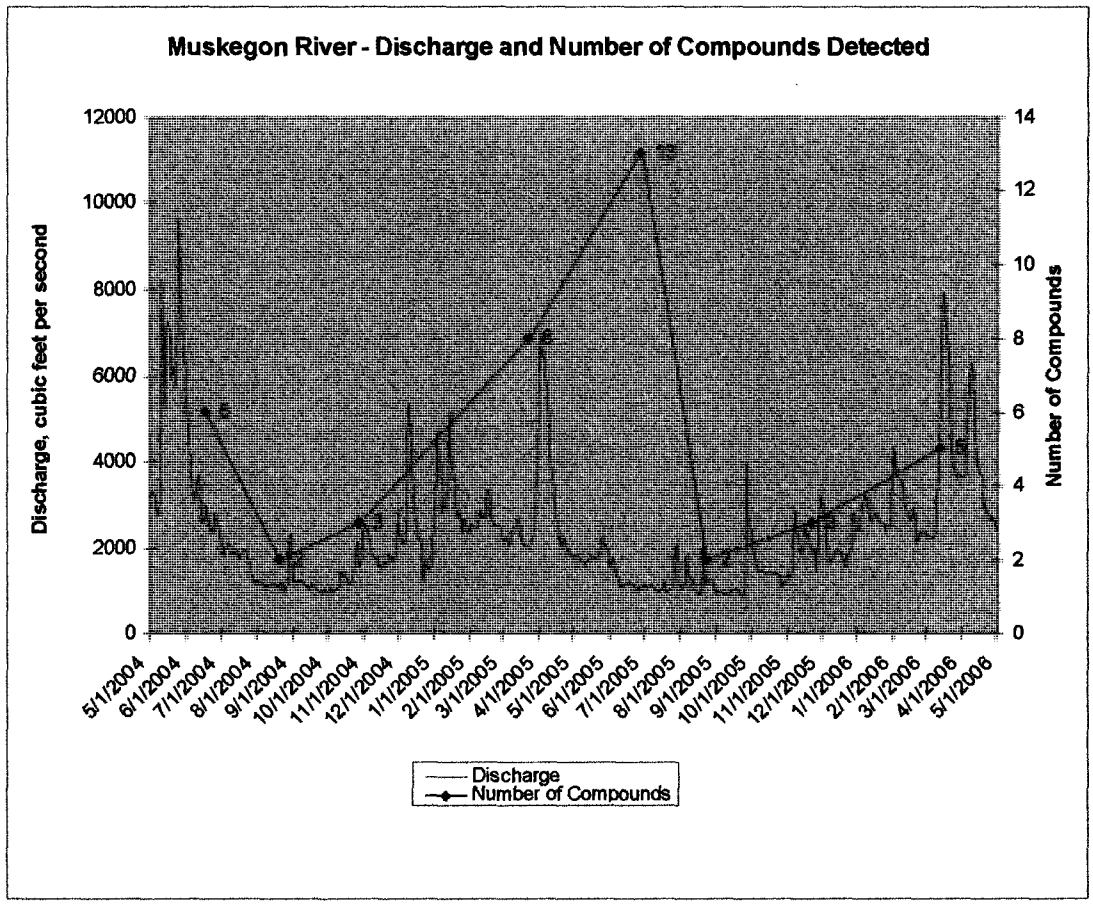



Figure 7: River discharge and the number of compounds detected versus time for the Muskegon River. The river discharge data were obtained from the USGS.

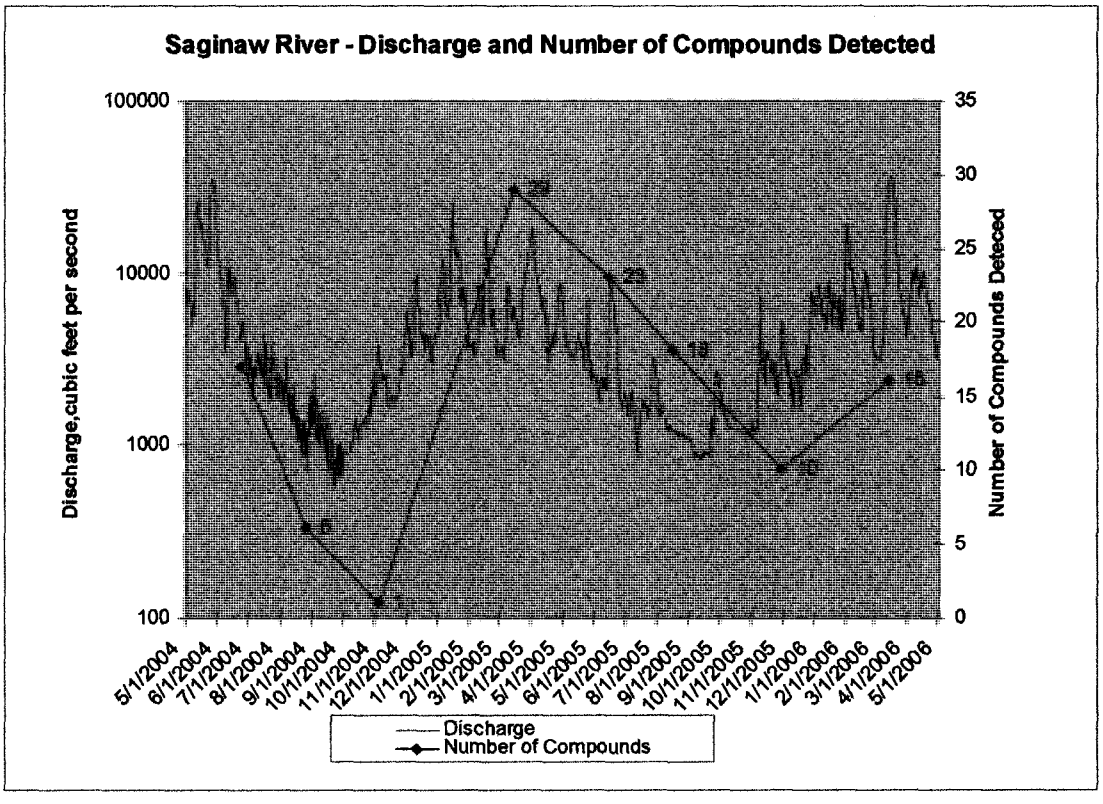



Figure 8: River discharge and the number of compounds detected versus time for the Saginaw River. The river discharge data were obtained from the USGS.

Endocrine Disruptors

As discussed in the introduction, some of the pharmaceutical and personal care products studied have been known to cause endocrine disruption in wildlife, even at very low concentrations (ppb). The endocrine system is responsible for regulating the growth and sex hormones within an organism. Known or suspected endocrine disrupting compounds were found in varying degrees in all of the rivers sampled.

Over the sampling period, the following compounds which are known or suspected to be endocrine disruptors were detected in the Clinton River at least once: 4-t-octylphenol, bisphenol A, diethoxynonylphenol, diethoxyoctylphenol, 4-nonylphenol, carbaryl, p-cresol, benzophenone, triclosan, diazinon, and dichlorvos.

The Grand River contained the following compounds at least once: 4-nonylphenol, triclosan, diethoxyoctylphenol, diethoxynonylphenol, 4-t-octylphenol, benzophenone, and bisphenol A .

The following suspected or known endocrine disruptors were detected in the Saginaw River over the study period: 4-t-octylphenol, bisphenol A, diethoxynonylphenol, diethoxyoctylphenol, 4-nonylphenol, p-cresol, benzophenone, and triclosan.

For the Kalamazoo River, the following compounds were detected at least once over the sampling period: 4-nonylphenol and benzophenone.

Finally, the Muskegon River was shown to contain the following known or suspected endocrine disrupting compounds: 4-nonylphenol, benzophenone, and p-cresol.

The Clinton River, which has been identified throughout the text as being the most impacted by pharmaceuticals and personal care products, also has the highest

number of endocrine disruptors detected overall. This may be because the Clinton River had the highest number of compounds detected and the greatest amount of compounds detected at least once, so statistically there was a higher probability that some of these compounds will be endocrine disruptors. The trend wasn't as clear for the other rivers, but it can be said that the Saginaw and Grand Rivers have the next highest number of compounds known or suspected to be endocrine disruptors. Then, the Muskegon and Kalamazoo have the lowest number of endocrine disruptors found in general.

Detection Issues and Low Concentrations

As evident on Tables 3-8, the vast majority of the compound detections are well below 1 ppm and most are given an "E" demarcation, which means estimate. The concentration is given an estimate qualifier when the value is between the laboratory reporting level and the long-term method detection level. The National Water Quality Lab developed this reporting convention to prevent the over-censoring of data. Historically, if the minimum reporting level was set too high for a compound, data would be lost; as lower concentrations would be reported as non-detections. Now that analytical methods are proven for lower concentrations of compounds, it is important not to lose resolution. Even though the estimated values have less certainty, the researcher is given the opportunity to use or censor the data which is usually determined by how the data will be used. For example, if the detections are to be used in a regulatory sense, higher confidence in the data is probably warranted. However, if the data are to be used in an occurrence study and there is a large volume of data, such as in this study, the detections can be considered to be quite valid.

Even though most of the values are reported as estimates, there is confidence in these values. Many replicate or duplicate samples were taken with high correlation of the types of compounds and the concentrations. The replicate results can be found in Tables 4-8 as well.

Table 10 below is a summary of the concentration ranges for each river. The highest concentrations occurred in the Clinton River. The Clinton River consistently seems to be the most impacted river out of the five sampled. Again, the Saginaw and the Grand Rivers fall in the middle with moderate concentrations. The Kalamazoo and the Muskegon River show the lowest concentrations found. This indicates again, the lower impact from the compounds sampled.

Table 10
Compound Concentration Ranges per River

| River | Concentration range (µg/L) |
|---|---|
| Clinton | .0052 – 8.0 |
| Saginaw | .0041 – 3.5 |
| Grand | .0036 – 2.3 |
| Kalamazoo | .0030 – 1.1 |
| Muskegon | .0049 - .78 |

Chemical Compound Discharge and Area of Drainage

A modified discharge formula was used to compare the total discharge of pharmaceuticals and personal care products from each river. The following equation was used:

$\sum \sum C \times Q \times 0.0027$ = Total Chemical Compound Discharge (tons/day)

Where C = concentration of each compound in mg/L and Q = discharge of the river in $ft^3/s$. The 0.0027 is a factor used to convert the values to tons/day. For

each river and for each sample round, the compound concentrations were first divided by 1000 to convert the units from µg/L to mg/L. Then, they were multiplied by the discharge (Q) reported by the USGS for the river on the same day the sample was collected. Table 11 shows the sample dates and the corresponding river discharge values ($ft^3/s$) used for each river. Discharge (Q) values were determined as described in the Seasonal Trends section above. Next, they were multiplied by 0.0027. Finally, these numbers were added to get a total tons/day of pharmaceuticals and personal care products during that sample round. The second sum ($\sum$) in the equation above is to signify that after the totals were calculated for each sample round (eight total for each river) they were added together to give a total for the entire study period for each river. See Table 12 below for the results. The total pharmaceutical and personal care product discharge was also computed in units of mg/l per $ft^3/s$. This was calculated as described above, except the factor of 0.0027 is not used in the multiplication. The results of this calculation for each river are also in Table 12.

Table 11
Sample Dates and Corresponding River Discharge Values ($ft^3/s$) for Each River

| | Clinton | Grand | Kalamazoo | Muskegon | Saginaw |
|---|---|---|---|---|---|
| Sample Dates | | | | | |
| June 2004 | 550 | 7706 | 3120 | 2741 | 4420 |
| August 2004 | 183 | 1749 | 1320 | 1031 | 899 |
| November 2004 | 577 | 2194 | 1560 | 1670 | 3790 |
| March 2005 | 619 | 6222 | 3000 | 2016 | 6030 |
| June 2005 | 301 | 2025 | 1210 | 1103 | 8180 |
| August 2005 | 191 | 1134 | 1090 | 1124 | 1190 |
| November 2005 | 442 | 2226 | 1350 | 1922 | 4260 |
| March 2006 | 3250 | 12190 | 3930 | 6300 | 34800 |

Table 12
Total Discharge of Pharmaceuticals and Personal Care Products for Each River for the Entire Study Period and Area of Drainage

| River | Area of drainage ($mi^2$) | Total Pharmaceutical and Personal Care Product Discharge (tons/day) \ (mg/l per $ft^3/s$) |
|---|---|---|
| Saginaw | 6440 | 0.3566 \ 132.1 |
| Grand | 5230 | 0.2141 \ 79.29 |
| Clinton | 734 | 0.0650 \ 24.07 |
| Kalamazoo | 1994 | 0.0378 \ 14.02 |
| Muskegon | 2420 | 0.0219 \ 8.100 |

The total discharge values for the rivers were compared and contrasted. As the table above shows, the area of drainage was also considered for each river. The area of drainage for each river watershed was obtained from USGS Lansing, Michigan field staff, but can also be found on its website (http://water.usgs.gov/waterwatch/?m=real&r=mi). Area of drainage for each river is important here because it helps to explain the data for total discharge of chemical compounds. Recall that in the previous results sections, the Clinton River always seems to be the most heavily impacted of the five rivers sampled, followed by the Grand and Saginaw Rivers which trend toward the middle. The Kalamazoo and Muskegon Rivers tend to be the least impacted. However, here, the Clinton River total chemical compound discharge falls below that of the Saginaw and Grand Rivers. But, for the river with the smallest drainage area and therefore, typically the smallest Q values, the Clinton River could be considered to have quite a high discharge of chemical compounds. The Clinton River had a higher number of

compounds detected and higher concentrations as well, which help to place it ahead of the Kalamazoo and Muskegon Rivers which have larger Q values and drainage areas than the Clinton River. The Saginaw and Grand Rivers have the largest drainage areas, higher Q values, and moderate chemical detections and concentrations, which help to place them at the top for chemical compound total discharge. With these trends in mind, the Muskegon River, with a higher drainage area than the Kalamazoo River, might be expected to have a higher chemical compound discharge as well. However, its lower compound discharge can be explained by the lower number of compounds detected and their lower concentrations for the Muskegon River as compared to the Kalamazoo River. This shows, again, that the rural nature of the Muskegon River lessens its impact from these compounds.

To provide a visual reference, the watershed areas are presented in the figures that follow (figures 9 – 18). These maps or graphics were obtained from a USGS website (http://water.usgs.gov/wsc/reg/04.html). An explanation of the water resource region hierarchy that the USGS uses is needed, as it is shown in the figures that follow. The United States is subdivided into water resource regions or hydrologic units specified with a numbering system (hydrologic unit code or HUC). To specify a more detailed area, two digits are added each time in succession. An example is the best way to illustrate this numbering system. The Great Lakes watershed or water resource region is specified by 04. This region is then divided further into several subregions, one of which is 0409. The subregions contain a number of accounting units, one of which is 040900. Finally, the accounting units are further divided into cataloging units, one of which is 04090003, which happens to be the Clinton River watershed (refer to figures 9 -11 for this specific example).

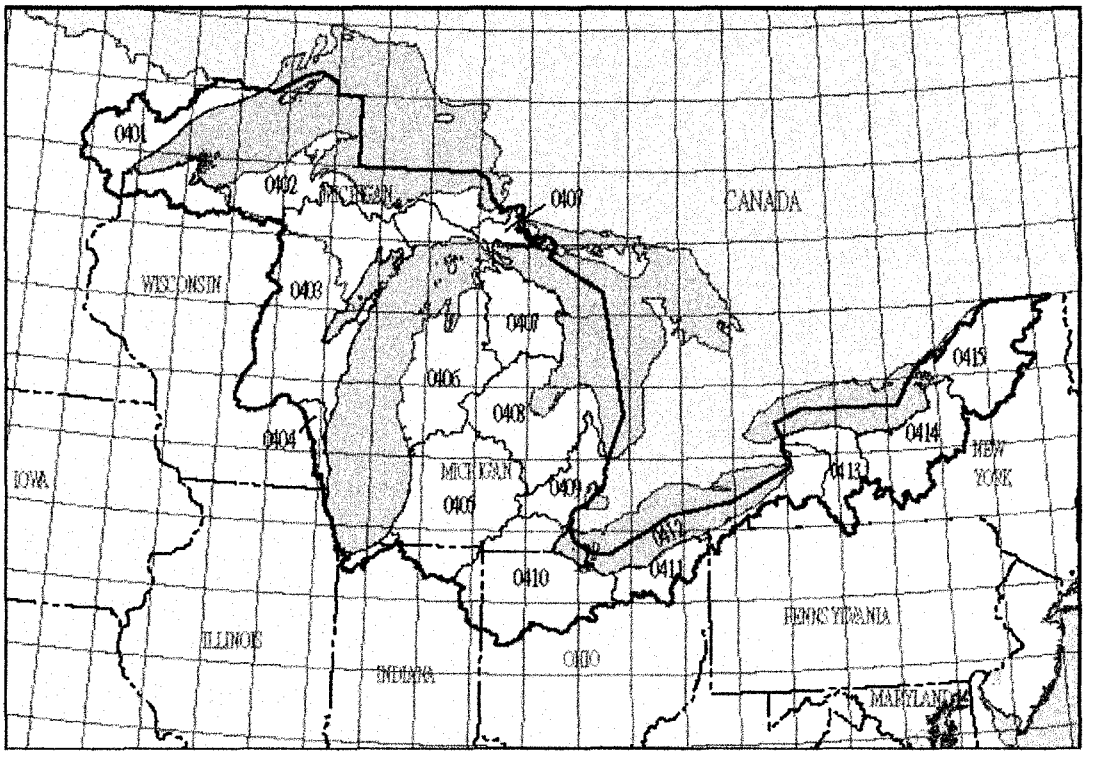



Figure 9: The watersheds of the Great Lakes Basin (04). Graphic provided by USGS website http://water.usgs.gov/wsc/reg/04.html.

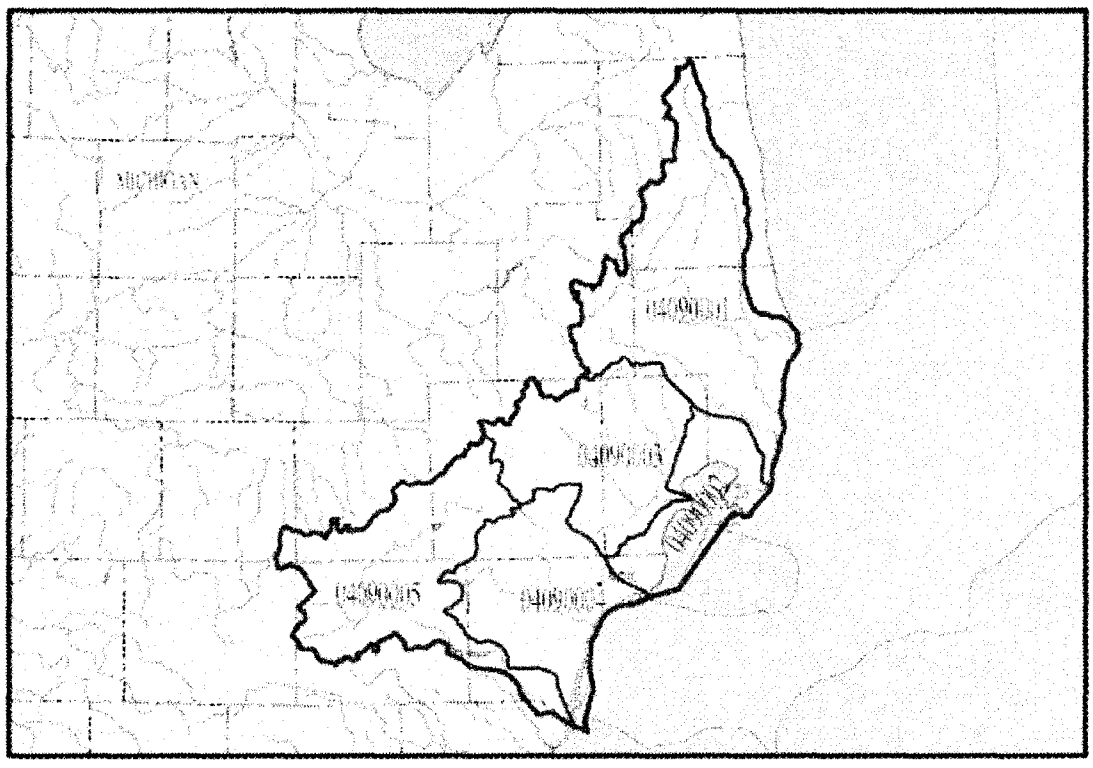


Figure 10: A closer view of the Lake St. Clair and Detroit River watershed (040900). *Graphic provided by USGS website* http://water.usgs.gov/wsc/reg/04.html

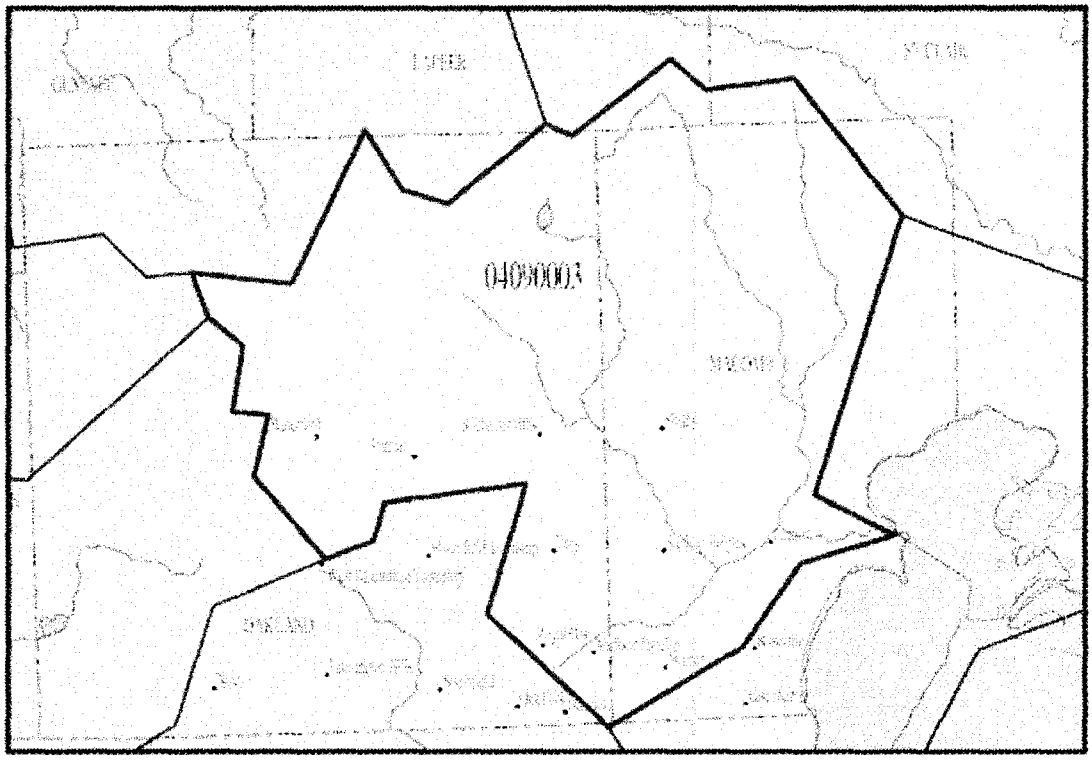


Figure 11: The Clinton River watershed (04090003). Graphic provided by USGS website http://water.usgs.gov/wsc/reg/04.html

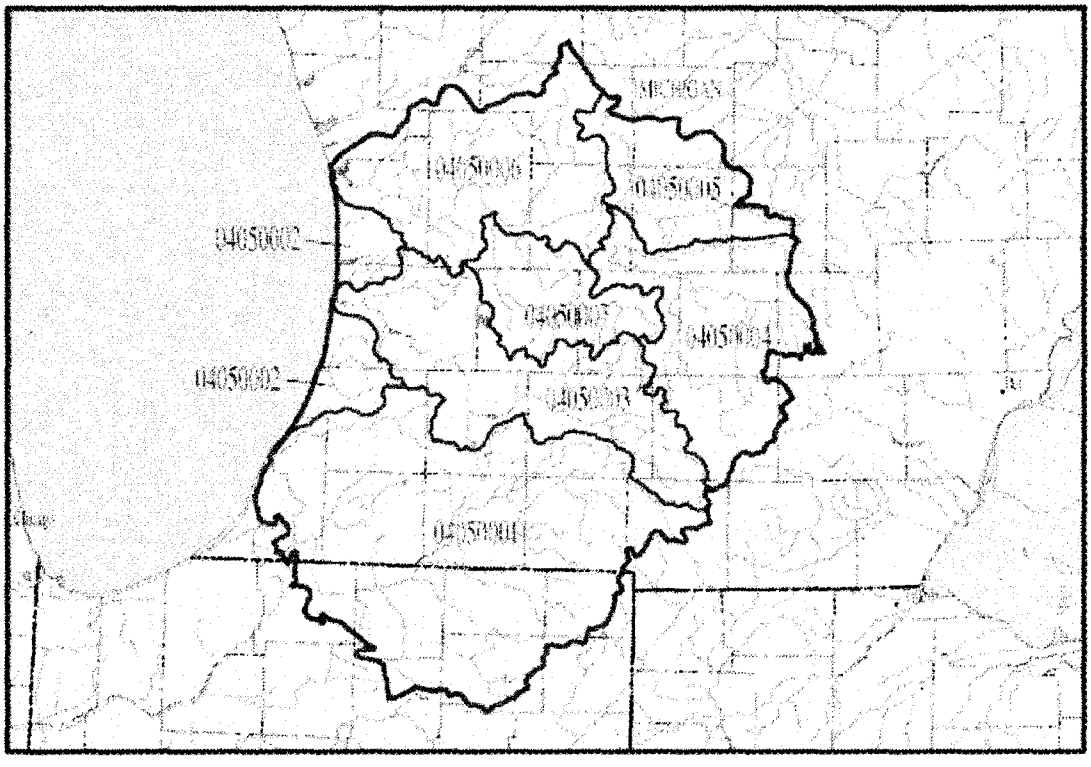


Figure 12: A closer view of the Southeastern Lake Michigan watershed (040500). Graphic provided by USGS website http://water.usgs.gov/wsc/reg/04.html

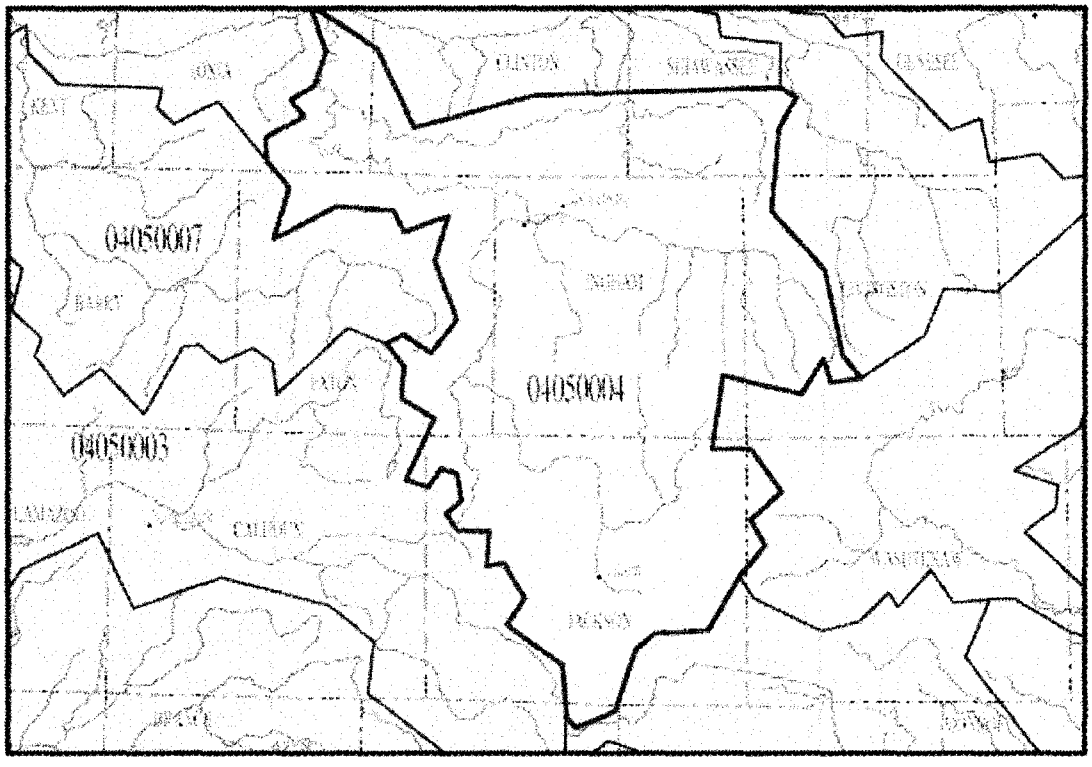



Figure 13: The Upper Grand River watershed (04050004). Combined with the Lower Grand watershed in Figure 14, they compose the entire Grand River watershed. Graphic provided by USGS website http://water.usgs.gov/wsc/reg/04.html

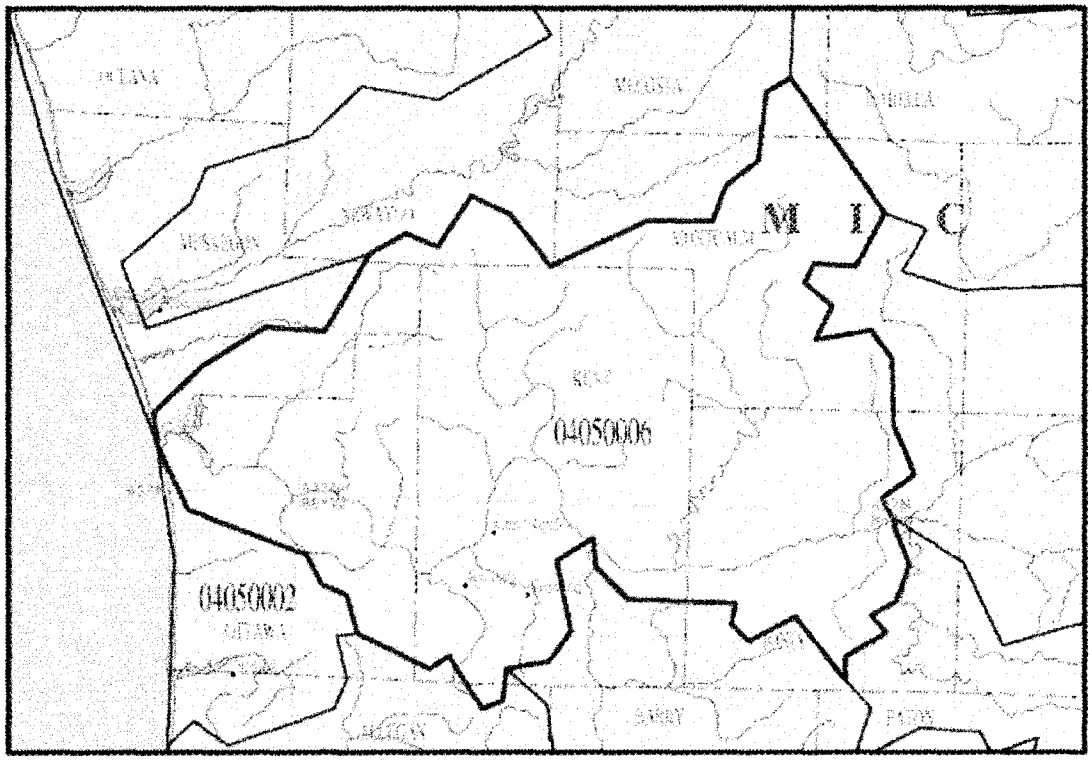



Figure 14: The Lower Grand River watershed (04050006). Combined with the Upper Grand River watershed in Figure 13, they compose the entire Grand River watershed. Graphic provided by USGS website http://water.usgs.gov/wsc/reg/04.html

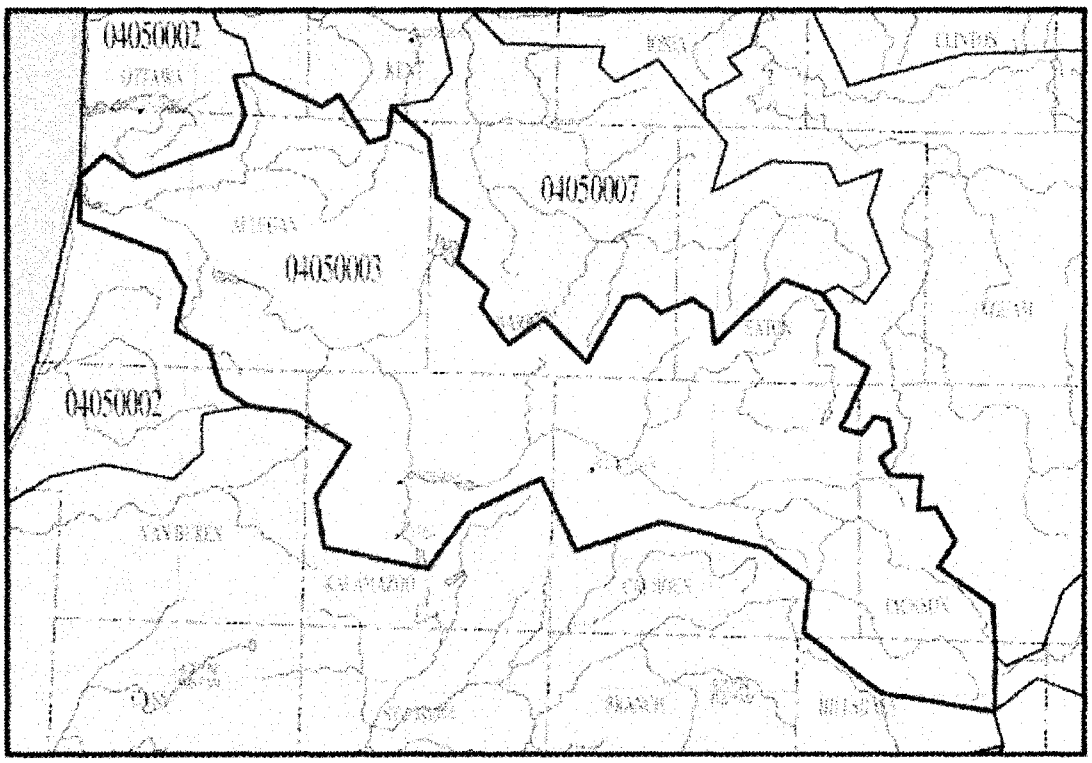



Figure 15: The Kalamazoo River watershed (04050003). Graphic provided by USGS website http://water.usgs.gov/wsc/reg/04.html

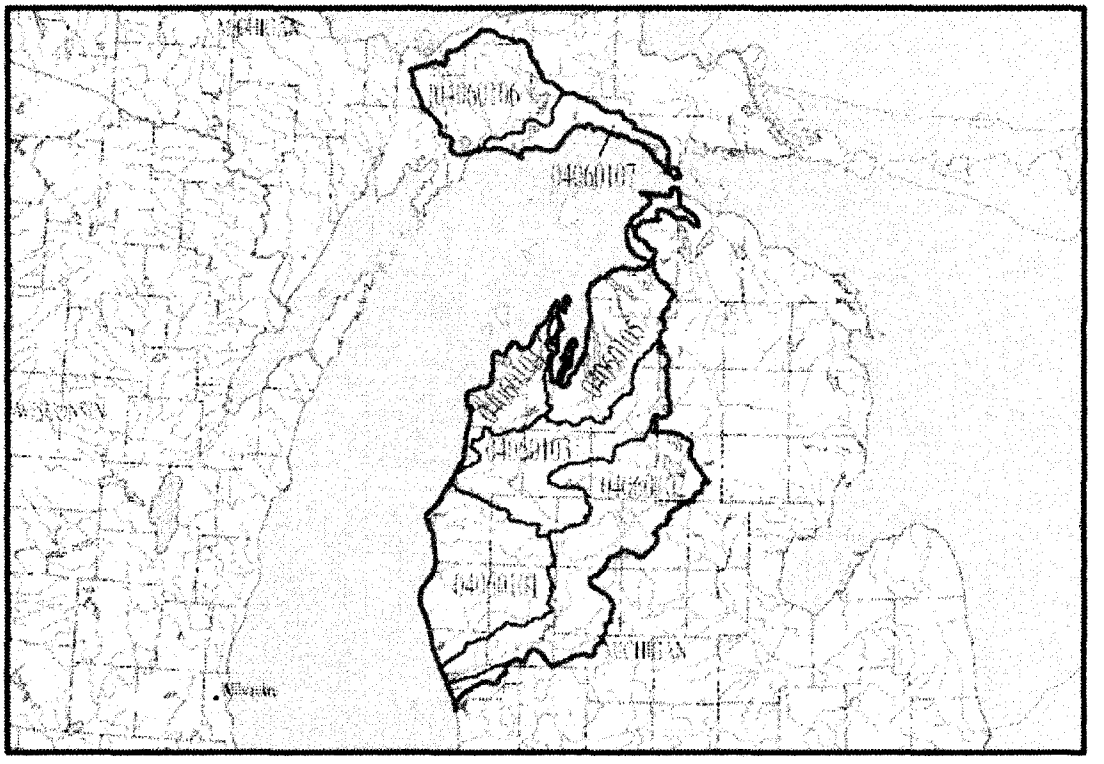


Figure 16: A closer view of the Northeastern Lake Michigan watershed (040601). Graphic provided by USGS website http://water.usgs.gov/wsc/reg/04.html

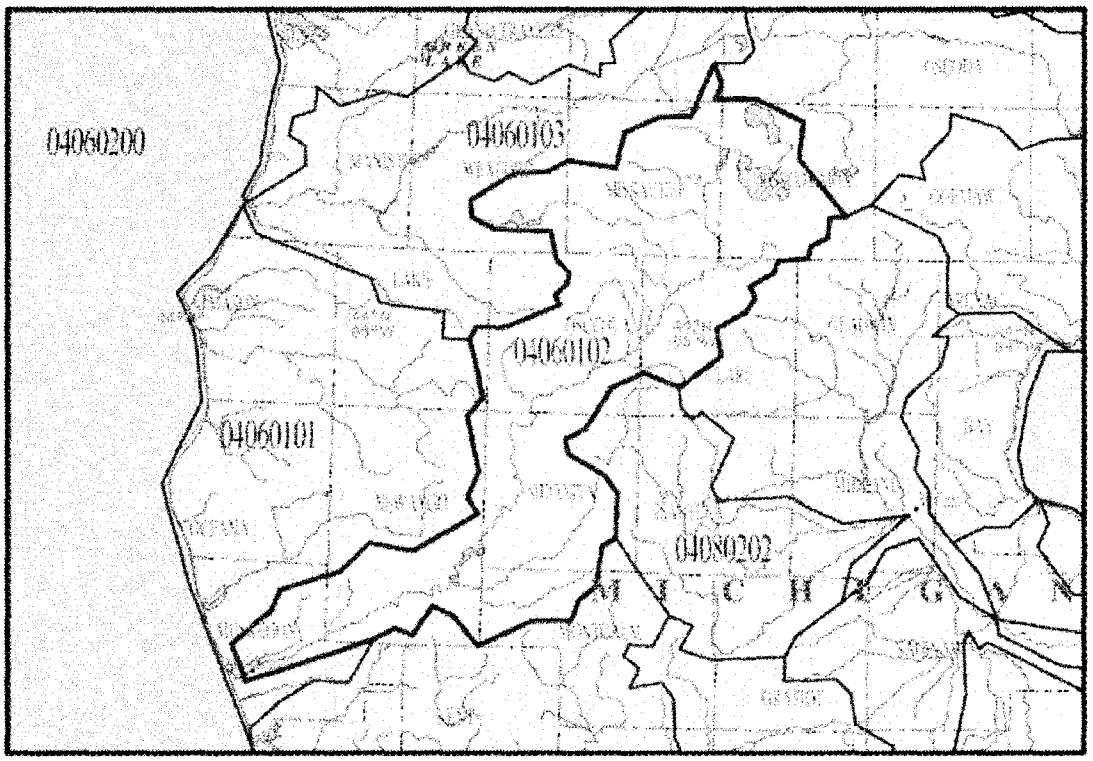



Figure 17: The Muskegon River watershed (04060102). Graphic provided by USGS website http://water.usgs.gov/wsc/reg/04.html

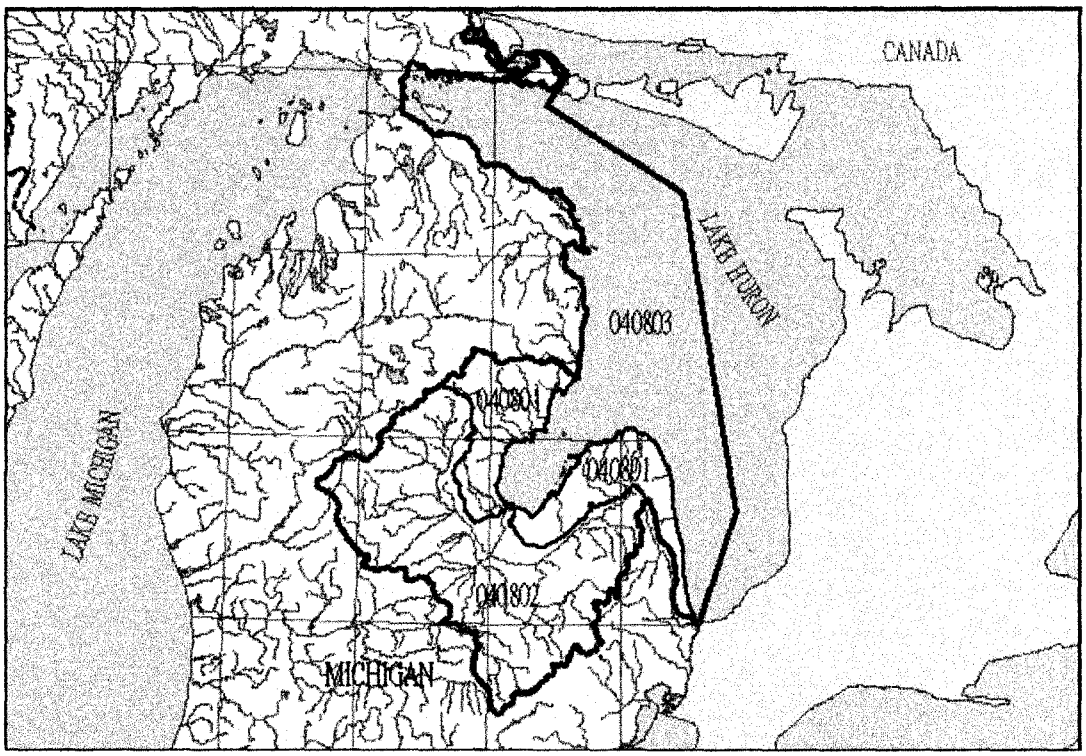



Figure 18: A closer view of the Southwestern Lake Huron watershed (0408). The Saginaw River watershed is shown as the area 040802 and is thought to be used for area calculations. Graphic provided by USGS website http://water.usgs.gov/wsc/reg/04.html

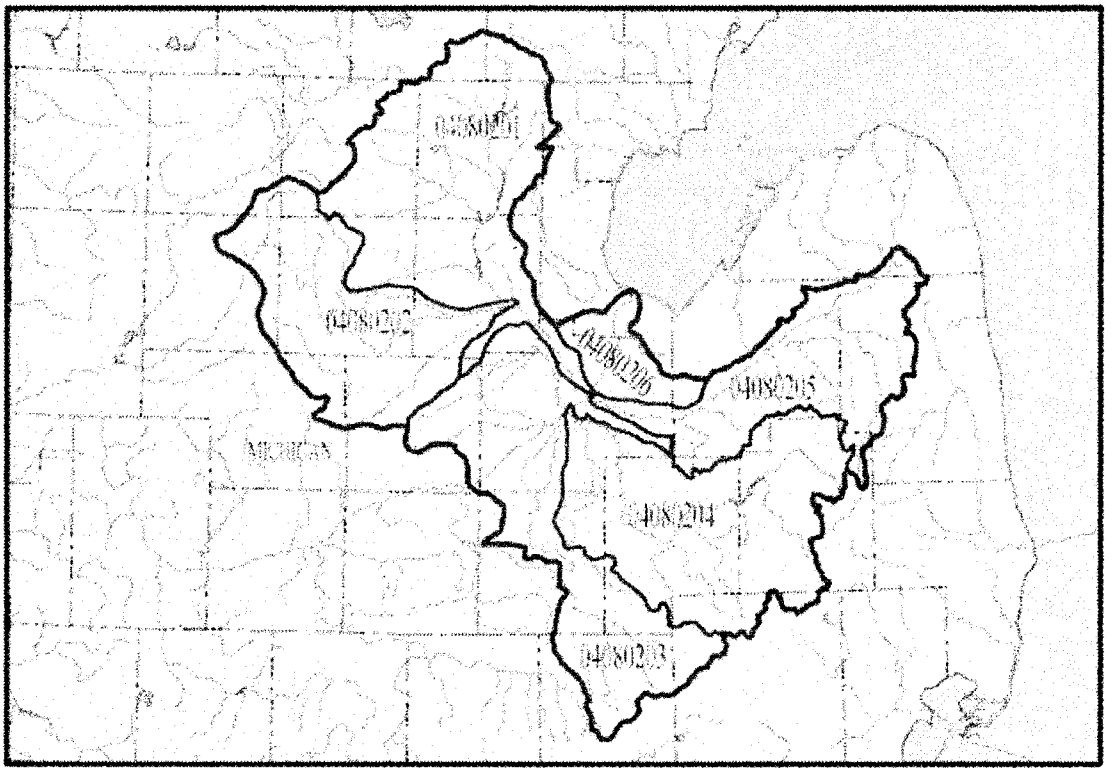


Figure 19: A closer view of the Saginaw River watershed. The watershed is divided into six different watersheds that make up the entire Saginaw River watershed. Graphic provided by USGS website http://water.usgs.gov/wsc/reg/04.html

Waste Water Discharge into Rivers

An analysis of the types and quantity of waste water discharge into each river basin was performed. This was completed by consulting the National Pollution Discharge Elimination System (NPDES) permits for each river on the EPA envirofacts website (http://www.epa.gov/enviro/index.html). Every company, industry, or municipality that discharges waste water legally to a U.S. waterway must obtain a NPDES permit to do so. First, a list of counties contained in each river watershed was made. All counties within each watershed were included, as the sample points are so near the mouth of each river, except for the Muskegon River.

Muskegon County was not included for the Muskegon River analysis, because the sample site is upstream from this county. Then, by entering the water section of the envirofacts website the option to look up NPDES permits by county is given. Because watersheds often cross county boundaries, the proper number and type of NPDES permits for each watershed was determined by cross referencing them with their proper hydrologic unit code (as described in the previous section). The results are compiled in Table 13 below. The EPA granted the State of Michigan primacy for the NPDES permit program, therefore the program and permitting are under the authority of the Michigan Department of Environmental Quality.

Table 13
NPDES Permits for Each River Watershed

| River Watershed | Total NPDES Permits | Number of Sewerage Permits of Total | Total Design Flow Discharge from Sewerage in million gallons per day (mgd) |
|---|---|---|---|
| Saginaw | 168 | 69 | 209.78 |
| Grand | 146 | 49 | 209.13 |
| Kalamazoo | 82 | 19 | 87.24 |
| Clinton | 46 | 9 | 72.31 |
| Muskegon | 28 | 9 | 10.94 |

It was important to single out the discharge from municipal sewerage systems as this is the major point source of pharmaceuticals and personal care products into streams and rivers. The design flow for each of these waste water discharges was also found on the website above and added together to give a total design flow from sewerage for each river (Table 13). The remaining NPDES permits, those that are not from sewerage, consist of those from industry such as

steel and automakers, storm water management, and confined animal feeding operations or CAFOs, just to name a few. Also of interest is the presence of discharge permits from two pharmaceutical production companies, both within the Kalamazoo River watershed. The data in Table 13 are as accurate as the EPA website allows. For example, some of the non-major NPDES discharge permits did not include a HUC within the database, making it impossible to assign them to a watershed. These without a HUC were disregarded as it would be an exhaustive process to look up each address and assess which watershed they were located in. This is thought to bring only a small amount of error to the numbers above, as non-major NPDES permits discharge less than 1 million gallons per day. A major NPDES discharge permit is issued for those who discharge over 1 million gallons per day or for industrial sources that are determined by EPA or state criteria to qualify as a major discharger. No major NPDES discharge permits were found in the database to be without their respective HUC, so it is thought the analysis is a good representation of the majority of permits and discharge types. Another issue with some of the non-major NPDES permits was it appeared there were errors in entry for their design flow number. For example, if the municipal waste water discharger was listed as a non-major and the design flow was shown as 6 mgd, it was assumed to be 0.6 mgd. It also became easier to make these decisions by looking at the maps of the cities within the database. Based on the size of the community, it became clear that 0.6 better fit a small community that 6 mgd. Again, this may introduce some error to the total numbers within Table 13, but the data is still strong for general comparisons between discharges into each river.

The Saginaw River watershed was a special case in this analysis. For the four other rivers, their one hydrologic unit code was sufficient to find all the NPDES

permits in the watersheds. These HUCs are as follows: Clinton (04090003), upper and lower Grand combined (04050004 and 04050006), Kalamazoo (04050003), and Muskegon (04060102). However, the Saginaw river basin is subdivided differently. Figure 19 shows that the Saginaw River watershed is really composed of six different watersheds. This was determined, because if only the Saginaw River HUC of 04080206 were used, it would be a gross misrepresentation of the actual discharge to that river. The entire six HUCs numbers within the greater Saginaw watershed also better represents the area of 6440 $mi^2$ as given. Therefore, each of the six watersheds were assessed separately and then added together to give the numbers for the Saginaw River in Table 13. The six watersheds are as follows: Tittabawassee (04080201), Pine (04080202), Shiawassee (04080203), Flint (04080204), Cass (04080205), and Saginaw (04080206).

As is evident in Table 13, the Saginaw and Grand Rivers have the greatest number of NPDES permits, the greatest number of sewerage permits, and also the greatest amount of sewage discharge to their waters as compared to the other three rivers. Therefore, it is not surprising that these rivers tend to rank among the highest rivers impacted by pharmaceuticals and personal care products throughout this study. However, the Clinton River ranks near the bottom in Table 13. Only the Muskegon ranks below it in the number of permits and ranks the same in the number of sewerage permits at 9. Even though the Clinton and Muskegon Rivers have the same number of sewerage permits, there is over 8 times as much sewage discharged into the Clinton than into the Muskegon. This is because the Clinton River has municipal discharge from the City of Warren (36 mgd) and the City of Pontiac (25.5 mgd) to account for a major proportion of the treated sewage discharge. Because the Muskegon River sample site is up river of the City of

Muskegon, the municipal contributions are minor in comparison, with its major discharger being the City of Cadillac at only 3.2 mgd. Also, the reason the Clinton River consistently ranks as one of the highest rivers impacted by pharmaceuticals and personal care products in this study is due to its lower volume of flow. Previously, in this report, it was mentioned that USGS staff knew that during the summer months, the majority of the Clinton River flow was due to waste water discharge. This can be proven with the calculation that follows. During the summer sample dates of August 24, 2004 and August 15, 2005, the river discharge was 183 $ft^3/s$ and 191 $ft^3/s$ respectively. Knowing that 1 mgd equals 1.547 $ft^3/s$, the proportion of the river discharge that is sewerage waste water (72.31 mgd) can be found. So, 72.31 mgd equals 111.86 $ft^3/s$. Therefore, in the August months of this study, sewerage waste water accounted for 61% and 58% of the river discharge. The large proportion of waste water discharge and the probable addition of storm water runoff account for the Clinton River remaining one the most impacted rivers in this study. The Kalamazoo River falls in the middle with regard to number of NPDES permits, number of sewerage permits, and the total sewerage discharged, as expected. In this study, the Kalamazoo River tends to rank in the mid to low range regarding impact due to pharmaceuticals and personal care products.

Blank and Replicate Issues

As discussed briefly in the sample container section of the study design, blank issues early in the study forced the change of the sample container from HDPE to Teflon. The study design allowed for 10% blank and 10% replicate samples to be taken. However, it was learned through experience that for these low level values, at least one blank per sample round is helpful, if not necessary. The

blank data are shown in Tables 4 through 8. For the June, 2004 sample round, a blank sample was taken after the filter apparatus was properly cleaned following the Grand River sample preparation. These blank data are in Table 5. Many of the compounds mentioned in the sample container section above were detected in the blank. A blank for the river samples was not taken for the August, 2004 samples, as the contaminant problem with the HDPE churn had not yet been recognized. Therefore, similar blank results as the June, 2004 sample round were assumed for the August, 2004 sample round, as shown in Tables 4-8. The November, 2004 blank sample broke in shipment. It was analyzed, but not used due to probable contamination issues. The results for this blank are located in Table 6. The first sample round to use the Teflon sample containers instead of the HDPE churn was the November, 2004 sample round. Because of similar sample techniques, the March, 2005 blank data were also used for the November, 2004 data set, to be conservative. The March 2005 blank data are located in Table 4. There were far fewer compounds in this blank, showing the benefits of using the Teflon sample containers. The June, 2005 blank data are in Table 8. This was also a very successful blank sample, with only one compound being detected. The August, 2005 blank sample results are located in Table 7. The November, 2005 blank data are in Table 6. Finally, the March, 2006 blank sample results are in Table 4. These last three blank samples were also quite successful with low numbers of detections. Basically, once the problem with the HDPE sample container was found and corrected, great confidence can be placed in the blank samples and sample techniques.

All of the replicate samples taken for the river samples throughout this study are also located in Tables 4-8. A June, 2004 replicate was taken for the Grand River

sample and is located in Table 5. A replicate for the river samples during the August, 2004 sample round was not taken. Table 6 contains the replicate results for the Kalamazoo River for the November, 2004 sample event. The March, 2005 replicate sample for the Clinton River is located in Table 4. A replicate sample was taken for the Saginaw River during the June, 2005 sample round and is presented in Table 8. The August, 2005 replicate sample results for the Muskegon River are in Table 7. A replicate sample for the rivers was not taken during the November, 2005 sample round. The final replicate sample is shown in Table 4 for the Clinton River taken during the March, 2006 sample event. The replicate results show excellent correlation to the original river water sample. This is an indication that even though the analytical results are at very low levels, estimate values even, these results can be trusted because they are reproducible.

# Municipal Well Data

## Goal and Background

The municipal wells at Portland and Parchment, Michigan were sampled in order to determine if shallow, high capacity wells draw in river water through induced recharge that may contain pharmaceuticals and personal care products. Portland is situated on the Grand River in Ionia County, Portland Township, just to the northwest of Lansing. The City of Parchment is located on the Kalamazoo River in Kalamazoo County, Cooper Township, just north of the city of Kalamazoo. Figures 20-23 show maps of these two cities and field maps with water well locations.

The interaction between the Kalamazoo River and the Parchment municipal well field has been investigated previously (Laton, 1997). This research showed that predominantly, the Kalamazoo River receives recharge from the nearby aquifer. However, with the use of seepage meters and geochemical tracers it was shown, during periods of high river stage, the pumping of the well field can cause shifts in the hydraulic gradient toward the aquifer or induce recharge (Laton, 1997). The municipal supply wells have not shown adverse impact due to this potential induced recharge.

Evidence of induced recharge also exists in the literature. The Portland Basin contains a deep aquifer known as the Sand and Gravel Aquifer that spans portions of Oregon and Washington (Koreny and Fisk, 2000). The aquifer is an important source for drinking water in both states. Under low pumping conditions, the aquifer discharges to the Columbia River. However, during high demand and extended pumping, recharge is induced to the aquifer from the river through a buried

paleochannel (Koreny and Fisk, 2000). There is no mention of contaminants being introduced to the aquifer from the river system. In fact, it is suggested that this induced recharge may help to meet future demands for groundwater resources.

There is evidence of groundwater quality deterioration caused by induced recharge from the Katsura River in the Kyoto Basin, Japan (Yoneda et al., 2001). The induced recharge is caused by groundwater extraction through wells used for drinking water and for industry. This was shown through water quality trends (dissolved oxygen, chemical oxygen demand, electric conductivity, nitrate, etc.) in the alluvium aquifer and by a stochastic model (Yoneda et al., 2001).

Water Wells Sampled, Well Logs, and Geology

The well logs for the municipal water supply wells for the cities of Parchment and Portland are included in Appendix B. The well logs were obtained from the Michigan Department of Environmental Quality, Water Bureau Wellogic water well record system.

The city of Parchment utilizes three water wells that run in a north-south trending line approximately 800-850 feet from the Kalamazoo River; with well number 1 being the most southern and well number 3 the most northern well. The wells are approximately 300-400 feet apart. Well number 3 was selected to be sampled for this study. However, there were sample rounds where well number 3 was not available due to unforeseen mechanical issues and well number 2 was sampled in its place. Well number 2 was sampled instead of well number 3 in November of 2004, March of 2005, November of 2005, and March of 2006.

The well logs for the Parchment wells indicate that wells 1 and 2 were drilled in 1961 and well 3 was completed in 1973. The well logs indicate that they were

produced from limited well log information, which is probably not uncommon for the time they were drilled. Wells number 1 and 2 are 60 feet in depth, whereas well number 3 is 58 feet deep. No information was included regarding the screen length or where the screen was set for well 1. Parchment wells 2 and 3 have 15 foot screens that were set from 43 to 58 feet. These shallow glacial drift wells have a lithology that consists of alternating layers of clay and sand and gravel. The wells were set just into a clay layer and produce from an overlying 22 to 26 foot layer of sand and gravel. The pump capacities for the Parchment wells are 600 gallons per minute (gpm) for well 1 and 1000 gpm for wells 2 and 3.

Aquifer characteristic data were obtained from pump test results within the City of Parchment wellhead protection program report (Jones, 1992). During the pump test, well 1 was pumped for a 24 hour period at a rate of 500 gpm. Using the water level data and the Theis equation, it was determined that the average transmissivity for the aquifer was 17,915 $ft^2$/day, the average hydraulic conductivity was 407 ft/day, and the average storativity was .00037 (Jones, 1992). The pump test results also show the drawdown cone of well 1 intercepted the river during the test. The report indicated the groundwater flow is to the northwest (Jones, 1992).

The Parchment well field is located in the Kalamazoo River Valley which was formed by a catastrophic outburst flood originating from under the Saginaw Lobe during the Quaternary (Kozlowski, 2004). The source of the subglacial meltwater is not yet known, but a subglacial lake is a possibility (Kozlowski, 2004). The well field location is characterized by glacial outwash and flood plain deposits. These deposits consist of coarse bedded sand, gravel, and cobbles of Pleistocene outwash and Holocene flood plain deposits of silty sand, muck, and braided streams (Kozlowski,

2004). The description of these deposits is consistent with the well logs for the Parchment municipal wells, which indicate flood plain sediments are present.

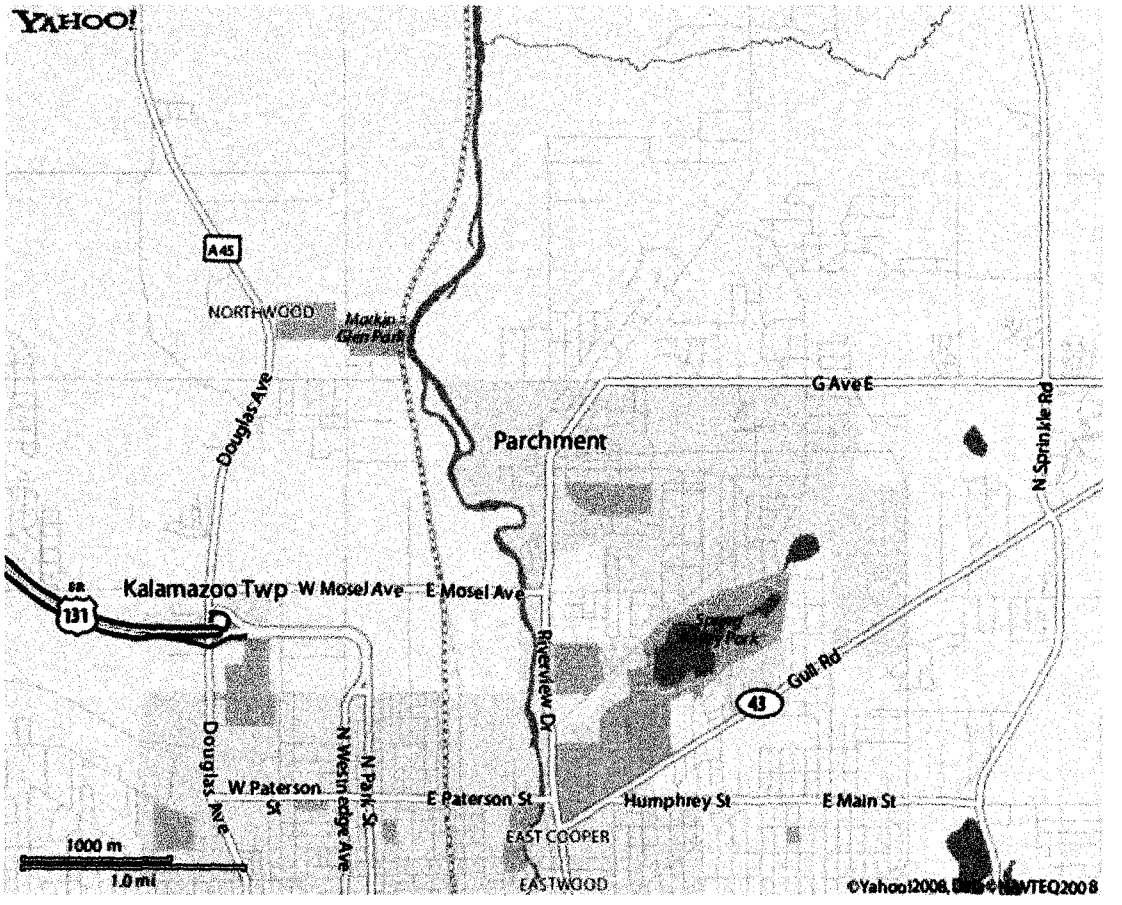



Figure 20: Map of the City of Parchment, located just to the north of Kalamazoo. Map obtained from web-based Yahoo maps.

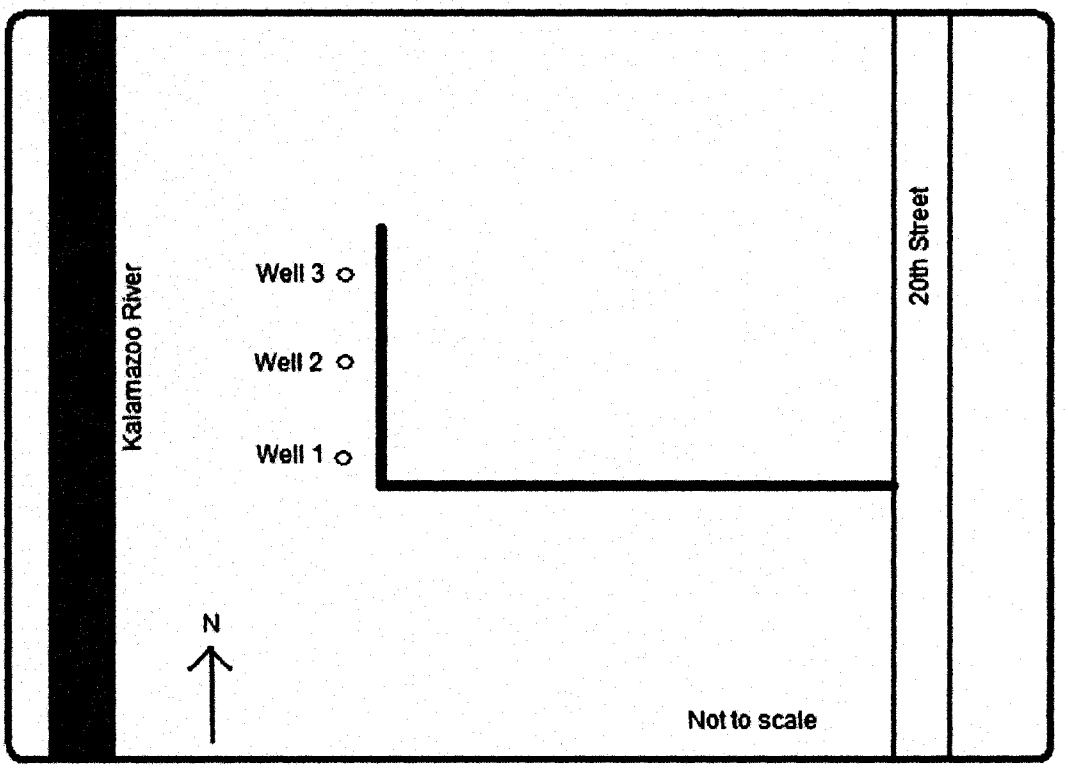



Figure 21: Field map of the City of Parchment municipal well field.

The city of Portland utilizes at least five wells for municipal water supply. Four of these wells, designated as wells 3, 4, 5, and 6 are located near each other on the banks of the Grand River. Well 3 is a bedrock well over 250 feet deep. The fifth well, well 7, is located offsite and is also a bedrock well that is 435 feet in depth. These bedrock wells are not pertinent to this study due to their depth and will not be discussed further. Well number 6 was chosen to be sampled throughout this study and is located approximately 750-800 feet from the Grand River and 500 feet from well 4.

The well logs for the Portland wells indicate that well 4 was drilled in 1942, well 5 was drilled in 1954, and well 6 was drilled in 1967. These wells are also considered quite shallow as well number 4 is 59 feet in depth, well number 5 is 78 feet deep, and well number 6 is listed as being 79 feet deep. The well logs show well 4 has a 15 foot screen set from 44 to 59 feet. Well 5 has a 20 foot screen, but the well log does not indicate where the screen was set. It could be assumed the screen is set from 58 to 78 feet, since the total well depth is 78 feet. Well 6 has a 25 foot screen set from 54 to 79 feet in sediments consisting of sand and gravel. According to the well logs, the lithology is unknown for wells 4 and 5. Again, because of the age of the wells, this is probably not uncommon. There is record of the lithology for well 6. The glacial drift well was drilled in sediments consisting of sand and gravel. The pump capacities for the wells are listed as 450 gpm for well 4, 650 gpm for well 5, and not listed for well 6.

Aquifer characteristic data were obtained from pump test results within the City of Portland wellhead protection program report (Fleis and Vandenbrink, 2000). During the pump test, well 6 was pumped for a 96 hour period at a rate of 615 gpm. Using the water level data and the Neuman equation, it was determined that the

average transmissivity for the aquifer was 11,345 $ft^2$/day, the average hydraulic conductivity was 189 ft/day, and the average storativity was .002 (Fleis and Vandenbrink, 2000). The report indicated the groundwater flow is to the southwest.

The City of Portland well field is located in the Grand River Valley which served as a drainage way for the Saginaw Lobe as it retreated in the Quaternary (Kehew, 1993). The Grand River Valley also connected lakes in the Huron and Erie basins to the Michigan basin. Research has shown that the Grand River Valley was formed by at least one catastrophic outburst event from glacial Lake Saginaw to glacial Lake Chicago (Kehew, 1993). The city well field is located to the south of the main drainageway where the deposits are characterized by glacial outwash deposits of sand and gravel from the Pleistocene. These sand and gravel deposits are confirmed by the well log of well 6.

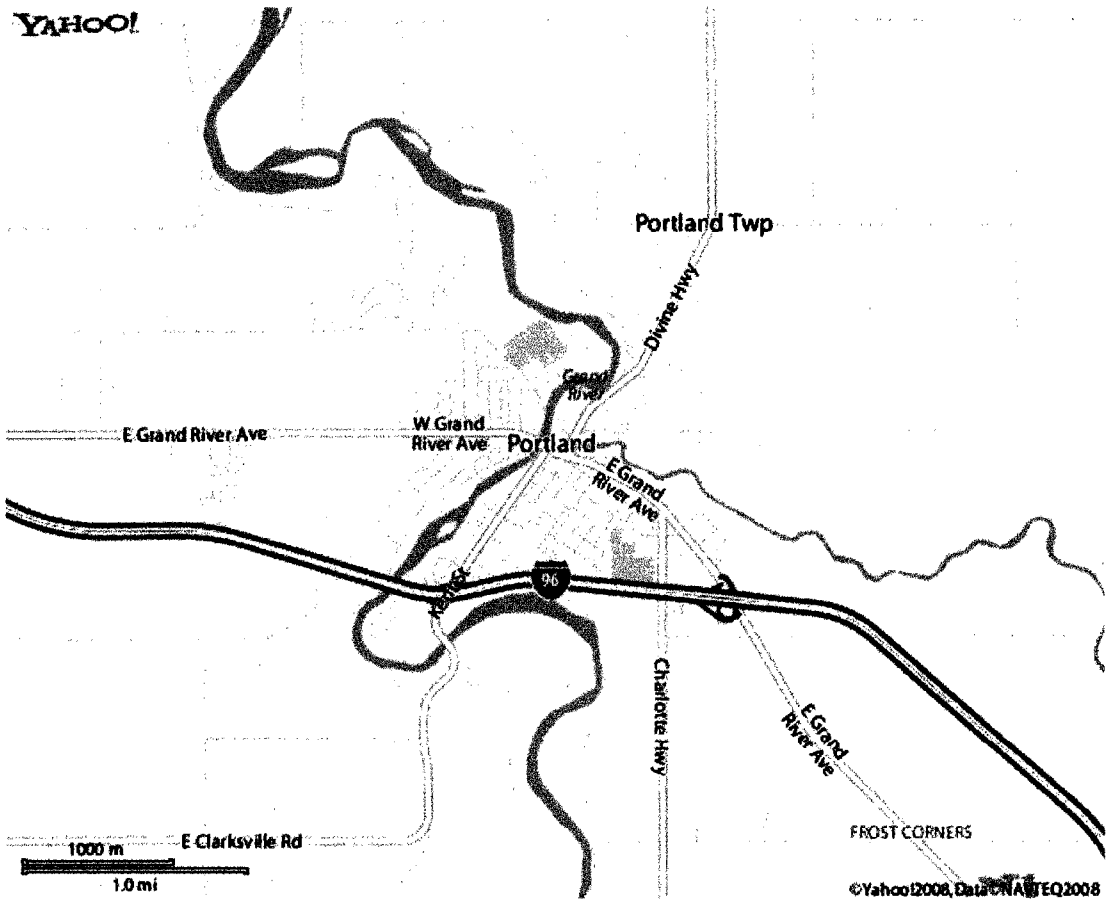



Figure 22: Map of the City of Portland, located to the northwest of Lansing. Map obtained from web-based Yahoo maps.

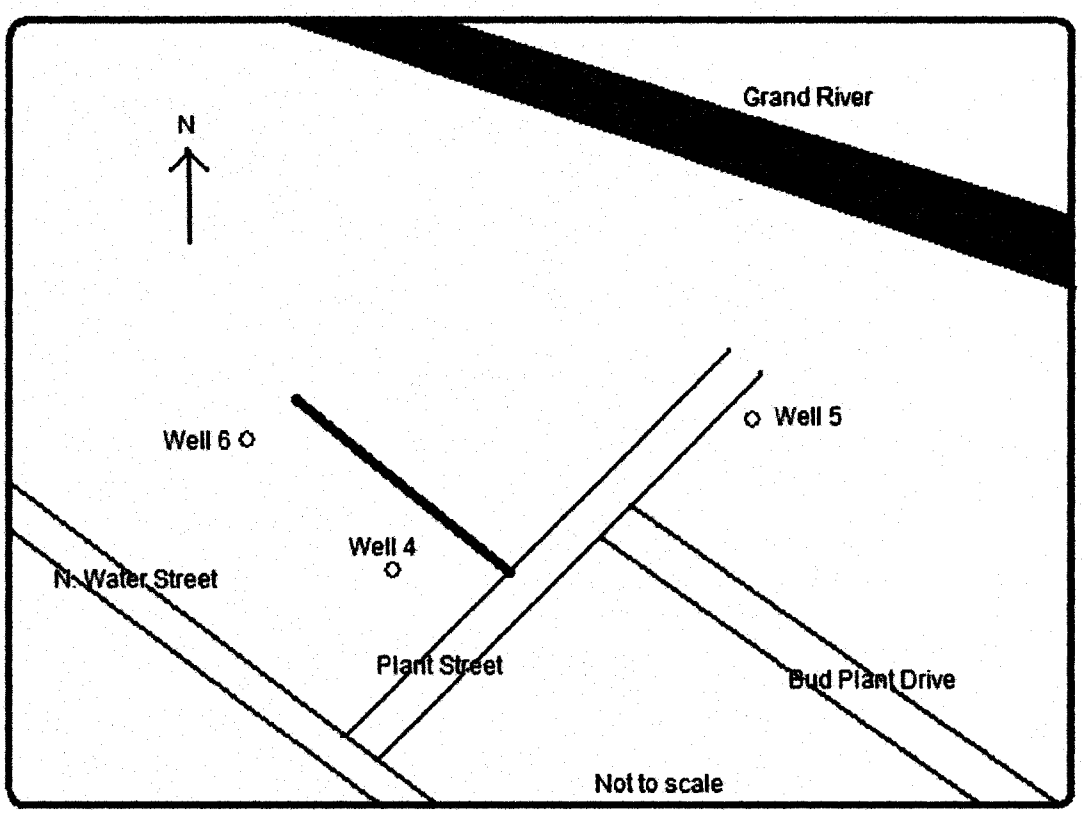



Figure 23: Field map of the City of Portland municipal well field.

Water Well Sample Results

Forty three percent (43%) of the water well samples from the City of Parchment had 1 or more compounds detected. Seventy one percent (71%) of the water well samples from the City of Portland had 1 or more compounds detected. The analytical results for the municipal wells can be found in Tables 14 and 15. The sample results for the November 2005 sample round proved troublesome. The analytical results showed that the exact same eleven compounds were found in both the Portland and Parchment well (Tables 14 and 15). This seems highly unlikely without some sort of sample contamination. Therefore, the sample results for

November 2005 for the Parchment and Portland wells were discarded and not used for further analysis in this report. Also, any compound that was detected in the blank samples for the municipal wells was disregarded in the data analysis in the following sections, including statistics, occurrence, endocrine disruptors, etc. The compounds detected in the blanks are listed in Table 14 and 15 and are shown in brown instead of black ink for ease in identification.

To summarize the results in Tables 14 and 15, the first three sample rounds showed little indication of induced recharge of the compounds of concern. The June 2004 sample event showed that phenol was present in both wells along with diethoxyoctylphenol in the Parchment well and tetrachloroethene in the Portland well. Phenol was present in the blank samples and was disregarded as a detection. Portland municipal personnel knew that they had a minor tetrachloroethene impact. So, the only compound that may have been present from the river was diethoxyoctylphenol, a detergent metabolite, in the Parchment well.

The August 2004 sample round showed no detections for either well. The November 2004 sampling showed no detections for Parchment and the presence of phenol again for Portland. But, again, since phenol was present in the blank samples it was disregarded.

Then, in the March and June 2005 samples, more compounds were detected in both wells. August 2005 also showed the presence of more compounds in the Portland well. The Parchment well showed no detections for the August 2005 sample, as the compounds that were detected were also in the blank and disregarded. The blank samples are considered of good quality; therefore, confidence in the data was high for the March, June, and August 2005 sample results.

However, the November 2005 sample results were discarded. The final sample round in March of 2006 showed the presence of isopropylbenzene in the Portland well and another non-detect sample round for the Parchment well, as the 1,4 Dichlorobenzene detected is also found in the blank samples taken for the water wells.

The municipal well results indicate that there could be some impact from the river water due to induced recharge, but with the data set currently available it would be difficult to assert that with a large amount of certainty.

## Table 14
## Analytical Results
## Parchment Municipal Well

**June 28, 2004**

| Compound | Conc. (µg/L) |
|---|---|
| Diethoxyoctylphenol | .1100 E |
| Phenol | .2400 E |

**August 31, 2004**

| Compound | Conc. (µg/L) |
|---|---|
| No detections | |

**Replicate (Aug. 31, 2004)**

| | |
|---|---|
| Phenol | 0.57 |

**Blank (Aug. 31, 2004)**

| | |
|---|---|
| 1,4 Dichlorobenzene | .0250 E |
| Phenol | .2200 E |

**November 9, 2004**

No detections

**March 29, 2005**

| Compound | Conc. (µg/L) |
|---|---|
| Benzophenone | .0180 E |
| Camphor | .0072 E |
| Isophorone | .0170 E |
| Menthol | .0430 E |

**June 29, 2005**

| Compound | Conc. (µg/L) |
|---|---|
| 1,4 Dichlorobenzene | .0290 E |
| Benzophenone | .0920 E |
| Camphor | .0066 E |
| HHCB | .0140 E |
| Isophorone | .0190 E |
| Menthol | .0560 E |
| Phenol | .1700 E |

**August 25, 2005**

| Compound | Conc. (µg/L) |
|---|---|
| 1,4 Dichlorobenzene | .0300 E |
| Phenol | .2600 E |

**Blank (Aug. 25, 2005)**

| | |
|---|---|
| 1,4 Dichlorobenzene | .0390 E |
| Isophorone | .0073 E |
| Phenol | 0.58 |

**Table 14 - Continued**

| November 23, 2005 | | March 22, 2006 | |
|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0890 E | 1,4 Dichlorobenzene | .0077 E |
| 1-Methylnaphthalene | .0180 E | | |
| 2-Methylnaphthalene | .0260 E | | |
| Acetophenone | .0810 E | | |
| Benzophenone | .0550 E | | |
| DEET | .0120 E | | |
| D-Limonene | .0320 E | | |
| Menthol | .0310 E | | |
| Methyl salicylate | .0120 E | | |
| Phenanthrene | .0110 E | | |
| Phenol | .2800 E | | |

**Key:**

Conc. (µg/L) = concentration of compound in micrograms per liter

E = Estimated value

Name of compound with no underline – waste water scan – Schedule 1433

Name of compound in brown - compound found in August 2004 blank and/or August 2005 blank

**Table 15**
**Analytical Results**
**Portland Municipal Well**

**June 28, 2004**

| Compound | Conc. (µg/L) |
|---|---|
| Phenol | .2800 E |
| Tetrachloroethene | .0190 E |

**August 31, 2004**

No detections

**November 9, 2004**

| Compound | Conc. (µg/L) |
|---|---|
| Phenol | .3100 E |

**March 29, 2005**

| Compound | Conc. (µg/L) |
|---|---|
| Isophorone | .0120 E |
| Menthol | .0270 E |

**June 16, 2005**

| Compound | Conc. (µg/L) |
|---|---|
| 1,4 Dichlorobenzene | .0360 E |
| Acetophenone | .0930 E |
| AHTN | .0120 E |
| Benzophenone | .3200 E |
| Camphor | .0200 E |
| HHCB | .0390 E |
| Isophorone | .0460 E |
| Menthol | .1600 E |
| Methyl salicylate | .0130 E |
| Phenol | .2100 E |
| Tributyl phosphate | .0180 E |

**August 18, 2005**

| Compound | Conc. (µg/L) |
|---|---|
| 1,4 Dichlorobenzene | .0300 E |
| Benzophenone | .0510 E |
| Camphor | .0070 E |
| DEET | .0690 E |
| Isophorone | .0310 E |
| Menthol | .1200 E |

**Table 15 - Continued**

| **November 23, 2005** | | **March 23, 2006** | |
|---|---|---|---|
| **Compound** | **Conc. (µg/L)** | **Compound** | **Conc. (µg/L)** |
| 1,4 Dichlorobenzene | .0890 E | 1,4 Dichlorobenzene | .0108 E |
| 1-Methylnaphthalene | .0220 E | Isopropylbenzene | .0035 E |
| 2-Methylnaphthalene | .0310 E | | |
| Acetophenone | .1000 E | **Replicate (Mar. 23, 2006)** | |
| Benzophenone | .0720 E | 1,4 Dichlorobenzene | .0084 E |
| DEET | .0130 E | | |
| D-Limonene | .0240 E | | |
| Menthol | .0500 E | | |
| Methyl salicylate | .0130 E | | |
| Phenanthrene | .0100 E | | |
| Phenol | .2200 E | | |

**Key:**

Conc. (µg/L) = concentration of compound in micrograms per liter
E = Estimated value
Name of compound with no underline – waste water scan – Schedule 1433
Name of compound in brown - compound found in August 2004 blank and/or August 2005 blank

Statistics

Below, Table 16 is a compilation of the minimum, mean, and maximum number of compounds detected for each well individually and overall.

Table 16
Compound Detection Statistics for the Water Wells Sampled

| | Overall | Parchment | Portland |
|---|---|---|---|
| Minimum | 0 | 0 | 0 |
| Mean | 1.6 | 1 | 2 |
| Maximum | 8 | 4 | 8 |

The table shows that the mean number of compounds detected overall for the water wells is 1.6 or rounded up to 2 compounds. The minimum number of compounds detected overall is 0 or what would be referred to as no detections. The maximum number of detections overall is 8 in a single water sample.

The national reconnaissance study of these chemicals in groundwater showed that mixtures were common (Barnes et al., 2008). 47 groundwater samples were evaluated; the mean number of detections was 2, with a maximum of 14 detections in a single sample (Barnes et al., 2008). The results of this study correlate with the nationwide results despite study design differences. The nationwide study included only one sample from each well, whereas the Parchment and Portland wells were sampled quarterly for 2 years.

The statistical data for each water well individually may not look significant, especially when compared to the statistical results for the river water samples. The

numbers for the water wells are low and as shown in Tables 14 and 15, there were numerous sample rounds where no detections were recorded for either well. However, when it is considered that these water wells supply drinking water to customers in each municipality, any detection at all is of interest. As stated above, the detections may even indicate that the wells may be obtaining these compounds from the river water systems nearby. If this is true, it is evident from the data above, that the Portland well is impacted to a greater degree than the Parchment well.

The national groundwater reconnaissance study concluded that as well depth increased, the number of compounds detected decreased (Barnes et al., 2008). However, this study indicated the inverse, as the Portland well is deeper than the Parchment well, but shows a greater impact. The Portland well is 79 feet deep and the Parchment well is 60 feet deep. This approximate 20 foot difference in depth may not be a large enough to statistically correlate with the national results. The nationwide study included wells of a much greater depth range, between 2.4 to 310.9 meters (median of 19.2 meters) (Barnes et al., 2008). Sources near the wellhead and inadequate shallow seals and gravel packs have been implicated to explain higher detections in the shallow wells (Barnes et al., 2008).

Occurrence

In an effort to understand occurrence trends and the degree of impact from the compounds studied, the number of compounds detected at least once per water well was determined. The results are shown in Figure 24 below.

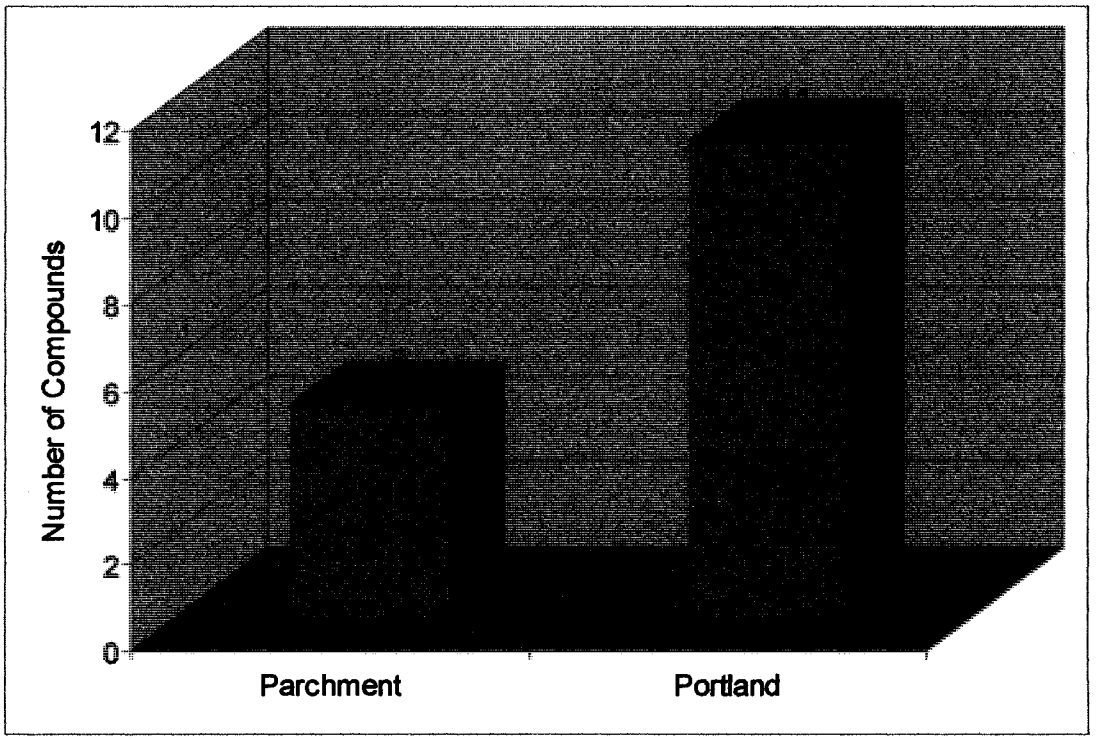



Figure 24: The number of compounds detected at least once per water well for the municipalities of Parchment and Portland.

As the figure shows, Parchment had only 5 compounds detected at least once over the sample period, whereas, Portland had 11 different compounds detected at least once during this study. Again, using this measure, the Portland well is more impacted by pharmaceuticals and personal care products than the Parchment well.

The following classes of compounds were detected frequently including: fragrances, detergent metabolites, fire retardants, and solvents.

Endocrine Disruptors

As previously discussed in this report, the identification of endocrine disrupting compounds was an important goal of this study. Known or suspected

endocrine disrupting compounds were identified in both the Parchment and Portland water wells sampled.

The Parchment well showed the presence of diethoxyoctylphenol in June of 2004 and benzophenone in March and June of 2005. The Portland well showed the presence of benzophenone in June and August of 2005.

It is acknowledged that the detected endocrine disrupting compounds were present at very low concentrations and in all likelihood pose little risk to the water consumers. However, as studies continue, it could be possible that maximum contaminant levels are developed for these compounds in the future, as more is learned about long term, low level exposure to them.

Detection Issues and Low Concentrations

As is evident in the analytical data Tables 14 and 15, the water well results show all of the detections are well below 1 ppm. Also notice that most of the analytical results have an "E" demarcation after the concentration. This "E" signifies an estimated value. The implications of estimated values are discussed above. As with the river results, even though most of the water well data are estimated, higher confidence in the data can be achieved with quality blanks and replicate samples. Tables 14 and 15 contain the replicate and blank data, which show high correlation and blank quality that is to be expected. The section below contains a more thorough discussion of the blank and replicate results.

Table 17 below shows the concentration ranges for each water well sampled. Again, these concentrations are quite low: however, the Portland well did have a higher maximum concentration than the Parchment well. The Parchment well has a higher minimum concentration than the Portland well, however.

Table 17
Compound Concentration Ranges per Water Well

| Water Well | Concentration Range (µg/L) |
|---|---|
| Parchment | .0066 - .1700 |
| Portland | .0035 - .3200 |

When comparing the concentrations detected in this study to the national groundwater reconnaissance study (Barnes et al., 2008), the groundwater concentrations found in Michigan were generally lower. 87% of the compound detections nationwide were below 1 µg/L; however no estimated values were listed as in this study (Barnes et al., 2008). The national reconnaissance study was biased toward sampling wells near or downgradient of waste water contaminant sources. The same cannot be said of the wells sampled in this study, which may help explain the lower concentrations detected in Michigan

Blank and Replicate Issues

As discussed in the River results section of the same name, blank and replicate samples became very important in this study. The results from the blank and replicate samples taken with the water well samples are located in Tables 14 and 15.

Table 14 contains the blank and replicate results for the water samples obtained on August 31, 2004. The blank shows the presence of 1,4 Dichlorobenzene and phenol. Both were common compounds detected in the blank samples. The replicate results show phenol was detected. Since this compound was also in the blank, it can be disregarded. Therefore, the replicate sample can be

considered a sample with no detections, which is what was also indicated for the Parchment water sample for that sample round.

Table 14 also contains the results for the blank sample taken on August 25, 2005. The blank shows the presence of 1,4 Dichlorobenzene, isophorone, and phenol. Again, these compounds were common contaminants of the blank samples.

Table 15 shows the results for the replicate sample obtained on March 23, 2006. The results show the presence of 1,4 Dichlorobenzene. The replicate shows good correlation with the actual sample taken on that day; however, the presence of isoproplybenzene was not detected. A blank sample was also taken during this sample round, but it broke in shipment and was not analyzed.

Overall, quality blank and replicate samples were achieved for the water well samples.

Implications of Induced Recharge

As stated previously, the analytical results from the municipal water wells implicates induced recharge from the rivers as a source for the compounds of interest in the groundwater. Seasonal trends for the contaminant detections are difficult to ascertain, especially with the loss of data and the low frequency of detections. It might be expected that induced recharge would be more prevalent during periods of high river stage and high demand from the municipal wells, as the study by Laton, 1997 determined.

Previous studies (Barnes et al., 2008; Focazio et al., 2008) have shown the presence of pharmaceutical and personal care products in groundwater, including wells used as drinking water sources. However, these studies do not include information that indicates if these compounds could result from induced recharge. It

seems to be much more common for the sources of these groundwater contaminants to originate from animal feedlots, on-site septic systems, land application of waste water effluent, and water re-use projects utilizing treated waste water.

The literature does show that induced recharge has been documented as a source of pharmaceuticals, personal care products, and other organic waste water compounds to the groundwater. As mentioned in the Introduction, the use of induced recharge or bank filtration to purify surface water to produce drinking water in Berlin, Germany has occurred for over a century (Heberer et al., 2004). Six compounds were shown to enter the groundwater by this process. Samples were collected from the surface water and groundwater for six months, from May to October 2002, so seasonal variations were not discussed (Heberer et al., 2004). Low-flow conditions (summer) are thought to potentially provide higher proportions of these compounds to the groundwater as they will be a greater portion of the surface water. The induced recharge and bank filtration occurs between lakes and the groundwater in Germany. However, for this study the sources of the compounds to the groundwater are river systems. The process is not expected to be different, but the expected analytical results may be as inputs, residence time in the surface water bodies, and pumping capacities probably differ. There is a real need to continue the research of induced recharge as a source of waste water compounds from rivers or lakes to nearby water wells.

# FUTURE RESEARCH SUGGESTIONS

## River Sampling

It is my hope that this study will foster continued research into the presence of pharmaceuticals and personal care products in the waters of Michigan. Much was learned during this study regarding how to improve the quality of the data. This was partly due to the fact the sampling methods and analytical scans were new or still in development and from the analytical results themselves. The importance of blank samples cannot be stressed enough. Future research involving these compounds should have as many blank samples as the funding will allow. At a minimum, there should be an equipment blank per sample round. A field blank is also recommended. There should also be another equipment blank for each different sampling method, if any, or if different types of sample containers are used. Future research should also plan for at least 10% replicate samples if not higher. It is also recommended to have both scans (if not more, as they become available), the waste water and pharmaceutical scans, run on all water samples taken.

Continued quarterly sampling at the same river sites chosen in this study could offer further insight into the presence and seasonal trends of pharmaceuticals and personal care products in these rivers. It would be better if numerous sites along the path of each river were sampled quarterly for these compounds; especially near the point sources that are the waste water treatment plant outfalls. This would probably allow for seasonal trends to be more apparent and for higher numbers and concentrations of these compounds to be detected. If higher concentrations are

detected near cities and/or waste water treatment plants, these data would be important in the future as toxicity studies progress the possibility for regulation exists.

It is also important to be prepared for the large amount of data produced in future studies regarding pharmaceuticals and personal care products in Michigan or any waters. It is essential to have a general plan for data analysis. Hopefully, the statistics, occurrence trends, seasonal trends, the presence of endocrine disrupting compounds, the discharge equation, and the use of NPDES permits in this report will act as a baseline and be used as a guideline to better analyze this type of data in the future.

## Municipal Water Well Sampling

The results of the municipal water well samples did not produce large amounts of data like the river samples; however, it is not of less importance; especially when it is considered that people consume this water. Even though the concentrations are extremely low, only time and further study will determine if there are risks to such long term exposure. Just as with the river sampling above, future studies of pharmaceuticals and personal care products in groundwater should include numerous of blank samples, at least one per sample round, and at a minimum 10% replicate samples. Also, Teflon bottles should be used for sample collection instead of glass. This would make it the standard sample bottle for both the river and water well samples.

Continued quarterly sampling of the municipal water wells in Parchment and Portland would be desirable. If funding were available, it would be ideal if more than just one well was sampled at each site. Perhaps this would provide the evidence needed to say for sure that the shallow water wells can be influenced by the nearby

river water through induced recharge or maybe prove the opposite. Monitoring wells between the rivers and the municipal wells could also be added and sampled for these compounds. This would allow for recharge and discharge trends to be monitored more closely and to identify these compounds along the flow path in the aquifer. Additional monitoring wells around the municipal wells could also be added to determine if other sources of these compounds, such as septic systems, animal feedlots, industry, etc., contribute to the municipal well impact. Again, as above, both the waste water scan and the pharmaceutical scan could be used to analyze the water samples. Municipal wells in other communities that have a similar setting, shallow and near a river system, should be located and sampled.

# CONCLUSIONS

This paper is the result of a two year study, in which five rivers and two municipal wells in Michigan were sampled quarterly for low level pharmaceuticals and personal care products. The extent and importance of research regarding these compounds in surface water, drinking water, and other media were demonstrated early on in this dissertation. Thousands of these compounds exist. They are utilized for their designed purpose and then many end up in our waste water treatment plants. The analytical scans in this study and others cited in this paper only account for a fraction of the compounds with the potential to occur in our waters. The compounds that have been analyzed for to date were chosen based on their high usage rate and their potential for toxicity to the ecosystem. It has been proven that these compounds find their way into our streams and even at low concentrations can be problematic for aquatic organisms. Of particular interest, is the fact some of these compounds can have little to no effect on an organism, but in combination with one or more other compounds can be quite toxic. Mixtures are common in the environment and studies indicate that both acute and chronic effects of these compounds need to be considered when risk assessments are completed and evaluated for existing or new pharmaceuticals and personal care products. Another very important aspect of this research is the potential for some of these compounds to have endocrine disrupting affects on aquatic organisms; even at very low concentrations. This may inhibit the reproductive success of some organisms and therefore potentially cause changes in a food web.

Research continues regarding the occurrence, fate and transport, and

degradation of these compounds. Much has been learned regarding the fate and transport of these compounds in the environment. It is especially important to understand their chemical behavior, such as partition coefficients, to determine the likelihood of finding them in the soil or water phase. It is also important to evaluate how these chemicals respond to different treatment scenarios in waste water treatment plants. For example, some pharmaceuticals and personal care products are subject to microbial degradation and/or photodegradation. Some studies even propose using some of these compounds as tracers for the presence of human sewage in surface waters. It is expected that global research into these compounds will only continue and there is much yet to learn regarding effects and how best to address the presence of these compounds in our waters.

The research within this dissertation sought to verify the existence of pharmaceuticals and personal care products in the rivers sampled. Then, the data was analyzed to determine occurrence and seasonal trends, concentration ranges, the presence of known or suspected endocrine disrupting compounds, and provide statistical information. The data were also used to determine the total discharge of these compounds to each river in tons per day. Finally, NPDES permits were researched to investigate sewerage inputs to each river. These last two exercises proved to be significant to the character and environmental pressure, or lack of, each river is under. Another goal of this study was to sample two high capacity, shallow municipal wells, one on the Grand River and one on the Kalamazoo River, to determine if it were possible for them to draw pharmaceuticals and personal care products from these rivers. These data were also analyzed to determine occurrence trends, concentration ranges, the presence of known or suspected endocrine disrupting compounds, and to provide statistical information.

This study found that 100% of all river samples contained one or more pharmaceutical or personal care product. This is remarkable when it is considered each of the five rivers were sampled eight times for a total of 40 water samples. It is also significant when the low concentrations and the blank issues that caused some of the data to be censored were taken into account. There is no question this study has proven the existence of these compounds in the rivers of the State. The low concentrations were slightly problematic, but somewhat expected as the samples were collected near the mouth of each river for a cumulative source perspective. The confidence in the data is supported by successful blank and replicate samples.

As the analysis of the river data shows, there were some clear trends regarding impact to these rivers from pharmaceuticals and personal care products. Consistently, especially regarding the statistics and number of compounds detected at least once analysis; the Clinton River was the most impacted river. The Grand and Saginaw Rivers trend toward the middle regarding impact. Finally the Kalamazoo and Muskegon Rivers seem to be the least impacted. The same trends were found for compound concentration ranges and the number of endocrine disrupting compounds found. Of particular interest is that at least one or more endocrine disrupting compound was detected in each river.

Maybe some of the most compelling analysis came from the modified compound discharge formula and the NPDES research. This analysis showed that when the river discharge values, watershed area, sewerage inputs, and the environmental pressure it is under are considered, the Clinton River consistently, throughout the entire study, is the most impacted river out of the five sampled. Continued and more extensive sampling of these rivers for pharmaceuticals and personal care products would be of interest.

The data generated from the municipal water well samples shows that it is possible these shallow (58-79 feet deep), high capacity wells may be drawing some water from the nearby rivers through induced recharge. This is indicated by the presence of pharmaceuticals and personal care products in some of the samples. The concentrations of these compounds were extremely low in each well and well below any known maximum contaminant level for these compounds. However, just their presence is of interest and warrants further study. It is also of interest that at least one endocrine disrupting compound was identified in each well during the sample period.

The water well results show that 43% of the Parchment water samples and 71% of the Portland water samples had the presence of one or more of the compounds analyzed for. The Portland well exhibits slightly more impact from these compounds than the Parchment well; although quite minor. Portland had more compounds detected at least once and higher statistical results regarding the minimum, mean, and maximum number of compounds detected, than the Parchment well.

Again, further study is warranted regarding impact to both of these wells as well as other municipal wells near river systems. This is urged because data were lost due to the November 2005 sampling issue. Also, the sample bottles for the water well samples should have been standardized throughout the study and Teflon should have been used. It would be interesting to see if the same or different compounds are detected over time and to monitor concentrations of these compounds.

The research contained within this dissertation may serve as a starting point or as a baseline for continued research into pharmaceuticals and personal care

products in the waters of Michigan. There are many more avenues to pursue regarding this type of research; both in Michigan and globally. As more is discovered regarding the risks and effects of these compounds in the environment and in our drinking water, it will be interesting to see the course chosen. Perhaps we as a society will find the money to upgrade our waste water treatment plants for more effective methods of removing these compounds. Or work to reduce the sources of these compounds and perhaps search for more natural or environmental friendly versions of industrial and household chemicals. It is certain that pharmaceutical use will not be reduced, due to its role in the improvement of people's lives. But perhaps we can work to increase the awareness and frequency of pharmaceutical drop off sites so that they are incinerated instead of being placed in a landfill or worse, flushed. For all of the research and findings regarding pharmaceuticals and personal care products in the environment, it seems unlikely that nothing will be done in the future to reduce their presence in surface water and groundwater.

# Appendix A

## Fact Sheets Prepared for the MDEQ

# Pharmaceuticals and Personal Care Products in the Clinton River - Fact Sheet

**Sample Location:** Macomb County, Clinton township, Shadyside Park, Gratiot Avenue, City of Mt. Clemens, Latitude 42.58417° N, Longitude 82.88278° W.

**Sample Dates:** June 24, 2004, August 24, 2004, November 3, 2004, March 14, 2005, June 14, 2005, August 15, 2005, November 22, 2005, March 14, 2006.

**Analytical Scan:** A waste water scan was performed by the United States Geological Survey (USGS) lab in Colorado. The waste water scan consists of 62-67 compounds (the method developed and changed throughout the study duration); including diazinon, 4-nonlyphenol, camphor, naphthalene, bisphenol A, triclosan, and caffeine.

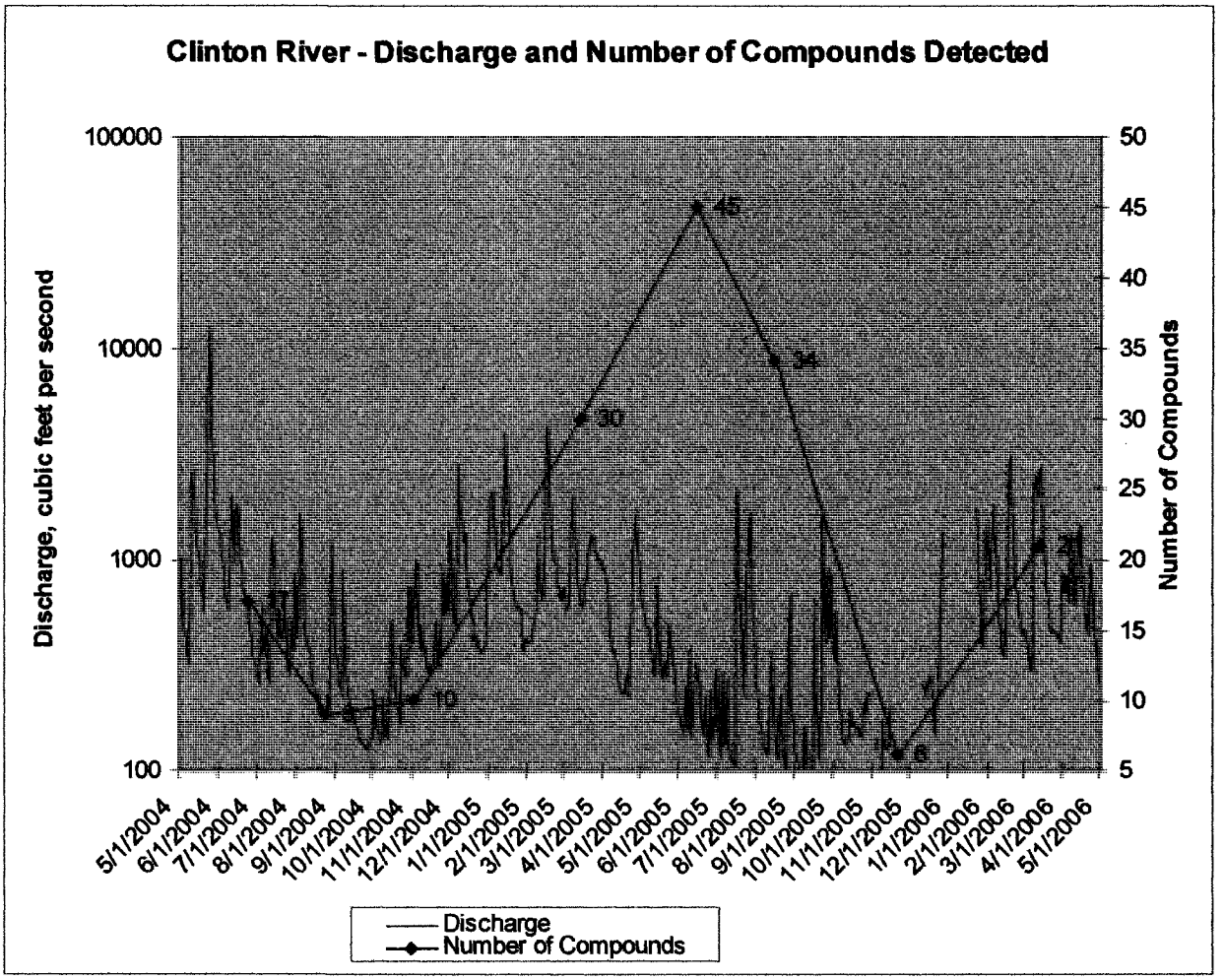
**Background Information:** Pharmaceuticals and personal care products are used by most of us everyday. These compounds become a part of our waste stream; many are not removed and are discharged into the environment. Recently, some of these compounds have been studied and are a cause for concern. The USGS spearheaded this research and developed analytical techniques to detect these compounds in the part per billion (ppb) range. In 2002, the USGS published the paper titled *Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance.* Streams that were likely impacted were sampled and many compounds were found. Research has only increased since then in areas of occurrence, toxicity, fate, and transport. It has been shown that some of the compounds, even in the small ppb range, act as endocrine disruptors in wildlife. The endocrine system regulates growth and sex hormones in an organism.

The results found below are the product of a 2 year study funded by the Michigan Department of Environmental Quality with monies from the Clean Michigan Initiative. The goals of the study include verifying these chemicals exist in the waters of the State, looking for seasonal and occurrence trends, and identifying known or suspected endocrine disrupting compounds.

**Results:**

- Compound detection statistics for 8 sample events on the Clinton River:
  Number of compounds detected (concentrations ranged from .0052 – 8.0 µg/L)
  - Low - 6
  - Mean - 22
  - High - 45

- Seasonal trends were investigated using the number of compounds detected per sample event and how that relates to river discharge data. It is thought that as the river discharge increases, dilution will cause the number of detections to decrease. A clear inverse trend was not found (see graph below). This may indicate that other mechanisms, other than just dilution, are a factor; such as non-point source contributions from storm runoff. The river discharge data was obtained from the USGS.




- Known or suspected endocrine disruptors found: 4-t-octylphenol, bisphenol A, diethoxynonylphenol, diethoxyoctylphenol, 4-nonylphenol, carbaryl, p-cresol, benzophenone, triclosan, diazinon, and dichlorvos.

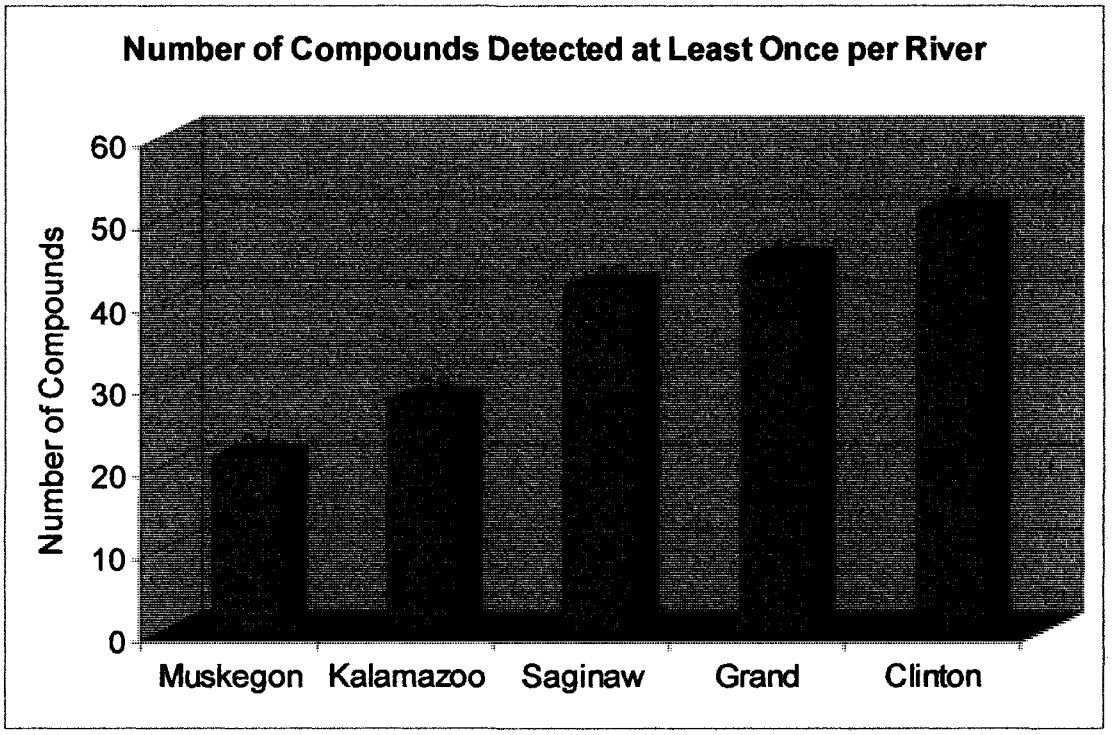
**Statewide Comparison:** Four other rivers in the State of Michigan were sampled as a portion of this project; including the Kalamazoo, Grand, Muskegon, and Saginaw rivers.

- 100% of all river samples had 1 or more compounds detected.

- Compound detection statistics for all sample rounds, all rivers:
  Number of compounds detected
  Low - 1
  Mean - 14
  High - 45

- Seasonal trends: None of the five rivers exhibited a consistent inverse relationship regarding river discharge and the number of compounds detected.

- Number of compounds found at least once per river (see graph below):




- Classes of compounds found overall include: flame retardants, gasoline constituents, dyes, solvents, plasticizers, fragrances, detergent metabolites, pesticides, and pharmaceuticals (Kalamazoo and Grand Rivers analyzed only).
- Known or suspected endocrine disrupting compounds were found in all five of the rivers sampled.

DEQ Department of Environmental Quality

WESTERN MICHIGAN UNIVERSITY

# Pharmaceuticals and Personal Care Products in the Grand River - Fact Sheet

**Sample Location:** Ottawa County, Robinson township, Riverside Park in the vicinity of Ottawa Center, Latitude 43.02667° N, Longitude 86.03389° W.

**Sample Dates:** June 15, 2004, August 18, 2004, November 17, 2004, March 22, 2005, June 27, 2005, August 23, 2005, November 21, 2005, March 13, 2006.

**Analytical Scans:** A waste water scan and a pharmaceutical scan were performed by the United States Geological Survey (USGS) lab in Colorado. The waste water scan consists of 62-67 compounds (the method developed and changed throughout the study duration); including diazinon, 4-nonlyphenol, camphor, naphthalene, bisphenol A, triclosan, and caffeine. The pharmaceutical scan includes 15 or 24 compounds (the number of compounds analyzed was reduced from 24 to 15 during the last two sample rounds); including cotinine, acetaminophen, carbamazepine, fluoxetine, and codeine.

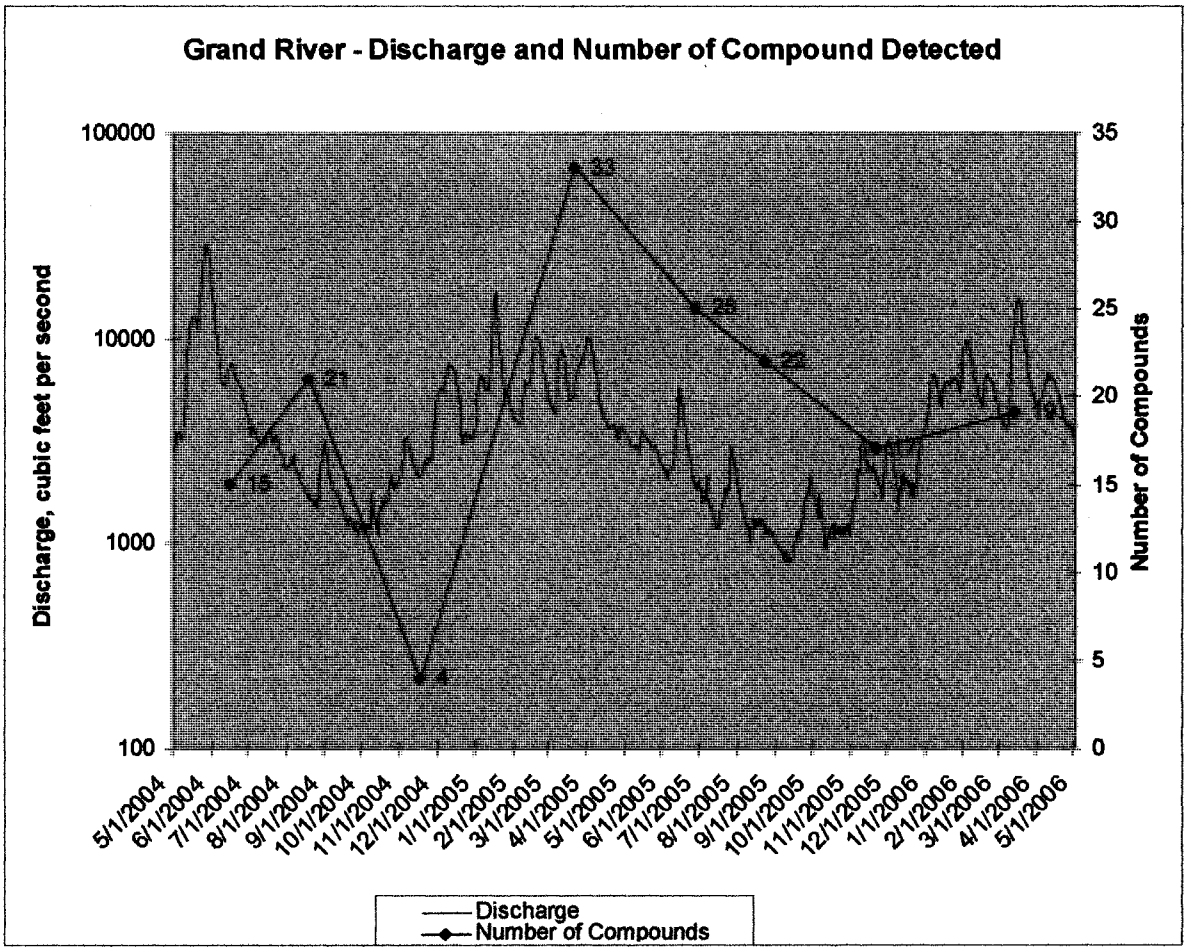
**Background Information:** Pharmaceuticals and personal care products are used by most of us everyday. These compounds become a part of our waste stream; many are not removed and are discharged into the environment. Recently, some of these compounds have been studied and are a cause for concern. The USGS spearheaded this research and developed analytical techniques to detect these compounds in the part per billion (ppb) range. In 2002, the USGS published the paper titled *Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance.* Streams that were likely impacted were sampled and many compounds were found. Research has only increased since then in areas of occurrence, toxicity, fate, and transport. It has been shown that some of the compounds, even in the small ppb range, act as endocrine disruptors in wildlife. The endocrine system regulates growth and sex hormones in an organism.

The results found below are the product of a 2 year study funded by the Michigan Department of Environmental Quality with monies from the Clean Michigan Initiative. The goals of the study include verifying these chemicals exist in the waters of the State, looking for seasonal and occurrence trends, and identifying known or suspected endocrine disrupting compounds.

**Results:**

- Compound detection statistics for 8 sample events on the Grand River:
  Number of compounds detected (concentrations ranged from .0036 - 2.3 µg/L)
  Low - 4
  Mean - 20
  High - 33

- Seasonal trends were investigated using the number of compounds detected per sample event and how that relates to river discharge data. It is thought that as the river discharge increases, dilution will cause the number of detections to decrease. A clear inverse trend was not found (see graph below). This may indicate that other mechanisms, other than just dilution, are a factor; such as non-point source contributions from storm runoff. The river discharge data was obtained from the USGS.



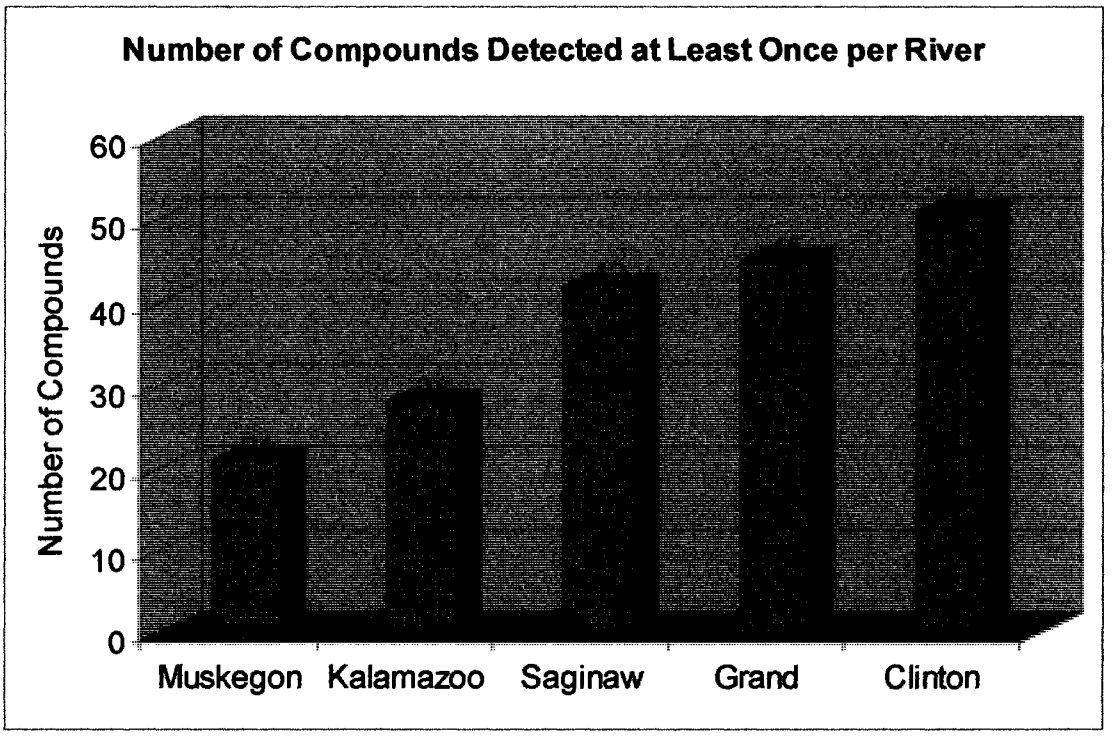

- Known or suspected endocrine disruptors found: 4-nonylphenol, triclosan diethoxyoctylphenol, diethoxynonylphenol, 4-t-octylphenol, benzophenone, and bisphenol A .

**Statewide Comparison:** Four other rivers in the State of Michigan were sampled as a portion of this project; including the Kalamazoo, Muskegon, Saginaw, and Clinton rivers.

- 100% of all river samples had 1 or more compounds detected.

- Compound detection statistics for all sample rounds, all rivers:
  Number of compounds detected
  Low - 1
  Mean - 14
  High - 45
- Seasonal trends: None of the five rivers exhibited a consistent inverse relationship regarding river discharge and the number of compounds detected.

- Number of compounds found at least once per river (see graph below):




- Classes of compounds found overall include: flame retardants, gasoline constituents, dyes, solvents, plasticizers, fragrances, detergent metabolites, pesticides, and pharmaceuticals (Kalamazoo and Grand Rivers analyzed only).
- Known or suspected endocrine disrupting compounds were found in all five of the rivers sampled.

DEQ Department of Environmental Quality

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# Pharmaceuticals and Personal Care Products in the Saginaw River - Fact Sheet

**Sample Location:** Bay County, Bangor township, Main Street, City of Essexville, Latitude 43.61751° N, Longitude 83.84278° W.

**Sample Dates:** June 23, 2004, August 24, 2004, November 4, 2004, March 14, 2005, June 15, 2005, August 16, 2005, November 29, 2005, March 14, 2006.

**Analytical Scan:** A waste water scan was performed by the United States Geological Survey (USGS) lab in Colorado. The waste water scan consists of 62-67 compounds (the method developed and changed throughout the study duration); including diazinon, 4-nonlyphenol, camphor, naphthalene, bisphenol A, triclosan, and caffeine.

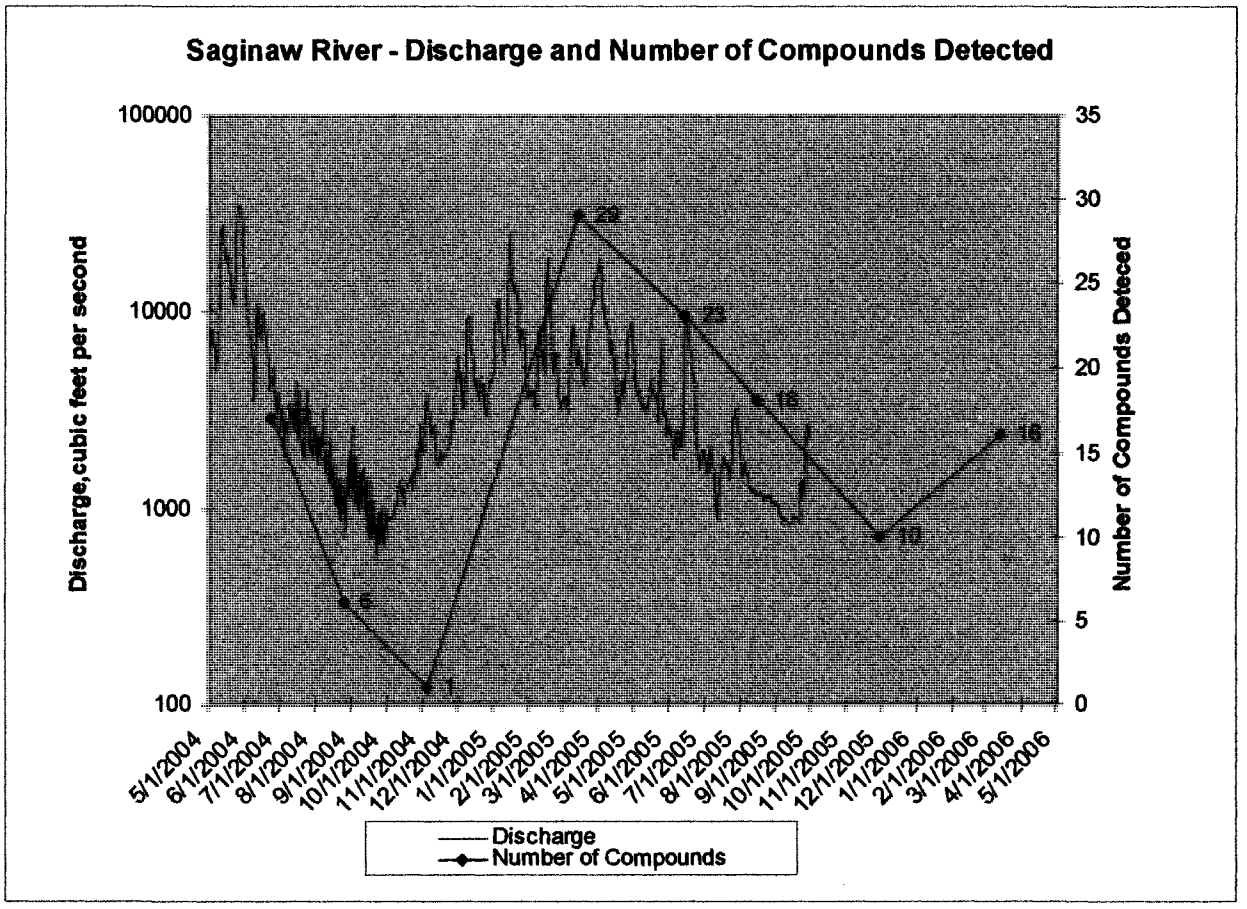
**Background Information:** Pharmaceuticals and personal care products are used by most of us everyday. These compounds become a part of our waste stream; many are not removed and are discharged into the environment. Recently, some of these compounds have been studied and are a cause for concern. The USGS spearheaded this research and developed analytical techniques to detect these compounds in the part per billion (ppb) range. In 2002, the USGS published the paper titled *Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance*. Streams that were likely impacted were sampled and many compounds were found. Research has only increased since then in areas of occurrence, toxicity, fate, and transport. It has been shown that some of the compounds, even in the small ppb range, act as endocrine disruptors in wildlife. The endocrine system regulates growth and sex hormones in an organism.

The results found below are the product of a 2 year study funded by the Michigan Department of Environmental Quality with monies from the Clean Michigan Initiative. The goals of the study include verifying these chemicals exist in the waters of the State, looking for seasonal and occurrence trends, and identifying known or suspected endocrine disrupting compounds.

**Results:**

- Compound detection statistics for 8 sample events on the Saginaw River:
  Number of compounds detected (concentrations ranged from .0041 - 3.5 µg/L)
  Low - 1
  Mean - 15
  High - 29

- Seasonal trends were investigated using the number of compounds detected per sample event and how that relates to river discharge data. It is thought that as the river discharge increases, dilution will cause the number of detections to decrease. A clear inverse trend was not found (see graph below). This may indicate that other mechanisms, other than just dilution, are a factor; such as non-point source contributions from storm runoff. The river discharge data was obtained from the USGS (discharge data collection for the Saginaw River was discontinued by the USGS after September 30, 2005).




- Known or suspected endocrine disruptors found: 4-t-octylphenol, bisphenol A, diethoxynonylphenol, diethoxyoctylphenol, 4-nonylphenol, p-cresol, benzophenone, and triclosan.

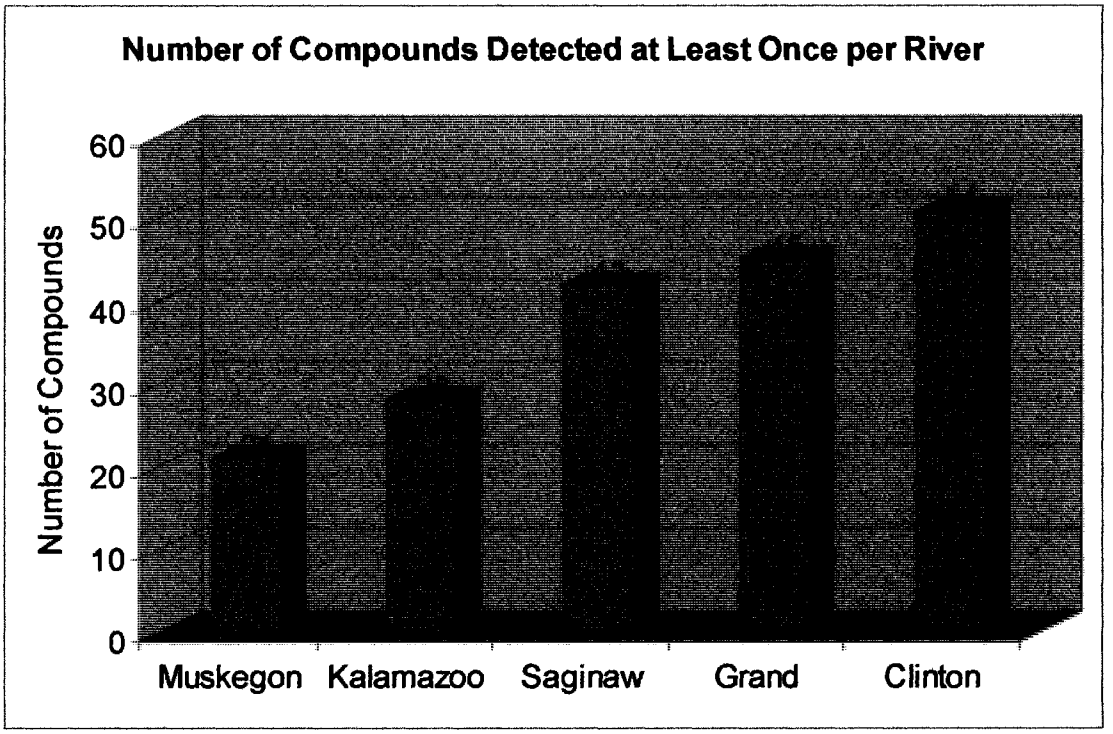
**Statewide Comparison:** Four other rivers in the State of Michigan were sampled as a portion of this project; including the Kalamazoo, Grand, Muskegon, and Clinton rivers.

- 100% of all river samples had 1 or more compounds detected.

- Compound detection statistics for all sample rounds, all rivers:
  Number of compounds detected
  Low - 1
  Mean - 14
  High - 45

- Seasonal trends: None of the five rivers exhibited a consistent inverse relationship regarding river discharge and the number of compounds detected.

- Number of compounds found at least once per river (see graph below):




- Classes of compounds found overall include: flame retardants, gasoline constituents, dyes, solvents, plasticizers, fragrances, detergent metabolites, pesticides, and pharmaceuticals (Kalamazoo and Grand Rivers analyzed only).

- Known or suspected endocrine disrupting compounds were found in all five of the rivers sampled.

DEQ Department of Environmental Quality

WESTERN MICHIGAN UNIVERSITY

# Pharmaceuticals and Personal Care Products in the Kalamazoo River - Fact Sheet

**Sample Location:** Allegan County, Manlius township, 57th Street in the vicinity of New Richmond, Latitude 42.6511° N, Longitude 86.10611° W.

**Sample Dates:** June 15, 2004, August 18, 2004, November 17, 2004, March 21, 2005, June 28, 2005, August 24, 2005, November 22, 2005, March 13, 2006.

**Analytical Scans:** A waste water scan and a pharmaceutical scan were performed by the United States Geological Survey (USGS) lab in Colorado. The waste water scan consists of 62-67 compounds (the method developed and changed throughout the study duration); including diazinon, 4-nonlyphenol, camphor, naphthalene, bisphenol A, triclosan, and caffeine. The pharmaceutical scan includes either 15 or 24 compounds (the number of compounds analyzed was reduced from 24 to 15 during the last two sample rounds); including cotinine, acetaminophen, carbamazepine, fluoxetine, and codeine.

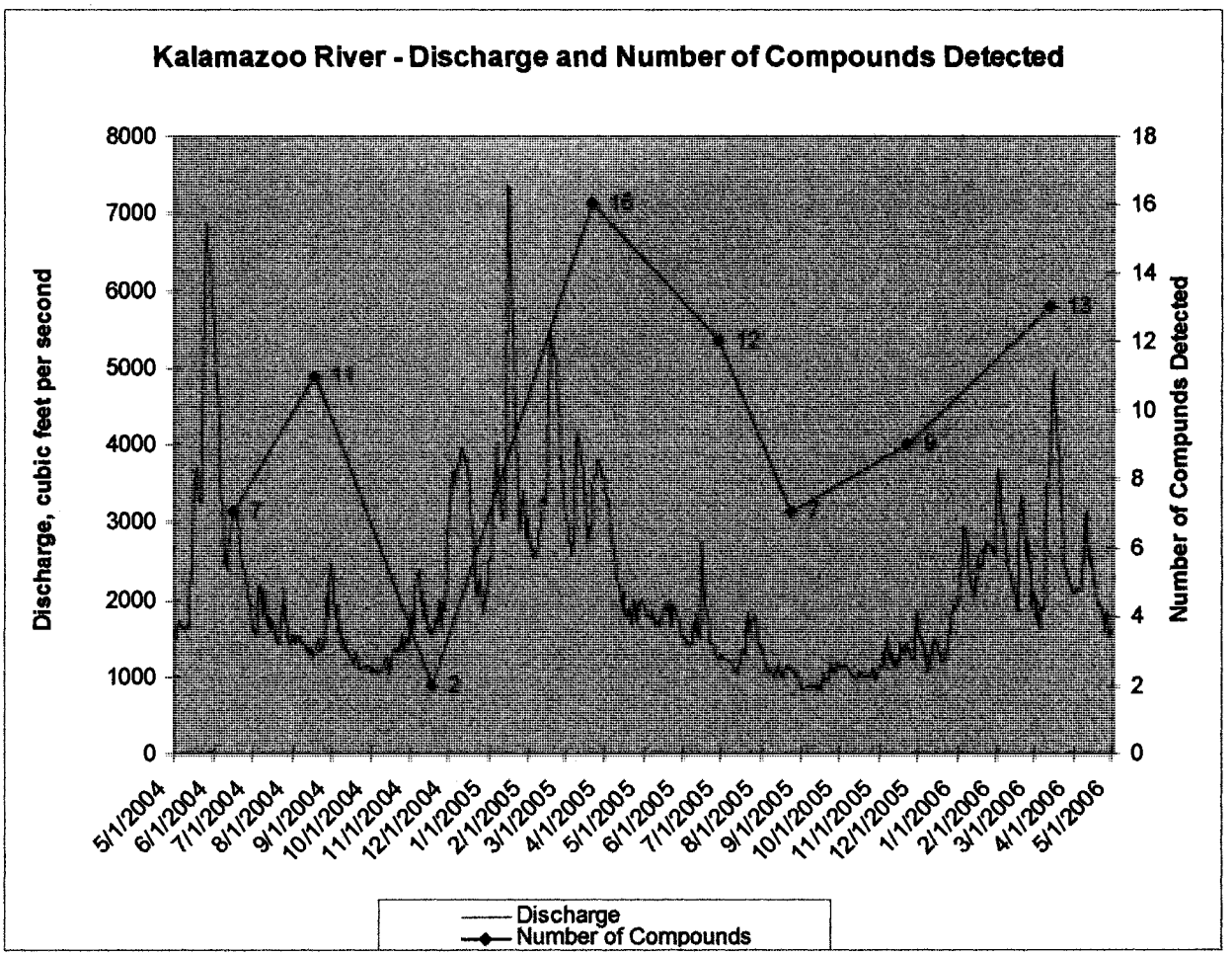
**Background Information:** Pharmaceuticals and personal care products are used by most of us everyday. These compounds become a part of our waste stream; many are not removed and are discharged into the environment. Recently, some of these compounds have been studied and are a cause for concern. The USGS spearheaded this research and developed analytical techniques to detect these compounds in the part per billion (ppb) range. In 2002, the USGS published the paper titled *Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance*. Streams that were likely impacted were sampled and many compounds were found. Research has only increased since then in areas of occurrence, toxicity, fate, and transport. It has been shown that some of the compounds, even in the small ppb range, act as endocrine disruptors in wildlife. The endocrine system regulates growth and sex hormones in an organism.

The results found below are the product of a 2 year study funded by the Michigan Department of Environmental Quality with monies from the Clean Michigan Initiative. The goals of the study include verifying these chemicals exist in the waters of the State, looking for seasonal and occurrence trends, and identifying known or suspected endocrine disrupting compounds.

**Results:**

- Compound detection statistics for 8 sample events on the Kalamazoo River:
  Number of compounds detected (concentrations ranged from .0030 - 1.1 µg/L)
  - Low - 2
  - Mean - 10
  - High - 16

- Seasonal trends were investigated using the number of compounds detected per sample event and how that relates to river discharge data. It is thought that as the river discharge increases, dilution will cause the number of detections to decrease. A clear inverse trend was not found (see graph below). This may indicate that other mechanisms, other than just dilution, are a factor; such as non-point source contributions from storm runoff. The river discharge data was obtained from the USGS.



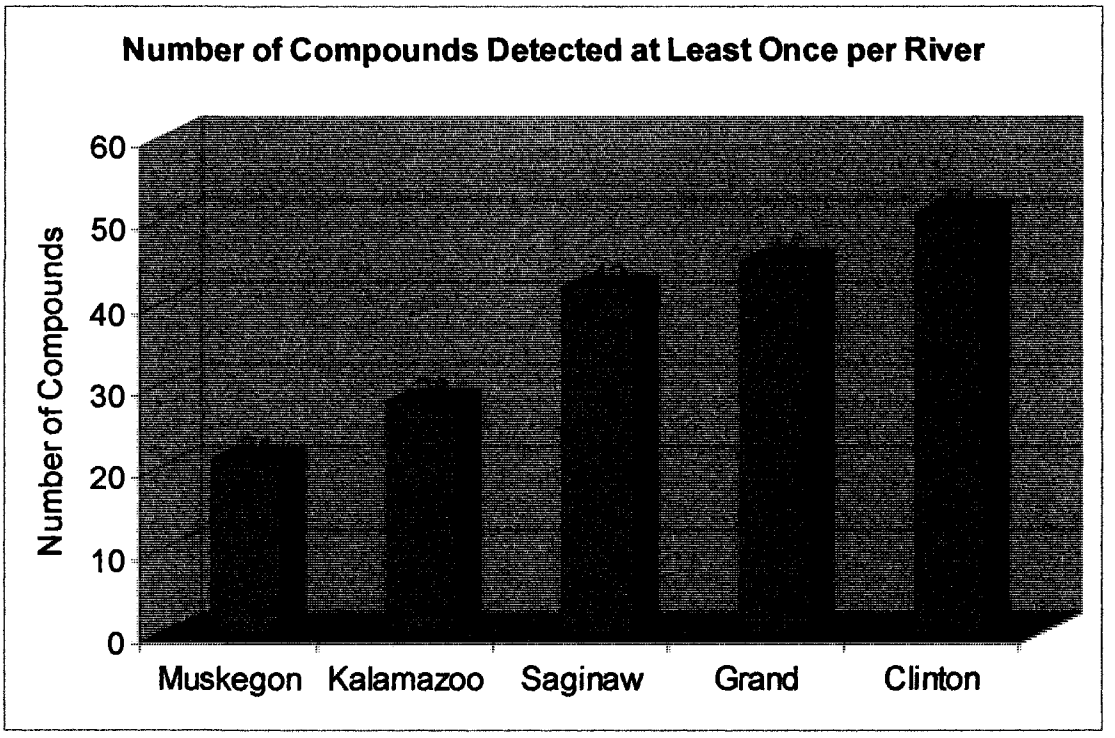

- Known or suspected endocrine disruptors found: 4-nonylphenol and benzophenone.

**Statewide Comparison:** Four other rivers in the State of Michigan were sampled as a portion of this project; including the Grand, Muskegon, Saginaw, and Clinton rivers.

- 100% of all river samples had 1 or more compounds detected.

- Compound detection statistics for all sample rounds, all rivers:
  Number of compounds detected
  Low - 1
  Mean - 14
  High - 45
- Seasonal trends: None of the five rivers exhibited a consistent inverse relationship regarding river discharge and the number of compounds detected.

- Number of compounds found at least once per river (see graph below):




- Classes of compounds found overall include: flame retardants, gasoline constituents, dyes, solvents, plasticizers, fragrances, detergent metabolites, pesticides, and pharmaceuticals (Kalamazoo and Grand Rivers analyzed only).
- Known or suspected endocrine disrupting compounds were found in all five of the rivers sampled.

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# Pharmaceuticals and Personal Care Products in the Muskegon River - Fact Sheet

**Sample Location:** Muskegon County, Cedar Creek township, Maple Island Road, Latitude 43.31778° N, Longitude 86.03889° W.

**Sample Dates:** June 16, 2004, August 19, 2004, October 27, 2004, March 22, 2005, June 27, 2005, August 23, 2005, November 21, 2005, March 13, 2006.

**Analytical Scan:** A waste water scan was performed by the United States Geological Survey (USGS) lab in Colorado. The waste water scan consists of 62-67 compounds (the method developed and changed throughout the study duration); including diazinon, 4-nonlyphenol, camphor, naphthalene, bisphenol A, triclosan, and caffeine.

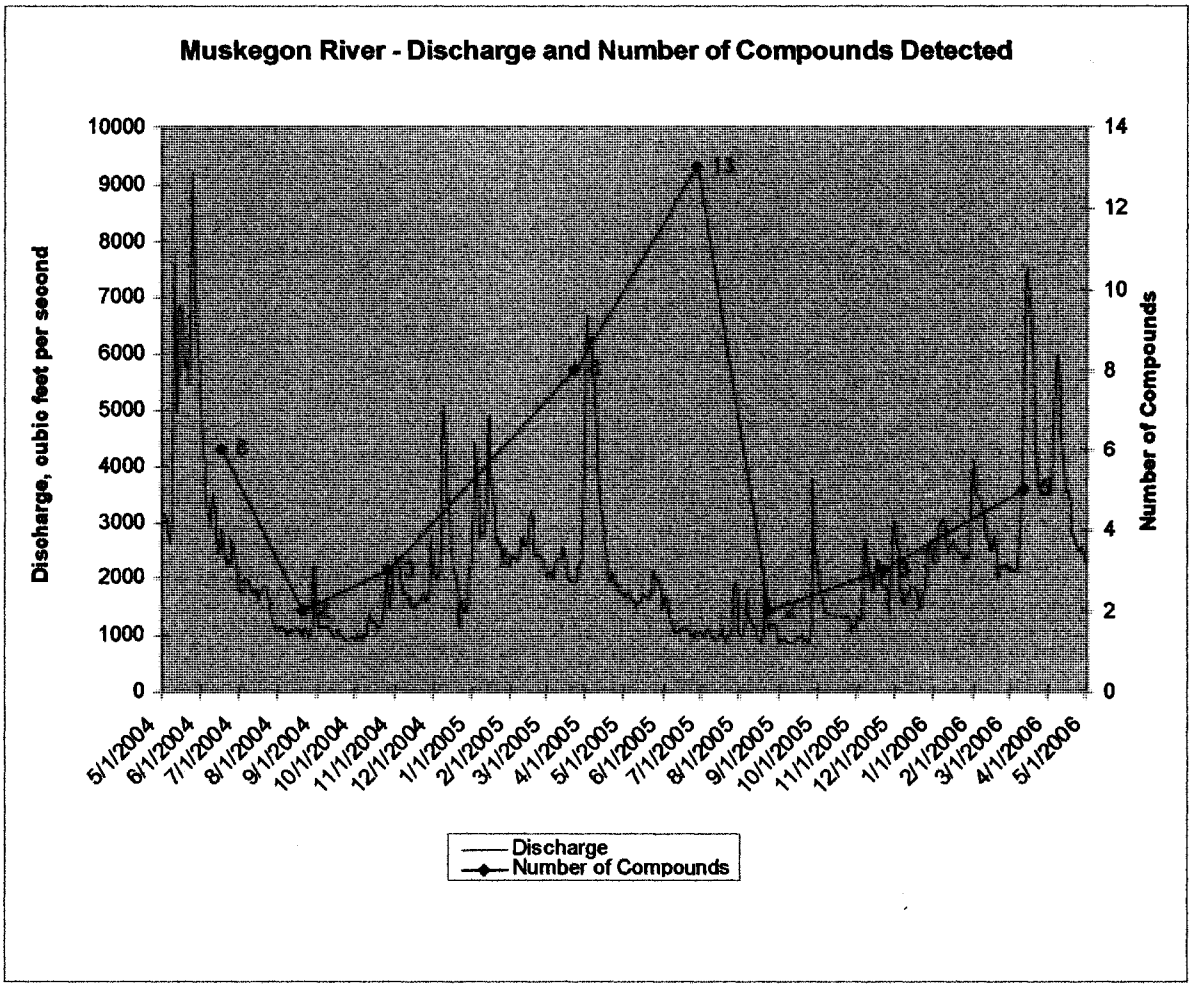
**Background Information:** Pharmaceuticals and personal care products are used by most of us everyday. These compounds become a part of our waste stream; many are not removed and are discharged into the environment. Recently, some of these compounds have been studied and are a cause for concern. The USGS spearheaded this research and developed analytical techniques to detect these compounds in the part per billion (ppb) range. In 2002, the USGS published the paper titled *Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance*. Streams that were likely impacted were sampled and many compounds were found. Research has only increased since then in areas of occurrence, toxicity, fate, and transport. It has been shown that some of the compounds, even in the small ppb range, act as endocrine disruptors in wildlife. The endocrine system regulates growth and sex hormones in an organism.

The results found below are the product of a 2 year study funded by the Michigan Department of Environmental Quality with monies from the Clean Michigan Initiative. The goals of the study include verifying these chemicals exist in the waters of the State, looking for seasonal and occurrence trends, and identifying known or suspected endocrine disrupting compounds.

**Results:**

- Compound detection statistics for 8 sample events on the Muskegon River:
  Number of compounds detected (concentrations ranged from .0049 - .7800 µg/L)
  - Low - 2
  - Mean - 5
  - High - 13

- Seasonal trends were investigated using the number of compounds detected per sample event and how that relates to river discharge data. It is thought that as the river discharge increases, dilution will cause the number of detections to decrease. A clear inverse trend was not found (see graph below). This may indicate that other mechanisms, other than just dilution, are a factor; such as non-point source contributions from storm runoff. The river discharge data was obtained from the USGS.



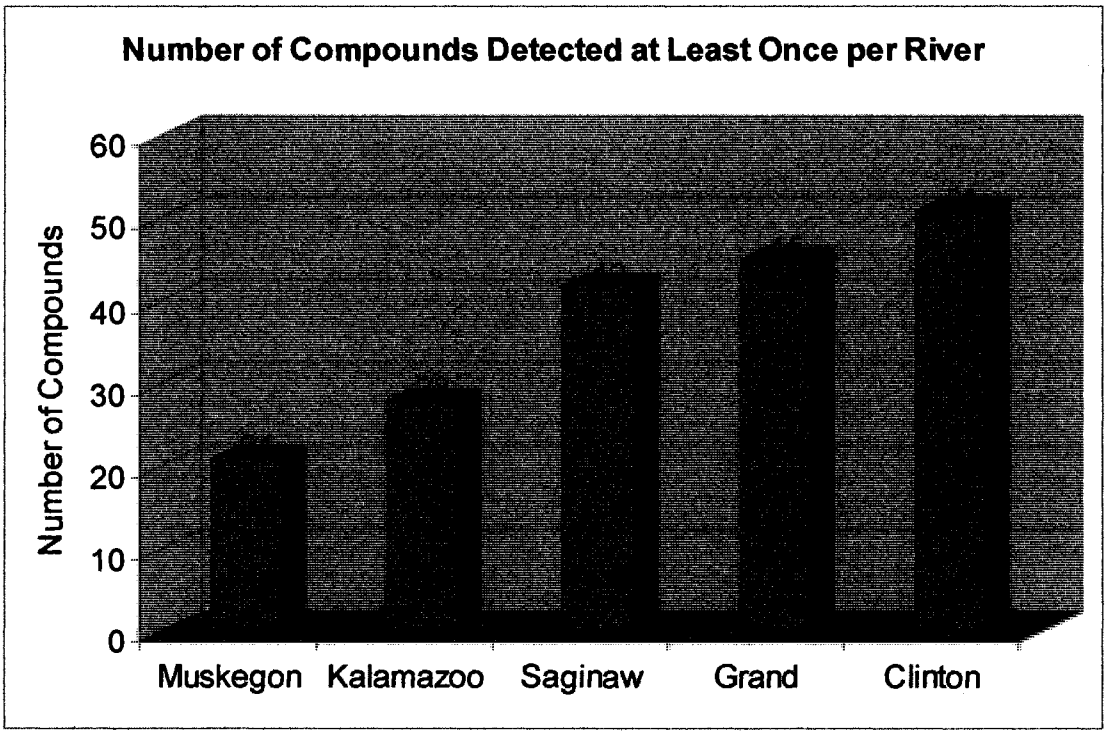

- Known or suspected endocrine disruptors found: 4-nonylphenol, benzophenone, and p-cresol.

**Statewide Comparison:** Four other rivers in the State of Michigan were sampled as a portion of this project; including the Kalamazoo, Grand, Saginaw, and Clinton rivers.

- 100% of all river samples had 1 or more compounds detected.

- Compound detection statistics for all sample rounds, all rivers:
  Number of compounds detected
  Low - 1
  Mean - 14
  High - 45

- Seasonal trends: None of the five rivers exhibited a consistent inverse relationship regarding river discharge and the number of compounds detected.
- Number of compounds found at least once per river (see graph below):




- Classes of compounds found overall include: flame retardants, gasoline constituents, dyes, solvents, plasticizers, fragrances, detergent metabolites, pesticides, and pharmaceuticals (Kalamazoo and Grand Rivers analyzed only).

- Known or suspected endocrine disrupting compounds were found in all five of the rivers sampled.

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# Pharmaceuticals and Personal Care Products in the Surface Waters of Michigan - Fact Sheet

**Sample Locations:** Kalamazoo River, Allegan County, Manlius township, 57th Street in the vicinity of New Richmond, Latitude 42.6511° N, Longitude 86.10611° W.

Grand River, Ottawa County, Robinson township, Riverside Park in the vicinity of Ottawa Center, Latitude 43.02667° N, Longitude 86.03389° W.

Muskegon River, Muskegon County, Cedar Creek township, Maple Island Road, Latitude 43.31778° N, Longitude 86.03889° W.

Saginaw River, Bay County, Bangor township, Main Street, City of Essexville, Latitude 43.61751° N, Longitude 83.84278° W.

Clinton River, Macomb County, Clinton township, Shadyside Park, Gratiot Avenue, City of Mt. Clemens, Latitude 42.58417° N, Longitude 82.88278° W.

**Sample Dates:** June 2004, August 2004, October/November 2004, March 2005, June 2005, August 2005, November 2005, March 2006.

**Analytical Scans:** A waste water scan and a pharmaceutical scan were performed by the United States Geological Survey (USGS) lab in Colorado. The waste water scan consists of 62-67 compounds (the method developed and changed throughout the study duration); including diazinon, 4-nonlyphenol, camphor, naphthalene, bisphenol A, triclosan, and caffeine. The pharmaceutical scan includes either 15 or 24 compounds (the number of compounds analyzed was reduced from 24 to 15 during the last two sample rounds); including cotinine, acetaminophen, carbamazepine, fluoxetine, and codeine. The waste water scan was performed on all rivers sampled. The pharmaceutical scan was performed on the Kalamazoo and Grand Rivers only.

**Background Information:** Pharmaceuticals and personal care products are used by most of us everyday. These compounds become a part of our waste stream; many are not removed and are discharged into the environment. Recently, some of these compounds have been studied and are a cause for concern. The USGS spearheaded this research and developed analytical techniques to detect these compounds in the part per billion (ppb) range. In 2002, the USGS published the paper titled *Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance*. Streams that were likely impacted were sampled and many compounds were found. Research has only increased since then in areas of occurrence, toxicity, fate, and transport. It has been shown that some of the compounds, even in the small ppb range, act as endocrine disruptors in wildlife. The endocrine system regulates growth and sex hormones in an organism.

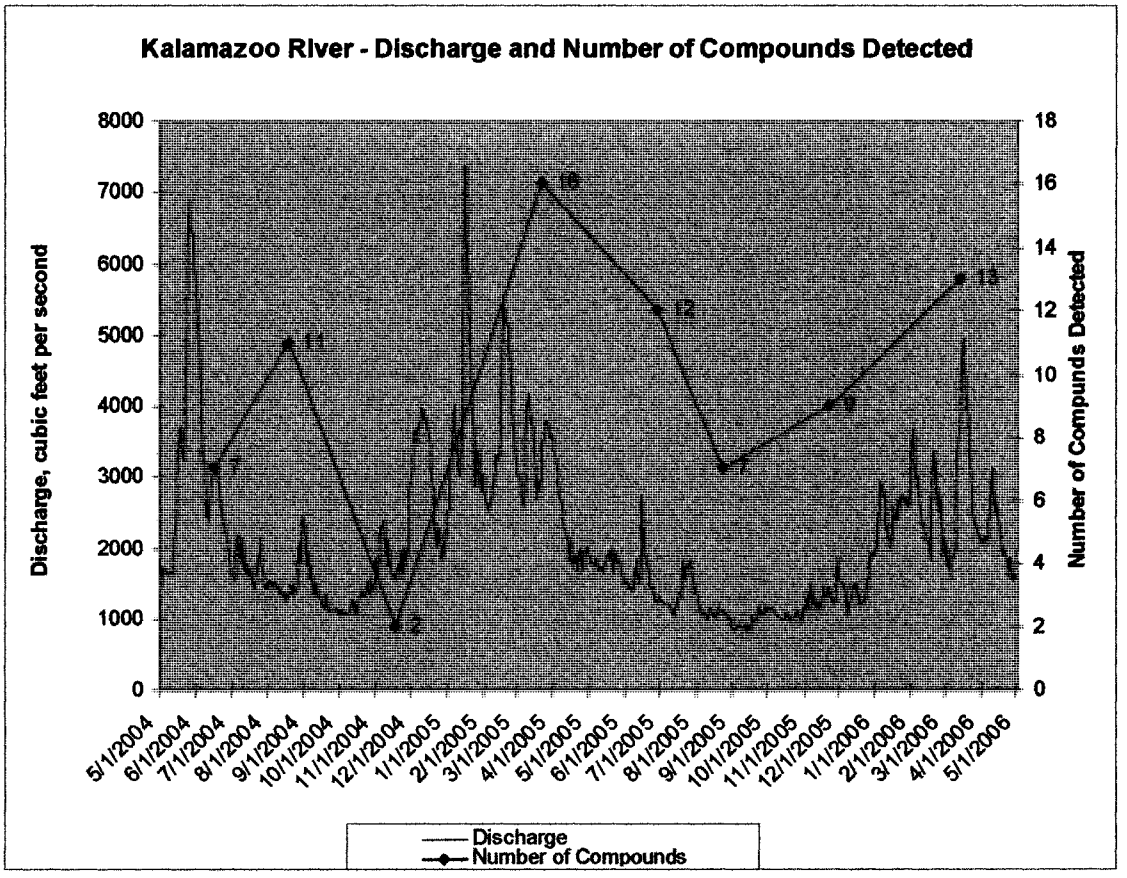
The results found below are the product of a 2 year study funded by the Michigan Department of Environmental Quality with monies from the Clean Michigan Initiative. The goals of the study include verifying these chemicals exist in the waters of the State, looking for seasonal and occurrence trends, and identifying known or suspected endocrine disrupting compounds.

**Results:**

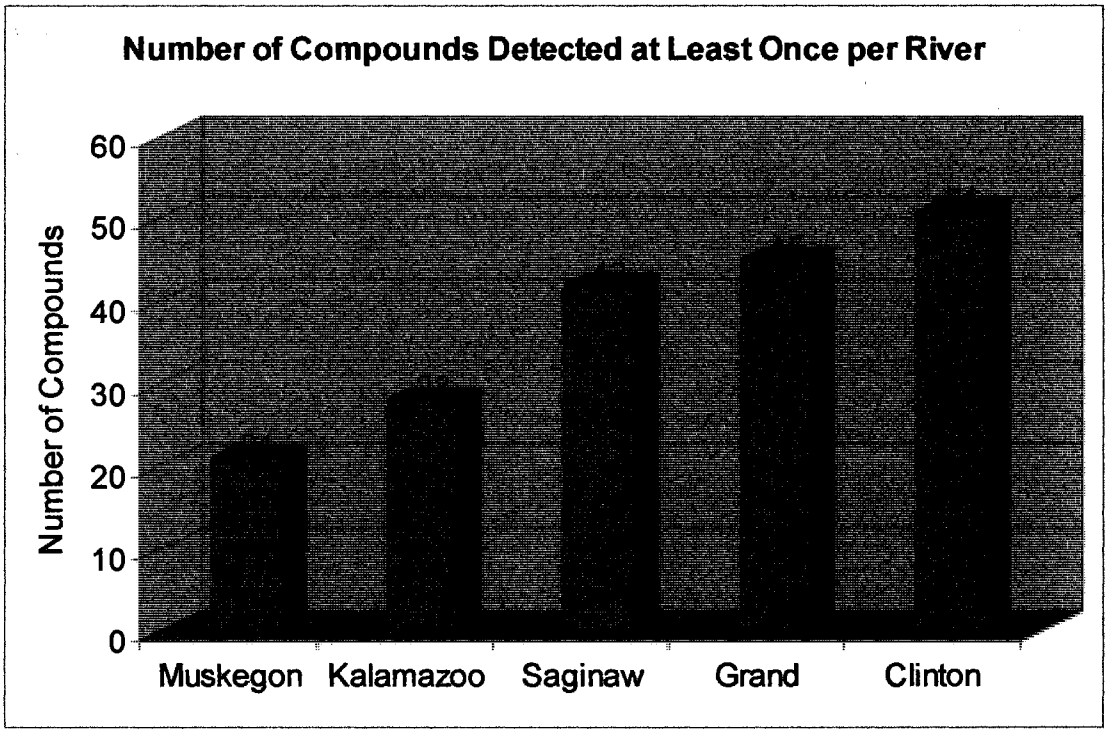
- 100% of all river samples had 1 or more compounds detected.

- Compound detection statistics for all sample rounds, all rivers:
  Number of compounds detected
  Low - 1
  Mean - 14
  High - 45

- Seasonal trends were investigated using the number of compounds detected per sample event and how that relates to river discharge data. It is thought that as the river discharge increases, dilution will cause the number of detections to decrease. A clear inverse trend was not found for any of the five rivers sampled (see the graph below for the Kalamazoo River as an example). This may indicate that other mechanisms, other than just dilution, are a factor; such as non-point source contributions from storm runoff. The river discharge data was obtained from the USGS.



- Number of compounds found at least once per river (see graph below):




- Classes of compounds found overall include: flame retardants, gasoline, constituents, dyes, solvents, plasticizers, fragrances, detergent metabolites, pesticides, and pharmaceuticals (Kalamazoo and Grand Rivers analyzed only).
- Known or suspected endocrine disrupting compounds were found in all five of the rivers sampled.

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# Current State of PBDE Analysis of Various Media Summer 2007 - Fact Sheet

**PBDE Introduction:** Polybrominated Diphenyl Ethers (PBDEs) are a class of fire retardant compounds. Although many are now banned worldwide, the compounds have been used in many consumer products including textiles, plastics, and furniture that are still in use today. The fate and toxicity of PBDEs in the environment are a concern and as a result, many studies have been completed to determine their behavior in most, if not all, environmental media. The purpose of this fact sheet is to summarize the current state of the analysis of PBDEs in various media. The search for researchers currently completing PBDE analysis was not exhaustive, but the goal was to show that PBDE analysis is currently occurring all over the globe and in media including water, air, sediment, sludge, and animal tissue.

**Water:** Sea water was sampled in 2005 in Hong Kong, China by researchers from the National University of Singapore and the City University of Hong Kong. To look for PBDEs in these samples they used a gas chromatograph (GC) and tandem mass spectrometry (MS/MS) (1). A leaching experiment was conducted by scientists from Japan and Korea to determine if PBDEs would leach from television housings in an effort to simulate landfill conditions. High resolution GC and high resolution MS (HRGS/HRMS) were used to analyze the samples (2). Scientists from the University of Minnesota sampled Lake Michigan water in 2004 and studied fish tissue from 2000-2002 in and effort to find PBDEs. A gas chromatograph and mass spectrometer (GC/MS) was used in electron capture negative ionization mode to analyze the samples (3).

**Air:** Researchers from the Department of Environmental Science at Lancaster University, Lancaster, United Kingdom (UK) sampled the air in the UK during the annual bonfire festival in 2000. The air was tested for PBDEs and analyzed using GC/MS (4). A group of scientists from The University of Maryland, the United States Department of Agriculture, the University of Delaware, and Oregon State University studied air sampled in 2001-2003 near sewage spray irrigation areas. They also used GC/MS to analyze the air samples for PBDEs (5). Banu Cetin and Mustafa Odabasi from the Dokuz Eyulul University in Izmir Turkey also used GC/MS to analyze their paired air and water samples taken from Izmir Bay, Turkey when they looked for PBDEs in 2005 (6).

**Sediment:** A group of scientists from the University of Illinois at Chicago searched for PBDEs in sediment cores from Lake Superior in 2001-2002. They used GC/MS to process their sampled (7). In 2002, researchers from Barcelona, Spain obtained sediment and fish samples from the Cinca River in Spain in an effort to find PBDEs. A GC/negative ION chemical ionization (NICI)/MS was used to analyze the samples (8). Sediment and shrimp specimens were analyzed for PBDEs using GC/negative chemical ionization (NCI)/MS in 2001 by researchers from Belgium and The Netherlands. The samples were obtained from the Scheldt estuary, The Netherlands (9).

**Sludge:** Scientists from the University of Windsor in Ontario, Canada sampled sludge from a waste water treatment plant in Windsor, Ontario, Canada in 2004. They used a GC/MS to analyze the sludge for PBDEs (10). Another group of researchers from Canada also tested sewage sludge from Ontario for BDE-209 and decabromodiphenylethane (DBDPE). Their goal was to show that DBDPE can be used as a surrogate standard. They used HRGC/HRMS for the analysis (11). Swiss scientists studied the anaerobic degradation of DecaBDE in sewage sludge from Dubendorf, Switzerland to determine degradation rates. They used GC/HRMS to analyze the samples (12).

**Soil and Plants:** Soil and earthworm samples were taken from field plots in Sweden that had been amended with sewage sludge. The researchers then analyzed the samples for PBDEs using GC/MS (13). A group of scientists from the University of Birmingham, United Kingdom sampled air and soil in the UK from 2003 to 2004. They also used GC/MS to analyze these samples for PBDEs (14). Researchers from the University of Cincinnati, Ohio studied the fate of PBDEs in soil and its uptake by plants by using GC/mass selective detector (MSD)/MS to analyze the samples (15). Archived pasture grasses from the UK were analyzed for PBDEs to investigate the atmospheric burden of these compounds over time. The scientists from the UK analyzed samples from 1930 to 2004 for PBDEs using a GC/MS (16).

**Fish and Other Non-human Animal Tissue:** It would appear that there is a large volume of studies completed on fish and other animals. Researchers search for the fate of PBDEs in the environment and their effects on these species and the food chain. Many scientists have studied the PBDE content of fish, including a study of archived Great Lakes fish from 1980-2000 by researchers at Indiana University. They used a GC/MS to analyze their samples (17). A group from the California Department of Toxic Substances Control in Berkley, California sampled fish from the San Francisco Bay in 2000 and the California coast in 2001 and also used a GC/MS to look for PBDEs in their samples (18). Fish and mussels from Portugal were sampled in 2002-2004 by scientists from Portugal and Spain. They used a GC/NCI/MS in their quest to detect PBDEs (19). Researchers from Taiwan, Republic of China sampled fish within Taiwan and used a GC/HRMS to look for PBDEs (20). The PBDE content of fish and crab from British Columbia, Canada was the focus of researchers from the Marine Environmental Quality of Canada and Columbia University, New York. They used samples obtained in 1992-2002 and used GC/HRMS to analyze the samples for PBDEs (21).

Researchers from Japan, China, and California, USA focused their study on dolphins that live within the waters of Hong Kong, China. They used specimens that were found dead from 1995-2001 and used a GC/MSD to analyze the samples to determine PBDE content (22). Canadian researchers studied the content of PBDEs in grizzly bears from British Columbia obtained in 2003. They used HRGC/HRMS to find PBDE in the tissue samples (23).

**Human Tissue or Fluids:** Researchers from the United Kingdom and New Zealand obtained human blood serum samples from New Zeeland residents in 2001. They used a GC/MS to analyze the samples for PBDEs (24). Adipose tissue from women living is Spain was sampled in 2003 and analyzed using a GC/MS also. This research was conducted by scientists from Spain and Finland (25). Researchers from Poland and Belgium studied the PBDE content of human breast milk. The samples were obtained in 2004 from Polish woman living within the Wielkopolska region. The sample analysis was completed using a GC/MS (26).

**Summary:** It is evident from the research cited above that PBDE research is very active and is occurring worldwide. It appears there are many options for sample analysis; with the GC/MS method being the most commonly used.

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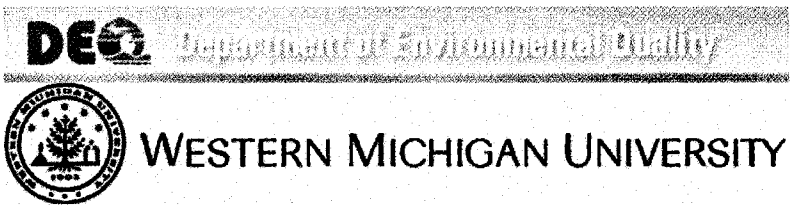

# Appendix B

## Water Well Logs for the Municipal Wells of Parchment and Portland, Michigan

# WATER WELL AND PUMP RECORD

Completion is required under authority of Part 127 Act 368 PA 1978.

Failure to comply is a misdemeanor.

Well ID: 39000002412 Import ID: 39711134301

| Tax No: | Permit No: | County: Kalamazoo | Township: Cooper |
|---|---|---|---|

**Well ID: 39000002412**

Elevation: 752 ft

Latitude: 42.3434273078

Longitude: -85.5742032066

| Fraction: | Section: | Town/Range: | WSSN: | Source ID/Well No: |
|---|---|---|---|---|
| NE¼ SW¼ NE¼ | 34 | 01S 11W | 5200 | PARCHMENT WELL #1 |

Distance and Direction from Road Intersection: WSSNW 05208; 900' WEST 201H ST & 800'E OF KAZOO RIVER

Well Owner: City Of Parchment

Well Address: PARCHMENT WELL #1 PARCHMENT MI

Owner Address: PARCHMENT MI

Drilling Method: Cable Tool
Well Depth: 60.00 ft. Well Use: Type Ipublic
Well Type: Replacement Date Completed: 1/5/1961
Casing Type: Unknown
Casing Joint: Unknown
Diameter: 8.00 in. to 0.00 ft. depth

Bore Diameter 1:
Bore Diameter 2:
Bore Diameter 3:
Height: 0.00 ft. above grade
Casing Fitting: None

Static Water Level: 3.00 ft. Below Grade(Not Flowing)
Yield Test Method: Unknown
Measurement Taken During Pump Test:

Abandoned Well Plugged: No
Reason for not plugging Well:

Abandoned well ID:

Screen Installed: No Well Intake: Unknown
Filter Packed:
Screen Diameter: Length:
Screen Material Type:
Slot:
Blank:
Fittings:

Well Grouted: Yes Grouting Method: Unknown
No. of Bags: Additives: None
Grouting Materials:
Unknown From 0.00 ft. to 0.00 ft.

Well Head Completion: Unknown

Nearest source of possible contamination:

| Type | Distance | Direction |
|---|---|---|
| Unknown | 0.00 ft. | |
| Unknown | | |

Drilling Machine Operator Name:

Employment: Unknown

Pump Installed: No Pump Installation only: No
Pump Installation date: HP:
Manufacturer: Pump Type:
Model Number: Pump Capacity: 600.00 GPM
Length of Drop Pipe: Id of Well:
Diameter of Drop Pipe:
Draw Down Seal Used: No

Pressure Tank Installed: No
Pressure Tank Type:
Manufacturer:
Model Number: Tank Capacity: Gallons
Pressure Relief Valve Installed: No

| Formation Description | Thickness | Depth to Bottom |
|---|---|---|
| Topsoil | 1.00 | 1.00 |
| Clay Gravely | 2.00 | 3.00 |
| Sand & Gravel | 15.00 | 18.00 |
| Clay Silty | 14.00 | 32.00 |
| Sand & Gravel Gray | 26.00 | 58.00 |
| Clay | 2.00 | 60.00 |

Geology Remarks: 1. [TOP SOIL] [1] [1] 2. [GRAVELY CLAY] [3] [2] 3. [SAND & GRAVEL] [18] [15] 4. [SILTY CLAY] [32] [14] 5. [SAND & GRAVEL (GREY)] [58] [26] 6. [CLAY] [60] [2]

Contractor Type: Unknown
Registration Number:
Business Name:
Business Address:

WATER WELL CONTRACTOR'S CERTIFICATION:
This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

Signature of Registered Contractor Date

General Remarks: LIMITED INFORMATION ON WELL LOG;
OTHER REMARKS

EQP 2017C (2/2000)

**ATTENTION WELL OWNER: FILE WITH DEED**

2/17/2000 13:03

DEQ

# WATER WELL AND PUMP RECORD

Completion is required under authority of Part 127 Act 368 PA 1978.

Well ID: 39000002413 — Failure to comply is a misdemeanor. — Import ID: 39711134302

| Tax No: | Permit No: | County: Kalamazoo | Township: Cooper |
|---|---|---|---|

## Well ID: 39000002413

Elevation: 752 ft

Latitude: 42.3437197309

Longitude: -85.5725016778

| Fraction: | Section: | Town/Range: | WSSN: | Source ID/Well No: |
|---|---|---|---|---|
| SW¼ NE¼ NE¼ | 34 | 01S 11W | 5200 | PARCHMENT WELL #2 |

Distance and Direction from Road Intersection: WSSNW 05200; 400' NORTH OF CITY WELL #1

Well Owner: City Of Parchment

| Well Address: | Owner Address: |
|---|---|
| PARCHMENT WELL #2<br>PARCHMENT MI | PARCHMENT MI |

Drilling Method: Rotary
Well Depth: 58.00 ft. | Well Use: Type I public
Well Type: New | Date Completed: 11/20/1961
Casing Type: Unknown
Casing Joint: Unknown
Diameter: 34.00 in. to 28.00 ft. depth

Bore Diameter 1:
Bore Diameter 2:
Bore Diameter 3:
Height: 0.00 ft. above grade
Casing Fitting: None

Pump Installed: No — Pump Installation only: No
Pump Installation date: — HP:
Manufacturer: — Pump Type:
Model Number: — Pump Capacity: 1,000.00 GPM
Length of Drop Pipe: — Id of Well:
Diameter of Drop Pipe:
Draw Down Seal Used: No

Pressure Tank Installed: No
Pressure Tank Type:
Manufacturer:
Model Number: — Tank Capacity: Gallons
Pressure Relief Valve Installed: No

Static Water Level: 8.00 ft. Below Grade(Not Flowing)
Yield Test Method: Unknown
Measurement Taken During Pump Test:
0.00 ft. after 0.00 hrs. pumping at 1,640.00 GPM

Abandoned Well Plugged: No
Reason for not plugging Well:
Abandoned well ID:

| Formation Description | Thickness | Depth to Bottom |
|---|---|---|
| Lithology Unknown Fill | 7.00 | 7.00 |
| Topsoil | 1.00 | 8.00 |
| Sand & Gravel Coarse | 15.00 | 23.00 |
| Sand Fine | 2.00 | 25.00 |
| Clay | 3.00 | 28.00 |
| Sand & Gravel Coarse | 3.00 | 31.00 |
| Clay | 7.00 | 38.00 |
| Sand & Gravel Coarse | 22.00 | 60.00 |

Screen Installed: Yes — Well Intake:
Filter Packed: No
Screen Diameter: 12.00 in. — Length: 15.00 ft.
Screen Material Type:
Slot: 15.00 in. Set Between 43.00 ft. and 58.00 ft.
Blank: 0.00 ft. Above
Fittings:
None

Well Grouted: Yes — Grouting Method: Unknown
No. of Bags: — Additives: None
Grouting Materials:
Unknown — From 0.00 ft. to 0.00 ft.

Well Head Completion: Unknown

Geology Remarks: 1. [FILL] [7] [7] 2. [TOP SOIL] [8] [1] 3. [COARSE SAND - GRAVEL] [23] [15] 4. [FINE SAND] [25] [2] 5. [CLAY] [28] [3] 6. [COARSE SAND - GRAVEL] [31] [3] 7. [CLAY] [38] [7] 8. [COARSE SAND AND GRAVEL] [60] [22]

Nearest source of possible contamination:

| Type | Distance | Direction |
|---|---|---|
| Unknown | 0.00 ft. | |
| Unknown | | |

Contractor Type: Unknown
Registration Number:
Business Name:
Business Address:

Drilling Machine Operator Name:

Employment: Unknown

WATER WELL CONTRACTOR'S CERTIFICATION:
This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

Signature of Registered Contractor — Date

General Remarks: LIMITED WELL LOG PROVIDED; DRILLERS STOPPED IN HARD SANDY CLAY; SCREEN TYPE LISTED AS EVERDUR LAYNE SHUTTER;
OTHER REMARKS

EQP 2017C (2/2000)

ATTENTION WELL OWNER: FILE WITH DEED

2/17/2000 13:03

# WATER WELL AND PUMP RECORD

Completion is required under authority of Part 127 Act 368 PA 1978.
Failure to comply is a misdemeanor.

Well ID: 39000002414 | Import ID: 39711134303

| Tax No: | Permit No: | County: Kalamazoo | Township: Cooper |
|---|---|---|---|

**Well ID: 39000002414**

Elevation: 751 ft
Latitude: 42.3423077917
Longitude: -85.5741822963

| Fraction: | Section: | Town/Range: | WSSN: | Source ID/Well No: |
|---|---|---|---|---|
| SE¼NE¼NE¼ | 34 | 01S 11W | 6280 | PARCHMENT WELL #3 |

Distance and Direction from Road Intersection: WSSNW 06280; 400' NORTH OF WELL #2

Well Owner: City Of Parchment

| Well Address: | Owner Address: |
|---|---|
| PARCHMENT WELL #3<br>PARCHMENT MI | PARCHMENT MI |

Drilling Method: Rotary
Well Depth: 58.00 ft. | Well Use: Type I public
Well Type: New | Date Completed: 4/11/1973

Casing Type: Unknown
Casing Joint: Unknown
Diameter: 34.00 in. to 38.00 ft. depth

Bore Diameter 1: 42.00 in. to 38.00 ft. depth
Bore Diameter 2:
Bore Diameter 3:
Height: 2.00 ft. above grade
Casing Fitting: None

Static Water Level: 8.00 ft. Below Grade(Not Flowing)
Yield Test Method: Unknown
Measurement Taken During Pump Test:
14.00 ft. after 0.00 hrs. pumping at 1,000.00 GPM

Abandoned Well Plugged: No
Reason for not plugging Well:
Abandoned well ID:

Screen Installed: Yes | Well Intake:
Filter Packed: No
Screen Diameter: 0.80 in. | Length: 15.00 ft.
Screen Material Type:
Slot: 60.00 in. Set Between 43.00 ft. and 58.00 ft.
Blank: 0.00 ft. Above
Fittings:
None

Well Grouted: Yes | Grouting Method: Unknown
No. of Bags: | Additives: None
Grouting Materials:
Neat cement | From 0.00 ft. to 38.00 ft.

Well Head Completion: Unknown

Nearest source of possible contamination:

| Type | Distance | Direction |
|---|---|---|
| Unknown | 0.00 ft. | |
| Unknown | | |

Drilling Machine Operator Name: PAUL WYATT

Employment: Unknown

Pump Installed: No | Pump Installation only: No
Pump Installation date: | HP:
Manufacturer: | Pump Type:
Model Number: | Pump Capacity: 1,000.00 GPM
Length of Drop Pipe: | Id of Well:
Diameter of Drop Pipe:
Draw Down Seal Used: No

Pressure Tank Installed: No
Pressure Tank Type:
Manufacturer:
Model Number: | Tank Capacity: Gallons
Pressure Relief Valve Installed: No

| Formation Description | Thickness | Depth to Bottom |
|---|---|---|
| Lithology Unknown Fil | 7.00 | 7.00 |
| Clay | 2.00 | 9.00 |
| Sand & Gravel Coarse | 13.00 | 22.00 |
| Clay | 10.00 | 32.00 |
| Sand & Gravel Coarse | 26.00 | 58.00 |

Geology Remarks: 1. [FILL] [7] [7] 2. [CLAY] [9] [2] 3. [COARSE SAND AND GRAVEL] [22] [13] 4. [CLAY] [32] [10] 5. [COARSE SAND AND GRAVEL] [58] [26]

Contractor Type: Unknown
Registration Number:
Business Name:
Business Address:

**WATER WELL CONTRACTOR'S CERTIFICATION:**
This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

Signature of Registered Contractor | Date

General Remarks: LIMITED WELL LOG PROVIDED; DRILLERS STOPPED IN CLAY
OTHER REMARKS

EQP 2017C (2/2000)

**ATTENTION WELL OWNER: FILE WITH DEED**

2/17/2000 13:03

DEQ

# WATER WELL AND PUMP RECORD

Completion is required under authority of Part 127 Act 368 PA 1978.

Failure to comply is a misdemeanor.

Well ID: 34000000015 | Import ID: 34060528301

| Tax No: | Permit No: | County: Ionia | Township: Portland |
|---|---|---|---|

| Fraction: | Section: | Town/Range: | WSSN: | Source ID/Well No: |
|---|---|---|---|---|
| NE¼ NW¼ SE¼ | 28 | 06N 05W | 5530 | PORTLAND #4 |

## Well ID: 34000000015

Elevation: 711 ft

Latitude: 42.877837

Longitude: -84.904404

Distance and Direction from Road Intersection: WSSN# 05530; GRAND RIVER FLOOD PLAIN - N SIDE OF CITY.

Well Owner: City Of Portland

| Well Address: | Owner Address: |
|---|---|
| PORTLAND #4<br>PORTLAND MI | PORTLAND |

Drilling Method: Unknown

Well Depth: 59.00 ft. | Well Use: Type I public

Well Type: New | Date Completed: 1/1/1942

Casing Type: Unknown
Casing Joint: Unknown
Diameter: 58.00 in. to 29.00 ft. depth
26.00 in. to 58.00 ft. depth

Bore Diameter 1:
Bore Diameter 2:
Bore Diameter 3:
Height: 1.50 ft. above grade
Casing Fitting: Drive shoe

Pump Installed: Yes | Pump Installation only: No
Pump Installation date: | HP:
Manufacturer: Other | Pump Type: Unknown
Model Number: | Pump Capacity: 450.00 GPM
Length of Drop Pipe: 0.00 ft. | Id of Well:
Diameter of Drop Pipe:
Draw Down Seal Used: No

Pressure Tank Installed: No
Pressure Tank Type:
Manufacturer:
Model Number: | Tank Capacity: Gallons
Pressure Relief Valve Installed: No

Static Water Level: 21.00 ft. Below Grade(Not Flowing)
Yield Test Method: Unknown
Measurement Taken During Pump Test:
30.00 ft. after 1.00 hrs. pumping at 450.00 GPM

Abandoned Well Plugged: No
Reason for not plugging Well:
Abandoned well ID:

| Formation Description | Thickness | Depth to Bottom |
|---|---|---|
| Lithology Unknown | 59.00 | 59.00 |

Screen Installed: Yes | Well Intake:
Filter Packed: No
Screen Diameter: 26.00 in. | Length: 15.00 ft.
Screen Material Type:
Slot: 0.00 in. Set Between 44.00 ft. and 59.00 ft.
Blank: 0.00 ft. Above
Fittings:
None

Well Grouted: Yes | Grouting Method: Unknown
No. of Bags: | Additives: None
Grouting Materials:
Unknown | From 0.00 ft. to 0.00 ft.

Well Head Completion: Unknown

Geology Remarks: 1. [LITHOLOGY UNKNOWN,BUT MDFH INDICATES DRIFT WELL] [59] [59]

Nearest source of possible contamination:

| Type | Distance | Direction |
|---|---|---|
| Unknown | 0.00 ft. | |
| Unknown | | |

Contractor Type: Unknown
Registration Number:
Business Name:
Business Address:

WATER WELL CONTRACTOR'S CERTIFICATION:
This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

Drilling Machine Operator Name:

Employment: Unknown

Signature of Registered Contractor | Date

General Remarks: ORIGINAL WELLID WAS 28001 AND USE WAS OTH; PUMP INST. LAYNE NORTHERN CO.
OTHER REMARKS: Pump Manufacturer: DEMING

EQP 2017C (2/2000)

ATTENTION WELL OWNER: FILE WITH DEED

2/17/2000 10:45

DEQ

# WATER WELL AND PUMP RECORD

Completion is required under authority of Part 127 Act 368 PA 1978.

Failure to comply is a misdemeanor.

Well ID: 34000000016 | Import ID: 34060628302

| Tax No: | Permit No: | County: Ionia | Township: Portland |
|---|---|---|---|

| Fraction: | Section: | Town/Range: | WSSN: | Source ID/Well No: |
|---|---|---|---|---|
| NE¼ NW¼ SE¼ | 28 | 06N 05W | 5530 | PORTLAND #5 |

## Well ID: 34000000016

Elevation: 701 ft

Latitude: 42.87767

Longitude: -84.902027

Distance and Direction from Road Intersection: WSSNW 05530; KENT ST.

Well Owner: City Of Portland

| Well Address: | Owner Address: |
|---|---|
| PORTLAND #5<br>PORTLAND MI | PORTLAND |

Drilling Method: Unknown

Well Depth: 78.00 ft. | Well Use: Type I public

Well Type: New | Date Completed: 1/1/1954

Casing Type: Unknown
Casing Joint: Unknown
Diameter: 12.00 in. to 58.00 ft. depth

Bore Diameter 1:
Bore Diameter 2:
Bore Diameter 3:
Height: 0.00 ft. above grade
Casing Fitting: Drive shoe

Static Water Level: 30.00 ft. Below Grade(Not Flowing)
Yield Test Method: Unknown
Measurement Taken During Pump Test:
39.00 ft. after 0.00 hrs. pumping at 0.00 GPM

Abandoned Well Plugged: No
Reason for not plugging Well:
Abandoned well ID:

Screen Installed: Yes | Well Intake:
Filter Packed: No
Screen Diameter: 0.00 in. | Length: 20.00 ft.
Screen Material Type:
Slot: 0.00 in. Set Between 0.00 ft. and 0.00 ft.
Blank: 0.00 ft. Above
Fittings:
None

Well Grouted: No | Grouting Method:
No. of Bags: | Additives:
Grouting Materials:

Well Head Completion: Unknown

Nearest source of possible contamination:

| Type | Distance | Direction |
|---|---|---|
| Unknown | 0.00 ft. | |
| Unknown | | |

Drilling Machine Operator Name:

Employment: Unknown

Pump Installed: Yes | Pump Installation only: No
Pump Installation date: | HP:
Manufacturer: Other | Pump Type: Unknown
Model Number: | Pump Capacity: 650.00 GPM
Length of Drop Pipe: 0.00 ft. | Id of Well:
Diameter of Drop Pipe:
Draw Down Seal Used: No

Pressure Tank Installed: No
Pressure Tank Type:
Manufacturer:
Model Number: | Tank Capacity: Gallons
Pressure Relief Valve Installed: No

| Formation Description | Thickness | Depth to Bottom |
|---|---|---|
| Lithology Unknown | 78.00 | 78.00 |

Geology Remarks: 1. [LITHOLOGY UNKNOWN][78][78]

Contractor Type: Unknown
Registration Number:
Business Name:
Business Address:

WATER WELL CONTRACTOR'S CERTIFICATION:
This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

Signature of Registered Contractor | Date

General Remarks: ORIGINAL WELLID WAS 28002 AND USE WAS OTH; PUMP INST: LAYNE NORTHERN
OTHER REMARKS: Pump Manufacturer: DEMING

EQP 2017C (2/2000)

ATTENTION WELL OWNER: FILE WITH DEED

2/17/2000 10:45

# WATER WELL AND PUMP RECORD

Completion is required under authority of Part 127 Act 368 PA 1978.

Failure to comply is a misdemeanor.

Well ID: 34000000017 Import ID: 34060528303

| Tax No: | Permit No: | County: Ionia | Township: Portland |
|---|---|---|---|

| Fraction: | Section: | Town/Range: | WSSN: | Source ID/Well No: |
|---|---|---|---|---|
| NW¼ NW¼ SE¼ | 28 | 06N 05W | 6530 | PORTLAND #6 |

## Well ID: 34000000017

Elevation: 712 ft

Latitude: 42.878045

Longitude: -84.906621

Distance and Direction from Road Intersection: WSSN# 06530; 54FT N OF C&O RR R/W 500FT W OF #4 WELL.

Well Owner: City Of Portland

Well Address:
PORTLAND #6
PORTLAND MI

Owner Address:
PORTLAND MI

Drilling Method: Cable Tool
Well Depth: 79.00 ft. | Well Use: Type I public
Well Type: New | Date Completed: 1/11/1967

Casing Type: Unknown
Casing Joint: Unknown
Diameter: 30.00 in. to 20.00 ft. depth
16.00 in. to 54.00 ft. depth

Bore Diameter 1: 34.00 in. to 0.00 ft. depth
Bore Diameter 2:
Bore Diameter 3:
Height: 2.00 ft. above grade
Casing Fitting: None

Pump Installed: Yes | Pump Installation only: No
Pump Installation date: | HP:
Manufacturer: Other | Pump Type: Unknown
Model Number: | Pump Capacity: 0.00 GPM
Length of Drop Pipe: 0.00 ft. | Id of Well:
Diameter of Drop Pipe:
Draw Down Seal Used: No

Pressure Tank Installed: No
Pressure Tank Type:
Manufacturer:
Model Number: | Tank Capacity: Gallons
Pressure Relief Valve Installed: No

Static Water Level: 19.00 ft. Below Grade(Not Flowing)
Yield Test Method: Unknown
Measurement Taken During Pump Test:
38.00 ft. after 0.00 hrs. pumping at 0.00 GPM

Abandoned Well Plugged: No
Reason for not plugging Well:
Abandoned well ID:

| Formation Description | Thickness | Depth to Bottom |
|---|---|---|
| Sand & Boulders | 7.00 | 7.00 |
| Gravel Sandy | 18.00 | 25.00 |
| Sand | 20.00 | 45.00 |
| Sand W/Gravel Fine | 5.00 | 50.00 |
| Gravel | 25.00 | 75.00 |
| Sand & Gravel Fine Fine | 4.00 | 79.00 |

Screen Installed: Yes | Well Intake:
Filter Packed: No
Screen Diameter: 12.00 in. | Length: 25.00 ft.
Screen Material Type:
Slot: 70.00 in. Set Between 54.00 ft. and 79.00 ft.
Blank: 0.00 ft. Above
Fittings:
None

Well Grouted: Yes | Grouting Method: Unknown
No. of Bags: | Additives: None
Grouting Materials:
Neat cement | From 0.00 ft. to 40.00 ft.

Well Head Completion: Unknown

Geology Remarks: 1. [SAND BOULDERS] [7] [7] 2. [SANDY GRAVEL] [25] [18] 3. [SAND] [45] [20] 4. [SAND & FINE GRAVEL] [50] [5] 5. [GRAVEL] [75] [25] 6. [SAND, FINE GRAVEL] [79] [4]

Nearest source of possible contamination:

| Type | Distance | Direction |
|---|---|---|
| Unknown | 0.00 ft. | |
| Unknown | | |

Contractor Type: Unknown
Registration Number:
Business Name:
Business Address:

Drilling Machine Operator Name: STEADMAN

Employment: Unknown

WATER WELL CONTRACTOR'S CERTIFICATION:
This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

Signature of Registered Contractor Date

General Remarks: ORIGINAL WELLID# WAS 28003; WELL LOG 67A
OTHER REMARKS: Pump Manufacturer: DEMMING

EQP 2017C (2/2000)

ATTENTION WELL OWNER: FILE WITH DEED

2/17/2000 10:45

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