Minnesota Pollution Control Agency

Endocrine Disrupting Compounds

A Report to the Minnesota Legislature

January 15, 2008

Acknowledgments

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This Legislative report was completed by the MPCA to fulfill the requirements of the 2007 Minnesota Session Laws Chapter 57:

Sec. 160. ENDOCRINE DISRUPTOR REPORT.
(a) The commissioner of the Pollution Control Agency, in consultation with the commissioner of agriculture, the commissioner of health, the commissioner of natural resources, the University of Minnesota, and the United States Environmental Protection Agency, shall prepare a report on strategies to address endocrine disruptors in waters of the state. The report shall include:
(1) a review of the current literature of known endocrine-disrupting compounds to determine which ones are most likely to be of significance to humans, fish, and wildlife in Minnesota;
(2) a review of scientific studies to determine whether these compounds have the potential to account for known effects on humans, fish, and wildlife in Minnesota;
(3) a review of the comparative risk posed by endocrine-disrupting compounds to the long-term viability of populations of fish and wildlife; and
(4) an evaluation of the practicability and the cost of prevention and remediation strategies for any endocrine-disrupting compounds found in clauses (1) and (2), as well as other potential endocrine disruptors.
(b) By January 15, 2008, the commissioner shall submit the report to the house of representatives and senate committees and divisions with jurisdiction over environment and natural resources policy and finance.

Hours to prepare this report: 700
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Executive Summary

This report to the Minnesota Legislature provides an overview of concerns associated with endocrine disrupting compounds (EDCs) in the environment.

The endocrine system is an internal chemical signaling system that regulates many important functions in humans, and in all other mammals, birds, fish, amphibians, and many invertebrates. Several effects of chemical exposure may be brought about through disruption of the endocrine system. Endocrine disruption is a *means* by which a chemical exerts an adverse effect or endpoint; it is not a discrete toxic effect of the chemical itself.

Suspected effects of EDCs have been observed in humans, fish, wildlife, and laboratory animals. A wide array of effects has been attributed to EDCs including impacts on growth, development, reproduction, changes in behavior, immune suppression, and cancer. Effects may occur at multiple levels of biological organization, including the molecular, cellular, tissue, individual organism, and population levels.

Population-level effects of EDCs have been observed in several species of fish and wildlife. Many of the prominent examples of population-level impacts have been associated with exposure to organochlorine (e.g., polychlorinated biphenyls, DDT, etc.) and organometallic (e.g., tributyltin) compounds, many of which are now banned in several countries. Synthetic estrogen found in birth control pills may also pose a risk to fish populations at concentrations found in the environment.

As we strive to understand how EDCs enter and move in the environment, it is important to note that EDCs are not a single, discrete class of chemicals. Known and potential EDCs exist among many classes of chemicals including pharmaceuticals and personal care products, general anthropogenic (man-made) compounds, pesticides, biogenic (naturally occurring) compounds, and inorganics and organometallic compounds. Currently, there are more than 87,000 chemicals produced and used worldwide and more are being produced all the time. Many of these chemicals may have endocrine-disrupting potential.

Effectively managing environmental contamination by EDCs is difficult and complex. Due to the widespread, continual, low-level contamination associated with EDCs, reduction in use and release of EDCs will likely be more effective in reducing environmental contamination than remediation. Upgrading wastewater treatment facilities to remove more potential EDCs, product stewardship, and educating consumers about ways to minimize their exposure may reduce the impact of EDCs on the environment and human health.

The potential for EDCs to have long-term effects on both humans and wildlife is of global concern. While there are still many unanswered questions, the hypothesis that chemicals can have an adverse impact on endocrine function in humans, fish and wildlife has been corroborated by laboratory and field research. Ongoing research is needed to better understand the potential long-term ecological effects of EDCs in the environment.

Introduction

Purpose

The Minnesota Pollution Control Agency (MPCA) prepared this report to the Legislature on endocrine disrupting compounds, as directed by statute enacted in 2007. The report provides:

- a brief description of the endocrine system and how it works,
- a review of the potential effects of EDC exposure on humans, fish, and wildlife,
- a review of risk to long-term fish and wildlife population viability,
- a review of the current state of knowledge of EDCs, and
- an evaluation of prevention and remediation strategies for EDCs in the environment.

This report should be regarded as a general overview of EDCs in the environment aimed at providing a basis for continued discussion of endocrine disrupting compounds in Minnesota. The limited scope and timeframe of this report precludes a discussion of every known, potential, or suspected EDC and their potential effects, although several such extensive reviews are referenced. Agency staff consulted with federal, state and university scientists (as noted below) in preparing this report, and reviewed a total of 139 scientific papers and sources, which are listed at the end. Readers should keep in mind that the scientific literature around the broad subject of endocrine disruption is enormous, and it grows and changes with completion of new studies.

Definition of Endocrine Disrupting Compounds (EDCs)

In order to facilitate meaningful discussion it was necessary to develop a working definition of what constitutes an EDC (see Appendix A). The MPCA helped organize a meeting of twenty-three Minnesota researchers from four federal agencies (EPA, US Geological Survey, US Fish and Wildlife Service, National Park Service), four state agencies (MPCA, Minnesota Department of Health, Minnesota Department of Agriculture, Minnesota Department of Natural Resources), and three universities (University of Minnesota, St. Cloud State University, University of Nebraska) to discuss and formulate the following definition:

"An EDC is an anthropogenic* chemical [human-made compound or natural compounds at unnatural concentrations due to human activity] that may have an *adverse* effect on reproduction or development, mediated directly through the endocrine system of fish, wildlife, and humans."

While differing in its scope, this definition is in general agreement with definitions previously set forth by other agencies including the EPA, European Commission, Swedish Environmental Protection Agency and the World Health Organization (Appendix C).

*A glossary of acronyms, terms, and units is included as Appendix B.

Endocrine System

The endocrine system is a complex internal chemical signaling system composed of ductless glands, organs and tissues that secrete hormones into the bloodstream (Fig. 1). Hormones are chemical messengers that are critical to the regulation of many bodily processes, including maintenance of internal equilibrium, growth and development, metabolic processes, and sexual differentiation [1]. The endocrine system produces both non-steroid and steroid hormones. Non-steroid hormones are water-based molecules that bind to receptors on cell membranes to elicit a response within the cell. Steroid hormones are lipid-based molecules that bind to receptors within the nucleus of a cell where they exert an effect by activating or inhibiting mRNA transcription (an intermediate step leading to gene expression) and protein production [2]. A receptor is a protein that is located in the nucleus of a cell or on a cell membrane that can bind with a specific molecule (i.e. a hormone).

In addition to having a direct effect on a target tissue, hormones produced by one gland can regulate the function of another gland and the function of other systems as well. The nervous system interacts with the endocrine system via the hypothalamus, the central gland of the endocrine system. The hypothalamus regulates hormone release throughout the endocrine system of glands through a cascade of stimulating and releasing hormones and in turn is up- and down-regulated through feedback loops that utilize blood hormone concentrations as indicators of glandular activity. One example of this is the hypothalamus-pituitary-gonadal axis [2]. The hypothalamus produces gonadotropin-releasing hormone that stimulates the pituitary to release gonadotropins; the gonadotropins then stimulate the follicle cells in ovaries to produce and release estrogen in females and the Leydig cells of the testis to produce testosterone in males. It follows, then, that disruption of one hormone or gland could have an effect on the entire endocrine system.

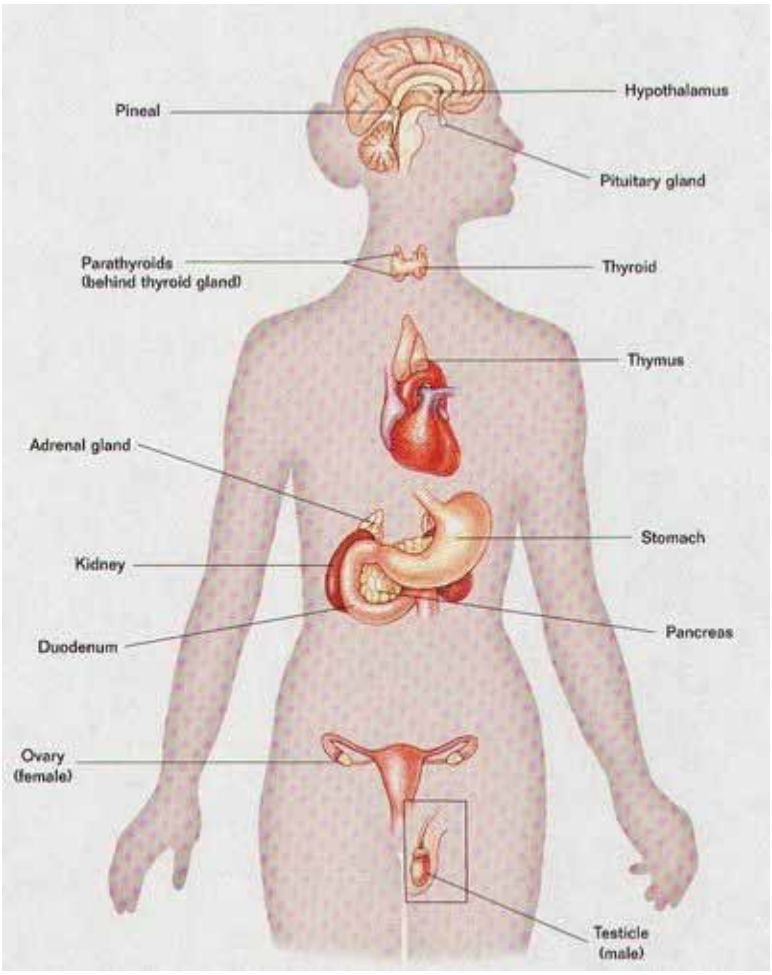

Figure 1. Human Endocrine System [3].

All vertebrates (organism with a backbone) and many invertebrates (organism without a backbone) have endocrine systems that control biological processes using essentially the same strategy but with different components [4]. Estrogens, androgens, and progestins are among the most prominent sex steroid hormones present in all vertebrates (Table 1) and some invertebrates [5]. Sex determination, and sexual development and differentiation are the primary functions of steroid hormones; sex steroids, in addition to other steroid hormones, also affect growth, metabolism, and brain development [2]. Androgens and estrogens have similar functions in all classes of vertebrates [5].

Non-steroid hormones are also critical in the regulation of a number of bodily processes. For example, thyroid hormones play an important role in metabolism, brain development, and growth [1]. Hypothalamic hormones in the brain regulate pituitary function as well as maternal behavior, metabolism, and blood pressure [1]. The pituitary gland controls sex organ function, thyroid function, some aspects of pregnancy and childbirth, and growth and metabolism [1]. The functional interrelationship between different glands and hormones makes it important to consider the effects of disruption of all hormones, not just steroid hormones. There are many other non-steroid hormones including amines (epinephrine and norepinephrine), peptides

(oxytocin), proteins (insulin, growth hormone), and glycoproteins (follicle-stimulating hormone, thyroid-stimulating hormone).

Table 1. Five major groups of vertebrate steroid hormones and their functions.

Steroid Hormone Classification	Origin	Function
Estrogens	Adrenal cortex and gonads	Female sex determination Maturation
Androgens	Adrenal cortex and gonads	Male sex determination Maturation
Progestins	Ovaries and placenta	Menstrual cycle Pregnancy
Mineralocorticoids	Adrenal cortex	Salt and water balance
Glucocorticoids	Adrenal cortex	Metabolism Decreases inflammation Mediates stress response

What is Endocrine Disruption?

Some chemicals are capable of mimicking or blocking normal hormonal function in animals and humans in a process known as endocrine disruption. When a chemical binds with a hormone receptor it can elicit a particular response. Some chemicals may bind with the receptor to block normal hormonal action, or trigger an unexpected response (Fig. 2). Endocrine disruption can also occur when exposure to a chemical alters normal hormone production, metabolism, or organ system interactions [6]. It is important to note that endocrine disruption is not a discrete toxic effect; rather it is a means by which a toxic effect may occur. It is also important to note that, while EDCs can cause reproductive and developmental toxicity, not all reproductive or developmental toxins are EDCs.

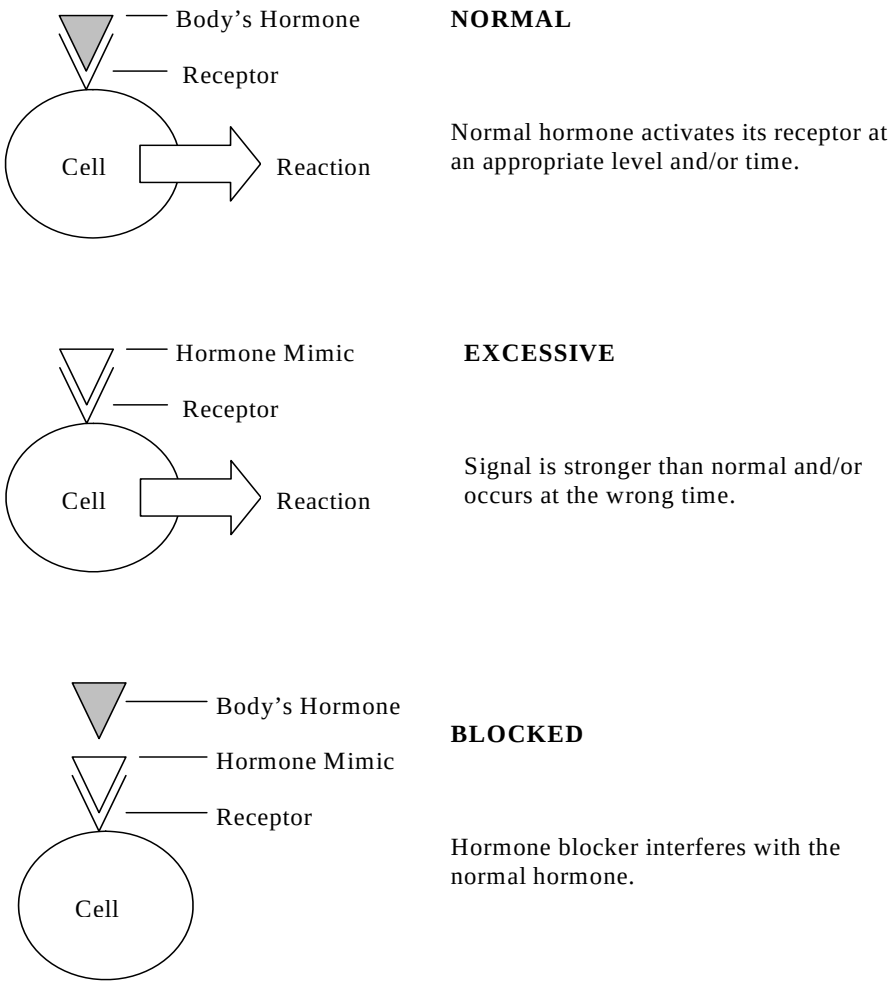

Figure 2. Modes of action for hormones and EDCs [7].

Some EDCs (particularly synthetic estrogens and androgens) are presumed to be active at levels similar to those of circulating hormones, as low as parts per trillion [8]. When the effects of chemical exposure do not follow a linear dose-response curve, it is called a non-monotonic response (Fig. 3). For some chemicals, greater effects may be seen at low and high doses, with reduced effects occurring at intermediate doses (Fig. 3b). Other chemicals may produce greater effects in the intermediate dose range and reduced effects at lower and higher doses (Fig. 3c). This represents a shift from the long-held paradigm of "the dose makes the poison" and has important implications for future research. The potential for low-dose effects is rather controversial because many studies that have shown low-dose effects have not been reproducible. The US National Toxicology Program evaluated the low-dose effects of several chemicals in 2001 [9]. The panel concluded that although low-dose effects have been seen in some studies, the results cannot always be replicated and that standard testing protocol should be reevaluated.

The timing of exposure may be as important or more important than the dose. A great deal of research has focused on determining the effects of low-level exposure to EDCs during critical stages of development [10-13] because many EDCs may not have impacts if exposure occurs during non-developmental stages of an individual's life.

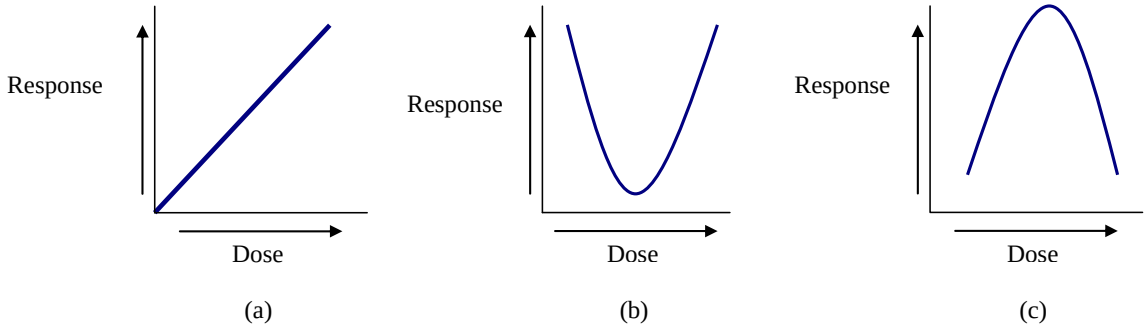

Figure 3. Traditional linear dose-response curve (a) in which the effects of a chemical increase in response to increased doses. U-shaped non-monotonic dose-response curve (b) in which very low and very high doses produce a greater response. Inverted u-shaped non-monotonic dose-response curve (c) in which intermediate doses produce the greatest response.

A further complication is that humans, fish, and wildlife are exposed to mixtures of chemicals rather than one chemical at a time. The effects of exposure to chemical mixtures are unknown. There are potential synergistic, additive, or inhibitory effects that could affect outcomes of exposure. Although some recent research has addressed the effects of chemical mixtures it is unlikely that all the possible effects of all possible chemical mixtures could ever be thoroughly evaluated. Assessing the effects of chemical mixtures is a major challenge facing toxicologists and regulators alike. In spite of these challenges, it is important to continue to look for effective ways of managing exposure to EDCs.

Why Should We Care?

EDCs are found virtually everywhere in the environment, and the exposure of humans, fish and wildlife to them is widespread. However, the consequences of exposure to EDCs in the environment are largely unknown for free-living organisms. While several effects of exposure to EDCs have been documented in laboratory studies, it is very difficult to conclusively establish a cause-and-effect relationship in nature. It is also difficult to extrapolate effects in laboratory animals to humans or animals in the wild. In spite of these challenges, there is growing evidence that EDCs can impact humans and wildlife. Diminished intelligence, altered behavior and development, and decreased immunity to disease are just a few of the consequences that have been associated with human exposure to EDCs. In animals, several effects of exposure to EDCs have been observed including reduced reproductive success, reduced survival, altered sex ratios, occurrence of intersex, and developmental abnormalities. Species that are already stressed due to other environmental factors could be further impacted by EDCs, which may result in species decline.

With so many complexities and unknowns regarding the consequences of exposure of free-living organisms to EDCs, further study is needed to better understand the long-term implications. This ongoing need for further study should not, however, preclude consideration of strategies to minimize or avoid environmental releases of EDCs. Such strategies are discussed in the Practicability and Cost of Prevention and Remediation section of this report.

Potential Effects on Humans, Fish, and Wildlife

Effects of exposure to EDCs have been observed in humans, fish, wildlife, and laboratory animals. A wide array of effects have been attributed to EDCs including impacts on growth, development, reproduction, changes in behavior, immune suppression, and cancer [2, 6]. Effects may occur at multiple levels of biological organization, from the molecular level to the population level.

Molecular-Level Effects

At the molecular level, EDCs can bind to nuclear receptors, including estrogen, androgen, and thyroid receptors [2]. Once an EDC is bound to a receptor it can stimulate mRNA transcription resulting in the production of specific proteins. For example, vitellogenin (VTG) is an egg yolk precursor that is typically only produced in female egg-laying animals. VTG is commonly used as an indicator or biomarker to detect exposure to environmental estrogens [14, 15], because exposure of male fish to estrogenic compounds in water can induce VTG production in males which they do not normally produce [16, 17]. Male walleye collected downstream of the Metropolitan Council Environmental Services wastewater treatment plant in St. Paul had measurable levels of VTG as well as decreased serum testosterone and increased 17β-estradiol (E2) [18] as a result of exposure to estrogenic effluent. A recent study in the Mississippi River detected VTG in three species of male fish (Fig. 4) [19].

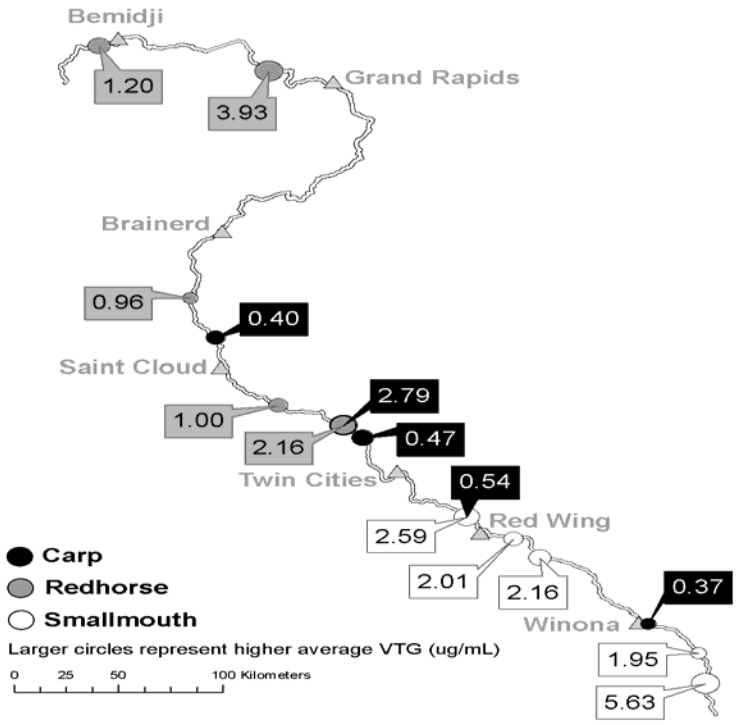

Figure 4. Highest plasma vitellogenin (VTG) averages in male fish (carp, redhorse, and smallmouth bass) [19].

Several compounds have been shown to have varying effects at the molecular level. For example, acetochlor (a herbicide used on corn) can accelerate thyroid hormone-induced metamorphosis in tadpoles [20]. Acetochlor may also effect the expression of thyroid receptors in the brain of frog tadpoles (*Rana catesbeiana*) [21]. Several organochlorine compounds as well as nonylphenol (an industrial surfactant) can significantly inhibit binding of the organism's natural androgens and estrogens to their respective receptors *in vitro* (a controlled experiment conducted outside of a living organism) [22]. Bisphenol A (a compound found in many plastics) was shown to suppress gene expression by displacing thyroid hormone (T_3) from the thyroid receptor [23]. Endocrine disrupting chemicals have also been shown to interfere with plant signaling by inhibiting the production of plant estrogens that legumes use to attract soil bacteria for nitrogen fixation to stimulate plant growth [24].

Cellular-Level Effects

Effects at the molecular level could lead to changes in cellular activity. Most biological processes at the cellular level take place under the influence of enzymes. Changes in enzyme (protein that accelerates chemical reactions) activity at the cellular level may occur as a result of exposure to EDCs. For example, aromatase is an enzyme that converts testosterone to estrogen. If aromatase production is stimulated (induced), excess estrogen will be produced; if it is inhibited testosterone will remain unaltered, resulting in a shift in normal hormone concentrations.

The ability of EDCs to alter aromatase activity has been studied by several researchers [25-29]. The herbicides atrazine, simazine, and propazine induced aromatase in a human cancer cell line [29], and several fungicides inhibited aromatase activity in the same cell line [30]. Increased levels of estrogen have been associated with an increased risk of cancer, so there may be an association between aromatase induction and increased cancer risk *in vivo* (in a living animal). Indeed, some drugs used in the treatment of breast cancer are aromatase inhibitors.

Tissue-Level Effects

Tissue-level effects may be observed as a result of changes in cellular activity. For example, permanent anatomical changes in several species have been associated with changes in aromatase activity. Suppression of aromatase following exposure of female marine snails to tributyltin (a biocide in paint used to treat boat hulls) was correlated with a condition known as imposex in which females have both male and female sex organs (refer to the section on Population-Level Effects for more detail) [31]. It has been hypothesized that demasculinized larynges (voiceboxes) and hermaphroditism (condition of having both male and female reproductive organs) observed in male frogs following exposure to low levels of atrazine (≥ 0.1 ppb) may be caused by aromatase induction [26].

Intersex is a term used to describe a tissue-level response in which male fish have female oocytes (eggs) present in their testes and/or the reproductive ducts of males have female characteristics [32]. Varying levels of intersex have been noted in wild fish. In mild cases of intersex, a few primary and secondary oocytes may be spread throughout the testes, while in more severe cases large areas of distinct ovarian tissue may present [32].

To date, very little research has been conducted to determine whether the occurrence of intersex can reduce the reproductive potential of an organism. The sperm of severely feminized wild roach (*Rutilus rutilus*) exhibited a 50% decrease in sperm motility and a 75% decrease in fertilization success compared to normal males [33]. A more recent comprehensive study in the Mississippi River did not observe any intersex fish, but did observe widespread vitellogenin induction [19].

Organism-Level Effects

Adverse effects of EDCs such as reduced fertility and reproductive capacity would first occur at the level of the individual organism before being noticed at the population level (Fig. 5).The possibility that the occurrence of intersex can reduce the reproductive capacity of fish is one example of how EDCs may have impacts on the organism as a whole and perhaps on populations of individuals as well.

Changes in the behavior of exposed individuals can also reduce their reproductive success. Male fathead minnows exposed to either estrogenic wastewater effluent or estradiol were able to spawn successfully but were unable to compete with control males for nest sites or females [16] resulting in almost total reproductive failure.

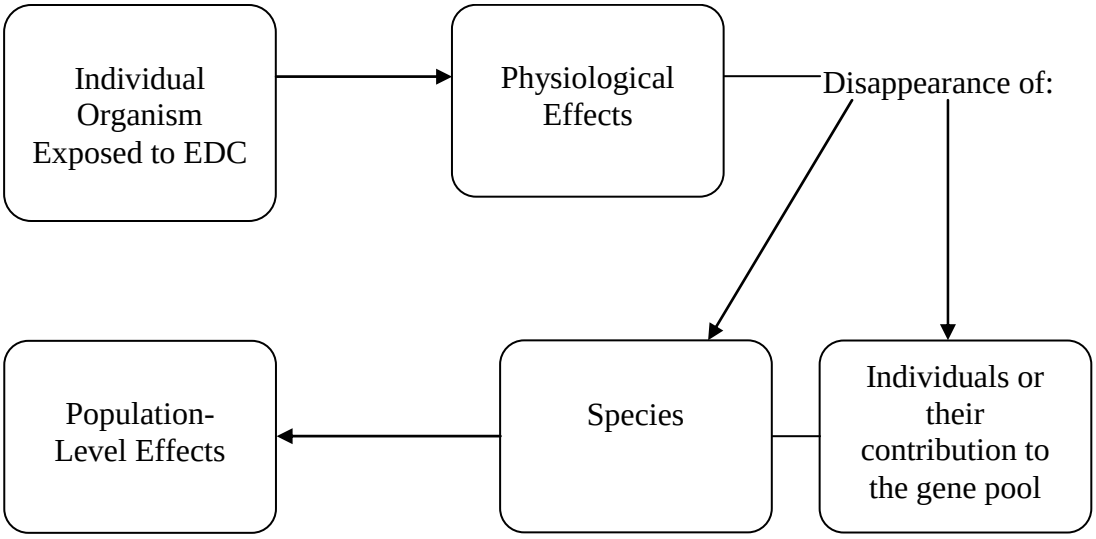

Figure 5. Effects in individuals can lead to effects in populations (adapted from [34]).

Transgenerational effects were observed following exposure of pregnant female rats to vinclozolin (a fungicide) and methoxychlor (an insecticide) during a critical period of fetal sexual development [35]. Adult males in the first generation (F_1) had reduced sperm viability and increased incidence of infertility. These effects were transferred to all subsequent generations studied (through F_4) [35, 36] indicating that the DNA of the F1 generation had been altered by chemical exposure in the womb. These findings suggest potential for long-term ecological implications of EDCs. If exposure to EDCs can change the genetic makeup of individuals, genetic diversity and adaptability at the population level may be adversely affected.

Population-level Effects

Population-level effects of EDCs have been observed in several species of fish and wildlife. The most prominent examples have been associated with exposure to organochlorine and organometallic compounds, many of which are now banned in several countries [34, 37]. Exposure to a synthetic estrogen at concentrations found in the environment (i.e. environmentally relevant concentrations) has recently been shown to have effects on fathead minnow populations [38]. Several examples of endocrine effects at the population level are described below.

Fathead Minnows and Lake Trout
Environmentally relevant concentrations of ethinylestradiol (EE2, a synthetic estrogen found in birth control pills) were added to a lake in the Experimental Lakes Area (ELA) in Canada [38]. The food web, water chemistry, and limnological properties of these lakes are very well understood making it much easier to assess the impacts of chemical addition. While the addition of 6 nanograms EE2/L had no impact on the invertebrate species in the lake, the fathead minnow population crashed within 2 years due to a loss of the young-of-the-year. This reproductive failure continued to impact the fathead minnow population for two years after the addition of EE2 was stopped. The fact that invertebrate prey species, the food source for the minnows, were not impacted indicates that fathead minnows were directly impacted by exposure to EE2 rather than a bottom-up food chain effect. Lake trout, however, were adversely affected by the loss of their prey species, the fathead minnow. When the minnow population crashed, the condition and fitness of the lake trout were negatively impacted. Two years after dosing with EE2 was discontinued, the fathead minnow population recovered while the lake trout population remained depressed. Lake trout are a long-lived species and will likely show a lag time in recovering from a loss of prey species.

Lake Trout
Native populations of Great Lakes lake trout collapsed in the 1950s. While some experts have cited over-fishing, habitat loss, and predation by sea lamprey as the cause of the collapse, there is evidence associating impaired reproduction in lake trout to exposure to 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD, hereafter referred to as dioxin) and dioxin-like polychlorinated biphenyl (PCB) congeners [8]. Blue sac disease, a condition characterized by abnormal fluid accumulation in the yolk sac, and increased early-life mortality have been associated with exposure to dioxin and PCBs in laboratory studies [37]. Although concentrations of PCBs and dioxins are now low enough in Lake Superior that this is no longer a concern, lake trout populations in Lake Ontario and possibly in Lake Michigan are thought to be impacted by the endocrine disrupting effects of exposure to PCBs and dioxin [39].

Colonial Fish-Eating Birds
Exposure to PCBs, dichloro-diphenyl-trichloroethane (DDT), and dichloro-diphenyl-dichloroethylene (DDE, a breakdown product of DDT) in the 1960s and 1970s resulted in severe deformities and increased mortality in colonial fish-eating birds (herring gulls, cormorants, terns) in the Great Lakes region [40, 41]. A consistent set of symptoms known as Great Lakes Edema, Mortality, and Embryo Deformity Syndrome is characterized by cardiac edema, and skeletal and beak malformations, and is correlated primarily with the bioaccumulation of dioxin-like PCB

congeners [42]. Female-female pairing and abnormal nesting behavior was observed in gulls living in DDT-contaminated areas [42]. This unusual behavior has been attributed to possible estrogenic effects of DDT in birds. In addition to DDT, other organochlorine pesticides that can impact avian reproduction include aldrin, dieldrin, endrin, toxaphene, chlordane, hexachlorobenzene, lindane, mirex, and kepone [42]. Although all of these pesticides are banned (except lindane which is severely restricted) in the U.S. [34], they are persistent in the environment and continue to be present in aquatic food webs [6].

Bald Eagles

The reproductive success of bald eagles in the Great Lakes region was severely affected by exposure to DDE [43, 44]. Prostaglandin (a hormone with a variety of strong physiological effects) synthesis is inhibited by DDE which results in eggshell thinning by limiting calcium deposition during eggshell formation [44]. While populations of bald eagles have increased since the ban of DDT in the 1970s, the recovery has not been uniform; as of 1995, populations around the Great Lakes continued to be impacted compared to interior populations [44]. The incidence of deformities such as crossed bills, bilateral foot deformities, and fused vertebrae has increased from 12.5 deformities per 10,000 chicks in the period from 1968 – 1989 to 42.3 deformities per 10,000 chicks (1990 – 1995) [44]. These deformities have been associated with exposure to dioxin-like PCB congeners.

Mink

Declines in populations of wild mink in the Great Lakes region led to the hypothesis that exposure to organochlorines in the food chain may result in reduced reproductive success [37]. Laboratory studies in which mink were fed Great Lakes fish resulted in impaired reproduction, reduced kit survival, and lower body weight of exposed kits compared to controls [45, 46]. Great Lakes fish are contaminated with a number of synthetic compounds, including PCBs [37]. A study by Aulerich and Ringer [47] showed that mink are particularly sensitive to PCBs; mink fed PCB-contaminated coho salmon from Lake Michigan exhibited symptoms similar to those of mink given diets supplemented with PCBs [47].

American Alligators

Population decline, decreased clutch viability and abnormal sex organ development in American alligators in Lake Apopka (central Florida) were attributed to an extensive spill of the pesticides dicofol and DDT [48]. DDT and dicofol have the ability to bind to the estrogen receptor to produce estrogenic effects [8]. Female juvenile alligators had elevated levels of plasma 17β-estradiol and abnormal ovaries, while male juvenile alligators had significantly lower levels of plasma testosterone, abnormal testes, and unusually small penises compared to control specimens. Changes in the gonads of juvenile alligators appeared to be permanent, which may explain why alligator populations continue to be low years after contamination [48].

Marine Snails

A prominent example of endocrine effects at the population level is the masculinization of female marine snails following early-life exposure to tributyltin, a biocide in paint used to treat boat hulls [31]. Tributyltin acts as an aromatase inhibitor, reducing estrogen production by inhibiting the conversion of testosterone to estrogen [31]. Female snails exposed to tributyltin exhibited an irreversible reproductive abnormality known as imposex in which females

developed male sex organs as well as female sex organs; the male structures often impeded normal female reproductive function leading to impaired reproductive ability. Abundant field evidence has linked tributyltin to imposex and the decline of marine snails [31]. Marine snail populations eventually recovered following a ban of tributyltin in many countries [37].

Amphibians

Several studies have documented the worldwide decline of amphibian populations [8, 27, 49, 50]. A number of hypotheses have been suggested to explain this phenomenon including habitat destruction and global climate change [51], increased exposure to ultraviolet light [50], and exposure to environmental contaminants [8, 27, 50]. Recently, a fungus was found to cause mortality in frogs and may be a significant contributor to worldwide amphibian declines [52]. The endocrine system drives much of the immune response of an organism. If the immune system is weakened by endocrine disruption, an organism may be more susceptible to infections, fungi, and parasites than an unexposed organism. At this time it is not clear what impact EDCs may be having on amphibians at the population level. However, there is growing evidence that EDCs, particularly pesticides, may be impacting amphibian metamorphosis, reproduction, and survival [26, 27, 53].

It should be noted that a direct causal relationship between a specific chemical and impact in the wild is very difficult to establish conclusively, and the modes of action are complex and poorly understood. Many environmental contaminants are ubiquitous and contamination occurs as mixtures, making it particularly difficult to identify the effects of a single compound [34]. Furthermore, interactions between chemicals can produce unexpected, unknown effects [6].

Many factors unrelated to endocrine disruption (i.e. food availability, disease, habitat loss) can have an impact on wildlife reproduction, development, growth, and survival [37]. It can be very difficult in some instances to differentiate between potential endocrine effects and effects caused by other environmental stressors. On the other hand, it is possible that exposure to EDCs may exacerbate the effects of non-chemical stressors, which may add another level of stress to already compromised species.

Endocrine Disrupting Compounds: What are they and where are they found?

EDCs are not a discrete class of chemicals. Known and potential EDCs include many classes of chemicals including pharmaceuticals and personal care products, general anthropogenic compounds, pesticides, biogenic compounds, and inorganics and organometallic compounds. Currently, there are more than 87,000 chemicals produced and used worldwide, many of which may have endocrine disrupting potential [54]. While there is clearly a concern about the possible adverse effects of EDCs, many of these compounds are used because of their benefits to society.

The number and diversity of chemicals makes identifying those with endocrine disrupting potential very difficult, because there is no scientific consensus on what makes a chemical an EDC. The complexity of the endocrine system and the multitude of possible interactions of a chemical (or chemical mixtures) with the endocrine system complicates matters further. More efficient, accurate, and comprehensive screening tools are needed to properly identify and evaluate potential EDCs.

Several lists of potential and known EDCs have been assembled by various agencies and organizations (Appendix D). While there is some overlap among these lists, no two lists are exactly the same. The UK Institute for Environment and Health published a list of 966 known and potential EDCs that is a compilation of several previously published lists [55]. The lack of a definitive list of EDCs underscores the many complications associated with determining a chemical's potential to disrupt hormonal systems in humans and wildlife. Also, any list published today would require continuous updating as more EDCs are identified over time. For these reasons as well as a lack of time, this report will not establish a list of EDCs specific to Minnesota. The following discussion provides a description of some EDCs in each of the five chemical categories described above.

Pharmaceuticals and Personal Care Products (PPCPs)

Pharmaceuticals and personal care products (PPCPs) comprise a class of potential EDCs that includes synthetic hormones, over-the-counter and prescription medication, and ingredients found in cosmetics, toiletries, detergents, and cleaning products. Unlike many other potential EDCs, pharmaceuticals are purposely designed to have a biological effect. Exposure of humans, fish and wildlife to low levels of PPCPs is widespread as a result of intentional consumption or application to the skin and subsequent environmental release in wastewater effluents. A pharmaceutical may be of environmental concern if it is a high production volume chemical, is persistent in the environment, and has biological activity [56]. Although many of these compounds are not persistent, PPCPs may act like persistent compounds because of their continual release into the environment [57].

Steroid hormones, estrogens in particular, are among the most thoroughly studied EDCs. Estrone (E1), estradiol (E2), and estriol (E3) are examples of natural estrogens; ethinylestradiol (EE2) is a synthetic estrogen found in birth control pills. Diethylstilbestrol (DES) is a potent synthetic estrogen that was given to women to prevent miscarriage and morning sickness. Natural estrogens have been classified as known human carcinogens [58], thus it is likely that synthetic estrogens may have similar carcinogenic effects. Prenatal exposure to both natural and synthetic estrogens has been associated with increased occurrence of vaginal and breast tumors in humans and uterine tumors in animals [58]. Exposure to natural and synthetic steroid hormones will likely elicit an effect because these hormones can readily bind to receptors to activate transcription and protein synthesis.

DES is one of the most extensively studied synthetic estrogens. While it is not an environmental contaminant and is no longer prescribed to women, it is a useful model in determining the potential effects of other estrogenic EDCs [59]. Several adverse effects have been observed in humans and laboratory animals following *in utero* (in the womb) exposure to DES. In females, vaginal, cervical, and ovarian cancer, infertility, and abnormal uterine development have been observed. Testicular cancer, hypospadias, cryptorchidism (undescended testicles), and impaired semen quality and quantity have been observed in exposed males [6]. The effects of DES have been thoroughly reviewed elsewhere [6, 59].

Synthetic androgens are also released into the environment. For example, trenbolone is a synthetic testosterone administered to cattle to promote growth. It is relatively stable in animal waste and is more potent than endogenous (naturally produced in the body) testosterone [60].

Contaminated effluent can enter surface waters directly or in runoff providing a possible means of exposure to aquatic animals [60]. Researchers have observed alterations in secondary sexual characteristics and reduced reproductive capacity in fish in waters receiving feedlot effluent [60, 61]. Female fathead minnows exhibited masculine secondary sexual characteristics upon exposure to low levels of 17β-trenbolone [60]. Also, female rats exposed *in utero* exhibited reproductive abnormalities as adults [61].

Several ingredients in cosmetics and other personal care products have been identified as potential EDCs. Parabens, siloxanes, phthalates, and musks have all been suggested as possible EDCs. Many ingredients in personal care products are high production volume chemicals that are used by people on a daily basis [62]. Routes of human exposure to personal care products differ from those of other EDCs in that many of these ingredients are applied to and absorbed through the skin [63]. Parabens are the most commonly used preservatives in cosmetic preparations. They have demonstrated estrogenic effects both *in vivo* and *in vitro,* are readily absorbed by the skin and have been detected in human breast cancer tissue [63]. Synthetic musks are fragrances used in perfumes, detergents, soaps and cosmetics. Musks are ubiquitous environmental contaminants that have been detected in human adipose tissue, surface water, mussels and shrimp [64], sewage sludge [65], and wastewater, surface water, and ground water [66]. The polycyclic musks AHTN (acetyl-hexamethyl-tetrahydro-naphthalene) and HHCB (hexahydrohexamethyl-cyclopentabenzopyran) can exert anti-estrogenic effects on human estrogen receptors [67]. An epidemiological study of women being treated for gynecological problems found a significant correlation between mild ovarian dysfunction and blood levels of musk ketone and musk xylene [68].

Although several pharmaceuticals have been identified in surface and ground water [69], to date very few have been identified as EDCs [62]. One type, the selective serotonin (a naturally-occurring neurotransmitter that regulates mood, among other things) reuptake inhibitors (SSRIs) fluvoxamine and fluoxetine are widely used prescription antidepressants. These have been shown to induce spawning in zebra mussels in the laboratory at very low concentrations within an hour of exposure [70]. More research needs to be conducted to determine the potential endocrine disrupting effects of other pharmaceuticals in the environment.

General Anthropogenic Compounds

It is difficult to categorize the wide variety of man-made, industrial-use compounds that are potential EDCs. Industrial chemicals that are known or potential EDCs include polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins and furans, plasticizers, alkylphenols, naphthols and naphthalenes, siloxanes, polynuclear aromatic hydrocarbons (PAHs) and others [55]. While many of these compounds are banned in the U.S., their persistence and bioaccumulative potential can lead to exposure via intake of contaminated food, air, and water [2, 6]. Also, several of these compounds are still widely used in the U.S. and the world and are likely contributing to the ongoing occurrence of EDCs in the environment.

PCBs and dioxins are known EDCs that have been implicated in a multitude of effects on both wildlife and humans. Both are persistent, bioaccumulative, toxic at low doses, and ubiquitous in the environment [6]. PCBs are environmental estrogens that were used in a number of industrial applications until their ban in 1977 [6]. Dioxins are the byproduct of incineration and industrial

processes; they can exert estrogenic, anti-estrogenic, androgenic and anti-androgenic effects depending on the dose, species, and timing of exposure [8]. A recent study that calculated hazard quotients (ratio of daily intake to reference dose) of organochlorine contaminants in human breast milk indicated that PCBs are the most critical breast-milk contaminant in the U.S. [71].

Bisphenol A (BPA, 2,2-bis(4-hydroxyphenyl)propane) is an industrial chemical that was shown to have estrogenic effects as early as 1936 [72]. It is the chemical building block of many plastics that are used in a number of consumer goods such as polycarbonate plastics, food can linings, white dental sealants, electrical sheathings, adhesives, and polyvinyl chloride, and is capable of leaching into food and water [73]. In 2003, more than 6.4 billion pounds of bisphenol A was produced worldwide, making it one of the highest-volume chemicals in production [10]. In a recent study of over 2,500 individuals over the age of 6, BPA was detected in the urine of 92.6% of the participants, indicating that human exposure to BPA is widespread [74]. Children had the highest concentrations, followed by adolescents and adults [74].

The primary route of exposure to BPA is via ingestion of contaminated food, but BPA can also be present in drinking water. Exposure to BPA has been associated with fetal toxicity [75], changes in maternal behavior [76], enlarged prostate [77], reduced sperm count [78], obesity and diabetes [79] in mice, and the proliferation of human breast cancer cells [80]. Several studies have indicated that BPA can exert effects at low doses, although this has been the subject of some debate [9, 10].

Phthalates are a large group of structurally similar compounds that have a number of uses in industrial and consumer products. They are used to make plastics soft, as solvents in perfumes, hairsprays and insect repellents, and are also used in floorings, paints, and adhesives [81]. Human exposure to phthalates is likely widespread and is a concern because phthalates can be absorbed through the skin, ingested with contaminated food or water, and can also enter the bloodstream directly via leaching from plastic IV bags during transfusion [81]. In a study of over 2,500 individuals from the U.S., breakdown products of phthaltes were detected in the urine of over 75% of the participants [81]. Phthalates may have a number of adverse effects in humans and laboratory animals including carcinogenicity (ability to cause cancer) and teratogenicity (ability to produce fetal malformations), and have been shown to damage DNA in sperm [81]. Exposure to phthalates has also been associated with the early onset of puberty and premature breast development in young girls [82] and abnormal sexual differentiation in male rats [83]. In 2007, California passed a bill to ban phthalates in children’s products.

Alkylphenol polyethoxylates (APEs) are non-ionic surfactants that have numerous agricultural, industrial and household applications in detergent, paints, fragrances, spermicides, and inert ingredients in some pesticide formulations. Nonylphenol and octylphenol are breakdown products of APEs that are commonly found in wastewater effluents [84, 85]. Alkylphenols were first shown to be estrogenic in 1938 [86]. Humans and wildlife are likely exposed to APs and their breakdown products due to their widespread presence in the environment. Nonylphenols have been detected in the atmosphere, which may be an important albeit less well-characterized route of exposure to these EDCs [87]. Exposure of fish to estrogenic APs has been shown to induce the production of vitellogenin [14, 16, 88, 89] an egg yolk precusor typically produced by

female egg-laying animals. Male fathead minnows that are exposed to alkylphenols are less likely to reproduce in a competitive mating scenario [16].

Pesticides

Several pesticides have been identified as known or potential EDCs, including some organochlorine pesticides, organophosphate pesticides, pyrethroids, herbicides, fungicides and carbamates. While most organochlorine pesticides have been banned or severely restricted, organophosphates are the most widely used insecticides in the U.S. and the world [90]. Several organophosphates have been identified as potential EDCs including acephate, chlorpyrifos, diazinon, dimethoate, malathion, and parathion [55]. Vinclozolin is a fungicide that has demasculinized male rats in laboratory expirments due to the fungicide's anti-androgenic activity [91]. Exposure to acetochlor in the laboratory may affect thyroid-hormone induced metamorphosis in frogs (*Xenopus laevis*) [20] and may induce anti-thyroid and mutagenic (able to cause genetic mutations) activity in rats [92]. The herbicide 2,4-D has also been identified as a potential EDC [55] although supporting data are very limited [93]. Please refer to Appendix E for more detailed information regarding pesticide sales, use, environmental distribution, and Best Management Practices in Minnesota.

DDT is an organochlorine pesticide that has been used extensively around the world. Although the use of DDT was banned in the United States and many other developed countries, it is still used in tropical regions to control mosquitoes that carry malaria. The World Health Organization is once again recommending the indoor use of DDT in regions where malaria transmission is high [94] which will increase the release of DDT into the environment. DDT, like many other persistent organic pollutants, can be found in remote regions of the world due to long-range atmospheric transport [95]. DDT and its breakdown products DDD and DDE are persistent, bioaccumulative toxics that have demonstrated endocrine disrupting effects in humans, wildlife, and laboratory animals. For example, p,p'-DDE has been associated with egg-shell thinning in the eggs of fish eating birds [43, 44], increased risk of breast cancer in women exposed to p,p'-DDT before the age of 14 [96], and abnormal development and sexual differentiation in mice exposed to o,p'-DDT [97].

Atrazine is a widely applied pre-emergent herbicide used in the production of corn. In 2005, atrazine was used on 24% of surveyed corn acres in Minnesota, a decrease of 6% compared to 2003 [98]. More than 1.8 million pounds of atrazine were sold in Minnesota in 2005, although it should be noted that all of the pesticide sold may not be used in the same year or may never be used in Minnesota [99].

Atrazine is a known EDC with demonstrated effects in animals and human cell lines at high concentrations. Male rats exposed to 100 and 200 mg/kg/day had decreased levels of testosterone and luteinizing hormone (a hormone necessary for proper reproductive function) and reduced prostate weight [100]. Altered hypothalamic control of luteinizing hormones was seen in female rats given a single dose of 300 mg atrazine/kg [101]. Larval gray tree frogs exposed to 200 – 2000 µg atrazine/L had reduced length and weight at metamorphosis compared to controls [102]. Two species of frogs (*Rana pipiens*, *Rana sylvatica*) and one toad (*Bufo americanus*) all showed an increase in larval deformities when exposed to relatively high levels of atrazine [103]. Atrazine also has been shown to induce aromatase in human adrenocortical carcinoma cells [29].

While most of the effects seen in laboratory studies are associated with relatively high doses, some effects have also been attributed to low-level exposure to atrazine. Gonadal abnormalities, including hermaphroditism, were seen in male African clawed frogs (*Xenopus laevis*) at concentrations of atrazine as low as 0.1 part per billion (ppb) [26]. In the same study, male frogs exposed to 1 ppb atrazine also had abnormally small voiceboxes which affects their ability to call a mate.

The finding of an association between female oocytes in male testes and low-level atrazine exposure has been very controversial and the focus of much debate. The EPA recently released a review of the effects of atrazine on amphibian gonadal development [104]. Although a total of 19 studies on gonadal development were initially reviewed, only one study (submitted by the registrant) met all of the design elements required by the EPA. Although this study suffered from a subset of contaminated controls, it was deemed to be of high quality by the reviewers. Contrary evidence was presented by a number of independent researchers, but EPA concluded that atrazine has no effects on amphibian gonadal development and that no further study is warranted. However, this is clearly an unresolved issue. The effects of atrazine on amphibian gonadal development are currently being analyzed by independent scientific advisory panels convened by the EPA; their final report on amphibian gonadal development is due in 2008.

Glyphosate is a widely used herbicide that may have endocrine disrupting effects. Roundup, a commercial formulation containing glyphosate and inert ingredients, disrupted aromatase activity and mRNA levels in human placental cells; the Roundup formulation was always more toxic than glyphosate alone [28] suggesting that increased endocrine activity may be due to the adjuvants (thought to be inert) in the formulation. Glyphosate may also disrupt the cell cycle in sea urchin eggs [105]. While there is limited evidence to conclusively determine the endocrine disrupting potential of glyphosate, its widespread use indicates that exposure of humans and wildlife is highly likely. Glyphosate was used on 48% of corn acres and 89% of soybean acres surveyed in Minnesota in 2005 [98]. Roundup is also used in residential applications. Further study is needed to determine the potential endocrine disrupting effects of glyphosate.

Biogenic Compounds

Several non-steroidal estrogen-like compounds derived from plants, known as phytoestrogens, occur naturally in the environment. There are three major categories of phytoestrogens: isoflavones, coumestans, and lignans [106]. Fungal metabolites (zearalenone), vitamins (betacarotene, folic acid, and trans-retinoic acid), plant sterols (resveratrol, beta-sitosterol), anthraquinones, and natural animal and human steroids are all examples of biogenic compounds with potential hormone-like action [55]. Unlike many suspected EDCs, biogenic compounds do not persist in the environment nor do they bioaccumulate. Natural steroid hormones (human and animal) were discussed along with synthetic steroids (see PPCPs section) for ease of comparison.

The literature describing the potential adverse endocrine effects of exposure to biogenic compounds is somewhat limited. One human epidemiological study correlated a significant increase in the risk of giving birth to a boy with hypospadias (a condition in males in which the urethra opens on the underside of the penis rather than the tip) when the mother consumed a soy-rich vegetarian diet during pregnancy [107]. Female mice that were injected with genistein, a soy

isoflavone, had longer estrous cycles, altered ovarian function, early reproductive maturity, and subfertility or infertility [108]. Sheep that grazed on estrogen-rich clover showed reduced reproductive capacity [2].

At this time the extent of the risk associated with exposure to phytoestrogens is uncertain. It has been suggested that prenatal and neonatal exposure to soy isoflavones may have an adverse impact on fetal development [109], but more study is needed to characterize the possible effects. A recent study linked phytoestrogens present in commercial diets commonly fed to laboratory rats with early sexual maturity and rapid growth [110]. This could be a confounding factor in studies of other estrogenic EDCs using sexual endpoints as indicators of endocrine disruption.

Inorganics and Organometallic Compounds

Many metals and organometallic complexes (compounds with a bond between carbon and a metal) have been suggested as potential EDCs [55]. Tributyltin is a well-known EDC that caused imposex in marine snails. Several organotin complexes (tin bound to hydrocarbons) are also potential EDCs [55], as are some elemental metals including aluminum, arsenic, chromium, lead, and mercury [55]. For example, non-toxic doses of arsenite can interact directly with glucocorticoid receptors in rat liver cancer cells to inhibit transcription [111], and cadmium can activate estrogen receptor-α [112] and can bind with estrogen receptors in breast cancer cells [113]. One epidemiological study of occupationally exposed males linked a decrease in sperm quality with blood levels of lead and cadmium commonly found in the general population [114, 115]. Mercury has been associated with decreased sperm quality and quantity as well as hyperthyroidism in the Florida panther [116]. Human exposure to arsenic, cadmium, lead, and mercury is primarily through consumption of contaminated food, but contaminated drinking water (arsenic), air (lead), and smoking (cadmium) may also be important routes of exposure [117].

Sources, Fate, and Distribution of EDCs in the Environment

Wastewater treatment plant (WWTP) effluent and paper mill effluent are two major point sources of EDC release in the environment. Several classes of potential EDCs have been detected in WWTP effluent including low levels of pharmaceuticals [56], alkylphenols, PAHs, triclosan, bisphenol A, musks, and pesticides [66]. In a study of organic wastewater compounds in wastewater effluent in Minnesota, a total of 11 different EDCs were detected, with the greatest number of detections occurring in effluent from the Metropolitan Council Environmental Services WWTP in St. Paul and the Western Lake Superior Sanitary District WWTP in Duluth (9 EDCs each) [66] (Appendix F). Paper mill effluent can be a source of estrogenic, androgenic and progestegenic compounds to surface waters [118, 119].

Other known sources of EDCs include landfill leachate [56, 66], confined animal feeding operations [120], application of sewage sludge to fields, and aquaculture [56]. Incineration of municipal waste [121] and backyard burning of household trash [122] can release dioxins and furans into the atmosphere. Intentional use, as with agricultural and household pesticides and PPCPs, is another important source of EDCs in the environment.

Long-range atmospheric transport can play an important role in the distribution of EDCs in the environment. A study of fish in Siskiwit Lake, a remote, isolated lake on Isle Royale in Lake

Superior, confirmed the presence of PCBs and several organochlorine pesticides [123]. Since this lake receives no inflow from Lake Superior, the only possible source of these compounds was atmospheric transport and deposition. Similarly, PCBs and organochlorine pesticides have been detected in remote arctic regions where deposition from the atmosphere is the only likely source [124].

Depending on its molecular structure, a particular chemical may be completely broken down, changed only slightly, or remain unaltered in the environment for decades. PCBs, for example, are extremely resistant to breakdown. Though they can break down slowly in the environment under some conditions, they are still present many years after being released into soil, surface water, and sediment. Because of their persistence, PCBs and similar persistent, bioaccumulative chemicals tend to "cycle" in freshwater ecosystems, where they are continually available to fish and wildlife. The pesticide DDT has not been used in the U.S. for over 30 years, but it is still present in the environment along with its partial degradation products, DDE and DDD.

WWTPs are partially effective in removing some EDCs from sewage. Studies on the fate of estrogens that enter WWTP in sewage, for example, show that they are not always broken down in a WWTP, and can be released to surface waters in the effluent [66, 120]. WWTPs that employ activated sludge treatment systems may remove greater than 85% of estradiol, estriol, and estrone [125, 126]. Of the estrogens, ethinylestradiol appears to be the most resistant to degradation. About 5% of the estrogens appear to be sorbed to sewage sludge [125]. Incomplete degradation of estrogens explains why these compounds are found in surface water downstream of WWTPs at concentrations often greater than 1 part per trillion [127]. Once in surface water, estrogens break down at varying rates. 17β-estradiol, for example, has a half-life of up to 9 days in surface water where it is biodegraded [128]. However, ethinylestradiol was found to be much more resistant to biological degradation in surface water. Estrogens are also susceptible to degradation in sunlight.

Alkylphenol polyethoxylates (APEs), which are used in detergent, pesticide, deicing, and other industrial applications, can partially break down to form the endocrine-disrupting alkylphenols in WWTPs as well as in the environment. Some studies indicate that roughly 40% of APEs entering WWTPs are released as alkylphenols and other breakdown products [129]. Alkylphenols are present in Minnesota surface waters, where they are associated with endocrine disruption in fish [66]. Some researchers have found that alkylphenol at a concentration of 1 ppb was detectable in river water 11 kilometers downstream of the WWTP, representing a 2-4 day residence time in the river [84].

Once in ground water, some EDCs can persist there for many years. Studies done at one landfill showed that the plasticizers bisphenol A and phthalates, as well as nonylphenol and other alkylphenols, were found in the ground water near the landfill 20 years after it was closed [130]. Studies on hormones used in animal feedlots show that they may leach through soil. Testosterone appears to move through soil more readily than other hormones, with some studies showing that more than 40% of testosterone and 30% of estradiol applied to soil appears in the leachate [131]. This suggests that ground water may be at some risk to contamination from hormones when applied to soils. Other laboratory studies seem to show that most of the testosterone binds to soil, with over 20% breaking down in the soil environment [132]. For alkylphenols, their mobility is

apparently reduced in aerobic (oxygenated) soils. Octylphenol and nonylphenol concentrations decrease by 80% under aerobic soil conditions [129]. However, under anaerobic conditions, alkylphenols appear to be more mobile. Some pesticides (acetochlor, alachlor, atrazine, dimethenamid, metolachlor, and metribuzin) have been detected in ground water in Minnesota (Appendix E).

EDCs in Minnesota

While the presence of EDCs in the environment is a global concern, there may be some sources of particular importance to Minnesota. Agricultural operations (i.e. crops, large animal feeding operations) are likely sources of pesticides and hormones. Hormones are often added to animal feed to promote growth, resulting in the release of these hormones in animal waste. Paper mill effluents have been shown to contain estrogenic, androgenic, and progestegenic compounds [118, 119]. Biofuel operations may also be an emerging source of EDCs in Minnesota and elsewhere, although pertinent research is still in the early stages [133, 134].

EDCs have been detected in rivers and streams throughout Minnesota. Some potential EDCs (as defined by the USGS) were detected by the USGS in a study of organic wastewater compounds in Minnesota waters [66] (Fig. 6). Potential EDCs that were detected in surface water included AHTN, metolachlor (a pesticide), β-sitosterol, bisphenol A, diazinon (a pesticide), octylphenol, nonylphenol, and nonylphenol diethoxylate. EDCs (AHTN, bisphenol A, octylphenol monoethoxylate, and nonylphenol diethoxylate) were also detected in ground water samples.

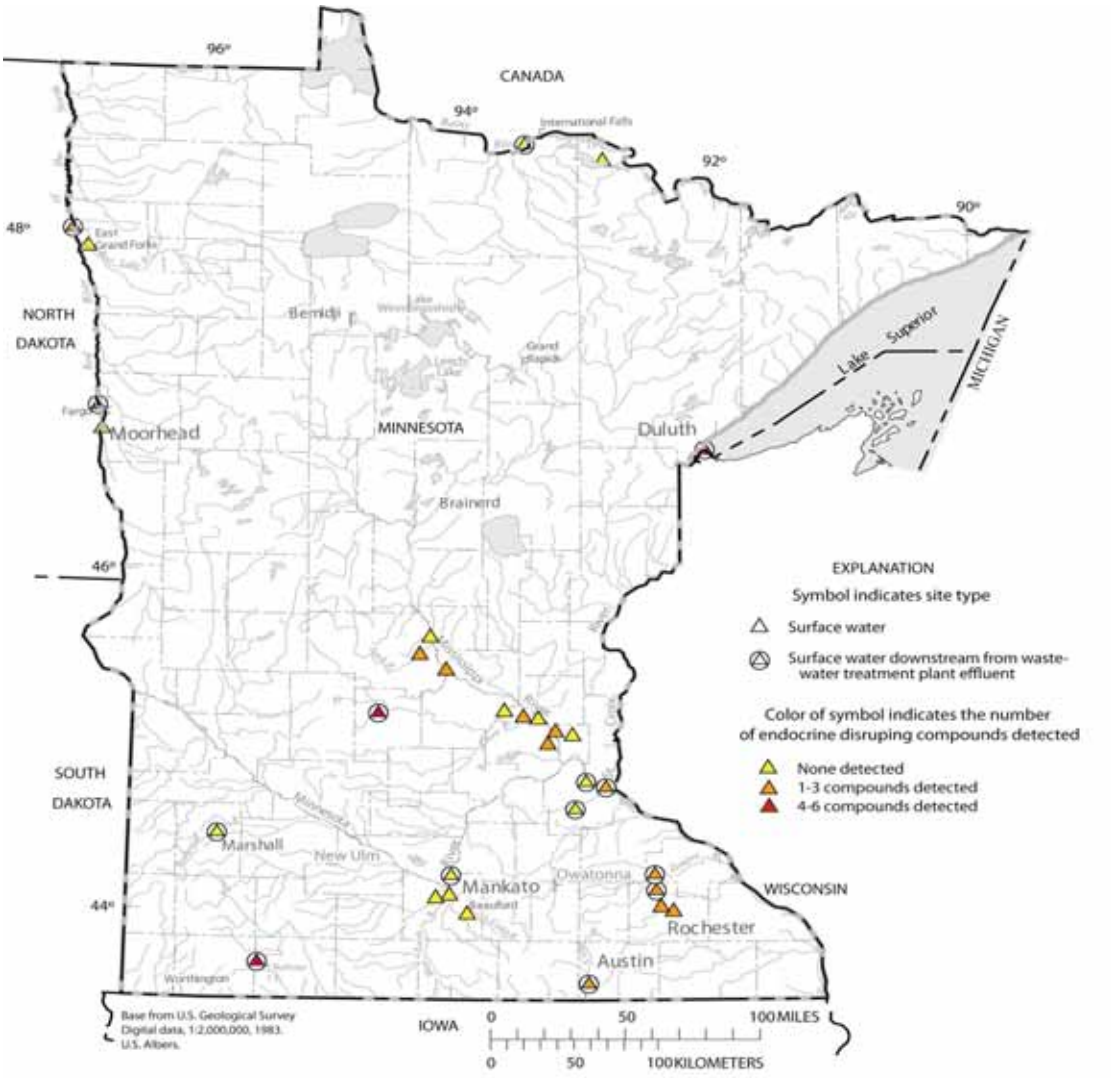

Figure 6. Number of EDCs detected in surface water in Minnesota during 2000-2002 as part of a cooperative effort by the U.S. Geological Survey and MPCA [66].

In 2006, sediment samples were collected and analyzed for potential EDCs from 41 sites in the Mississippi River [19] (Fig. 7; Appendix F). More potential EDCs at greater concentrations were detected near Bemidji and from St. Cloud south to Red Wing. The occurrence of EDCs in bottom sediment seems to be correlated with population density and urban or agricultural land use. The results of these studies suggest that the presence of potential EDCs in Minnesota waters is widespread.

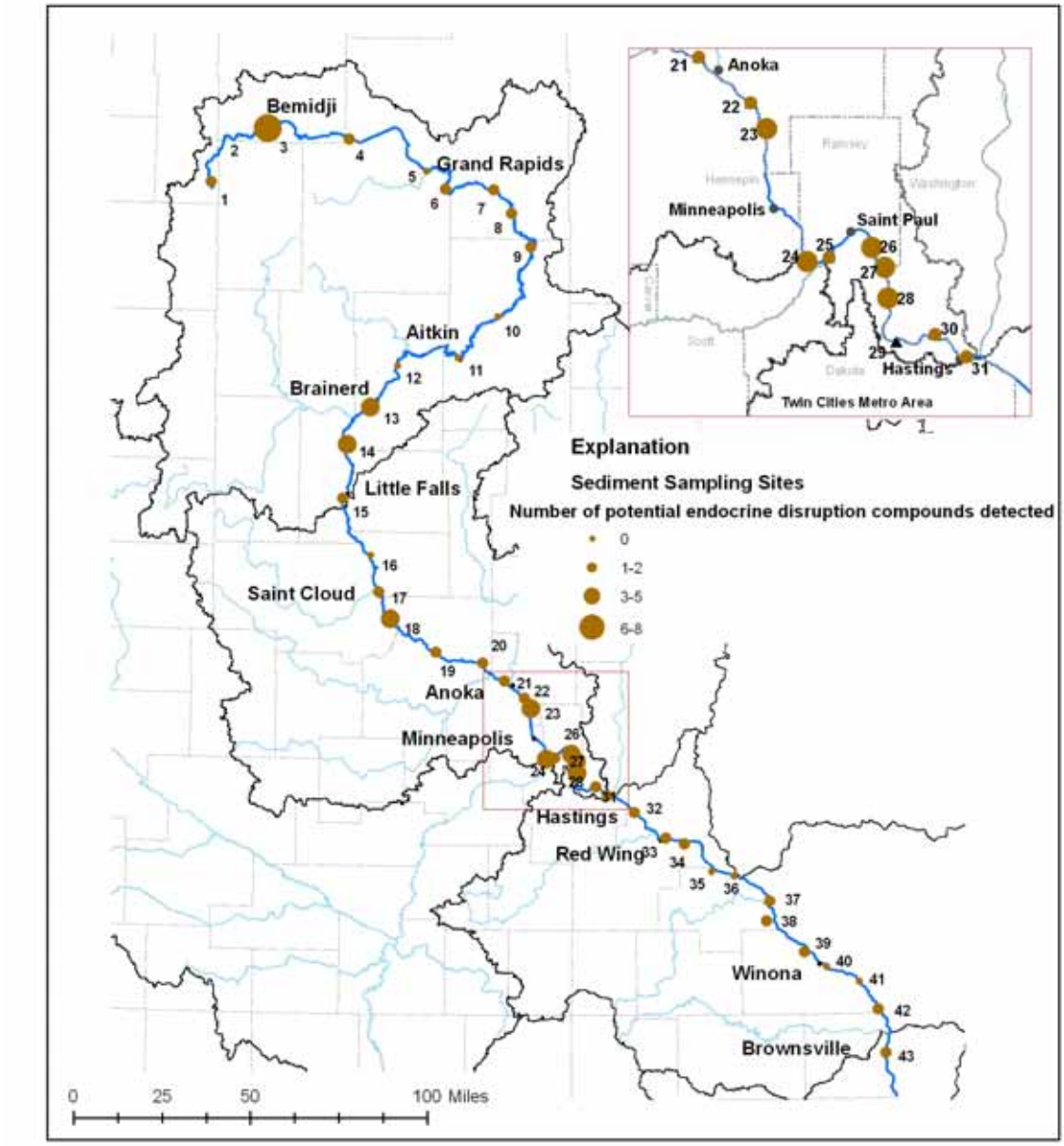

Figure 7. Number of potential EDCs detected in bottom sediment at 41 sites sampled as part of the Mississippi River Longitudinal Study during the months of June, July and August 2006 [19].

Practicability and Cost of Prevention and Remediation

Effectively managing contamination of the environment by EDCs is a difficult and complex task. The diverse nature of the compounds in question and their widespread presence in the environment preclude the possibility of finding a “quick fix” or a “one size fits all” answer. The widespread, continual, and low-level contamination associated with EDCs does not lend itself to remediation. Therefore, preventing the initial use and release of EDCs will likely be more effective in reducing environmental contamination.

The Endocrine Disruptor Screening Program (EDSP) at the EPA was initiated in response to a mandate in the 1996 Food Quality Protection Act. The EPA has compiled a list of pesticide active and inert ingredients to undergo initial EDC screening. Currently, the EPA is in the process of validating EDC screens and tests, setting priorities for determining which chemicals to test, and developing policies and procedures that will be used to require testing [135]. The EPA is working with other agencies and researchers internationally to develop peer-reviewed assays in order to identify relevant toxic doses of EDCs. See Appendix G for more details regarding the EDSP.

The information presented in this report indicates that preventing the release of known or potential EDCs to our environment is clearly beyond the ability of one particular state agency or program. Collaboration between state agencies, county governments, manufacturers, and academia would be needed to implement programs that might effectively eliminate EDCs from the waste stream or from certain high-volume industrial or consumer products. The MPCA, Minnesota Department of Agriculture (MDA), Minnesota Department of Health (MDH), and Minnesota Department of Natural Resources (DNR), and local wastewater authorities would all have important roles in efforts to eliminate EDCs from the waste stream, prevent human exposure to them, or otherwise prevent their release to the environment. These collaborative efforts would likely include human and ecological risk assessments, permitting activities, assessments of various consumer and agricultural products that include EDCs, WWTP optimization, and other strategies aimed at intercepting EDCs prior to their release to surface water. In addition, the widespread contamination along with the complexity of the issue means that effectively dealing with EDCs is beyond the capabilities of state government. Collaboration among government agencies and researchers worldwide already exists, which is appropriate considering the scope of the problem.

Wastewater Treatment

One way to minimize EDC contamination locally may be to treat point sources of environmental contamination of EDCs. Since WWTPs are major conduits for the release of EDCs, upgrading treatment processes may effectively reduce contaminated emissions to surface waters. To effectively remove all the types of EDCs present in wastewater effluents consecutive treatment technologies may be required. However, since most of the EDCs present are organic compounds, the best available technology that is economically feasible to remove EDCs would be granular activated carbon (GAC) technology or treatment. GAC has been used very successfully for treatment of municipal and industrial wastewater effluents. While this method is effective, it is very expensive and requires regular maintenance to ensure proper performance. This method could also be used as a final treatment for finished drinking water. Please refer to Appendix H for a more detailed description of wastewater treatment options.

Collection Programs

Pharmaceutical collection programs may reduce the amount of potential EDCs that enter the environment as a result of improper disposal. For example, the Western Lake Superior Sanitary District in Duluth recently sponsored a weekend-long pharmaceutical take-back program in which individuals could bring in their unwanted medication for incineration. A total of 258 pounds of medication was collected from 166 households. Police officers were on site to handle controlled substances and pharmacists were present to sort and record data on the drugs received.

The event was considered a success and a similar collection event may be held in the spring of 2008.

Product Stewardship

Product stewardship, or extended product responsibility, may also be an effective way to reduce EDC pollution. Product stewardship means that all parties involved in designing, manufacturing, selling and using a product take responsibility for environmental impacts at every stage of that product's life. Manufacturers have the greatest responsibility for minimizing the impact their products have on the environment because they generally have the greatest ability to limit those impacts [136]. Retailers can encourage product stewardship by preferring environmentally-conscious providers and educating consumers, and consumers can make better choices and take the initiative to dispose of products properly.

Product stewardship can be achieved in part by designing products to minimize the use of potential EDCs from the outset. In the MPCA Design for the Environment (DfE) process [137], the manufacturer evaluates the need for a particular compound, and if feasible, designs the product to avoid the use of any potentially harmful chemicals. For example, S.C. Johnson and Seagate Technology, Inc. have developed lists of materials to avoid using in products with the specific goal of eliminating or "designing out" the use of dozens of hazardous substances in the conceptual and preliminary design phases of new products and programs. As opposed to waiting until it is known that something is harmful to the environment, a cautious approach can be adopted; compounds can be eliminated from products when sufficient doubt exists regarding its safety.

Informed Individual Choices

Individuals can also reduce their exposure to some EDCs by making informed choices regarding diet and lifestyle. For persistent, bioaccumulative environmental contaminants found at relatively low levels globally (i.e., PCBs, PBDEs, and DDT), exposure prevention is likely the best way to avoid the potential endocrine disrupting effects of these compounds. For example, women of childbearing age should avoid excessive consumption of contaminated food in order to minimize their exposure to bioaccumulative compounds that could be passed on to the fetus in the womb or to infants via breast milk. Using less plastic for food storage and choosing baby bottles made from special plastics may reduce exposure to phthalates and bisphenol A. Education would be an important first step in helping consumers choose better alternatives.

Costs of Inaction

While effectively addressing environmental contamination by EDCs will be a difficult and expensive undertaking, not doing anything to address this issue may also be costly. For example, impaired reproductive capacity and increased mortality in fish exposed to pollution can drastically reduce populations of affected species. The value of the commercial fishery in Lake Superior declined due to a reduction in the number of larger, more valuable species of fish such as lake trout (due in part to impacts of chemical exposure) as well as federal laws banning the sale of fish contaminated with toxic pollutants [138]. Costs associated with an increase in birth defects and childhood diseases such as cancer and neurobehavioral disorders have been estimated at over $1 billion per year in Minnesota; environmental pollution (not just EDCs) has been indicated as a possible contributor to the increased incidence of childhood disease [139].

Summary

This report provides an overview of selected concerns associated with EDCs in the environment. Several effects of chemical exposure may be mediated through the endocrine system. Endocrine disruption is a mode of action by which a toxic effect or endpoint may be reached; it is not a toxic effect itself. As demonstrated by several of the studies cited in this report, endocrine disruption can involve more than just the sex hormones. In fact, there are many hormones produced by the endocrine systems of humans and wildlife, all of which have important roles in maintaining bodily processes. While there are still many unanswered questions, the evidence that chemicals can adversely impact endocrine function in humans, fish and wildlife is mounting. Ongoing research will be important to better understand the potential long-term ecological effects of EDCs in the environment.

As policy makers consider options to address the challenge of EDCs, it is important to keep in mind that a combination of strategies is needed. While conventional “end of pipe” treatment approaches may be feasible, a broad approach to preventing EDC release into the environment may ultimately have a greater impact. Such strategies could include product stewardship, Design for the Environment, minimizing the use of EDCs, collection programs, and better-informed consumer choices.

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Appendix A

Description of the Consultation Process

The Minnesota Pollution Control Agency (MPCA) consulted with the following agencies and academic institutions:

- Minnesota Department of Agriculture (MDA)
- Minnesota Department of Health (MDH)
- Minnesota Department of Natural Resources (DNR)
- U.S. Environmental Protection Agency (USEPA)
- University of Minnesota (U of M)

In addition, the MPCA also consulted with St.Cloud State University (SCSU), U.S. Geological Survey (USGS), U.S. Fish and Wildlife Service (USFWS), National Park Service (NPS) and University of Nebraksa.

The consultation process included three multi-agency meetings held on the following dates:

- September 18, 2007
- September 19, 2007
- October 3, 2007

A working definition of endocrine disrupting compounds was formulated at the October 3, 2007 meeting in St. Cloud, MN. That meeting is summarized here.

Individuals from the various agencies and institutions were also consulted separately in meetings and via e-mail and telephone conversations. A copy of the draft report was submitted to individuals from MDA, MDH, DNR, USEPA, U of M, SCSU, and USGS for review and comment. All comments were considered and changes were made where appropriate. A response to all comments was sent to the reviewers.

Endocrine Disrupting Compounds in Minnesota Waters

October 3, 2007

Review

Synopsis

On Wednesday, October 3, 2007 the MN Pollution Control Agency in conjunction with the St. Cloud State University Aquatic Toxicology Laboratory hosted an endocrine disruption roundtable meeting. Twenty-three participants from four federal agencies (US EPA, USGS, US Fish & Wildlife Service, National Park Service), four state agencies (MN Pollution Control Agency, MN Department of Health, MN Dept. of Agriculture, MN Dept. of Natural Resources), and three Universities (U. Minnesota, U. Nebraska, St. Cloud State U.). The roundtable developed a working definition of "endocrine disruptors" with several tiers of specificity, discussed ongoing and planned projects on endocrine disruption, established a list of research priorities and gaps, and developed several possible communication avenues to improve efficiency and effectiveness of research efforts in the field of endocrine disruption.

Review of Meeting Discussions

The meeting hosts set forth six goals for the round table discussion:

1. Derive a working definition of an EDC.
2. Gain an understanding of what projects are being conducted. (see also goal 5)
3. Identify gaps in understanding of EDCs in environment
4. Develop a means of secure communication between researches and agencies doing work on EDCs in Minnesota
5. Encourage collaboration on overlapping areas of research
6. Set tentative meeting for next spring.

Goal 1. The morning session focused on a working definition of endocrine disruptors. The group agreed that an updated definition with greater specificity was needed in communicating a common message to stakeholders and interested parties. There was some discussion of the utility of a “working” definition that needed to be applicable to the needs of the regulatory agencies, the press, the public, or the legislature as opposed to detailed definitions that are more appropriate to academic research focus. There was concern that a definition could be so simple and so broad that it was meaningless, as well as concern that a detailed definition would be too complicated for public consumption. An in-depth discussion of differing approaches for such a definition highlighted three necessary components of the definition: (1) the compound in question; (2) the effect or effects classified as endocrine disrupting in nature; and (3) the target organism. The group developed the following definition as a baseline for public

organism. The group developed the following definition as a baseline for public comments and discussed several qualifiers that would allow users of the definition to expand its specificity based on particular research needs and audiences:

"An Endocrine Disruptor is an Anthropogenic Compound[1] that may have an Adverse Effect[2] Mediated Directly through the Endocrine System on Fish, Wildlife, or Humans."

[1] Human-made or at unnatural concentrations.
[2] Effects on reproduction or development

It was agreed that this definition should be further defined through tiered annotations such as annotations 1 & 2. It was also suggested that endocrine disrupting compounds be segregated in some way based on source or origin and not focus on individual chemicals. Naturally occurring compounds that demonstrate endocrine disrupting activity might not elicit as much concern as anthropogenic endocrine disruptors. However, they are of greater concern when associated with large-scale operations, such as confined animal feedlot operations. Participants are encouraged to submit additional annotations that will be posted in the near future on a web-page (see below).

Goal 2. Roundtable participants briefly described projects being conducted by their agencies and in their laboratories, or projects planned for the near future. A common perception developed that a substantial amount of endocrine disruption research is being conducted in the Upper Midwest and that greater collaboration would further improve the efficiency of these projects.

Goal 3. A spirited discussion ensued as participants described their perceived gaps in our research and knowledge of endocrine disrupting compounds. The group developed the following list of possible gaps:

- Fate and transport of endocrine disrupting compounds and their breakdown pathways and products are largely unknown. The fate of particular compounds is an important component of risk assessment. Alternative transport, other then through water (i.e., air) was briefly discussed.
- The lack of tools for environmental sampling geared specifically to endocrine disruption research was considered a hindrance in gaining a better understanding of this issue.
- Our lack of understanding of the temporal and spatial variability of endocrine disrupting compounds in the environment is a major obstacle to understanding the overall risk they pose to organisms.
- A better definition and understanding of what constitutes "environmentally relevant concentrations" and the effects on organisms exposed at these concentrations is needed.
- A dearth of data on F1 and F2 generation offspring of endocrine disrupting compounds exposed parent generations.
- We need more information on the apparent variations in species sensitivity and on the sensitivity of endangered species to EDCs.
- More data is needed on the food chain effects of endocrine disrupting compounds.

- Study is needed on co-located trophic levels and the assessment of the potential for biomagnification.
- The effects of mixtures or synergies of endocrine disrupting compounds needs further study.
- Study of run-off contributions to endocrine disruptors to aquatic ecosystems and defining other non-point sources of endocrine disruption is needed.
- Defining source-mixtures and their signature profiles was seen as a crucial research need.
- Addressing creative source-prevention and source-treatment solutions was discussed as an important future step to alleviate and mediate some of the problems caused by endocrine disrupting compounds.
- The fate of EDCs in wastewater treatment plants should be studied in greater detail.

Goal 4. The round table brainstormed on potential avenues by which effective communication between researchers, agencies and stakeholders could continue. The US EPA system of web-portals for user groups was mentioned as a potential option or model for such a secure communication pathway that would allow participants to share ideas, data, and research objectives.

Goal 5. Participants agreed that collaborations should be strengthened in future years and projects. A suggestion to develop an interactive map of Minnesota that would allow researchers to quickly mark proposed field sites will be investigated further in the coming weeks. A general consensus was that on many occasions, combing field sampling locations of multiple studies would benefit all participants and may justify moving a field site in order to benefit from the overall greater data set.

Goal 6. The meeting concluded with a discussion of the need and possible location of a follow-up round table meeting. Participants suggested a tentative meeting before or after the Midwest SETAC meeting in March 31 - April 2, 2008 in Duluth, MN, possibly at the EPA facility. This option and date will be investigated in the coming weeks.

Appendix B

Glossary of Acronyms, Terms, and Units

Glossary of Acronyms

Agencies and Programs

Acronym	Definition
DfE	Design for the Environment
DNR	Minnesota Department of Natural Resources
EDSP	Endocrine Disruptor Screening Program
EDSTAC	Endocrine Disruptor Screening and Testing Advisory Committee
ELA	Experimental Lakes Area
IEH	Institute for Environment and Health
MDA	Minnesota Department of Agriculture
MDH	Minnesota Department of Health
MPCA	Minnesota Pollution Control Agency
NPS	National Park Service
NTP	National Toxicology Program (US)
SAP	Scientific advisory panel
SCSU	Saint Cloud State University
SEPA	Swedish Environmental Protection Agency
U of M	University of Minnesota
USEPA	United States Environmental Protection Agency
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
WHO	World Health Organization
WLSSD	Western Lake Superior Sanitary District
WWTP	Wastewater treatment plant

Compounds

Acronym	Definition
AHTN	acetyl-hexamethyl-tetrahydro-naphthalen (a musk)
AP	alkylphenol
APE	alkylphenol polyethoxylate
BPA	bisphenol A
DDD	dichloro-diphenyl-dichloroethane
DDE	dichloro-diphenyl-dichloroethylene
DDT	dichloro-diphenyl-trichloroethane
DES	diethylstilbestrol (a synthetic estrogen)
E1	estrone (a natural estrogen)
E2	estradiol (a natural estrogen)
E3	estriol (a natural estrogen)
EDC	endocrine disrupting compound
EE2	ethinylestradiol (synthetic estrogen found in birth control pills)
HHCB	hexahydrohexamethyl-cyclopentabenzopyran (a musk)
PAH	polynuclear aromatic hydrocarbon

Acronym	Definition
PBDE	polybrominated diphenyl ether
PCB	polychlorinated biphenyl
PPCP	pharmaceutical and personal care products
TCDD	2,3,7,8-tetrachloro-dibenzo-p-dioxin (dioxin)
DNA	deoxyribonucleic acid
GAC	granular activated carbon
GLEMEDS	Great Lakes Embryo Mortality, Edema, and Deformity Syndrome
mRNA	messenger ribonucleic acid
T_3	triiodo-thyronine (thyroid hormone)
VTG	vitellogenin

Glossary of Terms

Additive effect: combined effect of two or more chemicals is the sum of their individual effects

Adjuvant: in the case of pesticides, the non-active ingredients in pesticide formulations

Anthropogenic: man made

Biogenic: naturally produced or occurring

Carcinogenicity: cancer causing

Degradate: breakdown product of a chemical

Down regulate: process by which the amount of a cellular component (i.e. RNA or a protein) is decreased in response to external stimuli

Endogenous: chemical produced within the body

Exogenous: chemical coming from outside the body

Gene expression: process in which inheritable information in a gene is made into a gene product (i.e., protein or RNA)

Hermaphroditism: condition of having both male and females sex organs

Homeostasis: process by which a living organism maintains stable internal conditions

Imposex: formation of male reproductive organs in female snails

Induce: to stimulate the production of a protein or enzyme by increasing gene transcription

Inhibit: to decrease, limit, or block the production of a protein or enzyme by decreasing gene transcription

In utero: in the uterus; used to describe the state of an embryo or fetus

Invertebrate: organism that lacks a backbone

In vitro: controlled experiment conducted outside of a living organism

In vivo: in a living organism

Inhibitory effect: to restrain or hinder the normal effect of a hormone

Metabolite: breakdown product of a chemical

mRNA transcription: synthesis of RNA from DNA

Mutagenicity: capable of inducing mutation

Non-monotonic: toxics effects do not follow a linear dose-response curve

Oocyte: female germ cell involved in reproduction (egg)

Phytoestrogen: plant estrogen

Recalcitrant: resistant to breakdown

Receptor: protein in the nucleus of a cell or on a cell membrane that can bind with a specife molecule such as a hormone

Syngeristic effect: combined effect of two or more chemicals is greater than the sum of their individual effects

Teratogenicity: capable of inducing malformations

Up regulate: process by which the amount of a cellular component (i.e. RNA or a protein) is increased in response to external stimuli

Vertebrate: organism that has a backbone

Glossary of Units

"Parts-per" Notation

Units	Abbreviation	Definition
Parts per hundred	%	1 in 100
Parts per thousand	‰	1 in 1000
Parts per million	ppm	1 in 1,000,000
Parts per billion	ppb	1 in 1,000,000,000
Parts per trillion	ppt	1 in 1,000,000,000,000

Metric System

Units of Mass	Abbreviation	Definition
kilogram	kg	10^{3} g
gram	g	1 g
milligram	mg	10^{-3} g
microgram	µg	10^{-6} g
nanogram	ng	10^{-9} g
pictogram	pg	10^{-12} g
Units of Volume		
liter	L	1 L
milliliter	mL	10^{-3} L

Appendix C

Definition of Endocrine Disrupting Compounds from Other Agencies

United States Environmental Protection Agency (USEPA)

"The EDSTAC describes an endocrine disruptor as an exogenous chemical substance or mixture that alters the structure or function(s) of the endocrine system and causes adverse effects at the level of the organism, its progeny, populations, or subpopulations of organisms, based on scientific principles, data, weight-of-evidence, and the precautionary principle."

European Commission (EC)

"An endocrine disrupting compound is an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse effects in an intact organism, or its progeny, or (sub)populations."

Swedish Environmental Protection Agency (SEPA)

"An endocrine disrupter is an exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to changes in endocrine function."

World Health Organization (WHO)

"An endocrine disruptor is an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations."

A potential endocrine disruptor is an exogenous substance or mixture that possesses properties that might be expected to lead to endocrine disruption in an intact organism, or its progeny, or (sub)populations."

Appendix D

Published Lists of Known and Potential Endocrine Disrupting Compounds

Web links to published lists of EDCs:

UK Institute of Environment and Health

http://www.silsoe.cranfield.ac.uk/ieh/pdf/w20.pdf

Scorecard

http://www.scorecard.org/health-effects/chemicals-2.tcl?short_hazard_name=endo&all_p=t

Our Stolen Future

http://www.ourstolenfuture.org/Basics/chemlist.htm

King County, Washington

http://dnr.metrokc.gov/wtd/community/edc/chart.htm

Appendix E

Pesticide Sales, Usage, Environmental Distribution, and Best Management Practices in Minnesota

Information Provided Courtesy of the Minnesota Department of Agriculture

Thank you for the opportunity to meet on November 5th to discuss the Endocrine Disruptor Report you are preparing for the legislature in January 2008. The Minnesota Department of Agriculture (MDA) takes seriously its role as a participant in preparation of the report as part of the consultative process outlined under statute.

At our meeting, we discussed several pesticide-related issues, and we offered to provide you with additional information related to pesticides sales, usage, water quality monitoring data and MDA prevention and mitigation programs. In providing this information, it is not the MDA's intent to make any inferences about the status of individual pesticides as known or potential Endocrine Disrupting Compounds (EDCs). Rather, as we work jointly to identify known or potential EDCs of likely significance to humans, fish, and wildlife, the MDA believes it is important to share critical facts and figures related to pesticide usage and occurrence in the environment, regardless of their status as EDCs.

Pesticide Sales and Usage:

Several pesticides are sold and used in relatively high volumes, or are used over relatively large land areas. Glyphosate, acetochlor, atrazine and metolachlor are used in the production of corn or soybeans. Glyphosate is also as a common landscape herbicide in urban environments. 2,4-D is an herbicide used in agriculture, landscape applications and in aquatic plant control. Alachlor, historically a commonly used herbicide and still registered for use in Minnesota, is not currently sold or used to a significant degree.

Figure 1 illustrates agricultural sales and usage trends for these pesticide active ingredients. Note that MDA sales information shown in Figure 1 represents total pounds of select active ingredients used in crop production (glyphosate and 2,4-D data points may include or omit certain non-crop sales, but it is likely that such sales contribute insignificantly to the totals shown). The data is for active ingredients contained in products that were reported as being sold in Minnesota. The data summarizes information reported to the MDA on annual pesticide sales in Minnesota. Pesticides sold in Minnesota may not be used in the same year they are sold, or in some cases may never be used in Minnesota. However, sales data provide a general indication of long-term pesticide use trends.

Figures 2 – 5 illustrate actual pesticide usage data for corn and soybeans. Note again that alachlor, historically a commonly used herbicide and still registered for use in Minnesota, is not currently sold or used to a significant degree. It would appear that any increases in individual herbicide usage (total pounds) is due to expansion of planted acres rather than increases in individual producer usage rates (pounds/acre).

Additional pesticide usage information and surveys compiled by the MDA Pesticide & Fertilizer Management Division are available at http://www.mda.state.mn.us/chemicals/pesticides/pesticideuse.htm

Pesticide Water Quality Monitoring Data:

Monitoring of groundwater, drinking water, surface water and springs has focused on many of the same agricultural pesticides that account for the largest statewide use by volume and land area. These pesticides and their degradates, as well as other pesticides, are captured according to available laboratory methods and capacities.

The *Summary of Pesticide Detections in Groundwater and Surface Water Resources MDA 2006 Annual Monitoring Report*, January 7, 2008, (sent separately) represents a compilation of monitoring data from the more comprehensive annual reports of the past few years. Similar summaries have been created for deliberations of the Pesticide Management Plan Committee (PMPC), to which the MPCA has assigned a representative. PMPC members provide recommendations to the Commissioner of Agriculture after review of such data and participation in annual meetings.

Any MDA designation of "common detection" for a pesticide under the Groundwater Protection Act (Minn. Stat. 103H) adheres to authority to make such designation based on detection of the "pollutant or *pollutant breakdown product*" [emphasis added]. Five pesticides (acetochlor, alachlor, atrazine, metolachlor and metribuzin) are considered "common detection," though this designation is generally made irrespective of concentration relative to exposure and human health risk as established by the Minnesota Department of Health. Thus, while acetochlor, alachlor and metolachlor have been designated "common detection," the available data led the MDA to make the designation based primarily on their breakdown products (degradates), not on the detection of the parent compounds. This is appropriate since MDA program management of degradates will be driven by management of pesticide products containing the parent compounds. Given that several of the degradates account for the vast majority of detection frequencies and concentrations in samples, and given that the human health toxicological endpoints for several degradates differ from those of the parent, any inferences made about groundwater or drinking water exposure and health risks due to acetochlor, alachlor and metolachlor might need to consider such issues.

Also, please note the difference between groundwater concentrations vs. drinking water concentrations when considering known or potential human exposure.

For surface water, the MDA considers designating a pesticide as a "surface water pesticide of concern" when 10-50% of an aquatic toxicity reference value (typically established through consultation with the MPCA and linked to MPCA-evaluated aquatic animal and plant toxicity endpoints). Currently, acetochlor and atrazine have each been named a "surface water pesticide of concern" based on seasonal concentration exceedances of 10-50% or more of chronic reference values. The MPCA makes pesticide impairment decisions based on pesticide concentrations sustained over time-periods established by MPCA rule.

All surface water chronic standards or aquatic reference values cited in the summary are current as of January 7, 2008.

Finally, note that detection frequencies, concentrations, exposure significance and general environmental impact profiles differ for groundwater, drinking water and surface water, and that "common detection" is not a relevant statutory term for surface water.

Water Quality Impact Prevention and Mitigation Programs:

The legislation authorizing preparation of the Endocrine Disruptor Report also recommends assessment of cost and practicability of prevention and remediation strategies for known EDCs.

The MDA has developed, is promoting the adoption of, and is evaluating the effectiveness of Best Management Practices (BMPs) for alachlor, acetochlor, atrazine, metolachlor and metribuzin for groundwater (based on frequent detection of the parent or degradates), and for acetochlor and atrazine (based in surface water concentrations). These pesticide-specific BMPs, as well as core BMPs for all agricultural herbicides, represent the first step in preventing current and future impacts from pesticides groundwater and surface water contamination by pesticides.

A copy of the BMPs have been sent separately, and they are available online at http://www.mda.state.mn.us/protecting/bmps/voluntarybmps.htm

Figure 1: Sales of major crop production pesticide active ingredients. Rank of sales for 2005 is glyphosate =1; acetochlor =2; atrazine = 3; metolachlor = 4; 2,4-D = 5; and alachlor = 43.

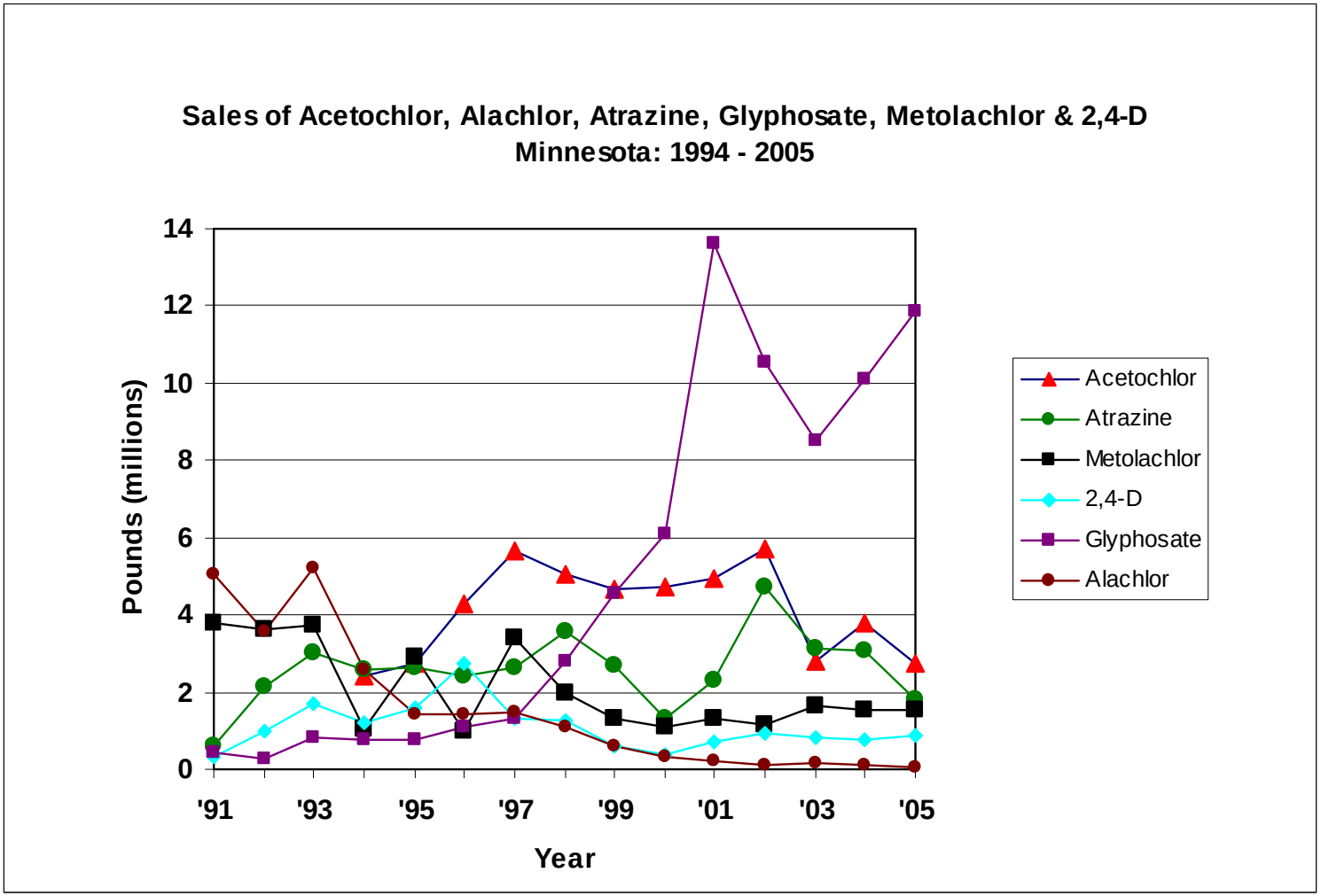


Figure 2: Usage (total pounds) of select corn herbicide active ingredients.

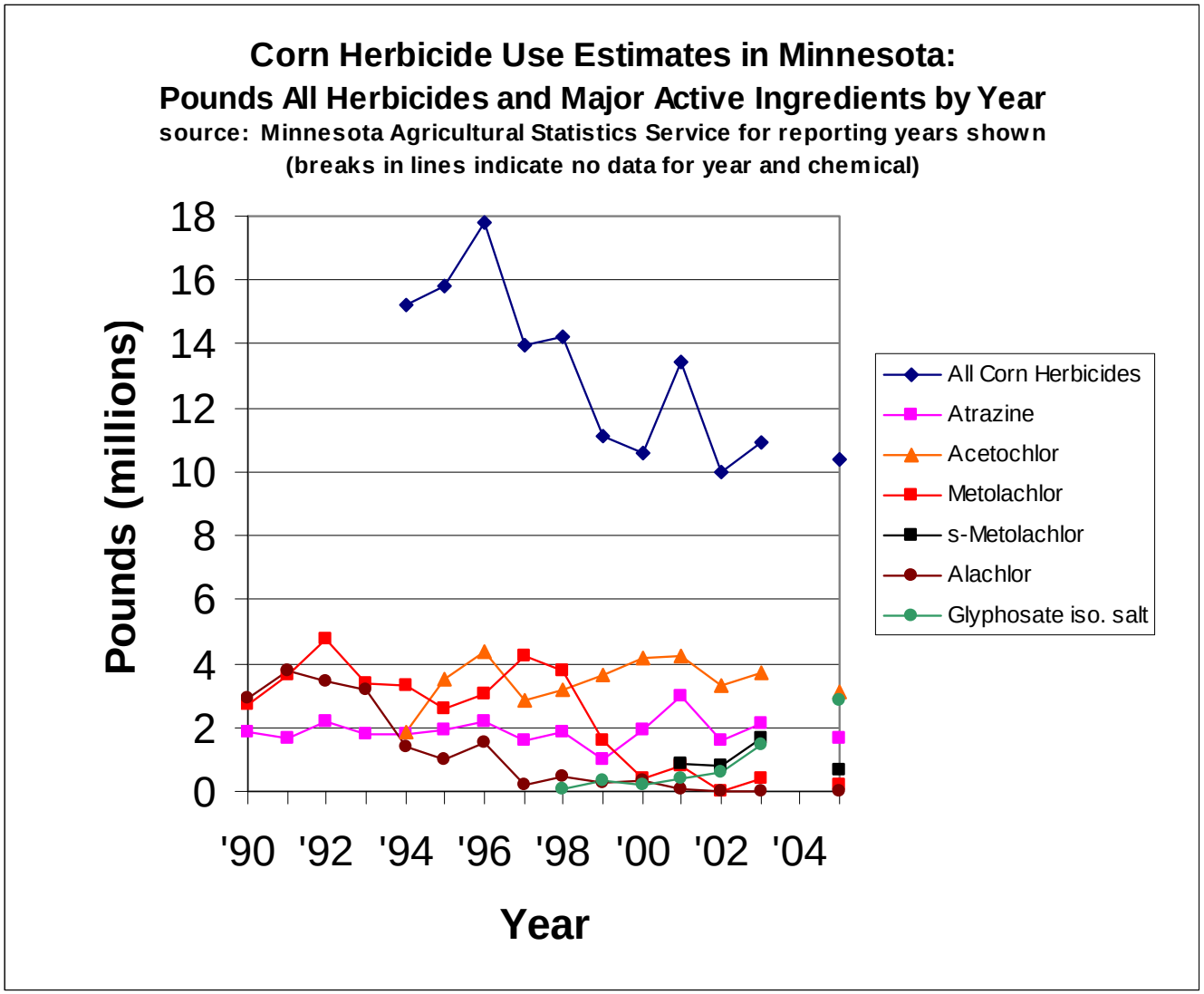


Figure 3: Usage (pounds/acre) of select corn herbicide active ingredients.

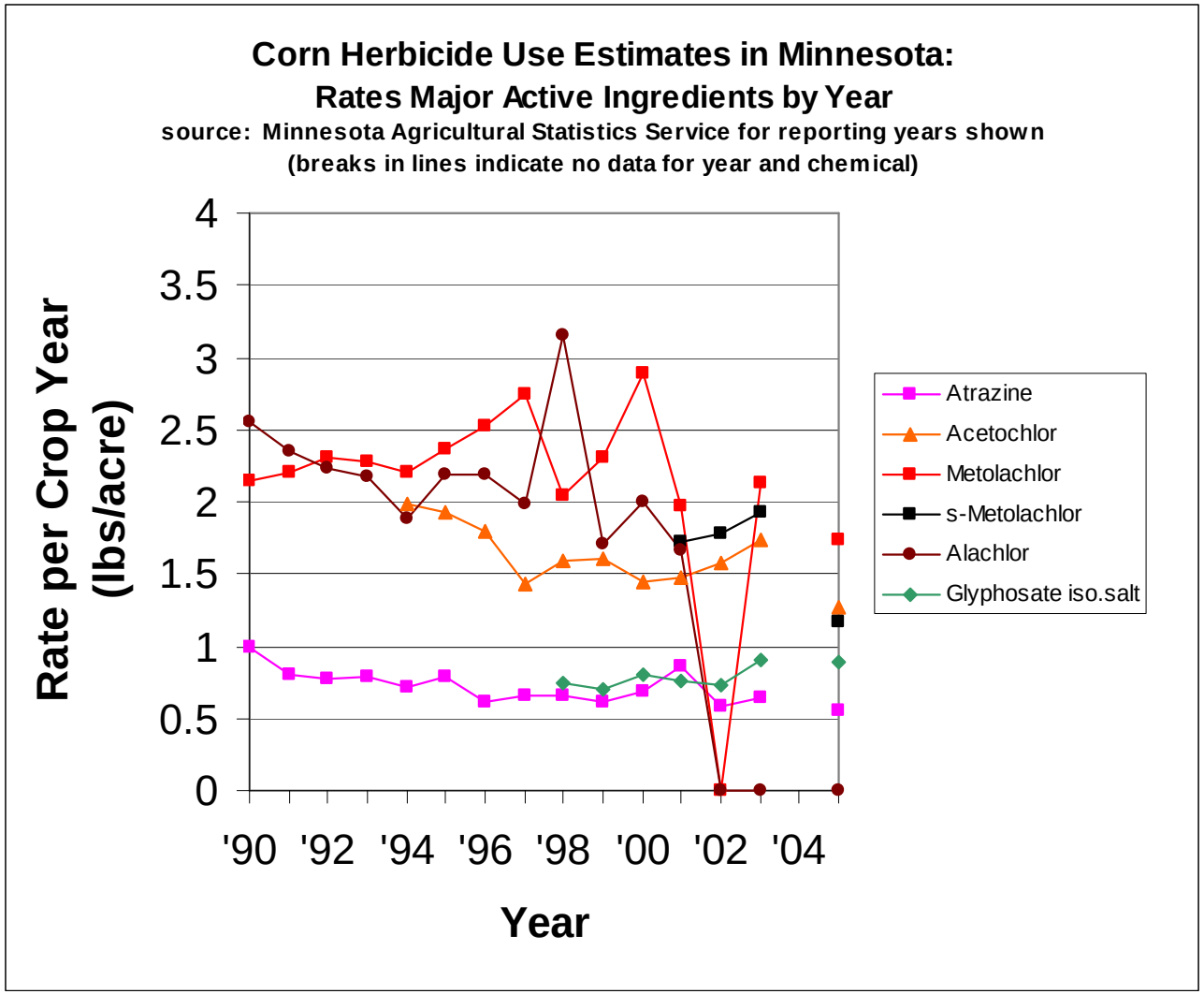


Figure 4: Usage (total pounds) of select soybean herbicide active ingredients.

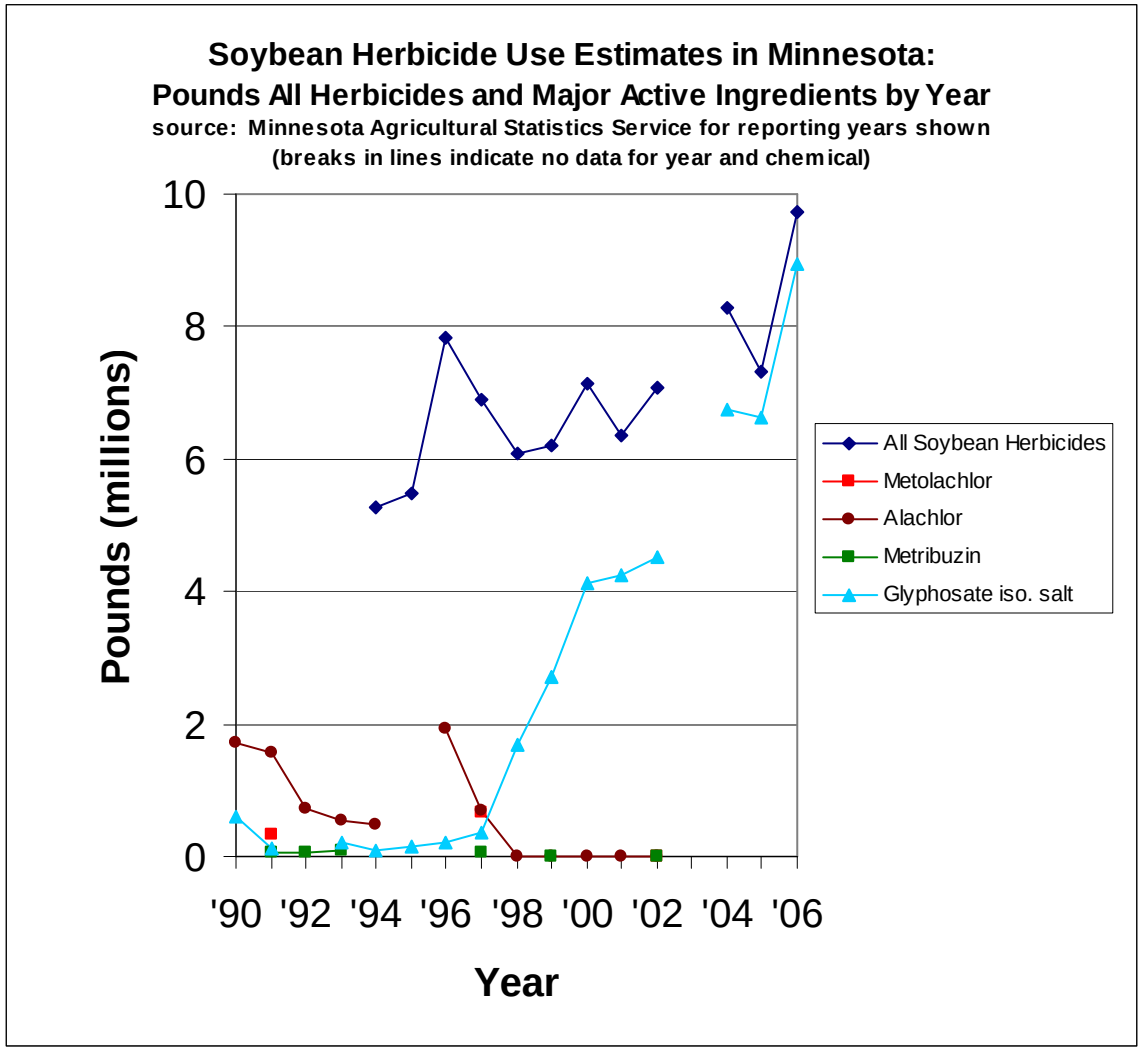
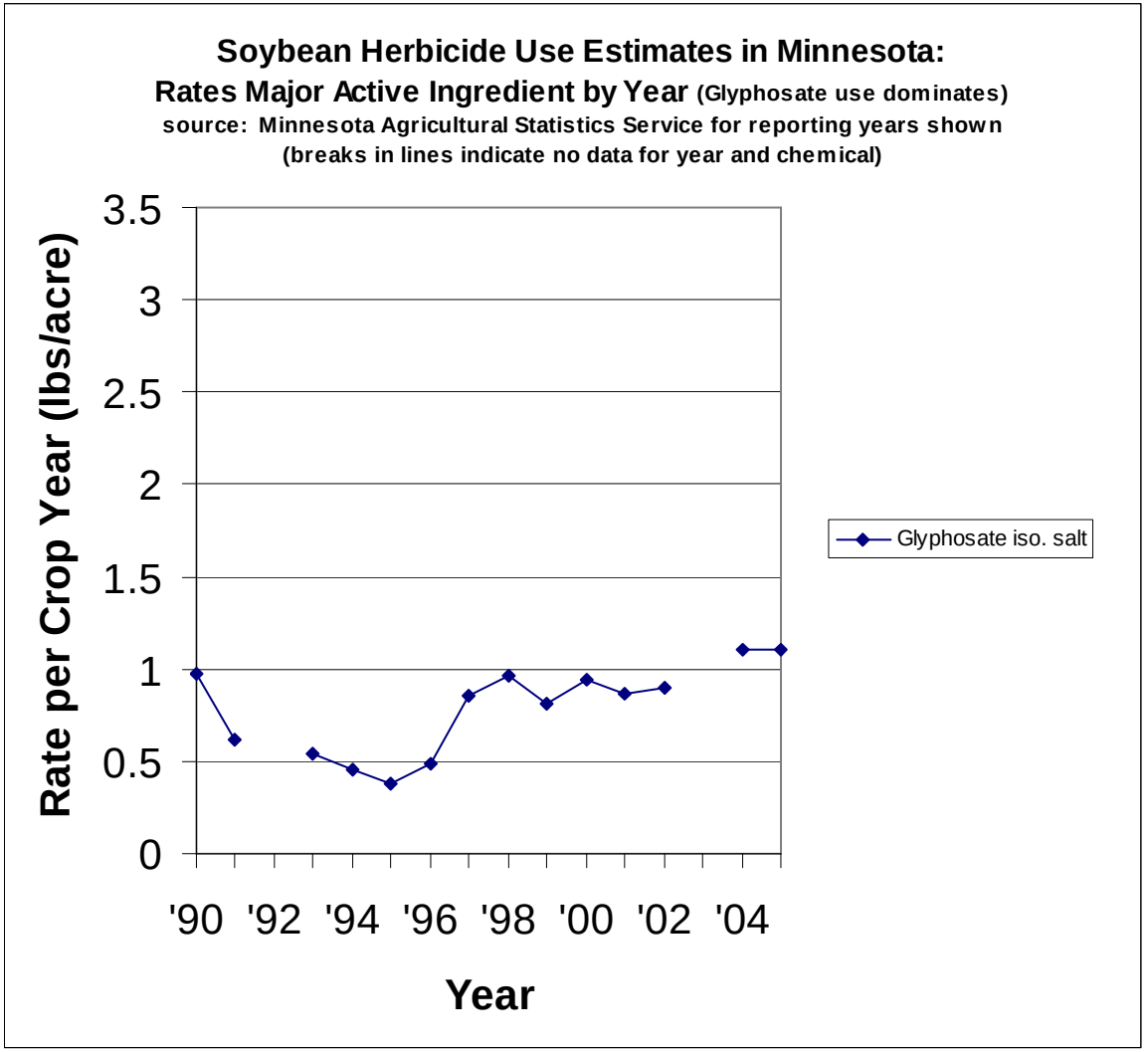


Figure 5: Usage (pounds/acre) of select soybean herbicide active ingredients.



Summary of Pesticide Detections in Groundwater and Surface Water Resources
MDA 2006 Annual Monitoring Report

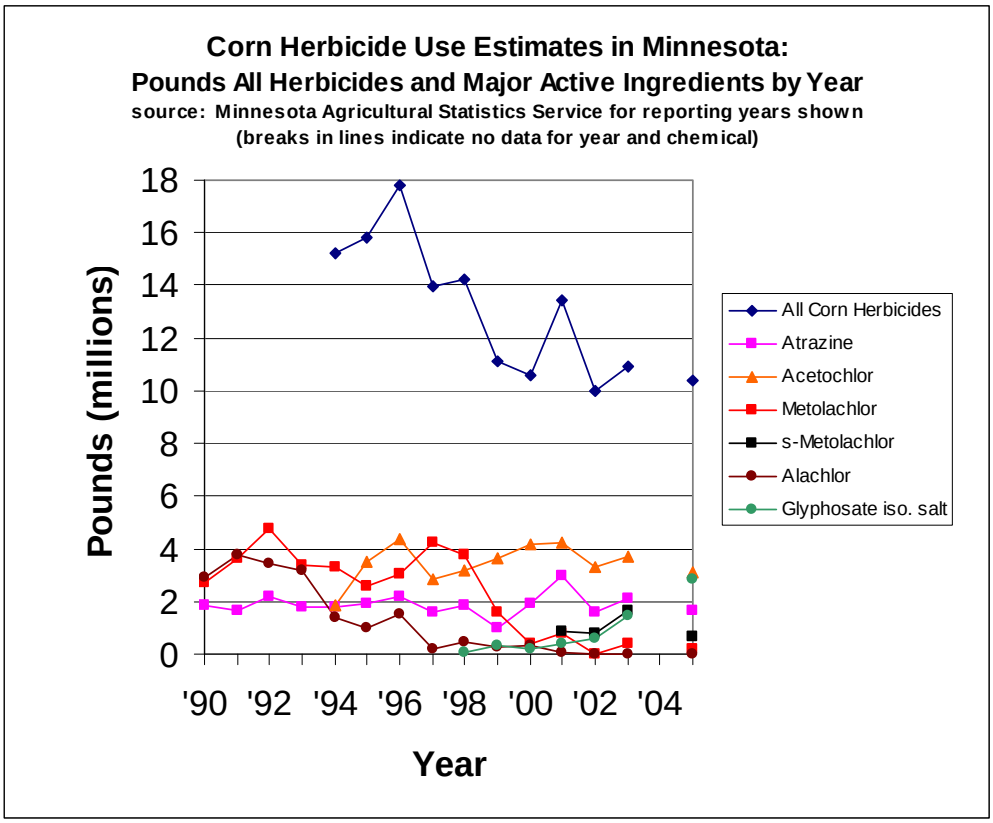
Abbreviations:

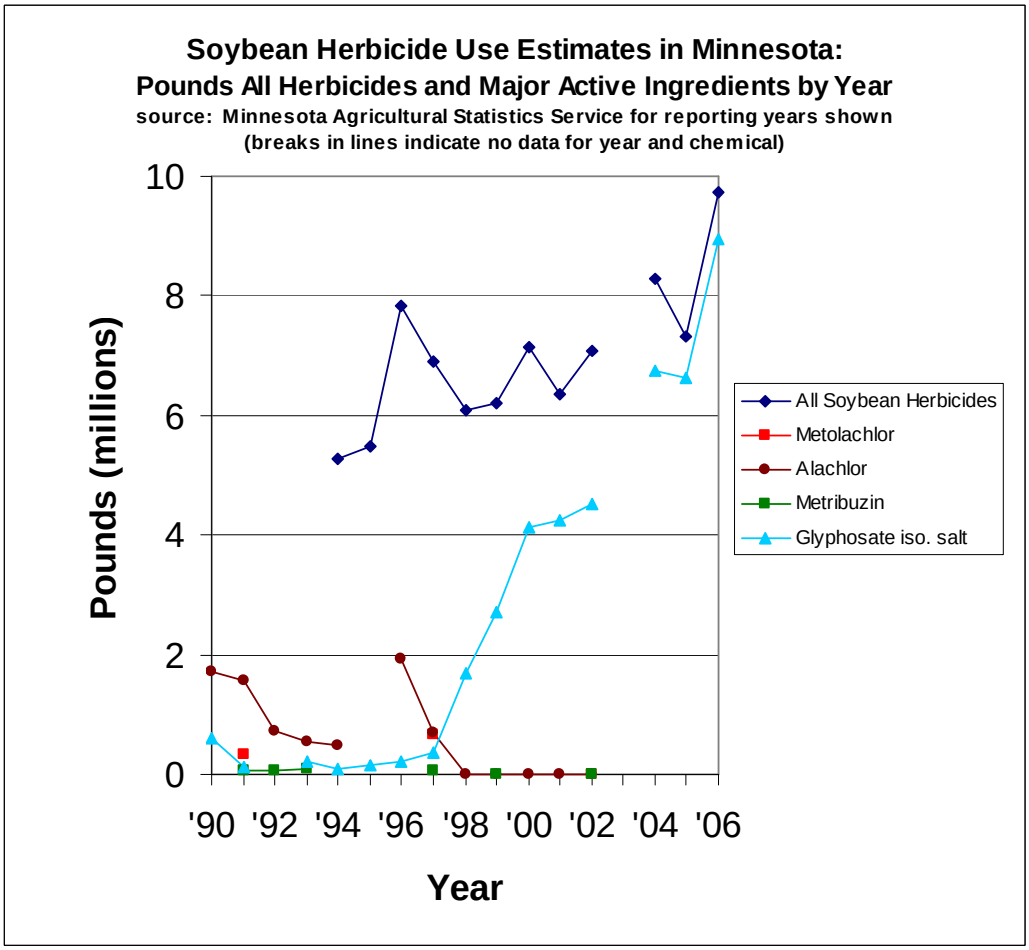
ND = Pesticide or degradate "Not Detected" during laboratory analysis

P = Pesticide or degradate is "Present" as an unquantifiable peak during laboratory analysis; a reported concentration represents a value equal to one half the method reporting limit (MRL) or estimated reporting limit (ERL).

Note: All Minnesota Department of Health groundwater Health Risk Limits (HRLs) included in this summary are those current as of July 1, 2007 and are appropriately cited until such time that new HRLs are promulgated or other guidance is provided. Minnesota Pollution Control surface water aquatic standards for acetochlor and metolachlor are proposed and pending federal approval.

Pesticide Use: Corn and Soybean (major active ingredients)

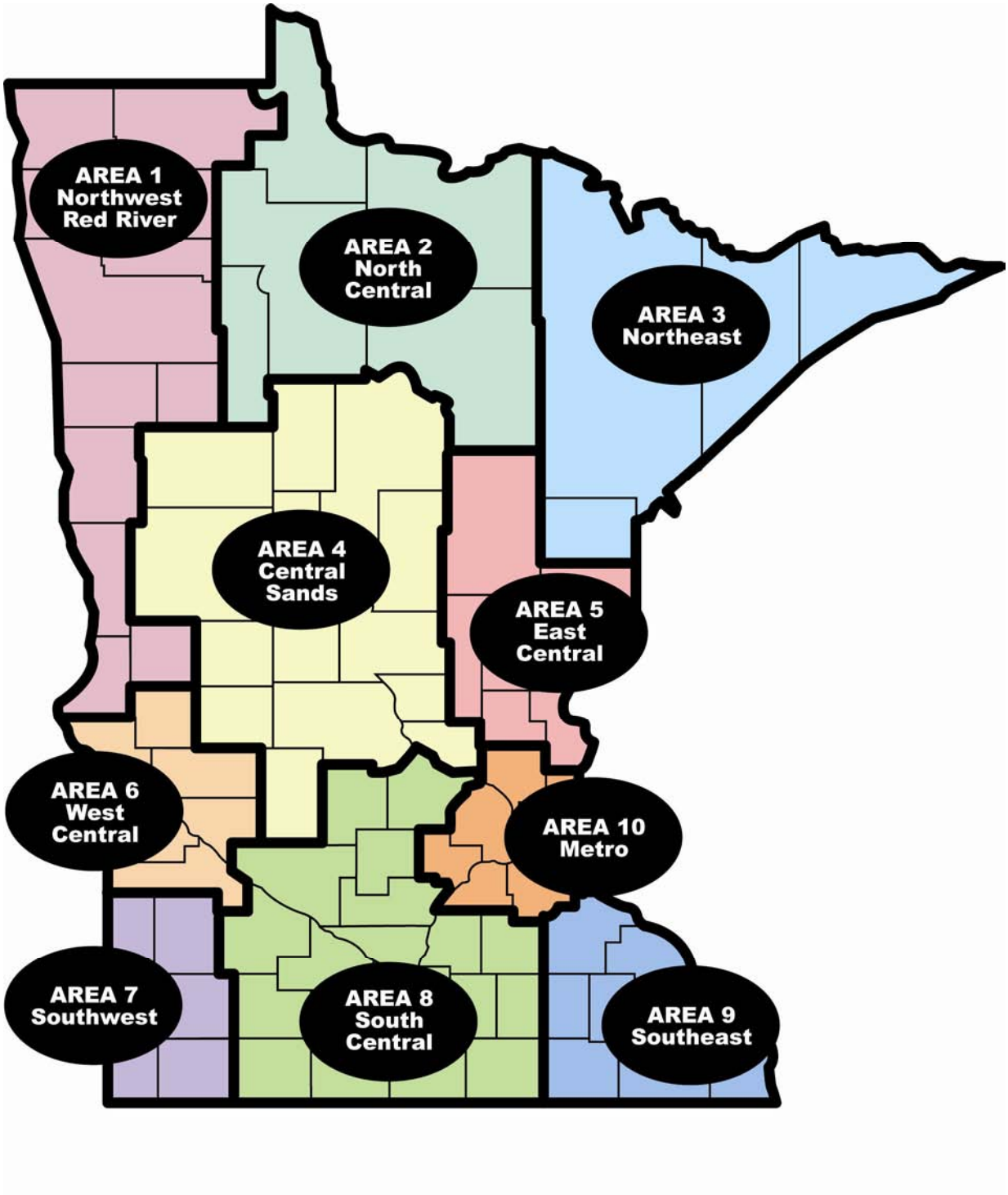




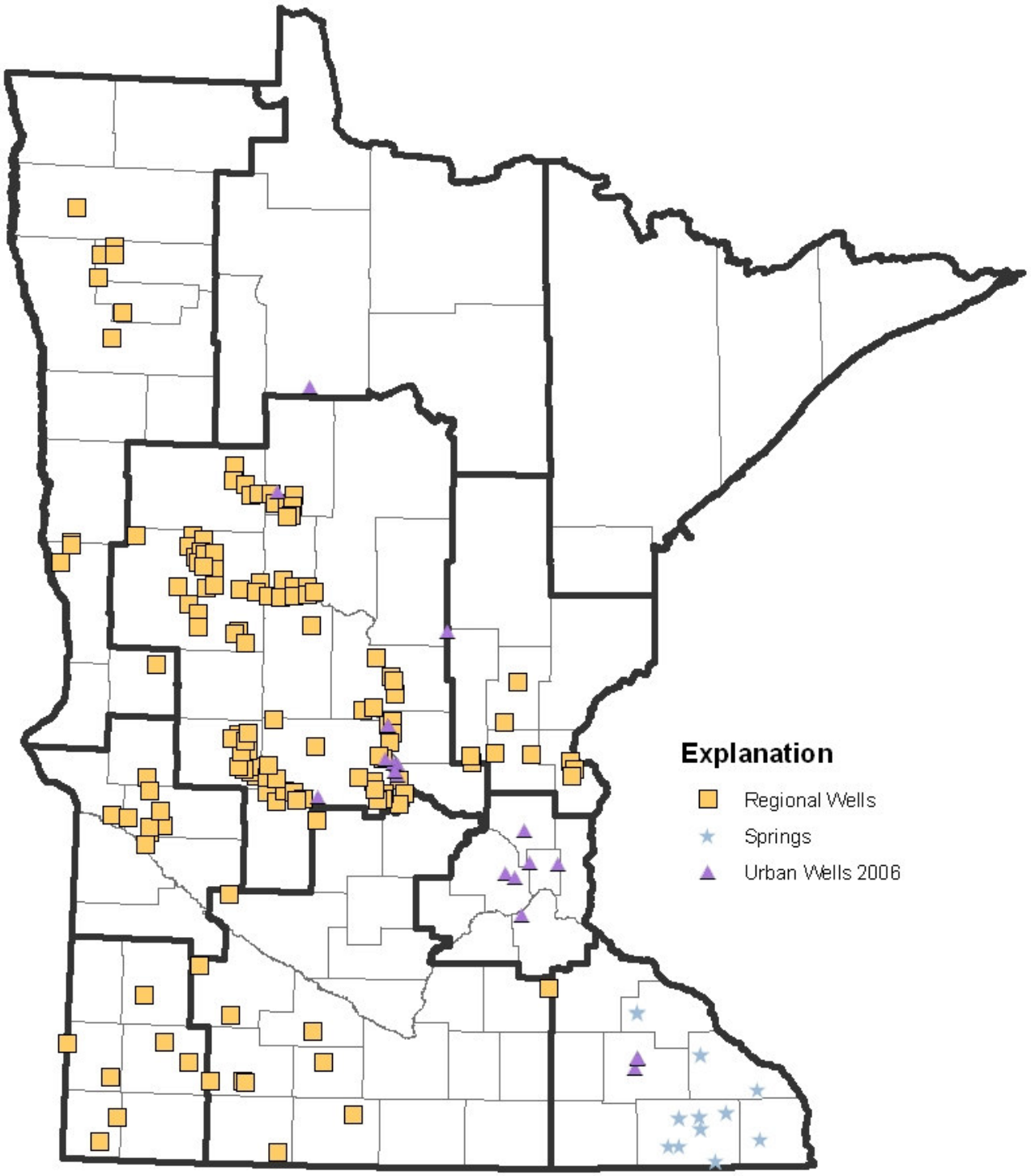
Minnesota's Pesticide Management Areas (PMAs)

The PMAs have boundaries that stratify the state according to pesticide contamination risks and management practices. They are designed to guide water quality monitoring strategies and BMP development, promotion and evaluation.

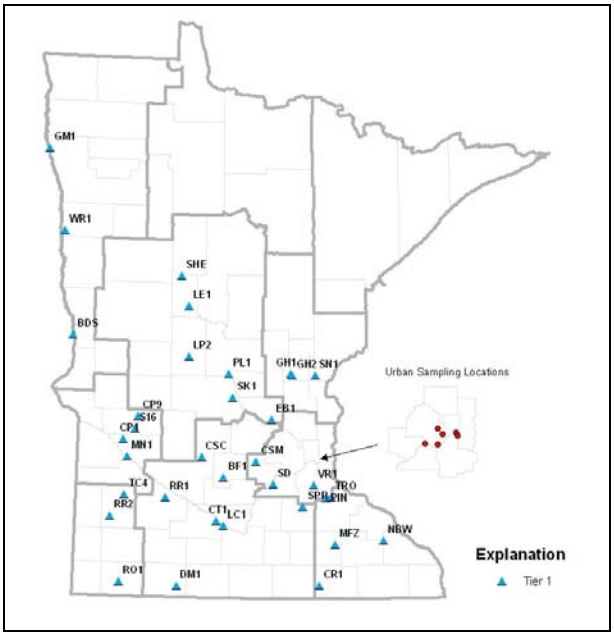
1 = Northwest Red River
2 = North Central
3 = Northeast
4 = Central Sands
5 = East Central
6 = West Central
7 = Southwest
8 = South Central
9 = Southeast
10 = Metro



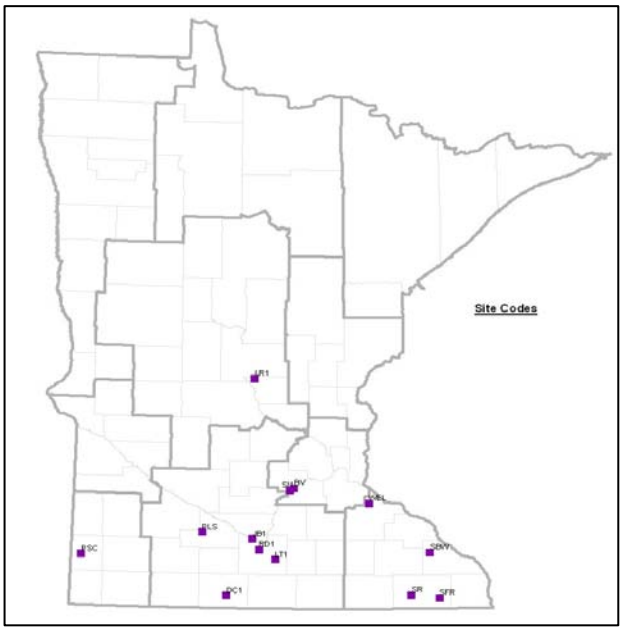
MDA Groundwater Monitoring Locations, 2006



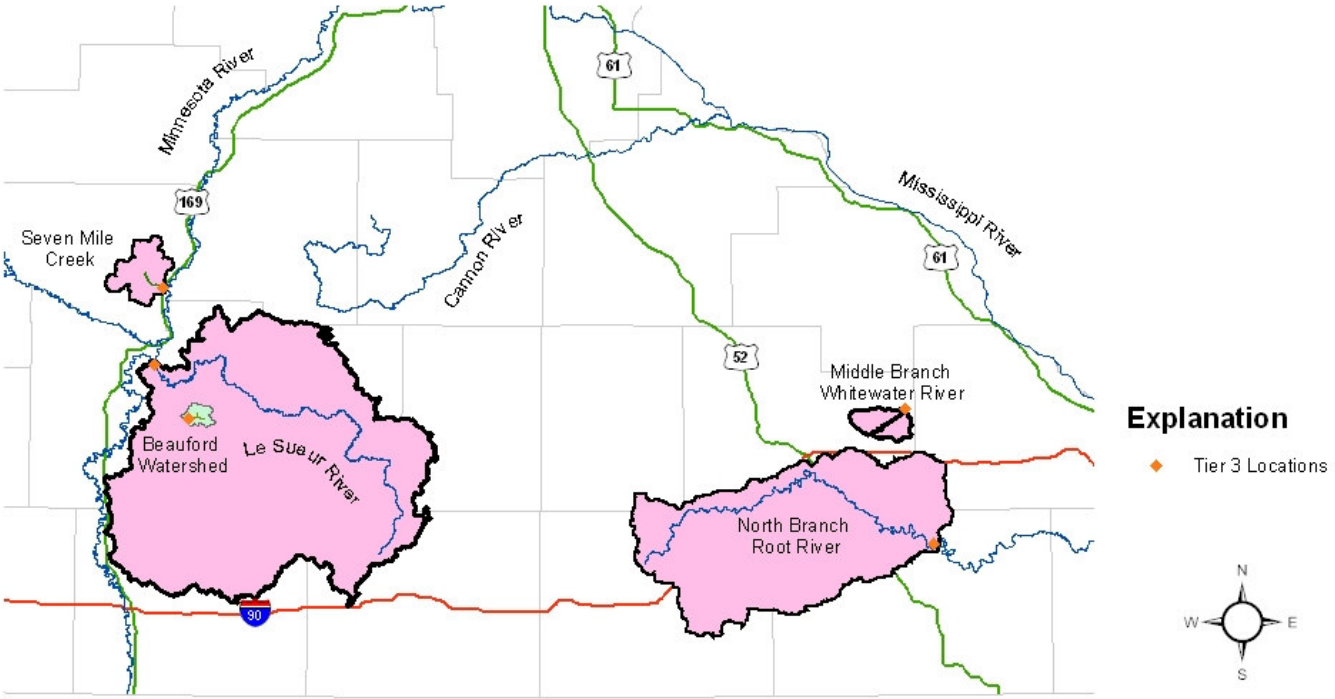
MDA Surface Water Monitoring Sites – Tier 1 2006



MDA Surface Water Monitoring Sites – Tier 2 2006



MDA Surface Water Monitoring Sites – Tier 3 2006



Groundwater Contaminant: **Acetochlor & Degradates**

HBV Parent: 10 ug/L

HBV ESA Degradate: 50 ug/L; OXA Degradate: 50 ug/L

Data comparison to HRLs or HBVs serves to screen data but is not equivalent to a health risk assessment.

1. MDA Central Sands Network: see also attached graphs

Detections (2004 - 2006)

Pesticide or Degradate	Detections (% Detections by Sample)			Concentration values of samples; all values in ug/L (ND = non detect)								
				Median			75th Percentile			Maximum		
	2004 – 108 samples	2005 – 113 samples	2006 – 113 samples	2004	2005	2006	2004	2005	2006	2004	2005	2006
Acetochlor	4 (4%)	0 (0%)	1 (1%)	ND	ND	ND	ND	ND	ND	0.025	ND	0.14
Acetochlor ESA	27 (25%)	33 (29%)	20 (18%)	ND	ND	ND	0.04	0.10	ND	5.97	16.40	26.5
Acetochlor OXA	3 (3%)	3 (3%)	2 (2%)	ND	ND	ND	ND	ND	ND	1.12	7.89	2.21
Acetochlor + Degradates	32 (30%)	34 (30%)	21 (19%)	Acetochlor ESA & OXA concentrations not additive with parent for risk comparisons								

Exceedances (2004 - 2006)

Pesticide or Degradate (number of samples collected for pesticide or degradate from 2004 through 2006)	State Health Risk Limit (HRL) – ug/L for private well drinking water supplies and for public supplies when < MCL	Number of HRL Exceedances
Acetochlor (334)	no HRL (see HBV)	not applicable
Acetochlor ESA		
Acetochlor OXA		

State Health Based Value (HBV) – ug/L an "interim" HRL; not promulgated in Minnesota Rules	Number of HBV Exceedances
10	0
50	0
50	0

Federal Maximum Contaminant Level (MCL) – ug/L for federally-regulated public drinking water supplies	Number of MCL Exceedances
no MCL	not applicable

2. MDA Regional (non-Central Sands); Sampling Sites = 34 wells (34 samples) & 11 springs (40 samples):

2006

Pesticide Monitoring Region	Pesticide or Degradate	Sites with Detections	Samples with Detections	Median (ug/L)	75th Percentile (ug/L)	Maximum (ug/L)
9 (Southeast; springs)	Acetochlor	2	2	ND	ND	P[1]
	Acetochlor ESA	3	6	ND	0.13	0.62
	Acetochlor OXA	2	3	ND	ND	0.66

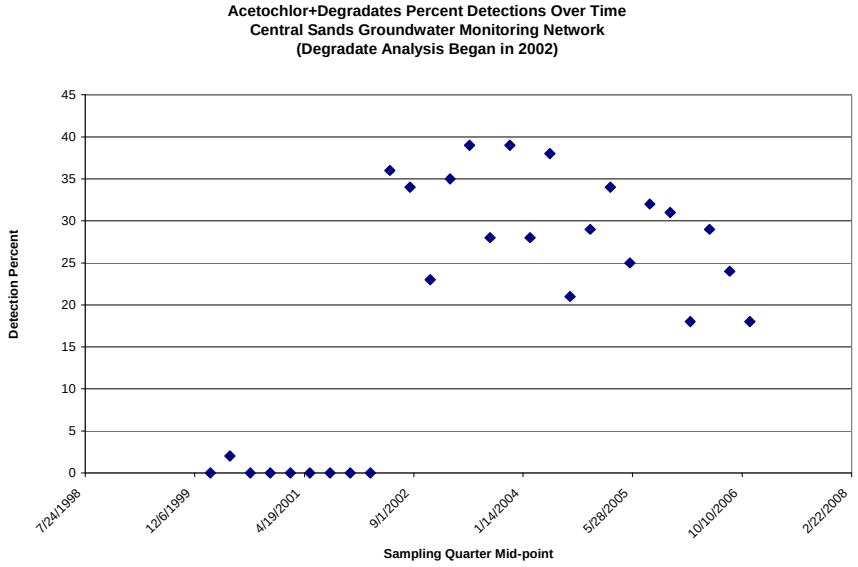
[1] P indicates that the pesticide was detected at or below the Method Reporting Limit or Estimated Reporting Limit.

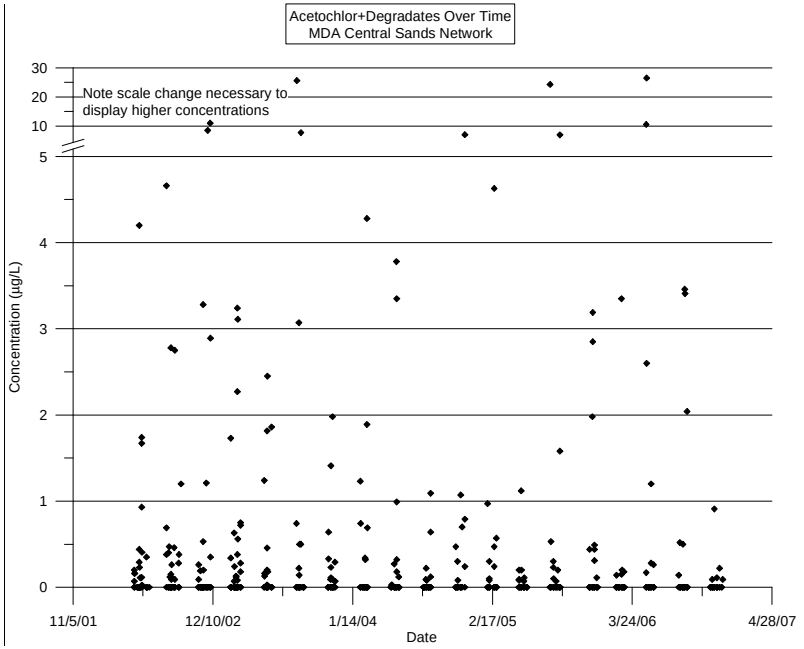
3. MDA Drinking Water Detections; 71 wells statewide:

2004

Pesticide or Degradate	Detections (% Detections by Sample)	Median of all Samples (ug/L)	90th Percentile of all Samples (ug/L)	Maximum Detected Concentration (ug/L)
Aceotchlor ESA	5 (7%)	ND	ND	3.68
Acetochlor OXA	1 (1%)	ND	ND	0.12

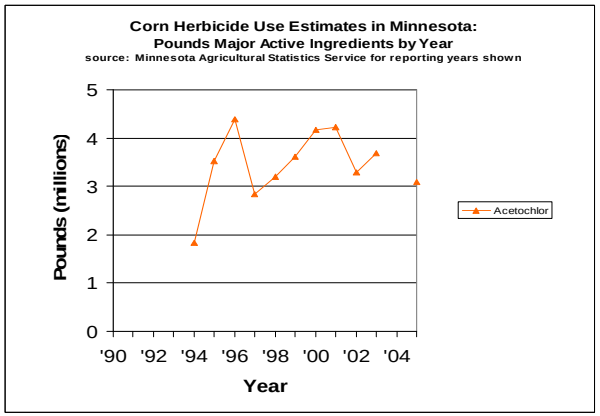
4. Acetochlor Trends: Detections & Concentrations in Central Sands Monitoring Network



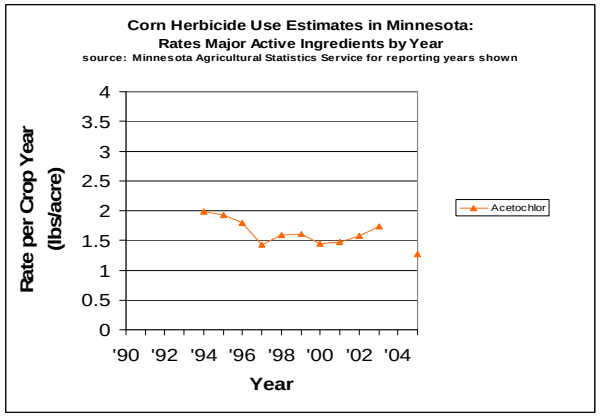


5. Acetochlor Trends: Pesticide Use & Sales

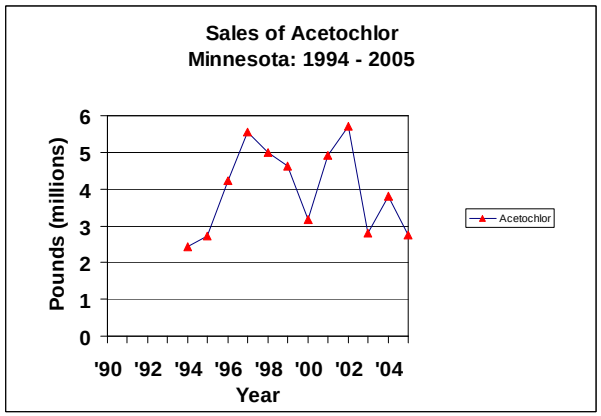
NASS: Use (Pounds)



NASS: Rate (lbs/acre)



MDA: Sales (Pounds)



Groundwater Contaminant: **Alachlor & Degradates**

HRL Parent, OXA Degradate: 2 ug/L (MCL-based July 1, 2007)
HBV ESA Degradate: 40 ug/L
Data comparison to HRLs or HBVs serves to screen data but is not equivalent to a health risk assessment.

1. MDA Central Sands Network: see also attached graphs

Detections (2004 - 2006)

Pesticide or Degradate	Detections (% Detections by Sample)			Concentration values of samples; all values in ug/L (ND = non detect)								
				Median			75th Percentile			Maximum		
	2004 – 108 samples	2005 – 113 samples	2006 – 113 samples	2004	2005	2006	2004	2005	2006	2004	2005	2006
Alachlor	0 (0%)	0 (0%)	0 (0%)	ND	ND	ND	ND	ND	ND	ND	ND	ND
Alachlor ESA	55 (51%)	50 (48%)	40 (48%)	0.10	ND	ND	0.69	0.26	0.17	8.93	4.26	4.55
Alachlor OXA	8 (7%)	7 (7%)	6 (7%)	ND	ND	ND	ND	ND	ND	1.55	1.2	1.5
Alachlor + OXA	56 (52%)	50 (48%)	40 (48%)	ND	ND	ND	ND	ND	ND	1.55	1.2	1.5

Exceedances (2004 - 2006)

Pesticide or Degradate (number of samples collected for pesticide or degradate from 2004 through 2006)	State Health Risk Limit (HRL) – ug/L for private well drinking water supplies and for public supplies when < MCL	Number of HRL Exceedances	State Health Based Value (HBV) – ug/L an "interim" HRL; not promulgated in Minnesota Rules	Number of HBV Exceedances	Federal Maximum Contaminant Level (MCL) – ug/L for federally-regulated public drinking water supplies	Number of MCL Exceedances
Alachlor (334)	2	0	not applicable	not applicable	2	0
Alachlor ESA	no HRL (see HBV)	not applicable	40 ug/L	0	comparison of degradate concentrations to parent MCL not applicable	
Alachlor OXA	use parent HRL	0	not applicable	not applicable		
Alachlor + OXA		0				

2. MDA Regional (non-Central Sands); Sampling Sites = 34 wells (34 samples) & 11 springs (40 samples):

2006

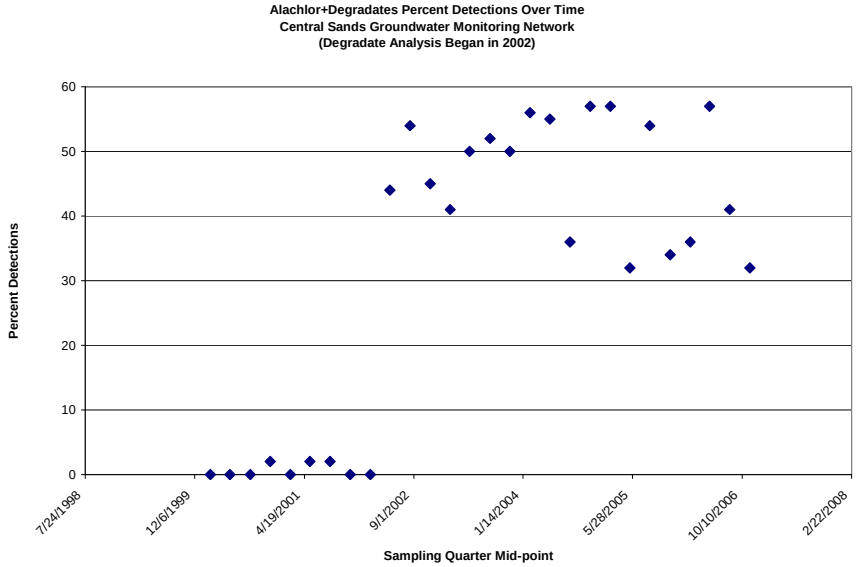
Pesticide Monitoring Region	Pesticide or Degradate	Sites with Detections	Samples with Detections	Median (ug/L)	75th Percentile (ug/L)	Maximum (ug/L)
9 (Southeast; springs)	Alachlor ESA	9	23	0.13	0.40	0.78

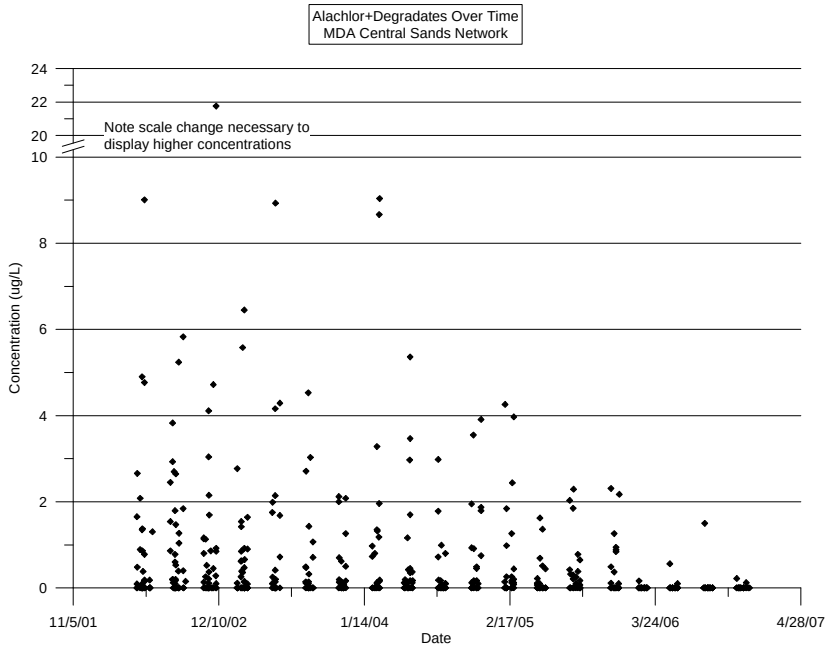
3. MDA Drinking Water Detections; 71 wells statewide:

2004

Pesticide or Degradate	# of Wells Positive	% Positive	Median of all Samples (ug/L)	90th Percentile of all Samples (ug/L)	Maximum Detected Concentration (ug/L)
Alachlor ESA	11	15.5	ND	0.56	3.46
Alachlor OXA	1	1.4	ND	ND	0.35
Alachlor + Alachlor OXA	1	1.4	ND	ND	0.35

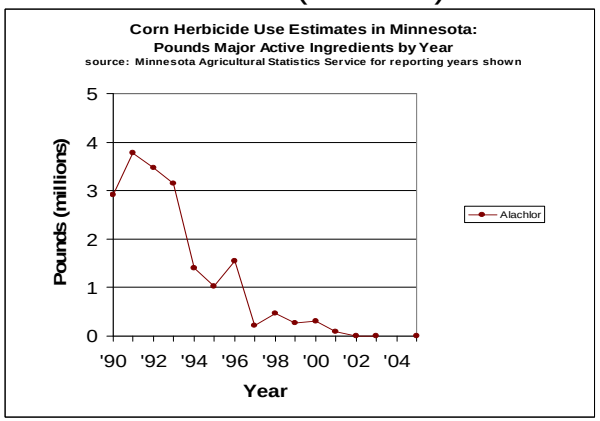
4. Alachlor Trends: Detections & Concentrations in Central Sands Monitoring Network



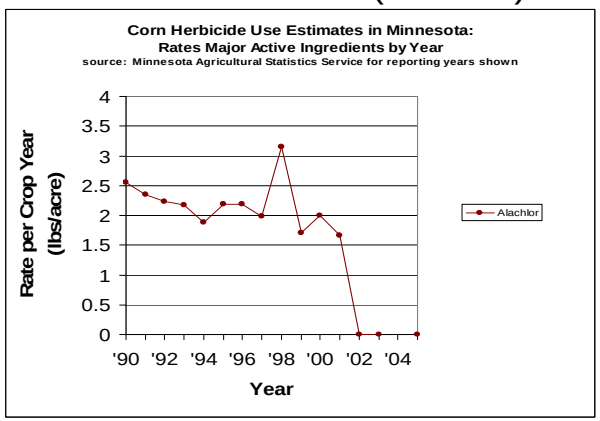


5. Alachlor Trends: Pesticide Use & Sales

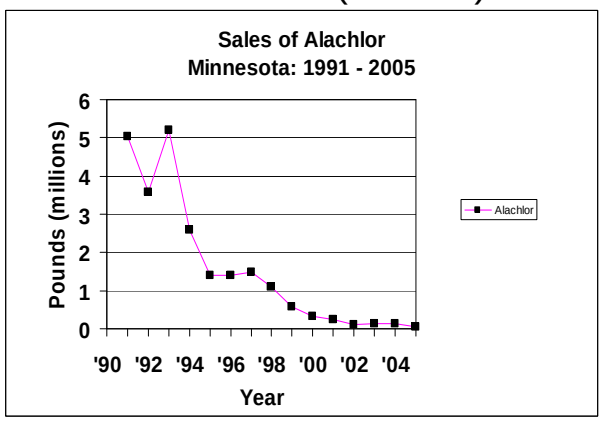
NASS: Use (Pounds)



NASS: Rate (lbs/acre)



MDA: Sales (Pounds)



Groundwater
Contaminant: **Atrazine & Degradates** **HRL Parent & Degradates: 3 ug/L (MCL-based July 1, 2007)**
Data comparison to HRLs or HBVs serves to screen data but is not equivalent to a health risk assessment.

1. MDA Central Sands Network: see also attached graphs

Detections (2004 - 2006)

Pesticide or Degradate	Detections (% Detections by Sample)			Concentration values of samples; all values in ug/L (ND = non detect)								
				Median			75th Percentile			Maximum		
	2004 – 108 samples	2005 – 113 samples	2006 – 113 samples	2004	2005	2006	2004	2005	2006	2004	2005	2006
Atrazine	55 (51%)	58 (51%)	55 (49%)	0.025	0.025	0.025	0.025	0.025	0.025	0.26	0.32	0.2
Deethylatrazine	89 (82%)	96 (85%)	79 (70%)	0.07	0.06	0.025	0.12	0.09	0.08	0.63	0.42	0.37
Deisopropylatrazine	36 (33%)	32 (28%	25 (22%)	ND	ND	ND	0.10	0.10	ND	1.43	0.72	0.42
Atrazine + Degradates	91 (84%)	97 (86%)	81 (72%)	0.12	0.085	0.075	0.22	0.185	0.15	2.32	1.17	0.91

Exceedances (2004 - 2006)

Pesticide or Degradate (number of samples collected for pesticide or degradate from 2004 through 2006)	State Health Risk Limit (HRL) – ug/L for private well drinking water supplies and for public supplies when < MCL	Number of HRL Exceedances
Atrazine (334)	3	0
Deethylatrazine	use parent HRL	0
Deisopropylatrazine		0
Atrazine + Degradates		0

State Health Based Value (HBV) – ug/L an "interim" HRL; not promulgated in Minnesota Rules	Number of HBV Exceedances
not applicable	not applicable

Federal Maximum Contaminant Level (MCL) – ug/L for federally-regulated public drinking water supplies	Number of MCL Exceedances
3	0
use parent MCL	0
	0
	0

2. MDA Regional (non-Central Sands); Sampling Sites = 34 wells (34 samples) & 11 springs (40 samples):

2006

Pesticide Monitoring Region	Pesticide or Degradate	Sites with Detections	Samples with Detections	Median (ug/L)	75th Percentile (ug/L)	Maximum (ug/L)
1 (Northwest Red River)	Atrazine	1	1	ND	ND	P[1]
	Deethylatrazine	1	1	ND	ND	0.11
6 (West Central)	Atrazine	2	2	ND	ND	P
	Deethylatrazine	2	2	ND	0.04	0.08
8 (South Central)	Atrazine	1	1	ND	ND	P
	Deethylatrazine	2	2	ND	ND	0.06
9 (Southeast; springs)	Atrazine	10	35	P	0.08	0.26
	Deethylatrazine	9	18	P	P	P
	Deisopropylatrazine	11	40	0.1	0.13	0.15

[1] P indicates that the pesticide was detected at or below the Method Reporting Limit or Estimated Reporting Limit.

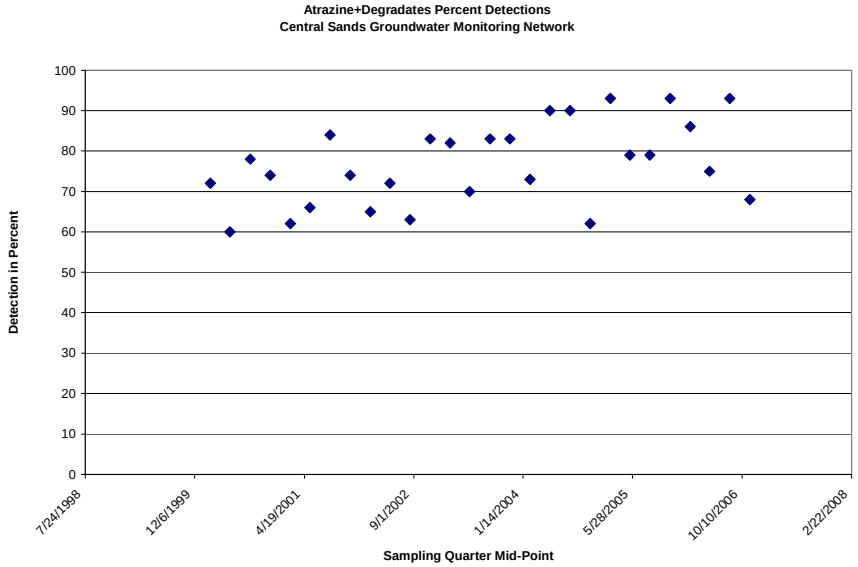
Groundwater
Contaminant: **Atrazine & Degradates** **HRL Parent & Degradates: 3 ug/L (MCL-based July 1, 2007)**
Data comparison to HRLs or HBVs serves to screen data but is not equivalent to a health risk assessment.

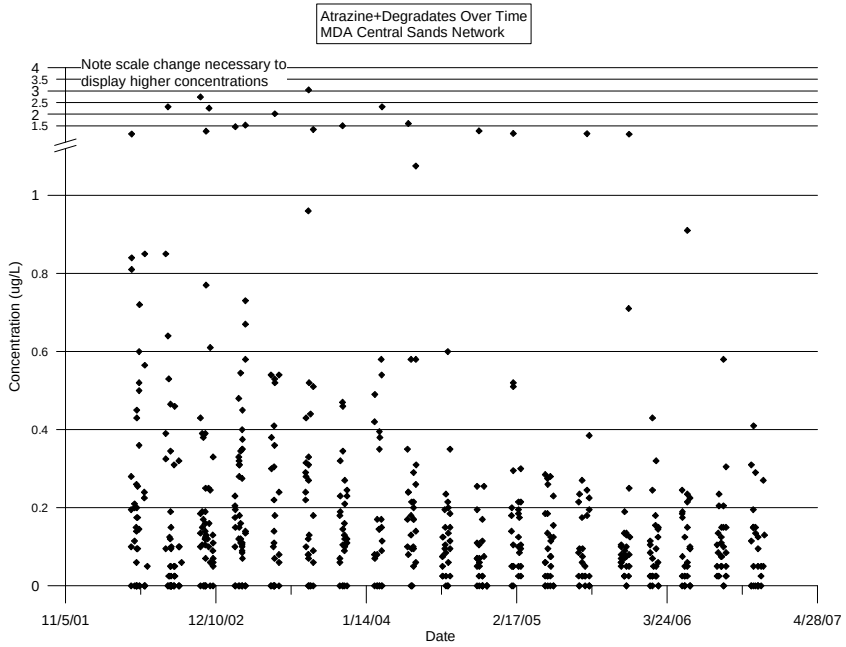
3. MDA Drinking Water Detections; 71 wells statewide:

2004

Pesticide or Degradate	# of Wells Positive	% Positive	Median of all Samples (ug/L)	90th Percentile of all Samples (ug/L)	Maximum Detected Concentration (ug/L)
Atrazine	4	5.6	ND	ND	1.52
Deisopropylatrazine	2	2.8	ND	ND	0.35
Deethylatrazine	10	14.1	ND	0.09	0.65
Atrazine + Degradates	10	14.1	ND	0.09	2.52

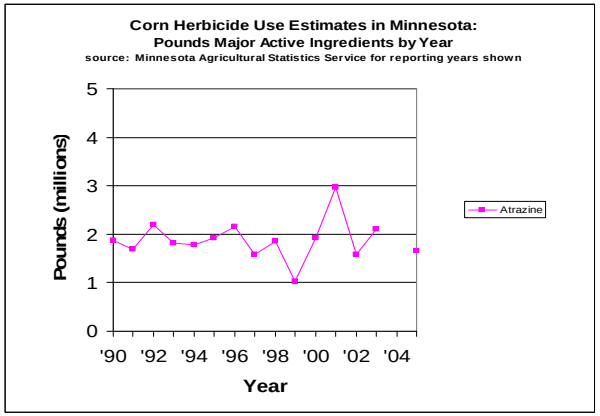
4. Atrazine Trends: Detections & Concentrations in Central Sands Monitoring Network



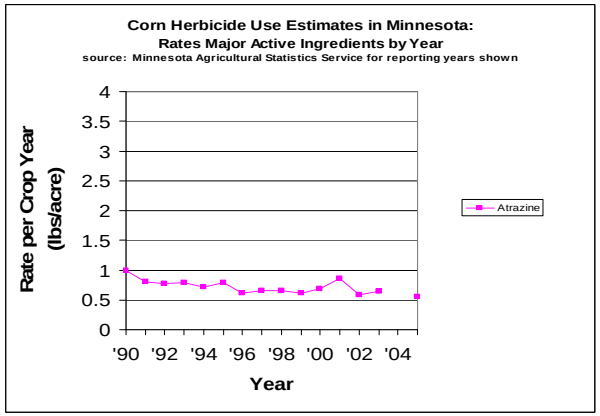


5. Atrazine Trends: Pesticide Use & Sales

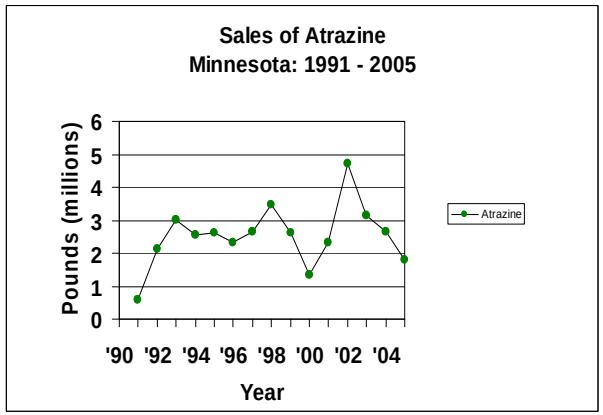
NASS: Use (Pounds)



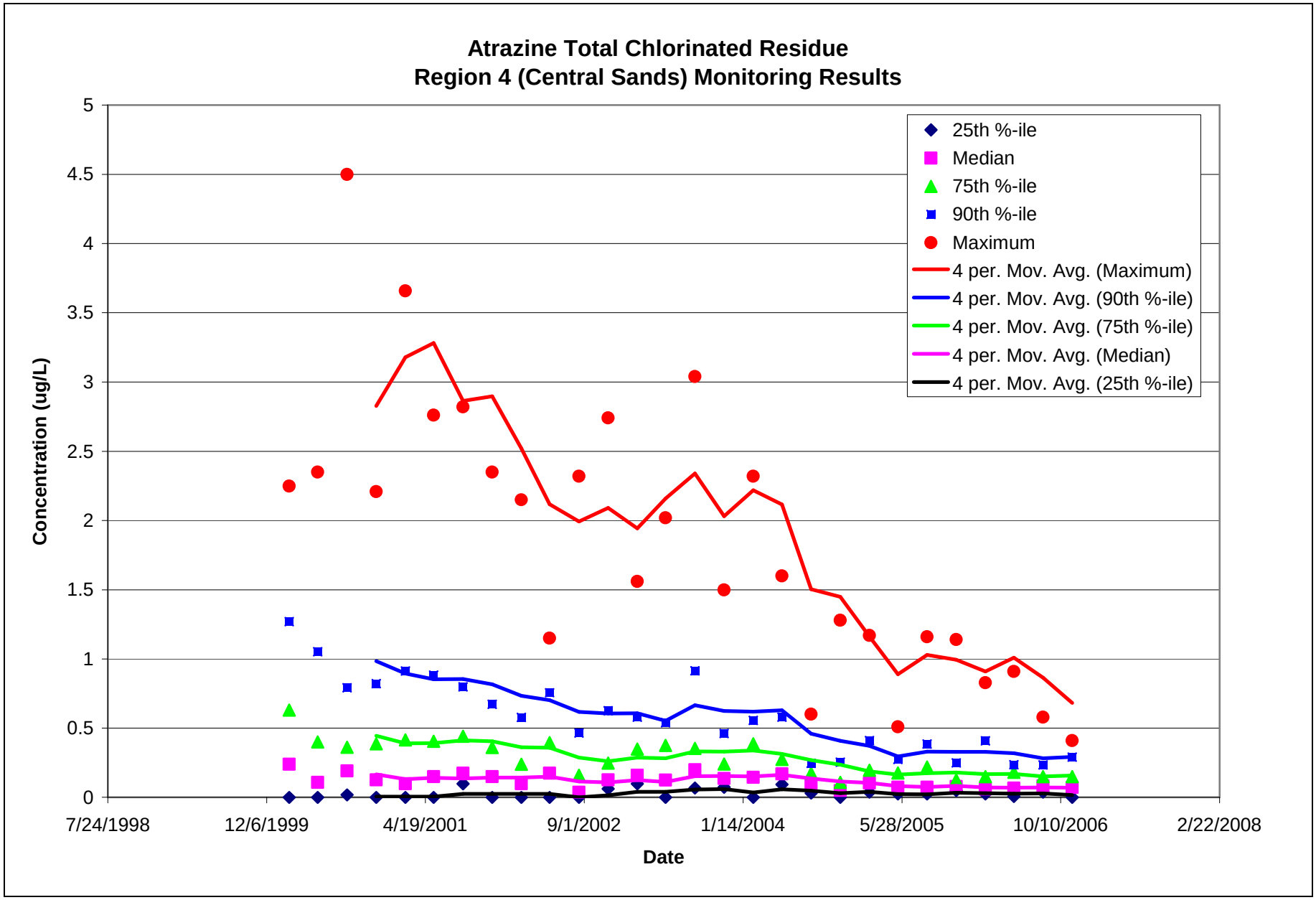
NASS: Rate (lbs/acre)



MDA: Sales (Pounds)



6. Graphical Summary of All Atrazine Data from Central Sands Network: (1999-2006):



Groundwater Contaminant: **Dimethenamid & Degradates** **HBV Parent & Degradates: 40 ug/L**

Data comparison to HRLs or HBVs serves to screen data but is not equivalent to a health risk assessment.

1. MDA Central Sands Network: see also attached graphs

Detections (2004 - 2006)

Pesticide or Degradate	Detections (% Detections by Sample)			Concentration values of samples; all values in ug/L (ND = non detect)								
				Median			75th Percentile			Maximum		
	2004 – 108 samples	2005 – 113 samples	2006 – 113 samples	2004	2005	2006	2004	2005	2006	2004	2005	2006
Dimethenamid	0 (0%)	2 (2%)	0 (0%)	ND	ND	ND	ND	ND	ND	ND	0.07	ND
Dimethenamid ESA	7 (6%)	12 (11%)	8 (7%)	ND	ND	ND	ND	ND	ND	2.22	7.06	2.06
Dimethenamid OXA	2 (2%)	5 (4%)	5 (4%)	ND	ND	ND	ND	ND	ND	1.09	3.01	0.65
Dimethenamid + degradates	7 (6%)	12 (11%)	8 (7%)	ND	ND	ND	ND	ND	ND	3.06	10.07	2.71

Exceedances (2004 - 2006)

Pesticide or Degradate (number of samples collected for pesticide or degradate from 2004 through 2006)	State Health Risk Limit (HRL) – ug/L for private well drinking water supplies and for public supplies when < MCL	Number of HRL Exceedances
Dimethenamid (334)	no HRL (see HBV)	not applicable
Dimethenamid ESA		
Dimethenamid OXA		
Dimethenamid + degradates		

State Health Based Value (HBV) – ug/L an "interim" HRL; not promulgated in Minnesota Rules	Number of HBV Exceedances
40	0
use parent HBV	0
	0
	0

Federal Maximum Contaminant Level (MCL) – ug/L for federally-regulated public drinking water supplies	Number of MCL Exceedances
no MCL	not applicable

2. MDA Regional (non-Central Sands); Sampling Sites = 34 wells (34 samples) & 11 springs (40 samples):

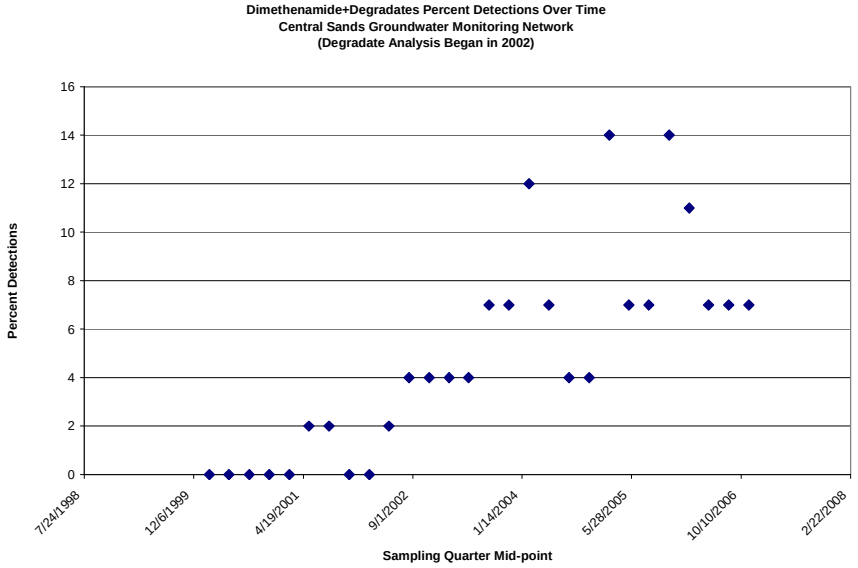
2006

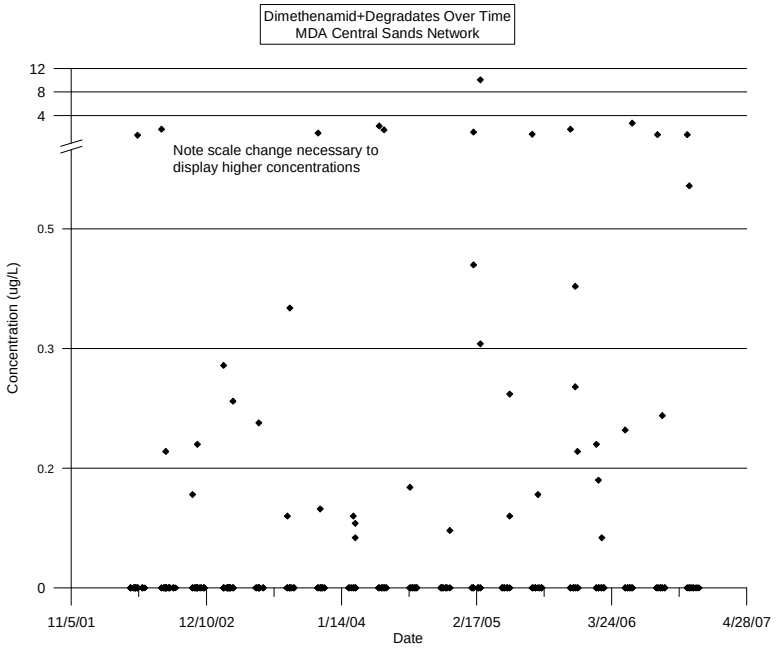
Pesticide Monitoring Region	Pesticide or Degradate	Sites with Detections	Samples with Detections	Median (ug/L)	75th Percentile (ug/L)	Maximum (ug/L)
9 (Southeast; springs)	Dimethenamid	4	10	ND	ND	0.58
	Dimethenamid ESA	9	26	0.11	0.74	2.77
	Dimethenamid OXA	4	6	ND	0.12	0.61

3. MDA Drinking Water Detections; 71 wells statewide: no detections

2004

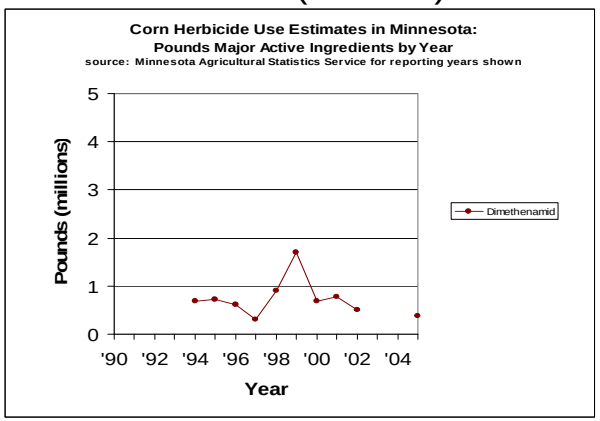
4. Dimethenamid Trends: Detections & Concentrations in Central Sands Monitoring Network



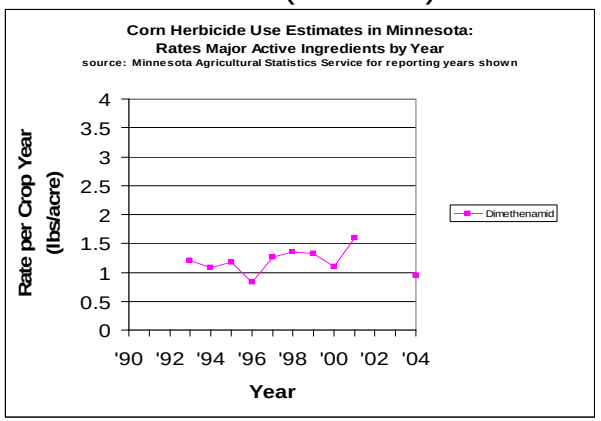


5. Dimethenamid Trends: Pesticide Use & Sales

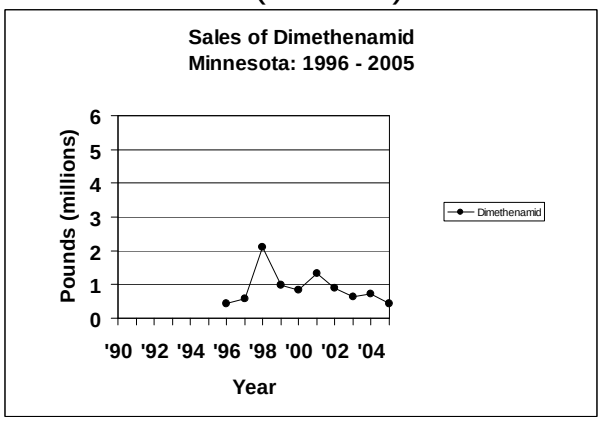
NASS: Use (Pounds)



NASS: Rate (lbs/acre)



MDA: Sales (Pounds)



Groundwater Contaminant: **Metolachlor & Degradates**

HRL Parent: 100 ug/L

HBV ESA Degradate: 1000 ug/L; OXA Degradate: 1000 ug/L

Data comparison to HRLs or HBVs serves to screen data but is not equivalent to a health risk assessment.

1. MDA Central Sands Network: see also attached graphs

Detections (2004 - 2006)

Pesticide or Degradate	Detections (% Detections by Sample)			Concentration values of samples; all values in ug/L (ND = non detect)								
				Median			75th Percentile			Maximum		
	2004 – 108 samples	2005 – 113 samples	2006 – 113 samples	2004	2005	2006	2004	2005	2006	2004	2005	2006
Metolachlor	10 (9%)	9 (8%)	10 (9%)	ND	ND	ND	ND	ND	ND	0.27	1.87	0.76
Metolachlor ESA	68 (63%)	74 (65%)	57 (50%)	0.18	0.23	0.13	1.72	1.13	1.2	15.60	10.2	12.7
Metolachlor OXA	34 (31%)	30 (27%)	26 (23%)	ND	ND	ND	0.14	0.10	0.07	8.54	6.75	4.9
Metolachlor + degradates	68 (63%)	74 (65%)	57 (50%)	Metolachlor ESA & OXA concentrations not additive with parent for risk comparisons								

Exceedances (2004 - 2006)

Pesticide or Degradate (number of samples collected for pesticide or degradate from 2004 through 2006)	State Health Risk Limit (HRL) – ug/L for private well drinking water supplies and for public supplies when < MCL	Number of HRL Exceedances
Metolachlor (334)	100	0
Metolachlor ESA	no HRL (see HBV)	not applicable
Metolachlor OXA		

State Health Based Value (HBV) – ug/L an "interim" HRL; not promulgated in Minnesota Rules	Number of HBV Exceedances
not applicable	not applicable
1000 ug/L	0
1000 ug/L	0

Federal Maximum Contaminant Level (MCL) – ug/L for federally-regulated public drinking water supplies	Number of MCL Exceedances
no MCL	not applicable

2. MDA Regional (non-Central Sands); Sampling Sites = 34 wells (34 samples) & 11 springs (40 samples):

2006

Pesticide Monitoring Region	Pesticide or Degradate	Sites with Detections	Samples with Detections	Median (ug/L)	75th Percentile (ug/L)	Maximum (ug/L)
8 (South Central)	Metolachlor	1	1	ND	ND	P
9 (Southeast; springs)	Metolachlor	4	10	ND	ND	0.58
	Metolachlor ESA	9	26	0.11	0.74	2.77
	Metolachlor OXA	4	6	ND	0.12	0.61

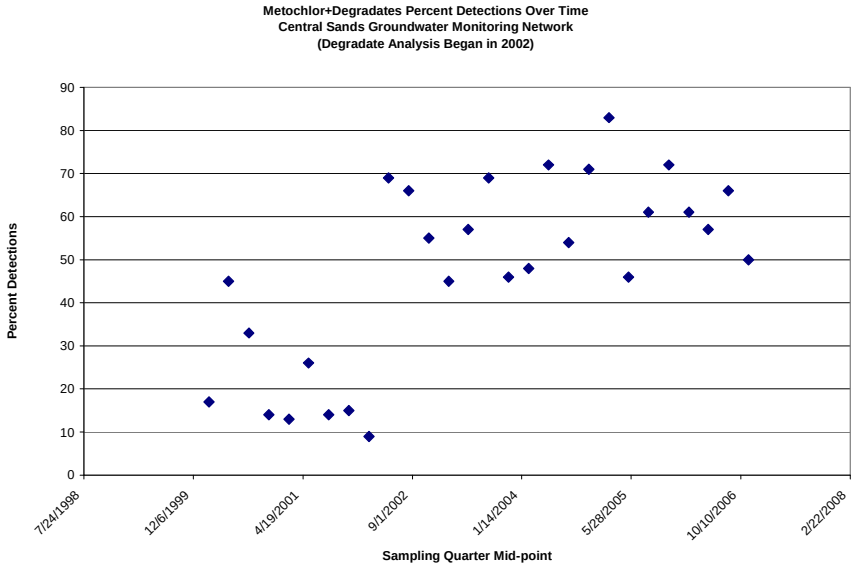
[1] P indicates that the pesticide was detected at or below the Method Reporting Limit or Estimated Reporting Limit.

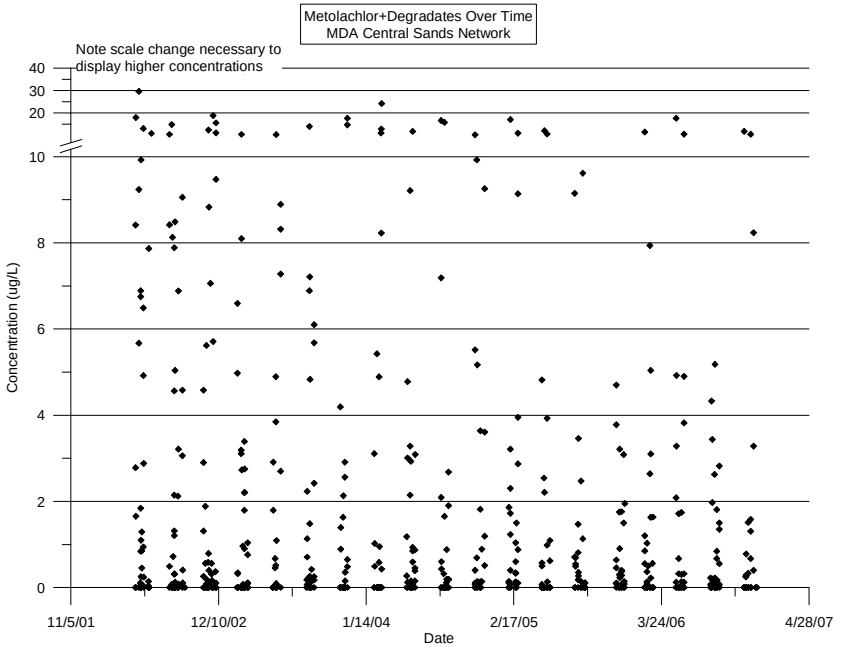
3. MDA Drinking Water Detections; 71 wells statewide:

2004

Analyte Detected	# of Wells Positive	% Positive	Median of all Samples (ug/L)	90th Percentile of all Samples (ug/L)	Maximum Detected Concentration (ug/L)
Metolachlor	3	4.2	ND	ND	P
Metolachlor ESA	9	12.6	ND	0.25	6.74
Metolachlor OXA	5	7.0	ND	ND	0.45

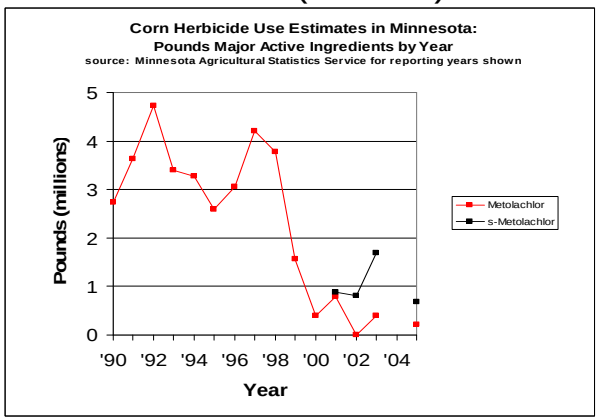
4. Metolachlor Trends: Detections & Concentrations in Central Sands Monitoring Network



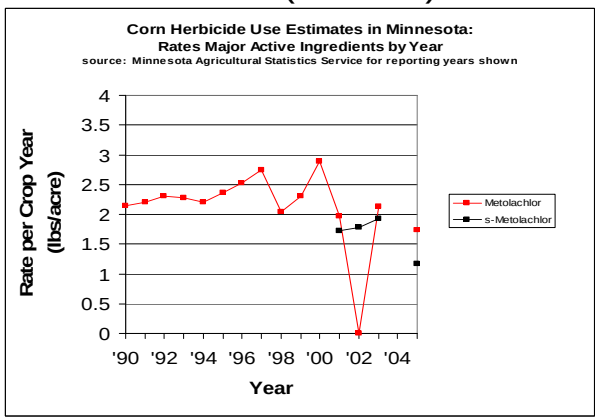


5. Metolachlor Trends: Pesticide Use & Sales

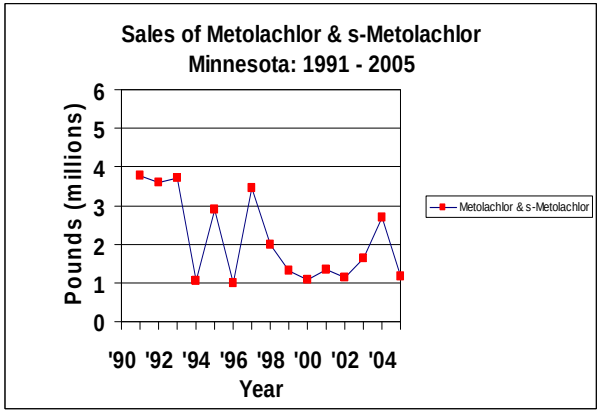
NASS: Use (Pounds)



NASS: Rate (lbs/acre)



MDA: Sales (Pounds)



Groundwater Contaminant: **Metribuzin & Degradates** **HRL Parent & Degradates: 200 ug/L**

Data comparison to HRLs or HBVs serves to screen data but is not equivalent to a health risk assessment.

1. MDA Central Sands Network: see also attached graphs

Detections (2004 - 2006)

Pesticide or Degradate	Detections (% Detections by Sample)			Concentration values of samples; all values in ug/L (ND = non detect)								
				Median			75th Percentile			Maximum		
	2004 – 108 samples	2005 – 113 samples	2006 – 113 samples	2004	2005	2006	2004	2005	2006	2004	2005	2006
Metribuzin	14 (13%)	14 (12%)	12 (11%)	ND	ND	ND	ND	ND	ND	0.43	1.24	1.06
Metribuzin DADK	24 (23%)	23 (20%)	21 (19%)	ND	ND	ND	ND	ND	ND	8.55	5.60	9.28
Metribuzin DK	15 (14%)	8 (7%)	15 (13%)	ND	ND	ND	ND	ND	ND	1.06	1.20	1.49
Metribuzin DA	7 (7%)	4 (4%)	7 (6%)	ND	ND	ND	ND	ND	ND	1.17	0.05	0.5
Metribuzin + Degradates	26 (26%)	25 (22%)	22 (20%)	ND	ND	ND	0.09	ND	ND	10.54	7.84	10.52

Exceedances (20004- 2006)

Pesticide or Degradate (number of samples collected for pesticide or degradate from 2004 through 2006)	State Health Risk Limit (HRL) – ug/L for private well drinking water supplies and for public supplies when < MCL	Number of HRL Exceedances
Metribuzin (334)	200	0
Metribuzin DADK	use parent HRL	0
Metribuzin DK		0
Metribuzin DA		0
Metribuzin + Degradates		0

State Health Based Value (HBV) – ug/L an "interim" HRL; not promulgated in Minnesota Rules	Number of HBV Exceedances
not applicable	not applicable

Federal Maximum Contaminant Level (MCL) – ug/L for federally-regulated public drinking water supplies	Number of MCL Exceedances
no MCL	not applicable

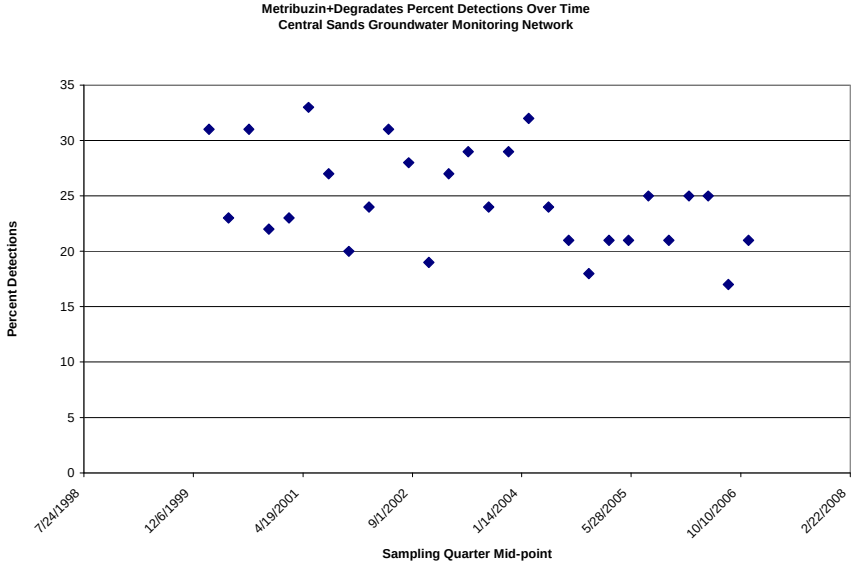
2. MDA Regional (non-Central Sands) Sampling Sites = 34 wells (34 samples) & 11 springs (40 samples): no detections

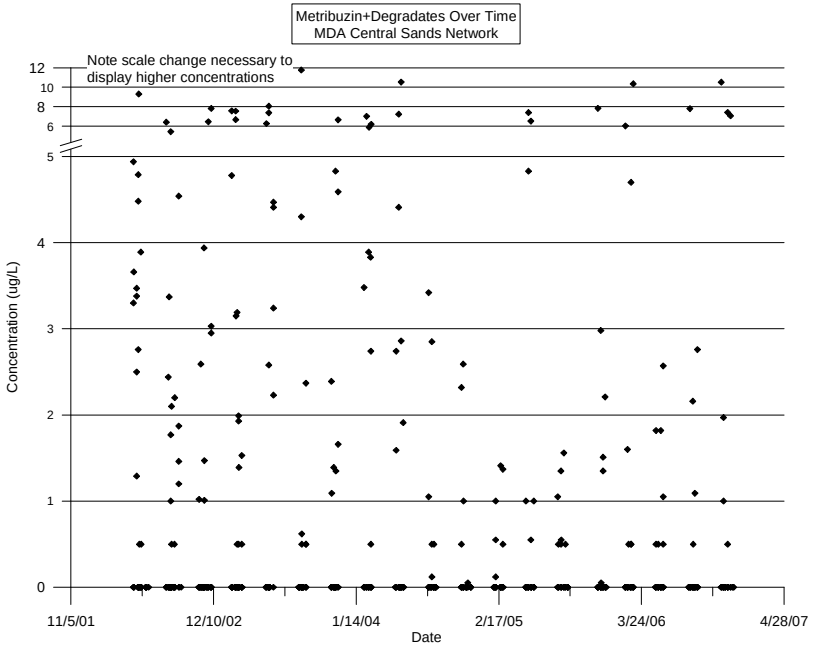
2006

3. MDA Drinking Water Detections; 71 wells statewide: no detections

2004

4. Metribuzin Trends: Detections & Concentrations in Central Sands Monitoring Network



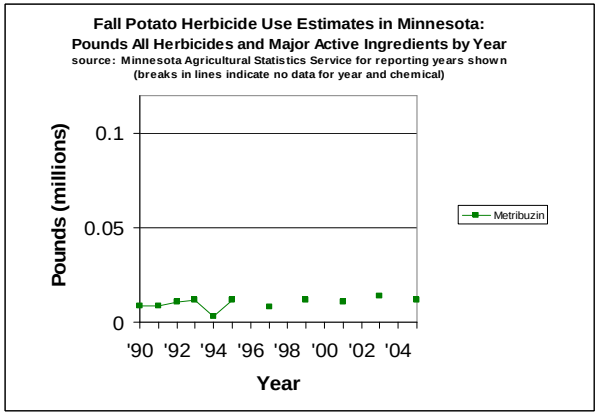


5. Metribuzin Trends: Pesticide Use & Sales

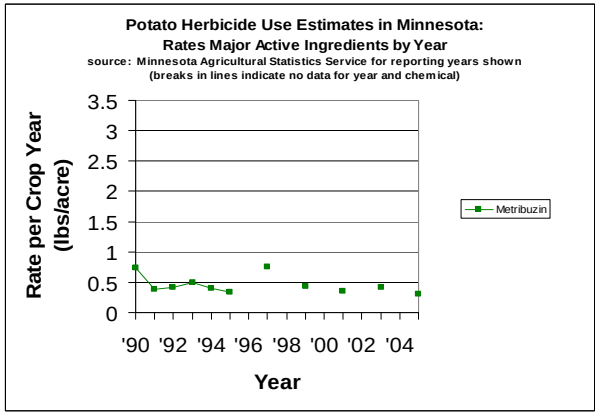
NASS: Use (Pounds)

Data shown only for fall potatoes

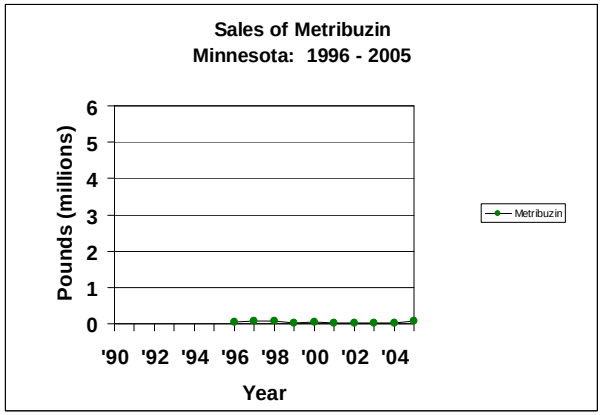
Use in soybeans no longer significant



NASS: Rate (lbs/acre)



MDA: Sales (Pounds)



Surface Water Contaminants:	Reference Value(s)
Acetochlor	**1.4 ug/L (current advisory value; 4-day aquatic toxicity); 3.6 ug/L (proposed standard; 4-day aquatic toxicity)**
Atrazine	**10 ug/L standard (4-day aquatic toxicity)**
Chlorpyrifos	**0.041 ug/L (4-day aquatic toxicity)**
Diazinon	**0.1 ug/L (EPA/Office of Pesticide Programs – acute invertebrate)**
Metolachlor	**10 ug/L (current advisory value; 4-day aquatic toxicity); 23 ug/L (proposed standard; 4-day aquatic toxicity)**

Exceedance of reference value or fraction thereof does not imply a violation of water quality standards or impairment for a given use.

1. Tier 1 Surface Water Monitoring; Sites Exceeding 50 Percent of Reference Value in 2006
   (Sites exceeding 50 percent of the reference value become candidates for Tier 2 sampling the subsequent year)

Site Name	PMR	Stream Class	Pesticide Evaluated	Maximum Concentration Measured (ug/L)	Date of Maximum Concentration	50% of Reference Value (ug/L)	Reference Value Source
Buffalo River-Dilworth	1	2B	Chlorpyrifos	Present = 0.05	7/17/2006	0.020	MPCA 7050
Snake River	1	2B	Chlorpyrifos	Present = 0.05	7/18/2006	0.020	MPCA 7050
Nine Mile Creek [a]	10	2B	Diazinon	Present = 0.06	7/12/2006	0.05	EPA Reference

[a] Urban Tier 1 sampling sites included analysis for and detections of acid herbicides diazinon, oxadiazon, 2,4-D, dicamba, dichlorprop, MCPA, MCPP and Triclopyr.

2. Tier 2 Surface Water Monitoring: No Sites Exceeded Reference Values in 2006
   (Sites exceeding reference values become candidates for Tier 3 sampling the subsequent year)

Surface Water Contaminants:	Reference Value(s)
Acetochlor	**1.4 ug/L (current advisory value; 4-day aquatic toxicity); 3.6 ug/L (proposed standard; 4-day aquatic toxicity)**
Atrazine	**10 ug/L standard (4-day aquatic toxicity)**
Metolachlor	**10 ug/L (current advisory value; 4-day aquatic toxicity); 23 ug/L (proposed standard; 4-day aquatic toxicity)**

Exceedance of reference value or fraction thereof does not imply a violation of water quality standards or impairment for a given use.

3. Tier 1 & 2 Annual Maximums and Medians by Pesticide Monitoring Region; 2004-2006

Acetochlor

	Annual Maximum				Field Season Median (Mid-May to Mid-July)		
Pesticide Monitoring Region	**2004**	**2005**	**2006**		**2004**	**2005**	**2006**
1	0.12	0.44	0.09		0.00	0.00	0.00
4	0.13	0.23	0.035		0.025	0.025	0
5	---[1]	0.06	---		---	0.00	---
6	0.05	0.48	0.025		0.00	0.025	0.00
7	---	1.16	0.2		---	0.025	0.00
8	1.85	1.43	0.75		0.09	0.05	0.025
9	1.01	1.35	0.23		0.06	0.00	0.00
10	1.44	0.92	0.07		0.12	0.00	0.00

Atrazine

	Annual Maximum				Field Season Median (Mid-May to Mid-July)		
Pesticide Monitoring Region	**2004**	**2005**	**2006**		**2004**	**2005**	**2006**
1	0.16	0.83	0.16		0.07	0.025	0.025
4	0.20	1.87	0.35		0.08	0.08	0.025
5	---	0.16	---		---	0.025	---
6	0.26	3.20	0.10		0.14	0.26	0.025
7	---	5.70	1.26		---	0.17	0.05
8	2.00	1.10	1.73		0.38	0.12	0.07
9	7.40	5.70	1.59		1.49	0.08	0.07
10	1.39	13.2	0.54		0.44	0.14	0.05

Metolachlor

	Annual Maximum				Field Season Median (Mid-May to Mid-July)		
Pesticide Monitoring Region	**2004**	**2005**	**2006**		**2004**	**2005**	**2006**
1	0.18	0.18	0.11		0.035	0.00	0.00
4	0.07	1.45	0.035		0.00	0.035	0.00
5	---	0.035	---		---	0.00	---
6	0.10	0.53	0.035		0.06	0.035	0.00
7	---	0.98	0.50		---	0.035	0.035
8	0.31	0.87	0.99		0.08	0.07	0.035
9	14.0	3.10	1.04		0.33	0.035	0.035
10	2.02	2.74	0.36		0.23	0.05	0.00

[1] --- = No sample collected for year/region indicated.

Surface Water Contaminant:	**Acetochlor**	Reference Value **1.4 ug/L (current advisory value; 4-day aquatic toxicity);** **3.6 ug/L (proposed standard; 4-day aquatic toxicity)**

Exceedance of reference value or fraction thereof does not imply a violation of water quality standards or impairment for a given use.

4. Tier 3 Intensive Monitoring Sites Occurrence Data; Trends 2004 – 2006:

Acetochlor

Storm Samples Positive/Number Storm Samples = % Positive for Pesticide			Base Flow Samples Positive/Number Base Flow Samples = % Positive for Pesticide			Site Sample Results Status: Comparisons Made to Available 4-day Chronic Aquatic Toxicity Reference Values[1]	Beauford Ditch			Blue Earth River- Rapidan Dam (Moved to Tier 2 in 2005)			Le Sueur River- Hwy 66			Middle Branch- Whitewater River			Minnesota River- Judson Bridge (Moved to Tier 2 in 2005)			North Branch- Root River			Seven Mile Creek #3		
2004	2005	2006	2004	2005	2006		2004	2005	2006	2004	2005 (T2)[2]	2006 (T2)	2004	2005	2006	2004	2005	2006	2004	2005 (T2)	2006 (T2)	2004	2005	2006	2004	2005	2006
						Detected in?	Not monitored	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
						# > 10% Current Advisory Value		10	2	9	4	2	13	4	5	18	2	0	10	0	1	9	0	2	9	4	3
						# > 10% Proposed Standard		9	1	5	0	0	10	3	3	11	2	0	6	0	0	7	0	1	5	3	3
87/120 = 73%	36/63 = 57%	22/34 = 65%	33/83 = 40%	28/64 = 44%	14/29 = 48%	# > 50% Current Advisory Value		7	1	4	0	0	5	3	1	4	2	0	2	0	0	6	0	1	4	1	0
						# > 50% Proposed Standard		5	0	0	0	0	0	2	0	1	1	0	0	0	0	1	0	0	1	0	0
						# > Current Advisory Value		5	1	2	0	0	2	2	0	2	1	0	0	0	0	1	0	1	2	0	0
						# > Proposed Standard		4	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0

[1] The acetochlor proposed standard has a corresponding 30-day human health chronic standard for surface waters protected as potential sources of drinking water and associated fish consumption (Middle Branch-Whitewater River and Seven Mile Creek #3).

[2] T2 = Tier 2 sampling site; Indicates that up to 8 samples were collected at that location from Mid-May to Mid-July.

Surface Water Contaminant:	Reference Value
Atrazine	**10 ug/L standard (4-day aquatic toxicity)**

Exceedance of reference value or fraction thereof does not imply a violation of water quality standards or impairment for a given use.

Atrazine

Storm Samples Positive/Number Storm Samples = % Positive for Pesticide			Base Flow Samples Positive/Number Base Flow Samples = % Positive for Pesticide			Site Sample Results Status: Comparisons Made to Available Chronic Aquatic Toxicity Reference Values[1]	Beauford Ditch			Blue Earth River-Rapidan Dam			Le Sueur River-Hwy 66			Middle Branch-Whitewater River			Minnesota River-Judson Bridge			North Branch-Root River			Seven Mile Creek #3		
2004	2005	2006	2004	2005	2006		2004	2005	2006	2004	2005 (T2)[2]	2006 (T2)	2004	2005	2006	2004	2005	2006	2004	2005 (T2)	2006 (T2)	2004	2005	2006	2004	2005	2006
						Detected in?	Not monitored	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
120/120 = 100%	61/63 = 97%	28/34 = 82%	75/83 = 83%	63/64 = 98%	27/29 = 93%	# > 10% Standard		3	0	3	1	0	3	0	0	24	1	0	3	0	0	7	2	0	3	2	3
						# > 50% Standard		0	0	0	0	0	0	0	0	8	0	0	0	0	0	2	0	0	0	1	0

[1] The atrazine standard has a corresponding 30-day human health chronic standard for surface waters protected as potential sources of drinking water and associated fish consumption (Middle Branch-Whitewater River and Seven Mile Creek #3).

[2] T2 = Tier 2 sampling site; Indicates that up to 8 samples were collected at that location from Mid-May to Mid-July.

Surface Water Contaminant:	**Metolachlor**	Reference Value
		10 ug/L (current advisory value; 4-day aquatic toxicity);
		23 ug/L (proposed standard; 4-day aquatic toxicity)

Exceedance of reference value or fraction thereof does not imply a violation of water quality standards or impairment for a given use.

Metolachlor

Storm Samples Positive/Number Storm Samples = % Positive for Pesticide			Base Flow Samples Positive/Number Base Flow Samples = % Positive for Pesticide			Site Sample Results Status: Comparisons Made to Available Chronic Aquatic Toxicity Reference Values[1]	Beauford Ditch			Blue Earth River-Rapidan Dam			Le Sueur River-Hwy 66			Middle Branch-Whitewater River			Minnesota River-Judson Bridge			North Branch-Root River			Seven Mile Creek #3		
2004	2005	2006	2004	2005	2006		2004	2005	2006	2004	2005 (T2)[2]	2006 (T2)	2004	2005	2006	2004	2005	2006	2004	2005 (T2)	2006 (T2)	2004	2005	2006	2004	2005	2006
						Detected in?		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
						# > 10% Current Advisory Value		2	0	0	0	0	2	0	0	3	1	0	0	0	0	6	1	1	4	0	0
116/120 = 97%	56/63 = 89%	33/34 = 97%	61/83 = 73%	43/64 = 67%	18/29 = 62%	# > 10% Proposed Standard	Not monitored	1	0	0	0	0	0	0	0	0	1	0	0	0	0	2	0	0	1	0	0
						# > 50% Current Advisory Value		0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0
						# > 50% Proposed Standard		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

[1] The metolachlor proposed standard has a corresponding 30-day human health chronic standard for surface waters protected as potential sources of drinking water and associated fish consumption (Middle Branch-Whitewater River and Seven Mile Creek #3).

[2] T2 = Tier 2 sampling site; Indicates that up to 8 samples were collected at that location from Mid-May to Mid-July.

Surface Water Contaminants:	Reference Value(s)
Acetochlor	**1.4 ug/L (current advisory value; 4-day aquatic toxicity); 1.7 ug/L (proposed standard; 4-day aquatic toxicity)**
Atrazine	**10 ug/L standard (4-day aquatic toxicity)**
Metolachlor	**10 ug/L (current advisory value; 4-day aquatic toxicity); 23 ug/L (proposed standard; 4-day aquatic toxicity)**

Exceedance of reference value or fraction thereof does not imply a violation of water quality standards or impairment for a given use.

5. Tier 3 Intensive Monitoring Sites – Concentration Trends:

Annual *Maximum* Concentration Trends – ug/L

Acetochlor	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**
Beauford Ditch	---[1]	---	---	---	---	12.10	1.58
Blue Earth River	3.80	6.50	1.50	0.86	1.76	0.35 (T2)[3]	0.27 (T2)
Le Sueur River	3.55	9.00	7.10	2.38	1.52	5.30	1.24
Middle Branch of the Whitewater River	4.89	8.00	9.60	1.19	2.17	2.20	0.025
Minnesota River at Judson	0.62	0.42	1.09	0.43	0.85	0.12 (T2)	0.17 (T2)
North Branch of the Root River	---	---	---	0.42 (T1)[2]	1.83	0.06	1.71
Seven Mile Creek	---	---	---	2.19	2.45	1.18	0.48
Atrazine	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**
Beauford Ditch	---	---	---	---	---	2.85	0.03
Blue Earth River	1.38	2.20	2.87	0.98	1.88	1.10 (T2)	0.40 (T2)
Le Sueur River	2.80	3.80	2.97	0.43	1.95	0.72	0.29
Middle Branch of the Whitewater River	16.5	17.4	29.4	7.15	32.0	2.00	0.16
Minnesota River at Judson	0.77	0.98	2.24	0.55	1.40	0.41(T2)	0.64 (T2)
North Branch of the Root River	---	---	---	4.8 (T1)	7.40	1.27	0.72
Seven Mile Creek	---	---	---	2.59	1.35	10.0	1.06
Metolachlor	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**
Beauford Ditch	---	---	---	---	---	3.70	0.17
Blue Earth River	1.13	2.52	0.52	0.46	0.71	0.46 (T2)	0.13 (T2)
Le Sueur River	1.41	1.44	0.65	0.68	1.30	0.98	0.24
Middle Branch of the Whitewater River	7.79	0.69	4.30	3.90	1.62	3.70	0.035
Minnesota River at Judson	6.65	3.36	0.65	0.37	2.46	0.13 (T2)	0.30 (T2)
North Branch of the Root River	---	---	---	1.09 (T1)	5.80	1.59	1.55
Seven Mile Creek	---	---	---	1.65	3.20	0.90	0.40

[1] ---Indicates no samples collected during that year.
[2] T1 = Tier 1 sampling site; Indicates that 4 samples were collected at that location from Mid-May to Mid-July
[3] T2 = Tier 2 sampling site; Indicates that up to 8 samples were collected at that location from Mid-May to Mid-July.

Acetochlor – *Median* Concentration Trends – ug/L

Tier 3 Field Season (April - July)

Beauford Ditch

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	---[1]	---	---	---	---	0.025	0.04
Storm Flow Grab	---	---	---	---	---	4.20	---
Storm Flow Composite	---	---	---	---	---	0.68	---
Storm Time Composite	---	---	---	---	---	---	0.21

Blue Earth River

Type of Sample	2000	2001	2002	2003	2004	2005 (T2)[2]	2006 (T2)
Base Flow Grabs	0.06	0.05	0.00	---	0.11	0.025	0.025
Storm Flow Grab	---	0.40	0.19	0.07	0.07	0.20	0.10
Storm Flow Composite	0.26	0.26	0.28	0.11	0.72	---	---

Le Sueur River

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	0.12	0.50	0.05	0.00	0.21	0.06	0.04
Storm Flow Grab	0.07	0.28	0.87	0.11	0.10	0.04	0.00
Storm Flow Composite	0.57	0.46	0.35	0.16	0.42	0.00	0.45
Storm Time Composite	---	---	---	---	---	---	0.27

Middle Branch of the Whitewater River

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	0.00	0.025	0.16	0.025	0.06	0.00	0.00[3]
Storm Flow Grab	0.09	0.00	---	0.60	---	0.88	---
Storm Flow Composite	0.43	0.00	1.71	0.27	0.31	0.05	---
Storm Time Composite	---	---	---	---	---	---	0.00

Minnesota River at Judson

Type of Sample	2000	2001	2002	2003	2004	2005 (T2)	2006 (T2)
Base Flow Grabs	0.00	---	0.00	0.00	0.01	0.00	0.025
Storm Flow Grab	---	0.06	0.13	0.00	0.50	0.04	0.08
Storm Flow Composite	0.10	0.12	0.025	---	0.25	---	---

North Branch of the Root River

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	---	---	---	0.39	0.00	0.00	0.025
Storm Flow Grab	---	---	---	---	0.17	0.00	0.00
Storm Flow Composite	---	---	---	---	---	---	---
Storm Time Composite	---	---	---	---	---	---	0.04

Seven Mile Creek

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	---	---	---	0.03	0.19	0.025	0.025
Storm Flow Grab	---	---	---	0.36	0.25	0.06	0.38
Storm Flow Composite	---	---	---	0.23	0.36	0.025	---
Storm Time Composite	---	---	---	---	---	---	0.07

[1] ---Indicates no samples collected during that year.
[2] T2 = Tier 2 sampling site; Indicates that up to 8 samples were collected at that location from Mid-May to Mid-July.
[3] Median concentrations that were less than 1/2 the Method Reporting limit of 0.050 ug/L are shown as 0.

Atrazine – *Median* Concentration Trends – ug/L

Tier 3 Field Season (April - July)

Beauford Ditch

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	---[1]	---	---	---	---	0.025	0.025
Storm Flow Grab	---	---	---	---	---	0.13	---
Storm Flow Composite	---	---	---	---	---	0.08	---
Storm Time Composite	---	---	---	---	---	---	0.00[2]

Blue Earth River

Type of Sample	2000	2001	2002	2003	2004	2005 (T2)[3]	2006 (T2)
Base Flow Grabs	0.13	0.18	0.31	---	0.14	0.12	0.04
Storm Flow Grab	---	0.32	0.07	0.13	0.41	0.22	0.21
Storm Flow Composite	0.66	0.09	1.28	0.05	1.12	---	---

Le Sueur River

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	0.09	0.33	0.33	0.06	0.28	0.14	0.09
Storm Flow Grab	0.55	0.34	1.29	0.29	0.62	0.06	0.04
Storm Flow Composite	1.02	0.10	1.56	0.16	0.53	0.13	0.04
Storm Time Composite	---	---	---	---	---	---	0.05

Middle Branch of the Whitewater River

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	0.19	0.18	0.94	0.20	0.46	0.24	0.08
Storm Flow Grab	0.70	0.10	---	5.70	---	0.72	---
Storm Flow Composite	4.60	0.10	8.00	0.52	2.4	0.55	---
Storm Time Composite	---	---	---	---	---	---	0.14

Minnesota River at Judson

Type of Sample	2000	2001	2002	2003	2004	2005 (T2)	2006 (T2)
Base Flow Grabs	0.05	---	0.38	0.06	0.13	0.025	0.05
Storm Flow Grab	---	0.06	0.90	0.07	0.46	0.17	0.27
Storm Flow Composite	0.44	0.06	0.00	---	0.91	---	---

North Branch of the Root River

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	---	---	---	4.08	0.22	0.16	0.11
Storm Flow Grab	---	---	---	---	0.85	0.11	0.13
Storm Flow Composite	---	---	---	---	---	---	---
Storm Time Composite	---	---	---	---	---	---	0.48

Seven Mile Creek

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	---	---	---	0.07	0.27	0.06	0.025
Storm Flow Grab	---	---	---	0.12	0.96	0.14	1.02
Storm Flow Composite	---	---	---	0.74	0.54	0.025	---
Storm Time Composite	---	---	---	---	---	---	0.16

[1] ---Indicates no samples collected during that year.
[2] Median concentrations that were less than 1/2 the Method Reporting limit of 0.050 ug/L are shown as 0.
[3] T2 = Tier 2 sampling site; Indicates that up to 8 samples were collected at that location from Mid-May to Mid-July.

Metolachlor – *Median* Concentration Trends – ug/L

Tier 3 Field Season (April - July)

Beauford Ditch

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	---[1]	---	---	---	---	0.035	0.00[2]
Storm Flow Grab	---	---	---	---	---	0.63	---
Storm Flow Composite	---	---	---	---	---	0.21	---
Storm Time Composite	---	---	---	---	---	---	0.035

Blue Earth River

Type of Sample	2000	2001	2002	2003	2004	2005 (T2)[3]	2006 (T2)
Base Flow Grabs	0.14	0.13	0.00	---	0.10	0.035	0.035
Storm Flow Grab	---	0.26	0.11	0.09	0.19	0.09	0.035
Storm Flow Composite	0.27	0.63	0.21	0.13	0.38	---	---

Le Sueur River

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	0.10	0.10	0.035	0.035	0.18	0.035	0.035
Storm Flow Grab	0.15	0.22	0.25	0.12	0.08	0.11	0.035
Storm Flow Composite	0.32	0.57	0.19	0.13	0.16	0.13	0.06
Storm Time Composite	---	---	---	---	---	---	0.035

Middle Branch of the Whitewater River

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	0.07	0.035	0.28	0.08	0.035	0.035	0.035
Storm Flow Grab	0.33	0.035	---	1.04	---	0.97	---
Storm Flow Composite	2.06	0.07	2.12	3.90	0.18	0.11	---
Storm Time Composite	---	---	---	---	---	---	0.035

Minnesota River at Judson

Type of Sample	2000	2001	2002	2003	2004	2005 (T2)	2006 (T2)
Base Flow Grabs	0.06	---	0.00	0.00	0.06	0.035	0.035
Storm Flow Grab	---	0.15	0.10	0.08	0.30	0.08	0.12
Storm Flow Composite	0.18	0.94	0.25	---	0.3	---	---

North Branch of the Root River

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	---	---	---	1.04	0.10	0.07	0.035
Storm Flow Grab	---	---	---	---	0.83	0.07	0.07
Storm Flow Composite	---	---	---	---	---	---	---
Storm Time Composite	---	---	---	---	---	---	0.27

Seven Mile Creek

Type of Sample	2000	2001	2002	2003	2004	2005	2006
Base Flow Grab	---	---	---	0.08	0.38	0.035	0.035
Storm Flow Grab	---	---	---	0.23	0.72	0.16	0.18
Storm Flow Composite	---	---	---	0.16	0.62	0.08	---
Storm Time Composite	---	---	---	---	---	---	0.05

[1] ---Indicates no samples collected during that year.
[2] Median concentrations that were less than 1/2 the Method Reporting limit of 0.050 ug/L are shown as 0.
[3] T2 = Tier 2 sampling site; Indicates that up to 8 samples were collected at that location from Mid-May to Mid-July.

Additional MDA Pesticide Water Quality Data for 2006

Groundwater

1. Urban/Suburban Monitoring Wells; 22 Wells/22 Samples:

Pesticide Analyte	**Detections/ wells**	**Maximum concentration** (ug/L)
Acetochlor ESA	1/22	0.16
Alachlor ESA	2/22	0.15
Atrazine	4/22	0.08
Deethylatrazine	10/22	0.10
Deisopropylatrazine	1/22	P
Clopyralid	1/22	0.28
MCPP	1/22	P
Metolachlor ESA	4/22	1.59
Prometon	1/22	P
2,4-D	2/22	0.20
P indicates that the pesticide was detected at or below the Method Reporting Limit or Estimated Reporting Limit		

2. Cyanazine Analysis/Reconnaissance:

Pesticide Analyte	**Number of Samples Collected**	**Number of Samples w/ Detections**	**90th Percentile Concentration** (ug/L)	**Maximum Concentration** (ug/L)	**Number of exceedences of health guidelines** (ug/L)
Cyanazine	27	1	ND	0.04	0
cyanazine amide	27	2	ND	0.05	0
cyanazine-acid	27	2	ND	0.14	0
deethylcyanazine acid	27	2	ND	0.10	0
deethylcyanazine amide	27	0	ND	ND	0
Cyanazine + degradates	27	2	0.046	0.33	0

Additional MDA Pesticide Water Quality Data for 2006

Surface Water

3. Glyphosate and Degradate (aminomethylphosphonic acid; AMPA) Detections in Select Monitoring Locations;

EPA/Office of Pesticide Programs benchmarks for glyphosate –
chronic fish > 25,700 ug/L
acute nonvascular plant 850 ug/L

Samples Collected for Glyphosate Analysis in 2006	STORM FLOW SAMPLES[a]				BASE FLOW SAMPLES[a]				TOTAL SAMPLES			
	Of 27 Storm Flow Samples, Number Positive (and %) for Pesticide	11 Monitoring Sites Sampled: Maximum Value Detected (ug/L)	Date of Maximum	Median Value of Samples (ug/L)[b]	Of 20 Base Flow Samples, Number Positive (and %) for Pesticide	5 Monitoring Sites Sampled: Maximum Value Detected (ug/L)	Date of Maximum	Median Value of Samples (ug/L)[b]	Of 47 Total Samples, Number Positive (and %) for Pesticide	Maximum Value Detected (ug/L)	Date of Maximum	Median Value of Samples (ug/L)[b]
Pesticide Analyte												
Glyphosate	22 (81%)	0.94	2-Aug	0.25 (P)	8 (40%)	1.00	12-Jun	ND	30 (64%)	1.00	12-Jun	0.25 (P)
AMPA	12 (44%)	0.85	25-Aug	ND	3 (15%)	0.25 (P)	multiple	ND	15 (32%)	0.85	25-Aug	ND

[a] Storm flow samples are grabs, and time and flow based composites taken during peak flow periods. Base flow samples are grabs and time based composites taken during base or low flow periods.

[b] nd = non detect. na = sample was not analyzed for the compound indicated. In cases where Max. Concentration is reported as a number value, a corresponding Median Concentration reported as "nd" indicates that the calculation of the median resulted in zero or a number below one half the Method Reporting Limit or Estimated Reporting Limit.

Additional non-MDA Pesticide Water Quality Data

1. Nutrients, Suspended Sediment, and Pesticides in Water of the Red River of the North Basin, Minnesota and North Dakota, 1990–2004

   Christensen, V.G., 2007, Nutrients, suspended sediment, and pesticides in water of the Red River of the North River Basin, Minnesota and North Dakota, 1990–2004: U.S Geological Survey Scientific Investigations Report 2007–5065, 36 p.

   a. MDA data from the region was considered in the analysis of USGS data. See report for complete details.

   b. SW: From 1990 – 2004, pesticide data that met the selection criteria established in the Methods section of at least 8 samples over 2 years were found for 12 sites—2 sites on the Red River, 3 sites in Minnesota, and 7 sites in North Dakota.

Table 5. Summary of the most frequently detected pesticides from 12 surface-water sites in the Red River of the North Basin, 1990–2004.

[U.S. Geological Survey data from National Water Information System; µg/L, micrograms per liter; <, less than]

Pesticide	Concentration range (µg/L)	Median reported concentration (µg/L)	Number of observations greater than reporting level	Number of observations
Acetochlor	<0.002–0.585	<0.002	14	90
Alachlor	<0.002–0.284	<0.002	16	145
Atrazine	<0.001–0.54	0.016	19	145
Cyanazine	<0.004–0.25	<0.004	47	144
De-ethylatrazine	<0.002–0.056	0.004	89	144
EPTC	<0.002–0.488	<0.002	54	143
Metolachlor	<0.002–0.103	0.004	83	145
Simazine	<0.005–0.07	<0.005	18	144
Triallate	<0.001–0.21	<0.001	67	143
Triazine[1]	<0.1–0.7	<0.1	13	67
Trifluralin	<0.002–0.132	<0.002	54	143

[1]Triazines are a group of pesticides, which include atrazine, cyanazine, and simazine.

c. GW: Ninety-nine wells were sampled in North Dakota and 157 wells were sampled in Minnesota for 1990–2004. Results for 156 pesticides were available for 1990–2004 in the NWIS data base. All concentrations were less than the reporting level for 127 pesticides. Of the remaining 29 pesticides, only 5 had more than 10 percent of values that exceeded their respective reporting level.

Table 6. Summary of the most frequently detected pesticides in ground water from 263 sites in the Red River of the North Basin, 1990–2004.

[U.S. Geological Survey data from National Water Information System; µg/L, micrograms per liter; ESA, ethanesulfonic acid; <, less than]

Pesticide	Concentration range (µg/L)	Median reported concentration (µg/L)	Number of observations greater than reporting level	Number of observations
Alachlor ESA	<0.02–0.96	<0.02	10	61
Atrazine	<0.001–0.54	0.007	58	286
De-ethylatrazine	<0.002–1.9	0.006	13	285
Picloram	<0.01–0.02	<0.01	2	10
Triazine[1]	<0.1–3	<0.1	8	69

[1]Triazines are a group of pesticides, which include atrazine, cyanazine, and simazine.

Water Quality ***Best Management Practices for AGRICULTURAL HERBICIDES***

February 2004

In order to protect Minnesota's water resources, the Minnesota Department of Agriculture (MDA), along with the University of Minnesota Extension Service and other interested parties, has developed a set of core voluntary Best Management Practices (BMPs). The core voluntary BMPs are provided on the opposite side of this page and should be adopted when applying all agricultural herbicides in Minnesota. The BMPs may also refer to mandatory label use requirements. Always read product labels. Additional information and references accompany the BMPs.

The MDA has also developed unique voluntary BMPs (on separate pages) for the use of specific herbicides due to their presence in Minnesota's groundwater or surface water from normal agricultural use. The herbicide-specific BMPs should be adopted when using herbicides that have been, or whose breakdown products have been, frequently detected in groundwater (acetochlor, alachlor, atrazine, metolachlor and metribuzin) or those detected at concentrations of concern in surface water (acetochlor and atrazine). If the BMPs are proven ineffective, mandatory restrictions on herbicide use and practices may be required. For information on monitoring results for herbicides in Minnesota's water resources, refer to the MDA's Monitoring and Assessment webpage: http://www.mda.state.mn.us/appd/ace/maace.htm

Careful planning in the use of herbicides – as part of an Integrated Weed Management Plan – can help protect water resources from future contamination and help reduce the levels of herbicides currently in Minnesota's waters. Planning also promotes the efficient and economical use of herbicides and may result in reduced application rates that can save you money.

State and federal law can require that the use of a pesticide be limited or curtailed due to the potential for adverse impacts on humans or the environment. The Minnesota Pesticide Control Law (Minn. Stat. 18B) outlines state regulatory authority to prevent these impacts. The Minnesota Groundwater Protection Act (Minn. Stat. 103H) outlines a process that can lead to regulations on the use of herbicides frequently detected in groundwater. In addition, there are other state and federal laws that could lead to restrictions on the use of herbicides contributing to surface water impacts. Adopting these BMPs, and a cautious and respectful attitude regarding the proper use of herbicides, will help growers to maintain access to a variety of herbicides as important and diverse tools in the effort to control weeds and protect water resources.

Best Management Practices (BMPs) for herbicide use

- The purpose of voluntary BMPs is to prevent and minimize the degradation of Minnesota's water resources while considering economic factors, availability, technical feasibility, implementability, effectiveness, and environmental effects.

Integrated Weed Management

Reducing crop losses by combining *cultural*, *chemical* and *mechanical* techniques in ways that favor the crop and suppress weed populations and vigor.

See "Additional Information & References" for more details and practical examples.

- From a practical standpoint, these BMPs are intended to reduce the loss of herbicides to the environment and to encourage the efficient use of herbicides, chemistry-rotation, and non-chemical approaches to weed control as part of an Integrated Weed Management program to save costs, reduce development of herbicide resistant weeds and increase profitability.

The BMPs are provided as a series of options. Producers, crop consultants and educators should select options most appropriate for a given farming operation, soil types and geography, tillage and cultivation practices, and irrigation and runoff management. The MDA encourages development of Integrated Weed Management Plans for every Minnesota farm (see "Additional Information and References" for more information). **Always read the product label. Label use requirements and application setbacks are legally enforceable.**

Water Quality *Best Management Practices for All Agricultural Herbicides*

Core Practice*	Description	Benefit
1. Scout fields for weeds and match the management approach to the weed problem.	Scout for weeds, then map infestations throughout the year. Determine whether weed control will result in significant crop yield benefits. Carefully match weed control options – including non-chemical control – to weed pressures. Use herbicides only in situations where they are necessary and will be cost-effective. Use herbicides with long-lasting effect ("residual control") only in fields that have high densities of target weeds or in fields where weed information is lacking (e.g., newly rented or purchased acres). Consider post-emergent weed control alternatives.	Responding accurately to specific weed pressures, using post-emergent control and using alternative chemical and non-chemical (e.g., cultivation) controls can lower costs and prevent water resource impacts.
2. Evaluate reduced or split herbicide application rates.	Evaluate a reduced-rate herbicide program. Banding – especially in ridge-till rotations – can significantly reduce herbicide inputs. Use split applications to reduce the amount of herbicide loss in runoff during early spring rains. Consider using the lowest labeled rate in a "rate range." Start on a small area to test what works best on your farm. Be prepared for follow-up weed management including post-emergent herbicide application, rotary hoeing, or inter-row cultivation.	In many cases, banding and a carefully planned reduced-rate herbicide program can result in effective weed control, reduced costs, and a reduction in herbicide loss to the environment.
3. *For Surface Water protection*: Soil incorporate herbicides.	When the timing of application and the product label allow, incorporate herbicides to reduce runoff losses. Use a field cultivator or other implement to incorporate products to the greatest recommended depth. Easily adopted when tilling prior to planting.	Incorporated herbicide is less vulnerable to being lost in runoff and reaching nearby streams and surface tile inlets.
4. *For Surface Water protection*: Evaluate surface drainage patterns in your field and install filter strips and establish buffer zones for streams, sinkholes and tile inlets.	Work with crop consultants and other ag professionals. Study Natural Resources Conservation Service (NRCS) listings for herbicides and soil properties that can lead to herbicide losses in runoff to surface waters (rivers, streams & lakes). Consider herbicides that NRCS lists as having low loss ratings for runoff from your soils, or consider non-chemical weed control methods in sensitive areas. Then, in addition to required label setbacks or buffers, install vegetative filter strips and establish buffers along vulnerable surface waters, karst features, tile inlets and sinkholes.	Filters and buffers reduce field runoff and setbacks eliminate applications where losses are most likely. Reducing use of herbicides known to move to surface water reduces the potential for surface water contamination.
5. *For Ground Water protection:* Determine the depth to groundwater in your fields and consider protective practices in vulnerable areas.	Work with crop consultants and other ag professionals. Study Department of Natural Resources groundwater pollution sensitivity maps and Natural Resources Conservation Service (NRCS) listings for herbicides and soil properties that contribute to herbicide losses by leaching. Consider herbicides that NRCS lists as having low loss ratings for leaching from your soils, or consider non-chemical weed control methods in sensitive areas. Follow label requirements or recommendations where water tables are shallow.	Reducing herbicide use in sensitive areas reduces the potential for groundwater contamination. Adhering to label groundwater advisories and exclusions reduces aquifer pollution.
6. Rotate herbicide modes of action (chemistry).	Avoid more than two consecutive applications of herbicides with the same mode of action (chemistry) to the same field. Evaluate this practice in the context of other effective control practices in the management system (e.g., use of tank mixes with multiple modes of action; crop rotation; planned, periodic use of herbicide-resistant crops in a rotation; mechanical weed control; field scouting).	This practice serves to reduce development of herbicide resistance in weeds or weed species shifts and, in the long term, can help reduce the total annual loss of particular herbicides to water resources and the environment.
7. Consider precision application of herbicides.	Precision application of herbicides (spot spraying or use of variable rate technologies) is based on weed scouting and variation in soil properties (soil organic matter and texture). Adjust application rates according to weed pressures and soils information.	Precision applications result in less total herbicide applied when compared to broadcast applications; this means less potential loss to the environment.
8. *For Ground Water protection:* Develop an Irrigation Water Management Plan.	If you irrigate, implement a water management scheduling plan that uses a soil probe, rain gauge, daily crop water use estimations and a soil water balance worksheet.	Effective irrigation management reduces leaching of chemicals to groundwater.

***For practices related to the use of specific herbicides refer to MDA's herbicide-specific Best Management Practices. *All BMPs are available at http://www.mda.state.mn.us/appd/bmps/bmps.htm* See "Additional Information & References" for access to detailed guidance on all recommended practices.**

ADDITIONAL INFORMATION & REFERENCES

This information accompanies the State of Minnesota's voluntary Water Quality Best Management Practices (BMPs) for agricultural herbicides. The information and references are not additional BMPs; rather, they provide more detailed guidance to support a producer's management program for the proper use of all herbicides, and are provided in support of the voluntary BMPs.

Applied Weed Research

University of Minnesota Applied Weed Science Research program (assistance with *general weed and herbicide information*, *mode of action*, *crop injury*, *pesticide trials* and links to many other helpful sources of information) http://appliedweeds.coafes.umn.edu/

"Herbicide Resistant Weeds" (helpful information on *rotating chemistries & herbicide modes of action*) J.L. Gunsolus, 1999, U of M, http://www.extension.umn.edu/distribution/cropsystems/DC6077.html

Pesticide Use

Minnesota Department of Agriculture: *Best Management Practices for pesticide use* http://www.mda.state.mn.us/appd/bmps/bmps.htm; *Pesticide sales and use* information http://www.mda.state.mn.us/appd/pesticides/pesticideuse.htm; *Plant pest survey* information http://www.mda.state.mn.us/pestsurvey/default.htm; and *Integrated pest management information* http://www.mda.state.mn.us/ipm/default.htm

Natural Resources Conservation Service (NRCS) offices (offers access to a helpful document on *integrated weed management* entitled *"Protecting Wisconsin's Resources through Integrated Weed Management"* and includes the *"Minnesota Insert"*); the same publication (without the insert) can be obtained at http://ipcm.wisc.edu/pubs/pdf/Int_Weed.pdf Additional helpful information is available at http://www.mn.nrcs.usda.gov/technical/ecs/pest/pest.htm

Iowa State University Extension Service (descriptions of ways in which farmers have saved money in herbicide costs and reduced herbicide use while effectively managing weeds), see *"Eight Ways to Reduce Pesticide Use,"* at http://www.pme.iastate.edu/resources/default.htm (publication #IPM 59).

University of Wisconsin-Extension (information on *development and implementation of a reduced-rate herbicide program*) http://ipcm.wisc.edu/pubs/pdf/a3563-reduced01.pdf

Soils & Water

Local SWCD offices (assistance with *water table information*, *soil maps*, *groundwater and surface water maps*) http://www.bwsr.state.mn.us/directories/index.html

Minnesota Department of Natural Resources (information for some areas of the state for identifying *water table depth*, *groundwater pollution sensitivity, karst features*) http://www.dnr.state.mn.us/waters/groundwater_section/mapping/index.html

Natural Resources Conservation Service (NRCS) (assistance with *water table information*, *soil maps*, identification of *vulnerable soils* in your county, *pest and weed management planning*) http://www.mn.nrcs.usda.gov/ and click on "Technical Resources." To locate offices for local assistance, click on "Find a Service Center" For information on protective filter strips, go to http://www.mn.nrcs.usda.gov/technical/ecs/agron/crp/cp21.doc

University of Minnesota Extension Service offices (assistance with *Integrated Weed Management Plan development* and implementation, and *soils and water information*) http://www.extension.umn.edu/offices/ See also Extension Bulletin "Tillage Best Management Practices for Water Quality Protection in Southeast Minnesota," BU-07694-S (2002) http://www.extension.umn.edu/distribution/cropsystems/DC7694.html

University of Minnesota Extension Service (assistance with *irrigation water management plans*) at http://www.extension.umn.edu/distribution/cropsystems/DC1322.html Also see the University of Wisconsin's irrigation decision support and record-keeping software "WISDOM" http://ipcm.wisc.edu/apps/wisdom/default.htm

Minnesota Department of Agriculture (information about *pesticide management programs, monitoring and assessment of water resources for pesticide impacts, pesticide use and sales, Best Management Practices*) http://www.mda.state.mn.us/appd/ace/pestmgmt.htm

ADDITIONAL INFORMATION & REFERENCES

Integrated Weed Management

Use one or more of the following strategies to help you cost effectively manage weeds while protecting the environment. Develop an Integrated Weed Management Plan in consultation with the local University of Minnesota Regional Extension Educators, Natural Resources Conservation Service and Soil & Water Conservation District personnel, certified crop advisors and local crop consultants.

- ✓ **Develop an Integrated Weed Management Plan for your field(s) –** The MDA encourages the development of Integrated Weed Management plans for every Minnesota farm (*see opposite side of this page for additional information and references)*. Start slow if you like…try the practices on a few fields and build from there!

- ✓ **Document recent chemical use.** This information is important when planning for rotating herbicide chemistries and establishing reduced rate programs.

- ✓ **Introduce a post-harvest cover crop, introduce a small grain or perennial forage**, and rotate among a wider variety of crops to disrupt weed life cycles and control weeds while using fewer chemicals.

- ✓ **Don't assume that more is better!** It may cost more to achieve 100% elimination of weeds than is gained through increased yield. Work with a crop consultant to determine the economic level of injury your field can sustain with reduced or no herbicide use.

- ✓ **Proper application timing.** Apply herbicides under optimal environmental conditions and at the appropriate time of year, crop growth stage, and weed growth stage specified on the label. Doing so can reduce the availability of herbicides for runoff or leaching.

- ✓ **Use a rotary hoe, harrow or cultivator** as part of integrated approaches to weed control. Mechanical weed control can reduce herbicide program costs and reduce herbicide environmental impacts.

- ✓ **Consider planned, periodic use of herbicide-resistant (HR) crops** into cropping sequences, but don't rely on this technology to solve all weed problems. HR crops should be considered as part of a planned rotation of herbicide chemistries (to avoid the buildup of herbicide resistant weeds or weed species shifts).

- ✓ **Apply herbicides as split applications** to reduce the amount of herbicide on the soil surface during periods of higher rainfall intensities.

- ✓ **Work with your local crop consultant and regional Extension Educators** to determine where reduced rates or alternative weed control practices can be introduced.

Water Quality ***Best Management Practices for ACETOCHLOR***

February 2004

The Minnesota Department of Agriculture (MDA) has developed voluntary Best Management Practices (BMPs) to address the presence of acetochlor and its breakdown products in Minnesota's groundwater and surface water from normal agricultural use (see reverse side of page for acetochlor-specific BMPs). If the BMPs are proven ineffective, mandatory restrictions on herbicide use and practices may be required. The BMPs may also refer to mandatory label use requirements. Always read product labels. For information on monitoring results for acetochlor and other pesticides in Minnesota's water resources, refer to the MDA's Monitoring and Assessment webpage: http://www.mda.state.mn.us/appd/ace/maace.htm

Example trade names for products and package mixtures containing acetochlor. List is not all-inclusive and can change with the introduction of new products; always check the label, or consult MDA's product registration database at http://state.ceris.purdue.edu/doc/mn/statemn.html and search for Active Ingredient.*

Acetochlor is an active ingredient in:	
Confidence products	Harness products
Certainty products	Keystone products
Channel products	Ruler products
Degree products	Shot Blast products
Doubleplay products	Stall products
Fieldmaster	Surpass products
Fortitude products	Top Notch products
FS Acetochlor products	Volley products
FulTime products	

* Reference to commercial products or trade names is made with the understanding that no discrimination is intended and no endorsement is implied.

The acetochlor BMPs are companions to a set of core BMPs for use with all agricultural herbicides. Herbicide-specific BMPs have also been developed for use with alachlor, atrazine, metolachlor and metribuzin. If you use any of these herbicides in the production of crops, be sure to consult each herbicide-specific BMP prior to applying these herbicides. State and federal law can require that the use of a pesticide be limited or curtailed due to the potential for adverse impacts on humans or the environment.

Information about ACETOCHLOR

- Acetochlor is a Restricted Use Pesticide that can only be purchased and applied by properly licensed or certified individuals. All pre-mixes and tank mixes containing acetochlor are also Restricted Use Pesticides.

- Acetochlor demonstrates the properties and characteristics associated with chemicals detected in groundwater. Its use in areas where soils are permeable, particularly where the groundwater is shallow, may result in groundwater contamination. Combined detections of acetochlor and its breakdown products have been frequently detected in Minnesota groundwater beneath areas with coarse-textured soils.

- Acetochlor has properties that may result in surface water contamination from runoff or erosion. It has been found at concentrations of concern in Minnesota surface waters. Acetochlor is toxic to fish.

- Acetochlor belongs to the class of "chloracetamide herbicides" that manage weeds through a similar mode of action (chemistry). Other herbicides in this class include alachlor and metolachlor. Herbicides in this class should be considered in the context of an Integrated Weed Management (IWM) Plan. All chloracetamide herbicides have similar potential to contaminate water resources.

Certain soils, regions and watersheds are more vulnerable to losses of acetochlor. Sensitive areas include those with highly permeable geologic material, highly erodible soils or seasonally high water tables (including areas with drain tiles). Note that portions of every Minnesota county may include one or more of these conditions.

Contact your Natural Resources Conservation Service or Soil & Water Conservation District for further information on specific soil and water resource conditions on and near your farm. Then work with crop consultants and educators to select and adopt the Best Management Practices that are appropriate for your field and farm.

The BMPs are provided as a series of options. Producers, crop consultants and educators should select options most appropriate for a given farming operation, soil types and geography, tillage and cultivation practices, and irrigation and runoff management. The MDA encourages development of Integrated Weed Management Plans for every Minnesota farm (see "Additional Information and References" for more information). **Always read the product label. Label use requirements and application setbacks are legally enforceable.**

Water Quality *Best Management Practices for ACETOCHLOR*

To be used in conjunction with MDA's core "BMPs for All Agricultural Herbicides"

Acetochlor-Specific Practice*	Description	Benefit
1. Adopt the core "BMPs for All Agricultural Herbicides" when applying acetochlor.	MDA's core "BMPs for All Agricultural Herbicides" are designed as the baseline set of options to mitigate or prevent losses of herbicides to water resources. The core BMPs are available at http://www.mda.state.mn.us/appd/bmps/bmps.htm	Adoption of core BMPs with those specific for acetochlor and adherence to mandatory label use requirements and application setbacks result in opportunities for multiple water quality protection benefits.
2. Evaluate surface drainage patterns in your field, then identify points where surface runoff leaves the field and consider protective practices in vulnerable areas, including tile inlets.	Work with crop consultants and other ag professionals. Identify and implement appropriate acetochlor application setbacks and planted buffers for your farm. Application setbacks from points where runoff enters perennial or intermittent streams and rivers, or around natural or impounded lakes and reservoirs can be adopted to help minimize the potential for acetochlor losses in dissolved runoff and/or runoff erosion. Setbacks or buffers could also be adopted around surface inlets on tile-drained fields for further water quality protection benefits.	Protects vulnerable streams, rivers, lakes and reservoirs from acetochlor impacts.
3. Determine your soil's texture and organic matter content, then limit acetochlor application rates to the indicated label recommendation.	The practice is especially important for acetochlor (and other chloracetamide herbicides). Weed control with acetochlor is sensitive to differences in soil organic matter and texture. Limit unnecessary and costly use of acetochlor and protect the environment by carefully reviewing the label and adjusting the application rate to match your soil organic matter content and soil texture.	Proper acetochlor application rates mean cost-effective use and efficient weed control with minimal risk of water resource impacts.
4. Adopt conservation tillage practices appropriate for your farm's topography and in SE Minnesota karst areas.	Conservation tillage controls soil erosion that can contribute to losses of acetochlor attached to soil particles during field runoff events and from fields with tile drain surface inlets. It also helps slow movement of water across the landscape when acetochlor is dissolved in runoff water. Consult your Natural Resources Conservation Service and Soil & Water Conservation District offices for current tillage guidelines.	Controlling loss of soil and runoff helps reduce acetochlor losses to surface waters.
5. Rotate use of acetochlor (and alachlor, metolachlor and other chloracetamide herbicides) with herbicides from a different chemical class.	Evaluate this practice in the context of other effective control practices in the management system (e.g., use of tank mixes with multiple modes of action; crop rotation; planned, periodic use of herbicide-resistant varieties in a rotation; mechanical weed control; field scouting). Determine which crop in the rotation is in greatest need of chloracetamide herbicides, and reserve their use for that crop.	With time, this practice will reduce development of herbicide resistant weeds or weed species shifts, and means less annual availability of these herbicides for loss to the environment.

***For core practices and for practices related to the use of other specific herbicides, visit MDA's Best Management Practices webpage at *http://www.mda.state.mn.us/appd/bmps/bmps.htm* See "Additional Information & References" for access to detailed guidance on all recommended practices.**

Water Quality ***Best Management Practices for ALACHLOR***

February 2004

The Minnesota Department of Agriculture (MDA) has developed voluntary Best Management Practices (BMPs) to address the presence of alachlor and its breakdown products in Minnesota's groundwater from normal agricultural use (see reverse side of page for alachlor-specific BMPs). If the BMPs are proven ineffective, mandatory restrictions on herbicide use and practices may be required. The BMPs may also refer to mandatory label use requirements. Always read product labels. For information on monitoring results for alachlor and other pesticides in Minnesota's water resources, refer to the MDA's Monitoring and Assessment webpage: http://www.mda.state.mn.us/appd/ace/maace.htm

Example trade names for products and package mixtures containing alachlor. List is not all-inclusive and can change with the introduction of new products; always check the label, or consult MDA's product registration database at http://state.ceris.purdue.edu/doc/mn/statemn.html and search for Active Ingredient.*

Alachlor is an active ingredient in:	
Alachlor	Lasso products
Bronco	Micro-Tech
Bullet	Partner products
Freedom	Shroud
Lariat	

* Reference to commercial products or trade names is made with the understanding that no discrimination is intended and no endorsement is implied.

The alachlor BMPs are companions to a set of core BMPs for use with all agricultural herbicides. Herbicide-specific BMPs have also been developed for use with acetochlor, atrazine, metolachlor and metribuzin. If you use any of these herbicides in the production of crops, be sure to consult each herbicide-specific BMP prior to applying these herbicides. State and federal law can require that the use of a pesticide be limited or curtailed due to the potential for adverse impacts on humans or the environment.

Information about ALACHLOR

- Alachlor is a Restricted Use Pesticide that can only be purchased and applied by properly licensed or certified individuals. All pre-mixes and tank mixes containing alachlor are also Restricted Use Pesticides.
- Alachlor can leach through the soil to groundwater, especially where soils are coarse and groundwater is near the surface. Combined detections of alachlor and its breakdown products have been frequently detected in Minnesota groundwater beneath areas with coarse-textured soils.
- Alachlor may reach surface water bodies including streams, rivers and reservoirs following application and during rainfall events that cause runoff.
- Alachlor belongs to the class of "chloracetamide herbicides" that manage weeds through a similar mode of action (chemistry). Other herbicides in this class include acetochlor and metolachlor. Herbicides in this class should be considered in the context of an Integrated Weed Management (IWM) Plan. All chloracetamide herbicides have similar potential to contaminate water resources.

Certain soils, regions and watersheds are more vulnerable to losses of alachlor. Sensitive areas include those with highly permeable geologic material, highly erodible soils or seasonally high water tables (including areas with drain tiles). Note that portions of every Minnesota county may include one or more of these conditions.

Contact your Natural Resources Conservation Service or Soil & Water Conservation District for further information on specific soil and water resource conditions on and near your farm. Then work with crop consultants and educators to select and adopt the Best Management Practices that are appropriate for your field and farm.

February 2004

The BMPs are provided as a series of options. Producers, crop consultants and educators should select options most appropriate for a given farming operation, soil types and geography, tillage and cultivation practices, and irrigation and runoff management. The MDA encourages development of Integrated Weed Management Plans for every Minnesota farm (see "Additional Information and References" for more information). **Always read the product label. Label use requirements and application setbacks are legally enforceable.**

Water Quality *Best Management Practices for ALACHLOR*

To be used in conjunction with MDA's core "BMPs for All Agricultural Herbicides"

Alachlor-Specific Practice*	Description	Benefit
1. Adopt the core "BMPs for All Agricultural Herbicides" when applying alachlor.	MDA's core "BMPs for All Agricultural Herbicides" are designed as the baseline set of options to mitigate or prevent losses of herbicides to water resources. The core BMPs are available at http://www.mda.state.mn.us/appd/bmps/bmps.htm	Adoption of core BMPs with those specific for alachlor and adherence to mandatory label use requirements and application setbacks result in opportunities for multiple water quality protection benefits.
2. Determine your soil's texture and organic matter content, then limit alachlor application rates to the indicated label recommendation.	The practice is especially important for alachlor (and other chloracetamide herbicides). Weed control with alachlor is sensitive to differences in soil organic matter and texture. Limit unnecessary and costly use of alachlor and protect the environment by carefully reviewing the label and adjusting the application rate to match your soil organic matter content and soil texture.	Proper alachlor application rates mean cost-effective use and efficient weed control with minimal risk of water resource impacts.
3. Adopt conservation tillage practices appropriate for your farm's topography and in SE Minnesota karst areas.	Conservation tillage controls soil erosion that can contribute to losses of alachlor attached to soil particles during field runoff events and from fields with tile drain surface inlets. It also helps slow movement of water across the landscape when alachlor is dissolved in runoff water. Consult your Natural Resources Conservation Service and Soil & Water Conservation District offices for current tillage guidelines.	Controlling loss of soil and runoff helps reduce alachlor losses to surface waters.
4. Rotate use of alachlor (and acetochlor, metolachlor and other chloracetamide herbicides) with herbicides from a different chemical class.	Evaluate this practice in the context of other effective control practices in the management system (e.g., use of tank mixes with multiple modes of action; crop rotation; planned, periodic use of herbicide-resistant varieties in a rotation; mechanical weed control; field scouting). Determine which crop in the rotation is in greatest need of chloracetamide herbicides, and reserve their use for that crop.	With time, this practice will reduce development of herbicide resistant weeds or weed species shifts, and means less annual availability of these herbicides for loss to the environment.

***For core practices and for practices related to the use of other specific herbicides, visit MDA's Best Management Practices webpage at *http://www.mda.state.mn.us/appd/bmps/bmps.htm* See "Additional Information & References" for access to detailed guidance on all recommended practices.**

Water Quality ***Best Management Practices for ATRAZINE***

February 2004

The Minnesota Department of Agriculture (MDA) has developed voluntary Best Management Practices (BMPs) to address the presence of atrazine and its breakdown products in Minnesota's groundwater and surface water from normal agricultural use (see reverse side of page for atrazine-specific BMPs). If the BMPs are proven ineffective, mandatory restrictions on herbicide use and practices may be required. The BMPs may also refer to mandatory label use requirements. Always read product labels. For information on monitoring results for atrazine and other pesticides in Minnesota's water resources, refer to the MDA's Monitoring and Assessment webpage: http://www.mda.state.mn.us/appd/ace/maace.htm

Example trade names for products and package mixtures containing atrazine. List is not all-inclusive and can change with the introduction of new products; always check the label, or consult MDA's product registration database at http://state.ceris.purdue.edu/doc/mn/statemn.html and search for Active Ingredient.*

Atrazine is an active ingredient in:		
Aatrex	Degree Xtra	Lariat
Atrazine	Expert products	Leadoff
Axiom AT	Field Master	Liberty ATZ
Basis Gold	FulTime products	Lumax
Bicep II products	Guardsman	Marksman
Buctril + atrazine	Harness Xtra	Moxy + atrazine
Bullet	Keystone products	Shotgun
Cinch products	Laddok	

* Reference to commercial products or trade names is made with the understanding that no discrimination is intended and no endorsement is implied.

The atrazine BMPs are companions to a set of core BMPs for use with all agricultural herbicides. Herbicide-specific BMPs have also been developed for use with acetochlor, alachlor, metolachlor and metribuzin. If you use any of these herbicides in the production of crops, be sure to consult each herbicide-specific BMP prior to applying these herbicides. State and federal law can require that the use of a pesticide be limited or curtailed due to the potential for adverse impacts on humans or the environment.

Information about ATRAZINE

- Atrazine is a Restricted Use Pesticide that can only be purchased and applied by properly licensed or certified individuals. All pre-mixes and tank mixes containing atrazine are also Restricted Use Pesticides.

- Atrazine can travel (seep or leach) through soil and can enter groundwater used as drinking water. Users are advised not to apply atrazine to sand and loamy sand soils where the water table (groundwater) is close to the surface and where these soils are very permeable. Atrazine and its breakdown products have been frequently detected in Minnesota groundwater beneath areas with coarse-textured soils.

- Atrazine can also be lost to surface water through field runoff, and has been found at concentrations of concern in Minnesota surface waters. Atrazine is toxic to aquatic invertebrates, and runoff from treated areas may be hazardous to aquatic organisms in neighboring areas.

- Atrazine is a photosynthesis inhibiting herbicide that manages weeds through a particular mode of action (chemistry). When used in an Integrated Weed Management (IWM) Plan, its use should be considered jointly with other photosynthesis inhibiting herbicides. Use of herbicides with different modes of action (e.g., plant growth regulators, pigment inhibitors or sulfonylurea herbicides), alone or in tank mixes, may be desirable in an IWM Plan to effectively control weeds while protecting the environment.

Certain soils, regions and watersheds are more vulnerable to losses of atrazine. Sensitive areas include those with highly permeable geologic material, highly erodible soils or seasonally high water tables (including areas with drain tiles). Note that portions of every Minnesota county may include one or more of these conditions.

Contact your Natural Resources Conservation Service or Soil & Water Conservation District for further information on specific soil and water resource conditions on and near your farm. Then work with crop consultants and educators to select and adopt the Best Management Practices that are appropriate for your field and farm.

The BMPs are provided as a series of options. Producers, crop consultants and educators should select options most appropriate for a given farming operation, soil types and geography, tillage and cultivation practices, and irrigation and runoff management. The MDA encourages development of Integrated Weed Management Plans for every Minnesota farm (see "Additional Information and References" for more information). **Always read the product label. Label use requirements and application setbacks are legally enforceable.**

Water Quality *Best Management Practices for ATRAZINE*

To be used in conjunction with MDA's core "BMPs for All Agricultural Herbicides"

Atrazine-Specific Practice*	Description	Benefit
1. Adopt the core "BMPs for All Agricultural Herbicides" when applying atrazine.	MDA's core "BMPs for All Agricultural Herbicides" are designed as the baseline set of options to mitigate or prevent losses of herbicides to water resources. The core BMPs are available at http://www.mda.state.mn.us/appd/bmps/bmps.htm	Adoption of core BMPs with those specific for atrazine and adherence to mandatory label use requirements and application setbacks result in opportunities for multiple water quality protection benefits.
2. Limit total atrazine use per year to 0.8 lbs of active ingredient per acre on coarse-textured soils by using premixes and tank mixes.	This practice is especially important on coarse-textured soils (e.g., where sand, loamy sand or sandy loam soil textural classifications make up more than 25% of the field). These soils are common in central Minnesota, but are also present in many other locations.	Effective weed control for many small-seeded broadleaf weeds can be obtained using premixes and tank mixes with low atrazine content. Lower rates mean less potential loss to water resources.
3. *For Southeast Minnesota:* Limit total atrazine use per year to 0.8 lbs of active ingredient per acre on all soils *except* on medium and fine textured soils, where a total of 1.0 lb of active ingredient per year can be used for pre-emergence weed control.	This practice is important on any soils in the following ten counties in southeastern Minnesota with karst geology and features: *Dakota, Dodge, Fillmore, Goodhue, Houston, Mower, Olmsted, Rice, Wabasha and Winona.* The slightly higher rate of atrazine for pre-emergence applications on medium- and fine-textured soils is allowed to maintain efficacy of early season weed control and reduce potential losses from leaching and runoff.	Effective weed control for many small-seeded broadleaf weeds can be obtained using premixes and tank mixes with low atrazine content. Lower rates mean less potential loss to water resources.
4. Evaluate surface drainage patterns in your field, then identify points where surface runoff leaves the field and consider protective practices in vulnerable areas, including tile inlets, wells and sinkholes; follow label requirements for application setbacks and planted buffers.	Work with crop consultants and other ag professionals. Identify and implement appropriate label-required setbacks and planted buffers for your farm. Atrazine, and premixes or tank mixes containing atrazine, may not be applied within 66 feet of the points where runoff enters perennial or intermittent streams and rivers, within 200 feet around natural or impounded lakes and reservoirs, or within 50 feet of wells or sinkholes. Setbacks or buffers could also be adopted around surface inlets on tile-drained fields for further water quality protection benefits.	Protects vulnerable wells, sinkholes, streams, rivers, lakes and reservoirs from atrazine impacts.
5. Adopt conservation tillage practices appropriate for your farm's topography and in SE Minnesota karst areas.	Conservation tillage controls soil erosion that can contribute to losses of atrazine attached to soil particles during field runoff events and from fields with tile drain surface inlets. It also helps slow movement of water across the landscape when atrazine is dissolved in runoff water. Consult your Natural Resources Conservation Service and Soil & Water Conservation District offices for current tillage guidelines.	Controlling loss of soil and runoff helps reduce atrazine losses to surface waters.
6. Rotate use of atrazine (and metribuzin and other photosynthesis inhibiting herbicides) with herbicides from a different chemical class.	Evaluate this practice in the context of other effective control practices in the management system (e.g., use of tank mixes with multiple modes of action; crop rotation; planned, periodic use of herbicide-resistant varieties in a rotation; mechanical weed control; field scouting). Determine which crop in the rotation is in greatest need of photosynthesis inhibiting herbicides, and reserve their use for that crop.	With time, this practice will reduce development of herbicide resistant weeds or weed species shifts, and means less annual availability of these herbicides for loss to the environment.

***For core practices and for practices related to the use of other specific herbicides, visit MDA's Best Management Practices webpage at *http://www.mda.state.mn.us/appd/bmps/bmps.htm* See "Additional Information & References" for access to detailed guidance on all recommended practices.**

Water Quality ***Best Management Practices for METOLACHLOR***

February 2004

The Minnesota Department of Agriculture (MDA) has developed voluntary Best Management Practices (BMPs) to address the presence of metolachlor and its breakdown products in Minnesota's groundwater from normal agricultural use (see reverse side of page for metolachlor-specific BMPs). If the BMPs are proven ineffective, mandatory restrictions on herbicide use and practices may be required. The BMPs may also refer to mandatory label use requirements. Always read product labels. For information on monitoring results for metolachlor and other pesticides in Minnesota's water resources, refer to the MDA's Monitoring and Assessment webpage: http://www.mda.state.mn.us/appd/ace/ maace.htm

Example trade names for products and package mixtures containing metolachlor. List is not all-inclusive and can change with the introduction of new products; always check the label, or consult MDA's product registration database at http://state.ceris.purdue.edu/doc/mn/statemn.html and search for Active Ingredient.*

Products containing:

s-metolachlor		**metolachlor**
Bicep II products	Dual Magnum	Stalwart C
Bicep Lite II	Dual II products	
Boundary	Expert	
Cinch	Lumax	
Camix	Medal products	

* Reference to commercial products or trade names is made with the understanding that no discrimination is intended and no endorsement is implied.

The metolachlor BMPs are companions to a set of core BMPs for use with all agricultural herbicides. Herbicide-specific BMPs have also been developed for use with acetochlor, alachlor, atrazine, and metribuzin. If you use any of these herbicides in the production of crops, be sure to consult each herbicide-specific BMP prior to applying these herbicides. State and federal law can require that the use of a pesticide be limited or curtailed due to the potential for adverse impacts on humans or the environment.

Information about METOLACHLOR

- There are two categories of metolachlor herbicides: those listing "metolachlor" as a registered active ingredient, and those listing "s-metolachlor" as a registered active ingredient. Products in both categories contain s-metolachlor as the primary herbicidal chemical. The active ingredient "s-metolachlor" is considered a reduced risk for potential water resource impacts by the Environmental Protection Agency because a lesser amount of the product is needed to achieve the same level of weed control as that achieved with the active ingredient "metolachlor."

- Products containing metolachlor herbicides have the potential to leach through soil into groundwater under certain conditions as a result of agricultural use. Groundwater contamination may result if used in areas where soils are permeable, particularly where the water table is shallow. These herbicides and their breakdown products have been frequently detected in Minnesota groundwater beneath areas with coarse-textured soils.

- Products containing metolachlor herbicides may, under some conditions, have a high potential for runoff into surface water primarily via dissolution in runoff water, for several months post application. These conditions include poorly draining or wet soils with readily visible slopes toward adjacent surface waters, frequently flooded areas, areas over-laying extremely shallow groundwater, areas with in-field canals or ditches that drain to surface water, areas not separated from adjacent surface waters with vegetated filter strips, and areas over-laying tile drainage systems that drain to surface water.

Certain soils, regions and watersheds are more vulnerable to losses of metolachlor. Sensitive areas include those with highly permeable geologic material, highly erodible soils or seasonally high water tables (including areas with drain tiles). Note that portions of every Minnesota county may include one or more of these conditions.

Contact your Natural Resources Conservation Service or Soil & Water Conservation District for further information on specific soil and water resource conditions on and near your farm. Then work with crop consultants and educators to select and adopt the Best Management Practices that are appropriate for your field and farm.

- Metolachlor belongs to the class of "chloracetamide herbicides" that manage weeds through a similar mode of action (chemistry). Other herbicides in this class include acetochlor and alachlor. Herbicides in this class should be considered in the context of an Integrated Weed Management (IWM) Plan. All chloracetamide herbicides have similar potential to contaminate water resources.

The BMPs are provided as a series of options. Producers, crop consultants and educators should select options most appropriate for a given farming operation, soil types and geography, tillage and cultivation practices, and irrigation and runoff management. The MDA encourages development of Integrated Weed Management Plans for every Minnesota farm (see "Additional Information and References" for more information). **Always read the product label. Label use requirements and application setbacks are legally enforceable.**

Water Quality *Best Management Practices for METOLACHLOR*

To be used in conjunction with MDA's core "BMPs for All Agricultural Herbicides"

Metolachlor-Specific Practice*	Description	Benefit
1. Adopt the core "BMPs for All Agricultural Herbicides" when applying metolachlor.	MDA's core "BMPs for All Agricultural Herbicides" are designed as the baseline set of options to mitigate or prevent losses of herbicides to water resources. The core BMPs are available at http://www.mda.state.mn.us/appd/bmps/bmps.htm	Adoption of core BMPs with those specific for metolachlor and adherence to mandatory label use requirements and application setbacks result in opportunities for multiple water quality protection benefits.
2. Determine your soil's texture and organic matter content, then limit metolachlor application rates to the indicated label recommendation.	The practice is especially important for metolachlor (and other chloracetamide herbicides). Weed control with metolachlor is sensitive to differences in soil organic matter and texture. Limit unnecessary and costly use of metolachlor and protect the environment by carefully reviewing the label and adjusting the application rate to match your soil organic matter content and soil texture.	Proper metolachlor application rates mean cost-effective use and efficient weed control with minimal risk of water resource impacts.
3. When using metolachlor herbicides, choose products with "s-metolachlor" listed as the registered active ingredient.	The active ingredient "s-metolachlor" is considered a reduced risk for water resource impacts because a lesser amount of the product is needed to achieve the same level of weed control as that achieved with the active ingredient "metolachlor."	Use of products containing "s-metolachlor" at recommended label rates can mean fewer potential impacts to water resources.
4. Adopt conservation tillage practices appropriate for your farm's topography and in SE Minnesota karst areas.	Conservation tillage controls soil erosion that can contribute to losses of metolachlor attached to soil particles during field runoff events and from fields with tile drain surface inlets. It also helps slow movement of water across the landscape when metolachlor is dissolved in runoff water. Consult your Natural Resources Conservation Service and Soil & Water Conservation District offices for current tillage guidelines.	Controlling loss of soil and runoff helps reduce metolachlor losses to surface waters.
5. Rotate use of metolachlor (and acetochlor, alachlor and other chloracetamide herbicides) with herbicides from a different chemical class.	Evaluate this practice in the context of other effective control practices in the management system (e.g., use of tank mixes with multiple modes of action; crop rotation; planned, periodic use of herbicide-resistant varieties in a rotation; mechanical weed control; field scouting). Determine which crop in the rotation is in greatest need of chloracetamide herbicides, and reserve their use for that crop.	With time, this practice will reduce development of herbicide resistant weeds or weed species shifts, and means less annual availability of these herbicides for loss to the environment.

***For core practices and for practices related to the use of other specific herbicides, visit MDA's Best Management Practices webpage at *http://www.mda.state.mn.us/appd/bmps/bmps.htm* See "Additional Information & References" for access to detailed guidance on all recommended practices.**

Water Quality ***Best Management Practices for METRIBUZIN***

February 2004

The Minnesota Department of Agriculture (MDA) has developed voluntary Best Management Practices (BMPs) to address the presence of metribuzin and its breakdown products in Minnesota's groundwater from normal agricultural use (see reverse side of page for metribuzin-specific BMPs). If the BMPs are proven ineffective, mandatory restrictions on herbicide use and practices may be required. The BMPs may also refer to mandatory label use requirements. Always read product labels. For information on monitoring results for pesticides in Minnesota's water resources, refer to the MDA's Monitoring and Assessment webpage: http://www.mda.state.mn.us/appd/ace/maace.htm

Example trade names for products and package mixtures containing metribuzin. List is not all-inclusive and can change with the introduction of new products; always check the label, or consult MDA's product registration database at http://state.ceris.purdue.edu/doc/mn/statemn.html and search for Active Ingredient.*

Metribuzin is an active ingredient in:		
Axiom products	Domain	Canopy
Boundary	Sencor	

* Reference to commercial products or trade names is made with the understanding that no discrimination is intended and no endorsement is implied.

The metribuzin BMPs are companions to a set of core BMPs for use with all agricultural herbicides. Herbicide-specific BMPs have also been developed for use with acetochlor, alachlor, atrazine, and metolachlor. If you use any of these herbicides in the production of crops, be sure to consult each herbicide-specific BMP prior to applying these herbicides. State and federal law can require that the use of a pesticide be limited or curtailed due to the potential for adverse impacts on humans or the environment.

Information about METRIBUZIN

- Metribuzin can travel (seep or leach) through soil and contaminate groundwater which may be used as drinking water. Users are advised not to apply metribuzin where the water table (groundwater) is close to the surface and where the soils are very permeable i.e., well drained soils such as loamy sands. Metribuzin and its breakdown products have been frequently detected in Minnesota groundwater beneath areas with coarse-textured soils.

- Metribuzin is a photosynthesis inhibiting herbicide that manages weeds through a particular mode of action (chemistry). When used in an Integrated Weed Management (IWM) Plan, its use should be considered jointly with other photosynthesis inhibiting herbicides. Use of herbicides with different modes of action (e.g., plant growth regulators, pigment inhibitors or sulfonylurea herbicides), alone or in tank mixes, may be desirable in an IWM Plan to effectively control weeds while protecting the environment.

Certain soils, regions and watersheds are more vulnerable to losses of metribuzin. Sensitive areas include those with highly permeable geologic material, highly erodible soils or seasonally high water tables (including areas with drain tiles). Note that portions of every Minnesota county may include one or more of these conditions.

Contact your Natural Resources Conservation Service or Soil & Water Conservation District for further information on specific soil and water resource conditions on and near your farm. Then work with crop consultants and educators to select and adopt the Best Management Practices that are appropriate for your field and farm.

The BMPs are provided as a series of options. Producers, crop consultants and educators should select options most appropriate for a given farming operation, soil types and geography, tillage and cultivation practices, and irrigation and runoff management. The MDA encourages development of Integrated Weed Management Plans for every Minnesota farm (see "Additional Information and References" for more information). **Always read the product label. Label use requirements and application setbacks are legally enforceable.**

Water Quality *Best Management Practices for METRIBUZIN*

To be used in conjunction with MDA's core "BMPs for All Agricultural Herbicides"

Metribuzin-Specific Practice*	Description	Benefit
1. Adopt the core "BMPs for All Agricultural Herbicides" when applying metribuzin.	MDA's core "BMPs for All Agricultural Herbicides" are designed as the baseline set of options to mitigate or prevent losses of herbicides to water resources. The core BMPs are available at http://www.mda.state.mn.us/appd/bmps/bmps.htm	Adoption of core BMPs with those specific for metribuzin and adherence to mandatory label use requirements and application setbacks result in opportunities for multiple water quality protection benefits.
2. Limit total metribuzin rate, including amounts in premixes and tank mixes: **- on sand soils to no more than 0.4 lbs active ingredient per acre per year.** **- on loamy sands and sandy loams to no more than 0.5 lbs active ingredient per acre per year.**	Following these application limits is especially important on coarse-textured and irrigated soils (where sand, loamy sand or sandy loam soil textural classifications make up more than 25% of the field). These soils are common in central Minnesota, but are also present in many other locations.	By reserving metribuzin for use on the crop/weed association most in need of its effectiveness (e.g., during the potato year of a corn-bean-potato or bean-potato rotation) – and by limiting its annual application rate – environmental losses are minimized.
3. Rotate use of metribuzin (and atrazine and other photosynthesis inhibiting herbicides) with herbicides from a different chemical class.	Evaluate this practice in the context of other effective control practices in the management system (e.g., use of tank mixes with multiple modes of action; crop rotation; planned, periodic use of herbicide-resistant varieties in a rotation; mechanical weed control; field scouting). Determine which crop in the rotation is in greatest need of photosynthesis inhibiting herbicides, and reserve their use for that crop.	With time, this practice will reduce development of herbicide resistant weeds or weed species shifts, and means less annual availability of these herbicides for loss to the environment.

***For core practices and for practices related to the use of other specific herbicides, visit MDA's Best Management Practices webpage at *http://www.mda.state.mn.us/appd/bmps/bmps.htm* See "Additional Information & References" for access to detailed guidance on all recommended practices.**

Appendix F

Recent Studies of Endocrine Disrupting Compounds in Minnesota Waters and Sediments

Presence and Distribution of Organic Wastewater Compounds in Wastewater, Surface, Ground, and Drinking Waters, Minnesota, 2000–02

By Kathy E. Lee, Larry B. Barber, Edward T. Furlong, Jeffery D. Cahill, Dana W. Kolpin, Michael T. Meyer, and Steven D. Zaugg

Prepared in cooperation with the Minnesota Department of Health and the MInnesota Pollution Control Agency

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Conversion Factors and Water-Quality Units

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
cubic yard (yd^3)	0.7646	cubic meter (m^3)
	Flow rate	
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C=(°F-32)/1.8$$

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

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PRESENCE AND DISTRIBUTION OF ORGANIC WASTEWATER COMPOUNDS IN WASTEWATER, SURFACE, GROUND, AND DRINKING WATERS, MINNESOTA, 2000-02

By Kathy E. Lee, Larry B. Barber, Edward T. Furlong, Jeffery D. Cahill, Dana W. Kolpin, Michael T. Meyer, and Steven D. Zaugg

ABSTRACT

Selected organic wastewater compounds (OWCs) such as household, industrial, and agricultural-use compounds, pharmaceuticals, antibiotics, and sterols and hormones were measured at 65 sites in Minnesota as part of a cooperative study among the Minnesota Department of Health, Minnesota Pollution Control Agency, and the U.S. Geological Survey. Samples were collected in Minnesota during October 2000 through November 2002 and analyzed for the presence and distribution of 91 OWCs at sites including wastewater treatment plant influent and effluent; landfill and feedlot lagoon leachate; surface water; ground water (underlying sewered and unsewered mixed urban land use, a waste dump, and feedlots); and the intake and finished drinking water from drinking water facilities

There were 74 OWCs detected that represent a wide variety of use. Samples generally comprised a mixture of compounds (average of 6 OWCs) and 90 percent of the samples had at least one OWC detected. Concentrations for detected OWCs generally were less than 3 micrograms per liter. The ten most frequently detected OWCs were metolachlor (agricultural-use herbicide); cholesterol (sterol primarily associated with animal waste); caffeine (stimulant), N,N-diethyl-*meta*-toluamide (DEET) (topical insect repellant); bromoform (disinfection by product); tri(2-chloroethyl)phosphate (flame-retardant and plastic component); *beta*-sitosterol (plant sterol that is a known endocrine disruptor); acetyl-hexamethyl-tetrahydro-naphthalene (AHTN) (synthetic musk widely used in personal care products, and a known endocrine disruptor); bisphenol-A (plastic component and a known endocrine disruptor); and cotinine (metabolite of nicotine).

Wastewater treatment plant influent and effluent, landfill leachate, and ground water underlying a waste dump had the greatest number of OWCs detected. OWC detections in ground-water were low except underlying the one waste dump studied and feedlots. There generally were more OWCs detected in surface water than ground water, and there were twice as many OWCs detected in the surface water sites downstream from wastewater treatment plant (WWTP effluent than at sites not directly downstream from effluent. Comparisons among site classifications apply only to sites sampled during the study.

Results of this study indicate ubiquitous distribution of measured OWCs in the environment that originate from numerous sources and pathways. During this reconnaissance of OWCs in Minnesota it was not possible to determine the specific sources of OWCs to surface, ground, or drinking waters. The data indicate WWTP effluent is a major pathway of OWCs to surface waters and that landfill leachate at selected facilities is a potential source of OWCs to WWTPs. Aquatic organism or human exposure to some OWCs is likely based on OWC distribution. Few aquatic or human health standards or criteria exist for the OWCs analyzed, and the risks to humans or aquatic wildlife are not known. Some OWCs detected in this study are endocrine disrupters and have been found to disrupt or influence endocrine function in fish. Thirteen endocrine disrupters, 3-*tert*-butyl-4-hydoxyanisole (BHA), 4-cumylphenol, 4-*normal*-octylphenol, 4-*tert*-octylphenol, acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), benzo[*a*]pyrene, *beta*-sitosterol, bisphenol-A, diazinon, nonylphenol diethoxylate (NP2EO), octyphenol diethoxylate (OP2EO), octylphenol monoethoxylate (OP1EO), and total *para*-nonylphenol (NP) were detected. Results of reconnaissance studies may help regulators who set water-quality standards begin to prioritize which OWCs to focus upon for given categories of water use.

INTRODUCTION

Household, industrial, and agricultural-use compounds (HIAs), pharmaceuticals, antibiotics, sterols, and hormones are newly recognized classes of organic compounds that are often associated with wastewater. These organic wastewater compounds (OWCs) are characterized by high usage rates, potential health effects, and continuous release into the environment through human activities (Halling-Sorensen and others, 1998; Daughton and Ternes, 1999). OWCs can enter the environment through a variety of sources and may not be completely removed in wastewater treatment systems (Richardson and Bowron, 1985; Stumpf and others, 1996; Ternes, 1998) resulting in potentially continuous sources of OWCs to surface, ground, and drinking waters. OWCs have been detected in surface and ground waters throughout the world (Stumpf and others, 1996; Heberer and others, 1997; Buser and others, 1998; Ternes, 1998; Heberer and others, 1998; Daughton and Ternes, 1999). Kolpin and others (2002) reported that 80 percent of 139 streams sampled across the United States contained at least one OWC.

The continual introduction of OWCs into the environment may have undesirable effects on humans and animals (Daughton and Ternes, 1999). Much of the concern has focused on the potential for endocrine disruption (change in normal processes in the endocrine system) in fish. Field investigations in Europe and the United States suggest that selected OWCs (nonionic-detergent metabolites, plasticizers, pesticides, and natural or synthetic sterols and hormones) have caused changes in the endocrine systems of fish (Purdom and others, 1994; Jobling and Sumpter, 1993; Folmar and others, 1996; Folmar and others, 2001; Goodbred and others, 1997). In Minnesota, male common carp (*Cyprinus carpio*) collected in the effluent channel from the St. Paul/Minneapolis Metropolitan Wastewater Treatment Plant showed signs of endocrine disruption (Folmar and others, 1996; Lee and others, 2000).

An additional concern is the introduction of antibiotics and other pharmaceuticals into the environment. Antibiotics and other pharmaceuticals administered to humans and animals are not always completely metabolized and are excreted in urine or feces as the original product or as metabolites (Daughton and Ternes, 1999). The introduction of antibiotics into the environment may result in strains of bacteria that become resistant to antibiotic treatment (Daughton and Ternes, 1999).

It is important to determine the presence and distribution of OWCs in Minnesota's wastewater, surface, ground, and drinking waters because of potential human and ecosystem health concerns. The U.S. Geological Survey (USGS), in cooperation with the Minnesota Department of Health (MDH), and the Minnesota Pollution Control Agency (MPCA) conducted a reconnaissance study to determine the presence and distribution of OWCs in wastewater, surface, ground, and drinking waters in Minnesota during October 2000 through November 2002. The purpose of this report is to describe the results of this study and to document the quality-assurance procedures used to evaluate data quality.

STUDY DESIGN AND METHODS

Sites were selected to determine the presence and distribution of selected OWCs in potential wastewater, ground, surface, and drinking water sources in Minnesota. A total of 65 sites were selected, which included classifications as wastewater, surface-, ground-, and drinking-water sites (figs. 1 and 2; table 1).

The wastewater site classification included wastewater treatment plant influent and effluent, leachate from landfills, and water underlying feedlot lagoons. Wastewater treatment plants (WWTPs) were selected based on major influent composition, processing techniques, and accessibility. WWTPs sampled during this study differed in design flows, treatment techniques, and composition of influent (table 2). Effluent was sampled from four WWTPs (Sites 2, 3, 4, 5). Both the influent (Site 1) and effluent (Site 2) were sampled from one WWTP (East Grand Forks).

Three landfills were selected for leachate sampling. Landfill leachate (water that had passed through waste and collected in perimeter drains) was expected to have high concentrations of OWCs and would provide an estimate of the greatest expected concentrations. Landfill leachate was included in the wastewater classification (as opposed to the ground-water classification) because leachate at the facilities sampled is collected and transported to WWTPs for treatment. Landfills were selected based on type of waste received and accessibility. Landfills varied with respect to total capacity, type of waste, and leachate amount generated (table 3). Two of the landfill locations (Sites 6 and 7) were sanitary landfills and one (Site 8) was an industrial landfill.

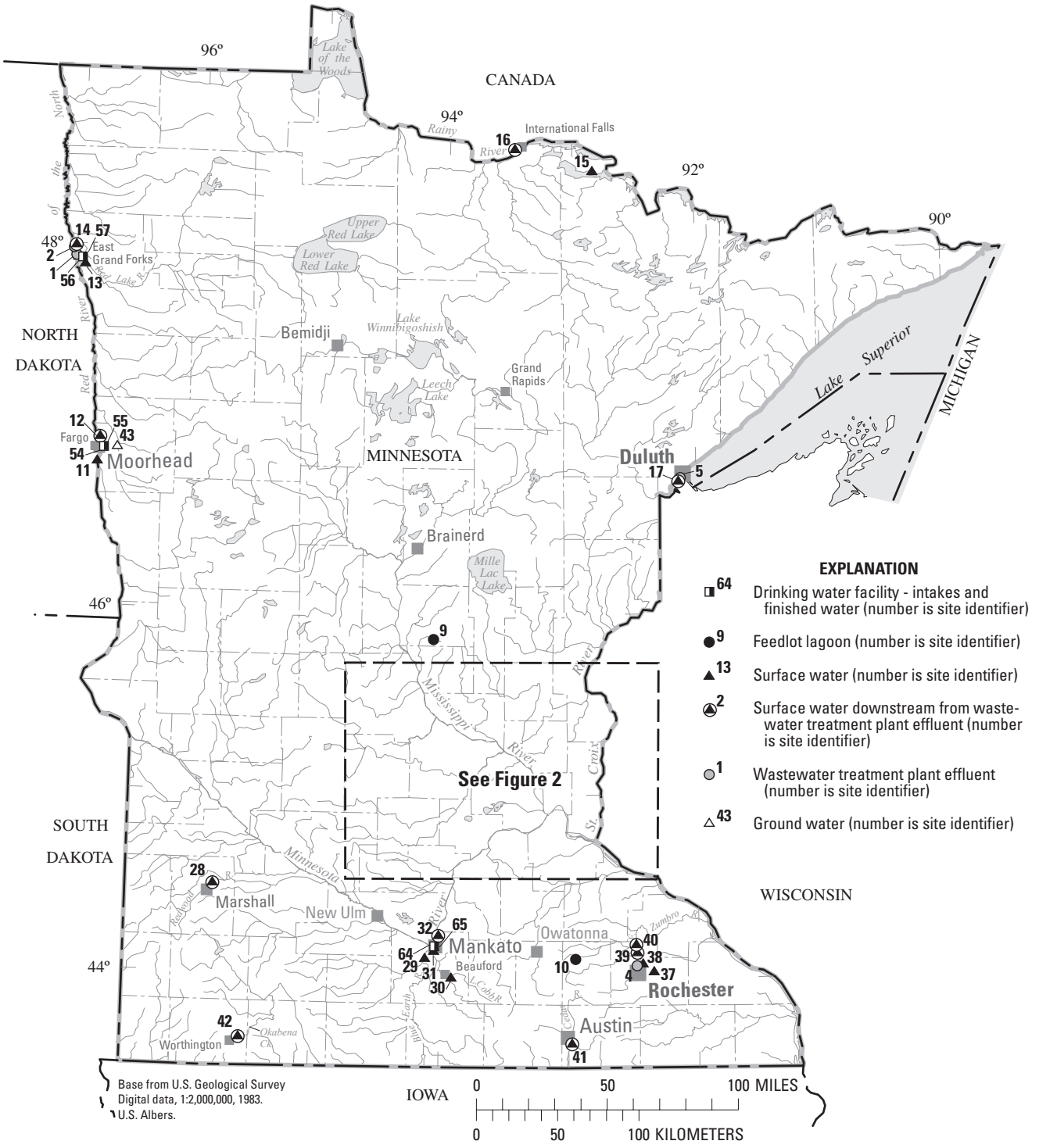

Figure 1. Location of study area and sampling sites (see table 1).

Two feedlot lagoons (Sites 9 and 10) used for livestock waste were selected to determine if OWCs in livestock waste pass through the compacted clay layer surrounding the lagoon basin. The two selected lagoons have systems to monitor the quantity and quality of seepage through compacted clay liners that underlie the sidewalls and bottoms of the lagoons. The systems consist of polyvinyl chloride (PVC) sheets that route seepage to a sump. Site 9 is located at a large hog farm, and holds a manure-water mixture from a nearby swine gestation barn (Ruhl, 1999). Site 10 holds waste from a small dairy farm (Wall and others, 1998). Selected

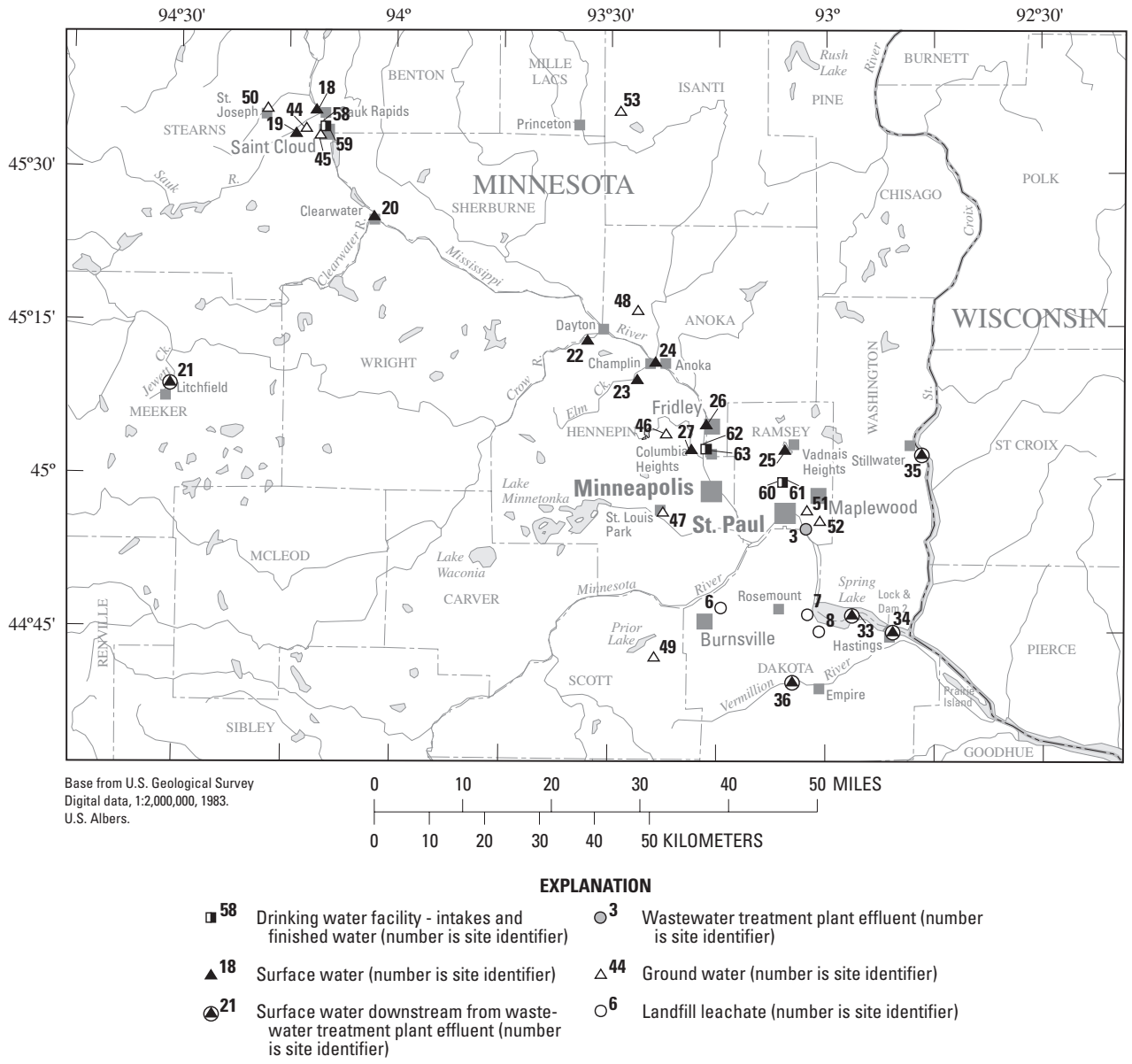

Figure 2. Location of sampling sites in east-central Minnesota, (see table 1).

feedlot lagoons were considered representative of other lagoons in the state of Minnesota.

There were 32 surface-water sites selected for this study (table 4). Surface-water sites were selected because of proximity to WWTP effluent discharge points and drinking-water-facility intakes, or basin land use. A remote lake in Voyageurs National Park with little human influence was selected as a reference location (Site 15). There were 11 sites selected on streams or lakes upstream from, and in close proximity to, drinking water-facility-intake pipes to determine potential sources of OWCs. There were 15 stream or lake sites (Sites 12, 14, 16, 17, 21, 28, 32, 33, 34, 35, 36, 39, 40, 41, and 42) selected downstream from WWTP effluent discharges (most within 1 mile of the discharge location) to determine if WWTP effluent is a potential source of OWCs to these streams.

This reconnaissance study included additional cooperative research. Three sites (Sites 38, 39, and 40) were sampled to determine the longitudinal change in OWCs upstream and downstream from WWTP effluent as part of a nationwide study by the U.S. Environmental Protection Agency and USGS Toxics Substances Hydrology Program. Site 38 is located upstream from WWTP effluent (Site 4), Site 39 is 250 ft downstream from the effluent discharge, and Site 40 is 1 mile downstream from effluent discharge. In addition, three sites (Sites 23,

Table 1. Selected sampling sites, and site classifications, Minnesota, 2000-02

[WWIF, wastewater treatment plant influent; WWEF, wastewater treatment plant effluent; WWTP, wastewater treatment plant; LFLCH, landfill leachate; FLLAG, feedlot lagoon; SW, surface water; SDW, surface water downstream from wastewater treatment plant effluent discharge; GWDW, ground water used for municipal drinking water supply; GWUI, ground water underlying mixed urban/residential/commercial/industrial land use that is sewered; GWUNSW, ground water underlying urban residential area that is unsewered; GWD, ground water underlying a waste dump; GWFLT, ground water underlying a feedlot; DWI, drinking water intakes; DWO, finished drinking water; HN, Hennepin County; MW, monitoring well].

Site identifier (fig.1 or 2)	Site name	Site classification
	Wastewater sites	
1	WWTP Lift Station Inflow at East Grand Forks	WWIF
2	WWTP Outflow at East Grand Forks	WWEF
3	Metropolitan Council Environmental Services WWTP Outflow in St. Paul	WWEF
4	WWTP outflow at Rochester	WWEF
5	Western Lake Superior Sanitary District WWTP outflow at Duluth	WWEF
6	Sanitary Landfill-1	LFLCH
7	Sanitary Landfill-2	LFLCH
8	Industrial Landfill-1	LFLCH
9	Morrison County feedlot lagoon	FLLAG
10	Dodge County feedlot lagoon	FLLAG
	Surface-water sites	
11	Red River of the North above Fargo, N.Dak.	SW
12	Red River of the North below Fargo, N.Dak.	SDW
13	Red Lake River at State Hwy 220 above East Grand Forks	SW
14	Red River of the North below WWTP at East Grand Forks	SDW
15	Ek Lake near International Falls	SW
16	Rainy River below International Falls	SDW
17	Lake Superior in St. Louis Bay at Duluth	SDW
18	Mississippi River above Sauk River near Sauk Rapids	SW
19	Sauk River near St. Cloud	SW
20	Mississippi River above Clearwater River near Clearwater	SW
21	Jewitt's Creek near Litchfield	SDW
22	Crow River below State Hwy 101 at Dayton	SW
23	Elm Creek near Champlin	SW
24	Mississippi River near Anoka	SW
25	Vadnais Lake at Pumping Station in Vadnais Heights	SW
26	Rice Creek at County Road 1 in Fridley	SW
27	Shingle Creek at Queen Ave. in Minneapolis	SW
28	Redwood River below WWTP near Marshall	SDW
29	Blue Earth River near Rapidan	SW
30	Little Cobb River near Beauford	SW
31	Blue Earth River at County Road 90 near Mankato	SW
32	Minnesota River at Mankato	SDW
33	Mississippi River at Ninninger	SDW
34	Mississippi River below Lock and Dam 2 at Hastings	SDW
35	St. Croix River below Stillwater	SDW
36	Vermillion River below Empire WWTP near Empire	SDW
37	Bear Creek Tributary near Chester	SW
38	South Fork Zumbro River at Rochester	SW
39	South Fork Zumbro River near Rochester	SDW
40	South Fork Zumbro River below WWTP near Rochester	SDW
41	Cedar River below WWTP at Austin	SDW
42	Okabena Creek near Worthington	SDW
	Ground-water sites	
43	Moorhead City well number 9	GWDW
44	Burlington Northern well near St. Cloud	GWUI
45	St. Cloud Rail Authority well	GWUI
46	HN-K well	GWUI
47	St. Louis Park well	GWUI
48	Anoka County observation well	GWUNSW
49	Prior Lake observation well	GWUNSW
50	St. Joseph observation well	GWUNSW
51	MW-6 at Pigs Eye Dump	GWD
52	MW-14 at Pigs Eye Dump	GWD
53	Isanti County Observation well near Princeton	GWFLT
	Drinking-water sites	
54	Moorhead Drinking Water Facility intake water at Moorhead	DWI
55	Moorhead Drinking Water Facility finished water at Moorhead	DWO
56	East Grand Forks Drinking Water Facility intake water at East Grand Forks	DWI
57	East Grand Forks Drinking Water Facility finished water at East Grand Forks	DWO
58	St. Cloud Drinking Water Facility intake water at St. Cloud	DWI
59	St. Cloud Drinking Water Facility finished water at St. Cloud	DWO
60	St. Paul Drinking Water Facility intake water at Maplewood	DWI
61	St. Paul Drinking Water Facility finished water at Maplewood	DWO
62	Minneapolis Drinking Water Facility intake water at Columbia Heights	DWI
63	Minneapolis Drinking Water Facility finished water at Columbia Heights	DWO
64	Mankato Drinking Water Facility intake water at Mankato	DWI
65	Mankato Drinking Water Facility finished water at Mankato	DWO

Table 2. Characteristics of wastewater treatment plants sampled, Minnesota, 2000-02

[WWTP, wastewater treatment plant; NA, not available; NPDES, National Pollutant Discharge Elimination System; SP, stabilization pond; AS, activated sludge; M, mechanical screen bars; MGD, million gallons per day; CHL/DCHL, chlorination/dechlorination; (Patricia King and Angela Preimesberger, Minnesota Pollution Control Agency, written commun., 2003)].

Site identifier (fig. 1 or 2)	Facility name (NPDES number)	Receiving water	Annual average wet; and (dry) design flow (MGD)	Treatment technique	Disinfection method	Description of significant influent sources
1, 2	WWTP inflow and outflow at East Grand Forks (MN0021814)	Red River of the North	1.4 (NA)	2 cell -SP	NA	Domestic waste, potato processing
3	Metropolitan Council Environmental Services WWTP outflow in St. Paul (MN0029815)	Mississippi River	314 (250)	Step aeration, AS	CHL/DCHL	Domestic waste; battery, coil and can coating; electroplating, food and dairy processing; iron and steel; laundry; leather and tanning; livestock; medical facilities; metal finishing; organic chemicals; energy/power; pharmaceutical manufacturing; plastics; pulp and paper; railroads; solid waste landfill leachate
4	WWTP outflow at Rochester (MN0024619)	South Fork Zumbro River	19.1 (11.1)	AS	CHL/DCHL	Domestic waste; food and dairy processing; gas stations; incinerators; landfill leachate; laundry; medical facilities; metal finishing; power generator
5	Western Lake Superior Sanitary District WWTP outflow at Duluth (MN0049786)	Lake Superior	48.4 (35.3)	AS, M	CHL/DCHL	Domestic waste; electroplating; foundry; inorganic chemical; metal finishing; organic chemical; pulp and paper; pharmaceutical manufacturing; steam and electric power; timber products

Table 3.

, written commun., 2003)

Site identifier (fig. 1 or 2)	Landfill	Capacity (cubic yards)	Capacity used (cubic yards)	Tons of municipal waste landfilled	Tons of demolition waste landfilled	Tons of industrial waste landfilled	Leachate generated (gallons)	Leachate disposal location
6	Sanitary Landfill-1	14,028,000	11,841,400	198,829	Separate area	111,251	1,750,235	Metropolitan Council Envrionmental Services WWTP in St. Paul, Minn. (Site 3)
7	Sanitary Landfill-2	24,000,000	20,207,320	277,130	205	222,853	8,533,596	Metropolitan Council Envrionmental Services WWTP in St. Paul, Minn. (Site 3)
8	Industrial Landfill-1	6,037,983	664,244	0	0	283,081	3,474,161	Metropolitan Council Envrionmental Services WWTP in St. Paul, Minn. (Site 3) when volume exceeds amount permitted at Rosemount WWTP

Table 4. Land use and land cover percentages, and drainage ares in the basin upsstream from surface-water sampling locations, Minnesota, 2000-02

[nd, not determined; the sum of land use/land cover percentages may not equal 100 due to absence of an 'other' category; mi², square miles; WWTP, wastewater treatment plant].

Site identifier (fig. 1 or 2)	Site name	Percent urban	Percent forest/ shrub	Percent agriculture	Percent wetland	Basin Area (mi²)
11	Red River of the North above Fargo, N.Dak.	0.6	7.5	79.0	7.8	6,621
12	Red River of the North below Fargo, N.Dak.	0.8	7.4	79.1	7.7	6,704
13	Red Lake River at St. Hwy 220 above East Grand Forks	0.5	14.5	41.5	33.6	5,710
14	Red River of the North below WWTP at East Grand Forks	0.7	7.6	76.0	11.6	25,713
15	Ek Lake near International Falls	0	80	0	20.0	1.21
16	Rainy River below International Falls	0.3	61.6	1.1	21.0	4,452
17	Lake Superior in St. Louis Bay at Duluth	1.5	46.9	7.5	37.6	3,719
18	Mississippi River above Sauk River near Sauk Rapids	0.9	38.8	25.5	24.7	12,582
19	Sauk River near St. Cloud	1.2	9.8	71.9	12.1	1,034
20	Mississippi River above Clearwater River near Clearwater	1.0	36.4	29.3	23.6	13,762
21	Jewitt's Creek near Litchfield	7.3	4.4	63.9	14.9	26.9
22	Crow River below State Hwy 101 at Dayton	1.5	6.7	73.9	12.4	2,750
23	Elm Creek near Champlin	8.7	1.6	84.0	2.8	85.8
24	Mississippi River near Anoka	1.2	30.1	37.8	21.6	19,092
25	Vadnais Lake at Pumping Station in Vadnais Heights	nd	nd	nd	nd	nd
26	Rice Creek at County Road 1 in Fridley	22.2	10.2	39.2	18.6	180.2
27	Shingle Creek at Queen Ave. in Minneapolis	71.0	0.9	20	0.7	28.2
28	Redwood River below WWTP near Marshall	1.8	2.8	87.8	4.8	268.9
29	Blue Earth River near Rapidan	1.7	3.2	91.0	2.6	2,430
30	Little Cobb River near Beauford	0.2	0.5	94.0	4.0	130
31	Blue Earth River at County Road 90 near Mankato	1.7	3.2	91.0	2.6	3,536
32	Minnesota River at Mankato	1.0	3.5	88.5	4.5	14,917
33	Mississippi River at Ninninger	2.5	19.0	66.0	7.1	37,000
34	Mississippi River at Lock and Dam 2 at Hastings	2.5	18.0	66.0	7.1	37,000
35	St. Croix River below Stillwater	0.6	49.0	28.8	17.0	7,025
36	Vermillion River below Empire WWTP near Empire	13.8	10.6	65.0	7.6	118.9
37	Bear Creek Tributary near Chester	nd	nd	nd	nd	nd
38	South Fork Zumbro River at Rochester	5.4	7.7	83.6	2.9	301.6
39	South Fork Zumbro River near Rochester	5.4	7.7	83.6	2.9	301.6
40	South Fork Zumbro River below WWTP near Rochester	5.4	7.7	83.6	2.9	301.6
41	Cedar River below WWTP at Austin	3.4	3.4	90.6	2.4	244.3
42	Okabena Creek near Worthington	28.1	0.9	68.0	0.8	8.2

27, and 30) were sampled cooperatively with the USGS National Water-Quality Assessment (NAWQA) Program. These sites have been sampled extensively by the NAWQA Program.

Ground-water sites (table 5) included 1 production well (Site 43), 8 monitoring wells (Sites 44-47, 50-53), and 2 temporary drive-point test wells (Sites 48 and 49). Ground-water sites were selected based on proximity to potential OWC sources and surrounding land-use characteristics, with the exception of Site 43 in the Quaternary aquifer near Moorhead, Minnesota that was sampled because it serves as a source of water for the Moorhead Drinking Water Facility (DWF).

The monitoring wells were less than 40 ft deep. There were four wells located in mixed urban residential/commercial/industrial land use in sewered areas, two wells located in the waste dump, and one well located in the feedlot. Two temporary drive-point test wells (Sites 48 and 49) and one monitoring well (Site 50) were selected in unsewered areas near individual sewage treatment system leach fields (septic systems).

Six drinking water facilities (DWFs) (Sites 54-65 shown in table 6) were selected for this study. Two DWFs were selected in the Red River of the North Basin (Moorhead, and East Grand Forks), and four DWFs were sampled in the Upper Mississippi River Basin (St. Cloud, St. Paul, Minneapolis, and Mankato). These facilities have different source waters and varying water-treatment techniques (table 6). Selected DWFs (except Mankato and Moorhead DWFs) utilize surface water as their source for drinking water production. Mankato DWF draws most of its water from Ranney collector wells adjacent to the Blue Earth and Minnesota Rivers. Ranney wells used by the Mankato DWF are approximately 60 ft below the land surface. Ground water at the Ranney wells could be influenced by recharge from the Blue Earth and Minnesota Rivers (George Rosati, City of Mankato Water Treatment Facility, oral commun., 2000). One water production well that serves as a source of intake water for Moorhead DWF also was sampled (Site 43). This well is used intermittently as a drinking water source in conjuction with surface water from the Red River of the North and was in production during two sampling periods (Fall of 2000, and Summer of 2001). Both intake and finished water from DWFs were sampled.

All samples were collected using protocols and procedures to obtain a representative sample and avoid sample contamination. Specific protocols and methods are documented for the collection and processing of water-quality samples (U.S. Geological Survey, 2003), and streamflow computation (Rantz and others, 1982 a and b; Morlock and others, 2002). During collection or processing of samples, sample collectors did not use personal care items (such as insect repellent, colognes, aftershave, and topical antibiotics), and they did not consume caffeinated products (coffee, tea, carbonated beverages). All samples were collected with inert materials such as Teflon, glass, or stainless steel. A multi-parameter probe was used to measure field parameters (specific conductance, pH, water temperature, and dissolved oxygen) at each site (U.S. Geological Survey, 2004a).

Integrated width-and depth-sampling techniques were used to sample WWTP effluent from the effluent discharge channels outside of three plants (Sites 3, 4, and 5) and from the treated effluent at Site 2 in the outflow of the settling pond during release to the Red River of the North (U.S. Geological Survey, 2003). Both raw and treated sewage were collected from the East Grand Forks WWTP (Sites 1 and 2). Untreated sewage influent was collected from an interceptor line at Site 1 by filling a Teflon sample bottle from the incoming waste stream.

Landfill leachate samples were collected with a Teflon bailer from leachate storage tanks and composited in glass or Teflon containers. The leachate at Site 6 was collected from an underground storage tank that collected water from selected locations within the landfill. Leachate from Site 7 was collected from an above ground storage tank representative of selected locations within the landfill. Leachate from Site 8 was collected from an above ground storage tank that was representative of the entire landfill.

Wastewater samples from feedlot lagoons used for animal waste (Sites 9 and 10) were collected from the drainage system underlying the lagoon. A sump pump was used to collect water passing through the compacted clay layer that was intercepted by a plastic liner.

Stream samples were collected using established USGS techniques (U.S. Geological Survey, 2003). Samples were collected from boats, bridges, or by wading, depending on stream size and streamflow conditions. Stream samples were collected with a depth-integrating sampler from 5-10 verticals and composited in a Teflon or glass container prior to processing. Lake samples (Sites 15 and 17) were collected with a depth-integrating sampler from 5-10 locations in the lake.

Table 5. Characteristics of ground-water sites sampled, Minnesota 2000-02 (Angel Preimesberger, Minnesota Pollution Control Agency, written commun., 2003)

[PVC, polyvinyl chloride; SS, stainless steel; ST, steel; HN, Hennepin County; MW, monitoring well; NA, not available]

Site identifier (fig. 1 or 2)	Local well number	Site name	Description	Screened interval (feet)	Well depth (feet)	Casing construction material
43	222050	Moorhead City well number 9	Water production well	78.0 - 111.3	114.0	ST
44	444225	Burlington Northern well near St. Cloud	Sewered, older residential and industrial	4.0 - 14.4	16.5	ST
45	594128	St. Cloud Rail Authority well	Sewered older residential, commercial, and industrial	16.5 - 21.5	23.2	PVC
46	560417	HN-K well	Sewered, older residential, commercial, and industrial	17.5 - 22.5	22.5	PVC
47	216031 (MW-2)	St. Louis Park well	Sewered industrial	31.0 – 36.0	36.0	SS
48	NA	Anoka County observation well	Temporary drive-point test well within 100 feet of a septic system	0 – 2.0	2.0	SS
49	NA	Prior Lake observation well	Temporary drive-point test well within 100 feet of a septic system	0 – 2.0	2.0	SS
50	540955	St. Joseph observation well	Observation well within 100 feet of a septic system	26.0 – 31.0	31.0	PVC
51	MW-6	MW-6 at Pigs Eye Dump	Closed dump	15.2 - 17.2	20.0	ST
52	MW-14	MW-14 at Pigs Eye Dump	Closed dump	22.3 - 27.6	27.6	ST
53	591791	Isanti County observation well near Princeton	Dairy feedlot with approximately 70 head of cattle	8.5 - 13.5	14.0	PVC

Table 6. Characteristics of drinking water facilities sampled, Minnesota, 2000-02

[MGD, million gallons per day]

Site identifier (fig.1 or 2)	Location	Source water	Approximate number of people served	Average daily water production (MGD)	Treatment objective	Treatment process or chemical
54-55	Moorhead Drinking Water Facility at Moorhead	80-90 percent is from the Red River of the North, and the remainder from Quaternary buried and water table aquifers.	36,200	4.1	Softening Coagulation pH control Disinfection and taste/odor control Filtration Corrosion control Prevent tooth decay Secondary disinfection	Lime-soda ash Ferric sulfate Carbon dioxide Ozone Dual media filters Sodium hexametaphosphate Fluoride Chloramines
56-57	East Grand Forks Drinking Water Facility at East Grand Forks	100 percent Red Lake River	7,500	1.5	Taste/odor control Coagulation Coagulation aid Softening Softening Corrosion control pH control Disinfection Prevent tooth decay Filtration Disinfection	Powdered activated carbon and/or potassium permanganate Alum Cationic polymer Lime-soda ash Sodium aluminateP olyphosphate Carbon dioxide Chlorine Fluoride Mixed media filters Choramines
58-59	St. Cloud Drinking Water Facility at St. Cloud	100 percent Mississippi River	59,000	7	Taste/odor control Coagulation Softening pH control Disinfection Corrosion control Disinfection Prevent tooth decay Filtration	Powdered activated carbon and/or potassium permanganate Alum Lime-soda ash Carbon dioxide Chlorine Polyphosphate Chloramines Fluoride Filters
60-61	St. Paul Drinking Water Facility at Maplewood	70 percent is from Mississippi River water that is passed through a chain of lakes including Vadnais Lake. The remaining 30 percent from the Prairie du Chien-Jordan aquifer and local watershed runoff	415,000	50	Taste/odor control Softening Coagulation Prevent tooth decay pH control\ Disinfection Disinfection Filtration Corrosion control	Powdered activated carbon and/or potassium permanganate LimeAlum Ferric chloride Fluoride Carbon dioxid Chlorine Chloramines Anthracite/sand filters Sodium hydroxide and stannous chloride
62-63	Minneapolis Drinking Water Facility at Columbia Heights	100 percent from the Mississippi River	500,000	70	Softening Coagulation Taste/odor control pH control Disinfection Prevent tooth decay Coagulation Filtration Corrosion control	Lime Alum Powdered activated carbon and potassium permanganate Carbon dioxide Chloramines Fluoride Ferric chloride Sand/mixed media filers Poly/ortho phosphate
64-65	Mankato Drinking Water Facility at Mankato	70 percent from the Ranney collector wells underlying (60-foot depth) the Blue Earth and Minnesota Rivers. The remain¬ing 30 percent from wells (700 feet) in the Mt.Simon/Hinckley aquifer.	33,000	4.5	Softening pH adjustment Filtration Prevent tooth decay Corrosion control Disinfection	Lime Carbon dioxide Sand filter Fluorides Phosphate Chlorine

Hydrographers measured streamflow concurrent with sample collection at most stream sites. Streamflow was measured using current meters (Rantz and others, 1982 a and b) where stream cross sections could be waded. A boat-mounted acoustic-Doppler measuring device aboard a boat traversing the river was used to measure streamflow where depths in stream cross sections precluded wading (Morlock and others, 2002). At selected sites with continuous recording gages, streamflow was obtained from the USGS National Water Information System (NWIS) (U.S. Geological Survey, 2004b).

Ground-water samples were collected from monitoring wells using USGS protocols (U.S. Geological Survey, 2003). Samples were collected after at least three well volumes had been pumped and field parameters had stabilized. A positive displacement pump with a stainless steel head, and Teflon tubing was used for sampling monitoring wells. The water production well (Site 43) was sampled from a faucet in the well house. Two drive-point temporary test holes (Sites 48 and 49) within 100 ft of an active septic system in unsewered urban areas were sampled with a peristaltic pump and polyethylene tubing inserted into a steel probe that had a stainless steel screen. Water samples were collected from the upper 2 ft of the water table.

Intake and finished water samples were collected inside DWFs. The samples were collected from an intake faucet and a finished-water faucet that also were used for internal DWF monitoring. Samples were collected from the faucets when field parameters had stabilized.

All sites were sampled at least once from October 2000 through November 2002. At 30 sites, 3-4 water samples were collected during: (1) fall baseflow, (2) winter baseflow, (3) spring-snowmelt runoff, and (4) summer-storm runoff.

Following collection, samples were composited into a glass container and chilled prior to processing. Chilled water samples were processed within 1-2 hours of collection. Each sample was filtered through a 0.7-µm glass fiber filter that was baked at 450°C for 2 hours. Approximately 100 mL of filtrate was wasted before sample collection to flush the filtration system. Once the system was flushed, water was filtered into precleaned amber glass bottles and refrigerated before shipping to selected laboratories (National Water-Quality Laboratory, Denver, Colorado; U.S. Geological Survey Laboratory, Ocala, Florida; and U.S. Geological Survey Laboratory, Boulder, Colorado).

USGS research and official production methods were used to analyze for the 114 selected OWCs in this study (appendix 1). This list of OWCs was developed during previous and ongoing studies by the USGS Toxics Substances Hydrology Program. OWCs were selected based upon usage, toxicity, potential estrogenic activity, and persistence in the environment (Barnes and others, 2002; Kolpin and others, 2002). Research methods are experimental in contrast to official production methods, and are not conducted in a routine-production capacity. Research methods typically are in development and extensive quality-control information is often not available; therefore, there is uncertainty associated with compound concentrations.

There were five different analytical methods used in this study. The following descriptions of analytical Methods 1-5 are intended to provide an overview. Methods 1, 2, 4, and 5 are USGS research methods, and Method 3 is an official USGS production method. Analytical data summarized in this report, and can be accessed electronically on the world wide web (U.S. Geological Survey, 2004 a-f).

Analytical Method 1 analyzes for 16 human prescription and nonprescription pharmaceuticals and their select metabolites in filtered water samples (including two antibiotics that also are analyzed using Method 2; and 2 pharmaceuticals that also are analyzed using Methods 3 and 4). Pharmaceuticals were extracted from water samples using hydrophilic-lipophilic-balance (HLB) solid phase extraction (SPE) cartridges. Sample extracts were separated and measured by reversed phase high-performance liquid chromatography/electrospray ionization mass spectrometry (HPLC/[ESI]MS) using selected ion monitoring (SIM). Additional details on this method are provided elsewhere (Barnes and others, 2002; Kolpin and others, 2002; Cahill and others, 2004).

Analytical Method 2 analyzes for 21 veterinary and human antibiotics in filtered water samples. These analyses were completed at the U.S. Geological Survey Laboratory in Ocala, Florida. Antibiotics were extracted by tandem SPE and analyzed by HPLC/[ESI]MS using SIM. The tandem SPE included an Oasis HLB cartridge (60 mg) followed by a mixed mode, HLB-cation exchange (MCX) cartridge (60 mg) (Waters Inc., Milford, Mass.). Additional details on this method are provided elsewhere (Meyer and others, 2000; Barnes and others, 2002; Kolpin and others, 2002).

Analytical Methods 3 and 4 analyze for 63 OWCs in filtered water including 57 HIAs, 2 pharmaceuticals, and 4 sterols (including 2 sterols also analyzed by Method 5). These analyses were completed at the U.S. Geological Survey National Water-Quality Laboratory in Denver, Colorado. Method 3 is an official USGS production method (USGS laboratory schedule 1433). Samples were extracted by vacuum through disposable SPE cartridges that contain polystyrene-divinylbenzene resin. Sorbed compounds were eluted with dicholoromethane-diethyl ether. Compounds were measured by capillary-column gas chromatography/mass spectrometry (GCMS). Additional details on this method are provided by Zaugg and others (2002).

Analytical Method 4 (custom laboratory method 8033) analyzed for the same compounds as Analytical Method 3. Water samples were extracted using continuous liquid-liquid extraction (CLLE) with methylene chloride at pH 2.0, and analyzed by GC/MS. Additional details on this method are provided elsewhere (Brown and others, 1999; Barber and others, 2000; Barnes and others, 2002; Kolpin and others, 2002; Zaugg and others, 2004).

Analytical Method 5 analyzes for 20 sterols and hormones (Barber and others, 2000; Barnes and others, 2002; Kolpin and others, 2002). These analyses were completed at the U.S. Geological Survey Laboratory in Boulder, Colorado. Extracts from Methods 3 and 4 were derivatized to deactivate the hydroxyl and keto functional groups and reanalyzed. The technique used in this method is the formation of the trimethylsilyl ethers of the hydroxyl groups and the oximes of the keto groups. After derivatization, the samples were analyzed by GC/MS.

Analyte identification for all methods had to meet qualitative and quantitative criteria (Barnes and others, 2002; Kolpin and others, 2002). A positive identification was based on elution within the expected retention time. In addition, the sample spectra and ion abundance ratio was required to match that of the reference standard analytes. After identification criteria were attained, analyte concentrations were calculated using a 5–8-point calibration curve (concentrations generally from 0.01 to 10.0 µg/L) using internal standard quantitation. The base-peak ion was used for quantitation, and, if possible, as many as two fragment qualifier ions were used for ion abundance ratio confirmation. Calibration standards are processed throughout the extraction procedure for Method 2, which generally corrects concentrations for method losses, but not for matrix effects. Methods 1, 3, 4 and 5 do not extract calibration standards; thus the reported concentrations are not corrected for method losses.

Method reporting levels (MRLs) were determined for each analyte by a previously published procedure (U.S. Environmental Protection Agency, 1992). Selected analyte concentrations were flagged with an “E” to indicate estimated values. These include all concentrations above or below the calibration curve, concentrations for analytes with average recoveries less than 60 percent, analytes routinely detected in laboratory blanks, and constituents with reference standards prepared from technical mixtures (Barnes and others, 2002; Kolpin and others, 2002).

QUALITY ASSURANCE

Because some research methods used in this study are newly developed and methods are not published, a description of the data quality (including properties of the measurement such as precision, bias, and detection limits) is included in this report. A quality-assurance plan was established to evaluate laboratory and field sampling techniques, to assess possible sources of contamination, and to assure representative samples. Laboratory quality-control samples were used to validate analytical data. Field quality-assurance samples were used to assess sample collection and processing.

Laboratory quality-control samples included laboratory blanks, reagent spikes, and surrogates. At least one fortified laboratory spike and at least one laboratory blank was analyzed with each set of 10–16 field samples. Laboratory reagent blanks were used to assess potential sample contamination. Recoveries for compounds spiked into reagent water, and surrogate compounds in field samples indicate the general proficiency of the laboratory methods. Most methods had surrogate compounds added to samples prior to extraction to monitor method performance. Surrogates are chemicals that have similar properties to the analytes of interest, but do not interfere with quantitation of the compounds of interest. A summary of the laboratory spikes, reagent blanks, and surrogates are included in this report (appendixes 2 and 3).

Among all the laboratory reagent blank samples processed and analyzed 50 OWCs were detected (appendix 2). There were few detections of OWCs in laboratory blank samples in Methods 1 and 2 except acetamino-

phen (detected in 10 percent of the blanks) and caffeine (detected in 20 percent of the blanks). There were 47 OWCs detected for Methods 3 and 4 combined. One or more of these compounds, including *d*-limonene, isophorone, naphthalene, nonylphenol diethoxylate (NP2EO), *para*-nonylphenol (NP), prometon, tetrachloroethylene (TCE), and tributyl phosphate, were detected in at least 30 percent of the laboratory reagent blanks. Many of these OWCs were detected in laboratory blanks at low concentrations that were below MRLs and below concentrations detected in most field samples with the exception of isophorone. In order to correct for laboratory blank contamination, environmental samples with an OWC concentration less than 10 times the concentration of an OWC in the corresponding set blank was reported as a nondetection.

The average percent recoveries for laboratory reagent spikes for Methods 1-4 were 72, 102, 75, and 82 percent, respectively. Acceptable recoveries for these methods at the USGS Laboratories range from 60 to 120 percent. Most OWC recoveries were in the range of 60–120 percent with the exception of diltiazem, diphenhydramine, ibuprofen, and ranitidine (analyzed by Method 1); ciprofloxacin and virginiamycin (analyzed by Method 2); and 1,4-dichlorobenzene, 3-*tert*-butyl-4-hydroxyanisole (BHA), cotinine, dichlorvos, *d*-limonene, isopropyl benzene, NP, and TCE (analyzed by either Method 3 or 4). Low laboratory spike recoveries for these OWCs could indicate that there are false negatives (error in not identifying an OWC that is actually present) in an environmental sample. False negatives are more likely than false positives (error in identifying a OWC that is not present in a sample) as each USGS laboratory (National-Water Quality, Ocala, and Boulder Laboratories) had stringent and conservative procedures for qualitative identification of the compound. Low laboratory recoveries for these OWCs may indicate that the frequency of detection is underestimated, and highlights the need to continue to refine the analytical procedures to obtain less variability, better recoveries, and lower detections limits.

Average surrogate recoveries ranged from 27 to 171 percent (appendix 3). High and low surrogate recoveries result from sample components that interfere with isolation, detection, and quantification of the surrogate. Field sample concentrations for those samples with low surrogate recoveries may be underestimated, while samples with high surrogate recoveries may be overestimated.

Potential contamination of samples because of collection and sample processing was assessed with field-blank samples. Two types of blank samples were collected: field blanks and office blanks. Field blanks were prepared at the selected site prior to, or following, a scheduled field sample. Office blanks were processed in the laboratory at the USGS Minnesota District field office. In both cases, blank samples were prepared by processing HPLC grade organic-free water (Baker Analyzed, J.T. Baker Co.) through the same equipment used to collect and process field samples. A total of 13 blanks were submitted for Method 1, 9 blanks for Method 2, 14 blanks for Method 3 and 4, and 7 blanks for Method 5, and generally analyzed for all OWCs (appendix 4).

Most OWCs were detected infrequently in field blank samples, were at estimated concentrations below the MRL, and were below field sample concentrations verifying the general effectiveness of sampling protocols used for this study. Nine of the 114 OWCs analyzed for in this study were detected in the field blank samples (appendix 4). Cholesterol (Method 5) was the most frequently detected OWC in field blank samples followed by phenol (Methods 3 and 4), and caffeine (Method 1). Phenol concentrations exceeded MRLs and some field sample concentrations. The frequency of detections and high concentrations at or exceeding the MRL for phenol may indicate a contamination source in field sampling procedures or demonstrates the ubiquitous nature of this compound. Environmental samples were not corrected for field blank contamination as there were no instances where the OWCs detected in field or office blanks coincided with the occurrence of the same OWC in an environmental sample during a similar time frame.

Field replicate samples were collected to determine variability of detections and concentrations resulting from sample and laboratory processing techniques (sample splitting, filtration, and transport). Replicate samples consist of a split of the field sample so the field and replicate samples should be nearly equal in composition. Samples were submitted for 5 replicates for Method 1, 7 replicates for Method 2, 9 replicates for Methods 3 and 4, and 4 replicates for Method 5 (appendix 4). Most were duplicate samples and one was a triplicate. Replicate samples were collected at locations where few OWC detections were expected (DWFs) and where OWC detections were expected (WWTP effluent, stream sites downstream of WWTP effluent, and feedlot lagoons). By collecting replicates at both ends of this spectrum the detection consistency and the variability in concentrations was evaluated. The detection consistency

was evaluated by determining the number of replicates that had consistent detections (and nondetections) of selected OWCs. Concentrations of detected compounds were compared by calculating a relative standard deviation (RSD) for each compound.

There was a wide range in RSDs (from 0 to 101.1 percent) among all OWCs and all replicates (appendix 4). The average RSD (11.2 percent) for all OWCs and all replicates is low considering the new research methods utilized in this study. Replicate samples from three DWFs were appropriate primarily for comparison of OWC detection consistency, but limited for concentration comparisons, as there were 12 OWC detections in the field and corresponding replicate samples, and a high percentage of the data were below the MRL. Detection and nondetection consistencies were confirmed for most OWCs in DWF samples.

Replicate samples for WWTP effluent, streams directly downstream from effluent, and feedlot lagoon samples had more OWC detections, and were useful for both determinations of detection consistency and concentration comparisons. Detection consistency was confirmed for most comparisons. The average RSD for OWCs in wastewater replicate samples was 11.3 percent, and RSDs were less than 20 percent for most OWCs. Cholesterol (Methods 3, 4, and 5), diazinon, 3-*beta*-coprostanol (Methods 3, 4, and 5), 3-methyl-1H-indole (skatol), and phenol had the greatest average RSDs. For most comparisons; however, field and replicate concentrations were within an order of magnitude, and were within the laboratory analytical error associated with these compounds. For example, 3-*beta*-coprostanol concentrations analyzed by Method 3 in field and replicate samples from Site 3 on March 28, 2001 (0.59 and 0.38 µg/L respectively) had a RSD of 30.1 percent. While this RSD is greater than the accepted standard of 10 percent, these two concentrations are low, and the difference in concentration is within laboratory analytical error.

OWCs measured by more than one analytical method described in this report also were used to evaluate the results for this study. Three types of comparisons were made. The first was a comparison of 34 samples using Methods 3 and 4. This was important as field samples were analyzed by a combination of these two methods. The second comparison was for six compounds analyzed for more than one of the methods listed in this report (3-*beta*-coprostanol, caffeine, cholesterol, cotinine, sulfamethoxazole, and trimethoprim). The third comparison was a limited investigation of bromoform concentrations between Method 3 and a USGS production method (USGS laboratory schedule 1307) (Connor and others, 1998).

Methods 3 and 4 were used to analyze for HIAs in 34 samples. A comparison was made between these two methods to determine if data from the two methods could be combined. The two methods were compared graphically (fig. 3), and in terms of detection consistency. Concentrations of all compounds (except bromoform) from each method were plotted against each other and a linear regression line was prepared. Bromoform concentrations were not included because subsequent investigation indicated they may be overestimated by both methods. This line provides a representation of how the two methods compare, but does not provide information about specific OWCs as there generally were too few detections per OWC to prepare a regression line for each.

Among the 34 samples analyzed, 54 OWCs were detected. Detection and nondetection consistencies were confirmed for greater than 90 percent of the comparisons. Selected OWCs (*d*-limonene, isophorone, and phenol) were detected more frequently in Method 3 than Method 4. Concentrations of most OWCs were consistently greater for Method 3 than for Method 4 based on the visual inspection and regression analyses (fig. 3). The concentration differences; however, did not vary substantially between Methods 3 and 4, and generally were within one order of magnitude and within the laboratory analytical error for selected OWCs for most comparisons. This pattern holds true for WWTPs and landfill leachate samples with relatively greater concentrations, and for more dilute DWF samples.

There is reasonable agreement between Methods 3 and 4 indicating that data from both methods can be compared for this discussion of OWC presence and distribution. There were some inconsistencies that were biased to a certain method (*d*-limonene, isophorone, and phenol). *d*-Limonene, isophorone, and phenol are expected to have greater detection frequencies in Method 3 than Method 4; therefore, they were removed from further comparisons among sites and site classifications.

Caffeine, cotinine, trimethoprim, sulfamethoxazole, cholesterol, and 3-*beta*-coprostanol were analyzed by more than one method described in this report. Cotinine and caffeine were analyzed by Methods 1, 3, and 4; sulfamethoxazole and trimethoprim were analyzed by Methods 1 and 2; and cholesterol and 3-*beta*-coprostanol were analyzed by Methods 3, 4, and 5. There were

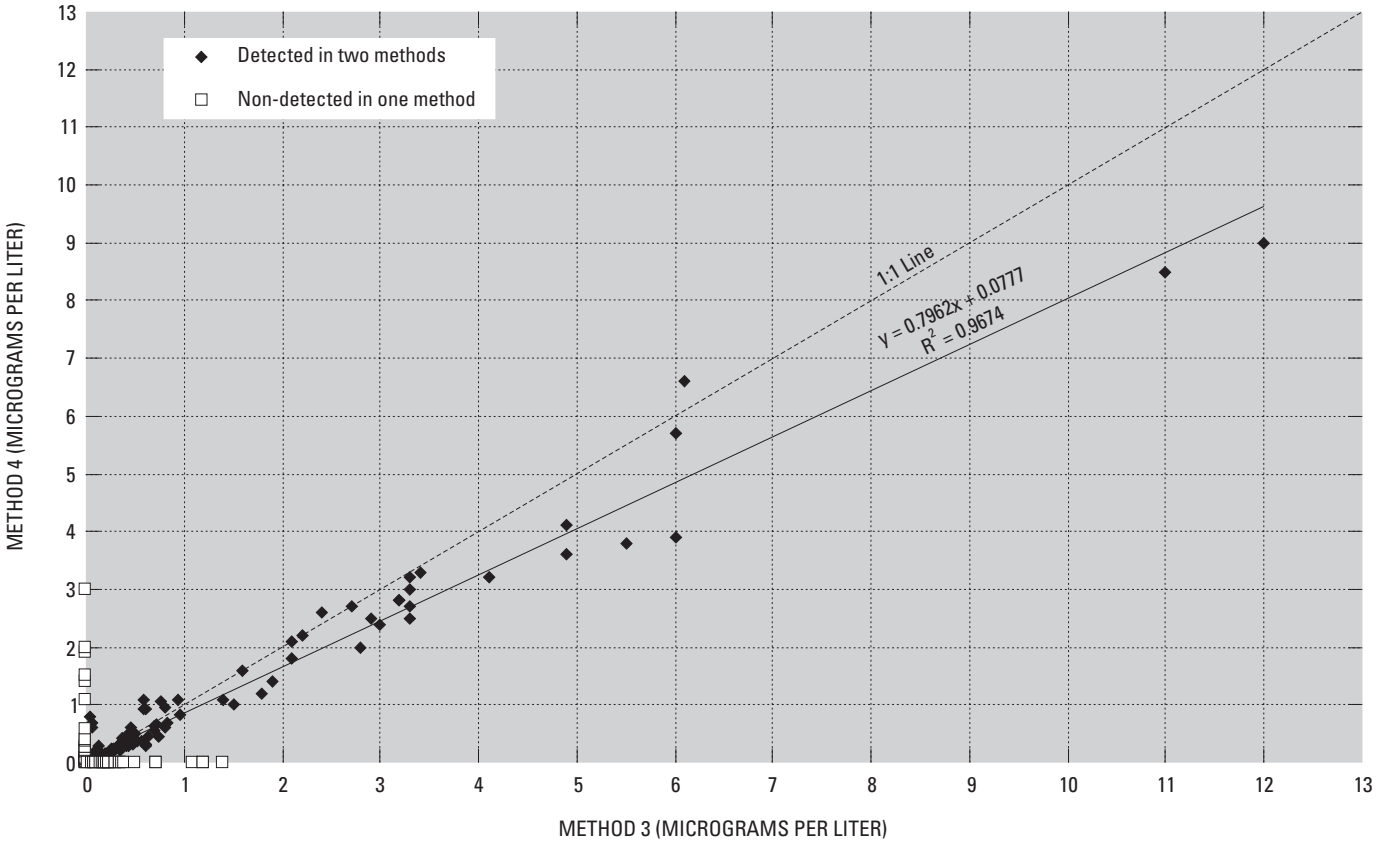

Figure 3. Comparison of results from U.S. Geological Survey analytical Methods 3 and 4 for selected organic wastewater compounds with the exception of bromoform. [Regression line (solid line) was prepared using detections only.]

different laboratory-method reporting limits (MRLs) among the methods. For example, the MRL for cotinine was 0.023 µg/L for Method 1, and 1.0 µg/L for Methods 3 and 4 (table 7). The detection frequency is not expected to be similar among methods with different MRLs. The frequency of detection was greater in those methods with lower detection limits as expected. For example, cotinine was detected in 23 samples analyzed by Method 1 and in 3 samples by methods 3 or 4 (table 7). Only 2 of the 23 samples analyzed by Method 1 had cotinine concentrations that were great enough to be detected in Methods 3 or 4, which equates to a detection consistency of 90 percent. The detection consistency of the remaining OWCs was confirmed in 99 percent of the determinations for cholesterol and 3-*beta*-coprostanol; 85 percent for trimethoprim; 80 percent for caffeine; and 50 percent for sulfamethoxazole.

Methods 3 and 4 target a wide variety of OWCs that serve as indicators of multiple types of wastewater. One of those OWCs, bromoform, is a regulated trihalomethane, and is a byproduct of drinking water or wastewater disinfection that is formed when chlorine reacts with organic matter and bromide. Methods 3 and 4 are appropriate for detection of bromoform based on spike recoveries (average of 71 percent) for 132 laboratory reagent spikes analyzed at the USGS NWQL for a separate study, and bromoform has a unique mass spectrum with little possibility of analytical interference (Steve Zaugg, U.S. Geological Survey, oral commun., 2004). The recoveries for spike samples analyzed with the environmental samples during this study also were in the same range (appendix 2). Sample processing for Methods 3 and 4, however, does not include a preservation step that is intended to stop the formation of bromoform in the sample bottle. It is possible; therefore, that bromoform could form in the sample bottle after sample collection and prior to sample analyses. This may result in an over estimation of bromoform concentrations in samples in comparison to a sampling methodology that includes preservation.

A limited sampling was completed to determine if bromoform concentrations from Methods 3 and 4 were similar to concentrations from sample processing and analytical techniques that include a preservation step (USGS laboratory schedule 1307 for volatile organic compounds) (Connor and others, 1998). One finished

Table 7. Basic summary statistics for 91 organic wastewater compounds among all environmental samples analyzed, Minnesota, 2000-02

[*d*-limonene, isophorone, and phenol were removed from this table because the combination of methods 3 and 4 were not appropriate for these compounds. Carbamazepine, diphenhydramine, and the sterols and hormones analyzed by method 5 (with the exception of cholestrerol, and 3-*beta*-coprostanol) are not included because they were not analyzed at all sites. Caffeine, cotinine, sulfamethoxazole, trimethoprim, 3-*beta*-coprostanol, and cholesterol were analyzed by more than one method. --, not applicable; µg/L, micrograms per liter].

Analytical method	Organic wastewater compounds	Method reporting limit (µg/L)	Minimum concentration (µg/L)	Maximum concentration (µg/L)	Number of detections	Frequency of detection (percent)
	Pharmaceuticals					
1	1,7-dimethylxanthine	0.018	0.008	3.29	15	11.5
1	Acetaminophen	0.009	0.004	16	20	15.3
1	Caffeine	0.014	0.0003	14	33	25.2
3,4	Caffeine	0.5	0.041	0.47	19	13.9
1	Codeine	0.024	0.007	0.203	9	6.9
1	Cotinine	0.023	0.0025	1.2	23	17.6
3,4	Cotinine	1.0	0.14	0.22	3	2.2
1	Dehydronifedipine	0.01	0.001	0.012	6	4.6
1	Diltiazem	0.012	0.005	0.146	9	6.9
1	Gemfibrozil	0.015	--	--	0	0
1	Ibuprofen	0.018	0.12	0.71	4	3.1
1	Ranitidine	0.01	0.0082	0.446	5	3.8
1	Salbutamol	0.029	0.002	0.006	2	1.5
1	Warfarin	0.001	--	--	0	0
	Antibiotics					
2	Carbadox	0.05-0.10	--	--	0	0
2	Chlorotetracycline	0.02-0.10	0.11	0.52	2	1.5
2	Ciprofloxacin	0.01	0.01	0.01	2	1.5
2	Doxycycline	0.05-0.1	--	--	0	0
2	Enrofloxacin	0.01-0.02	--	--	0	0
2	Erythromycin-H_2O	0.02-0.05	0.02	0.57	14	10.8
2	Lincomycin	0.01-0.05	0.01	0.37	3	2.3
2	Norfloxacin	0.01-0.02	--	--	0	0
2	Oxytetracycline	0.05	--	--	0	0
2	Roxithromycin	0.01-0.03	--	--	0	0
2	Sarafloxacin	0.01-0.02	--	--	0	0
2	Sulfadimethoxine	0.01-0.05	--	0.11	1	0.8
2	Sulfamerazine	0.02-0.05	--	--	0	0
2	Sulfamethazine	0.01-0.05	0.07	0.16	2	1.5
2	Sulfamethizole	0.05-0.1	--	0.07	1	0.8
1	Sulfamethoxazole	0.023	0.0039	0.342	14	10.7
2	Sulfamethoxazole	0.05-0.1	0.02	0.5	6	3.8
2	Sulfathiazole	0.05-0.1		0.05	1	0.8
2	Tetracycline	0.02-0.05	0.07	0.3	2	1.5
1	Trimethoprim	0.014	0.001	5.58	15	11.5
2	Trimethoprim	0.01-0.03	0.06	0.15	4	2.1
2	Tylosin	0.02-0.05	--	--	0	0
2	Virginiamycin	0.1	--	--	0	0
	Household, industrial, and agricultural use-compounds					
3,4	1,4-dichlorobenzene	0.5	0.12	7.5	10	7.5
3,4	1-methylnaphthalene	0.5	0.076	1.9	7	5.2
3,4	2,6-dimethylnaphthalene	0.5	0.091	1.1	6	4.5
3,4	2-methylnaphthalene	0.5	0.077	2	8	6.0
3,4	3-methyl-1H-indole (skatol)	1.0	0.013	27	18	13.5
3,4	3-tert-butyl-4-hydroxyanisole (BHA)	5.0	2.1	5.1	2	1.5
3,4	4-cumylphenol	1.0	0.6	1.2	3	2.2
3,4	4-*normal*-octylphenol	1.0	0.12	1.6	3	2.2
3,4	4-*tert*-octylphenol	1.0	0.18	2.8	6	4.5
3,4	5-methyl-1H-benzotriazole	2.0	0.45	24	10	7.5
3,4	Acetophenone	0.5	0.21	29	7	5.2

Table 7. Basic summary statistics for 91 organic wastewater compounds among all environmental samples analyzed, Minnesota, 2000-02—Continued

[*d*-limonene, isophorone, and phenol were removed from this table because the combination of methods 3 and 4 were not appropriate for these compounds. Carbamazepine, diphenhydramine, and the sterols and hormones analyzed by method 5 (with the exception of cholestrerol, and 3-*beta*-coprostanol) are not included because they were not analyzed at all sites. Caffeine, cotinine, sulfamethoxazole, trimethoprim, 3-*beta*-coprostanol, and cholesterol were analyzed by more than one method. --, not applicable; µg/L, micrograms per liter].

Analytical method	Organic wastewater compound	Method reporting limit (µg/L)	Minimum concentration (µg/L)	Maximum concentration (µg/L)	Number of detections	Frequency of detection (percent)
3,4	Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	0.5	0.059	5.3	25	18.7
3,4	Anthracene	0.5	0.044	0.33	4	3.0
3,4	Anthraquinone	0.5	0.056	0.81	15	11.2
3,4	Benzo[*a*]pyrene	0.5	--	0.051	1	0.7
3,4	Benzophenone	0.5	0.056	6.2	19	14.2
3,4	Bisphenol-A	1.0	0.084	26	24	17.9
3,4	Bromacil	0.5	0.02	1.4	6	4.5
3,4	Bromoform	0.5	0.13	74	31	22.4
3,4	Camphor	0.5	0.14	98	7	5.2
3,4	Carbaryl	1	--	--	0	0
3,4	Carbazole	0.5	0.031	0.72	6	4.5
3,4	Chlorpyrifos	0.5	--	--	0	0
3,4	Diazinon	0.5	0.025	0.083	5	3.7
3,4	Dichlorvos	1.0	--	--	0	0
3,4	Fluoranthene	0.5	0.057	0.32	9	6.6
3,4	Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)	0.5	0.049	1.5	13	9.7
3,4	Indole	0.5	0.012	1.4	8	6.0
3,4	Isoborneol	0.5	1.2	44	2	1.5
3,4	Isopropylbenzene (cumene)	0.5	0.056	2.2	5	3.7
3,4	Isoquinoline	0.5	--	--	0	0
3,4	Menthol	0.5	0.071	96	9	6.7
3,4	Metalaxyl	0.5	--	--	0	0
3,4	Methyl salicylate	0.5	0.013	3.2	6	4.5
3,4	Metolachlor	0.5	0.008	1.3	49	35.8
3,4	N,N-diethyl-*meta*-toluamide (DEET)	0.5	0.027	47	32	23.9
3,4	Naphthalene	0.5	0.093	10	8	6.0
3,4	Nonylphenol diethoxylate (NP2EO)	5.0	0.52	42	12	9.0
3,4	Octylphenol diethoxylate (OP2EO)	1.0	0.81	8.4	2	1.5
3,4	Otylphenol monoethoxylate (OP1EO)	1.0	0.4	7	3	2.2
3,4	*para*-cresol	1.0	0.049	1000	13	9.7
3,4	*para*-nonylphenol (NP)	5.0	0.76	56	15	11.2
3,4	Pentachlorophenol	2.0	0.018	0.62	14	10.4
3,4	Phenanthrene	0.5	0.04	0.38	5	3.7
3,4	Prometon	0.5	0.26	2	2	1.5
3,4	Pyrene	0.5	0.04	0.082	7	5.2
3,4	Tetrachloroethylene	0.5	0.055	17	10	7.5
3,4	Tri(2-butoxyethyl)phosphate	0.5	0.11	5.3	20	17.2
3,4	Tri(2-chloroethyl)phosphate	0.5	0.053	9.2	27	20.1
3,4	Tri(dichlorisopropyl)phosphate	0.5	0.053	2.5	20	14.9
3,4	Tributyl phosphate	0.5	0.058	13	18	13.4
3,4	Triclosan	1.0	0.088	4.3	10	8.2
3,4	Triethyl citrate (ethyl-citrate)	0.5	0.076	2.9	16	11.9
3,4	Triphenyl phosphate	0.5	0.051	0.24	14	10.4
	Sterols and Hormones					
3,4	3-*beta*-coprostanol	2.0	0.32	81	18	13.4
5	3-*beta*-coprostanol	0.005	0.001	2.607	18	13.4
3,4	*beta*-sitosterol	2.0	0.55	36	26	19.4
3,4	*beta*-stigmastanol	2.0	0.79	5.7	8	6.0
3,4	Cholesterol	2.0	0.48	130	35	26.1
5	Cholesterol	0.005	0.004	3.35	82	92.0

water sample from Site 65 was split into three samples. One sample was filtered and analyzed for Method 3 using the methodology described in this report, one sample was filtered, acidified with ascorbic acid, and analyzed using Method 3; and the remaining sample was not filtered, was acidified with ascorbic acid, and analyzed with the USGS laboratory schedule 1307 for volatile organic compounds. The results from this limited comparison show that bromoform concentrations reported for the filtered, unacidified, Method 3 samples, were approximately 100 times greater than those reported for either the acidified Method 3 sample or the schedule 1307 sample. Bromoform concentrations reported for Methods 3 and 4; therefore, may be overestimated in some samples (particularly wastewater effluent and finished drinking water samples) based on this limited comparison.

DATA EVALUATION

Evaluation of data includes several procedures to ensure consistent comparisons among samples. Although previously described, these procedures are consolidated and discussed in this section for clarity. Field sample concentrations for OWCs analyzed by Methods 1, 3, and 4 that were less than 10 times the concentrations in the corresponding laboratory reagent blanks were censored (reported as less than the MRL) to ensure that environmental concentrations did not reflect laboratory contamination. Data from Methods 2 and 5 were quality assured in the laboratory and censored prior to distribution. A large proportion of the OWC concentrations are reported as estimated values. Each laboratory had stringent and conservative procedures for qualitative identification of the compounds; therefore, all OWC detections (estimated and non estimated) were used in the analyses in this report. There is less certainty in the OWC concentrations generated by research methods because the analyses are in development and there are not enough quality-assurance data in some cases to determine concentrations within acceptable confidence limits.

Evaluation showed that detection consistency between Methods 3 and 4 generally were similar for most of the OWCs (with the exceptions of *d*-limonene, isophorone, and phenol); therefore, samples analyzed by both methods were combined for comparison. In the case where a sample was analyzed by both methods, Method 3 data were used. *d*-Limonene, isophorone, and phenol were not used for any comparisons because their detection frequency differed between Methods 3 and 4, and; therefore, could produce inconsistent results among samples.

Carbamazepine and diphenhydramine (Method 1), and the sterols and hormones (Method 5) were not used for comparisons because they were not analyzed at all sites. One laboratory method was selected for OWCs analyzed for more than one method. Trimethoprim, sulfamethoxazole, caffeine, and cotinine analyzed by Method 1; and cholesterol and 3-*beta*-coprostanol analyzed by Methods 3 and 4 were used.

In summary, USGS laboratories analyzed 114 OWCs for this study. Three HIAs (*d*-limonene, isophorone, and phenol), 2 pharmaceuticals (carbamazepine and diphenhydramine), and 18 sterols and hormones analyzed using Method 5 were removed from comparisons among sites or site classifications. This results in a total of 91 OWCs that are used for comparisons among sites and site classifications in the remainder of this report.

HYDROLOGIC SETTING AND BASIC WATER-QUALITY PARAMETERS

Differences in the hydrologic conditions and basic water-quality parameters among sites may contribute to the presence of OWCs and their fate and transport. A more focused study would be required to determine how these factors would influence OWC detections and concentrations.

Sampling occurred during four periods representing a variety of hydrologic conditions. Two of the sampling periods were during fall and winter baseflow when ground water was the primary source of water to the streams sampled. The remaining two sampling periods were during spring snowmelt and summer storm runoff when surface runoff was the primary source of water to streams sampled. During this reconnaissance study, no attempt was made to collect samples at the same place on the streamflow hydrograph (rising limb, peak flow, declining limb), which may influence detections and concentrations.

Basic water-quality parameters of specific conductance, pH, water temperature, and dissolved oxygen varied by site and period sampled. These parameters vary diurnally and seasonally due to weather, groundwater interactions, and internal factors such as microbial

and algal production. Differences in basic water-quality parameters among sites provide useful information about factors that could contribute to differences in presence and distribution of OWCs. For example, differences in pH, temperature, and dissolved oxygen, may indicate differences in microbial or algal productivity, which may contribute to different rates of OWC metabolism.

PRESENCE AND DISTRIBUTION OF ORGANIC WASTEWATER COMPOUNDS AMONG ALL SITES

The 74 OWCs (49 HIAs, 10 pharmaceuticals, 11 antibiotics, and 4 sterols or hormones) detected during this study (table 7) represent a wide variety of uses. Samples generally included a mixture of compounds (average of 6 OWCs per sample) and 90 percent of the samples had at least one OWC detected. The 10 most frequently detected OWCs among all samples were metolachlor (agricultural use-herbicide); cholesterol (sterol primarily associated with animal fecal matter); caffeine (stimulant in coffee, soft-drinks, and nonprescription medications), N,N-diethyl-*meta*-toluamide (DEET) (topical insect repellant); bromoform (by-product of waste- and drinking-water disinfection); tri(2-chloroethyl)phosphate (flame-retardant and plasticizer); *beta*-sitosterol (plant sterol and a known endocrine disruptor); acetyl-hexamethyl-tetrahydro-naphthalene (AHTN) (synthetic musk fragrance widely used in personal care products); bisphenol-A (plastic component used in the manufacture of polycarbonate resins and a known endocrine disruptor); and cotinine (metabolite of nicotine). With respect to individual classes of OWCs, caffeine, cotinine, and acetaminophen, were the three most frequently detected pharmaceuticals. Trimethoprim, an erythromycin metabolite (erythromycin H_20), and sulfamethoxazole were the most frequently detected antibiotics. Cholesterol, *beta*-sitosterol , and 3-*beta*-coprostanol were the most frequently detected sterols.

Concentrations of detected OWCs generally were less than 3 µg/L. Nearly 75 percent of the detections had estimated concentrations below MRLs. Concentrations of 3-*beta*-coprostanol, acetophenone, BHA, bromoform, caffeine, camphor, cholesterol, isoborneol, menthol, nonylphenol diethoxylate (NP2EO), octylphenol diethoxylate (OP2EO), *para*-cresol, and *para*-nonylphenol (NP) generally were above the MRL.

PRESENCE AND DISTRIBUTION OF ORGANIC WASTEWATER COMPOUNDS FOR SPECIFIC SITE CLASSIFICATIONS

WASTEWATER

Domestic WWTP influent and effluent, landfill leachate, and water underlying feedlot lagoons were selected as potential wastewater sources for this study. A total of 67 of the 91 OWCs were detected among wastewater samples. Wastewater influent and effluent, and landfill leachate had the greatest number of OWCs detected and water underlying feedlot lagoons had the least number detected. There were differences within site classifications and temporal variability among different sampling periods in terms of the number and the types of OWCs detected.

Wastewater Treatment Plants

WWTP samples were complex mixtures of OWCs likely due to the diversity of incoming domestic and industrial waste sources and treatment procedures. Most of the OWCs analyzed (63 of the 91 OWCs) were detected among all WWTP samples, averaging 27.1 OWCs per sample. Compounds detected included: 44 HIAs, 9 pharmaceuticals, 6 antibiotics, and 4 sterols. Among all WWTP samples, the untreated influent sample at Site 1 had the greatest number of OWCs detected, and the total number of OWCs detected in WWTP effluent was greatest at Site 5 (fig. 4). The most frequently detected OWCs in wastewater effluent samples included AHTN, benzophenone, cholesterol, erythromycin H_20, hexahydrohexamethyl-cyclopentabenzopyran (HHCB), NP2EO, tri(2-chloroethyl)phosphate, tributyl phosphate, tri(dichloroisopropyl)phosphate, and triethyl citrate. The prevalence of these OWCs in WWTP effluent is expected because they are widely used in products such as fragrances, antibiotics, plasticizers, flame retardants, and detergents, or are plant or animal sterols. Similar types of OWCs in WWTP effluent have been reported by Daughton and Ternes (1999), Barber and others (2000), Kummerer (2001), Wilkison and others (2002), and Buerge and others (2003).

The types of HIAs detected varied among WWTPs. For example, the WWTP effluent sample from Site 5 had

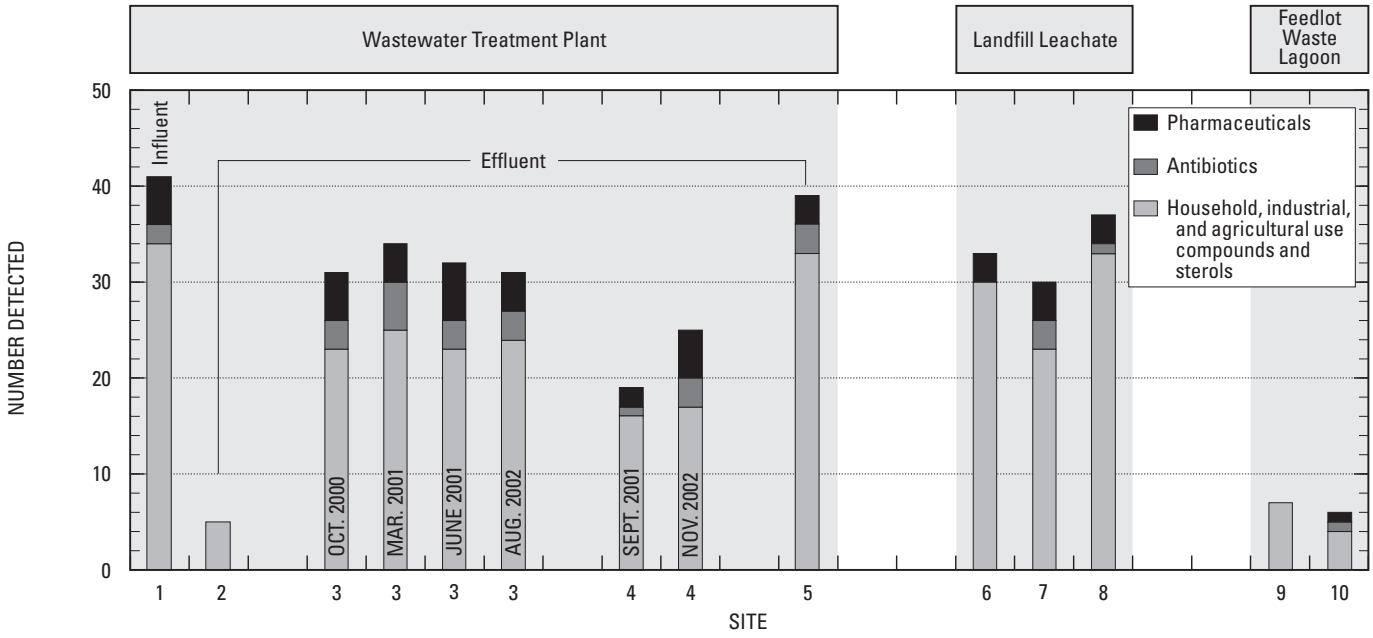

Figure 4. Organic wastewater compounds detected in wastewater treatment plant, landfill leachate, and feedlot waste lagoon samples, Minnesota, 2000-02. [Site identification numbers can be found in table 1 and figures 1 an 2.]

greater detections of polyaromatic hydrocarbons (PAHs) and nonionic detergent metabolites than other WWTPs. In contrast, the number of pharmaceuticals and antibiotics detected were similar among all WWTP samples with the exception of Site 2, where none were detected. With the exception of Site 2, there were 5 pharmaceuticals or antibiotics that were common to all WWTP effluent samples (caffeine, cotinine, diltiazem, erythromycin H_2O, and trimethoprim). Although acetaminophen, ibuprofen, and ranitidine are nonprescription pharmaceuticals and have high usage rates, they were not frequently detected in WWTP effluent, potentially due to degradation during treatment (Stumpf and others 1996; Ternes, 1998) or absence in the influent to the WWTP.

There was temporal variability in the number of OWCs detected in samples collected from Sites 3 and 4, with approximately 50 percent of the OWCs detected common to all sampling periods at any particular WWTP. For example, the number of OWCs ranged from 31-34 at Site 3 during four sampling events, and ranged from 19-25 at Site 4 during two sampling periods (fig. 4). Temporal changes in WWTP influent sources or treatment techniques may be the reason for this.

Difference in the types of compounds detected among WWTPs, and among multiple sampling periods at one WWTP may be due to differences in influent sources or treatment techniques. These spatial and temporal differences emphasize the importance of routine sampling to fully characterize the variability in chemical composition of WWTP effluent. This variability was likely not captured during this reconnaissance study.

Both the influent (Site 1) and effluent (Site 2) were sampled from the East Grand Forks WWTP, allowing a cursory investigation of OWC removal. The untreated influent water at Site 1 had 41 OWCs. In contrast, the treated water at Site 2 in the settling pond outflow (after the 6- month settling/treatment period) had 5 OWC detections. It was not possible to fully determine if treatment techniques influenced the types and concentrations of OWCs detected because of the 6-month settling/treatment period. The difference between OWC detections in influent and effluent water could be because many OWCs likely degraded during processing, partitioned into the sediment and biota in the treatment pond, or volatized.

There were 11 endocrine disrupting compounds (EDCs) detected among WWTP samples including 4-cumylphenol, 4-*normal*-octylphenol, 4-*tert*-octylphenol, AHTN, *beta*-sitosterol, bisphenol-A, diazinon, NP2EO, OP1EO, OP2EO, and NP. The number of EDCs detected in WWTP effluent among all sampling periods was greatest at Site 3 (9 EDCs) and Site 5 (9 EDCs).

Landfill Leachate

A total of 46 OWCs were detected among all three landfill leachate samples averaging 33.7 OWCs per

sample. OWCs detected included 35 HIAs, 4 pharmaceuticals (acetaminophen, caffeine, cotinine, ibuprofen), 3 antibiotics (chlorotetracycline, lincomycin, and trimethoprim), and 4 sterols (3-*beta*-coprostanol, *beta*-sitosterol, *beta*-stigmastanol, and cholesterol). The total number of OWC detections in leachate was greatest at Site 8, the industrial landfill (fig. 4).

A wide variety of OWCs were detected in landfill leachate including PAHs, fragrances, plastic components, flame retardants, and solvents. About one-half the OWCs detected among all landfill leachate samples were common among all three leachate samples, and 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, 4-*tert*-octylphenol, acetaminophen, acetophenone, benzophenone, bisphenol-A, caffeine, camphor, cotinine, isopropyl benzene, naphthalene, DEET, *para*-cresol, skatol, NP, tri(2-butoxyethyl)phosphate, tri(2-chloroethyl)phosphate, tributyl phosphate, tri(dichloro isopropyl)phosphate, and triethyl citrate were detected in all landfill leachate samples. The high number and variability in types of OWCs detected among landfill sites is likely due to diversity of waste that was landfilled and the spatial and temporal variability in waste types throughout a landfill. The composition of a leachate sample may depend on the day and the areas sampled. The presence of pharmaceuticals in the industrial landfill leachate was unexpected as domestic waste was not accepted at that location. Leachate from Sites 6, 7, and occasionally Site 8 is transferred to the Metropolitan WWTP (Site 3) for treatment. The removal efficiency of OWCs in WWTP is only documented for selected OWCs (Stumpf and others, 1996).

The number of OWCs detected per landfill leachate sample was similar to WWTP influent and effluent samples (fig. 4). Generally, there were more PAHs detected in landfill leachate than in other wastewater samples. PAHs are formed during incomplete combustion of organic materials such as coal, oil, and wood. PAHs are lipophilic (bind to organic matter) and may be prevalent in landfill leachate because there are relatively greater inputs of PAHs to landfills or slow degradation in the anaerobic conditions in landfills.

There were 7 EDCs found in landfill leachate samples: 4-cumylphenol, 4-*tert*-octylphenol, *beta*-sitosterol, BHA, bisphenol-A, OP1EO, and NP. The number of EDCs detected varied from 4-7 among landfills, and Site 8 (the industrial landfill) had the greatest number of EDCs detected.

Feedlot Lagoons

There were 11 OWCs (9 HIAs; 1 pharmaceutical (diltazem); and 1 antibiotic (lincomycin)) detected in the water underlying the two feedlot lagoons (Sites 9 and 10). The number of OWCs was similar between the two sites (fig. 4). Bisphenol-A, skatol and NP were detected at both sites. Camphor, indole, isopropyl benzene, *para*-cresol, and triphenyl phosphate were unique to Site 9, and diltiazem, lincomycin, and metolachlor were unique to Site 10.

While the sources of these OWCs are unknown, bisphenol-A, NP, and triphenyl phosphate could have leached from the polyvinyl chloride (PVC) pipes or liner in the feedlot lagoon drainage collection system. NP is a component in cleaning agents that may also be used in feedlot operations. Metolachlor (herbicide) could originate from surface runoff or atmospheric deposition into lagoons and subsequent leaching through the drainage collection system. The presence of lincomycin (antibiotic used for animal treatment), and indole and skatol (chemicals produced by bacteria in animal intestines) may be from the animal waste in the lagoon. The presence of diltazem (human antihypertensive medication), isopropyl benzene (solvent) and *para*-cresol (disinfectant) cannot be explained.

There were fewer OWCs and lower concentrations in feedlot lagoon samples than other identified wastewater sources. It was not possible to determine if the OWCs were removed as they passed through the compacted clay lining of the waste lagoon, or were not initially present in the lagoon. Each feedlot lagoon had two EDCs detected (bisphenol-A and NP).

SURFACE WATER

There were 56 OWCs detected among all surface-water samples (36 HIAs, 9 pharmaceuticals, 7 antibiotics, and 4 sterols), averaging 6 OWCs per sample. In descending order of detection frequency, the most frequently detected OWCs among all surface-water samples were metolachlor, caffeine, cholesterol, DEET, *beta*-sitosterol, AHTN, and acetaminophen. The total number of OWCs detected varied from 0 at the reference site at Ek Lake in Voyageurs National Park (Site 15) to 28 at Jewitt's Creek near Litchfield (Site 21), which is located downstream from a WWTP effluent discharge.

Table 8. Number of organic-wastewater compounds detected at surface-water sites, Minnesota 2000-02

[OWC, organic wastewater compound; HIA, household, industrial, and agricultural use compounds; --, not analyzed; WWTP, wastewater treatment plant; SW, sample taken from surface water site not directly influenced by WWTP discharge; SDW, sample taken from a surface water site directly downstream of a WWTP discharge. Sites 23, 27, and 30 were analyzed for USGS laboratory Methods 3 and 4 only].

Site identifier (fig. 1 or 2)	Site name	Site classification	Sample date (mm/dd/yy)	Pharmaceutical detections	Antibiotic detections	HIA detections	Total OWC detections
	Red River of the North Basin						
11	Red River of the North above Fargo, N.Dak.	SW	10/19/00	1	0	0	1
11	Red River of the North above Fargo, N.Dak.	SW	04/11/01	1	0	7	8
11	Red River of the North above Fargo, N.Dak.	SW	07/12/01	0	0	7	7
12	Red River of the North below Fargo, N.Dak.	SDW	10/18/00	0	2	7	9
12	Red River of the North below Fargo, N.Dak.	SDW	04/11/01	1	0	1	2
12	Red River of the North below Fargo, N.Dak.	SDW	07/12/01	0	0	2	2
13	Red Lake River at State Hwy 2220 above East Grand Forks	SW	10/23/00	0	0	1	1
13	Red Lake River at State Hwy 220 above East Grand Forks	SW	04/12/01	0	0	1	1
13	Red Lake River at State Hwy 220 above East Grand Forks	SW	07/09/01	--	1	0	1
14	Red River of the North below WWTP at East Grand Forks	SDW	10/25/00	2	0	3	5
14	Red River of the North below WWTP at East Grand Forks	SDW	07/10/01	0	0	2	2
	Rainy and Lake Superior Basins						
15	Ek Lake near International Falls	SW	09/20/01	0	0	0	0
16	Rainy River below International Falls	SDW	09/05/01	1	0	3	4
17	Lake Superior in St. Louis Bay at Duluth	SDW	09/05/01	4	0	9	13
	Mississippi River Basin						
18	Mississippi River above Sauk River near Sauk Rapids	SW	10/17/00	0	0	2	2
18	Mississippi River above Sauk River near Sauk Rapids	SW	04/16/01	0	0	1	1
18	Mississippi River above Sauk River near Sauk Rapids	SW	06/27/01	0	0	0	0
19	Sauk River near St. Cloud	SW	10/16/00	2	0	5	7
19	Sauk River near St. Cloud	SW	04/10/01	0	0	4	4
19	Sauk River near St. Cloud	SW	04/27/01	--	--	3	3
19	Sauk River near St. Cloud	SW	06/26/01	0	0	1	1
20	Mississippi River above Clearwater River near Clearwater	SW	10/17/00	2	0	0	2
20	Mississippi River above Clearwater River near Clearwater	SW	04/17/01	0	0	2	2
20	Mississippi River above Clearwater River near Clearwater	SW	06/26/01	0	0	1	1
21	Jewitt's Creek near Litchfield	SDW	09/06/01	5	2	21	28
22	Crow River below State Hwy 101 at Dayton	SW	10/11/00	3	1	3	7
22	Crow River below State Hwy 101 at Dayton	SW	04/09/01	1	0	4	5
22	Crow River below State Hwy 101 at Dayton	SW	06/21/01	0	0	1	1
23	Elm Creek near Champlin	SW	04/27/01	--	--	6	6
24	Mississippi River near Anoka	SW	10/03/00	1	0	3	4
24	Mississippi River near Anoka	SW	04/19/01	0	0	1	1
24	Mississippi River near Anoka	SW	06/22/01	0	0	2	2
25	Vadnais Lake at Pumping Station in Vadnais Heights	SW	10/10/00	0	0	2	2

Table 8. Number of organic-wastewater compounds detected at surface-water sites, Minnesota 2000-02—Continued

[OWC, organic wastewater compound; HIA, household, industrial, and agricultural use compounds; --, not analyzed; WWTP, wastewater treatment plant; SW, sample taken from surface water site not directly influenced by WWTP discharge; SDW, sample taken from a surface water site directly downstream of a WWTP discharge. Sites 23, 27, and 30 were analyzed for USGS laboratory Methods 3 and 4 only]."

Site identifier (fig. 1 or 2)	Site name	Site classification	Sample date (mm/dd/yy)	Pharmaceutical detections	Antibiotic detections	HIA detections	Total OWC detections
25	Vadnais Lake at Pumping Station in Vadnais Heights	SW	04/20/01	1	0	0	1
25	Vadnais Lake at Pumping Station in Vadnais Heights	SW	06/19/01	0	0	0	0
26	Rice Creek at County Road 1 in Fridley	SW	10/04/00	0	0	6	6
26	Rice Creek at County Road 1 in Fridley	SW	04/06/01	3	0	2	5
26	Rice Creek at County Road 1 in Fridley	SW	06/15/01	2	0	5	7
27	Shingle Creek at Queen Ave. in Minneapolis	SW	05/02/01	--	--	11	11
28	Redwood River below WWTP near Marshall	SDW	09/10/01	2	2	2	6
29	Blue Earth River near Rapidan	SW	10/12/00	0	0	2	2
30	Little Cobb River near Beauford	SW	05/04/01	--	--	3	3
31	Blue Earth River at County Road 90 near Mankato	SW	04/03/01	1	0	2	3
31	Blue Earth River at County Road 90 near Mankato	SW	07/02/01	0	0	4	4
32	Minnesota River at Mankato	SDW	10/13/00	0	0	2	2
32	Minnesota River at Mankato	SDW	04/04/01	1	0	3	4
32	Minnesota River at Mankato	SDW	07/02/01	0	0	--	0
33	Mississippi River at Ninninger	SDW	08/28/02	1	1	2	4
34	Mississippi River below Lock and Dam 2 at Hastings	SDW	10/02/00	1	2	6	9
34	Mississippi River below Lock and Dam 2 at Hastings	SDW	04/19/01	1	0	1	2
34	Mississippi River below Lock and Dam 2 at Hastings	SDW	06/25/01	1	0	6	7
35	St. Croix River below Stillwater	SDW	09/18/01	1	0	0	1
36	Vermillion River below Empire WWTP near Empire	SDW	09/17/01	4	3	10	17
37	Bear Creek Tributary near Chester	SW	08/27/02	0	1	2	3
38	South Fork Zumbro River at Rochester	SW	11/05/02	6	2	11	19
39	South Fork Zumbro River near Rochester	SDW	09/20/01	1	1	10	12
39	South Fork Zumbro River near Rochester	SDW	11/04/02	9	3	12	24
40	South Fork Zumbro River below WWTP near Rochester	SDW	11/05/02	9	3	8	20
41	Cedar River below WWTP at Austin	SDW	09/19/01	4	1	9	14
	Des Moines River Basin						
42	Okabena Creek near Worthington	SDW	09/10/01	3	0	14	17

The number and types of OWCs detected varied among sites (table 8). The number of OWCs detected and concentrations generally were greater in small streams (average of 8.9 OWCs) located within 1 mile downstream from WWTP effluent discharges (Sites 21, 28, 36, and 39-42) than at other surface-water sites (average of 3.6 OWCs) indicating that WWTP effluent may be a source of OWCs to surface water. There also were a greater number of OWCs detected at Site 17 in St. Louis Bay of Lake Superior (similar number of detections to small streams that are effluent dominated) near the WWTP effluent discharge from Site 5. Large river sites located downstream from WWTP effluent discharges (Sites 12, 14, 16, and 32-35) generally had fewer OWCs detected than small stream sites located downstream from WWTP effluent discharges. The greater number of OWCs in the small streams may be because effluent comprised a greater proportion of stream flow than large rivers.

OWCs that were frequently detected in WWTP effluent such as the animal sterol (3-*beta*-coprostanol), fragrances (AHTN and HHCB), flame retardants and plastic components (tri(2-butoxyethyl)phosphate, tri(2-chloroethyl)phosphate, tributyl phosphate, and tri(dich loroisopropyl)phosphate), and the pharmaceuticals or antibiotics (caffeine, cotinine, erythromycin H_2O, sulfamethoxazole, and trimethoprim) also were detected more frequently in streams directly downstream than upstream from WWTP effluent discharge. Some OWCs, such as *beta*-sitosterol, cholesterol, metolachlor, DEET (topical insect repellant), and skatol, were detected in streams directly and not directly downstream from WWTP effluent discharge suggesting that these OWCs may persist in streams from upstream WWTP sources or there may be other sources of these OWCs in addition to WWTP effluent. Cholesterol and *beta*-sitosterol are animal and plant sterols whose sources could be aquatic or terrestrial biota. Metolachlor (agricultural herbicide) is likely from runoff or atmospheric deposition, and DEET may enter streams directly through removal from treated skin during swimming.

OWC types and number of detections varied temporally at sites that were sampled more than once. For example, there were 2, 7, and 9 OWCs detected at Site 34 over three sampling periods (table 8). These temporal differences likely are influenced by upstream discharges, surface runoff, streamflow, water temperature, chemical characteristics, degradation rates, and biological metabolism and uptake.

Selected OWCs were detected more frequently during specific seasonal and hydrologic conditions. For example, metolachlor was detected more frequently during the spring or summer runoff periods (Sites 11, 12, 14, 18, 19, 20, 22, 24, 26, and 34), likely from runoff from agricultural land use. DEET was detected more frequently in fall or summer (Sites 11, 19, 24, 26, 31, and 34) possibly indicating increased human use during that period. *beta*-Sitosterol was more prevalent in the fall (Sites 12, 22, 25, 26, 31, and 32), which may result from senescing plants and algae or changes in the input or discharges of sterols from WWTPs. While patterns in detections were observed, this study did not fully characterize the sources and variability in OWC detections and concentrations due to limited temporal and spatial sampling.

A longitudinal study of the Zumbro River near Rochester (Sites 38-40) was useful for understanding the presence and distribution of OWCs upstream and downstream from WWTP effluent discharges and their fate in surface water. A series of sites, including upstream from an incoming WWTP effluent discharge (Site 38), the WWTP effluent (Site 4), 250 ft downstream from the effluent discharge (Site 39), and one-mile downstream from the effluent discharge (Site 40) were sampled. The total number of OWCs detected was lowest at Site 38 (19 OWCs), greater at Site 39 (24 OWCs), and reduced at Site 40 (20 OWCs). The relatively large number of OWCs detected upstream from WWTP effluent discharge (Site 38) was unexpected and may indicate upstream sources of OWCs in addition to WWTP effluent. There were several OWCs not detected in the WWTP effluent that were detected at Sites 39 and 40 (1,7-dimethylxanthine, acetaminophen, menthol, metolachlor, and salbutamol), and indicating potential sources other than the WWTP effluent.

Small streams (Sites 23, 26, and 27) draining urban land in the Minneapolis and St. Paul metropolitan area had a relatively large number of OWC detections considering that no direct source of WWTP effluent enters these streams directly upstream from the sampling location. The number of OWCs detected was similar to some stream sites located downstream from WWTP effluent even though Sites 23 and 27 were only analyzed for Methods 3 and 4, and; therefore, the number of OWCs may have been greater if analyzed using all methods. Potential sources of these OWCs in urban streams may be from individual sewage treatment systems, accidental discharge from sewer lines, or direct inputs through runoff or atmospheric deposition.

OWC detection frequency from this study for sites downstream from WWTPs compared closely to results by Kolpin and others (2002) for 139 streams in the United States located primarily downstream from WWTPs. The frequency of detection for OWCs was similar between the two studies with a few exceptions: 5-methyl-1H-benzotriazole, bisphenol-A, cholesterol, DEET, diazinon, fluoranthene, naphthalene, NP2EO, NP, pyrene, TCE, and triclosan, were more frequently detected by Kolpin and others (2002). This comparison indicates that there are similarities in the Minnesota and National results for surface waters influenced by wastewaters. The site types sampled, and analytical procedures, however, heavily influenced OWC detection frequencies. A more thorough analysis; therefore, would be required to place Minnesota results in context with National studies.

There were from one to five EDCs detected per surface-water site. Among all sites seven EDCs (AHTN, *beta*-sitosterol, bisphenol-A, diazinon, 4-*normal*-octylphenol, NP, and NP2EO) were detected. Site 21 had the greatest number and concentrations of EDCs among all surface-water sites.

GROUND WATER

For all ground-water samples, 31 OWCs (28 HIAs, 1 pharmaceutical (caffeine), and 2 antibiotics (sulfamethoxazole, and sulfamethazine)) were detected with an average of 3 OWCs detected per sample. There were few OWCs detected in the individual wells (0-5 OWCs) except those wells (Sites 51 and 52) underlying a waste dump (8 and 21 OWCs, respectively) (fig. 5).

The types of OWCs detected differed among sites. Components in sunscreen or topical linement products, fragrances, plasticizers, and pesticides were detected in municipal supply well (Site 43) samples (table 9). A total of 5 OWCs were detected at Site 43 and OWCs were detected twice during four samplings. The relatively greater number of OWCs detected at Site 43 in the March 2001 is unusual compared to the other sampling periods where none or one OWC was detected.

Three OWCs were detected in the mixed urban industrial/residential/commercial wells (Sites 44-47). Among those detected were industrial compounds such as solvents (TCE), nonionic-detergent metabolites (NP2EO) and flame retardants (tri(2-chloroethyl)phosphate). TCE concentrations at Site 47 (17 µg/L) exceeded the MCL of 5 µg/L and the HAL of 10 µg/L. Only two compounds; the antibiotic (sulfamethoxazole) and DEET, were detected in wells located in urban residential-unsewered areas (Sites 48-50).

A wide variety of OWCs were detected in ground-water samples underlying a waste dump (Sites 51 and 52). OWCs detected include: caffeine, insect repellants,

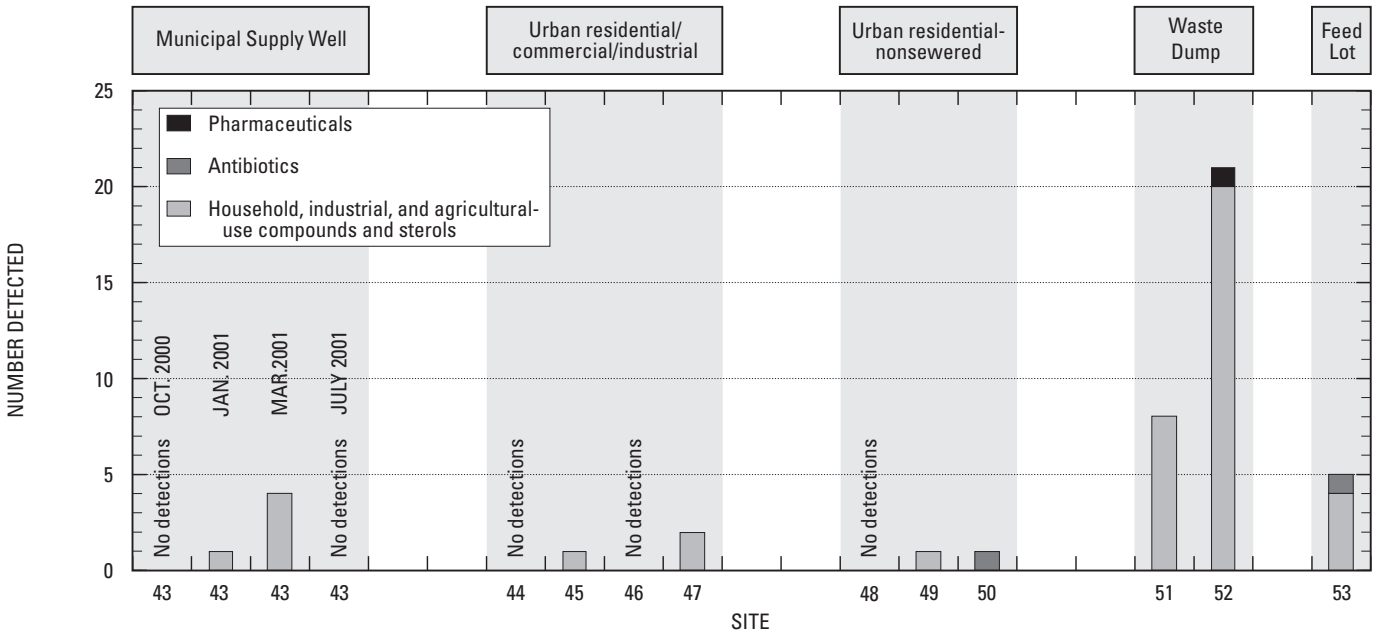

Figure 5. Organic wastewater compounds deteced in ground-water samples, Minnesota, 2000-02. [Site identification numbers can be found in table 1 and figures 1 an 2.]

Table 9. Organic wastewater compounds detected at Moorhead Drinking Water Facility and surface- and ground-water sites used as sources of drinking water

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydrologic condition	Source Waters		Moorhead Drinking Water Facility at Moorhead, Minn	
	Red River of the North above Fargo, N. Dak. (Site 11)	Moorhead City Well Number 9 (Site 43)	Intake Water (Site 54)	Finished Water (Site 55)
Compounds detected in fall 2000 baseflow	October 19, 2000 1,7-dimethylxanthine	October 18, 2000 none detected	October 18, 2000 none detected	October 18, 2000 bromoform
Compounds detected in winter 2001 baseflow	not sampled	January 23, 2001[1] benzophenone	January 23, 2001 benzophenone, bisphenol-A, cholesterol	January 23,2001 bromoform, methyl salicylate
Compounds detected in spring 2001 runoff	April 11, 2001 Acetyl-hexamethyl-tetrahydro-naphthalene(AHTN), *beta*-sitosterol, *beta*-stigmastanol, bisphenol-A, methyl salicylate, metolachlor, pentachlorophenol, *acetaminophen*	April 11, 2001[1] Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), bisphenol-A, methyl salicylate, metolachlor	April 11, 2001 *acetaminophen*, pentachlorophenol	April 11, 2001 bromoform
Compounds detected in summer 2001 storm runoff	July 12, 2001 Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), cholesterol, menthol, metolachlor, N,N-diethyl-*meta*-toluamide (DEET), *para*-nonylphenol (NP), triclosan	July 11, 2001 none detected	July 11, 2001 N,N-diethyl-*meta*-toluamide (DEET), metolachlor	July 11, 2001 Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), bromoform, *para*-nonylphenol (NP)

[1] Well not used as a source of drinking water on this date.

nonionic detergent metabolites, PAHs, and plastic components. Six of the eight compounds detected at Site 51 were detected at Site 52, but there were a greater number of OWCs and greater concentrations at Site 52 than Site 51. This may be explained by variability in the waste material and differences in locations and depths of the two wells. The dump is listed on the Minnesota Pollution Control Agency's State Superfund list of priorities, and various types of refuse were disposed at the site (Minnesota Pollution Control Agency, 2001; Minnesota Department of Health, 2003).

There were relatively greater number of OWCs detected from the well located in the feedlot (Site 53) than most other ground-water sites with the exception of Sites 51 and 52. An anticorrosive compound (5-methyl-1H-benzotriazole), an ingredient in liniments (camphor), a compound found in the intestines of animals (indole), a disinfectant (*para*-cresol), and an antibiotic used for animals (sulfamethazine) were detected in ground water underlying the feedlot (Site 53).

While the types of OWCs generally reflected the land use overlying monitoring wells, this study sampled a small number of wells and therefore the variability of specific OWCs in Minnesota ground-water resources is unknown. There were four EDCs detected in ground-water samples: AHTN (Site 43), bisphenol-A (Sites 43, 51, and 52), OP1EO (Site 51), and NP2EO (Site 47).

DRINKING WATER

The intakes and finished water from six drinking water facilities were sampled for this study (tables 9-14). Within the Red River of the North Basin, Moorhead, and East Grand Forks DWFs were sampled. Within the Upper Mississippi River Basin, the St. Cloud, St. Paul,

Table 10. Organic wastewater compounds detected at East Grand Forks Drinking Water Facility and surface water sites used as sources of drinking water

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydrologic condition	Selected Source Water	East Grand Forks Drinking Water Facility at East Grand Forks, Minn.	
	Red Lake River at County Rd. 220 above East Grand Forks, Minn. (Site 13)	Intake Water (Site 56)	Finished Water (Site 57)
Compounds detected in fall 2000 baseflow	October 23, 2000 triphenyl phosphate	October 24, 2000 none detected	October 24, 2000 bromoform
Compounds detected in winter 2001 baseflow	not sampled	January 24, 2001 tributyl phosphate, triphenyl phosphate	January 24, 2001 bromoform, benzophenone, methyl salicylate
Compounds detected in spring 2001 runoff	April 12, 2001 3-methyl-1H-indole (skatol)	April 12, 2001 bromacil, 3-methyl-1H-indole (skatol)	April 12, 2001 bromoform
Compounds detected in summer 2001 storm runoff	July 9, 2001 *sulfadimethoxine*; sample not analyzed by method 1	no pharmacuticals or antibiotics detected; sample not analyzed by methods 3 and 4	July 10, 2001 bromoform

Minneapolis, and Mankato DWFs were sampled. Surface and ground waters that serve as source waters for selected DWFs also were sampled to provide information regarding potential sources of OWCs that may be drawn into facility intakes. Among the source waters for the drinking water facilities, smaller streams tended to have greater numbers of OWCs detected than large rivers, lakes, or ground-water sources.

There were 26 OWCs detected in intake and 13 OWCs detected in finished-water samples (tables 9-14). In general, few OWCs (0-9 OWCs) were detected in each intake and finished DWF water sample, averaging 2 OWCs per sample. Differences in OWC detections among DWFs likely were due to differences in source waters, treatment processes, and sample timing. Minneapolis DWF had the greatest number of OWCs (12 OWCs) detected in intake samples while the Mankato DWF had the greatest number of OWCs detected in finished water samples (8 OWCs) during all sampling periods.

A wide variety of OWCs were detected in either intake or finished drinking water samples including: anthraquinone, *beta*-sitosterol, bisphenol-A, bromacil, caffeine, camphor, cholesterol, DEET, fluoranthene, metolachlor, and tri(2-chloroethyl)phosphate. The ten most frequently detected OWCs in drinking water facility intakes anthraquinone, *beta*-sitosterol, bisphenol-A, bromacil, caffeine, cholesterol, DEET, fluoranthene, metolachlor, and tri(2-chloroethyl)phosphate. Bromoform was detected in all finished DWF samples, as it is a chlorination disinfectant byproduct. Other OWCs that were detected in finished drinking water include anthraquinone, carbazole, and metolachlor. Seven EDCs were detected in DWF samples (AHTN, benzo[*a*]pyrene, *beta*-sitosterol, bisphenol-A, diazinon, NP, and NP2EO). EDCs generally were detected in intake samples, with the exception of Mankato DWF where one EDC (*beta*-sitosterol) was detected in finished water.

Inconsistencies in OWC detections between drinking and source waters probably were the result of differences in sampling area, sampling timing, introduction or removal of selected OWCs during treatment procedures, or analytical imprecision. For example: (1) OWCs detected in surface or ground water that are source waters for DWFs were not always detected in DWF intake waters, (2) OWCs detected in intake or finished waters were not in the source waters, and (3) OWCs detected in the intakes were not detected in finished water.

Variability in OWC detections among intake and source water samples could be due to differences in sampling location. A width and depth integrated sample was collected at all stream sites. These integrated samples are representative of the entire stream, whereas the drinking water intake sample generally is withdrawn from one specific area of the stream. Therefore, OWCs located in water near one bank of the stream, but not near the

Table 11. Organic wastewater compounds detected at St. Cloud Drinking Water Facility and surface water sites used as sources of drinking water.

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydrologic condition	Selected Source Waters		St. Cloud Drinking Water Facility at St. Cloud, Minn.	
	Mississippi River above Sauk River near Sauk Rapids, Minn (Site 18)	Sauk River near St. Cloud, Minn. (Site 19)	Intake Water (Site 58)	Finished Water (Site 59)
Compounds detected in fall 2000 baseflow	October 17, 20002-methylnaphthlene, naphthalene, *diphenhydramine*	October 16, 20001 methylnaphthalene, 2-methylnaphthalene, cholesterol, naphthalene, N,N-diethyl-*meta*-toluamide (DEET), *caffeine, 1,7-dimethylxanthine*	October 16, 2000 none detected	October 16, 2000 bromoform
Compounds detected in winter 2001 baseflow	not sampled	not sampled	January 22, 2001 3-*beta*-coprostanol, bisphenol-A, cholesterol, nonylphenol diethoxylate (NP2EO), triethylcitrate (ethyl citrate), *beta*-stigmastanol	January 22, 2001 bromoform
Compounds detected in spring 2001 runoff	April 16, 2001 metolachlor	April 10, 2001 *beta*-sitosterol, metolachlor, pentachlorophenol, 3-methyl-1H-indole (skatol) April 27, 2001 bisphenol-A, cholesterol, metolachlor; pharmaceuticals and antibiotics not analyzed	April 16, 2001 metolachlor	April 16, 2001 bromoform, metolachlor
Compounds detected in summer 2001 storm runoff	June 27, 2001 none detected	June 26, 2001 metolachlor	June 27, 2001 none detected	June 27, 2001 bromoform

other, would be detected in the stream sample, but not in the drinking water intake sample. Differences in OWC detections between the intake samples and ground water that served as source water may be due to differences in travel time of the ground water to the plant. Another potential factor contributing to these differences may be laboratory imprecision, as most OWCs were detected near their respective MRLs.

This study was designed to characterize the presence and distribution of OWCs in drinking and source waters. The time-of-travel from the sampling site to the drinking water DWF would be necessary to quantify inputs from source waters or removal rates during treatment.

COMPARISON AMONG SITE CLASSIFICATIONS

Among all site classifications, few OWCs were detected in the intake or finished water samples from DWFs. WWTP influent and effluent, and landfill leachate had the greatest average number of OWCs

Table 12. Organic wastewater compounds detected at St. Paul Drinking Water Facility and surface water sites used as sources of drinking water

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydrologic condition	Selected Source Waters			St. Paul Drinking Water Facility at Maplewood, Minn.	
	Crow River below State Hwy. 101 at Dayton, Minn. (Site 22)	Mississippi River near Anoka, Minn. (Site 24)	Vadnais Lake at Pumping Station in Vadnais Heights, Minn (Site 25)	Intake Water (Site 60)	Finished Water (Site 61)
Compounds detected in fall 2000 baseflow	October 11, 2000 1,7-dimethylxanthine, acetaminophen, beta-sitosterol, caffeine, cholesterol, sulfamethoxazole, tri(dichlorisopropyl)phosphate	October 3, 2000 tri(2-butoxyethyl) phosphate, fluoranthene, pyrene, caffeine,	October 10, 2000 *beta*-sitosterol, cholesterol	October 10, 2000 *beta*-sitosterol	October 10, 2000 bromoform
Compounds detected in winter 2001 baseflow	not sampled	not sampled	not sampled	January 17, 2001 anthraquinone, carbazole, N,N-diethyl-*meta*-toluamide (DEET)	January 17, 2001 anthraquinone, bromoform, carbazole, N,N-diethyl-*meta*-toluamide (DEET)
Compounds detected in spring 2001 runoff	April 9, 2001 acetaminophen, indole, pentachlorophenol, 3-methyl-1H-indole (skatol), metolachlor	April 19, 2001 metolachlor	April 20, 2001 cotinine	April 18, 2001 anthraquinone, erythromycin- H_2O, fluoranthene	April 19, 2001 bromoform
Compounds detected in summer 2001 storm runoff	June 21, 2001 metolachlor	June 22, 2001 metolachlor, N,N-diethyl-*meta*-toluamide (DEET)	June 19, 2001 none detected	June 19, 2001 none detected	June 19, 2001 bromoform

detected (table 15). This same pattern also was observed for selected general use categories (antibiotics, pharmaceuticals, fragrances and flavors, nonionic detergent metabolites, pesticides, and EDCs). The greater number and diversity of OWCs in these site classifications reflects the diversity of waste that is treated and/or stored at WWTP or landfill facilities. The average number of OWCs and the average number of OWCs in selected general use categories (except PAHs) were greater in surface water downstream than upstream from WWTP effluent discharge indicating that WWTP effluent may be a source of OWCs to streams.

More OWCs were detected in surface water than ground water, with the exceptions of ground water underlying the waste dump or underlying feedlots. This may be due to more potential sources of OWCs to surface water compared to ground water sampled in this study or more rapid loss of OWCs from ground water through adsorption, degradation, or transport. The greater number of OWCs in ground water underlying the waste dump reflects the diversity of waste that was deposited at this particular site.

Selected OWCs were more prevalent in particular site classifications. Antibiotic and pharmaceutical detections were rare, but were greatest at WWTP influent and effluent, landfill leachate, and surface water downstream from WWTPs. Antibiotics also were detected in ground water underlying a feedlot. PAHs were prevalent in the WWTP influent, landfill leachate, and ground water underlying the waste dump. EDCs were most commonly detected in landfill leachate, and WWTP influent and effluent.

These comparisons among site classifications are an attempt to understand the potential sources and presence of OWCs in Minnesota surface and ground water.

Table 13. Organic wastewater compounds detected at Minneapolis Drinking Water Facility and surface water sites used as sources of drinking water.

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydrologic condition	Selected Source Waters		Minneapolis Drinking Water Facility at Columbia Heights, Minn.	
	Mississippi River near Anoka, Minn(Site 24).	Rice Creek at County Road 1 in Fridley, Minn.(Site 26)	Intake Water(Site 62)	Finished Water(Site 63)
Compounds detected in fall 2000 baseflow	October 3, 2000 tri(2-butoxyethyl)phosphate, fluoranthene, pyrene, caffeine	October 4, 2000 Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), *beta*-sitosterol, cholesterol, fluoranthene, N,N-diethyl-*meta*-toluamide (DEET), pyrene	October 4, 2000 bisphenol-A, *beta*-sitosterol, cholesterol	October 4, 2000 bromoform
Compounds detected in winter 2001 baseflow	not sampled	not sampled	January 16, 2001 anthraquinone, tri(2-chloroethyl)phosphate	January 16, 2001 anthraquinone, bromoform, tri(2-chloroethyl) phosphate
Compounds detected in spring 2001 runoff	April 19, 2001 metolachlor	April 6, 2001 acetaminophen, caffeine, cotinine, pentachlorphenol, 3-methyl-1H-indole(skatol)	April 18, 2001 metolachlor	April 18, 2001 bromoform, metolachlor
Compounds detected in summer 2001 storm runoff	June 22, 2001 metolachlor, N,N-diethyl-*meta*-toluamide (DEET)	June 15, 2001 bromacil, caffeine, cholesterol, cotinine, diazinon, metolachlor, N,N-diethyl-*meta*-toluamide (DEET)	June 18, 2001 benzo[*a*]pyrene, beta-sitosterol, bromacil, cholesterol, caffeine, diazinon, fluoranthene, metolachlor, pyrene	June 18, 2001 bromoform

These results apply to this study only and are not meant to be extrapolated to all sites that fit into the selected site classifications. A random selection of a larger number of sites in each classification and increased sampling frequency may allow for confirmation of results from this study.

IMPLICATIONS FOR WATER QUALITY AND HUMAN AND AQUATIC HEALTH

This reconnaissance study indicates widespread presence of OWCs in wastewater, surface, ground, and drinking waters in Minnesota. The types of OWCs detected indicate a variety of sources and pathways to the environment including domestic and industrial disposal into WWTPs and landfills and subsequent discharge of treated effluent to surface waters, runoff from land surfaces, infiltration into ground water, direct disposal into surface water, and atmospheric deposition. Results of this study indicate that WWTP effluent is a major pathway of OWCs to surface waters and that landfill leachate from selected facilities is a potential source of OWCs to some WWTPs. Numerous pathways for these chemicals to enter the environment exist; however, and it was not possible to determine the relative contributions of various sources during this reconnaissance study.

The comparisons among site classifications only apply to sites sampled in this study. Some OWCs are likely removed through WWTP treatment processes and degradation in landfills although the efficiency at which they do so varies considerably (Stumpf and others, 1996). The presence of OWCs in surface water indicates that some OWCs are not removed through treatment processes or have additional sources other than treated wastewater. In general, there was insufficient temporal sampling to thoroughly understand the variability in

Table 14. Organic wastewater compounds detected at Mankato Drinking Water Facility and surface water sites used as sources of drinking water

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydrologic condition	Selected Source Waters[1]		Mankato Water Drinking Water Facility at Mankato, Minn.	
	Blue Earth River near Rapidan, Minn. (Site 29)	Blue Earth River at Co. Road 90 near Mankato, Minn. (Site 31)	Intake Water (Site 64)	Finished Water (Site 65)
Compounds detected in fall 2000 baseflow	October 12, 2000 *beta*-sitosterol, metolachlor	not sampled	October 12, 2000 metolachlor	October 12, 2000 bromoform, metolachlor
Compounds detected in winter 2001 baseflow	not sampled	not sampled	January 18, 2001 metolachlor, tri(2-chloroethyl)phosphate	January 18, 2001 anthraquinone, bromoform, carbazole, fluoranthene, metolachlor, pyrene, tri(2-chloroethyl)phosphate
Compounds detected in spring 2001 runoff	not sampled	April 3, 2001 acetaminophen, metolachlor, 3-methyl-1H-indole (skatol)	April 4, 2001 metolachlor	April 4, 2001 *beta*-sitosterol, bromoform, metolachlor
Compounds detected in summer 2001 storm runoff	not sampled	July 2, 2001 cholesterol, triphenyl phosphate, metolachlor, N,N-diethyl-*meta*-toluamide (DEET)	June 28, 2001 bromacil, caffeine, tetrachloroethylene	June 28, 2001 bromoform, metolachlor

[1] Ranney wells adjacent to the Blue Earth and Minnesota Rivers are used for source water for the Mankato Drinking Water Facility. The two surface water sites (Sites 29 and 31) were sampled because there was evidence that the ground-water quality at the depth of the Ranney wells would be similar to the overlying surface water.

OWC presence and distribution particularly with respect to ground water. The limited temporal sampling that was completed indicates high variability in OWC occurrence in WWTP effluent, as well as surface and drinking waters. This variability suggests that exposure to aquatic organisms or humans of OWCs measured in this study would be constantly in flux depending upon OWC use, disposal methods, treatment methods, and physical, chemical and biological processes.

Little information is readily available concerning the toxicity of many of the OWCs because few aquatic or human health standards, or criteria exist for the OWCs analyzed. Only one U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) was exceeded for tetrachloroethylene at a shallow well located in mixed urban land use; however, the MCL is only applicable, in this case, as a point of reference as this well is not used for drinking water supply. The state of Minnesota has stream water-quality standards for a small number of the OWCs measured (anthracene, bromoform, chlorpyrifos, fluoranthene, naphthalene, pentachlorophenol, phenanthrene, phenol, and tetrachloroethylene) and no sample concentrations exceeded those values. Results of this reconnaissance study may help regulators, who set water-quality health standards, begin to prioritize which OWCs to focus upon for given categories of water use.

While little toxicity information is available, selected OWCs detected in this study are known EDCs with respect to fish endocrine systems (Purdom and others, 1994; Jobling and Sumpter, 1993; Folmar and others, 1996; Goodbred and others, 1997; Lee and others, 2000). Thirteen EDCs were detected which include: BHA, 4-cumylphenol, 4-*normal*-octylphenol, 4-*tert*-octylphenol, AHTN, benzo[*a*]pyrene, *beta*-sitosterol, bisphenol-A, NP2EO, OP2EO, OP1EO, and NP.

Table 15. Summary statistics for selected general use categories among site classes, Minnesota, 2000-02

The number in parentheses indicates the number of organic wastewater compounds in a particular general use category that were summarized. The average number of compounds detected by site classification is not the sum of individual averages per general use categories (except GWUI and GWUNSW) because not all general use categories are shown (those categorized as 'other' in Appendix 1). The endocrine disrupting compound column is a subset of other categories. The number of compounds analyzed for this table do not include hormones or sterols analyzed by method 5; *d*-limonene, isophorone, or phenol analyzed by methods 3-4; or carbamazepine and diphenhydramine analyzed by method 1.

[WWIF, wastewater treatment plant influent; WWEF, wastewater treatment plant effluent; LFLCH, landfill leachate; FLLAG, water underlying a feedlot lagoon; SW, surface water; SDW, surface water downstream from wastewater treatment plant effluent discharge; GWDW, ground water used for municipal drinking water supply; GWUI, ground water underlying urban/residential/commercial/industrial land use; GWUNSW, ground water underlying urban residential area that is unsewered; GWD, ground water underlying a waste dump; GWFLT, ground water underlying a feedlot; DWI, drinking water intakes; DWO, finished drinking water].

Site classification	Number of samples analyzed	Average number of organic wastewater compounds detected per sample for selected general use categories [2]										
		Average number of compounds detected per sample (87)	Antibiotics (21)	Pharmaceuticals (12)	Plastic components and flame retardants (7)	Fragrances and flavors (9)	Nonionic detergent metabolites (7)	Polyaromatic hydrocarbons (9)	Pesticides (12)	Sterols (4)	Disinfectants, solvents, and antioxidants (6)	Endocrine disrupting compounds (14)
WWIF	1	41.0	2.0	5.0	4.0	8.0	3.0	8.0	2.0	4.0	2.0	4.0
LFLCH	3	33.7	1.7	3.3	6.3	4.0	3.0	5.7	2.7	2.0	2.0	5.0
WWEF	8	27.1	2.6	3.6	5.5	2.9	2.1	0.8	2.5	2.4	2.8	3.8
GWD	2	14.5	0	0.5	4.5	1.5	0.5	3.0	1.5	0	0.5	1.5
SDW	23	8.9	0.9	2.3	1.8	1.0	0.3	0	1.1	1.2	0.3	1.0
FLLAG	2	6.5	0.5	0.5	1.5	2.0	1.0	0	0.5	0	0.5	2.0
GWFLT	1	5.0	1.0	0	0	2.0	0	0	0	0	1.0	0
SW	[1]32-37	3.6	0.1	0.7	0.3	0.4	0.1	0.3	1.0	0.6	0.1	0.4
DWI	24	2.0	0	0.1	0.3	0	0	0.2	0.6	0.4	0	0.3
DWO	24	1.9	0	0	0.1	0	0	0.1	0.4	0	1.0	0.1
GWDW	4	1.3	0	0	0.3	0.3	0	0	0.3	0	0	0.5
GWUI	4	0.8	0	0	0.3	0	0.3	0	0	0	0.3	0.3
GWUNSW	3	0.7	0.3	0	0	0	0	0	0.3	0	0	0

[1] Number of samples analyzed varied slightly by laboratory method. There were 32, 33, and 37 SW samples analyzed by methods 1, 2, and 3-4 respectively.

[2] Organic wastewater compounds classified as general-use category "other" are listed in Appendix 1.

SUMMARY AND CONCLUSIONS

This report provides the results of a cooperative study of the Minnesota Department of Health, Minnesota Pollution Control Agency, and the U.S. Geological Survey to determine the presence and distribution of 91 organic wastewater compounds (OWCs) at 65 sites in Minnesota during October 2000 through November 2002. Sites included wastewater (wastewater treatment plant influent and effluent, leachate from landfills, and water underlying feedlot lagoons); surface water; ground water (sewered and unsewered mixed urban land use, a waste dump, and feedlots); and the intake and finished drinking water from drinking-water facilities. OWCs are newly recognized classes of compounds that include household, industrial, and agricultural-use compounds (HIAs), pharmaceuticals, antibiotics, and sterols and hormones, which are characterized by high usage rates, have potential health effects, and are continuously released into the environment through human activities.

Results of this study illustrate the ubiquitous distribution of these compounds in the environment. There were 74 OWCs (49 household, industrial, and agricultural use compounds, 10 pharmaceuticals, 11 antibiotics, and 4 sterols or hormones) detected that represent a wide variety of uses and sources. Samples generally were comprised of a mixture of compounds (average of 6 OWCs) and 90 percent of the samples had at least one OWC detected. Average concentrations for detected OWCs generally were less than 3 micrograms per liter. The most frequently detected OWCs among all samples were metolachlor, cholesterol, caffeine, N,N-diethyl-*meta*-toluamide, bromoform, tri(2-chloroethyl)phosphate, *beta*-sitosterol, acetyl-hexamethyl-tetrahydro-naphthalene, bisphenol-A, and cotinine.

The greatest number and diversity of OWCs was found in wastewater influent and effluent, and landfill leachate (averages of 41, 27.1, and 33.7 respectively) compared to other site classifications. The most common OWCs detected in wastewater effluent samples included widely used fragrances, plasticizers, flame retardants, nonionic detergent surfactants, and plant and animal sterols. The most commonly detected OWCs in landfill leachate samples were polyaromatic hydrocarbons, fragrances, plasticizers, flame retardants, and solvents.

Wastewater treatment plants (WWTPs) and landfills receive diverse waste sources from the communities they serve. There is likely OWC removal through treatment processes in WWTPs and degradation in landfills although the efficiency at which this occurs is not well understood and likely varies. This study showed differences in the types and numbers of OWCs detected among WWTPs and among time periods within one WWTP. These differences may be the result of varying sources of influent and treatment techniques. There was variability in types of OWCs detected among landfill sites, which is likely due to diversity of waste that was landfilled, and the spatial and temporal variability in waste type throughout a landfill.

The variety and number of OWCs detected in streams and lakes in this study indicate that there are numerous pathways for OWCs to enter surface water. A wide variety of OWCs (56 OWCs) were detected among all surface-water samples with an average of 6 OWCs per sample. Metolachlor, caffeine, cholesterol, N,N-diethyl-*meta*-toluamide (DEET), *beta*-sitosterol, acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), and acetaminophen were the most frequently detected OWCs among all surface-water samples. The number of OWCs detected and concentrations generally were greater in small streams (average of 8.9 OWCs), located within 1 mile downstream of WWTP effluent discharges than at other surface-water sites (average of 3.6 OWCs) indicating that WWTP effluent is a likely source of OWCs to selected surface waters. Small streams draining urban land use in the Minneapolis and St. Paul metropolitan area had a relatively high number of OWC detections considering that no direct source of WWTP effluent enters these streams directly upstream of the sampling location. Potential sources of these OWCs in urban streams may be individual sewage treatment systems, accidental discharge from sewer lines, or direct inputs through runoff or atmospheric deposition.

The types of OWCs detected at stream sites indicate diverse sources to streams. The animal sterol (3-*beta*-coprostanol), fragrances (AHTN and HHCB), flame retardants and plastic components (tri(2-butoxyethyl)phosphate, (tri(2-chloroethyl)phosphate, tributyl phosphate, and tri(dichloroisopropyl)phosphate)), and the pharmaceuticals (caffeine, cotinine, erythromycin H_2O, and trimethoprim) also were detected more frequently in streams directly downstream than upstream from WWTP effluent discharge. In contrast, *beta*-sitosterol, metolachlor, N,N-diethyl-*meta*-toluamide, and 3-methyl-1H-indole were detected in streams both directly and not directly downstream from WWTP effluent

discharge suggesting there may be other sources of these OWCs in addition to WWTP effluent.

In general, more OWCs were detected in surface water than in ground water. Among all ground-water samples, 31 OWCs were detected, and an average of 3 OWCs were detected per sample. There were few OWCs detected in the individual wells (0-4 OWCs) except those wells located in the waste dump site (8-21 OWCs), and a well located in a feedlot (5 OWCs).

Few OWCs were detected (0-9 detected per sample with an average of 2 per sample) at the six drinking water facilities sampled during this study. Among all facilities, 26 OWCs were detected in intake and 13 OWCs were detected in finished-water samples. The most frequently detected OWCs in drinking water facility intakes were anthraquinone, *beta*-sitosterol, bisphenol-A, bromacil, caffeine, cholesterol, DEET, fluoranthene, metolachlor, and tri(2-chloroethyl)phosphate. Bromoform was detected in all finished drinking water samples, as it is a disinfectant byproduct. Other OWCs that were detected in finished drinking water include anthraquinone, carbazole, and metolachlor.

OWCs in the source waters for each drinking-water facility may be taken in for processing and may be present in the intake or finished water samples. A variety of OWCs including fragrances, plasticizers, pharmaceuticals, pesticides, nonionic detergent metabolites, sterols, and disinfectants were detected in the source waters. Among the source waters for the drinking-water facilities, smaller streams tended to have greater numbers of OWCs detected than large rivers, lakes, or ground-water sources. The greater number of OWCs detected in small streams may be due to greater potential sources or relatively less dilution than larger rivers.

Inconsistencies exist between the OWCs detected in drinking and source waters. For example: (1) OWCs detected in surface or ground water that are source waters for drinking-water facilities were not always detected in the intake waters, (2) OWCs detected in intake or finished waters were not in the source waters, and (3) OWCs detected in the intakes were not detected in finished water. These inconsistencies probably are a result of differences in sampling area, timing of sampling, introduction or removal of selected OWCs during treatment procedures, or analytical imprecision.

This reconnaissance study indicates widespread presence of OWCs in wastewater, surface, ground, and drinking waters in Minnesota. Aquatic organism or human exposure to the OWCs would likely be in constant flux depending upon OWC use, disposal methods, treatment methods, and physical, chemical, and biological processes. Although exposure to OWCs is possible, concentrations generally are low and few aquatic or human health standards, or aquatic criteria exist for the OWCs analyzed. The risks of OWCs to humans or wildlife are not known, with the exception of selected OWCs detected in this study, that are known endocrine disrupters, and have been found to disrupt or influence endocrine function in fish. Results of this reconnaissance study, may help regulators who set water quality health standards, begin to prioritize which OWCs to focus upon for given categories of water use.

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Appendix 1. Potential uses of organic wastewater compounds analyzed in water samples, Minnesota 2000-02

[Analytical methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geological Survey production method; nd, not determined; HA, health advisory; MCL, maximum comtaminant level; µg/L, micrograms per liter].

Analytical method	Organic wastewater compound	General use category[1]	HA (MCL) µg/L[2]	CASRN[3]	Potential uses[4]
			Pharmaceuticals		
1	1,7-dimethylxanthine	PHARM	nd	611-59-6	Metabolite of caffeine
1	Acetaminophen	PHARM	nd	103-90-2	Nonprescription analgesic; anti-inflammatory
1,3,4	Caffeine	PHARM	nd	58-08-2	Stimulant or diuretic
1	Carbamazepine	PHARM	nd	298-46-4	Anticonvulsant; antiepileptic; antineuralgia treatment; bipolar disorders
1	Codeine	PHARM	nd	76-57-3	Narcotic analgesic
1,3,4	Cotinine	PHARM	nd	486-56-6	Primary metabolite of nicotine
1	Dehydronifedipine	PHARM	nd	67035-22-7	Metabolite of Procardia: a vasodilator
1	Diltiazem	PHARM	nd	33286-22-5	Antihypertensive; calcium channel blocker
1	Diphenhydramine	PHARM	nd	147-24-0	Antihistamine
1	Gemfibrozil	PHARM	nd	25812-30-0	Cholesterol regulator
1	Ibuprofen	PHARM	nd	15687-27-1	Nonprescription anti-inflammatory analgesic
1	Ranitidine	PHARM	nd	66357-35-5	Nonprescription antacid
1	Salbutamol	PHARM	nd	18559-94-9	Antiasthmatic bronchodilator
1	Warfarin	PHARM	nd	81-81-2	Anticoagulant
			Antibiotics		
2	Carbadox	ANTIB	nd	6804-07-5	Antibiotic to prevent and treat dysentery in swine and to maintain weight gain
2	Chloretetracycline	ANTIB	nd	57-62-5	Tetracycline antibiotic used for swine, poultry, cattle, and sheep
2	Ciprofloxacin	ANTIB	nd	85721-33-1	Fluoroquinolone antibiotic used for canine and swine
2	Doxycycline	ANTIB	nd	564-25-0	Tetracycline antibiotic used for humans and canines
2	Enrofloxacin	ANTIB	nd	93106-60-6	Fluoroquinolone antibiotic used for canine and swine
2	Erythromycin-H_2O	ANTIB	nd	114-07-8	Metabolite of erythromycin (a macrolide antibiotic) used for humans, poultry, and swine
2	Lincomycin	ANTIB	nd	154-21-2	Antibiotic used for poultry and swine
2	Norfloxacin	ANTIB	nd	70458-96-7	Fluoroquinolone antibiotic used for humans
2	Oxytetracycline	ANTIB	nd	6153-64-6	Tetracycline antibiotic used for poultry, fish, swine, cattle, sheep, bees, and lobster
2	Roxithromycin	ANTIB	nd	80214-83-1	Macrolide antibiotic
2	Sarafloxacin	ANTIB	nd	98105-99-8	Fluoroquinolone antibiotic used for poultry
2	Sulfadimethoxine	ANTIB	nd	122-11-2	Sulfonamide antibiotic used for fish and poultry
2	Sulfamerazine	ANTIB	nd	127-79-7	Sulfonamide antibiotic used for fish
2	Sulfamethazine	ANTIB	nd	57-68-1	Sulfonamide antibiotic used for swine and cattle
2	Sulfamethizole	ANTIB	nd	144-82-1	Sulfonamide antibiotic used for swine
1,2	Sulfamethoxazole	ANTIB	nd	723-46-6	Sulfonamide antibiotic used for humans
2	Sulfathiazole	ANTIB	nd	72-14-0	Sulfonamide antibiotic used for swine
2	Tetracycline	ANTIB	nd	60-54-8	Tetracycline antibiotic used for humans, canine, and cattle
1,2	Trimethoprim	ANTIB	nd	738-70-5	Antibiotic used for humans and canines
2	Tylosin	ANTIB	nd	1401-69-0	Antibiotic used for humans and canines
2	Virginiamycin	ANTIB	nd	11006-76-1	Antibiotic used for poultry, swine, and cattle
			Household, industrial, and agricultural use compounds		
3,4	1,4-dichlorobenzene	PEST	(75)	106-46-7	Deodorizer for restrooms; fumigant to control moths, molds, and mildew; suspected endocrine disruptor
3,4	1-methylnaphthalene	PAH	nd	90-12-0	Comprises 2-5 percent of gasoline, diesel, and crude
3,4	2,6-dimethylnaphthalene	PAH	nd	581-42-0	Indicator of diesel and kerosene, but not a significant component in gasoline

Appendix 1. Potential uses of organic wastewater compounds analyzed in water samples, Minnesota 2000-02—Continued

[Analytical methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geological Survey production method; nd, not determined; HA, health advisory; MCL, maximum comtaminant level; µg/L, micrograms per liter].

Analytical method	Organic wastewater compound	General use category[1]	HA (MCL) µg/L[2]	CASRN[3]	Potential uses[4]
3,4	2-methylnaphthalene	PAH	nd	91-57-6	Comprises 2-5 percent of gasoline, diesel, and crude
3,4	3-methyl-1H-indole (skatol)	FRAG	nd	83-34-1	Fragrance of the stench in feces and coal tar
3,4	3-*tert*-butyl-4-hydroxyanisole (BHA)	ANTIOX/EDC	nd	25013-16-5	Antioxidant and preservative; known endocrine disruptor
3,4	4-cumylphenol	NID/EDC	nd	599-64-4	Known endocrine disruptor
3,4	4-*normal*-octylphenol	NID/EDC	nd	1806-26-4	Known endocrine disruptor
3,4	4-*tert*-octylphenol	NID/EDC	nd	140-66-9	Known endocrine disruptor
3,4	5-methyl-1H-benzotriazole	ANTIOX	nd	136-85-6	Antioxidant in antifreeze and deicers; also an anti-corrosive agent
3,4	Acetophenone	FRAG	nd	98-86-2	Fragrance in soap and detergent; flavor in beverages and tobacco; solvent for cellulose ethers
3,4	Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	FRAG/EDC	nd	21145-77-7	Synthetic musk fragrance with widespread usage; known endocrine disruptor
3,4	Anthracene	PAH	nd	120-12-7	Wood preservative; also found in coal tar, diesel, and crude, but not gasoline
3,4	Anthraquinone	OTHER	nd	84-65-1	Manufacture of dye for textiles; seed treatments; bird repellant
3,4	Benzo[*a*]pyrene	PAH/EDC	(0.2)	50-32-8	Regulated polyaromatic hydrocarbon; known endocrine disruptor
3,4	Benzophenone	OTHER	nd	119-61-9	Fixative for perfumes and soaps; a photoinitiator in the curing of inks with ultra-violet light; suspected endocrine disruptor
3,4	Bisphenol-A	PLASTIC/EDC	nd	80-05-7	Manufacture of polycarbonate resins; used in PVC resins; antioxidant; known endocrine disruptor
3,4	Bromacil	PEST	nd	314-40-9	Herbicide used primarily for non-crop grass and brush control
3,4	Bromoform	DISINF	(80)	75-25-2	Trihalomethane; byproduct of water disinfection
3,4	Camphor	FLAV	nd	76-22-2	Flavor or odorant in ointments
3,4	Carbaryl	PEST/EDC	700	63-25-2	Insecticide for crop and garden uses; known endocrine disruptor
3,4	Carbazole	PEST	nd	86-74-8	Manufacture of dyes, explosives, and lubricants; also an insecticide
3,4	Chlorpyrifos	PEST/EDC	20	2921-88-2	Domestic pest/termite control; highly restricted; known endocrine disruptor
3,4	Diazinon	PEST/EDC	0.6	333-41-5	Insecticide for control of ants, flies, and grubs; known endocrine disruptor
3,4	Dichlorvos	PEST	nd	62-73-7	Insecticide in pet collars for control of flies; suspected endocrine disruptor
3,4	*d*-Limonene	FRAG	nd	5989-27-5	Antimicrobial; antiviral; a fragrance in aerosols
3,4	Fluoranthene	PAH	nd	206-44-0	Common in coal tar and asphalt, but not gasoline and diesel
3,4	Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)	FRAG	nd	1222-05-5	Musk fragrance with widespread usage
3,4	Indole	FRAG	nd	120-72-9	Produced by bacteria in swine intestines; coffee fragrance; inert ingredient in pesticides
3,4	Isoborneol	FRAG	nd	124-76-5	Fragrance and disinfectant
3,4	Isophorone	SOLV	100	78-59-1	Solvent for lacquers, plastics, oils, silicon, and resins
3,4	Isopropylbenzene (cumene)	SOLV	nd	98-82-8	Paint thinner in octane aviation fuel; used in styrene, acetone and phenol production
3,4	Isoquinoline	FLAV	nd	119-65-3	Flavor and fragrance
3,4	Menthol	FLAV	nd	89-78-1	Flavor or odorant in cigarettes, cough drops, liniment, and mouthwash
3,4	Metalaxyl	PEST	nd	57837-19-1	Fungicide for soil pathogens, mildew, and blight
3,4	Methyl salicylate	OTHER	nd	119-36-8	Used in liniments, food, beverages, and UV-adsorbing lotions
3,4	Metolachlor	PEST	(100)	51218-45-2	Herbicide used on corn
3,4	Naphthalene	PAH	(100)	91-20-3	Moth repellent; component in gasoline; found naturally in fossil fuels, burning tobacco or wood; used in dyes, resins, leather tanning agents, and in the insecticide carbaryl

Appendix 1. Potential uses of organic wastewater compounds analyzed in water samples, Minnesota 2000-02—Continued

[Analytical methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geological Survey production method; nd, not determined; HA, health advisory; MCL, maximum comtaminant level; µg/L, micrograms per liter].

Analytical method	Organic wastewater compound	General use category[1]	HA (MCL) µg/L[2]	CASRN[3]	Potential uses[4]
3,4	N,N-diethyl-*meta*-toluamide (DEET)	PEST	nd	134-62-3	Insecticide used for mosquito control
3,4	Nonylphenol diethoxylate (NP2EO)	NID/EDC	nd	26027-38-2	Nonionic detergent metabolite; known endocrine disruptor
3,4	Octylphenol diethoxylate (OP2EO)	NID/EDC	nd	26636-32-8	Nonionic detergent metabolite; known endocrine disruptor
3,4	Octylphenol monoethoxylate (OP1EO)	NID/EDC	nd	26636-32-8	Nonionic detergent metabolite; known endocrine disruptor
3,4	*para*-cresol	OTHER	nd	106-44-5	Intermediate for dyes, pigments, drugs, disinfectant, ultra violet absorbers and pesticides.; suspected endocrine disruptor
3,4	*para*-nonylphenol (NP)	NID/EDC	nd	84852-15-3	Nonionic detergent metabolite; known endocrine disruptor
3,4	Pentachlorophenol	PEST	(1)	87-86-5	Restricted -use pesticide for termite control; wood preservative for utility poles, railroad ties, and wharf pilings; suspected endocrine disruptor
3,4	Phenanthrene	PAH	nd	85-01-8	Manufacture of explosives; used in coal tar, diesel, or crude, but not gasoline
3,4	Phenol	DISINF	4000	108-95-2	Disinfectant; raw material in the production of phenolic resins; raw material for bisphenol-A and aniline.
3,4	Prometon	PEST	100	1610-18-0	Herbicide used as a soil sterilant
3,4	Pyrene	PAH	nd	129-00-0	In coal tar and asphalt, but not gasoline or diesel; used to make dyes, plastics, pesticides, and benzo[*a*]pyrene
3,4	Tetrachloroethylene (TCE)	SOLV	10 (5)	127-18-4	Solvent and degreaser; used in dry-cleaning products
3,4	Tri(2-butoxyethyl)phosphate	FIRE	nd	78-51-3	Flame retardant and plastic component
3,4	Tri(2-chloroethyl)phosphate	FIRE	nd	115-96-8	Flame retardant and plasticizer; suspected endocrine disruptor
3,4	Tri(dichlorisopropyl)phosphate	FIRE	nd	13674-87-8	Flame retardant used in rigid and flexible polyurethane foams; suspected endocrine disruptor
3,4	Tributyl phosphate	FIRE	nd	126-73-8	Flame retardant and antifoaming agent
3,4	Triclosan	DISINF	nd	3380-34-5	Antimicrobial disinfectant
3,4	Triethyl citrate (ethyl-citrate)	PLASTIC	nd	77-93-0	Used in cosmetics and pharmaceuticals; produced from citric acid; used to plasticize vinyl resins
3,4	Triphenyl phosphate	PLASTIC	nd	115-86-6	Plasticizer used in resins, waxes, finishes, roofing paper
			Sterols and Hormones		
5	11-ketotestosterone	HORMONE	nd	nd	Reproductive hormone
5	17-*alpha*-estradiol	HORMONE/EDC	nd	57-91-0	Reproductive hormone; known endocrine disruptor
5	17-*alpha*-ethynyl estradiol	HORMONE/EDC	nd	57-63-6	Ovulation inhibitor; known endocrine disruptor
5	17-*beta*-estradiol	HORMONE/EDC	nd	50-28-2	Reproductive hormone; known endocrine disruptor
5	19-norethisterone	HORMONE/EDC	nd	68-22-4	Ovulation inhibitor; known endocrine disruptor
3,4,5	3-*beta*-coprostanol	STER	nd	360-68-9	Usually a carnivore fecal indicator
5	4-androstene-3,17-dione	HORMONE	nd	63-05-8	Androgenic hormone
3,4	*beta*-sitosterol	STER/EDC	nd	83-46-5	A sterol in plant oils, legumes, and wood; known endocrine disruptor
3,4	*beta*-stigmastanol	STER	nd	19466-47-8	Generally a plant sterol
3,4,5	Cholesterol	STER	nd	57-88-5	Often a fecal indicator; also a plant sterol
5	cis-androsterone	HORMONE	nd	53-41-8	Urinary steroid; known endocrine disruptor
5	Diethylstilbestrol (DES)	HORMONE/EDC	nd	56-53-1	Synthetic estrogen; known endocrine disruptor
5	Epitestosterone	HORMONE	nd	481-30-1	Reproductive hormone

Appendix 1. Potential uses of organic wastewater compounds analyzed in water samples, Minnesota 2000-02—Continued

[Analytical methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geological Survey production method; nd, not determined; HA, health advisory; MCL, maximum comtaminant level; µg/L, micrograms per liter].

Analytical method	Organic wastewater compound	General use category[1]	HA (MCL) µg/L[2]	CASRN[3]	Potential uses[4]
5	Equilenin	HORMONE/EDC	nd	517-09-9	Estrogen replacement therapy; known endocrine disruptor
5	Equilin	HORMONE/EDC	nd	474-86-2	Estrogen replacement therapy; known endocrine disruptor
5	Estrone	HORMONE	nd	53-16-7	Reproductive hormone
5	Estriol	HORMONE/EDC	nd	50-27-1	Reproductive hormone; known endocrine disruptor
5	Mestranol	HORMONE/EDC	nd	72-33-3	Ovulation inhibitor; known endocrine disruptor
5	Progesterone	HORMONE/EDC	nd	57-83-0	Reproductive hormone; known endocrine disruptor
5	Stanalone	HORMONE	nd	10418-03-8	Synthetic anabolic steroid
5	Testosterone	HORMONE	nd	58-22-0	Reproductive hormone; known endocrine disruptor
5	Trenbolone	HORMONE	nd	10161-33-8	Synthetic anabolic sterol

[1]PLASTIC, plastic component; FIRE, fire retardant; EDC, endocrine disrupting compound for selected fish species; FRAG, fragrance; FLAV, flavor; NID, nonionic detergent metabolite; SOLV, solvent; PEST, pesticide; DISINF, disinfectants; ANTIOX, antioxidants; ANTIB, antibiotic; PHARM, pharmaceutical; PAH, polyaromatic hydrocarbons; STER, plant or animal sterols; HORMONE, natural and synthetic hormones. Compounds generally have multiple uses and sources. For purposes of this report compounds are characterized by the most common uses.

[2] Health advisories (HA) and maximum contaminant levels (MCL) are human health related advisories or standards (U.S. Environmental Protection Agency, 2002). HA are shown in italics and MCLs are in parentheses. The HA is an estimate of acceptable drinking water levels for a chemical substance based on health effects information. It is not a legally enforceable Federal standard, but serves as technical guidance to assist Federal, state, and local officials. The lifetime HA is the concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for a lifetime of exposure. The MCL is the highest level of a contaminant that is allowed in drinking water. MCLs are enforceable standards for community drinking water.

[3]The chemical abstracts registry number gistry database. A CASRN
is a numeric identifier that can contain up to 9 digits, divided by hyphens into 3 parts. For example, 58-08-2 is the CASRN for caffeine. The online database provides a source for the latest registry number information: http://www.cas.org/Support/lookup.html

[4] Sour
oxicology Program, 2003; National Institute of Standards and Technology, 2003; HealthCentral.com, 2003; Extension Toxicology Network, 2003).

Appendix 2: Quality-control data summary for laboratory reagent spike and blank samples for all analytes, Minnesota 2000-02.

[Analytical Methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geologcial Survey production method; RSD, relative standard deviation; µg/L; micrograms per liter; na, not available; nd, not detected; --not applicable; parentheses show results for method 4].

Analytical method	Organic wastewater compound	Reagent spike samples			Reagent blank samples			
		Average percent recovery	RSD	Number of samples	Minimum µg/L)	Average (µg/L)	Maximum (µg/L)	Number of samples with detections[1]
				Pharmaceuticals				
1	1,7-dimethylxanthine	104	42	40	0.001	0.002	0.003	2
1	Acetaminophen	87	37	40	0.0017	0.009	0.0139	4
1	Caffeine	81	30	40	0.001	0.004	0.008	8
3,4	Caffeine	73 (80)	31 (14)	21 (9)	0.0099 (nd)	0.010 (nd)	0.011 (nd)	3 (0)
1	Carbamazapine	73	42	30	--	--	--	0
1	Codeine	80	3	40	--	--	--	0
1	Cotinine	74	38	40	--	--	--	0
3,4	Cotinine	53 (66)	61 (39)	21 (11)	--	--	--	0
1	Dehydronifedipine	81	27	40	--	--	0.0056	1
1	Diltiazem	47	39	40	--	--	--	0
1	Diphenhydramine	56	33	36	--	--	--	0
1	Gemfibrozil	100	210	39	--	--	--	0
1	Ibuprofen	59	54	40	--	--	--	0
1	Ranitidine	34	53	40	--	--	--	0
1	Salbutamol	76	32	40	--	--	--	0
1	Warfarin	65	36	40	--	--	--	0
Antibiotics								
2	Carbadox	100	9.4	10	--	--	--	0
2	Chloretetracycline	114	17	10	--	--	--	0
2	Ciprofloxacin	125	6.5	10	--	--	--	0
2	Doxycycline	86	13	10	--	--	--	0
2	Enrofloxacin	135	17	10	--	--	--	0
2	Erythromycin-H_2O	103	11	10	--	--	0.01	1
2	Lincomycin	110	15	10	--	--	--	0
2	Norfloxacin	130	8	10	--	--	--	0
2	Oxytetracycline	74	4	10	--	--	--	0
2	Roxithromycin	115	13	10	--	--	--	0
2	Sarafloxacin	120	8	10	--	--	--	0
2	Sulfadimethoxine	91	5	10	--	--	--	0
2	Sulfamerazine	110		10	--	--	--	0
2	Sulfamethazine	86	5	10	--	--	--	0
2	Sulfamethizole	na	na	10	--	--	--	0
1	Sulfamethoxazole	61	48	40	--	--	--	0
2	Sulfamethoxazole	102	6	10	--	--	--	0
2	Sulfathiazole	95	7	10	--	--	--	0
2	Tetracycline	97	10	10	--	--	--	0
1	Trimethoprim	69	30	40	--	--	--	0
2	Trimethoprim	87	9	10	--	--	--	0
2	Tylosin	116	13	10	--	--	--	0
2	Virginiamycin	52	8	10	--	--	--	0

Appendix 2: Quality-control data summary for laboratory reagent spike and blank samples for all analytes, Minnesota 2000-02—Continued

[Analytical Methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geologcial Survey production method; RSD, relative standard deviation; µg/L; micrograms per liter; na, not available; nd, not detected; --not applicable; parentheses show results for method 4].

Analytical method	Organic wastewater compound	Reagent spike samples				Reagent blank samples		
		Average percent recovery	RSD	Number of samples	Minimum µg/L)	Average (µg/L)	Maximum (µg/L)	Number of samples with detections[1]
	Household, industrial, and agricultural use-compounds							
3,4	1,4-dichlorobenzene	75 (46)	19 (31)	21 (11)	0.006 (nd)	0.018 (nd)	0.019(nd)	5 (0)
3,4	1-methylnaphthalene	85 (70)	20 (22)	21 (7)	0.005 (nd)	0.011 (nd)	0.008 (nd)	3 (0)
3,4	2, 6-dimethylnaphthalene	83 (67)	21 (25)	21 (7)	0.014 (nd)	0.016 (nd)	0.018 (nd)	2 (0)
3,4	2-methylnapthalene	76 (80)	19 (13)	21 (7)	0.01 (nd)	0.018 (nd)	0.014 (nd)	3 (0)
3,4	3-methyl-1H-indole (skatol)	64 (79)	26 (16)	21 (7)	--	--	0.009 (nd)	1 (0)
3,4	3-*tert*-butyl-4-hydroxyanisole (BHA)	46 (33)	53 (42)	21 (10)	--	--	--	0
3,4	4-cumylphenol	83 (88)	23 (15)	21 (7)	--	--	(1.2)	0(1)
3,4	4-normal-octylphenol	64 (79)	31 (18)	21 (11)	--	--	--	0
3,4	4-*tert*-octylphenol	72 (63)	25 (27)	21 (7)	0.002 (nd)	0.014 (nd)	0.032 (nd)	6 (0)
3,4	5-methyl-1H-benzotriazole	86 (83)	25 (20)	21 (11)	--	--	--	0
3,4	Acetophenone	93 (81)	15 (21)	21 (11)	--	--	0.055 (nd)	1 (0)
3,4	Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	81 (80)	19 (14)	20 (7)	0.004 (nd)	0.008 (nd)	0.019 (nd)	4 (0)
3,4	Anthracene	82 (79)	21 (23)	21 (11)	--	--	--	0
3,4	Anthraquinone	78 (72)	21 (38)	21 (11)	--	--	--	0
3,4	Benzo[*a*]pyrene	68 (84)	27 (13)	21 (9)	--	--	0.009 (nd)	1 (0)
3,4	Benzophenone	90 (88)	20 (15)	21 (7)	--	--	0.0047 (nd)	1 (0)
3,4	Bisphenol-A	90 (77)	43 (27)	21 (9)	0.0091 (nd)	0.025 (nd)	0.041 (nd)	2 (0)
3,4	Bromacil	87 (86)	18 (12)	21 (7)	--	--	0.033 (nd)	1 (0)
3,4	Bromoform	73 (67)	21 (18)	21 (7)	--	--	--	0
3,4	Camphor	90 (88)	19 (16)	21 (7)	0.005 (nd)	0.006 (nd)	0.006 (nd)	3 (0)
3,4	Carbaryl	64 (66)	40 (24)	21 (7)	--	--	--	0
3,4	Carbazole	67 (86)	39 (15)	20 (7)	0.002 (nd)	0.002 (nd)	0.002 (nd)	1 (0)
3,4	Chlorpyrifos	82 (76)	19 (25)	21 (11)	nd (nd)	nd (nd)	nd (nd)	0
3,4	Diazinon	76 (82)	20 (15)	21 (11)	--	--	--	0
3,4	Dichlorvos	2 (84)	129 (10)	21 (7)	--	--	--	0
3,4	*d*-Limonene	60 (36)	35 (27)	21 (7)	0.026 (nd)	0.058 (nd)	0.16 (nd)	7 (0)
3,4	Fluoranthene	80 (79)	21 (26)	21 (10)	0.0037 (nd)	0.01 (nd)	0.017- (nd)	3 (0)
3,4	Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)	88 (90)	34 (18)	21 (7)	0.0012 (nd)	0.0017 (nd)	0.0023 (nd)	3 (0)
3,4	Indole	82 (69)	22 (25)	21 (7)	--	--	(0.075)	0 (1)
3,4	Isoborneol	90 (84)	19 (18)	21 (7)	--	--	--	0
3,4	Isophorone	96 (88)	17 (15)	21 (7)	0.05 (nd)	0.452 (nd)	4.4 (nd)	13 (0)
3,4	Isopropylbenzene (cumene)	65 (38)	31 (26)	21 (7)	0.002 (nd)	0.008 (nd)	0.019 (nd)	5 (0)
3,4	Isoquinoline	68 (80)	30 (14)	21 (7)	--	--	--	0
3,4	Menthol	82 (84)	21 (19)	21 (7)	0.026 (nd)	0.026 (nd)	0.026 (nd)	1 (0)
3,4	Metalaxyl	90 (89)	19 (17)	21 (7)	--	--	0.013 (0.012)	1 (1)
3,4	Methyl salicylate	89 (84)	16 (15)	21 (7)	0.007 (nd)	0.01 (nd)	0.01 (nd)	3 (0)
3,4	Metolachlor	88 (83)	20 (21)	21 (11)	0.003 (nd)	0.004 (nd)	0.005 (nd)	3 (0)
3,4	Naphthalene	86 (68)	19 (25)	21 (11)	0.006 (nd)	0.031 (nd)	0.08 (nd)	8 (0)
3,4	N,N-diethyl-meta-toluamide (DEET)	81 (81)	26 (27)	21 (9)	--	--	0.012 (nd)	1 (0)
3,4	Nonylphenol diethoxylate (NP2EO)	75 (76)	24 (28)	21 (9)	0.24 (nd)	0.717 (nd)	2.3 (nd)	16 (0)

Appendix 2: Quality-control data summary for laboratory reagent spike and blank samples for all analytes, Minnesota 2000-02—Continued

[Analytical Methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geologcial Survey production method; RSD, relative standard deviation; µg/L; micrograms per liter; na, not available; nd, not detected; --not applicable; parentheses show results for method 4].

Analytical method	Organic wastewater compound	Reagent spike samples			Reagent blank samples			
		Average percent recovery	RSD	Number of samples	Minimum µg/L)	Average (µg/L)	Maximum (µg/L)	Number of samples with detections[1]
3,4	Octylphenol diethoxylate (OP2EO)	68 (76)	31 (19)	21 (11)	0.02 (nd)	0.144 (nd)	0.26 (nd)	5 (0)
3,4	Octylphenol monoethoxylate (OP1EO)	81 (87)	25 (19)	21 (7)	0.014 (0.13)	0.31 (0.18)	1.1 (0.2)	4 (4)
3,4	*para*-cresol	82 (72)	31 (24)	21 (11)	--	--	--	0
3,4	*para*-nonylphenol (NP)	46 (57)	53 (33)	21 (7)	0.012 (nd)	0.815 (nd)	2.5 (nd)	8 (0)
3,4	Pentachlorophenol	63 (61)	36 (48)	21 (11)	--	--	--	0
3,4	Phenanthrene	88 (80)	25 (21)	21 (8)	0.001 (nd)	0.003 (nd)	0.003 (nd)	5 (0)
3,4	Phenol	96 (71)	28 (22)	21 (11)	0.048 (nd)	0.171 (nd)	0.4 (nd)	5 (0)
3,4	Prometon	89 (78)	18 (23)	21 (11)	0.005 (nd)	0.015 (nd)	0.028 (nd)	7 (0)
3,4	Pyrene	78 (75)	21 (32)	21 (11)	0.0034 (nd)	0.008 (nd)	0.017 (nd)	3 (0)
3,4	Tetrachloroethylene (TCE)	46 (27)	37 (33)	21 (11)	0.017 (nd)	0.065 (nd)	0.12 (nd)	9 (0)
3,4	Tri(2-butoxyethyl)phosphate	83 (82)	27 (19)	21 (7)	0.087 (nd)	0.088 (nd)	0.09 (nd)	2 (0)
3,4	Tri(2-chloroethyl)phosphate	86 (85)	23 (13)	21 (7)	--	--	0.12 (nd)	1 (0)
3,4	Tri(dichlorisopropyl)phosphate	85 (79)	19 (24)	21 (11)	--	--	--	0
3,4	Tributyl phosphate	90 (89)	20 (18)	21 (7)	0.007 (nd)	0.035 (nd)	0.063 (nd)	7 (0)
3,4	Triclosan	73 (81)	23 (14)	21 (8)	--	--	--	0
3,4	Triethyl citrate (ethyl-citrate)	93 (76)	20 (24)	21 (11)	0.003 (nd)	0.008 (nd)	0.018 (nd)	3 (0)
3,4	Triphenyl phosphate	80 (82)	24 (28)	21 (10)	0.0029 (nd)	0.03 (nd)	0.053 (nd)	3 (0)
	Sterols and hormones							
5	11-ketotestosterone	na	na	na	na	na	na	na
5	17-*alpha*-estradiol	na	na	na	na	na	na	na
5	17-*alpha*-ethynyl estradiol	na	na	na	na	na	na	na
5	17-*beta*-estradiol	na	na	na	na	na	na	na
5	19-norethisterone	na	na	na	na	na	na	na
3,4	3-*beta*-coprostanol	85 (88)	25 (23)	21 (7)	0.2 (nd)	0.338 (nd)	0.73 (nd)	6 (0)
5	3-*beta*-coprostanol	na	na	na	na	na	na	na
5	4-androstene-3,17-dione	na	na	na	na	na	na	na
3,4	*beta*-sitosterol	65 (89)	35 (41)	21 (7)	0.59 (nd)	0.895 (nd)	1.2 (nd)	2 (0)
3,4	*beta*-stigmastanol	72 (77)	35 (24)	21 (7)	0.46 (nd)	0.726 (nd)	1.2 (nd)	2 (0)
3,4	Cholesterol	77 (81)	26 (39)	21 (9)	0.31 (nd)	0.74 (nd)	1.9 (nd)	6 (0)
5	Cholesterol	na	na	na	na	na	na	na
5	*cis*-androsterone	na	na	na	na	na	na	na
5	diethylstilbestrol	na	na	na	na	na	na	na
5	Epitestosterone	na	na	na	na	na	na	na
5	Equilenin	na	na	na	na	na	na	na
5	Equilin	na	na	na	na	na	na	na
5	Estriol	na	na	na	na	na	na	na
5	Estrone	na	na	na	na	na	na	na
5	Mestranol	na	na	na	na	na	na	na
5	Progesterone	na	na	na	na	na	na	na
5	Stanalone	na	na	na	na	na	na	na
5	Testosterone	na	na	na	na	na	na	na
5	Trenbolone	na	na	na	na	na	na	na

[1]there were 39, 108, 23, and 11 laboratory blank samples analyzed for methods 1-4 respectively.

Appendix 3. Quality assurance summary for laboratory surrogate compounds in samples analyzed with field samples, Minnesota, 2000-02

[value in parentheses is for method 4]

Method	Surrogate compound	Average percent recovery	Relative standard deviation
Method 1	Caffeine $^{13}C_3$	100	14
	Ethyl nicotinate d_4	73	33
Methods 3 and 4	Decafluorobiphenyl	84 (27)	48 (48)
	Caffeine $^{13}C_3$	93 (40)	77 (28)
	Flouoranthene - d_{10}	92 (32)	77 (31)
	Bisphenol-A - d_3	73 (56)	71 (57)
Method 5	17-beta-estradiol d_4	134	64
	Testosterone d_3	141	37
	Cholesterol d_7	171	51

Appendix 4. Quality assurance summary of field replicates and blanks, Minnesota, 2000-02

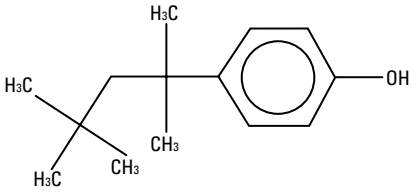
[Only those O ey research methods,
and Method 3 is an official U.S. Geolgoical Survey production method. There were 5 replicates and 13 blanks analyzed by USGS method 1; 7 replicates and 9 blanks analyzed by USGS
µg/L, micrograms per liter; -- not applicable; Relative Standard Deviation calculated using replicates with detections in both samples].

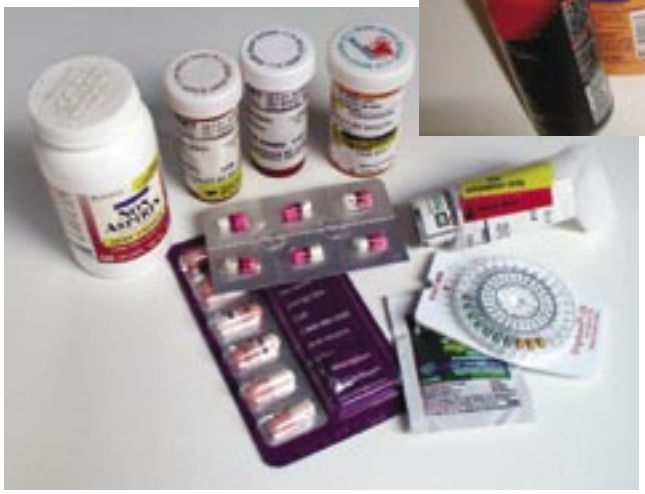
Analytical Method	Organic wastewater compound	Field replicate sample summary						Field blank sample summary	
		Relative standard deviations			Number of replicate pairs with:				
		Minimum	Average	Maximum	Detections in both samples	Nondetections in both samples	Inconsistent detections between samples	Number of blanks with a detection	Concentration range in blanks (µg/L)
Pharmaceuticals									
1	1,7-dimethylxanthine	5.2	8.8	12.5	2	2	1		
1	Caffeine	3.0	11.1	24.7	3	2	0	4	0.0023-0.0084
3, 4	Caffeine	2.3	7.1	17.1	4	5	0		
1	Carbamazepine	0.9	6.8	16.5	3	2	0		
1	Codeine	--	--	10.1	1	3	1		
1	Cotinine	5.2	10.9	20.8	3	1	1		
3, 4	Cotinine	19.4	19.8	20.2	3	6	0		
1	Diltiazem	5.2	12.0	22.3	3	2	0		
1	Diphenhydramine	8.4	14.7	24.7	4	1	0		
1	Ranitidine	--	--	2.3	1	4	0		
1	Trimethoprim	1.7	4.2	6.1	3	2	0		
Antibiotics									
2	Ciprofloxacin	--	--	--	0	6	1		
2	Erythromycin-H_2O	2.5	14.3	43.5	5	2	0		
2	Sulfadimethoxine	--	--	--	0	6	1		
2	Sulfamethizole	--	--	9.4	1	6	0		
1	Sulfamethoxazole	4.2	10.7	17.1	2	3	0		
2	Tetracycline	--	--	--	0	5	2		
1	Trimethoprim	1.7	4.2	6.1	3	2	0		
2	Trimethoprim	0.0	10.1	20.2	3	4	0		
Household, industrial, and agricultural-use compounds									
3, 4	1,4-dichlorobenzene	0.0	6.0	10.9	5	4	0		
3, 4	3-methyl-1H-indole (skatol)	2.5	28.0	53.5	2	7	0	1	0.024
3, 4	4-*tert*-octylphenol	--	--	7.4	1	7	1		
3, 4	5-methyl-1H-benzotriazole	2.2	6.3	12.4	5	4	0		
3, 4	Acetophenone	--	--	6.4	1	8	0		
3, 4	Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	3.5	8.6	18.0	6	3	0	1	0.24
3, 4	Anthraquinone	0.0	8.5	16.6	4	4	1		
3, 4	Benzo[*a*]pyrene	--	--	--	0	8	1		
3, 4	Benzophenone	0.0	4.8	8.8	5	4	0		
3, 4	Bisphenol-A	4.3	10.5	18.6	4	4	1		
3, 4	Bromacil	--	--	0.0	1	8	0		
3, 4	Bromoform	0.0	6.0	21.8	7	2	0		
3, 4	Diazinon	--	--	8.0	1	6	2		
3, 4	Fluoranthene	--	--	--	0	8	1		
3, 4	Hexahydrohexamethyl-cyclo-pentabenzopyran (HHCB)	0.0	4.5	11.5	6	3	0		
3, 4	Indole	--	--	20.2	1	8	0		
3, 4	Isophorone	--	--	--	0	7	2	1	0.11
3, 4	Metolachlor	1.4	7.5	15.7	3	5	1		
3, 4	N,N-diethyl-meta-toluamide (DEET)	4.6	5.1	5.7	3	5	1		
3, 4	Nonylphenol diethoxylate(NP2EO)	4.0	7.7	18.4	5	4	0		
3, 4	Octylphenol, diethoxylate (OP2EO)	8.3	9.8	11.2	2	6	1		
3, 4	*para*-cresol total	0.0	6.2	19.2	4	5	0		
3, 4	*para*-nonylphenol (NP)	6.0	8.6	11.2	2	7	0		

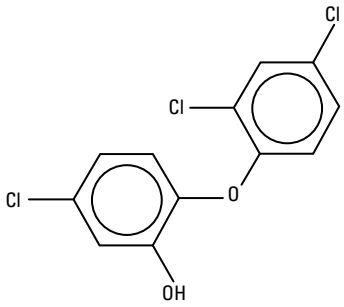
Appendix 4. Quality assurance summary of field replicates and blanks, Minnesota, 2000-02—Continued

[Only those O ey research methods,
and Method 3 is an official U.S. Geolgoical Survey production method. There were 5 replicates and 13 blanks analyzed by USGS method 1; 7 replicates and 9 blanks analyzed by USGS
µg/L, micrograms per liter; -- not applicable; Relative Standard Deviation calculated using replicates with detections in both samples].

Analytical Method	Organic wastewater compound	Field replicate sample summary						Field blank sample summary	
		Relative standard deviations			Number of replicate pairs with:				
		Minimum	Average	Maximum	Detections in both samples	Nondetections in both samples	Inconsistent detections between samples	Number of blanks with a detection	Concentration range in blanks (µg/L)
3, 4	Pentachlorophenol	1.5	13.4	27.5	4	5	0		
3, 4	Phenol	1.1	26.2	61.2	6	3	0	5	0.36-1.9
3, 4	Pyrene	--	--	--	0	8	1		
3, 4	Tetrachloroethylene (TCE)	2.6	8.8	12.3	3	6	0		
3, 4	Tri(2-butoxyethyl)phosphate	5.3	5.9	7.1	4	5	0		
3, 4	Tri(2-chloroethyl)phosphate	1.2	3.3	6.1	6	3	0		
3, 4	Tributyl phosphate	4.8	7.0	9.4	5	4	0	1	0.093
3, 4	Triclosan	4.5	8.6	19.0	4	5	0		
3, 4	Tri(dichlorisopropyl)phosphate	2.2	6.4	10.8	6	3	0		
3, 4	Triethyl citrate (ethyl citrate)	3.9	9.0	15.1	5	3	1		
3, 4	Triphenyl phosphate	0.8	4.7	8.5	2	6	1		
	Hormones and sterols								
3, 4	3-*beta*-coprostanol	15.7	40.6	99.8	3	4	2		
5	3-*beta*-coprostanol	29.6	30.9	32.2	2	1	1	2	0.004-0.069
3, 4	*beta*-sitosterol	2.5	9.1	15.7	2	4	3		
3, 4	*beta*-stigmastanol	--	--	--	0	8	1		
3, 4	Cholesterol	5.4	37.0	101.1	3	0	6		
5	Cholesterol	9.0	41.5	86.2	3	0	1	7	0.001-0.036
5	*cis*-androsterone	--	--	--	0	4	0	1	0.003
5	Stanalone	--	--	11.1	0	1	3		







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FINAL REPORT

APRIL 2007

INTEGRATED CHEMICAL AND BIOLOGICAL STUDY TO DEFINE THE OCCURRENCE OF INTERSEXUALITY IN MINNESOTA FISH WITHIN THE MISSISSIPPI RIVER: ASSESSMENT OF FISH HEALTH

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June 9, 2006 through April 30, 2007

SYNOPSIS

Endocrine disrupting compounds and their effects have been repeatedly measured in many locations along the Upper Mississippi River. However, no study had conducted an integrated survey of fish health and water and sediment chemistry load to encompass the entire Minnesota portion of the Mississippi River. As a result, the extent of endocrine disruption in the Upper Mississippi River and its frequency in different fish species was unknown. In this study we tested the hypothesis that treated wastewater effluents contribute significantly to the occurrence of endocrine disruption in Mississippi River fishes. The specific objectives of this study were:

(1) To determine the frequency of occurrence of intersex in four species of Mississippi River fishes.

(2) To determine the occurrence of plasma vitellogenin in male fishes commonly found in the Mississippi River.

(3) To assess whether occurrence of signs of endocrine disruption in the Mississippi River is correlated with major treated wastewater influents into the river.

Between June and September 2006 we collected almost 600 fish of four species: Redhorse, carp, smallmouth bass and walleye along 42 sites in the Mississippi River from upstream of Bemidji to near the Iowa border (Figure 1). We found that sex ratios did not differ between species and were roughly equal across the study (Figure 2). We also determined that plasma vitellogenin concentrations, an indication of a fish's acute exposure to endocrine disrupting compounds, were generally low in fish caught upstream of the St. Cloud Twin Cities urban corridor (with a few notable exceptions) but were largely elevated past the Twin Cities Metropolitan Area (Figure 3/4). In contrast to previous studies, we did not find any intersex condition among the sampled fish. Finally, we found that smallmouth bass were more sensitive to vitellogenin induction than redhorse and carp, the other two species of fish with large enough sample numbers to allow for comparison.

Figure 1. Sampling locations for longitudinal study of the occurrence of endocrine disruption in Mississippi River fishes.

SUMMARY OF STUDY

Between June 27 and August 21, 2006 we attempted to collect walleye, smallmouth bass, redhorse, and carp from 42 sites along the Mississippi River from upstream of Bemidji to the Iowa border. The two sampling months were noteworthy for their extremely dry conditions with average below normal precipitation totals for the State of Minnesota between 1-2.5" for each of the two months. Conversely, temperatures averaged 3-7ºF above normal for July and 2-5ºF for August 2006. As a result, the collection efforts were influenced by rapidly falling water levels and increasing water temperatures during the collection teams descent from Bemidji to the Iowa border. During the collection an effort was made to return collected fish samples (blood, testis, livers) to the laboratory with 15 hours but not more than 36 hours from the collection time. All specimens were maintained on ice until they could be processed according to analysis needs in the laboratory. The collection of samples from each fish proceeded as follows: the fish was stunned by the electrical current emitted by the electro shocking boat, netted and placed into a tub containing 2% clove oil (a fish anesthetic). Once sedated, a blood sample was drawn from the caudal vasculature (3-5mL) and transferred into a hematocrit tube which was stored on wet ice. The fish was then sacrificed. Within an hour of collection, all fish were processed near the collection site. Weight, total and standard length were recorded for each fish, as were weight of extirpated livers and testis. Scales were collected for later age determination. The abdominal cavity was opened, several liver samples were taken for later histological analysis, and placed into histo cassettes. In male fish, both testis were removed and a representative sample from anterior, middle, and posterior section of each testis was taken, marked with an ink for later identification, and placed into a histo cassette. In total, three histo cassettes were prepared from each male fish (liver, left testis, right testis). If gravid ovaries were present in the abdominal cavity, the sex was noted on the data sheets as female, but no attempt was made to weigh or collect these tissues for later histological analysis. The rationale for the exclusion of female reproductive tissue was that a clearly gravid female ovary was too fragile to be removed intact and that its histological analysis would not yield any further informational value. All histo cassettes

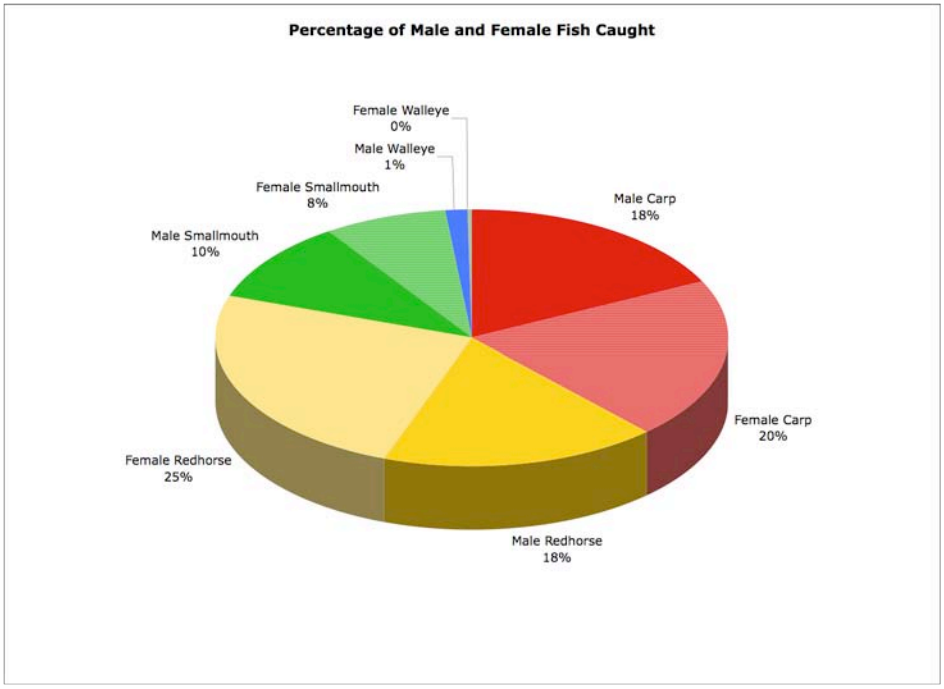
were then placed into a site-specific container with 4% formalin. Finally, a fillet was taken from each fish, wrapped in clean aluminum foil and placed on wet ice.
Upon return of the samples to the St. Cloud State University Aquatic Toxicology Laboratory, all samples were further processed. Whole blood samples in their hematocrit tubes were centrifuged for 5 minutes at 12,000 rpm before two aliquots of plasma were decanted. Almost all fish yielded enough plasma to collect two aliquots with more than 1ml plasma each. Aliquots were stored in two separate -80ºC freezer for the duration of the study. Blood plasma samples of carp and Redhorse were analyzed for plasma vitellogenin using a commercially available vitellogenin ELISA kit for carp with good cross-reactivity for redhorse. A special antibody for stripped bass was purchased to analyze vitellogenin concentrations in smallmouth bass plasma. Histo cassettes were further processed in a Leica tissue processor following an established histological protocol of dehydration and embedding in paraffin wax. Once embedded histological sections (3 per histo cassette) were produced and stained with H& E (2 sections) and reticular stains (1 section). Fish fillets were cataloged and stored in a -80ºC freezer as voucher specimens.

SUMMARY OF RESULTS

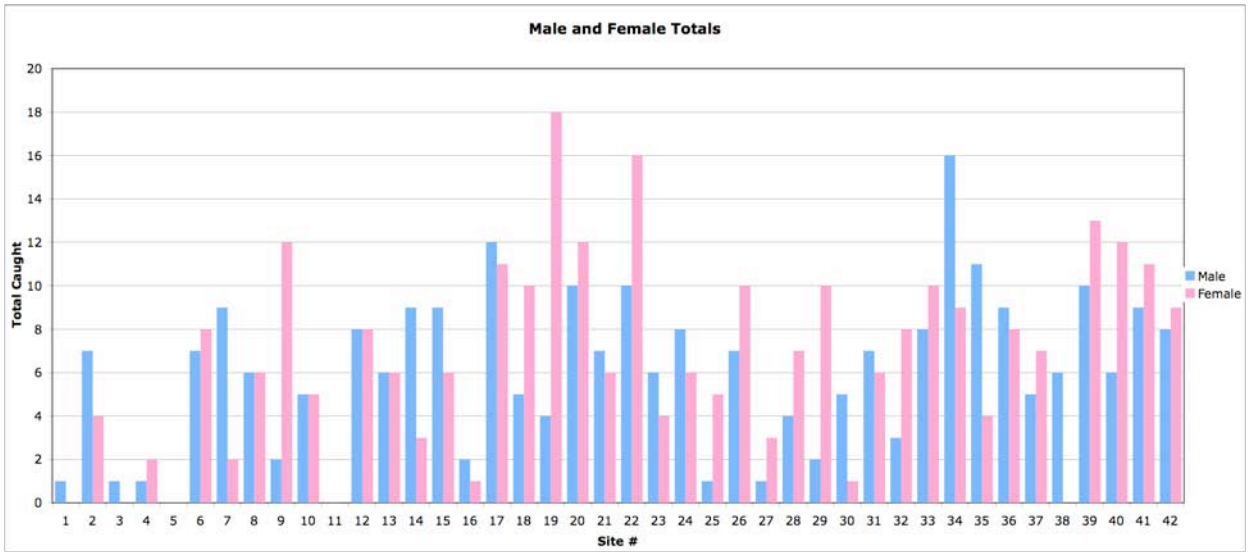
Fish Collection and Sex Ratio. We collected nearly 600 fish in the course of the study (Figure 2). Redhorse, carp and smallmouth bass were collected in sufficient numbers to be included in subsequent analysis. Due to the warm weather conditions, walleye retreated to deeper waters and were caught only infrequently. Several sites did not yield any fish due to the inaccessibility of sites with falling water levels. All sites that did not yield fish during the first collection effort were visited a second time near the end of the collection effort, however in most cases the second effort proofed to be as unsuccessful as the first attempt.

Figure 2. Sex ratios and fish numbers for 42 sampling sites on the Upper Mississippi River. (A) Summary. (B) Males/females per collection site.

(A)



(B)



Plasma Vitellogenin Concentrations. Plasma vitellogenin was measured in all fish collected in this study. Almost all female fish collected were vitellogenic with carp registering much higher plasma vitellogenin concentrations (20-160 mg/mL) than females of the other two species (2-200 µg/mL) (Figure 3; Figure 4a). Male fish of all three species were found to be less vitellogenic, but did exhibit plasma vitellogenin in measurable concentrations at several sites, especially along the urban corridor from St. Cloud to the Twin Cities as well as downstream of the Twin Cities to the Iowa border (Figure 3; Figure 4b).

Figure 3. Five highest plasma vitellogenin averages in male fish from each species.

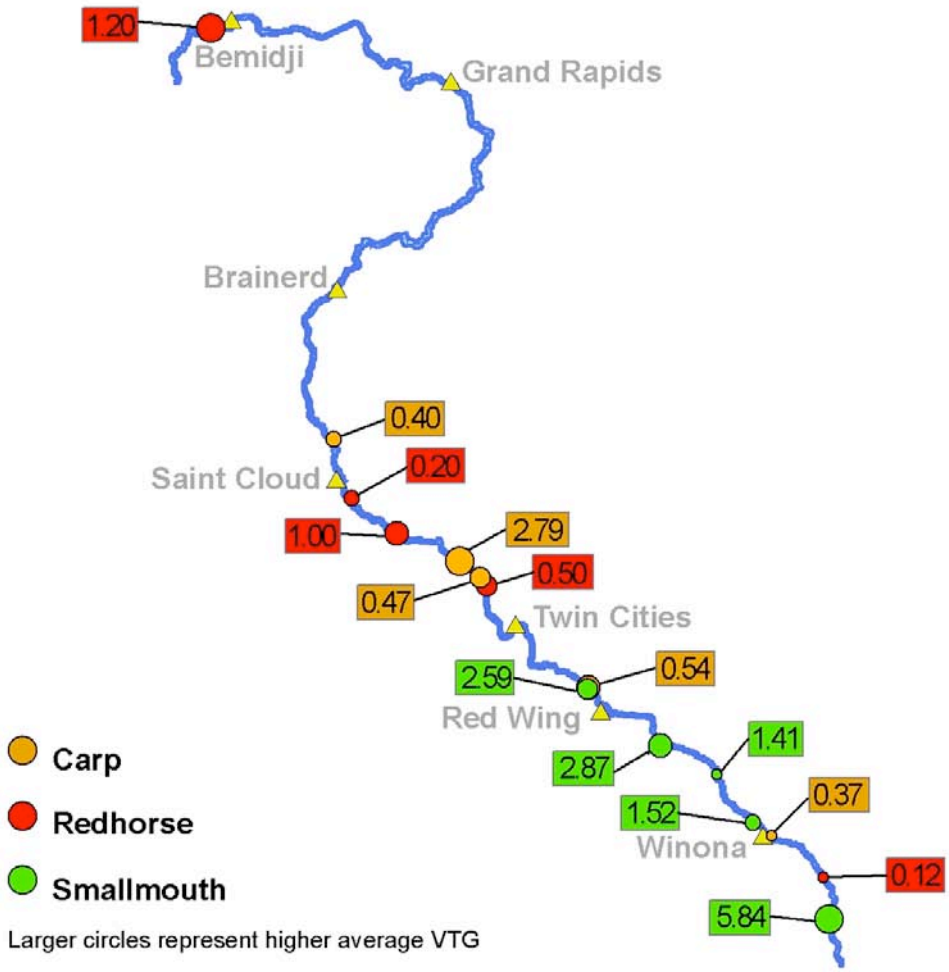
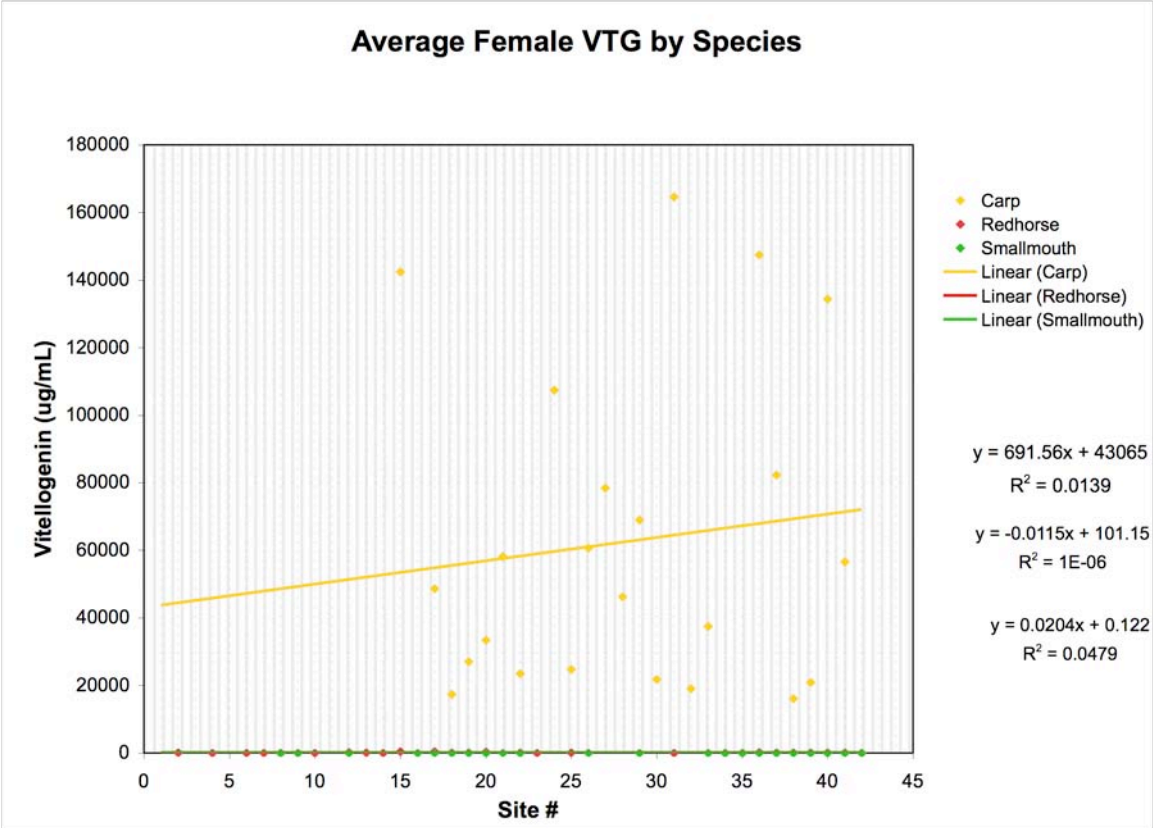
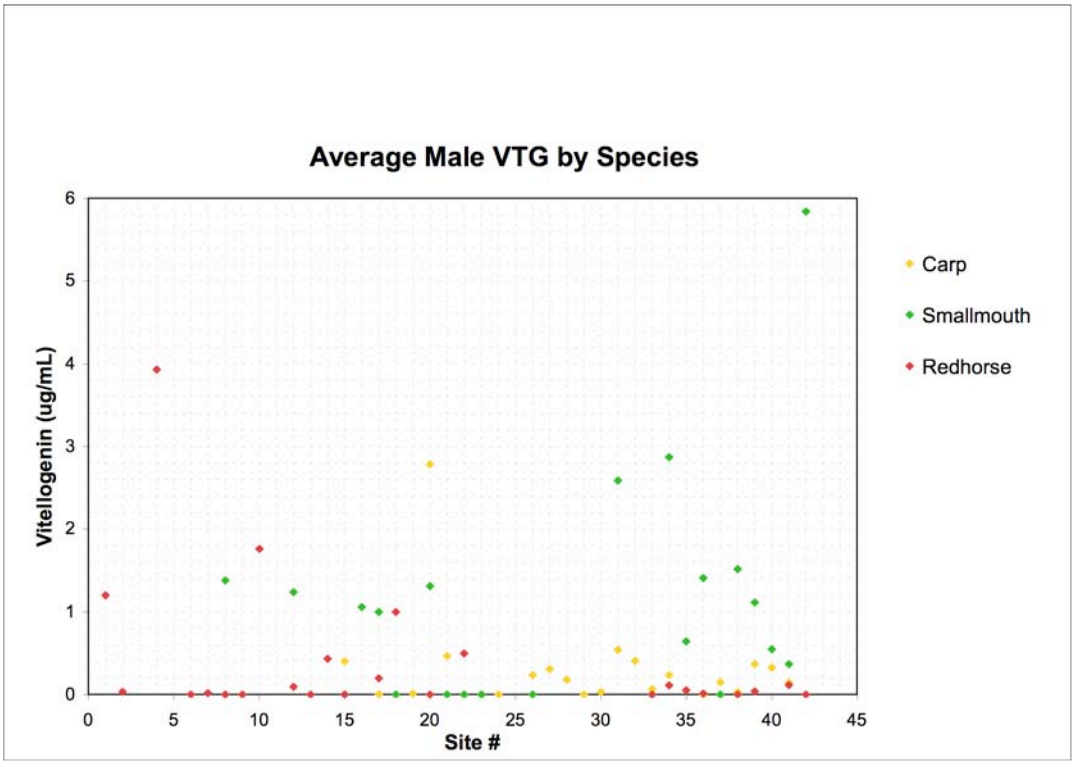


Figure 4. Plasma vitellogenin concentrations (A) female fish; (B) male fish.





Histological Analysis. Testis of all male (or perceived male) fish were extirpated and processed for histological analysis. 96 carp, 96 redhorse and 56 smallmouth bass were identified as being anatomically male. The reproductive condition of the fish indicated that carp were spermiating, redhorse were past reproductive activity and smallmouth bass were nearing the end of spermiation. As a result, redhorse testis were only analyzed for the occurrence of intersex, while carp and smallmouth testis were also evaluated for the state of spermiation and Sertoli cell proliferation. No intersex was found in any fish. Testis were analyzed across a matrix of parameters with each parameter being scored on a 0-3 scale by a trained observed. Seminiferous tubule Cohesiveness refers to the organization of these sperm producing tubules with 0 indicating no degeneration of tubules and 3 complete breakdown of tubular structure. A 0-3 scale was also applied to the abundance of early gametic cells (Spermatogonia) and completely developed sperm (Spermatozoa) with 0 indicating absence and 3 indicating great abundance of these cells. Sertoli cell abundance was also measured as these are generally non-proliferating support cells of the seminiferous tubules that are know to proliferate (higher score on 0-3 scale) in the presence of environmental pollutants.

Table 1. Testis development in male carp and smallmouth bass.

Parameter	Carp ± Stand. Dev.	Bass ± Stand. Dev.
Seminiferous Tubule Cohesiveness	0.67 ± 0.66	0.31 ± 0.65
Spermatogonia	0.99 ± 0.78	0.02 ± 0.14
Spermatozoa	2.6 ± 0.59	0.49 ± 0.54
Sertoli Cells	0.49 ± 0.76	0.47 ± 0.82

DISCUSSION

This study tested the hypotheses that treated wastewater effluents contribute significantly to the occurrence of endocrine disruption in Mississippi River fishes. Forty-two sites along the river were selected for collection of four species of fish. We were

unable to catch walleye due to the above normal air and water temperatures and the below normal precipitation during the collection months. We collected sufficient numbers of carp, redhorse and smallmouth bass to test our hypothesis. Our results indicate that male fish in the Upper Mississippi River are exposed to environmental estrogens that result in measurable plasma vitellogenin in male fish from many sampling sites. Most of these sites were located in the lower half of the sampling site, roughly beginning in the St. Cloud Twin Cities corridor and extending to the Iowa border. These sites coincide with much greater anthropogenic impact and resultant treated wastewater discharge than the sites upstream of St. Cloud, MN. Interestingly, one site in Bemidji, MN also exhibited relatively high plasma vitellogenin concentrations in male fish. This may be related to the sampling location just downstream of the Bemidji Wastewater Treatment Plant and the much smaller dilution factor through Mississippi River water at this site. In summary, our data corroborate the hypothesis that anthropogenic effluents may be responsible for some of the emerging contaminant impacts on aquatic organisms.

By comparing three species of fish widely found in the Mississippi River, we were also able to determine that their response to the acute exposure to environmental estrogens varies significantly. Male smallmouth bass exhibited much higher plasma vitellogenin concentrations than males of the other two species at the same sites. This suggests that smallmouth bass may be an excellent candidate to serve as a sentinel for emerging contaminant studies on wild fish in Minnesota waters.

In contrast to previous studies, no intersex was observed in any collected fish, even at sites with relatively high male plasma vitellogenin concentrations. Seminiferous tubule organization was usually well preserved and did not indicate structural problems. Furthermore, Sertoli cell numbers were similar between carp and smallmouth bass despite the differing reproductive status of the two species at the time of collection. Sertoli cells are nonproliferating support cells of the seminiferous tubules that protect and nurture the proliferating gametes (from Spermatogonia to Spermatozoa). Thus Sertoli cells provide an "internal control" for the health of the seminiferous tubule independent of the status of gametogenesis (sperm production) which can vary widely between species and seasons. Sertoli cells are known to proliferate if the testis are

severely impacted by environmental estrogens and our data indicate that this appears not to be the case in the collected specimens. Finally, sex ratios did not differ from the expected 50:50 ratio, further indicating that the effects of environmental estrogens and other emerging contaminants are either limited in geographic distribution or are not severe enough to cause population-level bias in sex ratios.

In summary, the Upper Mississippi River, upstream of St. Cloud appears to be little impacted by emerging contaminants, with the exception of "hotspots" at sites experiencing specific anthropogenic influx (i.e., municipal treated wastewater effluent discharge). However, the prevalence of plasma vitellogenin in fishes downstream of St. Cloud and more pronounced downstream of the Twin Cities should serve as a cautionary note that emerging contaminants may affect large portions of the Mississippi River in Minnesota and may have population level effects of unknown consequences in the future. The lack of intersex in any of the analyzed fish is contrary to previous reports at several of the sampled sites (which were matched to coincide with reports of intersex in smallmouth bass in previous studies). Several explanations may account for this discrepancy and would require further study to be explored: (1) Sampling bias - this is an unlikely explanation as we collected in the same month and location as previous studies reporting up to 100% intersex in male smallmouth bass. (2) Water quality improvements - it is possible that improved wastewater treatment methods and reduced production and disposal of alkylphenols (a major source of environmental estrogens) resulted in a reduction in the total estrogenicity of the Mississippi River downstream of the Twin Cities. A closer analysis of water and sediment sample data may be able to explore this explanation. (3) Resistance in fishes - it is possible that intersexed fish contribute less offspring to the fish population. As a consequence of this selective pressure the population may shift to a more estrogen-resistant genotype over several generations. We will test a component of this hypothesis in an upcoming study funded by the State of MN through the LCCMR program.

In the coming months we will be integrating our biological data set with sediment and water chemistry data collected in a parallel study concurrently at the same field sites. Our preliminary review indicates a high degree of consistency between these data sets

and should allow us to further strengthen the link between anthropogenic pollution and fish health effects in Minnesota waters.

RECOMMENDATIONS

(1) It is difficult to fully assess the effects of emerging contaminants on the health of fish populations without a complete understanding of the sources and fate of these compounds in the aquatic environment. This is difficult to achieve in a riverine system as large as the Mississippi River and could more readily be accomplished in smaller tributaries. The MN PCA has already provided funding for such a study and result are expected within a year.

(2) The biological consequences of emerging contaminant exposures are still poorly understood and further studies are necessary to elucidate the extend of these effects beyond the individual organism to the population level. The Legislative-Citizen Commission for MN Resources has given provisional approval to fund a population-genetics study that would begin such an analysis.

(3) Expanding studies of emerging contaminants beyond major municipal wastewater treatment plants is necessary to fully gauge the impact of these chemicals on Minnesota aquatic life. Preliminary discussions with the MN PCA to develop mobile exposure laboratory unit to investigate signs of emerging contaminant effects around the State may result in one approach to address this issue.

(4) Addressing emerging contaminant issues from a holistic mixture perspective appears to be needed to safeguard the aquatic environment from the adverse effects of these chemicals which always occur in mixtures that are often predictable in composition and relative concentration.

ACKNOWLEDGMENT

I would like to thank Kathy Lee and Larry Barber for helpful comments in the design of this study and their continued scientific expertise which greatly benefits the quality of my studies.

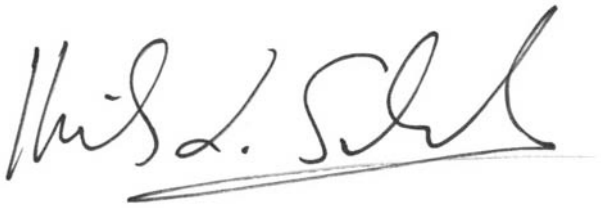
DISSEMINATION OF RESULTS

To date, preliminary data from this MN PCA funded study have been presented in several forums to the scientific and general public:

- January 2007 - MN House Natural Resources Finance Subcommittee - presentation by HL Schoenfuss.
- March 2007 - Midwest meeting of the Society for Environmental Toxicology & Chemistry, Chicago, IL - oral presentation by Nathan Jahns, graduate student in the SCSU Aquatic Toxicology Laboratory.
- March 2007 - MN meeting of the American Fisheries Society, St. Cloud, MN - oral presentation by Nathan Jahns, graduate student in the SCSU Aquatic Toxicology Laboratory.
- April 2007 - Bemidji League of Women Voters Earth Day Events - presentation by HL Schoenfuss.

A manuscript will be prepared later this summer for publication and reprints will be made available to the MN PCA.

Final report respectfully submitted on April 30, 2007,



Heiko L. Schoenfuss
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Appendix G

Summary of EPA Endocrine Disruptor Screening Program and Endocrine Disruptor Screening and Testing Committee

Since 1996, the EPA has been developing the Endocrine Disruptor Screening Program (EDSP) in response to two Congressional mandates. The 1996 Food Quality Protection Act (FQPA) gave the EPA the authority to test all pesticide chemicals and any other chemicals that may have effects "cumulative to the effects of pesticide chemicals". In addition, the 1996 amendments to the Safe Drinking Water Act (SDWA) gave the EPA the authority to test any chemicals found in drinking water for endocrine disrupting potential. Additional testing authority is given under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the Toxic Substances Control Act (TSCA). The Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) was chartered under the Federal Food, Drug, and Cosmetic Act (FFDCA) to aid EPA in fulfilling these Congressional mandates.

The EDSP has three primary components:

- Prioritization of chemicals for screening and testing
- Development and validation of assays
- Development of policies and procedures to require testing

The EDSP is developing and validating screening methods and assays to determine the potential estrogenic, androgenic, and thyroid effects of a chemical. The chemical screening process is a two-tiered approach. Tier 1 screening will identify chemicals with endocrine disrupting potential. Tier 2 testing will then determine effects related to endocrine disruption and provide information about the endocrine effects of specific chemicals at various doses. Following validation to assess the relevance and reliability of a test method, all assays will be subjected to scientific peer review.

Tier 1 and Tier 2 screens and assays are being developed and validated by multiple agencies and laboratories around the world. For example, a Tier 1 fish *in vivo* assay is being tested and validated by 14 laboratories in 7 countries. This is a major collaborative effort. Currently, several assays are in the pre-validation process. Only a few assays have been validated or have moved into the validation phase.

The EPA recently released the Draft List of Initial Pesticide Active Ingredients and Pesticide Inerts to be Considered for Screening under the Federal Food, Drug, and Cosmetic Act in the June 18, 2007 Federal Register. The list is comprised of 73 pesticide active and inert ingredients that will eventually undergo Tier 1 screening. The list is currently open for public comment until February 11, 2008.

The EPA is also in the process of evaluating the feasibility of using High Throughput Screening (HTPS) as a way to "pre-screen" thousands of chemicals for estrogenic and androgenic activity. HTPS is used by agrochemical and pharmaceutical industries to identify desirable or undesirable effects of a chemical, as well as a chemical's commercial potential. A feasibility study was conducted by the EPA in 2000 determined that HTPS technology and assays are not adequately developed for regulatory purposes at this time.

Quantitative Structure Activity Relationship (QSAR) computer models can be used to predict a chemical's behavior based on its structure. QSARs can be used to determine the how well a

chemical will fit into estrogen and androgen receptors based on structure (i.e. binding affinity). QSARs may eventually be used as a screening tool, but they are not adequately developed for regulatory purposes.

Recent budget cuts mean that fewer resources will be devoted to the EDSP which will greatly slow the pace of assay development and validation. Also, studies of potential EDCs in air were cut and an effort to develop risk assessment guidance was cancelled. Research emphasis will now be directed toward interpreting data for risk assessment.

Appendix H

Costs of Upgrading Wastewater Treatment Plants to Treat Endocrine Disrupting Compounds Using Granular Activated Carbon

Biological wastewater treatment plants function to aerobically, or in some cases anaerobically, degrade or transform organic materials and compounds, including organic compound EDCs, into smaller or low molecular weight molecules and into biomass that is attached to particulate matter. These organic molecules, or molecules attached to biomass, are then removed from the water phase by settling the biomass. For metals that are endocrine disruptive, they are removed primarily through the settling processes used at wastewater treatment facilities, although in limited cases metals may also be removed by chemical precipitation technologies. Chemical precipitation technologies are primarily used at industrial wastewater facilities where biological treatment may not be used, or as an addition to biological wastewater treatment systems.

As previously indicated wastewater treatment plants are only partially effective in the biodegradation and removal of EDCs. There are differences in the capability to degrade EDCs depending on the type of wastewater treatment processes used. For example, high rate or extended aeration activated sludge plants are somewhat more effective in removal of organic EDCs than other wastewater treatment plants. In some cases certain EDCs partially breakdown during treatment to form other endocrine disrupting compounds, such as the APE compounds degrading partially to alkylphenols. In some cases precursor compounds, such as the perfluorosurfactants and fluorotelemor alcohols found in various products discharged to sewer systems, may biotransform into other fluorochemicals that cause endocrine disruption and are more persistent. And in some instances, as in the case of fluorochemicals, there may be actual increases in levels of certain fluorochemical EDCs through the wastewater treatment process.

To effectively remove all the types of EDCs present in wastewater effluents consecutive treatment technologies may be required. However, since most of the EDCs present are organic compounds, the best available technology that is economically feasible to remove EDCs would be granular activated carbon (GAC) technology or treatment. GAC has been used very successfully for treatment of municipal and industrial wastewater effluents. GAC is used to adsorb relatively small concentrations of soluble organic compounds, and certain inorganic compounds, including some heavy metals,that remain in the wastewater following biological or physical/chemical treatment. GAC systems are placed at the end of the treatment plant and receive the effluent before it is discharged. Adsorption in the GAC occurs when the molecules adhere to the internal wall pores in carbon particles. GAC is very effective at removal of very low concentrations of organic compounds, generally to acceptable discharge standards or concentrations. However, the process may not always completely remove organics to non-detect levels. There are differences in the removal efficiency of specific EDC compounds through GAC systems, and the type of carbon used and the GAC design parameters may be adjusted in a particular effluent to maximize removal EDC efficiencies.

GAC systems are generally composed of carbon contactors or modules, with variations in the way in which they are operated. For wastewater treatment effluents, typically sand filtration is used ahead of the GAC system to remove particulate matter that may cause the GAC system to “foul” or become plugged, and therefore rendered less effective. The carbon modules are placed in series to allow monitoring of breakthrough of the compounds being removed. When the carbon is “spent”, as demonstrated by the breakthrough of compounds monitored, the carbon is replaced. The carbon is typically thermally regenerated to remove the adsorbed organics via a separate facility. The compounds are captured or destroyed in thermal regeneration.

GAC systems are relatively expensive. The estimated capital cost for a GAC system treating a relatively low effluent flow rate of 100,000 gallons per day, or a small wastewater treatment plant, is about $300,000. The estimated annual operating and maintenance (O and M) costs for this plant are estimated at about $40,000 to $70,000. The annual O and M costs are variable depending on the amount of carbon required to be changed annually. The estimated capital cost for a GAC system treating a larger wastewater treatment plant effluent flow rate of 1.0 million gallons per day is about $800,000 to $1.0 million, with annual O and M costs estimated at between $70,000 and $100,000. If these systems require sand filtration ahead of the GAC systems, the capital costs would be increased by a factor of about 25-30%, and O and M would be increased by a factor of about 10%.

Although GAC systems will remove some metallic EDCs, especially those attached to or complexed with organic compounds, carbon will not effectively remove all metals. Metal removal can be enhanced, however, by sand filtration technology. If further metals removal is required beyond sand filtration chemical precipitation may be needed. It is not anticipated that chemical precipitation technology would be required to remove EDC complexed metals in municipal wastewater treatment plant effluents, however, further study would be required to definitively understand EDC removal efficiencies.