

ABSTRACT

JONES, SAMANTHA JANE. Pesticide Residues in Surface Waters of North Carolina Rural and Urban Watersheds: Studies to Determine and Reduce Residues in Drinking Water. (Under the direction of Ross B. Leidy)

The practice of using pesticides on agriculture, commercial landscapes, residential lawns, highway rights-of-way, and recreational areas such as golf courses has resulted in non-point source contamination of surface waters via runoff. Assessment of human health implications of non-point sources within watersheds involved residues of selected pesticides monitored from 1999 to 2001 in surface waters that serve as drinking water sources of five rural and urban watersheds in North Carolina. Approximately 1500 samples from 90 sites were screened with Enzyme-Linked Immunosorbent Assay (ELISA) for atrazine, alachlor, simazine, chlorpyrifos, chlorothalonil, metolachlor, and 2,4-D. The residue concentrations exceeding 1.0 µg/L were extracted with C₁₈ Empore™ Disks and analyzed by gas chromatography/nitrogen phosphorous detection (GC/NPD) for confirmation.

The seven compounds showed similar pesticide concentrations in both rural and urban watersheds. The rural watersheds most often exhibited residues of atrazine, simazine, and 2,4-D while metolachlor and 2,4-D were chiefly found in urban areas. Pesticides intermittently exceeded established maximum contaminant levels (MCL) and led to further monitoring of raw and finished waters of treatment plants within the watersheds. Atrazine, simazine, metolachlor, 2,4-D residues were found in pre- and post-treated water at comparable levels, indicating little change in pesticide concentrations following standard treatment procedures.

Remediation efforts focused on prevention of non-point sources of atrazine in a rural watershed. Atrazine residue levels were lowered as a result of source prevention implementation with the cooperation of municipalities, farming community, and county agricultural extension agents. The prevention measures involved alternatives to atrazine applications and utilizing either less-persistent pesticides or genetically modified seed.

Additional remediation efforts involved the adsorbent ability of powdered activated carbon (PAC) as a treatment method for reducing pesticide residues in drinking water supplies. Studies with PAC combined with water fortified with a pesticide mixture of atrazine, chlorpyrifos, simazine, and metolachlor exhibited declines in residues from 25 to 100% of initial concentrations with 10 mg/L of carbon. Aluminum sulfate (alum) was combined with PAC in studies with atrazine and metolachlor to determine effects of contact time on the adsorption of the pesticide residues. Carbon alone adsorbed 5 to 30% more pesticide residues than carbon and alum combined and alum alone had minimal effects on residues of atrazine and metolachlor.

Further carbon studies simulated treatment plant procedures to determine effective points of PAC addition within the treatment train of a model drinking water treatment plant. A carbon concentration of 20 mg/L was most efficient in reducing pesticides residues and carbon added prior to or after alum resulted in adsorption of atrazine, metolachlor, simazine, and alachlor residues that was more effective than simultaneous addition of the two chemicals.

**PESTICIDE RESIDUES IN SURFACE WATERS OF NORTH CAROLINA RURAL
AND URBAN WATERSHEDS: STUDIES TO DETERMINE AND REDUCE
RESIDUES IN DRINKING WATER**

by
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DEDICATION

for my parents, Jane and Leo
who have supported me in everything I have ever done
or wanted to do...

for my sister, Stephanie
my ponchey...

BIOGRAPHY

Samantha Jane Jones is best known as the first daughter born to Leo and Jane Jones on August 7, 1975 Kinston, North Carolina. She began her education at the age of five and never stopped. An interest in human health and medicine led to undergraduate studies in pre-pharmacy at Campbell University in Buies Creek, North Carolina. Although, many friendships and adventures were founded at Campbell, a career in pharmacy was not. A love for the lab and science in general steered Samantha towards a double major in chemistry and biology. With the decision of post-college life looming, a casual stroll through the chemistry hall and a perchance sighting of a “Careers in Toxicology” advertisement resulted in the discovery of a seemingly perfect blend of chemistry and biology which also included her early interest in human health. Samantha was accepted into the doctorate program of the Department of Environmental and Molecular Toxicology at North Carolina State University in Raleigh, North Carolina and began her graduate studies with a focus on pesticide residues in surface waters. Her time at NC State has culminated in five years of research, classes, paperwork, research, exams, presentations, and research. Samantha is currently in the process of completing her graduate work and therefore, unemployed.

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CHAPTER ONE

PESTICIDES: A BRIEF INTRODUCTION TO HISTORICAL AND CURRENT USES WITH ASSOCIATED ENVIRONMENTAL INFLUENCES AND EFFECTS

INTRODUCTION

Chemicals used to control pests have been an inherent component of our lives for many years with documentation dating back several thousand years (Ware 1983, Cutkomp 1994). It was discovered about 150 years ago that a number of natural chemicals had capabilities to control pests and consequently use of these compounds increased with applications in and around the home, on the farm and anywhere pest elimination was desired. These agents included lime, sulfur, oil of citronella, nicotine, and arsenicals used to control insects, while copper sulfate and sodium chloride were shown to control weeds (Ware 1983, Stevens and Sumner 1991, Cutkomp and Eesa 1994). These chemicals were used to control various pest species but continuing research has since grown to accommodate newly discovered compounds and led to the development of synthetic versions of many naturally occurring chemicals now broadly classified as pesticides.

In the 1940s a group of synthetic compounds classified as the organochlorines gained recognition and popularity as effective materials to control insects (i.e., insecticides) and were used extensively. Particular attention was given to 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl) ethane, the compound commonly referred to as DDT. Vector-borne diseases such as malaria and typhus were controlled by insecticides like DDT, which suppressed insects responsible for transmittance of these diseases. Environmental persistence, one of the major advantages of DDT, eventually resulted in manufacture and use restrictions in many countries. Although DDT use is prohibited in the U.S., Canada, and Europe, it is still heavily used in less-developed countries. (Hayes and Laws 1991, Smith 1991, Levi 1997b)

Organophosphates, another class of insecticides discovered in the early 1940s, proceeded to replace organochlorines as the mainstay for insect control. Organophosphates possessed much shorter half-lives than the persistent organochlorines. These new compounds work effectively against a wide range of insects; however, most of the organophosphates exhibit toxic effects in mammals. While environmental persistence is short-term, the hazards associated with these chemicals prompted additional discoveries in the insecticide realm, including carbamates and pyrethroids (Ware 1983, Smith 1991, Levi 1997b).

Carbamates are short-lived pesticides similar to organophosphates in persistence and mode of action and were also preferred over the organochlorines. (Ware 1983, Levi 1997b). Pyrethroids, based on the natural insecticide, pyrethrum, are stable and effective insecticides that are comparable to the organophosphates and carbamates. Since their discovery in the 1970s, pyrethroids have gained considerable popularity, most likely a result of their low toxicities, and use of these compounds has increased substantially (Cutkomp and Eesa 1994).

Herbicides, another classification of synthetic pesticides introduced in the 1940s and 50s were effective in controlling unwanted plant growth and included paraquat, chlorophenoxy compounds, and the triazines (Cutkomp and Eesa 1994, Levi 1997a). Considering chemical discoveries of the twentieth century, the evolution of pesticides has been remarkable with regard to the ultimate engineering of compound selectivity against pests resulting in some 28 classes of pesticides that exist today.

Whether natural or anthropogenic, pesticides are presently found in many types of sites or samples analyzed including water, soil, sediment, plant, and animal. The ubiquitous nature of pesticides is most likely due to the many roles they play. Pesticides are employed in scores of situations including: increasing crop yields and productivity, deterring diseases spread by transmitting insects (i.e., mosquitoes), beautification of parks and lawns, and maintenance of structural and recreational areas. Pesticide applications protect wood and stored grains by thwarting pests such as termites and rodents. Herbicides, initially developed for use in agriculture for control of annual grasses and weeds, are now used for weed removal along railroads and highways which assists in providing safe travel and as a benefit, an ordered and kempt appearance.

Lawn care has become a multi-billion dollar industry in itself, prompting the use of various chemicals to increase the aesthetics related to private lawns, commercial sites (e.g., shopping centers, industrial parks), and campuses. Some sports, like golf, require turf specialists to maintain the courses for presentation and use. These lawn care specialists are responsible for reducing insects, fungi, and weeds associated with the turf and pesticide applications are usually the treatment of choice.

CONSEQUENCES OF PESTICIDES

While pesticide use has been beneficial in many facets of everyday life, negative environmental occurrences are associated with pesticides. Rachel Carson's Silent Spring (1962), raised questions concerning the potential for

increasing adverse effects linked to pesticide applications. One of the most popular examples of an extensively used pesticide that later became a problem is DDT. This chemical was responsible for wildlife injuries including eggshell thinning, reduced hatching success and subsequently dwindling populations. Several species of predatory birds were affected by exposure to DDT (bald eagle, peregrine falcon, and brown pelican). Exposure risk to humans and wildlife was associated with neurotoxic properties and interference of nerve impulse transmission produced by this compound. DDT along with major metabolites, 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane (DDD) and 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (DDE) currently remain persistent in the environment even after cancellation in 1970. The organochlorine's potential to bioaccumulate within the food chain increases the threat posed to the environment and human population (Smith 1991, USFWS 2003).

Similarly, mercury has been known to cause poisonings in areas where seed grain was treated with mercuric pesticides to curb fungal growth. These occurrences have exhibited toxic effects in humans as well as wildlife (e.g., birds). Seed grain contaminated with mercury was consumed by humans in Iraq in 1971 and resulted in numerous poisonings (Levi 1997b). Feeding birds are also susceptible to adverse effects of mercury-coated grain and several species have experienced reduced reproduction and increased mortality. Affected bird species include loons, pelicans, raptors, and pelagic seabirds (Franson and Friend 1999).

Furthermore, Agent Orange, a herbicide used in Vietnam as a defoliant was contaminated with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) during manufacture and is thought by some to be responsible for health impairments of many veterans.

In laboratory studies, it has been concluded that TCDD is one of the most toxic substances known, in relation to laboratory animals. Therefore, unintentional or indirect contamination also contributes to the problems associated with pesticides (Levi 1997b).

Thus, the unfortunate consequences of pesticide use include wildlife distress, interference with reproduction, birth defects, and depressed immunity which detrimentally affects wildlife populations and on a larger scale the surrounding ecosystem. Human exposure to pesticides is usually through food, water, and the atmosphere. These multiple avenues of exposure, the chemical diversity of pesticides, and their popularity are a source of great concern especially in view of the fact that little information is available for most pesticides and their effects.

In light of these discoveries, well-meaning organizations have called for complete elimination of pesticide use. Realistically, a pragmatic compromise that recognizes the risks and benefits involved when using pesticides must prevail. Rachel Carson said it best when she claimed: "It is not my contention that chemical pesticides must never be used. I do contend that we have put poisonous and biologically potent chemicals indiscriminately into the hands of persons largely or wholly ignorant of their potential for harm" (1962). Following the release of Silent Spring, environmental studies characterizing the risks and benefits associated with pesticide use increased at a rapid rate.

One of the major acknowledgments to result from the attention garnered by Carson's book was the need for an agency to focus on chemical usage and environmental effects in the U.S. In 1970, this responsibility was passed to the

newly formed United States Environmental Protection Agency (USEPA). Most of the authority associated with pesticide regulation was handed over by the Food and Drug Administration (FDA) and United States Department of Agriculture (USDA) which were formerly responsible for all pesticide regulation. The USEPA became responsible for the registration and regulation of pesticides (Ware 1983, Cutkomp and Eesa 1994).

The USEPA leads the nation in the efforts to establish regulations which are enforced by federal law. With focus on “air, water, land, communities and ecosystems, and compliance and environmental stewardship”, this agency attempts to promote public and environmental health safety (USEPA 2003). With regard to pesticides, the USEPA is responsible for registration, regulation, labeling, and use classification for these chemicals. Additionally, tolerances of pesticides in food, air, and water are determined and regulated by the USEPA. Health risks associated with pesticide exposure to humans and wildlife are identified, examined, and considered for appropriate risk management. Ideally, proper estimation of risk will ultimately prevent unsafe pesticide exposure and the subsequent adverse effects to the general public and environment, while still allowing the beneficial uses of pesticides (Jones 1993, USEPA 2003).

PESTICIDES IN THE ENVIRONMENT

In the arena of environmental pesticide studies origins can be categorized as either point or non-point sources. With point sources, the locations of chemical introduction into the environment can be directly determined, whereas non-point

sources involve chemical input distributed over expansive areas. Point sources are exclusive, for example an accidental chemical spill or an industrial outfall. Those inputs that cannot be directly linked to a specific source culminate as non-point source contamination; examples include vehicle exhaust, runoff of agricultural and suburban chemical applications (Ross *et al.* 1996, Schreiber *et al.* 1996, Shea 1997, Walker *et al.* 2000, Stover and Hamill 2002).

Non-point sources include surface runoff from land surfaces such as fields, lawns, or watersheds. Runoff often contains materials that are either dissolved or suspended. Nearby pesticide applications can introduce residues into the runoff and can consequently reach surrounding water bodies (Wauchope 1978, Leonard 1990, Signorella *et al.* 1993, Smith *et al.* 1993, Gallagher *et al.* 1996). A chemical with a water solubility of 5 mg/L or greater is readily dissolved in runoff. The transportation of pesticides that have been dissolved in surface flow and some non-water soluble compounds (e.g., water solubility of 1 mg/L or less) sorbed to soil particles can be facilitated by runoff (Thurman *et al.* 1998).

Many factors affect runoff. Ground water infiltration is influenced by soil type, moisture, pore size, organic matter content, agricultural practices, and pesticide chemical structure. Surface water runoff is more dependent on rainfall, volatilization, watershed characterization and drift (Spongberg and Martin-Hayden 1997, Leidy 2000). Rainfall distribution and intensity become important factors in the magnitude of the transient pollution event (Shreiber *et al.* 1996). Rain can affect pesticide movements and the duration and intensity of precipitation will greatly influence the fate of the chemical.

Soil infiltration capacity can be severely reduced following more than one rain event. Once the infiltration capacity of the soil is reached then all rainfall becomes surface flow. A light rain, classified as less than 2.5 centimeters will diminish the pesticide residues present on land surfaces and two consecutive rain events will amplify the depletion of residues at the beginning of the second precipitation event (Gu *et al.* 1992, Shueler 1995, Leidy 2000, James Gregory 2001, personal communication). Soil characteristics such as pore size and organic carbon content as well as pesticide physicochemical properties will determine the extent of infiltration and mobility within and upon the surrounding soil.

Albanis *et al.* (1998) reported peak pesticide concentrations in estuarine areas that were located some distance from the application sites. They concluded compounds were traveling considerable distances as a result of dispersion by runoff and air advection. This was corroborated by studies in which pesticide transport was discovered and tracked in both rainfall and fog (Hayes and Laws 1991, Walker 1992, Shueler 1995, Goolsby *et al.* 1997).

This runoff concept is well accepted; modeling programs and agencies are devoted to predicting environmental fate based on this premise. In some cases, indices are assigned to determine potential environmental hazards like the Runoff Potential and Drinking Water (UPRDW) index (Black and Veatch 1994).

Environmental fate models such as the Fugacity and ChemCAN models aid in predicting fate of contaminants in the environment based upon physicochemical properties of the pesticide and characteristics of the area (e.g., soil/sediment organic carbon content, vapor pressure, and octanol-water partition coefficient) (Mackay *et*

al. 1985, Di Guardo *et al.* 1994, CEMC 1996, Damian Shea 2000, personal communication). There are hundreds of models available that work towards predicting the fates of pesticides within the environment and are used extensively by many researchers.

Additionally, irrigation must also be considered with chemical fate processes. Transport of pesticide residues into ground water is facilitated by irrigation of dry soils which possess heightened infiltration capacities (Kolpin *et al.* 1996). If allowed to operate for a sufficient time, irrigation is a possible contribution to runoff simply by replicating natural precipitation events.

Following application, pesticides can infiltrate ground water by leaching through soil to the water table and moving into aquifers. Leaching is influenced by the pesticide water solubility and formulation, temporal and spatial points of application, total amount of pesticide applied, temperature, soil pH and texture, and organic matter content (Leidy 2000). As water moves the contaminants below the water table into groundwater, several situations could occur. Pesticides are degraded or parent and metabolite compounds move into surface water that draws its main source from the groundwater. The latter situation results in both ground and surface water contamination.

Surface waters receiving runoff might experience diminished water quality and pesticide contaminants could eventually partition into sediment. It is possible to have simultaneous contamination within the water column and sediment layer. Chemicals that have moved into sediment may remain there or partition through it into groundwater (Thurman *et al.* 1991, Kimbrough and Litke 1998). Regardless of

the endpoint, once pesticides have left agricultural fields any number of water contaminations can occur. All forms of precipitation events may transport contaminants that result in diminished water quality. Water bodies receiving the contaminating runoff would then be a concern, especially for those who utilize these sources of water for consumption.

Many studies have looked at groundwater contamination as a result of pesticide runoff and other sources (Moreau 1990, Hamilton and Shedlock 1992, Kellogg and Wallace 1995, Laroche and Gallichard 1995, Leonard *et al.* 1995, Gallagher *et al.* 1996, Kolpin *et al.* 1996, Thurman and Meyer 1996b, Wade *et al.* 1997, Albanis *et al.* 1998, Kolpin *et al.* 2000). Although groundwater quality is an important issue many recent studies have focused on surface water and the contamination and water quality issues raised as a result of pesticide runoff. The potentially diminished water quality is a concern because many surface waters are used as the principal sources for municipally-supplied drinking water.

AGRICULTURAL BACKGROUND

Herbicides and insecticides have long been used to protect crops and have played a significant role in increasing U.S. agricultural production efficiency. In fact, more than 66% of national pesticide expenditure is agriculturally related (Feagley *et al.* 1992, Curtis 1995). The USEPA reported that pesticide applications in 1999 reached 1.24 billion pounds of active ingredient (a.i.) and of this, agricultural practices accounted for approximately 706 million pounds. A substantial sum of money is spent each year to purchase agrochemicals used in the United States.

The sales of herbicides and insecticides in 1999 reached 5.0 and 1.4 billion dollars, respectively (USEPA 2002b).

The abundant food supply in the United States would be greatly reduced without pesticides. They are considered to be key components of modern farming. Applications in the agricultural regions of the U.S. were extensive and rose continually from 1966 to early 1980s. Pesticide use seemed to decrease throughout most of the 1980s until usage began once again to climb in 1988 (Stamer and Zelt 1994). Upon reviewing the literature, pesticide use from 1989 to 1999 appeared to reach a plateau with U.S. applications of annual pesticide active ingredient ranging from 1.19 to 1.24 billion pounds (Stevens and Sumner 1991, USEPA 2002b).

Because agriculture is one of the major outlets for pesticide use and considering the extensive application of pesticides in the agricultural community, surface water contamination from agricultural runoff was suspected in areas surrounding crop fields. These areas became the focus of numerous studies in the 1980s. Several researchers performed environmental studies in the Midwestern United States (Cooper *et al.* 1987, Pereira and Rostad 1990, Thurman *et al.* 1990, Thurman *et al.* 1991, Goolsby *et al.* 1991a, Goolsby *et al.* 1991b, Pereira and Hostettler 1993, Shreiber *et al.* 1996, Stamer and Wieczorek 1996). Given that these states produce much of the nation's grain crops (e.g., corn and wheat), the discovery of possible surface water contamination due to surface runoff suggested these harvesting states were compromising the quality of their water.

These studies found widespread evidence of pesticides in surface waters. A commonly used herbicide, alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-

(methoxymethyl)acetamide] was reported as high as 6.3 µg/L in raw and finished, drinking waters of Columbus, Ohio (USEPA 1986). In the Mississippi, Missouri, and Ohio Rivers, metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide] was detected as low as 0.3 µg/L and at an upper level of 4.4 µg/L (Datta 1986). The widely used herbicide, atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine], was found at a range of 1.7-18.0 µg/L (Stamer and Zelt 1994). These herbicides, alachlor, atrazine, and metolachlor were found in the Midwest Rivers due to their popularity, performance, low-cost, and wide-spread use in the predominant crop production of corn, wheat, and soybeans.

Atrazine was the prevalent compound in a Kansas River Basin study, residues were detected throughout the year at an average concentration of 1.2 µg/L. The summer months received a greater amount of runoff and atrazine concentrations were found above the established regulation concentration (3.0 µg/L) in June, July, and August from 1973 to 1986. Detection patterns of metolachlor and alachlor were similar to atrazine but found at lower concentrations (Stamer and Zelt 1994). Another study discovered runoff from nearby corn fields to an Italian lake was contributing to a constant detection of atrazine greater than 1 µg/L (Bacci *et al.* 1989).

In a study performed in the Mississippi River region, atrazine and metolachlor were detected in the majority of water samples collected and analyzed. In April, May, and June, one or more herbicides were identified in each of 146 samples of water (atrazine was present in all) collected from the Mississippi River and its major tributaries. Maximum concentrations ranged from 10 µg/L and greater for alachlor to

atrazine in excess of 100 µg/L. Metolachlor and cyanazine [2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile] were detected in 98 and 78% of samples, respectively (Goolsby *et al.* 1991a).

Other researchers reported multiple introductions of pesticides from runoff during the year (Stamer and Zelt 1994, Senseman *et al.* 1997). The studies conducted in the Midwest area of the U.S. demonstrated recurrent contamination in water bodies. Thus, based upon these data, the widespread detection of pesticides appeared to be universal in surface waters near agricultural areas (Thurman and Meyer 1996b).

REGULATION

Environmental studies that have helped to characterize contaminated ground and surface waters within the U.S. lend support to further monitoring of pesticide use and regulation which can aid in prevention of adverse outcomes such as those previously mentioned. The Environmental Fate and Ground Water Branch (EFGWB) monitoring has indicated that annual average atrazine and cyanazine concentrations could exceed maximum contaminant levels or health advisory levels in a few locales, particularly reservoirs and lakes with relatively long retention times (Nelson 1992).

Maximum contaminant levels (MCL), established by the USEPA, refer to the amount of a contaminant which can legally be present in municipally supplied waters. These values are calculated based on health advisory levels (HAL) and the best available control technologies. HALs are guidelines established by the USEPA

used to evaluate the health significance of a contaminant in drinking water when no MCL has been assigned for that contaminant. Health advisories are set at a concentration that if consumed in 2 liters of drinking water per day over the course of a 70 year lifetime is believed to present no adverse health effects (Nowell and Resek 1994, USGS 2001, USEPA 2002a). MCLs are enforceable by law, whereas HALs are not, and both refer to water that has been treated for human consumption.

In reviewing reports of Midwest studies, pesticide residue concentrations frequently exceeded regulatory values. Atrazine and alachlor exceeded MCLs of 3.0 and 2.0 µg/L, respectively, in the Missouri River throughout June, while simazine [6-chloro-*N,N'*-diethyl-1,3,5-triazine-2, 4-diamine] was present but did not exceed its MCL of 4.0 µg/L. Twenty-five percent of samples, collected from the Mississippi River, had atrazine present at concentrations exceeding its MCL of 3.0 µg/L (Goolsby *et al.* 1991a). Alachlor, atrazine, and cyanazine were found in the central Nebraska basins at levels exceeding their MCLs and HALs in 15% or greater of all samples analyzed (Stamer and Wieczorek 1996).

Problems with pesticide residues and other contaminants exceeding assigned MCLs have been sufficient to warrant agencies to develop monitoring programs like the United States Geological Survey's (USGS) National Water Quality Assessment (NAWQA) program. The long term goals of this program are to describe the status and trend in the quality of a large representative part of the nation's surface water and groundwater resources and to describe the primary natural and human factors that affect these resources (Skrobialowski 1996, Woodside and Simerl 1996). In 1999, NAWQA reported that at least one pesticide

was found in almost every water and fish sample collected from streams in the U.S. (USGS 1999).

SEASONAL VARIATION

The higher levels of pesticides found in water samples are attributed to precipitation events that quickly follow treatment of fields in which compounds either dissolve in surface flow and travel by means of runoff or become bound to soil particles and reach streams by erosion. To a large extent, the frequency of precipitation events would be a major contributing factor in the amount of pesticide loading that occurs.

The fluctuating concentrations of pesticides in water supplies appear to form a seasonal pattern. The general process of growing crops involves a seeding and growing period through the spring and summer followed by harvesting in the late summer and fall. Low levels of pesticides might persist in surface waters in winter and early spring but peak concentrations do not appear until late May and early June following spring applications (Pereira and Rostad 1990, Thurman *et al.* 1991). Such was the case with an atrazine study in which the contaminant was observed adsorbing to particles and became part of the suspended sediment in runoff but later desorbed as sediment became more dilute as the particles moved downstream (Gruessner and Watzin 1995).

Additional reports showed herbicide concentrations that increased in early May, began to decline in early to mid-June, and then gradually decreased over the remainder of the growing season. The decline in concentration was probably due to

degradation and the absence of subsequent pesticide applications (Goolsby *et al.* 1991a, Aga *et al.* 1996, Senseman *et al.* 1997, Lerch 1998, Holman and Leidy 2000a, Leidy *et al.* 2001). The concept of an annual cycle of contamination is well-accepted and entails pesticide applications followed by a series of flushing events during which compounds are transported to streams by rainfall in late spring and summer. The subsequent decrease in contamination is due to transport away from site, lack of additional applications, and chemical and biological degradation (Goolsby *et al.* 1991a).

METABOLITES

It is possible that reductions in concentration of specific pesticide detections are due to their breakdown to metabolites. Metabolites are the degradation products of the original, parent chemicals. However, the term degradation does not necessarily imply a less potent chemical as metabolites occasionally have an equal or greater toxicity than the parent compound. Two breakdown products of the herbicide atrazine are 2-chloro-4-ethylamino-6-amino-s-triazine and 2-chloro-4-amino-6-isopropylamino-s-triazine commonly referred to as deisopropylatrazine (DIA) and deethylatrazine (DEA), respectively. These metabolites are typically found and used as a marker for interaction between surface and ground water (Winkelman and Klaine 1991, Thurman *et al.* 1996a, Thurman and Meyer 1996b). While these metabolites are phytotoxic and somewhat equally potent, 2-[(2,6-diethylphenyl)(methoxymethyl) amino]-2-oxoethanesulfonic acid, the ethane sulfonic

acid (ESA) metabolite of alachlor, possesses greater stability than the parent compound but retains no herbicidal activity (Thurman *et al.* 1996a).

Pesticide metabolites are generally more stable and have a greater degree of polarity than the parent chemical. The molecular weights of breakdown products are usually lower and compounds are more completely oxidized. These differences render the metabolites more water soluble, thus, increasing mobility and the likelihood of transport (Barrett 1996, Kolpin *et al.* 1996, Mangiapan *et al.* 1997, Kalkhoff *et al.* 1998). Many assume metabolites are present later in the season, following initial degradation with no new input of the parent compound. Taking into account the amount of applied pesticides, which will most likely become degradation products, these metabolites with physicochemical properties favoring transport could be a hazard.

In the United States, there are approximately 100 frequently employed herbicides used in excess of 300 million pounds each year. This is an enormous supply of potential metabolites, but studying metabolites is costly and difficult and as a result, little is known about many of these compounds (Gianessi and Anderson 1995, Thurman *et al.* 1996a). While many researchers recognize the importance of metabolites and their behavior in the environment, most studies focus on parent compounds due to the scarcity of information available on the unmetabolized pesticides.

URBAN BACKGROUND

The monitoring of agricultural applications and subsequent surface and groundwater contamination remains a primary agenda for many researchers. While complete knowledge of all aspects of pesticide use is somewhat limited in the agricultural arena, the use of pesticides is obvious and acknowledged. However, information is very limited when trying to characterize non-point source contaminations in urban areas.

The realization of increased use of pesticides and the resulting presence of residues in urban areas began to reach the public when studies like the NAWQA report (USGS 1999) were issued and stated that pesticides were detected at a greater percentage in urban areas as opposed to rural areas (generally considered primarily agricultural) in the 1990s. Where agricultural applications appear more straightforward and visible, urban input is derived from many sources of unknown origin. Urban sources generally include recreational, industrial, residential areas, and stormwater drainage and all of these contribute to non-point sources of runoff contaminants (Holman and Leidy 2000a). A large concern of the past has been the massive quantities of pesticides applied in fields across the U.S., but when all the various input possibilities in urban areas are considered, pesticide loading from this source could be substantial. The identification of these sources is hard to come by; therefore, design and implementation of remediation efforts is extremely difficult.

Wotzka *et al.* (1994) found “a number of pesticides exclusively used for crops, such as atrazine, alachlor, cyanazine, and metolachlor, have been detected in stormwater runoff from residential watersheds located far away from agricultural

sources". In maintaining highway medians, railroads, and rights-of-way, herbicides like simazine have been frequently used to control weed growth. Sites of planned commercial centers must be cleared for construction where again herbicides would be beneficial. Once construction is complete, the landscape will be aesthetically maintained for these types of sites and this is largely done with pesticides.

Private lawns are also carefully maintained with pesticides. Professional care of lawns has been on the upswing since the 1990s. Landscaping companies servicing commercial and residential customers are sources of near constant pesticide application as is do-it-yourself landscape maintenance by homeowners. The diverse areas receiving pesticide applications require a variety of compounds for pest elimination; therefore, urban areas tend to have more individual sources of pesticide use when compared to agricultural settings resulting in a growing multi-billion dollar industry outside the agricultural market.

The potential for greater loading of pesticides is attributed to many people applying in urban areas versus several farmers applying in rural locales and applications vary with degree of knowledge and training possessed by applicators. There are numerous applications occurring throughout the season in urban areas compared to agriculture's one or two applications. Pesticides in the urban basins are typically detected throughout the year while pesticides in agricultural basins are found more often in the spring (Hippe *et al.* 1995). Agrochemicals are generally applied singly or in combination with one or more compounds such as a fungicide, herbicide, and/or fertilizer. Urban usage tends to involve application of many varieties of chemicals. "Urban land-use factors influence sediment quality by

introducing contaminants from sewage and industrial wastewater inputs as well as by activities associated with residential areas, and commercial, municipal, industrial, and transportation facilities” (Skrobalowski 1996). Thus, it is not surprising that many urban watersheds contained pesticide residues that were detected more frequently and at higher concentrations than other locales (Hippe and Garrett 1997, Holman *et al.* 2000b).

One study reported the number of U.S. farms using pesticides to be estimated at 0.94 million compared to the 74 million households that utilize, albeit in smaller volumes, pesticides (USEPA 2001). It has been estimated that approximately “70 million pounds of active pesticide ingredients are applied to urban lawns each year” (Shueler 1995). Therefore, any notions of overall pesticide residue contamination reductions due to the replacement of formerly agricultural-use land with urbanized areas can be dispelled. The nation now has the continual problems associated with agrochemicals in addition to the newer difficulties linked to urbanization.

Despite the large volumes of pesticides used in urban areas, limited studies have been performed in urban watersheds. However, a report by researchers in King County, Washington found 23 of 98 selected pesticides in ten urban watersheds in concentrations frequently exceeding levels considered safe by USEPA and other agencies. MCP [2-(4-chloro-2-methyl phenoxy) proprionic acid] and 2,4-D [(2,4-dichlorophenoxy)acetic acid] were among the several compounds applied to control pests in residential, recreational, and industrial locations. Urban

water bodies were found to be affected by the extensive applications of these pesticides (USGS 1999).

Additionally, a study in Baltimore found some 50 pesticides generally applied by homeowners and/or lawn-care applicators in 500 homes (Kroll and Murphy 1994). A survey of lawns and gardens discovered over 338 various active ingredients of pesticides applied to these urban areas (Immerman and Drummon 1985). While a number of researchers continue to characterize the agricultural aspect of surface and ground water contamination, others are concerned with the increased use and subsequent higher residue levels in urban areas.

Over the past ten years, lawn and garden specialists have represented an increasing portion of the market share from pesticide companies. These businesses have expanded to accommodate the increased demand for their skills and services. Comprehensive pesticide usage in many aspects of both rural and urban watersheds ultimately provides credence to the speculation that contamination is widespread; with surprising equanimity between the two types of watersheds (Reisch 2000). The consensus reached upon review of these reports was that urban pesticide applications are more of a threat than first believed.

SUMMARY

Pesticide residues have been found in a variety of sites and locations in rural and urban areas. These compounds are used extensively in some areas and minimally in others; however, it is clear that pesticides are present in non-target areas. The implications of this are diverse. Greater concentrations of pesticide

residues induce acute, occasionally lethal effects to exposed organisms, while low, chronic concentrations of pesticides can prove detrimental as well, affecting neuromuscular function and reproduction of organisms. Studies involving the identification and depiction of pesticide residue presence in surface waters from a watershed approach will enable researchers to assess the contamination issues within that watershed. The toxicological relevance of the residue levels found in the environment enable researchers to determine the risks and benefits associated with the pesticides. Implications of the pesticide usage can provide an understanding of the environmental effects and the means to develop a management plan to maintain a safe and healthy watershed.

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CHAPTER TWO

**ANALYSIS OF SELECTED PESTICIDE RESIDUES IN NORTH CAROLINA
SURFACE WATERS**

INTRODUCTION—NORTH CAROLINA

North Carolina contributes significantly to the overall agricultural production of the United States. Several high-yield crops, including corn, soybeans, cotton, peanuts, and tobacco are grown and cultivated in N.C and considerable pesticide applications are required to maintain acceptable production. Accurate records concerning pesticide usage do not exist in North Carolina (Moreau 1990, Gianessi and Anderson 1995b, McCarthy 2002). In order to determine pesticides being used researchers must rely on information provided by agricultural representatives (i.e., farmers and county agricultural extension agents). Rough estimates are prepared by calculating the projected use according to the acreage of crop and suggested application rates for commonly used pesticides. According to the North Carolina Department of Agriculture and Consumer Services, annual amounts of some agrochemicals applied within the State are in the hundreds of thousands of pounds range. For example, herbicides such as atrazine (737,000 lbs), metolachlor (272,200 lbs), alachlor (167,000 lbs), and 2,4-D (72,400 lbs) were applied in large quantities in North Carolina in 1999 (NCDA 2000).

With the exception of a few isolated studies, little is known about the presence of pesticide residues in North Carolina watersheds. Historically, the North Carolina Pesticide Board has performed broad experimental studies to characterize major river basins. The Board is appointed by the governor and is responsible for implementing the North Carolina Pesticide Law of 1971, which regulates pesticide use, application, sales, disposal, and registration. The law is designed to protect the

people of the State by promoting a safe, healthy living environment (Mather 1994, NCDA 2000).

The Interagency Work Group of the N.C. Pesticide Board sampled 152 monitoring wells throughout the State from 1990 to 1995. Twenty-six various pesticides and metabolites were identified in 33 of the 152 wells. Compounds repeatedly detected included hexazinone, prometon, simazine, atrazine, and several triazine metabolites (Wade *et al.* 1997). Additionally, infrequent groundwater studies conducted in North Carolina indicated many aquifers were susceptible to contamination from widespread pesticide applications (Moreau 1990). Mather (1994) reported that there was great potential for pesticide contamination in ground and surface waters of North Carolina. N.C. residents and researchers alike became more conscious of and attentive to the need for informative reports on pesticide usage and resulting environmental consequences.

Several researchers have focused on the Albemarle-Pamlico Drainage Basin (Harned *et al.* 1995, Ragland *et al.* 1995, Skrobialowski 1996, Woodside and Ruhl 1996, McCarthy 2002). Two popular chemicals, alachlor and atrazine are commonly used on a variety of crops in North Carolina and were identified as occurring in this drainage basin (Harned *et al.* 1995). A broad analysis revealed atrazine in 20 of 104 samples at levels as high as 0.1 µg/L (Skrobialowski 1996). The USGS-NAWQA program included the Albemarle-Pamlico drainage basin as part of a study looking at 60 major basins in the United States. Atrazine, alachlor, and metolachlor residues were a few of the continually detected pesticides in the Tar and Neuse Rivers.

These compounds were present at their highest levels in early spring and concentrations declined in mid-summer (USGS 2001).

Pesticides have been found in areas other than the Albemarle-Pamlico Drainage Basin. Corn and soybeans, two of the principal crops grown across North Carolina, commonly receive atrazine and metolachlor applications (Gianessi and Anderson 1995a). and these pesticides have been found in N.C. surface waters. A recent 16-month study of surface water intakes in North Carolina rural areas found herbicides: atrazine, metolachlor, 2,4-D, and aldicarb and the insecticide chlorpyrifos (Holman *et al.* 2000b, Walker *et al.* 2000). The occurrence of common rural and urban pesticides in surrounding waters was also observed in North Carolina in studies performed by Leidy *et al.* 2001, Woodside and Ruhl 2001, Holman and Leidy 2000a, and McCarthy 2002.

North Carolina is one of the many southeastern states that has shown a propensity towards development of previously rural areas. The state is primarily agricultural although the growth of relatively large cities and urbanization of rural lands throughout North Carolina have led to the development of expanding urban watersheds. Rural and urban regions are frequently in close proximity to each other leading to the potential for pesticide loading from surface runoff via both sources. Little is known about specific watersheds in North Carolina, but judging from past studies, areas of the State appear to be susceptible to pesticide contamination.

EXPERIMENTAL DESIGN

Based upon the preceding data, the author became interested in the potential for human health hazards associated with pesticides in drinking water. The presence of pesticide residues were monitored from input sites to streams, tributaries, and reservoirs that serve as sources for municipal drinking water. By locating and identifying residues, potential sources of the pesticides found in surface waters can be identified and human health implications considered.

Objectives of this study included surface water investigations to identify residue levels of selected pesticides in surface waters of five watersheds located in the Piedmont region of North Carolina. Concentrations of pesticide residues detected in surface waters were determined. Results were compared among the watersheds according to their categorization as either rural or urban. Differences within each watershed were also noted. This watershed approach provided for an assessment of these surface waters to determine the extent of pesticide presence and helped to characterize the chemical contamination within the watersheds. In developing a watershed assessment the author hoped to establish a foundation upon which to base future actions in watershed management which involves remediation as a response to the chemical contamination.

PESTICIDES

Pesticides were chosen based on recommendations from County Agricultural Extension, results of past studies, and reports of commonly used compounds (Harned *et al.* 1995, Ragland *et al.* 1995, Holman *et al.* 2000b, Walker *et al.* 2000).

The pesticides selected included five herbicides (alachlor, metolachlor, atrazine, simazine, 2,4-D), one fungicide (chlorothalonil), and one insecticide (chlorpyrifos) (Table 1).

Alachlor is predominantly used in rural areas and is a restricted use, Class III (slightly toxic); chloroacetanilide herbicide used to control nutsedge, annual grasses and broadleaf weeds. The more common crops requiring alachlor are corn, tobacco, cotton, and soybeans. The chemical can be applied prior to and following emergence of the crop plant. Alachlor is considered a selective systemic herbicide that interferes with protein production and root elongation in unwanted vegetation (Ware 1983, Briggs 1992, EXTOWNET 1996, Woodside and Ruhl 2001).

Another chloroacetanilide used in principally rural areas on pre-emerged plants is metolachlor. This herbicide is both a general and restricted use, Class III pesticide effective against annual grasses and broadleaf weeds (similar to alachlor) and used in corn, peanuts, and soybeans. Metolachlor selectively inhibits synthesis of chlorophyll, enzymes, and proteins (Ware 1983, Stevens and Sumner 1991, EXTOWNET 1996).

The triazines are a valuable and successful class of herbicides. Atrazine and simazine are both used in rural and urban locations. While atrazine is a Class III and restricted use pesticide, simazine is a Class IV (essentially non-toxic), general use pesticide. Atrazine is frequently used, pre and post-emergently, to selectively control broadleaf, grass, and pond weeds in corn, sorghum, sugarcane, nursery conifers, and forestry conservation, as well as non-selectively in fallow fields and non-crop lands. Simazine is an effective pre-emergent, systemic pesticide

selectively used in broadleaf and annual grass maintenance and non-selectively used around industrial areas. Historically, simazine was most often used to control submerged weeds and algae, but presently is also employed in the production of corn, peaches, and grapes, and along highway rights-of-way. Atrazine and simazine modes of action work to inhibit photosynthesis (Ware 1983, Stevens and Sumner 1991, EXTOWNET 1996).

The last herbicide chosen, 2,4-D is a commonly used rural and urban post-emergent, chlorophenoxy pesticide. This Class I (highly toxic, eye exposure) and III (slightly toxic, orally) compound controls broadleaf weeds such as pigweed and ragweed and is usually employed in combination with other herbicides, insecticides, and fertilizers. Applications to corn, cotton, apples, home gardens, pastures, forests, and aquatic vegetation are a few of the many uses for 2,4-D. The chemical is a systemic herbicide that interferes with plant growth processes, posing as a synthetic growth hormone (Ware 1983, Stevens and Sumner 1991, EXTOWNET 1996).

Chlorothalonil is a Class II (moderately toxic), general use chloronitrile fungicide. This broad spectrum fungicide is used in rural and urban areas to reduce fungi that affect vegetables, fruits, trees, ornamentals, turf, and agricultural crops. As a preservative, chlorothalonil is used in agriculture, horticulture, and silviculture. The agent is thought to act by uncoupling oxidative phosphorylation, inhibiting the electron transport chain (Ware 1983, Edwards *et al.* 1991, EXTOWNET 1996).

Chlorpyrifos, a widely used insecticide that is a restricted use, Class II organophosphate was once used to control mosquitoes. It is now banned for this use, chlorpyrifos currently serves as a broad spectrum insecticide on apples,

peaches, wheat, corn, and in and around structures to prevent termites.

Chlorpyrifos functions as an acetylcholinesterase inhibitor (Ware 1983, EXTTOXNET 1996, Woodside and Ruhl 2001).

STUDY LOCATIONS

Studies were performed to ascertain the identity and whereabouts of pesticides within the surface waters of the watersheds. Three rural watersheds and two urban watersheds were chosen. All are located in the Piedmont region of North Carolina and the water quality managers of these areas were interested in a comprehensive study to characterize the potential of pesticide contamination to their surface water supplies (maps of study locations in appendix).

Rural Watersheds: Burlington and Raleigh

The city of Burlington is located in Alamance County of North Carolina. Two reservoirs, Stony Creek and Lake Mackintosh, are the sources of drinking water for the city. Stony Creek, created in 1929, is located north of Burlington and receives water from Lake Cammack, previously called Lake Burlington. The capacity of Lake Cammack Reservoir exceeds 3 billion gallons and provides roughly 2 billion gallons of serviceable water. This contributes to the 10 million gallons per day (MGD) capacity of the Ed Thomas Water Treatment Plant, primarily supplied by Stony Creek Reservoir. The surrounding watershed that feeds into Stony Creek is comprised of 105 square miles of land that delivers drainage from rural north Alamance and southwest Caswell Counties (Holman and Leidy 1998a).

Lake Mackintosh, southwest of Burlington, utilizes Big Alamance Creek (since 1993) and feeds into J. D. Mackintosh Water Treatment Plant. This plant can supply 12 million gallons of water per day to customers due to the 5 billion gallons of serviceable water provided by the reservoir. Lake Mackintosh Watershed receives drainage from west Alamance County and a portion of neighboring Guilford County southeast of the city of Greensboro and consists of 135 square miles of land (Holman and Leidy 1998a).

Raleigh, one of North Carolina's prominent urban areas is still surrounded by significant agricultural land-use. These rural areas were monitored and were encompassed within the Falls of the Neuse Watershed. This watershed is 772 square miles and includes drainage from areas around Raleigh, including Durham, Hillsborough, and North Raleigh. Falls of the Neuse Lake, created by the Army Corps of Engineers in 1982, is a 1200 acre reservoir that makes up 12% of the Neuse River Basin. The E.M. Johnson Water Treatment Plant supplies 42 million gallons of serviceable water per day (Holman and Leidy 1998c).

Urban Watersheds: High Point and Greensboro

The High Point Watershed Study envelops both High Point Lake and Oak Hollow Lake Reservoirs. These water supply reservoirs are north of High Point in Guilford County. The eastern branch of Deep River flows into High Point Lake reservoir which was built in 1928 and has a surface area of 340 acres containing 1.25 billion gallons of water. The 30 square miles of High Point Lake Watershed drains northeast High Point. Oak Hollow Lake reservoir was built in 1971 and

receives water from the western branch of Deep River and holds 3.2 billion gallons of water. The 32 square miles of Oak Hollow Watershed drains western High Point. High Point and Oak Hollow Watersheds combined, contain 62 square miles of land drainage to the Frank L. Ward Water Treatment Plant to provide 12.5 MGD (Holman and Leidy 1998b).

Greensboro is located in Guilford County and contains part of the Lake Townsend Watershed. This 105 square mile watershed provides water from Lake Higgins, Lake Brandt, and Lake Townsend to the intake of the N. L. Mitchell Water Treatment Plant. The Townsend Plant impounds water from Lake Townsend, a 1450 acre water body in north central Guilford County, built in 1969 (City of Greensboro 2002). When all three reservoirs are full there are almost 8 billion gallons of water available.

The first three watersheds represent the rural portion of the study (Burlington and Raleigh) and pesticide contributions are regarded as agricultural. The participation of the City of Raleigh began in the last year of study; therefore, the majority of the rural data reported here was regarding the two Burlington watersheds. The next two watersheds characterize the urban section of the study (Greensboro and High Point) and although there is more of a gradient in land-use, they are considered urban.

For study purposes the watersheds were classified as either urban or rural; however, all four cities framing the watersheds contain both rural and urban areas. Of the four cities, Burlington possesses the greatest rural content followed by Raleigh and High Point. Greensboro possesses the least rural area of the four

cities, thereby rendering this city the most urban. Predominant land-uses of the rural watersheds were the agricultural crops of corn, tobacco, and soybeans. This was based upon visual confirmation and earlier studies in these North Carolina areas (Holman and Leidy 2000a, Holman *et al.* 2000b, Walker *et al.* 2000, Leidy *et al.* 2001).

There is a lack of knowledge associated with non-point source contamination combined with potentially numerous applications require greater characterization of urban watersheds. Considerations in the urban areas involved contributions from the many urban sources and practices, and no focus on agricultural applications. Lawn care for industrial parks, home-owners, parks, and other recreational areas involve some of the pesticide applications commonly observed in urban watersheds. Highway and railroad maintenance, golf courses, construction sites and numerous other possibilities are multiple inputs associated with non-agricultural pesticides applications.

Burlington and Raleigh still possess large parts of land dominated by agriculture and other uses, whereas Greensboro is characterized as having 68.2% of land that is residential and only 0.5% agricultural. High Point has more agricultural land than Greensboro and contribution from these sources is acknowledged although selected sites within High Point centered on non-agricultural areas. Population and urban growth rate for Greensboro were noted from 1999 to 2000, in which both increased 21.8% and 11.4%, respectively. Similar data were reported for High Point, although slightly higher increases in population (23.6%) and

urban growth (13.4%). These values are consistent with the downward trend of agricultural acreage noted since 1974 (City of Greensboro 2001).

MATERIALS AND METHODS

Site Selection: The approach to selecting sites to be sampled within each study location involved collecting samples along all the watershed's major water bodies and their tributaries as well as the reservoirs in proximity of water treatment plant intakes. At the beginning of the study a large number of sites were assigned to acquire a greater comprehension of possible sources of contamination within the watersheds. Site locations were modified at the end of each season after conferring with City Representatives and County Cooperative Agricultural Extension Agents participating in the study.

Those sites purged from the experimental sampling scheme had shown little to no contamination over the course of the previous years. Pesticide residue levels in the remaining locations were frequently found to be elevated and therefore sampled further to improve characterization. This experimental design allowed for a progressive refinement of the experiment that identified the "hot spots" of concern for each watershed (Holman and Leidy 1998a, 2000a, Holman *et al.* 2000b, Walker *et al.* 2000, Leidy *et al.* 2001).

Cooperating cities agreed to participate in the study. Surface water samples were collected from local watersheds using sampling techniques based on USGS procedures (Shelton 1994). Bimonthly collections, generally following a precipitation event of 2.5 cm or greater, if possible, were taken by participating city personnel.

The intent for collecting soon after rainfall was based upon the susceptibility of pesticide residues to surface runoff.

Samples were stored in 250 mL amber glass bottles with PTFE lined caps (I-Chem, Nalge Nunc International, Rochester, New York) following collection. Care was taken to minimize head space, thereby reducing potential volatilization. Samples were shipped on ice to NCSU's Department of Environmental and Molecular Toxicology Pesticide Residue Laboratory via a standard cooler, and stored at 4°C until analyses were performed, generally within one week of receiving samples.

The essential requirement of an analytical method necessitates identification and quantification of the chemical performed with a confidence that is to the level and extent of what is required (i.e., choose the best analytical method for a particular study) (Simon *et al.* 1998). Immunoassays became popular in the 1960s in the clinical market and twenty years later gained commercial acceptance and recognition by researchers as screening tools or even replacement for gas chromatography analysis (Jung *et al.* 1989).

The immunoassay technology has been refined and marketed in the form of enzyme-linked immunosorbent assay (ELISA) kits that provide swift, highly selective, on-site, cost-effective and relatively simple determinations of pesticide residue presence and concentration. The manner of screening samples prior to gas chromatography (GC) reduces the need for the chromatography process in some cases. ELISAs will adequately eliminate samples of little significance and allow researchers to focus on more crucial samples and reduce the quantity of GC

analyses. Therefore, immunoassays have replaced more costly forms of analysis (\$5 to \$10 per sample with immunoassays compared to \$250 with GC) and have occasionally shown better results than gas chromatography (Karu *et al.* 1991, Meulenberg *et al.* 1995).

Several studies were conducted that support the replacement of gas chromatography with immunoassays. Using fortified water samples with known concentrations of pesticides, examinations were done using both ELISA and GC analyses and results compared (concentrations ranging from 0.2 to 7 µg/L and 0.1 to 10 µg/mL). In most cases very little difference was observed and responses provided very strong correlation (r^2 values). Values were found ranging from 0.96 and greater (Thurman *et al.* 1990, Goolsby *et al.* 1991, Aga and Thurman 1993, Rodolico *et al.* 1997, Tessier and Clark 1998, Walker *et al.* 2000).

RaPID Assay[®] (Strategic Diagnostics, Inc., Newtown, Pennsylvania) kits were used to screen surface water samples for the seven previously described pesticides (Table 1). ELISAs effectively measure pesticide concentrations utilizing 200-250 µL of surface water and show little to no interference from humic materials present in unfiltered water, thereby reducing time spent in sample preparation (Thurman *et al.* 1990, Rittenburg *et al.* 1991). Multiple compounds present obstacles for some methods of analysis but immunoassays have shown no interference among chemicals of varying classes and minimal cross-reactivity of compounds within the same class. The selection of available kits was sufficient for the pesticides of interest and procedures were similar for all compounds. Steps for performing the ELISA procedures are outlined in the appendix.

Care was taken when delivering each solution and every tube treated in a precise manner for each step. All kits and samples were stored at approximately 4°C and allowed to rise to room temperature before the start of each process. The immunoassay involved antibodies of a specific pesticide bound to magnetic particles that were combined with enzyme-labeled standard conjugates of the pesticide and sample (potentially containing environmental pesticide residues).

This procedure utilized a magnetic separation rack, as the antibody was bound to magnetic particles, to retain those complexes of antibody and pesticide (enzyme-labeled and environmental) while free pesticide residues (unattached) were decanted. The immunochemical reaction was demonstrated with the assistance of a chromagen substrate mixture (3,3',5,5'-tetramethylbenzidine) analogous to the enzyme-bound conjugate. The competitive reaction presented both enzyme-labeled standard conjugate and environmental pesticide residue bound to antibodies although the color change only displayed the enzyme-labeled portion of the solution. The concentration of pesticide within the water solution was indirectly proportionate to the intensity of the sample color reaction.

The colorimetric procedure utilized an RPA-I™ RaPID Analyzer (Strategic Diagnostics Inc., Newtown, Pennsylvania) that measured the optical densities of the color change that occurred subsequent to the assay. This was an indirect indication of environmental pesticide presence. Absorbance measurements were calculated using linear regression and a standard curve of three known concentrations of the pesticide (SDI 1992).

Once pesticide residues were observed via ELISA samples with compound concentrations above 1 µg/L were reanalyzed by GC to confirm the elevated detection. Some of the recent technologies available include SPE cartridges and disks. The 3M Corporation (St. Paul, Minnesota) has developed a membrane filter consisting of a PTFE support that is compatible with both inorganic and organic solvents and a number of bonded phases. Depending upon experimental needs, specific disks can be used to selectively refine samples to isolate preferred analytes. Laboratory efficiency is enhanced by using the SPE disk. Solvent usage, manual labor, and amount of time required for preparation is reduced while through-put (1 L in 10 min.), velocity of flow, and the ability to handle multiple analytes simultaneously are improved with solid-phase extraction processes (Bolygó and Atreya 1991, Pavoni 1991, Markell and Hagen 1991, Dirksen *et al.* 1993, Mueller *et al.* 2000).

A SPE Empore™ Extraction Disk (47mm, 90% wt C₁₈ bonded phase and 10% wt PTFE support) (3M Corp., St. Paul, Minnesota) was used for sample concentration. Validity for the use of the Empore™ Extraction Disk over other extraction techniques was supported by an inter-laboratory study, in which the author participated. In-house and shipped water samples were compared with regard to recovery of an assortment of pesticides. The Empore™ disk provided a means to a more stable and cost-effective mode of transport with greater recoveries of the compounds (Mueller *et al.* 2000). The successful nature of this study further corroborated the preference for the extraction disk and steps for this procedure are outlined in the appendix.

The chosen methods utilizing ELISA kits in combination with Empore™ extraction disks and GC analysis were adequate and successful in screening, isolating, and subsequently detecting pesticides of interest. Considering the numerous samples the laboratory received within a year of study, the ability to process a large number of samples in a relatively short period of time was integral. Both ELISAs and Empore™ Disks fulfilled this requirement while minimizing quantities of solvents and materials and reduced preparation and procedural time.

Chromatographic analysis was used for confirmation of ELISA results. A Varian Star Model 3400 Gas Chromatograph equipped with a Model 8200 CX Autosampler and coupled with a nitrogen/phosphorous [Thermionic Specific Detector (TSD)] detector (Varian Inc., Walnut Creek, California) equipped with a DB-35 fused silica column (30 m by 0.25 mm i.d.) (0.25 µm film) (J & W Scientific Inc., Folsom, California).

The carrier and make-up gas was helium at a flow rate of 30.0 mL/min. Gases to the detector were air and hydrogen at flow rates of 175.0 and 4.0 mL/min, respectively. Temperatures were as follows: inlet, 175°C, detector, 300°C. The oven temperature program was as follows: initial, 160°C hold 2 minutes; to 170°C at 1.0°C/min, hold 2 minutes; to 280°C at 5°C /min, hold 2 minutes.

Samples with final extract volumes of 1.0 mL were interspersed with the analytical standards of interest at concentrations of 10 µg/L, placed on autosampler, with standards positioned at the start, between every five samples, and the last of the GC sample run. Volumes of 3.0 µL were injected onto the column for analysis. Data were quantified by comparison of peak areas against standards of known

concentration. Retention times (RT) were as follows: alachlor (10.2 min), atrazine (7.3 min), chlorothalonil (9.5 min), chlorpyrifos (11.5 min), metolachlor (11.2 min), simazine (7.5 min).

RESULTS AND DISCUSSION

This project incorporated variability in sampling and analysis to adequately characterize the watersheds. Sampling scheme and pesticide analyses were based upon previous findings and recommendations from participating NC Cooperative Agricultural Extension Agents (Gianessi and Anderson 1995, Holman and Leidy 2000a, Holman *et al.* 2000b, Walker *et al.* 2000, Leidy *et al.* 2001, Roger Cobb and Wick Wickliffe 1999, personal communications). Depending upon location, chemicals investigated varied so that those pesticides thought to be potentially agricultural were assigned to rural watersheds while urban watershed protocols incorporated compounds with non-agricultural uses. In view of the fact that the rural and urban watersheds were neither completely rural nor urban there was an overlap in chemical analyses for those pesticides that were used in both rural and urban settings (Appendix, Table 2).

Timing of the study adequately covered application periods with a sampling schedule that included early, pre-application stages to establish a background concentration; expected pre- and post-emergence application periods; and the parent compound degradation and metabolite development phase. This schedule also allowed for any potential fall treatments to suppress weed populations in preparation for winter and the following season's plantings.

For the purposes of this study values reported were a result of ELISA screening and those detections exceeding 1.0 µg/L were noted. This concentration was used to signal environmental concentrations that approached the MCLs of three of the seven pesticides studied (alachlor, atrazine, and simazine).

YEAR ONE—1999

Burlington: The study ran from March through September 1999 with the collection of 275 samples (1100 pesticide determinations). Early analyses of atrazine, chlorpyrifos, simazine, and 2,4-D exhibited little incidence of pesticide residues and it was well into the season before any residue levels were detected.

After sampling for two and a half months atrazine and simazine concentrations began to rise. Of the samples collected in May, atrazine was found at levels approaching the 3.0 µg/L MCL in the Lake Mackintosh Watershed; one locale (BULM-2B2) on Beaver (BVR) Creek and along various points of Rock (RK) Creek (BULM-2E1, 2E4, 2E5). Atrazine detections were minimal for the remainder of the year although there was a peak (4.27 µg/L) above the MCL in RK Creek (BULM-2E4) in September. Buttermilk (BM) Creek, in the Stony Creek watershed, had elevated levels of atrazine at a number of sites (BUSC-1D1, 1D2, 1D3, 1D4) in July (0.66-1.84 µg/L).

Early detections of simazine were infrequent and low in concentration (< 0.22 µg/L); however detections increased in May and levels along RK Creek (BULM-2E1, 2E4, 2E5) ranged from 0.68 to 1.52 µg/L. Residue levels of simazine were detected frequently in July in both watersheds but only exceeded the MCL once (mid-July), in

RK Creek (BULM-2E4), an area of rapid urbanization, with a concentration of 4.7 µg/L. Typically, detection of simazine after July was negligible, although slight increases in concentrations in RK Creek were noted in late August and early September (0.68-0.86 µg/L).

Chlorpyrifos was found infrequently throughout most of the season. This insecticide was first detected in May at 1.2 µg/L in RK Creek (BULM-2E2). The second detection was late in the sampling period (27 August) and found the pesticide in all three creeks of the watersheds (BVR, RK, and BM) ranging in concentration from 0.1 to 0.19 µg/L. Samples prior to and after this date exhibited no chlorpyrifos residues.

The herbicide 2,4-D was found once in May (0.77 µg/L) in BM Creek (BUSC-1D6) of the Stony Creek Watershed. The next observation of 2,4-D occurred in late July at which time the pesticide was present at elevated levels (0.71-7.08 µg/L) in all samples collected from BVR, RK, and BM Creeks. However, this widespread detection was not observed again and only sporadic detections of 2,4-D occurred in August in BM Creek (BUSC-1D7, 1.08 µg/L) and September in BM (BUSC-1D7, 4.11 µg/L) and BVR Creeks (BULM-2B2, 2.03 µg/L).

Summary: The pesticide residues detected in Burlington ranged in concentration (0.1-7.08 µg/L) and some levels approached MCLs with two detections exceeding regulatory values (atrazine; 4.27 µg/L and simazine; 4.7 µg/L). However, results predominantly showed a continual presence of low levels of the pesticides (Fig. 1).

Atrazine, simazine, and 2,4-D were the more prevalent compounds detected in rural watersheds in Burlington. Residues of atrazine and simazine surpassed their MCLs. On the other hand, chlorpyrifos was seldom present and was only found twice during the sampling period. Interestingly, chlorpyrifos was detected in all areas on the same date in August. This also occurred with 2,4-D in July, indicating a potentially brief but widespread application of these two compounds.

Pesticide detections were similar between the two watersheds of Burlington, Lake Mackintosh and Stony Creek and residue detection patterns for all of the pesticides investigated in Burlington exhibited similarities to the seasonal pattern associated with agricultural watersheds (Fig. 2). As previously mentioned, numerous factors influence pesticides. Timing of application and release into the environment as well as precipitation were expected to play large roles. Fluctuations in pesticide residues were most likely due to frequency, amount, intensity, and duration of a precipitation following an application. The presence of precipitation would determine runoff, transport, and subsequent detection of particular pesticides in sites of watersheds. Therefore, results would be expected to vary among locations and with time.

Greensboro: One hundred and ten samples from fifteen sampling sites were collected from April to December and analyzed for atrazine, chlorpyrifos, chlorothalonil, simazine, and 2,4-D. In the 547 determinations, pesticide residues were present for most of the year in the Greensboro Watershed.

Atrazine was found in many of the samples from April to December including the commercial sites (GBCS-6, GBCS-11) with residues of atrazine ranging from

0.05 to 1.18 µg/L. A maximum concentration of 2.66 µg/L (GBCS-11) was found in April along a tributary of North Buffalo (NB) Creek. Atrazine residues were detected in residential areas for the duration of the sampling period, although concentrations remained below 1 µg/L. The downtown sites also exhibited pesticide residues with a peak concentration of 6.66 µg/L along a tributary of NBC (GBUS-9) in early April. Levels of atrazine in downtown sites (GBUS-8, GBUS-9, GBUS-10) ranged from 0.06 to 1.59 µg/L for the remainder of the sampling period.

Simazine residues, ranging from 0.22 to 1.49 µg/L, were found near a commercial site (GBCS-11) along a NB tributary from April to August. The pesticide was detected once in residential areas. Simazine was found in December (GBRS-3) at 0.08 µg/L. Simazine was detected in downtown areas early in the sampling period at low levels (< 0.1 µg/L) and elevated concentrations were found at site GBUS-9 along NBC at 2.73 and 1.14 µg/L in April and May, respectively.

2,4-D residues were present at elevated levels in all three types of areas in Greensboro. Commercial site, GBCS-6, exhibited 2,4-D ranging from 1.03 to 1.92 µg/L in April and May and only once in the following months (December, 0.9 µg/L). Residential areas (GBRS-1, 2, 3, 4, 5, 7) presented multiple detections of 2,4-D at varying concentrations (0.80-4.87 µg/L) throughout the sampling period. There were several detections of the pesticide in downtown areas (GBUS-8, 9, 10) in April and May ranging from 0.85 to 3.55 µg/L. 2,4-D was found once more in the downtown areas in August along NBC (GBUS-8) at a concentration of 25.99 µg/L.

Chlorpyrifos residues were found infrequently in commercial, residential, and downtown sites. Only once was the pesticide found before August, in a downtown

site (GBUS-10) along a tributary of South Buffalo (SB) Creek at a concentration of 0.72 µg/L. Chlorpyrifos was found in the latter part of the sampling period in August and October in most of the sites in Greensboro and residue levels ranged from 0.07 to 0.28 µg/L.

Detections of chlorothalonil (0.07-0.66 µg/L) occurred in all samples near commercial sites (GBCS-6, GBCS-11) along NBC and downtown sites (GBUS-8, 9, 10) of NB and SB Creeks. Frequent detections in the residential areas (GBRS-1, 2, 3, 4, 5, 7) were noted throughout the sampling period. Although chlorothalonil residues were repeatedly present at multiple residential sites, all detected concentrations were below 0.28 µg/L.

Summary: The more common pesticides, atrazine, simazine, and 2,4-D were found in early April at elevated concentrations. This is earlier than was expected for concentrations exceeding 1 µg/L. Most likely area applications were performed earlier. Bearing in mind that the watershed is urban and may receive pesticide applications at different times from those in rural settings (e.g., golf courses, parks, housing, highway maintenance) the relatively premature appearance of chemical residues might have been a result of targets that are not common in agricultural locales. Time constraints associated with agrochemicals are not present when applying pesticides in urban areas in which treatments tend to be on an as needed basis.

Atrazine residues were present in all areas although the highest concentrations were detected at downtown sites where the 3.0 µg/L MCL was exceeded at GBUS-9 (Fig. 3). Simazine was not found in the residential sites but

was present in commercial and downtown areas and like atrazine was found at greater levels in the downtown, more urbanized areas. After May, concentrations of both atrazine and simazine dropped considerable and residue were found infrequently throughout the remainder of the sampling period.

Detection of 2,4-D occurred in commercial, residential, and downtown areas. While occasionally found in the commercial sites the residential areas exhibited multiple detections of 2,4-D at elevated levels. Greatest concentrations of the compound were in a downtown site (GBUS-9) along a tributary of NBC near Cumberland Park. Atrazine, simazine, and 2,4-D were present here at elevated levels in April and May while minimal levels were detected throughout the remainder of the season. 2,4-D residues were still prevalent as late as November. However, there was little concern for the 2,4-D concentrations because the current MCL is 70.0 $\mu\text{g/L}$ and the maximum concentration found (25.99 $\mu\text{g/L}$) was less than half of it's MCL.

Chlorpyrifos and chlorothalonil concentrations never rose above 1 $\mu\text{g/L}$ but were present throughout most of the sampling period (Fig 4). Levels found in April were similar to concentrations detected throughout the year. Although present in commercial, residential, and downtown sites, greater concentrations of chlorpyrifos and chlorothalonil were found in downtown and commercial areas, respectively. Persistence of these chlorine-containing compounds may account for their universal detection but the concentrations were low and neither chemical possesses an MCL upon which to base human health assessments. HAL values do exist for

chlorothalonil (150.0 µg/L) and chlorpyrifos (20.0 µg/L); however, these values far exceeded the residues found in this study.

Multiple pesticides were found in Greensboro with a majority of the detections in the downtown sites. Residues were found from April to December although detections between September and December were minimal for all compounds suggesting that little residues are present over the winter months. The pattern typical of an agricultural watershed was not evident in the urban watersheds. A greater temporal range and variation was observed in the detections and concentrations of pesticides within the urban areas (Fig. 5).

High Point: The sample quantity and number of collections in High Point were fewer than those from other watersheds due to staff time limitations; however, 52 samples were collected in High Point from April to June and analyzed for atrazine, chlorpyrifos, chlorothalonil, simazine, and 2,4-D. Residues of atrazine were found in May and June at sites (HPDL-1, 2, 3) along Davis Lake (DL) ranging from 0.84 to 2.1 µg/L. Atrazine concentrations detected in sites of High Point (HP) Lake, HPHP-2B, 4, 5 ranged from 0.6-0.54 µg/L. Commercial (MP) sites, HPMP-A, B, C, D, showed residue levels of 0.05 to 0.49 throughout the sampling period.

Simazine residues were not present until May in DL (1.24-2.58 µg/L) and HP Lake (0.05-0.3 µg/L). While all of the detections in DL were above 1.0 µg/L, residues of simazine along MP were found at low levels (0.04-0.35 µg/L). 2,4-D was present in May along DL; 7.97 µg/L at HPDL-1 and 4.72 at HPDL-2. HPL sites also exhibited elevated concentrations of the pesticide in May and June (0.75-2.9 µg/L). 2,4-D was found in most of the April and May samples and all of the June samples

of the four commercial sites (HPMP-A, HPMP-B, HPMP-C, HPMP-D) at concentrations ranging from 0.73 to 4.79 µg/L.

Chlorpyrifos was not detected in High Point throughout the sampling period. Chlorothalonil residues were found throughout the year in all areas. The fungicide was found in DL and HPL from April to June (0.07-0.14 µg/L) and frequently detected in MP sites ranging from 0.08 to 0.32 µg/L.

Summary: Atrazine, simazine, and 2,4-D were shown to be the prevalent pesticide compounds found occasionally at elevated levels (Figs. 6, 7). The greater concentrations of atrazine, simazine, and 2,4-D were in DL and levels approached but never exceeded the respective MCLs. 2,4-D was present at elevated levels in all areas of High Point with the largest concentrations occurring in Davis Lake. The 2,4-D residues peaked in commercial areas in late April while other areas of High Point exhibited peaks in pesticide concentration in mid May. Chlorothalonil was detected frequently but only at low levels with greater concentrations in commercial areas. Chlorpyrifos residues were not observed in High Point.

There was little evidence of a seasonal pattern in the pesticide detections of High Point. However, results were similar to the other urban watershed in that pesticide detections were notably present early in the year and varied throughout the sampling period (Fig. 8).

YEAR TWO—2000

Burlington: Between March and October, 145 samples were collected in sets of nine or twelve. Atrazine, alachlor, chlorpyrifos, simazine, and 2,4-D were the compounds investigated for the entire study period with metolachlor added in June. Pesticide residues detected prior to spring applications, referred to as background levels, were minimal to non-detectable. Detected chemical concentrations did not increase until May.

Low concentrations of atrazine (0.05-0.79 µg/L) were frequently found in BVR and RK Creeks and moderately detected in BM Creek. Residue levels were greatest in the summer months but only once approached the 3.0 µg/L MCL along RK Creek (BULM-2E5) in late July (1.16 µg/L). Detections of simazine were similar to atrazine in that low levels were present throughout the sampling period with the greatest concentrations found in the summer months. The pesticide was frequently detected along RK Creek (BULM-2E1, 4, 5) at concentrations ranging from 0.04 to 0.97 µg/L. Simazine residues approached the 4.0 µg/L MCL in BVR Creek (BULM-2B2, 1.63 and BULM-2B1, 2.7µg/L) in late June but remaining BVR and BM Creek detections were low ranging from 0.03 to 0.54 µg/L.

Alachlor was found at low levels (0.06-0.31 µg/L) in May, in all three creeks. Sporadic detections were observed throughout the rest of the sampling period for all areas although concentrations remained below 0.19 µg/L. Analysis for metolachlor did not begin until June although the majority of samples in the months following exhibited residues of the pesticide. In BVR Creek metolachlor concentrations ranged from 0.09 to 0.45 µg/L. Residue levels exceeded 1 µg/L in RK Creek at

BULM-2E1 (1.26 µg/L), BULM-2E4 (2.7 µg/L), and BULM-2E5 (2.24 µg/L) and remaining detections were less than 0.53 µg/L. BM Creek also frequently exhibited metolachlor residues with low concentrations (< 0.51 µg/L) and one detection of 1.44 µg/L (BUSC-1D4) in October.

2,4-D residues were not detected in sites along BVR Creek. The pesticide was found twice in RK Creek at 1.84 (BULM-2E4) and 1.29 µg/L (BULM-2E1) in June and August, respectively. A single detection of 0.89 µg/L was found in June along BM Creek in the BUSC-1D4 site.

Low concentrations of chlorpyrifos were detected in BVR, RK, and BM Creeks. A brief presence of the pesticide was observed in March (0.10-0.18 µg/L) for all areas. Similar concentrations were found in the three creeks in July and August ranging from 0.10 to 1.10 µg/L. One detection in each creek was observed in October; in BVR (BULM-2B3, 0.1 µg/L), RK (BULM-2E1, 0.14 µg/L), and BM (BUSC-1D4, 0.1 µg/L) Creeks.

Summary: Pesticide residues found in year two for this rural watershed were reduced from the preceding year. No MCLs were exceeded at any time throughout the sampling period (Fig. 9). As stated in prior discussions, rainfall or lack thereof might have had an influence over the transportation processes of compounds to surface waters as diminished precipitation can directly affect the frequency of pesticide detections. There was a decline in the monthly rainfall averages in from 1999 to 2000 in the months of April and May; however, the majority of elevated pesticide detections in 2000 were observed in May and June.

Detections continued to demonstrate a seasonal pattern even at low concentrations. All six pesticides (atrazine, simazine, 2,4-D, metolachlor, chlorpyrifos, alachlor) were detected in August at slightly elevated concentrations; however, minimal residues were present for the remainder of the sampling period. Metolachlor was an exception in which concentrations exceeded 1 µg/L in September and October. Residues of atrazine and simazine were not detected as frequently as the year before although several samples exceeded 1 µg/L. 2,4-D was remarkably reduced in the second year of this study with only 3 detections. Possibly, these rural areas were not using 2,4-D as frequently as anticipated.

Alachlor and metolachlor to the analyses were added in 2000 and low concentrations of both compounds were observed with metolachlor in higher concentrations than alachlor. Notably, metolachlor was found later in the season (August, September, and October). As in year one of the study, detected pesticides and residue concentrations were similar between Lake Mackintosh and Stony Creek Watersheds and occasionally detections fell on the same day.

Greensboro: From February to October, 241 samples were collected in sets of 15 to 23, and analyzed for atrazine, chlorpyrifos, chlorothalonil, simazine, and 2,4-D. Atrazine was found frequently in a majority of the sampling sites of Greensboro from March to October. The pesticide levels detected in commercial and residential areas were generally below 1 µg/L with one exception in GBRS-7 (2.02 µg/L). Atrazine residues were consistently detected in the downtown sites although concentrations at GBUS-8 and GBUS-10 along NBC and SBC, respectively, were

low (0.05-0.41 µg/L). However, a tributary of NBC at GBUS-9 exhibited elevated levels of the pesticide from March to May (0.96-6.25 µg/L).

Simazine residues first appeared in May and were detected throughout the sampling period in commercial and residential areas (Fig. 10). The commercial detections were low (< 0.49 µg/L) except in August at GBCS-6 (2.28 µg/L) and GBCS-11 (1.05 µg/L), while residential areas exhibited low concentrations ranging from 0.04 to 0.74 µg/L throughout the sampling period. Similar to atrazine, downtown residues of simazine were elevated in GBUS-9 (0.03-4.82 µg/L) and GBUS-8 and 10 presented simazine throughout the year at low concentrations (< 0.83 µg/L).

2,4-D was present at elevated concentrations in February and March in residential (1.71-5.44 µg/L), commercial (1.1-6.93 µg/L), and downtown areas (1.2-2.54 µg/L). Residues of 2,4-D generally exceeded 0.75 µg/L for the remainder of the sampling period (April to October). Commercial sites along a NBC tributary presented elevated levels of 2,4-D ranging from 1.05 to 6.93 µg/L. Residential detections of 2,4-D were frequently found May through late August (1.16-9.64 µg/L). The downtown sites exhibited the pesticide mostly in May, June, and July with concentrations ranging from 0.73 to 32.95 µg/L while early fall samples exhibited very little presence of 2,4-D (Fig. 11).

Chlorpyrifos was detected in commercial and residential areas in April at concentrations ranging from 0.12 to 0.23 µg/L and twice in the following months; in May (GBRS-4, 0.08 µg/L) and July (GBCS-11, 0.16 µg/L). Downtown areas presented the pesticide throughout most of the year, albeit in low concentrations,

and only one detection exceeded 1 µg/L, along a tributary of NBC at GBUS-9 (August, 1.24 µg/L).

Chlorothalonil was found repeatedly during the sampling period in the commercial and downtown areas and residues detected from February to August ranged from 0.07-0.58 µg/L. In the residential sites, most of the occurrences of chlorothalonil were present early in the year from February to April (0.08-0.16 µg/L). Although chlorothalonil was frequently found in all areas the concentrations detected were low and well below the HAL (150.0 µg/L).

As a result of a protocol error, the final 10 samples of the Greensboro sampling season were analyzed for metolachlor. The herbicide was found in the majority of these latter samples at elevated levels (1.32-6.85 µg/L). The error was advantageous in that metolachlor had been detected in an urban area and current chemical protocols for watersheds required revision.

Summary: The predominant pesticide detected in the urban watershed was 2,4-D. Present as early as February and in following months of the study, the compound seemed to be regularly used in many areas of the city. 2,4-D was frequently found at elevated levels; however, the MCL was not exceeded. The researcher found this pesticide could be purchased readily by homeowners. Commonly applied triazines, atrazine and simazine were frequently found but in low concentrations. The MCLs for atrazine and simazine were exceeded once in the downtown site GBUS-9.

Considering that 2,4-D, atrazine, and simazine are herbicides that are typically used for the same purposes it was possible that the chlorophenoxy acid or

perhaps another herbicidal compound were more accessible than atrazine and simazine to homeowners and applicators in the residential and downtown areas. Very little evidence of prolonged use of atrazine and simazine existed in the watershed. Although the sporadic detections indicated some use was occurring, it was difficult to determine sources of pesticide input considering the multiple possibilities for pesticide applications in urban areas.

As previously mentioned, most of the pesticide input in the rural areas was from farming practices predominant in those areas. However, in the urban watersheds a variety of inputs can occur from homeowners, city maintenance, park beautification, and professional lawn-care applicators for businesses and apartments. Multiple pesticide inputs coupled with a greater percentage of impervious surfaces, suggested increased surface runoff which was conducive to pesticide transport into area tributaries.

The variation between urban and rural pesticide runoff patterns was evident in the temporal detections of pesticide residues in which the urban areas produced a dampened version of the characteristic seasonal trend depicted in agricultural (rural) areas. Evidence of variation within the urban watershed was demonstrated in the diverse pesticide residue detections in each area of Greensboro sampling (commercial, residential, and downtown) and did not seem to follow the seasonal trends associated with rural areas.

The metolachlor findings in the downtown areas of Greensboro were interesting because the chemical was primarily thought of as an agricultural herbicide; however, existing concentrations in the urban watershed were relatively

high when compared to other pesticide levels. There is no MCL currently assigned to metolachlor, although the USEPA has proposed an MCL of 70.0 µg/L, same as the HAL. These values far exceeded any residue concentrations found; therefore, environmental significance of metolachlor detections within the realm of this study was not addressed. Given that samples analyzed for metolachlor in the second year (2000) of the study were limited, increased investigation in this area is needed.

The overall pesticide detections observed in the urban watershed of Greensboro demonstrated a wide variety of chemical concentrations intermittently present throughout the year. Residues appeared early in the year and varied from month to month. Most of the pesticides were more prevalent in the downtown areas with the greatest concentrations detected for those chemicals present in these locales. 2,4-D appeared to be present at elevated levels in all areas including commercial, residential, and downtown sites.

High Point: The second urban watershed was monitored from April to November and 134 samples were collected, 18 samples at a time. Analyses included investigation of atrazine, chlorpyrifos, chlorothalonil, simazine, and 2,4-D residues resulting in 690 determinations. Significant concentrations were not observed until late June. A slight increase in atrazine at a downtown weir (HPMP-B, 1.69 µg/L) was followed by only two other elevated atrazine residues; HPL (HPHP-4, 1.92 µg/L) in August and Regency Lake (HPHP-5, 36.78 µg/L) in October. The 3.0 µg/L MCL was exceeded with the latter detection which is an order of magnitude greater than the regulatory value. Detections of atrazine residues in all areas were otherwise sporadic and below 1 µg/L.

The HPL detection of atrazine in August was accompanied by simazine, exceeding its MCL with a peak concentration of 10.59 µg/L. This was the only elevated detection of simazine for the season aside from 2.62 µg/L found in the same area in July. All other simazine detections along DL and downtown sites were below 0.29 µg/L.

2,4-D residues were along DL (HPDL-1, 2, 3) from June to November at concentrations ranging from 0.93 to 3.25 µg/L. Commercial areas (MP) and HP Lake exhibited the pesticide at elevated concentrations throughout the sampling period April through November (0.71-3.9 µg/L). Chlorpyrifos residues were detected frequently in all areas. Most occurrences of the pesticide were from April to early August (0.1-0.44 µg/L) with an occasional detection in the following months (< 0.15 µg/L). Chlorothalonil residues were rarely observed in samples of High Point. Most detections occurred in June along DL, MP, and Regency Lake. All chlorothalonil residue levels detected fell below 0.75 µg/L.

Due to the protocol error with Greensboro samples, and the discovery of metolachlor in some of the urban samples, final analyses in High Point included the chemical as part of analysis procedure in October and November. The majority of samples (88%) exhibited metolachlor residues, although concentrations were low. However, October detections in DL (HPDL-1, 1.53 µg/L; HPDL-2, 2.09 µg/L) and Oak Hollow Lake (HPOH-6, 5.42 µg/L) presented metolachlor at elevated levels.

Summary: Overall detections of pesticides in High Point were low with a few cases of elevated levels. The majority of pesticide detections occurred later in the year mostly beginning in June. With the exception of simazine and 2,4-D, pesticide

detections were reduced (Fig. 12). This was possibly a result of variation in usage of the compounds of interest and/or influence of precipitation. The increased input of other chemicals as well as potentially dry conditions could have lessened the likelihood of pesticide transport in surface waters. Precipitation data for Greensboro provided by the National Climatic Data Center (Asheville, North Carolina) was similar for both 1999 and 2000 and did not indicate lack of pesticide detections were a result of diminished rainfall.

The detections of atrazine (HHP-5; 36.78 µg/L in October) and simazine (HHP-4; 10.59 µg/L in August) were inconsistent with the majority of other residue detections with no implications of increased use prior to or following the detections. These sites are located in close proximity to roads and a bridge; areas that occasionally received applications of pesticides. A culmination of excessive use or accidental spills within the vicinity of the site in a short period of time could explain these levels that appeared to be acute circumstances.

Atrazine, simazine, and 2,4-D residues were detected more frequently and at higher levels relative to the other pesticides. Chlorpyrifos and chlorothalonil were found several times throughout the sampling period although most concentrations were low (Fig. 13). Two years of monitoring for chlorpyrifos and chlorothalonil has shown little presence in the study areas; possibly a result of minimal use of chlorothalonil and chlorpyrifos in the vicinity of sampling sites.

Addition of metolachlor at the conclusion of the sampling year presented results similar to those of Greensboro. An agricultural pesticide was present in an urban watershed relatively late in season with no indication of its source. As with the

neighboring city, metolachlor was added to analysis protocol for High Point for the next year.

YEAR THREE—2001

Burlington: Two hundred eighty samples were collected from March to September and analyzed for atrazine and metolachlor. The other pesticides previously assigned to the chemical analysis protocol were eliminated because of extremely low concentrations or lack of detection. Focus on these two pesticides alone was founded on the recurrent predominance of atrazine and interest in characterizing the presence of metolachlor in a rural watershed.

The 557 determinations overall exhibited low concentrations for both compounds. Atrazine was present in almost all of the samples from BVR, Little Alamance, RK, Jordan, BM, and Stony Creeks from March to September. It was not until May that elevated concentrations of the herbicide were observed and found approaching or exceeding the 3.0 µg/L MCL, once in Rock Creek (BULM-2E1, 2.08 µg/L) and again in Buttermilk Creek (BUSC-1D1, 5.0 µg/L). Residues of atrazine were found in the following months in all areas although at low levels (0.05-0.41 µg/L).

Metolachlor was detected in a large majority of samples collected along the six creeks and analyzed in the third year (2001). Most detections of this pesticide were low in concentration but there were several exceptions. In March, both RK and Jordan Creek exhibited signs of metolachlor at BULM-2E5 (1.32 µg/L) and BUSC-1C (1.72 µg/L), respectively. Jordan Creek of the Lake Mackintosh Watershed was

found to contain metolachlor residues of 1.97 µg/L (BUSC-1C) in April.

Concentrations of metolachlor residues in all areas declined to earlier levels for the remainder of the season with one exception in July along BM Creek with a detection of 1.52 µg/L (BUSC-1D1).

Summary: The amended sampling protocols and chemical analyses allowed for greater characterization of the more prevalent compounds, atrazine and metolachlor. In conferring with County Cooperative Agricultural Extension Agents there was a slight drought situation in Burlington in 2001. Declining precipitation levels might have contributed to the abatement of elevated pesticide residues in area water bodies. As mentioned earlier, rainfall is required for most advection of chemicals from point of application to watershed surface waters; however, there was constant detection of both compounds throughout the year indicating some transport of these chemicals to surface waters (Fig. 14). Neither atrazine nor metolachlor prevailed over the other in detection and both were continually present, albeit at low levels.

Greensboro: Ninety-three samples were collected from March to September and analyzed for alachlor, atrazine, metolachlor, simazine, and 2,4-D (528 determinations). Residues of atrazine were found in commercial, residential, and downtown areas from March to September ranging from 0.06 µg/L to 0.41 µg/L. All the concentrations detected were relatively low levels and the MCL of 3.0 µg/L was not approached or exceeded.

Simazine residues were observed in many of the May and June samples of the commercial and residential areas (0.03-0.10 µg/L) although absent for the

remaining months. The site along a NBC tributary (GBUS-9) exhibited simazine residues in concentration ranging from 0.04 to 0.26 µg/L. Alachlor was present in commercial areas from July to September with concentrations ranging from 0.05 to 0.07 µg/L. One residential site (GBRS-1) exhibited alachlor in March at 0.23 µg/L while another (GBRS-4) presented the pesticide from May to September (0.05-0.44 µg/L). Alachlor residues were more prevalent in the downtown areas, found throughout the sampling period although concentrations never exceeded 0.65 µg/L.

Metolachlor, on the other hand, was found in most of the samples throughout the sampling period (Fig. 15). Residues of metolachlor were detected at elevated levels in residential (1.01-3.05 µg/L), commercial (1.42-3.80 µg/L), and downtown (1.09-8.26 µg/L) areas. Most of the elevated metolachlor concentrations were centered in a downtown area of four sub-sites, 9a, 9b, 9c, and 9d according to outfalls that impound this tributary of NBC. These sites were at GBUS-9, a site that has shown frequent contaminations. The primary site was broken down into individual sub-sites for further investigation of contamination.

2,4-D residues were found in many samples although earlier in the year from March to June. A September peak (6.26 µg/L) of 2,4-D was present in Richland Creek near a residential area (GBRS-1) and no other detections occurred after June in any sample or area. Elevated residues were found in commercial, residential, and downtown areas ranging from 0.78 to 6.50 µg/L. The greater concentrations of 2,4-D detected were generally found in May for all areas.

In a departure from the previous year, 2,4-D was more prevalent in the residential areas and not frequently found in the downtown sites. Analyses for 2001

exhibited 2,4-D in all types of areas including the residential, commercial, and downtown waters of Jordan Creek, Horse Pen Creek, and NBC and its tributaries.

Summary: Sample protocols were modified by adding alachlor and metolachlor and dropping chlorpyrifos and chlorothalonil. The latter two were eliminated due to complete lack of detections of environmentally relevant concentrations ($> 1 \mu\text{g/L}$) in the first two years of the study. It was concluded that these chemicals presented little threat to human health in the drinking water sources of this study. However, the chloroacetanilide compounds, alachlor and metolachlor, were briefly found in earlier studies and it was felt that a more extensive investigation was required.

Overall results of the urban pesticide analyses indicated a departure from more common pesticides, atrazine and simazine, to increased use of another herbicide, metolachlor. It was evident that metolachlor, formerly considered solely agricultural, was present in urban settings distant from potential agricultural deposits (e.g., parks, golf courses, ornamentals, rights-of-way) (Briggs 1992) as early as February and March throughout the summer and fall months.

Notably the elevated concentrations of 2,4-D ($0.78\text{-}6.5 \mu\text{g/L}$) that were found seemed to be consistently greater than previously observed in any of the other watersheds. The higher levels of 2,4-D observed in combination with earlier indications suggested that the compound was used more intensively. 2,4-D was commonly found as early as February and as late as November. However, the Greensboro detections in 2001 exhibited no presence of 2,4-D residues after June

indicating applications occurred at different times throughout the year and use of compounds varied from site to site and year to year.

High Point: Forty-three samples were collected from March to July and analyzed for alachlor, atrazine, metolachlor, simazine, and 2,4-D. When it became apparent that metolachlor was present in Greensboro this compound was added to the analysis protocol, along with alachlor, for the two urban watersheds (Greensboro and High Point). Analysis of chlorpyrifos and chlorothalonil was eliminated as detectable concentrations of both chemicals were low in the first two years of the study and indicated a minimal threat to surface water quality and human health.

Alachlor residues detected in High Point occurred in May for all areas and were infrequently present in areas along HPL (HPHP-5, 6) and OHL (HPOH-5) ranging from 0.07 to 0.13 µg/L. There were no detections of the pesticide in DL or its tributaries. Residues of alachlor were found in March and May along commercial sites (HPMP-B) although concentrations were low (< 0.12 µg/L). Atrazine was present from April to July for most of the sites in High Point. The concentrations detected were low with the exception of 1.13 µg/L found in a commercial area (HPMP-B) in May. Simazine residues were present from March to July but never at high concentrations (0.04-0.27 µg/L). There was little indication of alachlor, atrazine, or simazine being used in great quantities in the study areas.

Metolachlor residues were present at elevated levels in March for all areas. DL, HPL, Regency Lake, MP, and OHL exhibited metolachlor in March ranging from 0.66-2.1 µg/L. Concentrations tapered off until May when two notable detections occurred. OHL (HPOH-5) and a weir (HPMP-B) showed metolachlor residues at

levels of 4.04 and 3.22 µg/L, respectively. No other elevated detections were observed in the following months.

2,4-D was found frequently in all areas throughout the course of the year. Elevated levels were present in DL (HPDL-1) in March and May at 1.2 and 3.43 µg/L, respectively. HPL (HPHP-2, 4, 5, 6, 9) exhibited residues of 2,4-D ranging from 0.82 to 8.51 µg/L in March, May, and July. MP (HPMP-B) sites presented elevated concentrations of 2,4-D as high as 6.11 µg/L. Only one of these sites was sampled for the whole season while the other three sites (HPMP-B1, B2, B3) were sampled in March with levels of 2,4-D exceeded 1.0 µg/L (1.46-5.03 µg/L).

Summary: Sample quantity in 2001 was limited due to unavailability of city personnel to collect samples. Even with restricted amounts of data, it was evident that High Point presented similar pesticide detection patterns as Greensboro. Atrazine and simazine, two frequently used herbicides were continually present but in low concentrations. Other herbicides, metolachlor and 2,4-D, were found to a greater extent throughout most of the sampling period and at somewhat greater concentrations than were typically seen in this area (Fig. 16).

It cannot be confidently stated that atrazine and simazine were not used given that there was evidence of their presence, but rather they were used in a dwindling capacity or in locations distant from sampling sites rendering detected concentrations insignificant, relative to regulatory values. Detections of 2,4-D residues were further evidence of the continual use of this compound in urban areas as has been previously noted in earlier results of this study. Discovered and observed repeatedly, metolachlor was not used for agricultural purposes alone and

was most likely applied in and around urban areas possibly to highway rights-of way, recreational parks, fruit trees, and/or ornamentals.

Raleigh: An advantage of this study's experimental design was the ability to adapt procedures as data and implications of these results called for revision. In the third year of this study another rural watershed was added to the locations of interest, this being Raleigh's Falls of the Neuse watershed. Preliminary data were gathered to begin a more extensive characterization in subsequent studies.

Collections of 1 to 3 samples at a time yielded 52 total samples that were analyzed for atrazine and metolachlor. The pesticides investigated were based upon previous findings in the rural watersheds of Burlington. Samples were collected beginning in May and ending in September. Low concentrations of both pesticides were present throughout most of the season (Fig. 17). Atrazine residues were found along Buckhorn Creek and Chunky Pipe in May, June, August, and September at concentrations ranging from 0.05 to 0.65 $\mu\text{g/L}$. Metolachlor residues were found in all samples collected from May to late August (0.19-0.78 $\mu\text{g/L}$). The maximum metolachlor levels of the sampling period were found along Chunky Pipe Creek in August (RAFL-11, 0.93 and 1.16 $\mu\text{g/L}$).

Summary: This was a preliminary study; therefore, the limited data made an adequate characterization of pesticide residue presence in Raleigh impossible at this time. There was only one occasion in which pesticide levels were elevated above 1 $\mu\text{g/L}$; metolachlor at 1.16 $\mu\text{g/L}$. The residue values were low for most of the year and the one elevated concentration incited little concern considering metolachlor has no MCL and its HAL of 70.0 $\mu\text{g/L}$ far exceeded any environmental concentrations

found in this study. Concentrations of atrazine detected in Raleigh did not exceed its MCL of 3.0 µg/L and levels were considered safe with regard human health.

The lack of environmentally relevant pesticide residues was possibly influenced by reduced usage or precipitation events in this area in 2001. Most likely, results were limited by having only two sampling sites that did not represent a realistic depiction of the environmental presence of the pesticides of interest. However, by analyzing for only two pesticides instead of a larger base that began broadly and was narrowed down over several years, the foundation upon which to assess the watershed was restricted. Further monitoring of the area must be performed in order to create a basis of understanding for the environmental presence of pesticides used and any surface water contamination that might occur.

SUMMARY—THREE YEARS

Studies have shown pesticide contamination of surface water supplies occurs primarily by way of surface runoff as a result of precipitation events following pesticide applications. Increases in precipitation increase the likelihood of surface water runoff, providing ample surface flow and transport for chemicals away from application site to surface waters.

Other conditions to consider encompass duration and intensity of precipitations events, infiltration capacity of the soil and various soil characteristics. An example of pesticide surface runoff involved seasonal loading of atrazine from agricultural fields in which low levels were observed in April and early May following application. There was a large increase in atrazine concentrations in water supplies

following the first significant rain event, usually in late May and early June. Small peaks occurred throughout the summer and were followed by a continual decrease into the fall and winter months (Shea 1997).

These environmental trends have been observed numerous times and are generally accepted as runoff characteristics associated with pesticides. The decline was thought to be due to previously mentioned environmental factors and eventual breakdown of compounds to their metabolites. The seasonal trend described here was exhibited in the pesticide detections of rural watersheds.

In the rural watersheds, three of the five compounds studied were prevalent, atrazine, simazine, and 2,4-D. The seasonal pattern characteristic of pesticide detections observed in the rural watersheds exhibited the majority of elevated concentrations in May when spring rains usually occurred. Similar results were found in the two watersheds of Burlington, Lake Mackintosh and Stony Creek although some variations occurred most likely due to site specificity and location of pesticide applications. Late summer and early fall herbicide detections occurred in both watersheds as was expected due to typical pre-winter treatments in agricultural areas.

2000 and 2001 exhibited some discrepancies between the two watersheds in Burlington and some differences within respective watersheds. Lake Mackintosh comprised several sites that were arranged in groupings of sub-sites and various detections of different pesticides were discovered. Clearly, depending upon land-use and applicator, sites within close proximity of each other can differ as to the pesticides present and the concentrations.

The Greensboro watershed was separated based upon land-use such as commercial, residential, or strictly urban (referred to as downtown sites). 2,4-D and metolachlor, two herbicides commonly used, were the main compounds that appeared in this urban watershed. The characteristic peaks seemed to follow rain events but the pesticides appeared at atypical times of the sampling period. The urban pesticide detections did not follow seasonal patterns associated with agricultural runoff and residues were found for the duration of the sampling period.

Detections occurred early (February) and late (November) in the year. Some precedence was observed in the different land types. Commercial and residential sites mostly exhibited residue levels of 2,4-D and metolachlor while more densely developed urban sites exhibited residues all four of the herbicides, atrazine, simazine, metolachlor, and 2,4-D.

The High Point watershed exhibited a variety of contaminants, specifically atrazine, simazine, 2,4-D, and metolachlor. These compounds were present in many of the sites, although 2,4-D was the most prevalent. Chemical detections and concentrations varied throughout the course of the season. The seasonal trend was not followed. The urban watersheds were very similar with regard to pesticides that were present as well as the trends and detection patterns exhibited.

DETECTION RATES OF PESTICIDES

The percentage of chemical detections increased over the course of the three year study. This was expected as a result of the versatile sampling design that eliminated sites of little or no contamination and focused on those that were

considered problem areas. By directing efforts to the more contaminated sites detection was enhanced.

Representative rural watersheds include Lake Mackintosh and Stony Creek Watersheds of Burlington. Pesticide residues were detected at varying rates in the rural watersheds. Atrazine sample detections increased from 45 to 59% while simazine (41 to 33%) and 2,4-D (8 to 3%) declined from 1999 to 2000. There was greater diversity in the detection rates of chlorpyrifos; 4% in 1999 to 43% in 2000. Alachlor and metolachlor were analyzed for in 2000 and found in 13 and 56% of samples, respectively.

The third year of the project allowed for the comparison of another rural watershed. Samples collected in Raleigh rural areas provided for additional data comparison. Considering that the sampling protocol for 2001 was the only year in which all three rural watersheds were analyzed and only two pesticides were investigated; the characterization of distant and varying rural watersheds was limited to atrazine and metolachlor detections for one year.

Burlington had a higher detection rate for the compounds investigated and atrazine and metolachlor were present in 78 and 88% of samples, respectively. Raleigh samples exhibited atrazine in 63% and metolachlor in 80% of surface water samples collected. Although the results were similar between the watersheds the Raleigh data represented pesticide residue detections in three sites signifying a potential skewing of this data by the limited number of sites sampled.

The two urban watersheds were monitored for atrazine, simazine, and 2,4-D in all three years while chlorothalonil and chlorpyrifos were investigated in 1999 and

2000. Greensboro atrazine detection rates increased from 32% in 1999 to 43% in 2000, with a final rate of 46% in 2001. Samples in High Point showed atrazine in 48% (1999), 25% (2000), and 67% (2001). The Greensboro detections of simazine increased from 19% to 40% from 1999 to 2000. In 2001, the detection rate decreased with only 27% of samples positive for simazine. Rates varied for the other urban watershed. High Point simazine rates ranged from 33 to 21 to 28% for the three years of study. 2,4-D residues were detected at similar rates in both urban watersheds in 1999 (Greensboro 26%; High Point 35%), 2000 (Greensboro 30%; High Point 25%), and 2001 (Greensboro 39%; High Point 53%).

Similar to the rural areas, there was a greater degree of variation in detection rates of chlorothalonil and chlorpyrifos from year to year and between watersheds. Greensboro exhibited chlorothalonil and chlorpyrifos in 70 and 18%, respectively in 1999. The 2000 detections were closer in value with chlorothalonil in 38% and chlorpyrifos in 18% of samples. High Point detections of chlorothalonil (52%) and chlorpyrifos (0%) in 1999 varied considerably from the 2000 detection rates of chlorothalonil (9%) and chlorpyrifos (46%).

Metolachlor was added to the sampling protocol in the latter part of 2000 for both urban watersheds but was found in a large percentage of samples. The pesticide was found in 78% of samples in Greensboro and 90% of samples in High Point. Rates increased in the following year in which metolachlor was detected in Greensboro (92%) and High Point (95%). Alachlor was monitored in only 2001 and rates varied with 35% in Greensboro and 26% in High Point.

Four pesticides monitored over the three years of the study were compared to demonstrate any differences between rural and urban pesticides detection rates (Figs. 18-20). Differences were observed with various compounds, such as 2,4-D, which was observed regularly in the urban watersheds as opposed to minor detections in rural locales. Atrazine seemed to be detected to a slightly larger degree in rural areas, most likely due to its popularity in corn crop treatments of which Burlington has sizeable acreage. The other triazine, simazine, known for its use in both types of watersheds and commonly applied along highway rights-of-way, was found uniformly in all areas. Metolachlor was found in rural and urban sites although at a higher rate of detection in the urban areas.

The two types of watersheds, rural and urban, were surprisingly comparable in the pesticide residue detection rates. However the detection characteristics they possessed differed. The rural watersheds' pesticide detections tended to follow the typical characteristics associated with agricultural pesticide surface runoff patterns and atrazine, simazine, and 2,4-D were the primary pesticides detected. Urban watershed pesticide detections showed a variety of compounds with a predominance of metolachlor and 2,4-D residues. However, there was more variation between sites in the urban areas as opposed to rural locales. This was expected considering the similarity of rural watershed sites (agriculture) and the diversity of urban sites (commercial, residential, and downtown).

CONCLUSION

Watersheds categorized as either urban or rural were investigated for three years to determine if a select group of pesticides were present and at what concentrations. Areas of suspected contamination were analyzed for pesticides to identify those sites most likely receiving pesticide residues from runoff. Upon completion of this project, it was discovered that all seven compounds were present at various times in surface waters within the watersheds.

The presence of pesticide residues in urban watersheds varied throughout the year while rural watershed pesticide detections followed typical seasonal patterns. Residues found in both rural and urban watersheds were similar in concentrations, although the compounds found varied somewhat between the two different types of watersheds. Atrazine, simazine, and 2,4-D were chiefly found in the rural watersheds, while 2,4-D and metolachlor were commonly detected in the urban areas. Several sites within these watersheds were identified as potential problem areas; downtown areas of Greensboro (GBUS-8, 9, and 10) and commercial High Point (HPMP-A, B, C, and D) as well as residential areas of both urban watersheds. Rural watershed potential problem areas included the site groupings of 2B, 2E, and 1D.

The pesticide residues detected in the surface waters were generally below regulatory values, although the 3.0 µg/L for atrazine and 4.0 µg/L for simazine were exceeded in 6 and 3 samples throughout the sampling period of the three year study. The concentrations detected were most likely not a hazard to human health

considering the surface waters analyzed were raw, pre-treatment water supplies and MCLs refer to finished, drinking water.

While pesticide residue concentrations detected in this study were not immediately threatening to water quality and human health, there are other implications to consider. Initially, multiple pesticides were found in almost all water samples over the entire study; rarely did a sample contain only one compound. Even though detected concentrations of analytes were relatively low and less than their respective MCLs, there is little information available on the potential synergistic effects of multiple pesticides in the environment. Additionally, detection of low levels of pesticide residues over multiple sampling dates was indicative of a chronic presence of these compounds.

This study focused on more than detection of pesticide residues that exceeded regulatory values. Characterization of select areas in rural and urban watersheds provided a more in-depth understanding of the pesticide differences between rural and urban watersheds as well as individual sites within the urban areas. Discovery of multiple pesticides, chronically present, combined with limited information on these effects culminates in potential exposure in drinking water. This possibility for contamination requires further investigation to determine human health and environmental implications.

This study contributed to the assessment of the watersheds by collecting data concerning pesticide residues, identifying pesticides within the area water supplies and determining the concentrations present over the course of three years. As established earlier, the surface waters selected for this study were of concern

because they are drinking water sources for municipalities. These waters will eventually reach water treatment plant intakes and be treated to provide drinking water for the respective cities. Working with other stakeholders in the areas (e.g., county extension, university research, and city representatives) provided a variety of information and resources otherwise unavailable that allowed the foundation of watershed assessment in these select watersheds to take shape.

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Table 1. Pesticide Class, Toxicity, Use Classification, and Drinking Water Standards, the Maximum Contaminant Levels (MCL) and Health Advisory Levels (HAL) established by the USEPA.

Pesticide	Class	Toxicity Class	Description	Use	MCL or *HAL (µg/L)
Alachlor	Herbicide	III	Slightly Toxic	Restricted	2.0
Atrazine	Herbicide	III	Slightly Toxic	Restricted	3.0
Chlorothalonil	Fungicide	II	Moderately Toxic	General	*150.0
Chlorpyrifos	Insecticide	II	Moderately Toxic	General	*20.0
Metolachlor	Herbicide	III	Slightly Toxic	General/some Restricted	*70.0
Simazine	Herbicide	IV	Practically Nontoxic	General	4.0
2,4-D	Herbicide	III	Slightly Toxic	General	70.0

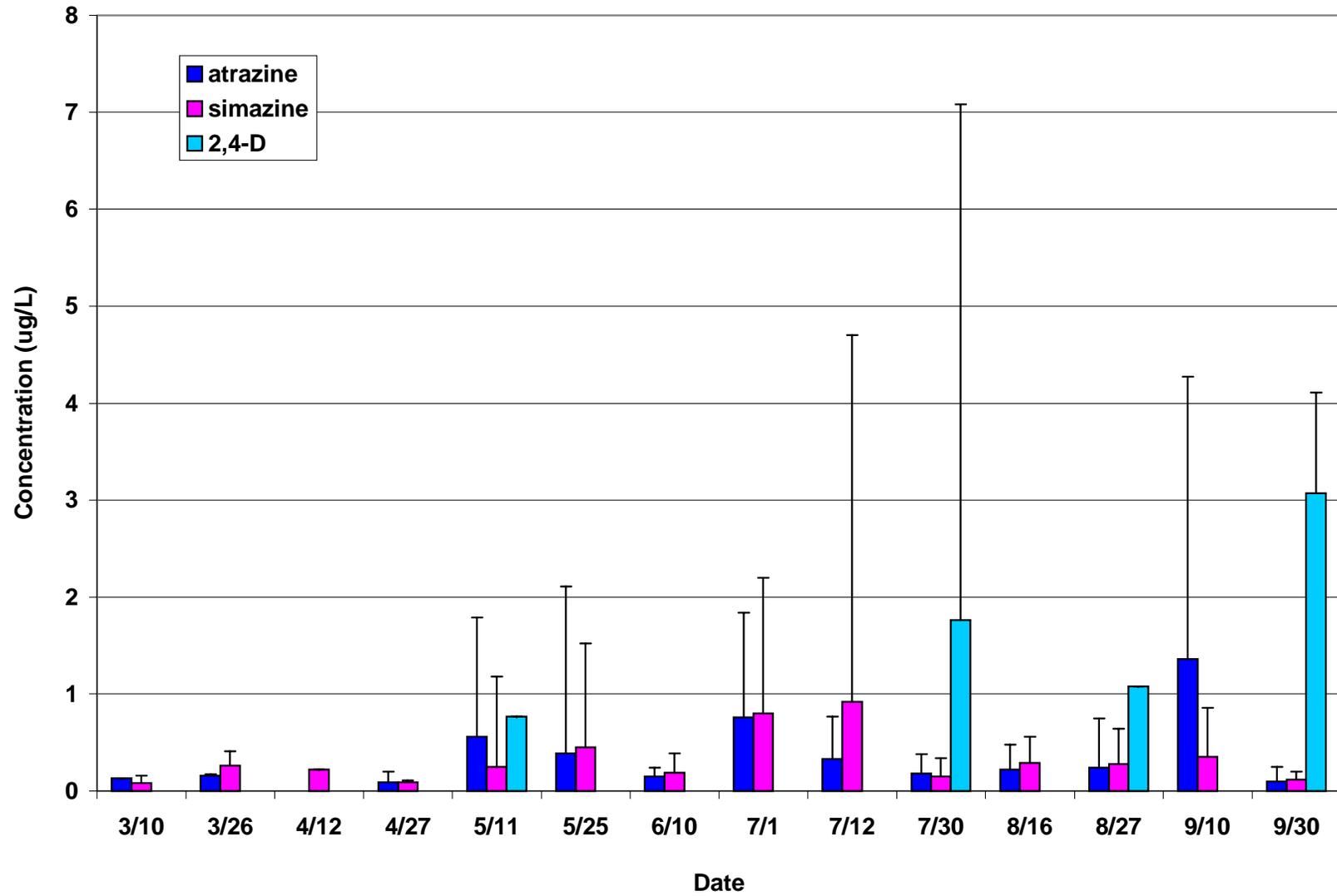


Figure 1. Average monthly pesticides concentrations for atrazine, simazine, and 2,4-D in Burlington 1999. Solid bars represent average concentration and narrow bars represent maximum concentration.

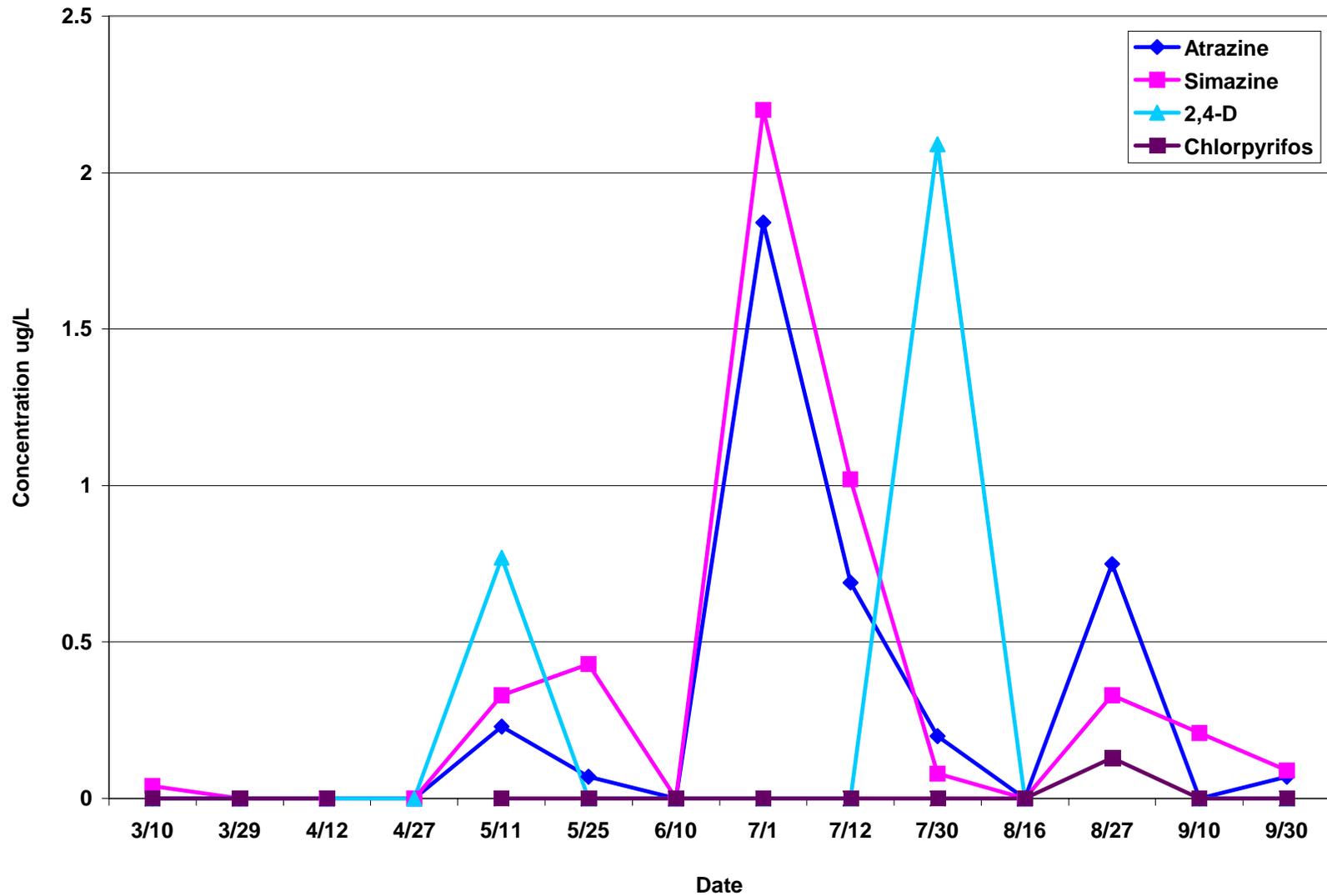


Figure 2. Atrazine, simazine, 2,4-D, and chlorpyrifos residues detected from March to September of 1999 in Rural Watershed 1 (Burlington).

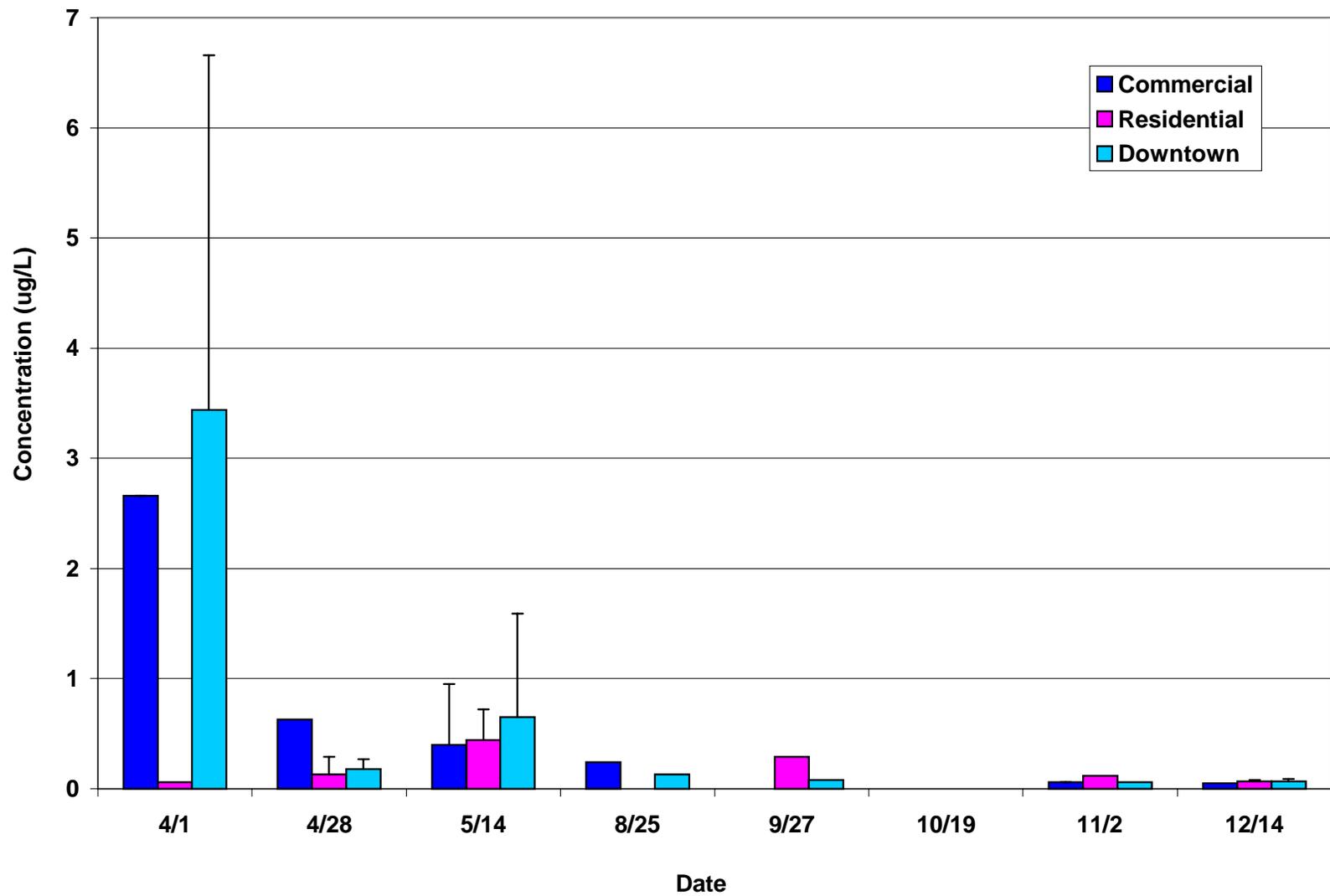


Figure 3. Average monthly atrazine concentrations in commercial, residential, and downtown areas of Greensboro in 1999. Solid bars represent average concentration and narrow bars represent maximum concentration.

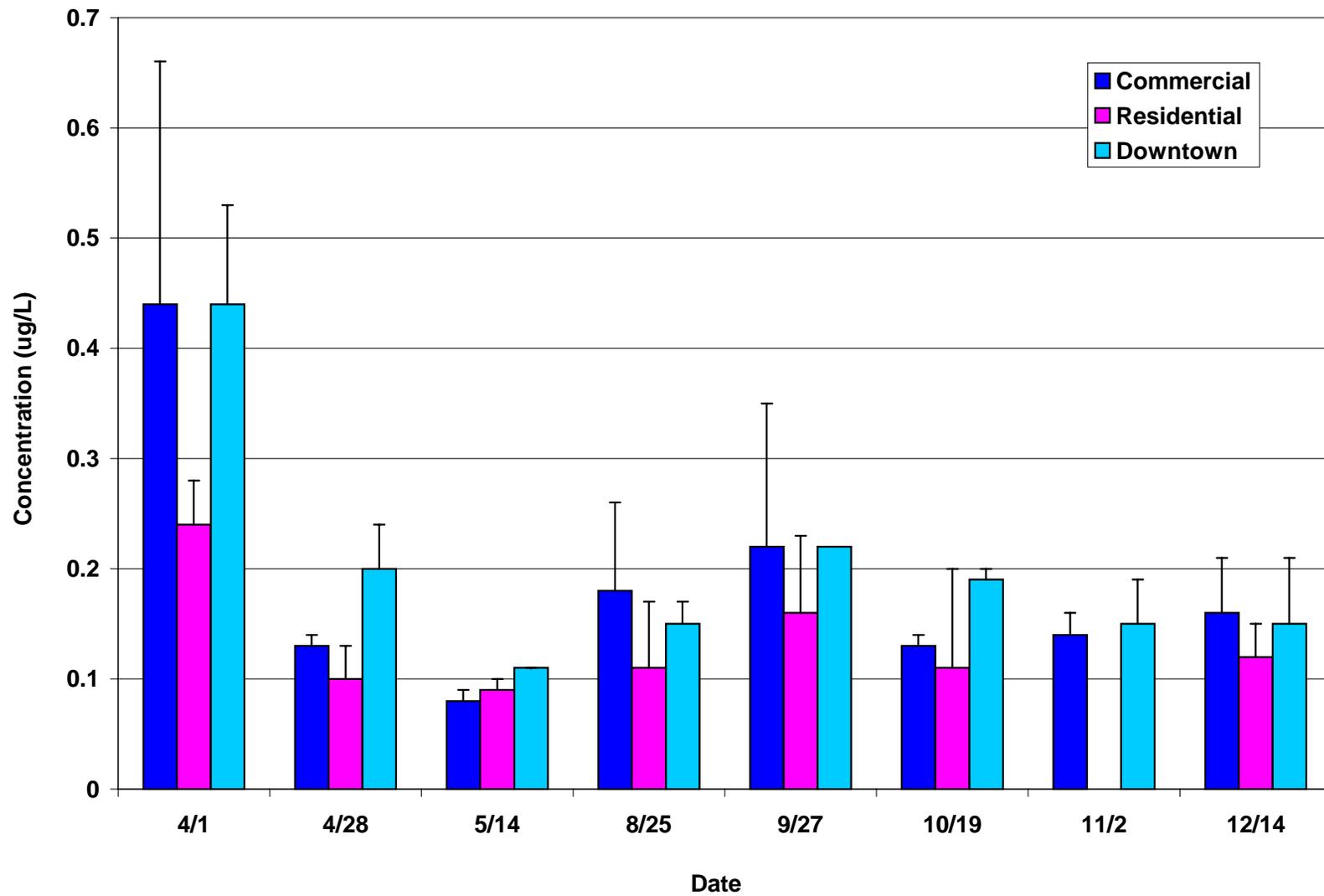


Figure 4. Average monthly chlorothalonil concentrations in commercial, residential, and downtown areas of Greensboro in 1999. Solid bars represent average concentration and narrow bars represent maximum concentration.

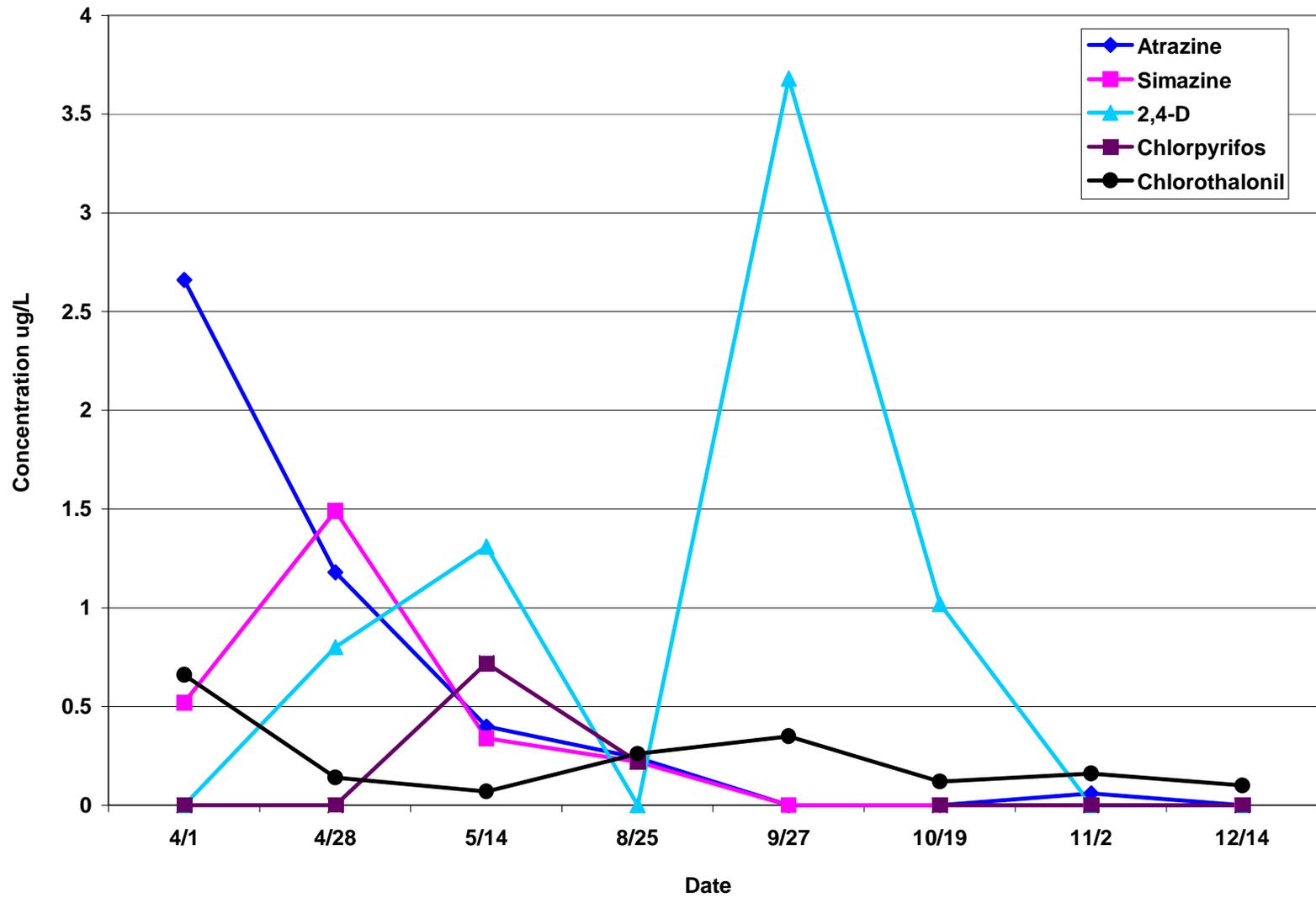


Figure 5. Atrazine, simazine, 2,4-D, chlorpyrifos, and chlorothalonil residues detected from April to December of 1999 in Urban Watershed 1 (Greensboro).

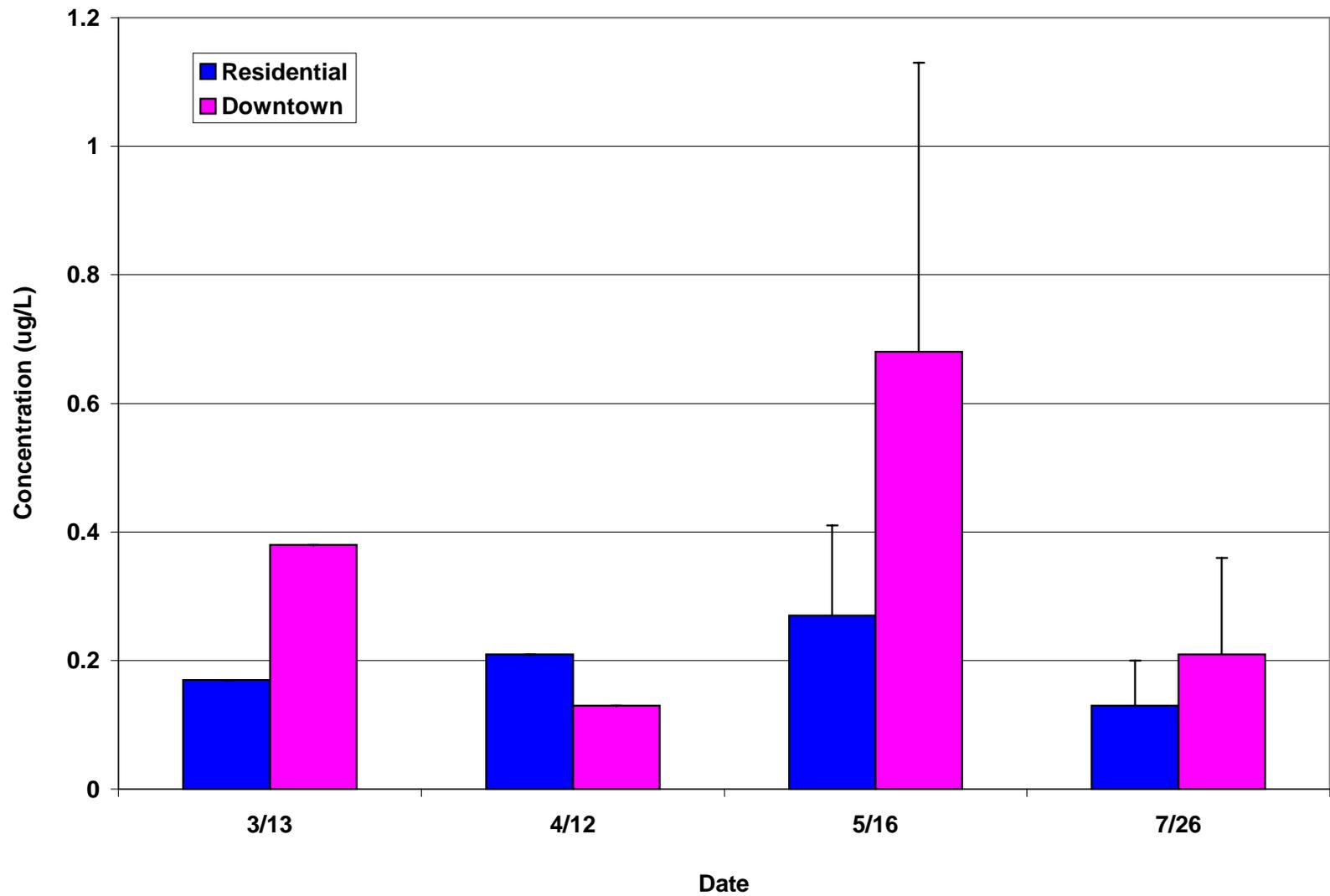


Figure 6. Average monthly atrazine concentrations in residential and downtown areas of High Point 1999. Solid bars represent average concentration and narrow bars represent maximum concentration.

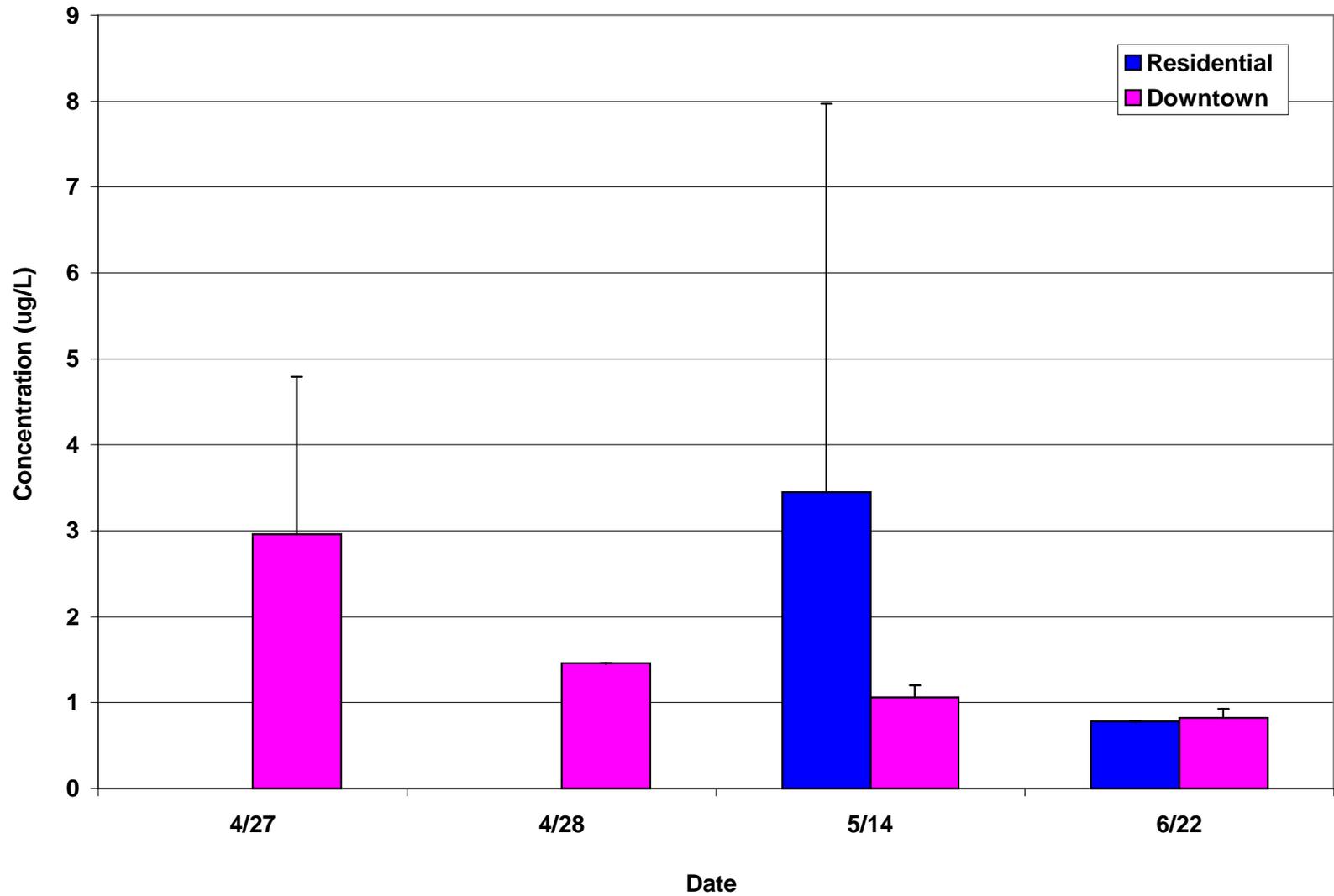


Figure 7. Average monthly 2,4-D concentration in residential and downtown areas of High Point 1999. Solid bars represent average concentration and narrow bars represent maximum concentration.

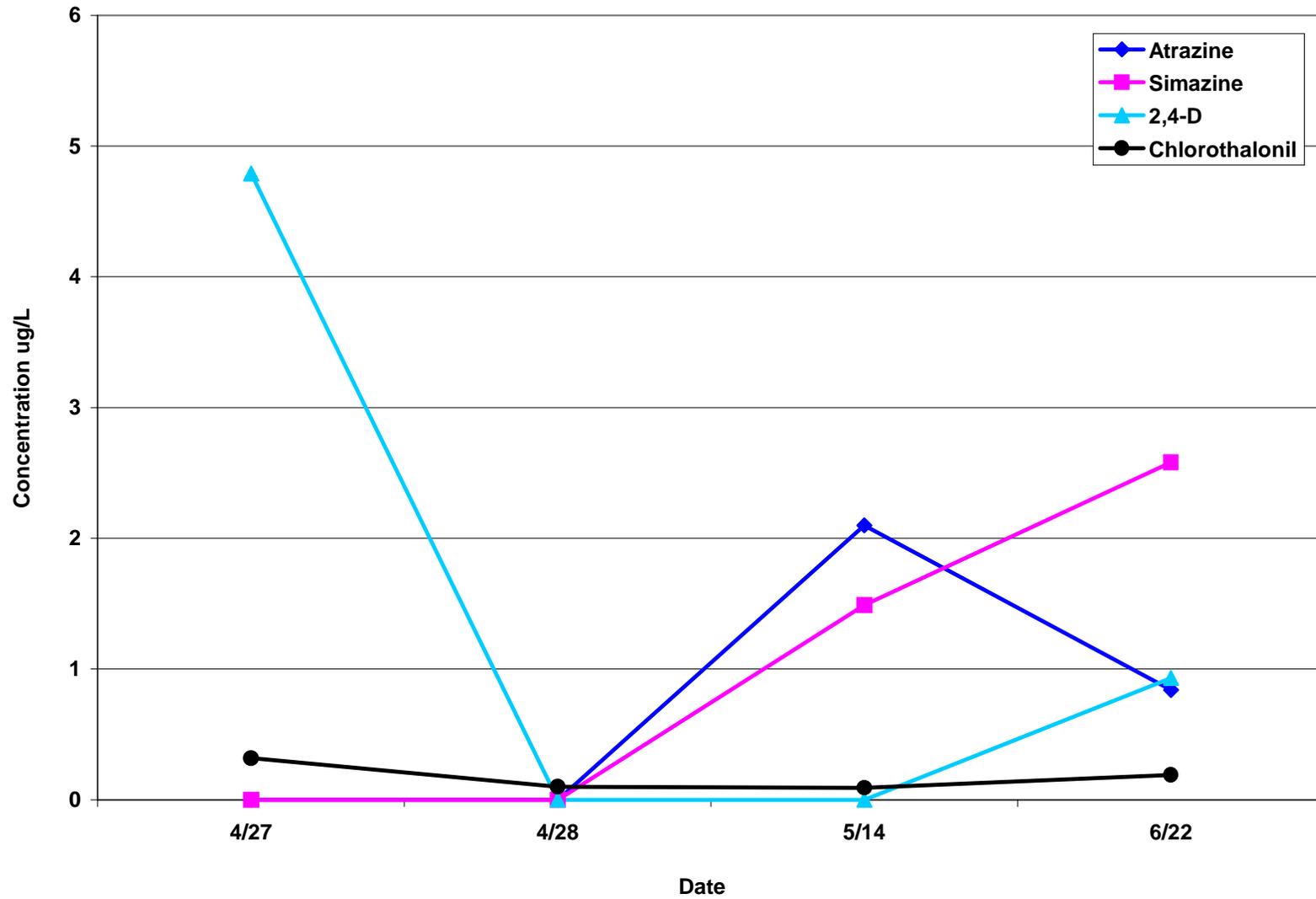


Figure 8. Atrazine, simazine, 2,4-D and chlorothalonil residues detected from April to June of 1999 in Urban Watershed 2 (High Point).

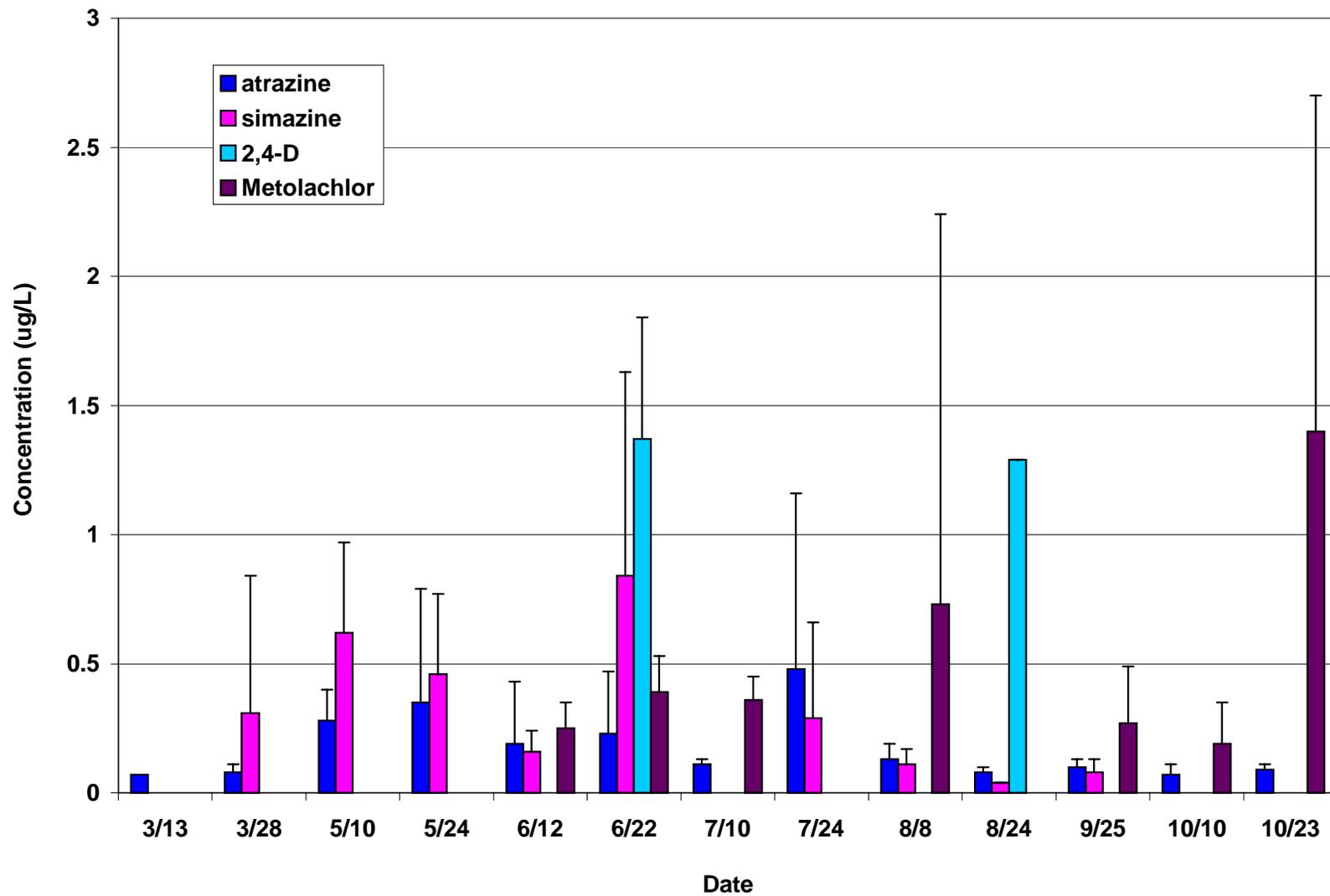


Figure 9. Average monthly atrazine concentrations in Burlington 2000. Solid bars represent average concentration and narrow bars represent maximum concentration.

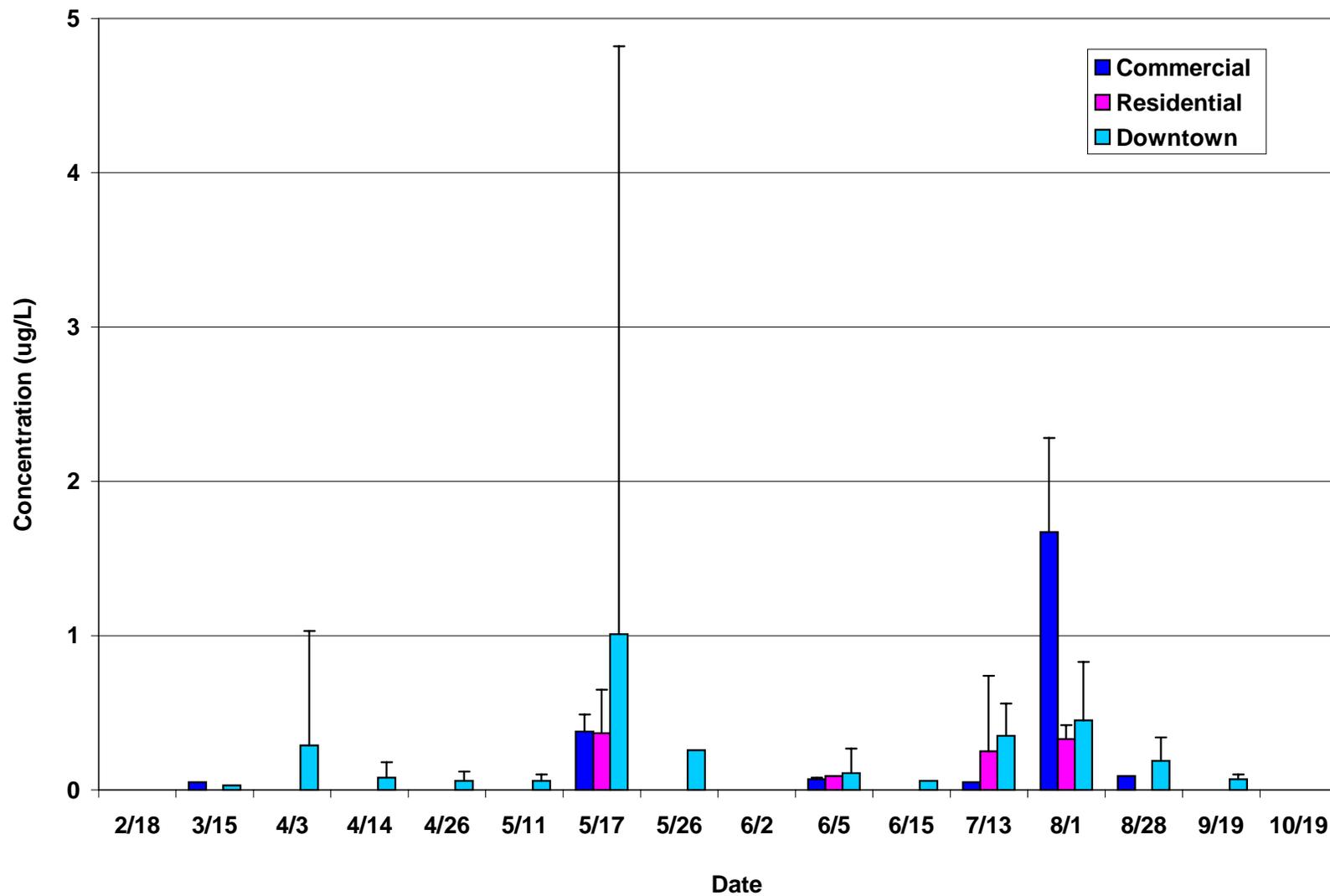


Figure 10. Average monthly simazine concentrations in commercial, residential, and downtown Greensboro 2000. Solid bars represent average concentration and narrow bars represent maximum concentration.

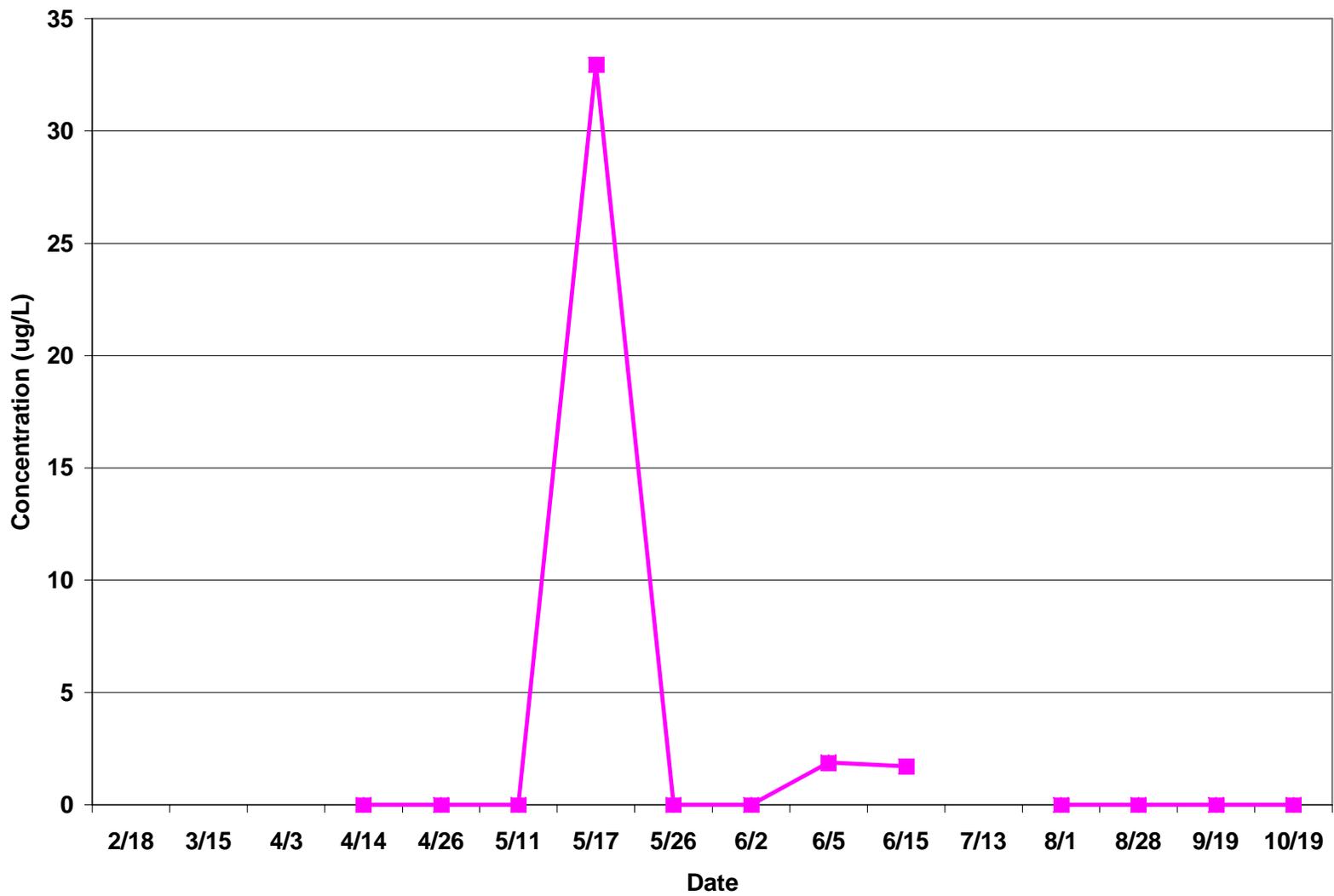


Figure 11. 2,4-D detections from February to October in Greensboro (GBUS-9c) 2000.

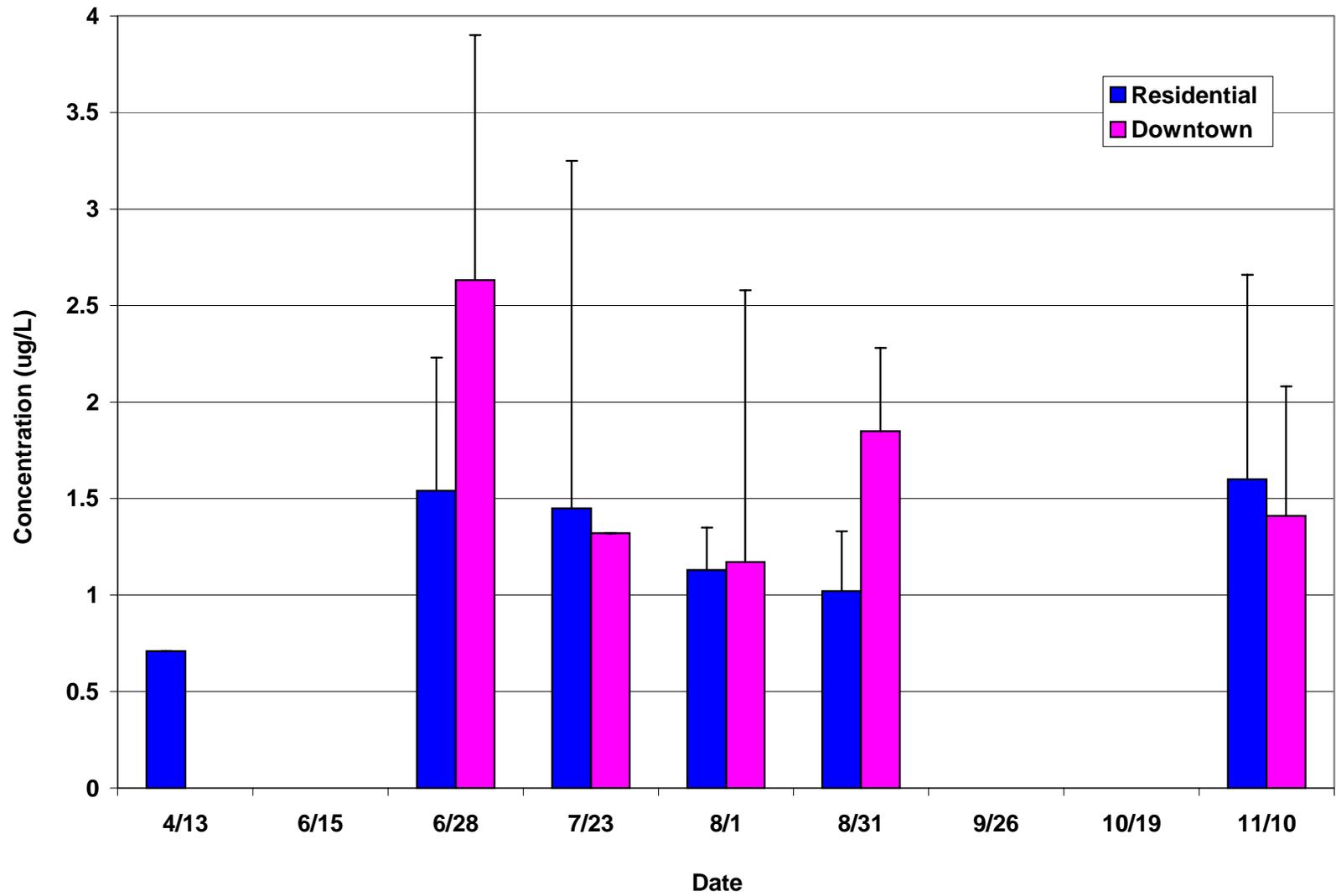


Figure 12. Average monthly 2,4-D concentrations in residential and downtown areas of High Point 2000. Solid bars represent average concentration and narrow bars represent maximum concentration.

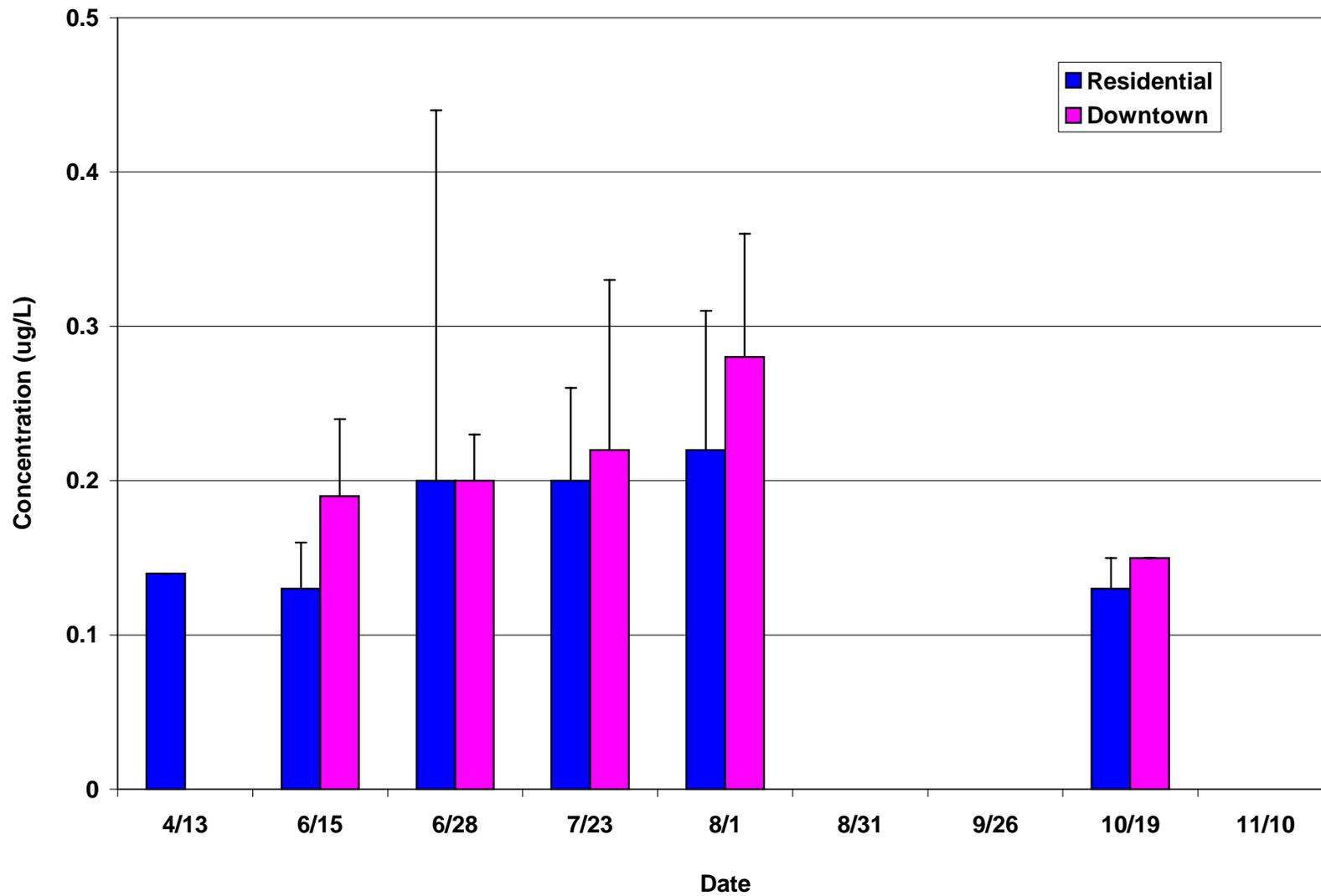


Figure 13. Average monthly chlorpyrifos concentrations in residential and downtown areas of High Point 2000. Solid bars represent average concentration and narrow bars represent maximum concentration.

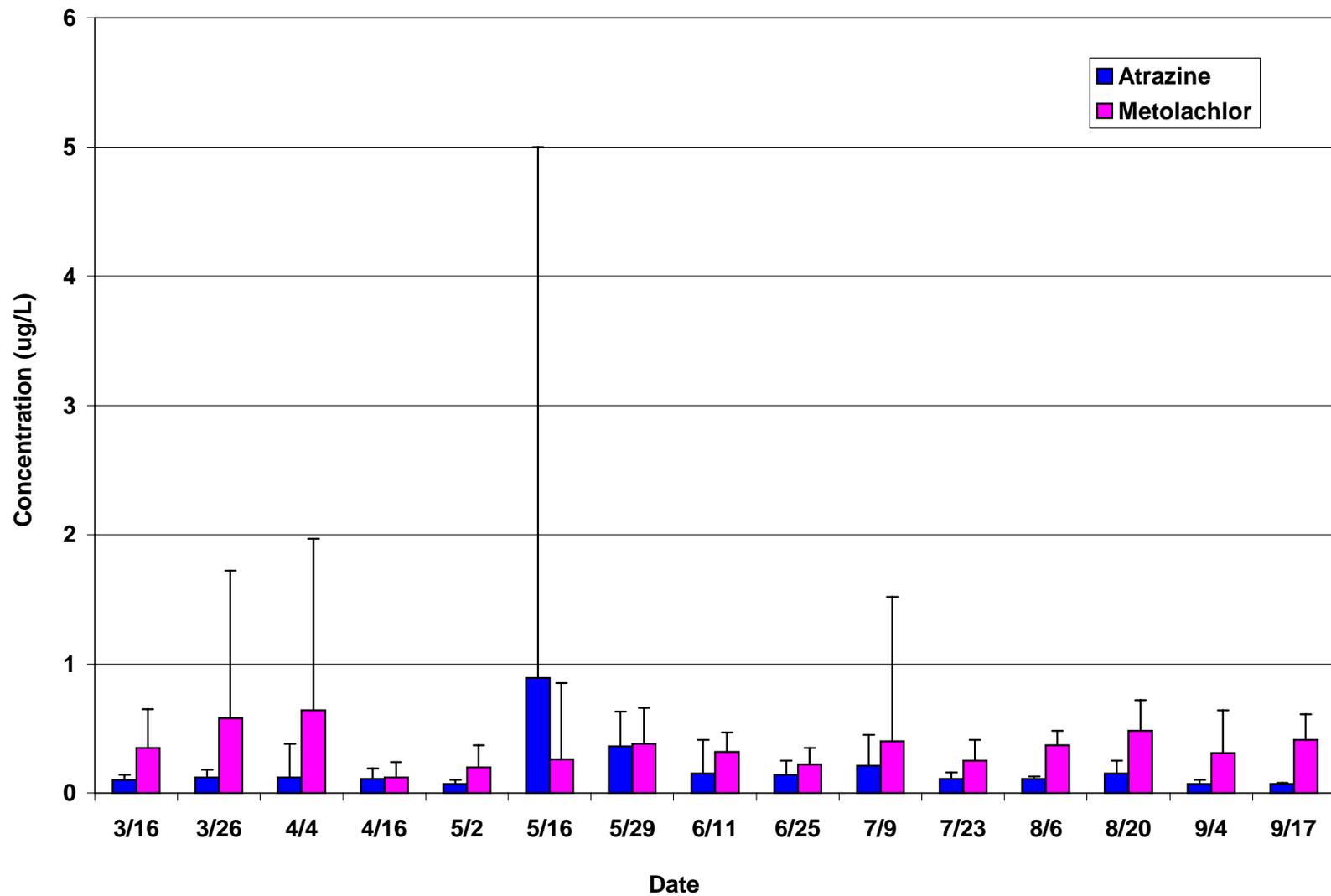


Figure 14. Average monthly atrazine and metolachlor concentrations in Burlington 2001. Solid bars represent average concentration and narrow bars represent maximum concentration.

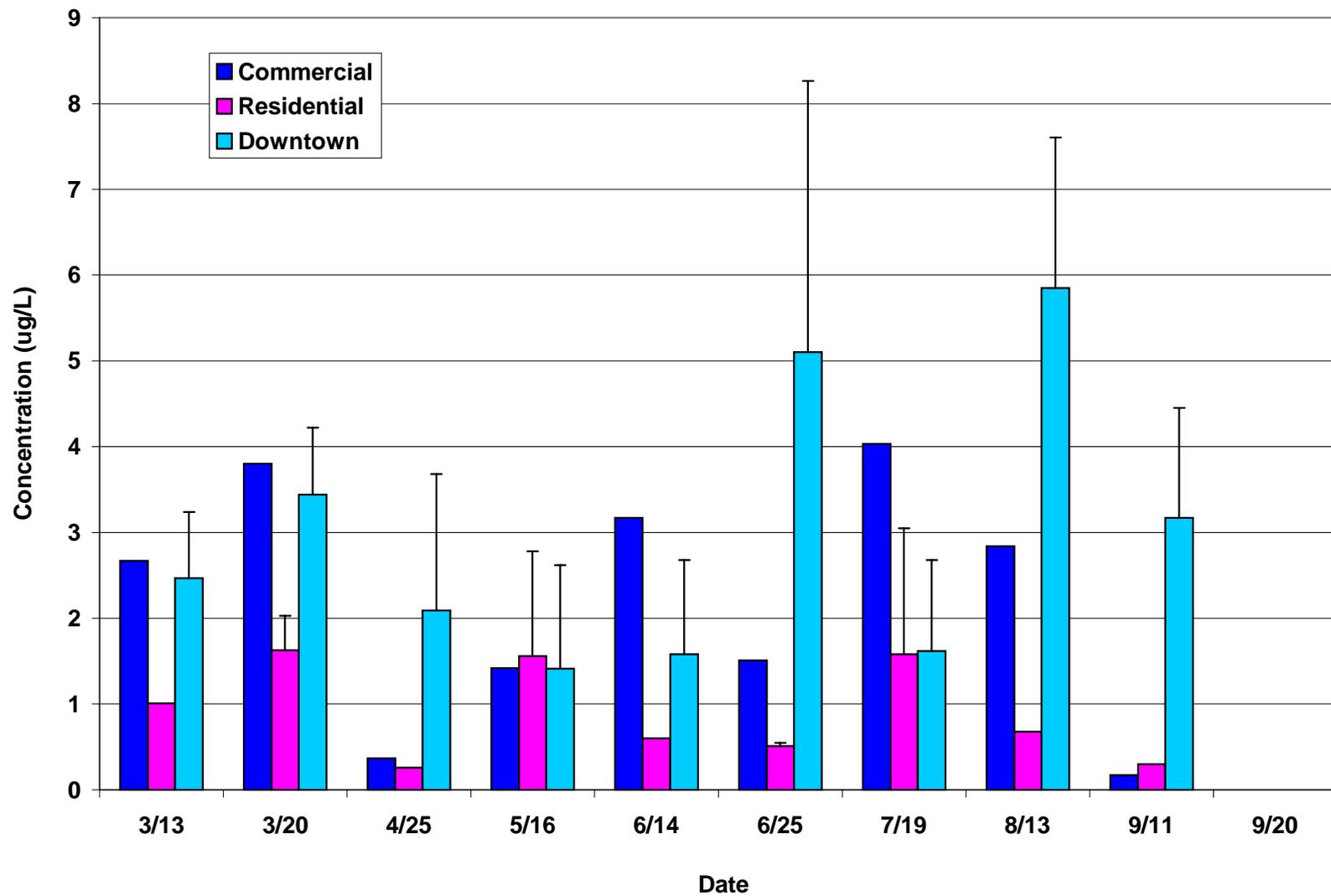


Figure 15. Average monthly metolachlor in commercial, residential, and downtown areas of Greensboro 2001. Solid bars represent average concentrations and narrow bars represent maximum concentration.

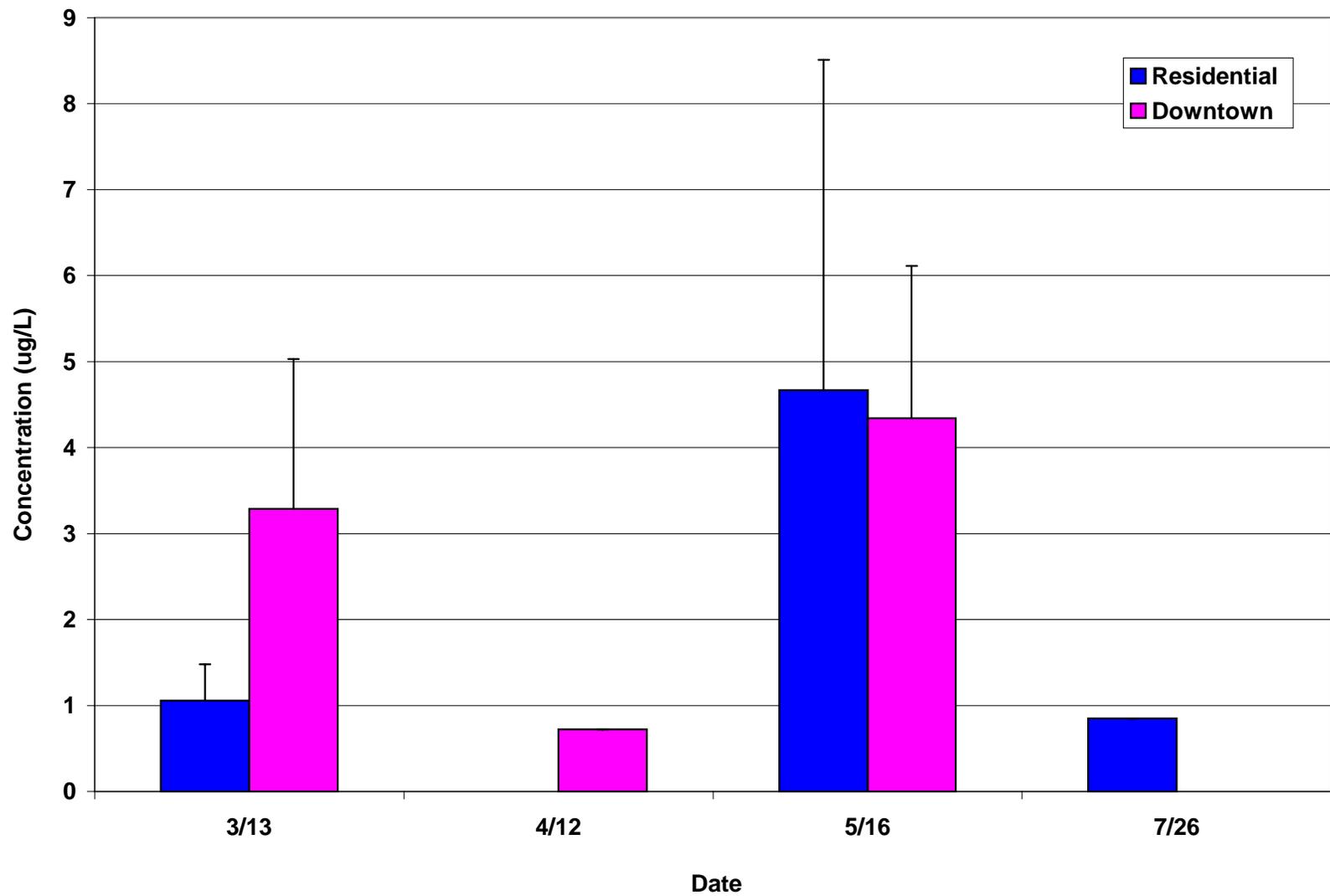


Figure 16. Average monthly 2,4-D concentrations in residential and downtown areas of High Point 2001. Solid bars represent average concentration and narrow bars represent maximum concentration.

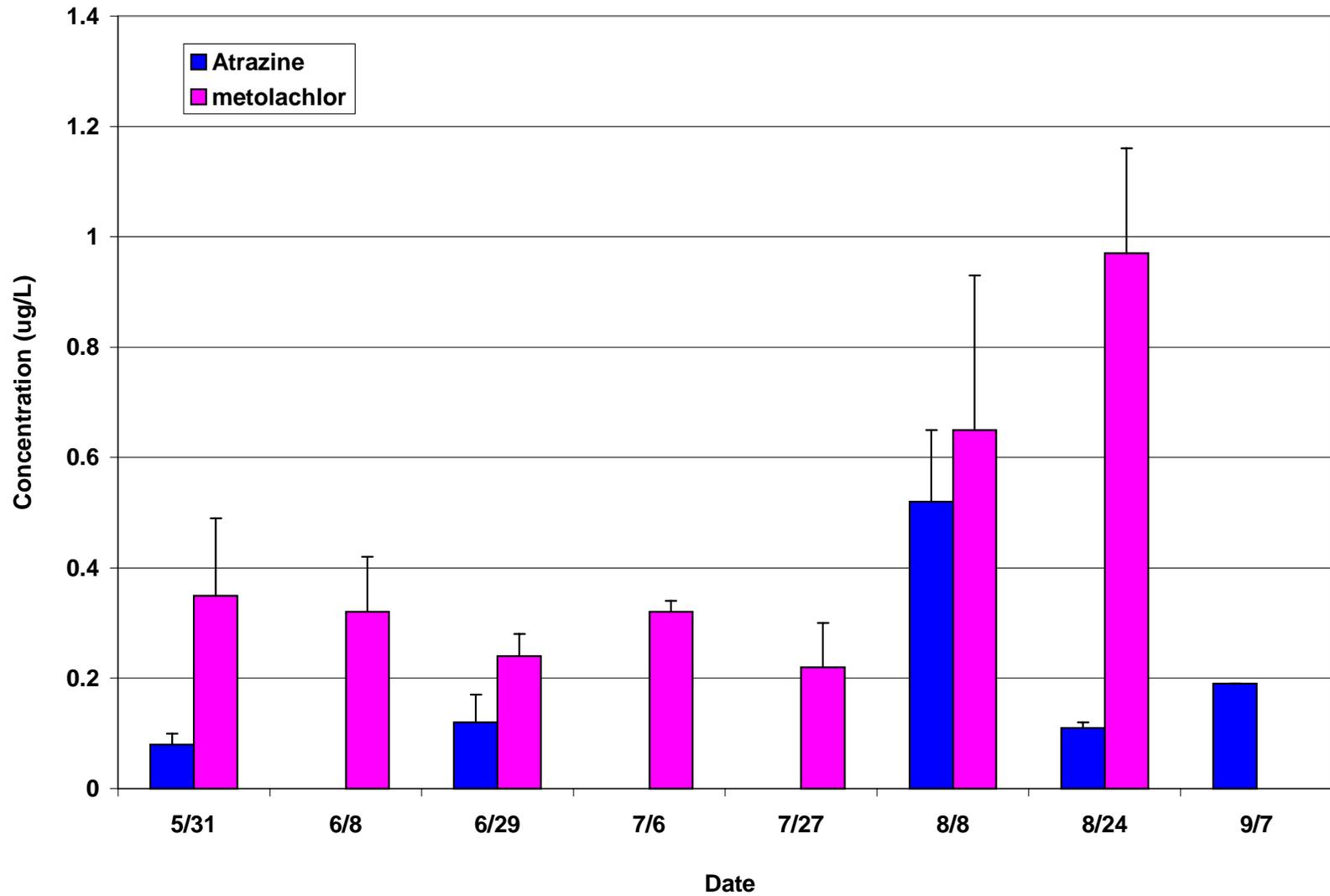


Figure 17. Average monthly atrazine and metolachlor concentrations in Raleigh 2001. Solid bars represent average concentration and narrow bars represent maximum concentration.

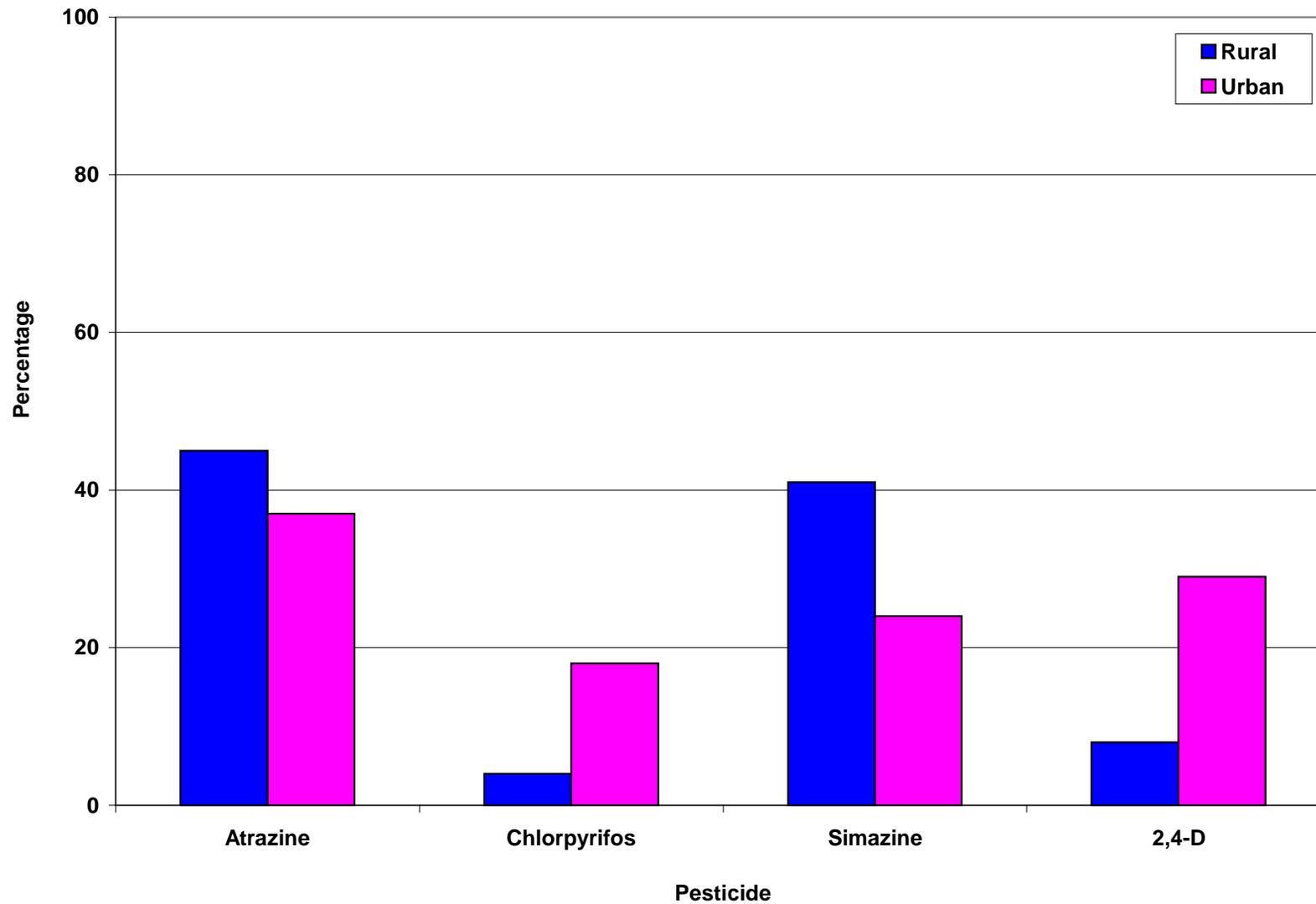


Figure 18. Metolachlor residues detected from March to September of 2001 in commercial, residential, and downtown areas of Urban Watershed 1 (Greensboro).

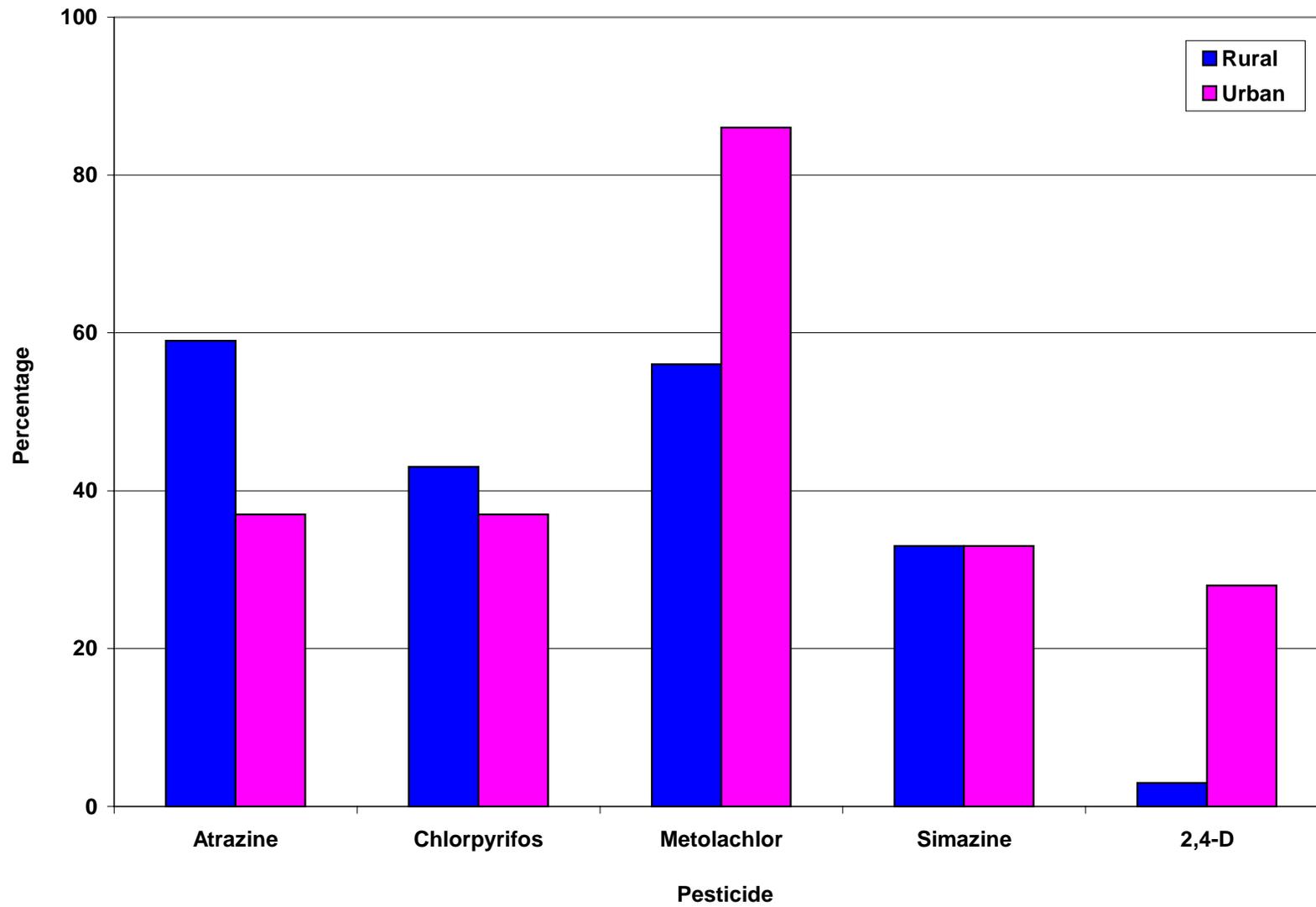


Figure 19. Atrazine, chlorpyrifos, metolachlor, simazine, and 2,4-D residue detection rates in Rural and Urban Watersheds in 2000.

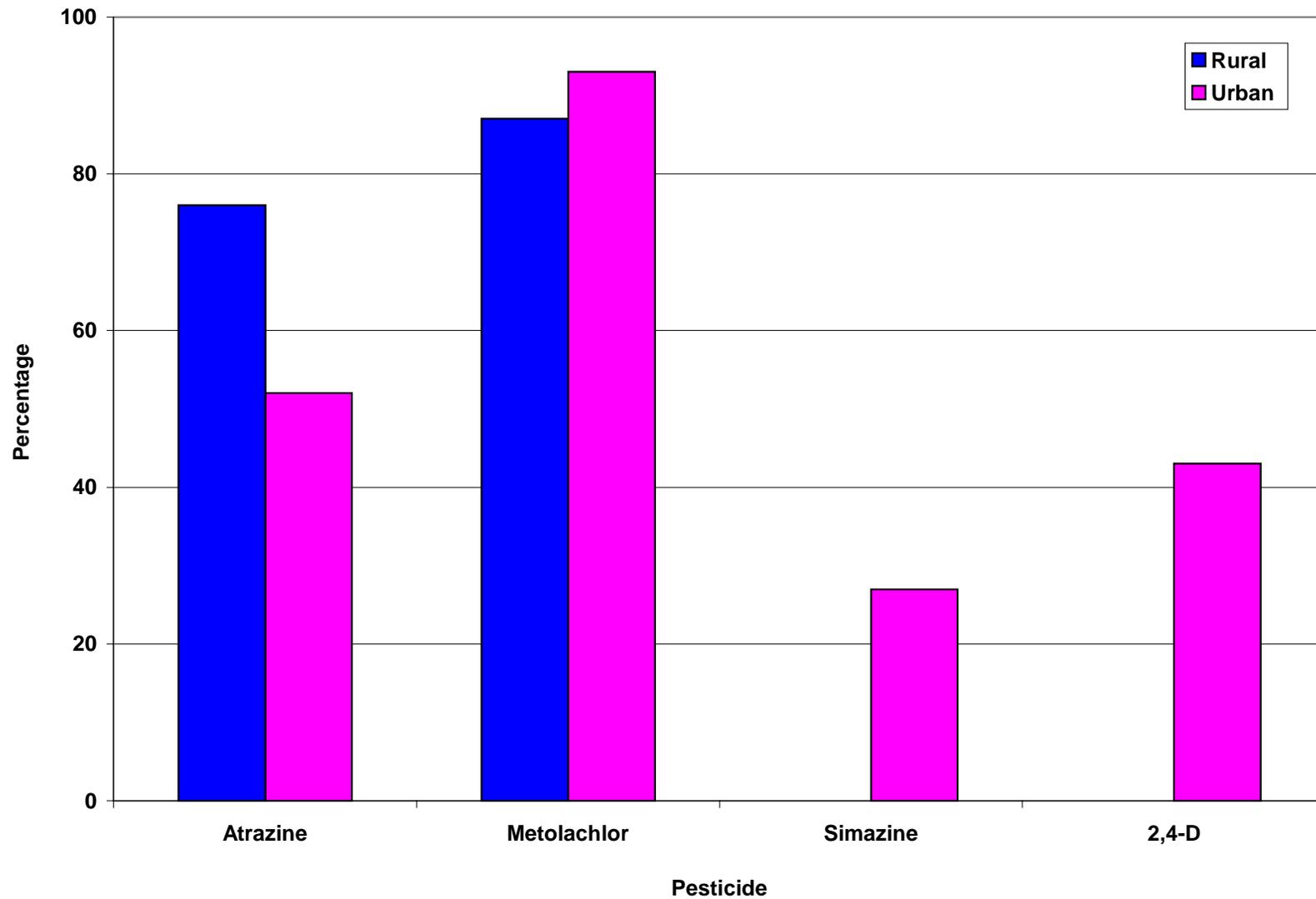


Figure 20. Atrazine, metolachlor, simazine and 2,4-D residue detection rates in Urban Watersheds with atrazine and metolachlor residue detection rates in Rural Watersheds in 2001 (Analysis of rural water samples did not include simazine and 2,4-D in 2001).

CHAPTER THREE

DESIGN AND IMPLEMENTATION OF SOURCE PREVENTION EFFORTS TO REDUCE PESTICIDE RESIDUES IN SURFACE WATERS OF AN AGRICULTURAL WATERSHED

INTRODUCTION

The difficulties encountered in managing environmental contamination are attributed to factors commonly associated with non-point sources, including seasonality, inherent variability and a multiplicity of origins (Pereira and Hostettler 1993, Albanis *et al.* 1998). With such diverse influences contributing to the non-point source contaminations, environmental studies are required to identify the contaminated waters and possibly characterize the sources of contamination. Distinguishing sources of pesticide input aids in evaluating and selecting the best method of remediation.

Failure to read pesticide labels by a number of handlers can result in improper preparation and application of pesticides. A number of non-point source contaminations could be reduced by reading and following label directions and through education of industrial and individual applicators. Pesticides used with an understanding of the properties and behaviors of chemicals, can promote greater awareness and insight into their environmental fate and potential to produce adverse effects.

While education is beneficial it is not enough to fully address environmental pesticide contamination issues; environmental monitoring and assessment is still required. Many studies have reported the presence of pesticide residues in surface waters and the potential for diminished surface water quality necessitating remediation efforts. Remediation is best carried out when a great deal is known about the selected areas. That information includes land-use, sources of contaminants, possible transport processes and receiving reservoirs. According to

Schreiber *et al.* (1996) “When contaminations associated with transient events reach aquatic ecosystems, emphasis shifts from transport to stress and impact”.

Preemptive action requires that attention be focused on sources that supply contaminants carried in transient events.

Remediation is chiefly executed through Best Management Practices (BMP) that combine “management, cultural, and structural practices that the agricultural scientists, local, State and Federal governments, and other planning agencies decide upon to be the most effective and economical way of controlling such problems without disturbing the quality of the environment” (Field and Engel 2002). Management approaches used in controlling sources of contamination include riparian buffers, structural changes, stormwater drainage, modified pesticide applications, planting variations, and conservation tillage.

Riparian buffers are vegetative strips that remove pesticides and nutrients from surface flow by infiltration and prevent these contaminants from entering surface waters. Stream restoration involves structural changes and environmental designs utilizing vegetation to divert flow of waterways and control runoff to reduce bank erosion while also avoiding areas of potential contamination (e.g., high traffic areas, construction, sites receiving pesticide applications).

Farming practices can influence surface runoff. Banding applications of pesticides require smaller amounts of active ingredient (a.i.) that subsequently reduces the amount of chemicals introduced into environment. Popular farming practices like conservation tillage can reduce losses of topsoil due to water and wind erosion. No-till and ridge-till agricultural practices help maintain surface soil particles

and reduce contaminants in surface runoff from entering surrounding water bodies (Bailey 1990, Bowman 1990, Clausen *et al.* 1996, Schreiber *et al.* 1996). Several studies have shown considerable reduction in contaminant laden surface runoff as a result of conservation tillage. A comparison of the two methods in Missouri and Iowa found that while both maintained erosion topsoil losses, no-tillage is less effective in reducing surface runoff and soil infiltration (Miller *et al.* 1999).

Conservation tillage, while greatly decreasing the amount of adsorbed compounds on soil particles and dissolved chemicals entering surface waters, can increase leaching potential and surface nutrient runoff. Herbicides are less likely to dissolve in runoff following tillage which mixes compounds within soil (Feagley *et al.* 1992). No-till or ridge-tilled practices can trap chemicals below or retain them on the surfaces of crop residue leaving the compounds vulnerable to precipitation. Therefore, pesticides, nutrients, and other potential contaminants are not completely eliminated with conservation tilling practices (Bailey 1990, Bowman 1990, Clausen *et al.* 1996, Schreiber *et al.* 1996).

Many types of remediation efforts have been employed and even those practices designed to specifically ameliorate environmental contaminations occasionally allow breakthrough. Conservation tillage while beneficially reducing surface runoff can occasionally increase pesticide leaching into groundwater, although the reverse may also be true given the tillage practice selected. It appears that one management practice is not sufficient in controlling contamination sources; thus, multiple management practices are required to effectively reduce levels of individual runoff contaminants. Successful remediation utilizes a combination of the

methods such as those above combined with ample knowledge of locations and sources of possible contaminants.

EXPERIMENTAL DESIGN

This study proposed an additional method to further increase and improve remediation efforts and involved going to the potential sources of contamination, specifically pesticide applications. Agricultural sites were chosen as the setting for the source prevention experiment. Numerous past studies suggest agrochemical inputs are a significant source of contaminants. The design of the surface water experiment incorporated a flexible sampling scheme that allowed progressive pesticide residue identification and investigation of potential sources. Using maps, visual scouting, and conferences with North Carolina Cooperative Extension Agents and city representatives, potential sources of contamination within surrounding areas of watersheds were identified and methods were initiated to reduce contaminants entering surrounding surface waters.

Most sampling areas were examined visually in combination with maps and Global Positioning System (GPS) in order to identify sites and surrounding land uses. Land-use varied and included croplands, forests, pastures, residential, urban, and commercial areas and served as a basis for estimating chemical compounds. Historical studies in combination with the first year (1999) of the overall study of monitoring surface water supplies (described in Chapter Two) provided significant information including land-use data, pesticides used and determination of residue

levels which culminated in a database specific to two rural watersheds. These provided a foundation upon which to determine remedial action.

The monitoring portion of this study included those pesticides found in surface waters that might affect drinking water quality. Project locations selected for implementations of source prevention were two, primarily agricultural areas; Lake Mackintosh and Stony Creek Watersheds. Both of these supply drinking water for Burlington and are located in Guilford and Alamance Counties. The cooperation of local County Agricultural Extension Agents and efforts by the City of Burlington were enlisted to successfully execute the remediation efforts.

MATERIALS AND METHODS

Herbicides commonly used on corn, such as atrazine, are popular and frequently used because they are relatively inexpensive yet still effective. Reduction in the amount of this and similar pesticides, especially those potentially harmful and persistent in the environment and available for runoff into surface waters, would be beneficial in improving water quality and decreasing potential hazard to human health. Source prevention in this study involved discussions with areas farmers through the County Agricultural Extension Agents who presented the experimental objectives and participant obligations.

Corn farmers were asked to use alternate methods in place of atrazine applications. Less-persistent herbicides or genetically modified seed were the alternative choices. Extension agents suggested several herbicides for the farmers to use including 3,6-dichloro-2-methoxybenzoic acid (dicamba), 2-[(4,6-

dimethoxypyrimidin-2-ylcarbamoyl) sulfamoyl]-*N,N*-dimethylnicotinamide (nicosulfuron), 2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide (metolachlor), and *N*-ethyl-*N'*-(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine (ametryn).

The genetically modified seed (GMO) utilized in this study was Round-Up[®] Ready corn seed. This seed produces corn that is scientifically engineered with a synthetic enzyme making the corn plant tolerant to Round-Up[®], a pesticide with the active ingredient glyphosate. Modification involves production of an enzyme, 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS). The EPSPS protein is inhibited in plants by glyphosate; thereby, killing the plant. The GMO produces a slightly altered EPSPS that is resistant to glyphosate and allows the corn plant to survive application of the pesticide. Using the GMO called for glyphosate to be applied as a substitute for atrazine. Therefore, the use of genetically modified seed also allowed for the application of a less-persistent herbicide that is lower in toxicity than atrazine.

The source prevention project was proposed and initiated in the first and second years of a surface water watershed assessment monitoring study (Chapter Two) performed by the author. An agreement was made where the City of Burlington would pay the increased cost of using alternative practices. Initially, \$22/acre were offered and over the course of experiment was increased to a final total of \$24/acre. This was a blind study in which the participating locations were not disclosed as a form of identity protection and experimental validation.

Samples analyzed for the surface water monitoring study served as the data for the source prevention project. Study results of the first year combined with historical data (Leidy *et al.* 2001, Holman and Leidy 2000a, Holman *et al.* 2000b, Walker *et al.* 2000) provided background concentrations while the second and third year of study exhibited the results of the alternative practices.

Upon receipt, surface water samples were screened with ELISA kits to determine presence and concentration of pesticide residues (RaPID Assay[®] Kits, Strategic Diagnostics, Inc., Newtown, Pennsylvania) (procedure outlined in appendix). Those samples with pesticide concentrations exceeding 1.0 µg/L were filtered with a 55 mm (pore size, 1.0 µm) glass fiber filter (Whatman[®] International, Maidstone, England) and extracted using the SPE procedure designed by Mueller *et al.* (2000).

Instrumental analyses of those samples exceeding 1.0 µg/L were performed using a Varian Star Model 3400 Gas Chromatograph equipped with a Model 8200 CX Autosampler and a nitrogen/phosphorous [Thermionic Specific Detector (TSD)] detector (Varian Inc., Walnut Creek, California). Injection volumes of 3.0 µL were introduced onto a DB-35 fused silica column (30 m by 0.25 mm i.d.)(0.25 µm film)(J & W Scientific Inc., Folsom, California). The flow rates of the carrier and make-up gas, helium, was 3.0 and 27.0 mL/min, respectively. Detector gases were air and hydrogen at flow rates of 175.0 and 4.0 mL/min, respectively.

Samples, concentrated to a final volume of 1.0 mL were loaded on the autosampler with analytical standards of interest at concentrations of 10 µg/L positioned at the start, between every five samples, and the last of the GC sample

run. Temperatures were as follows: inlet, 175°C, detector, 300°C. The oven temperature program was as follows: initial, 160°C hold 2 minutes; to 170°C at 1°C/min, hold 2 minutes; to 280°C at 5°C /min, hold 2 minutes. Quantification of data was performed by comparison of peak areas of samples and standards of known concentration. The retention time (RT) of atrazine was 7.3 min.

Pesticide residue detections in specific sites were monitored in rural areas and compared over the course of the three years to observe changes in concentration as a result of source prevention efforts. From March to October, samples were collected and screened for pesticides as previously described. Statistical analyses using paired t-tests ($p < 0.05$) were performed to ensure changes in atrazine concentration were significant.

RESULTS AND DISCUSSION

Atrazine is the most commonly used herbicide on corn in these areas. Therefore, the source prevention project focused on a change from atrazine to alternative methods including herbicides such as metolachlor, dicamba, and nicosulfuron, and more frequently Round-Up Ready[®] corn seed. Consequently, concentrations of atrazine in the Burlington region were averaged on a monthly basis (March through September) and compared from 1999 to 2001 (Fig. 1).

Concentrations of atrazine declined from 1999 to 2000. Residue levels in 2001 also exhibited decreased concentrations. March averages showed a reduction in pesticide residues with statistical differences between 1999 and both 2000 and 2001. Average monthly atrazine concentrations in July and August of 1999 were

statistically greater than those of 2001. There were some exceptions; April and July of 2000 showed levels of pesticides slightly higher in 2000 than the year before and similar concentrations were observed in April and May of 1999 and 2001.

A comparison of the yearly average atrazine concentrations also showed a decline from 1999 to 2001 in which the results of 1999 were statistically greater than both 2000 and 2001 (Fig. 2). This change was also apparent in the number of samples with atrazine concentrations exceeding 1 µg/L with a decrease from 8 in year one (1999), to 4 in year two (2000) and 1 in year three (2001) of this study (Table 1). To better demonstrate the changes in concentration from year to year, the pesticide residue concentrations were plotted as monthly averages with linear trendlines to determine if there were visible changes in the atrazine concentrations from 1999 to 2001 (Fig. 3). With the addition of the trendlines it was apparent that atrazine concentrations were lower in 2000 and 2001 than residue detections in 1999.

The changes in atrazine residues were observed in select areas of Burlington in which sites of suspected participation exhibited statistically significant declines in concentration (Fig. 4). However, those sites suspected of nonparticipation showed little evidence of change over the course of the study following implementation of source prevention. The results of atrazine analysis in these areas were statistically similar (Fig. 5). Pesticide analyses showed little detection of atrazine residues in areas that had discontinued or reduced usage of the chemical. Those locations that did not participate continued to show measurable concentrations of pesticides for the duration of the study.

County Agricultural Extension Agents confirmed an increased use of alternative pesticides and the genetically modified Round-Up Ready® seed. The use of alternate methods in place of atrazine applications served as a way to determine if it was possible to select an area of frequent pesticide use and implement changes through application variation and as a result alter environmental presence of a contaminant.

The replacement of a compound known to have adverse effects (e.g., atrazine) with other herbicides, such as metolachlor and dicamba, or using Round-Up® Ready corn that allowed for the use of glyphosate; another less-persistent, less toxic compound reduces the likelihood of atrazine presence in surface waters and potential exposure to wildlife and humans. While consequences associated with genetically modified seed usage remains unclear the use of glyphosate and other alternate pesticides in place of atrazine lowered the risk associated with surface runoff and human health implications with regard to MCLs.

PRECIPITATION INFLUENCES

Numerous factors are involved in transporting chemicals into environment: precipitation influences, weathering, advection, and degradation. Pesticide exposure is a result of a complex series of processes and the observed decrease in atrazine concentrations might not be only due to source prevention. Precipitation is one of the most influential factors in surface runoff and a lack of rainfall would facilitate a decrease in pesticide residue concentrations. Without excessive surface runoff from rain events, the movement of pesticides from field to water supplies is

lessened and subsequent declines in residue concentrations could lead to a false sense of security regarding successful source prevention.

Precipitation data for the agricultural areas was acquired through the National Climatic Data Center (Asheville, North Carolina) for the three years of the project. The rainfall was monitored to determine if reductions in atrazine concentrations were a result of declining precipitation events. Comparisons of the monthly average atrazine concentrations with the monthly average precipitation levels for each year showed variation month to month for the three years; however, these averages of rainfall were found to be statistically similar with paired t-tests ($p < 0.05$) (Fig. 6). There was no evidence of a diminishing effect or absence of pesticide residues as a result of precipitation changes. Reductions in atrazine concentrations were considered a direct result of the farmer's participation in the source prevention project.

CONCLUSION

Atrazine residues were either reduced or completely eliminated following source prevention implementation and the preventative measures seemed to be adequate additions to remediation efforts established to control surface water contamination. Therefore, in using less-persistent compounds potential exposure to atrazine was lowered and review of literature revealed no immediate human health threat posed by the alternate chemicals.

This was an innovative approach in which several points-of-view were taken into account to design, implement, and verify a remediation effort that focused on the

non-point sources of pesticides within a watershed to prevent surface water contamination from runoff containing these pesticide residues. Through collaboration common objectives such as remediation involving use of pesticides, their environmental monitoring, and chemical regulation can be achieved. This effort contributed to the watershed management process and also demonstrated that the various agencies involved are not required to be on opposing sides.

ACKNOWLEDGMENTS

This project was completed with the help of Steve Shoaf and the City of Burlington as well as the County Agricultural Extension Agents, Roger Cobb of Alamance County and Wick Wickliffe of Guilford County. Without the cooperation of the area farmers, this study would not have been possible.

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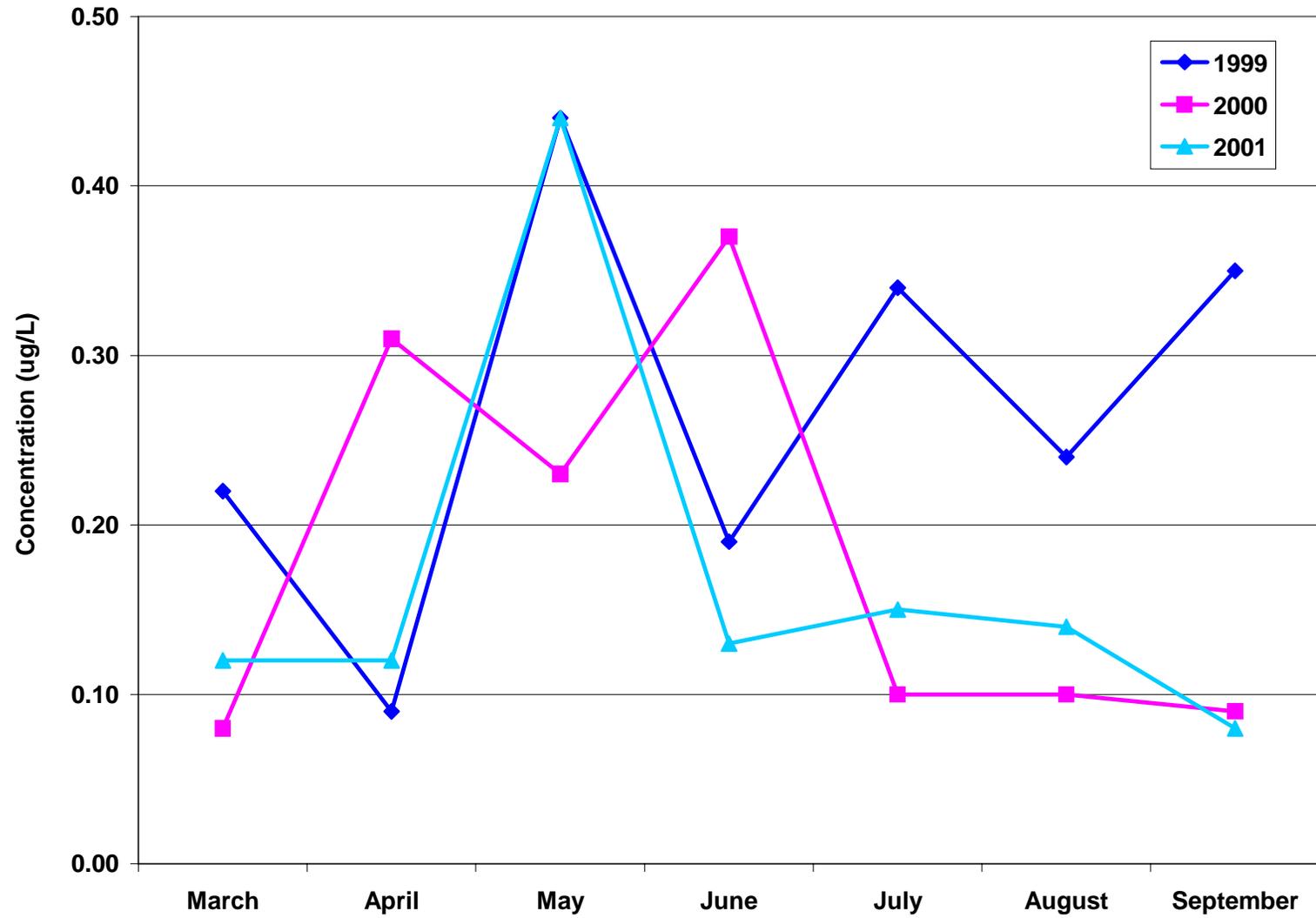


Figure 1. Average monthly atrazine concentrations from March to September of 1999, 2000, and 2001 for Rural Watershed 1 (Burlington).

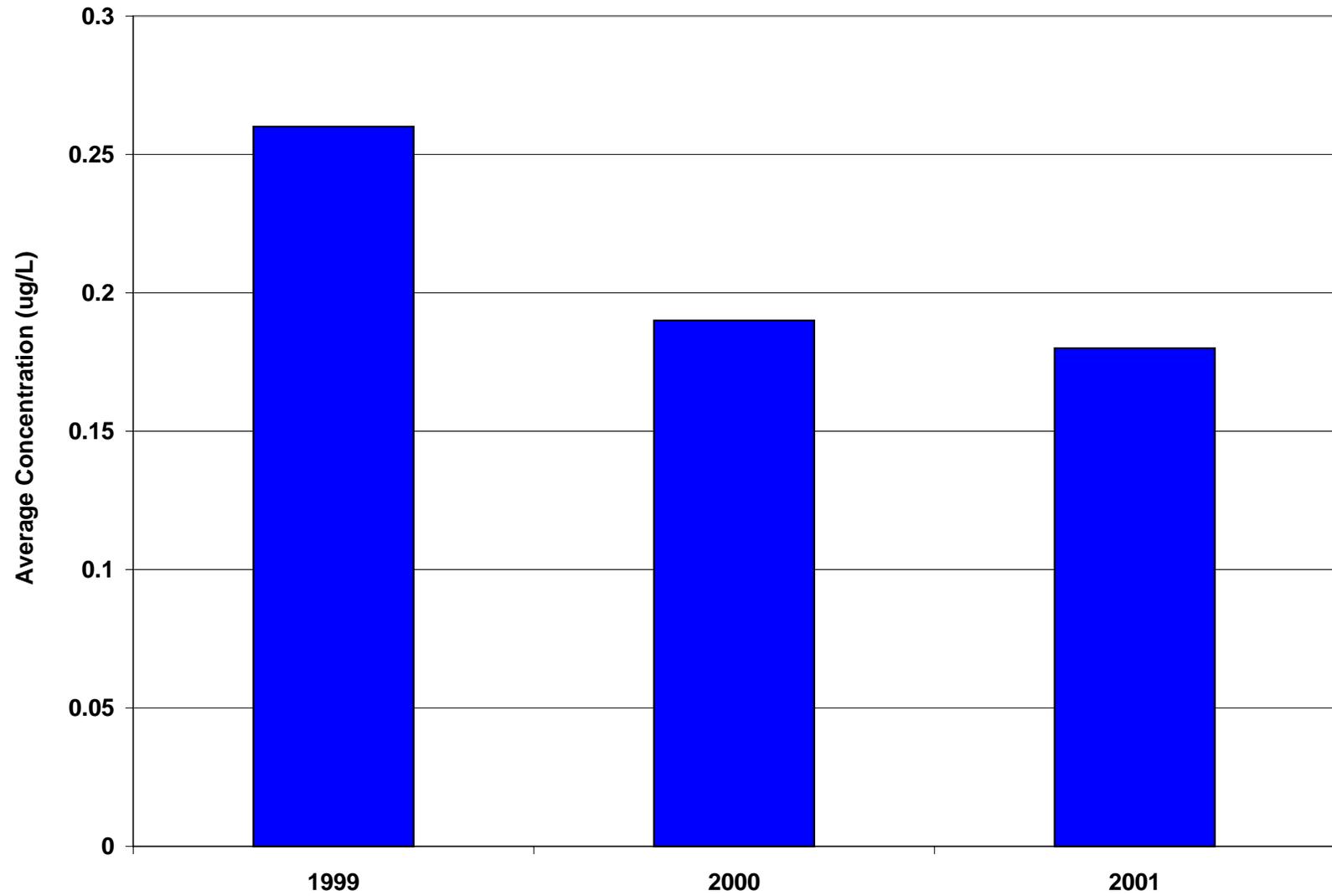


Figure 2. Average yearly atrazine concentrations from 1999 to 2001 in Rural Watershed 1 (Burlington).

Table 1. Yearly detections of atrazine, in Burlington, exceeding 1.0 µg/L and the ranges of concentration.

Year	No. Exceeding 1.0 µg/L	Conc. Range (µg/L)
1999	8	1.22-4.27
2000	4	1.16-4.16
2001	1	2.08

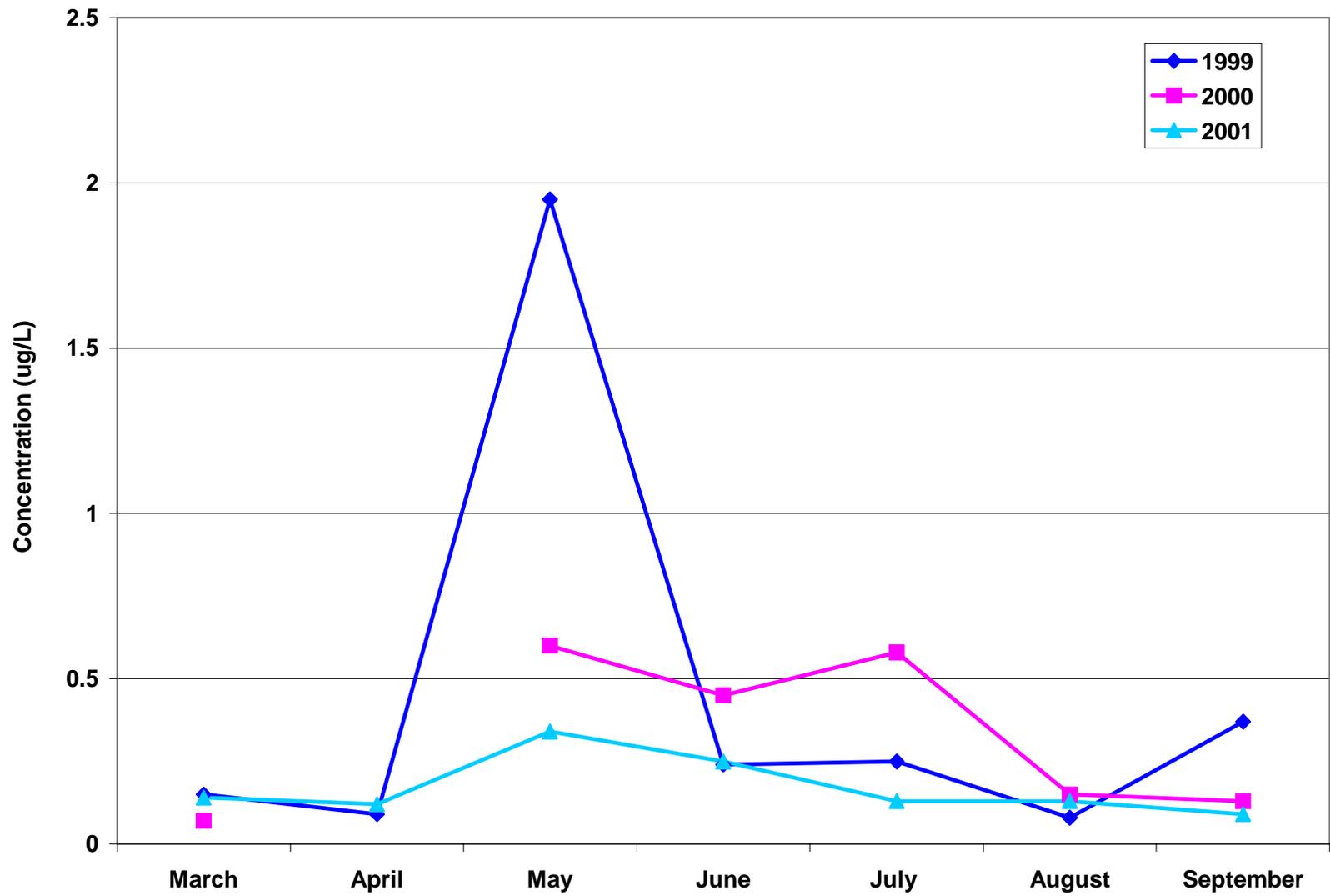


Figure 3. Atrazine detections in March to September from 1999 to 2001 in sites of suspected participation in Source Prevention Project.

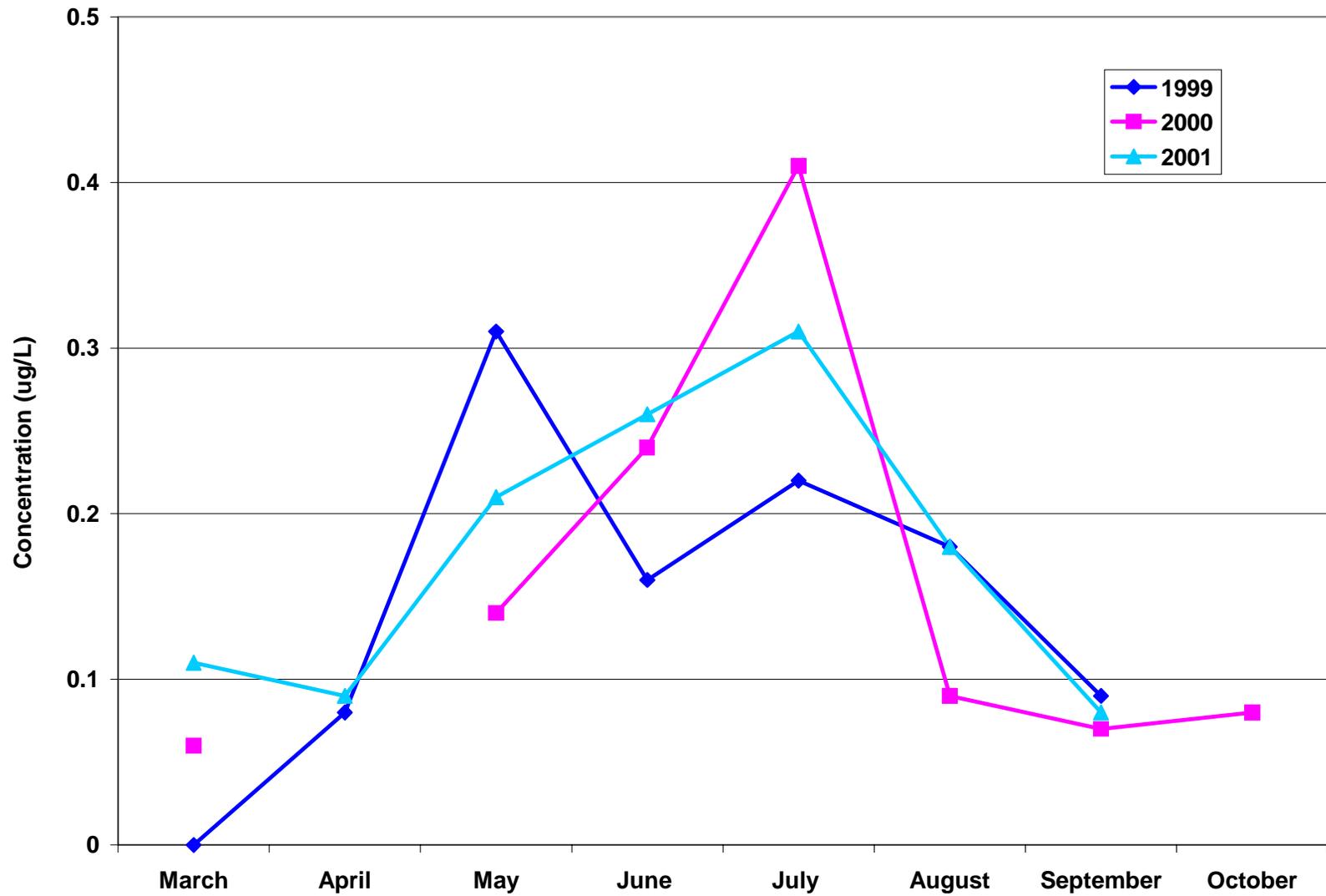


Figure 4. Atrazine detections in March to September from 1999 to 2001 in sites of suspected nonparticipation in Source Prevention Project.

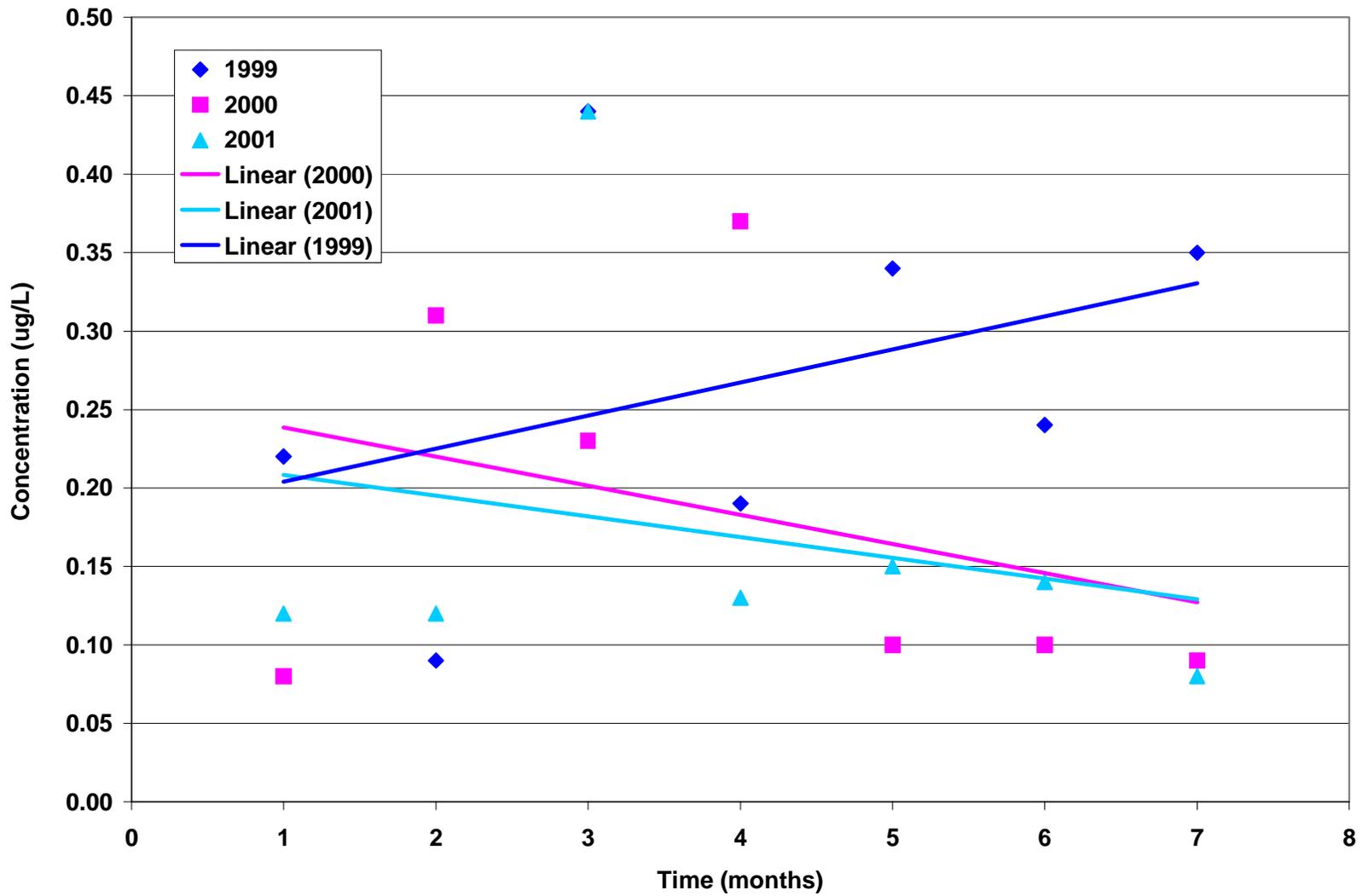


Figure 5. Atrazine detections in Burlington from March (1) to September (7) from 1999 to 2001 with trendlines.

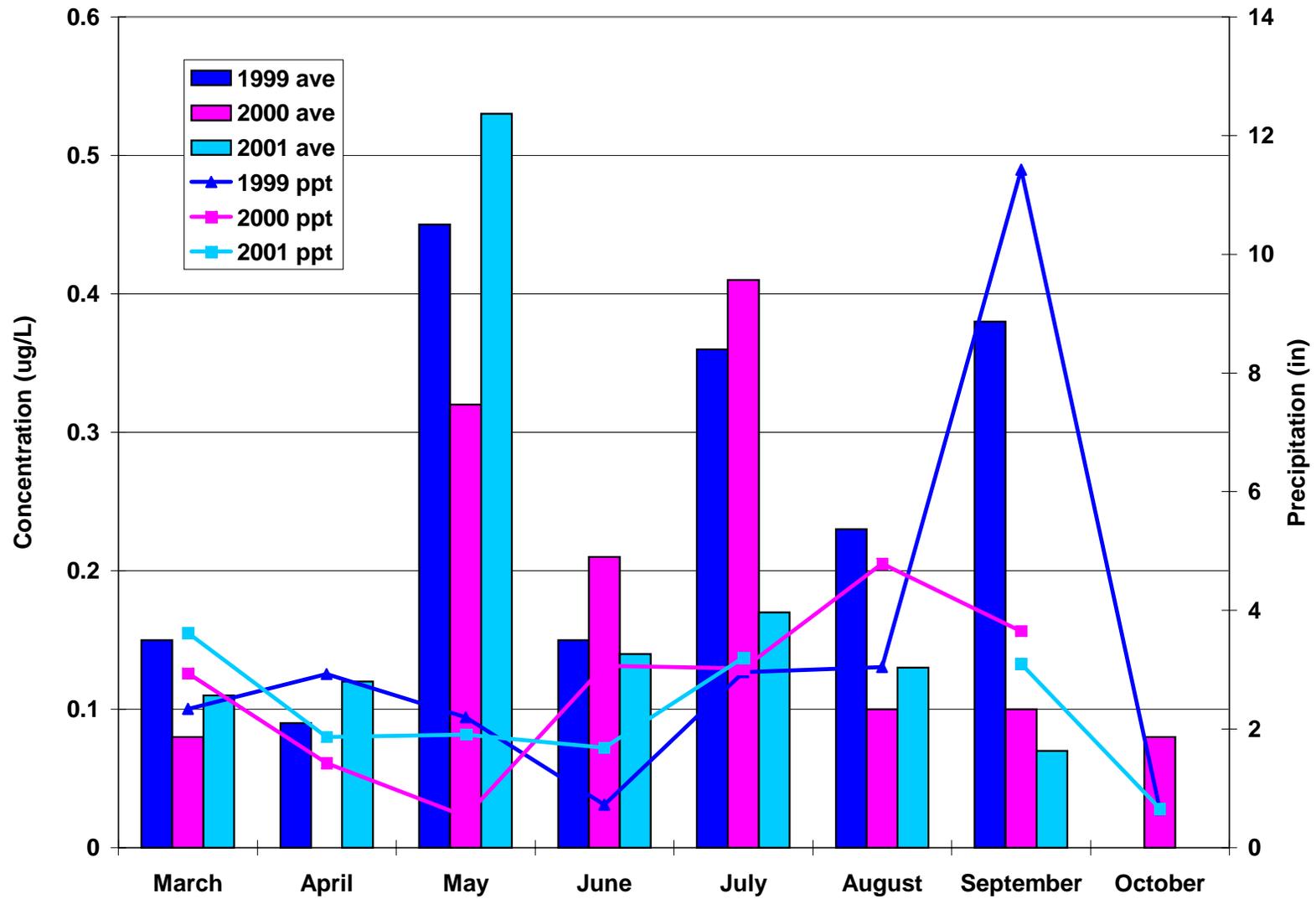


Figure 6. Average monthly levels of atrazine (solid bars) and precipitation (solid lines) in Burlington from March to October for 1999, 2000, and 2001.

CHAPTER FOUR

PESTICIDE RESIDUES IN RAW AND FINISHED WATER OF A NORTH CAROLINA DRINKING WATER TREATMENT PLANT

INTRODUCTION

Pesticide residue in surface runoff can affect more than the proximal surface waters receiving the contaminants. Recent studies in the author's lab have focused on contamination of rural and urban surface waters with pesticides. Interest became focused on raw and finished, drinking water because the previously monitored surface waters serve as drinking water sources for municipalities.

Several studies have monitored pesticide residues in drinking water treatment plants and found that standard treatment processes (flocculation, sedimentation, filtration, disinfection) were ineffective in reducing contaminant concentrations (Miltner 1989, Najm 1991). Pesticides commonly used and observed in surrounding surface waters flowing to the treatment plants were observed to determine if contaminant residues were entering intakes of area water treatment facilities.

The infiltration of pesticide residues into drinking water treatment plant would diminish the quality of drinking water and provide human exposure pathways for the pesticides. Raw water, collected at the intakes and finished, post-treatment water (collected within the plant prior to distribution) was monitored for the presence of pesticides to ascertain how efficiently chemical contaminants were removed with standard water treatment plant operating procedures.

MATERIALS AND METHODS

Drinking water treatment systems are responsible for reducing and removing contaminants from incoming raw water, which upon completion of water treatment becomes finished water that is distributed to the servicing area. In order to

determine potential the degree of infiltration of pesticide residues into treatment facilities, various samples were collected to represent raw and finished water.

Raw water samples were collected at water intakes located in reservoirs in close proximity to treatment plants. Finished water was collected from within the treatment facilities prior to distribution. Due to time constraints and sampling design, raw water samples collected and analyzed in this study were not the pre-treatment counterpart to the finished water samples that were collected and analyzed. Therefore, the raw and finished water data presented in this report do not accurately represent a before and after treatment measurement of pesticide residue concentrations. However, these raw water samples were regarded as an average representation of the raw water source that results in finished water.

Cooperating water treatment plants located in Burlington, Greensboro, High Point, and Raleigh, provided water samples that were collected by treatment personnel. Two drinking water treatment plants within Burlington took part in this study: Ed Thomas Water Treatment Plant drawing water from Stony Creek Watershed and J.D. Mackintosh Water Treatment Plant which draws water from the Lake Mackintosh Watershed.

Lake Townsend and N. L. Mitchell facilities were the water treatment systems located in Greensboro, and two watershed supply intakes in High Point supplied the Frank L. Ward Water Treatment Plant. The two intakes included the eastern High Point Lake Reservoir and the western, Oak Hollow Reservoir. In Raleigh raw water from Falls of the Neuse Reservoir and finished water samples were taken at the E.M. Johnson Water Treatment Plant. Each treatment facility participated in the

collection of raw and finished water samples over the course of the three year study, with the exception of Raleigh. Raleigh was not included until 2001, the concluding year of this study.

Samples were collected and stored in 250 mL amber glass bottles with PTFE-lined caps (I-Chem, Nalge Nunc International, Rochester, New York). Water samples were shipped on ice to NCSU's Department of Environmental and Molecular Toxicology Pesticide Residue Laboratory in a cooler and kept at 4°C until analysis. Pesticide residue analyses for the water samples were performed using Enzyme-Linked Immunosorbent Assay (ELISA) RaPID Assay[®] (Strategic Diagnostics, Inc., Newtown, Pennsylvania), and residue levels of 1.0 µg/L or greater were filtered with glass fiber filters (55 mm, pore 1.0 µm) (Whatman[®] International, Maidstone, England) and extracted as before with Empore[™] Extraction Disks (3M Corp., St. Paul, Minnesota)(Mueller *et al.* 2000). Procedures for both the ELISA kits and extraction methods are outlined in the appendix. Samples were analyzed by gas chromatography with a Varian Star Model 3400 Gas Chromatograph equipped with a Model 8200 CX Autosampler and coupled with a nitrogen/phosphorous [Thermionic Specific Detector (TSD)] detector (Varian Inc., Walnut Creek, California). A DB-35 fused silica column (30 m by 0.25 mm i.d.)(0.25 µm film)(J & W Scientific Inc., Folsom, California) was used with an injection volume of 3.0 µL. Helium was used as the carrier and make-up gas, at flow rates of 3.0 and 27.0 mL/min, respectively. The gases flowing to the detector were air and hydrogen at flow rates of 175.0 and 4.0 mL/min, respectively.

All samples and standards were concentrated to a final volume of 1.0 mL and placed on the autosampler. The analytical standards of interest (10 µg/L) were positioned at the start, between every five samples, and the last of the GC sample run. The temperature program was as follows: inlet, 175°C, detector, 300°C. The oven temperature program was as follows: initial, 160°C hold 2 minutes; to 170°C at 1°C/min, hold 2 minutes; to 280°C at 5°C /min, hold 2 minutes. Sample peak areas were quantified against standards of known concentration to determine sample pesticide concentrations. Retention times (RT) were as follows: alachlor (10.2 min), atrazine (7.3 min), chlorothalonil (9.5 min), chlorpyrifos (11.5 min), metolachlor (11.2 min), and simazine (7.5 min).

RESULTS AND DISCUSSION

Maximum Contaminant Levels (MCLs) are regulatory values assigned to chemicals thought to pose adverse health effects and are enforced by law. These values represent the greatest concentrations of a contaminant permitted in post-treatment potable water and are based upon empirical data on health risks and best available treatment technologies (USEPA 1992). MCLs were utilized in this study as a reference point for surface water and raw intake samples. Finished water can be directly compared to MCLs.

Presently, MCLs exist for four of the pesticides studied including: atrazine (3.0 µg/L), alachlor (2.0 µg/L), simazine (4.0 µg/L), and 2,4-D (70.0 µg/L). Contaminants lacking an MCL such as chlorpyrifos, chlorothalonil, and metolachlor

are not regarded as harmless, but sufficient data to establish a regulatory value is lacking.

While these three compounds had no legal regulatory value (MCL), Health Advisory Level (HAL) values do exist for these pesticides. Health advisories, also known as Maximum Contaminant Level Goals (MCLGs) were used in this report as a reference indicator, in place of MCLs for chlorpyrifos (20.0 µg/L), chlorothalonil (150.0 µg/L), and metolachlor (70.0 µg/L) (USEPA 1992). MCLGs represent the greatest concentration of a contaminant that does not exhibit a health risk when present in finished drinking water (USEPA 2002).

The HALs used here for chlorpyrifos and metolachlor were established by the USEPA and are the lifetime, non-cancer health advisories. Chlorothalonil's HAL is an exception as it is classified as B2 cancer group compound, defined as a chemical that exhibits "sufficient evidence in animals and inadequate or no evidence in humans" of acting as a carcinogen (USEPA 2002). The following summarizes the yearly findings from the individual regions studied.

YEAR ONE—1999

Burlington: Fourteen Lake Mackintosh Watershed raw water samples were collected from March to September and analyzed for atrazine, chlorpyrifos, simazine and 2,4-D. Of the four pesticides investigated only residues of atrazine and simazine were present and were detected in over 85% of the samples collected. However, concentrations were less than 0.6 µg/L for all samples with the exception

of one sample in Lake Mackintosh containing simazine (1.72 µg/L) in late August and one containing 2,4-D (1.93 µg/L) in July.

From May to September, ten samples were collected at the Stony Creek Watershed intake. Residues of atrazine and simazine were found in 46 and 69%, respectively, of the samples collected, but all detected residues measured below 0.5 µg/L. The herbicide, 2,4-D was detected once, at 1.59 µg/L in July.

Summary: Atrazine and simazine were found at both intakes in low concentrations over the course of the year (Fig. 1). These were also the two primary pesticides detected in field surface water samples. Simazine (1.72 µg/L) was the only pesticide found that approached its MCL of 4.0 µg/L. The two detections of 2,4-D were very low compared to the 70.0 µg/L MCL but occurred in July at both intakes. All residue detections in raw water collected from Burlington in 1999 were generally well below existing MCLs; therefore, pesticide residues present in surface water were not considered threatening to human health via drinking water.

Greensboro: The raw water intake of Townsend Treatment Plant was sampled eight times from April to December and analyzed for atrazine, chlorothalonil, chlorpyrifos, simazine, and 2,4-D. Three of the five compounds (chlorpyrifos, chlorothalonil, and simazine) were detected in low concentrations (e.g., <0.5 µg/L). The herbicide, 2,4-D was detected once, in December, at 1.01 µg/L.

Eight raw water samples were collected at the Mitchell intake from April to December and monitored for the five pesticides. Three of these compounds were detected in low concentrations (<0.5 µg/L) in the raw water samples including chlorothalonil and simazine present in 50% and chlorpyrifos in 25% of samples.

Finished water from both treatment facilities was analyzed for the five pesticides. From April to December, eight samples from each locale were collected and residue levels of chlorpyrifos, chlorothalonil, and simazine were found at various times throughout the year. Simazine was found in 25% of samples from Townsend and Mitchell Treatment Plants. Residue levels chlorpyrifos were detected in 13% of samples from both treatment plants. Chlorothalonil was found in 25% of Townsend and 38% of Mitchell finished water samples. The concentration levels of all pesticide residue detections never exceeded 0.15 µg/L.

Summary: Three pesticides were found at the intakes and in finished water and were also found at similar concentrations in the field surface water samples; however, rates of detection varied for field surface water samples in that chlorothalonil and chlorpyrifos were present in all samples while simazine was detected less frequently but in higher concentrations. In contrast, pesticide residues were found in less than 50% of all samples in both raw and finished water, and these concentrations were extremely low compared to regulatory or advisory levels. Pesticide detection rates varied in raw and finished waters of both treatment facilities with similar detection rates for chlorpyrifos and chlorothalonil in raw and finished water samples of Mitchell Treatment Plant.

High Point: The two raw water intakes selected for this portion of the study were sampled 4 times each from April to June and analyzed for atrazine, chlorpyrifos, chlorothalonil, simazine, and 2,4-D. Residues of atrazine, simazine, and 2,4-D were detected in concentrations greater than 1.5 µg/L and chlorothalonil was found at 0.20 µg/L from the City Lake intake, the eastern drainage area of Deep

River. Atrazine was found in 50% of samples with peaks in May at 1.61 µg/L and later in June at 1.2 µg/L. Simazine, present in 75% of samples, was found in April (< 0.5 µg/L) and in May and June at levels of 2.03 and 0.98 µg/L, respectively. The herbicide, 2,4-D, was detected in 50% of samples in May and June at concentrations between 0.83 and 1.7 µg/L.

Oak Hollow intake, a reservoir impounding water from the western fork of Deep River, also tested positive for the presence of atrazine, simazine, chlorothalonil, and 2,4-D, although at lower concentrations than City Lake Reservoir. Two of the four samples collected from April to June had residues present. In April, atrazine was found at 0.64 µg/L, and in June residues of chlorothalonil (0.24 µg/L), 2,4-D (0.84 µg/L), and simazine (0.6 µg/L) were detected. All of these chemicals were found only once throughout the course of the year in High Point.

The four finished water samples collected at the Frank Ward Treatment Plant from April to June were analyzed for atrazine, chlorpyrifos, chlorothalonil, simazine, and 2,4-D. Only three compounds were detected. Atrazine and simazine were found in 75 and 50% of finished water samples. Atrazine was found in low levels (ND-0.11 µg/L) in April, but in May at 1.61 µg/L, and in June at 0.97 µg/L. Residue levels of simazine were detected in finished water samples in May at 1.19 µg/L and June at 0.98 µg/L. Chlorothalonil was present in 25% of samples at concentrations ranging from non-detectable to 0.16 µg/L.

Summary: Atrazine, simazine, chlorothalonil, and 2,4-D were the pesticides detected in the raw and finished waters of High Point in 1999. These same compounds were also prevalent in field surface water samples. Residue levels at

City Lake found atrazine and simazine at levels approaching their MCLs.

Concentrations of 2,4-D were found at 1.0 and 2.0 µg/L, but considering its MCL of 70.0 µg/L and the untreated nature of the samples, these values were deemed insignificant in terms of human health risks. Pesticide residue levels found at the Oak Hollow intake were low in comparison to regulatory and advisory levels.

The finished water samples exhibited some values of interest. Atrazine and simazine were found at concentrations that measured approximately 54 and 30%, respectively, of their MCLs. Concentrations never exceeded MCLs and subsequently were not considered an immediate threat; however, most importantly the values detected in finished water were similar to raw water concentrations (Fig. 2).

YEAR TWO—2000

Burlington: Nine Lake Mackintosh intake water samples were collected from May through October and analyzed for atrazine, alachlor, chlorpyrifos, simazine, metolachlor, and 2,4-D. All analyzed pesticides were detected in the raw water samples at various times throughout the season. Atrazine, chlorpyrifos, and simazine were present in over 50% of samples, but levels rarely exceeded 0.5 µg/L. Residues of metolachlor were present in 63% of Lake Mackintosh samples and concentrations varied from 0.12 to 1.52 µg/L. Alachlor was detected once (May; 0.1 µg/L) and 2,4-D was found twice (July; 1.08 µg/L and October; 0.94 µg/L) throughout the whole season.

The ten raw water samples collected from May to October at the Stony Creek intake were analyzed for six pesticides: atrazine, alachlor, chlorpyrifos, simazine, 2,4-D, and metolachlor. Four of these pesticides were detected including atrazine and alachlor in 30%, chlorpyrifos in 38%, and metolachlor in 56% of the raw water samples, although concentrations remained below 0.75 µg/L.

The J. D. Mackintosh Plant receives water from Lake Mackintosh intake and was sampled 7 times. Samples, analyzed for atrazine, alachlor, chlorpyrifos, simazine, metolachlor and 2,4-D were found to contain atrazine (100%), chlorpyrifos (83%), simazine (57%), and metolachlor (57%). Residue levels of all four chemicals were below 0.75 µg/L.

Summary: Atrazine, simazine, chlorpyrifos, and metolachlor were the primary compounds detected in Burlington's raw and finished water samples. Low levels of these herbicides were also found in field surface water samples. Residue quantities detected at intakes and treatment plants did not approach regulatory or advisory levels at any time within the sampling season; therefore, threat to human health was considered negligible. However, analyses of these four pesticides showed residues found in finished water samples were similar in concentration to the raw water pesticide residue levels (Figs. 3,4).

Greensboro: The eight samples collected from February to August at the Townsend intake were analyzed for atrazine, chlorpyrifos, chlorothalonil, simazine, and 2,4-D. Rates of detection in raw water samples were as follows: chlorpyrifos (40%), atrazine (14%), and simazine (57%). However, residue levels of all pesticides detected never exceeded 0.27 µg/L.

The Mitchell intake was sampled on eight occasions from February to August and analyzed for atrazine, chlorpyrifos, chlorothalonil, simazine, and 2,4-D. Of these 5 pesticides only chlorothalonil and simazine were found in 29 and 86% of the samples, respectively. Residue concentrations never exceeded 0.5 µg/L.

The eight finished water samples collected from both the Townsend and Mitchell Treatment Plants from February to August were analyzed for 5 pesticides including atrazine, chlorpyrifos, chlorothalonil, simazine, and 2,4-D. The four pesticides found in both treatment plants were atrazine, simazine, chlorpyrifos, and chlorothalonil. Simazine was detected in 57% of Townsend and 75% of Mitchell samples, while the other chemicals were found in less than 50% of finished water samples for both plants. Residue levels were low across the board and the greatest concentration detected was simazine at 0.43 µg/L, found in both treatment systems.

Summary: Four pesticides, chlorothalonil, chlorpyrifos, atrazine, and simazine, were found in Greensboro's raw and finished water samples and also detected in field surface water samples. Pesticide residue levels detected at intakes and treatment plants were found in low quantities; well below regulatory and advisory values. Although all pesticide concentrations detected in raw and finished waters were low, the levels of simazine residues at both Mitchell and Townsend Plants were present at comparable levels in raw and finished water samples (Fig. 5).

High Point: From April to November, eight raw water samples were collected at both City Lake and Oak Hollow intakes and analyzed for atrazine, chlorpyrifos, chlorothalonil, simazine, and 2,4-D. City Lake intake exhibited three

pesticides, atrazine (14%), simazine (29%), and chlorpyrifos (57%) in samples collected, although concentrations detected were low, less than 0.25 µg/L.

Residues of atrazine, simazine, 2,4-D, and chlorpyrifos were found in Oak Hollow intake samples at concentrations generally below 0.5 µg/L. One exception was found in August when a 2,4-D value of 1.1 µg/L was observed. Residue concentrations were minimal and detection rates for atrazine and chlorpyrifos (25%), simazine (38%), and 2,4-D (13%) were slightly higher than City Lake results.

Finished water samples from Frank Ward Treatment Plant were collected on eight occasions from April to November and analyzed for atrazine, chlorpyrifos, chlorothalonil, simazine, and 2,4-D. Concentrations well below 0.5 µg/L of atrazine and simazine were found at rates of 13 and 38%, respectively in finished water samples. Chlorothalonil was present in 13% and chlorpyrifos in 50% of samples although concentrations never exceeded 0.25 µg/L.

Summary: Atrazine, simazine, and 2,4-D were the primary pesticides in field surface water samples while atrazine, simazine, and chlorpyrifos were commonly found in both raw and finished water. Concentrations in the field were considerably higher than those at the intakes and treatment facilities. Residue detections from all sources were well below regulatory and advisory values. Metolachlor residues were found in November at both raw water intakes and in the finished water. Although the compound was only found on one occasion, the levels detected were comparable for all three locales. Similar results were observed with simazine, chlorpyrifos, and atrazine (Fig. 6).

YEAR THREE—2001

Burlington: The twenty-eight samples collected at Lake Mackintosh intake from March to September were analyzed for atrazine and metolachlor. Atrazine was detected in all but one sample (96%) while concentrations were all below 0.5 µg/L. Metolachlor was present in 96% of samples at concentrations ranging from 0.07 to 1.38 µg/L.

From March to September, the Stony Creek Watershed intake was analyzed for atrazine and metolachlor in twenty-eight samples. Residue concentrations never exceeded 0.25 µg/L in the 68% found positive for atrazine. Metolachlor was detected in 89% of collected samples, with the majority of residues falling just above or below 0.5 µg/L.

The twenty-four finished water samples collected at J.D. Mackintosh plant from March to September were analyzed for atrazine and metolachlor. Atrazine was present in 63% and metolachlor in 70% of the water samples. Residue concentrations for both were equal to or less than 0.5 µg/L.

From April to September, seven finished water samples were collected from Stony Creek's Ed Thomas Plant and analyzed for atrazine and metolachlor. Although both atrazine (43%) and metolachlor (71%) were found in these samples, quantities were low and the greatest residue concentration detected was 0.44 µg/L of metolachlor, in September.

Summary: Atrazine and metolachlor residues were present in many of the raw and finished water samples collected in Burlington in 2001 and likewise in field surface water samples. Concentrations detected in the field were generally low with

a few values above 0.5 µg/L. Although these pesticides were detected repeatedly at the intakes and treatment plants, concentrations remained considerably lower than established MCLs and HALs. The regulatory values of atrazine and metolachlor were never exceeded; however, the concentrations detected were similar for the raw and finished water samples (Fig. 7).

Greensboro: Collections of raw and finished water were performed at only the Townsend Plant in 2001. From March to September, ten samples were analyzed for alachlor, atrazine, metolachlor, simazine, and 2,4-D. Four of the herbicides, atrazine, simazine, metolachlor, and 2,4-D were found at the intake throughout the year. Atrazine was detected in 30% and simazine in 20% of samples, but concentrations were below 0.10 µg/L. Measurable levels of 2,4-D and metolachlor were detected at rates of 20 and 78%, respectively. These two herbicides were frequently found at higher concentrations compared to the other pesticides (atrazine and simazine). Measurements of 2,4-D in May (2.31 µg/L) and metolachlor in August (2.04 µg/L) were the peak concentrations found within the study year.

The ten finished water samples collected from the Townsend Plant from March to September were analyzed for atrazine, alachlor, simazine, metolachlor, and 2,4-D. Metolachlor was found in 88% of samples, while the other four pesticides were detected in less than 25% of the samples. 2,4-D was observed in March at 3.25 µg/L and in May at 2.97 µg/L. Metolachlor residues reached 1.14 µg/L while all other pesticide levels were below 0.5 µg/L.

Summary: Simazine, 2,4-D, atrazine, and metolachlor were present in both raw and finished water samples of Greensboro in 2001. Field surface water detections also yielded these four compounds along with others not found at intakes or treatment facilities. 2,4-D was present in raw water samples at a concentration range of 0.79 to 2.31 µg/L, whereas finished water concentrations reached 2.97 and 3.25 µg/L. However, these values are considerably lower than the established MCL for 2,4-D (70.0 µg/L) and provided little support for human health risks.

Metolachlor was present at concentrations around 1.0 µg/L, but with an HAL of 70.0 µg/L these residue quantities were deemed insignificant. The raw water detections of metolachlor and 2,4-D were low but similar in concentration to the finished water samples (Fig. 8). All other detected values for simazine, atrazine, and alachlor were well below their MCLs and therefore posed minimal threat.

High Point: The eastern and western intakes of High Point were each sampled four times from March to July and analyzed for alachlor, atrazine, metolachlor, simazine, and 2,4-D. City Lake intake collections exhibited residues of all five pesticides with atrazine and metolachlor in 75%, alachlor and 2,4-D in 50%, and simazine in 25% of the samples. Although all five compounds were detected, only 2,4-D and metolachlor exceeded 1.0 µg/L with peak concentrations of 3.33 and 1.04 µg/L, respectively.

Atrazine, metolachlor, alachlor, and 2,4-D were detected at the Oak Hollow intake. Residues of atrazine and metolachlor residues were present in all samples, while alachlor and 2,4-D were found in only 50%. Concentrations remained at or below 0.5 µg/L for atrazine and alachlor, but metolachlor and 2,4-D exhibited

residues of larger quantities with peak concentrations of metolachlor, in March, at 2.1 µg/L and 2,4-D in May, at 2.56 µg/L.

The four Oak Hollow finished water samples collected from March to July were analyzed for alachlor, atrazine, metolachlor, simazine, and 2,4-D. Although concentrations were low, many of the samples exhibited pesticide residues including metolachlor (100%), atrazine (75%), simazine (25%), and alachlor (25%). Fifty percent of samples collected contained 2,4-D in concentrations ranging from 0.82 to 6.75 µg/L.

Summary: Residues of atrazine, simazine, metolachlor, alachlor, and 2,4-D were detected frequently in raw and finished water samples of High Point in 2001. These compounds were also commonly found in field surface water samples. Atrazine and simazine were present at extremely low levels (e.g., <0.5 µg/L), far below their MCLs. Elevated concentrations of 2,4-D and metolachlor were notable and similar residue concentrations were detected in raw and finished water samples for all pesticides analyzed (Fig. 9, 10). Comparisons of detected concentrations to regulatory and advisory levels deemed the pesticide residues found insignificant in terms of human health risks.

Raleigh: The twenty samples collected from May to September at E.M. Johnson intake were analyzed for atrazine and metolachlor. Atrazine was present in 60% of samples, yet all concentrations were below 0.5 µg/L. Metolachlor, found in 80% of samples, only exceeded 0.5 µg/L on two occasions, 0.84 and 2.0 µg/L in August.

From May to September, eight samples were collected at the Falls of the Neuse intake. The raw water was analyzed for atrazine and metolachlor and both chemicals were present in samples at 75 and 63%, respectively. Most concentrations fell below 1.0 µg/L except one sample collected in June containing atrazine at 2.65 µg/L and one in August containing metolachlor at 1.58 µg/L.

The ten finished water samples collected at E.M. Johnson Plant from July to September were analyzed for atrazine and metolachlor. Both herbicides were present with atrazine in 70% and metolachlor in 80% of samples collected. Detected residue concentrations never exceeded 0.65 µg/L.

Summary: Atrazine and metolachlor were present in nearly all of the samples collected in raw and finished water as well as field surface water samples. Most of detected pesticide residue concentrations were minimal (i.e., <0.5 µg/L) throughout the year. Atrazine was found in June, at a level of 2.65 µg/L at the Falls of the Neuse intake. This value is just 0.35 µg/L less than the established MCL for atrazine. However, the residue value was found in raw water for which no regulation is required and atrazine was not detected in finished water samples at a concentration above 0.46 µg/L. While pesticide concentrations in both raw and finished water remained below regulatory values the levels were similar in the pre and post-treated water (Fig. 11).

While MCLs and HALs provide a frame of reference when comparing raw and finished water pesticide detections, a hazard quotient (HQ) allows for the immediate assessment of the risk associated with pesticide concentrations in finished water. In addition to reported concentrations these values were also reported in relation to the

chemicals respective regulatory value by dividing the residue concentration by the MCL (Table 1) Therefore HQs greater than 1 would provide an alert to the presence of pesticide residues in finished drinking water that exceed regulatory values increasing the risk to human health. The yearly averages of atrazine, simazine, and 2,4-D residues in finished drinking water of the treatment facilities all exhibited HQs well below 1; therefore, concentrations detected in this study were considered an unlikely risk to human health.

CONCLUSION

For three years, participating treatment facilities and the intakes impounding surface waters to these plants were monitored for the presence of a variety of pesticides. Those studied were found frequently throughout the course of the treatment facility project in raw and finished water samples. Pesticide residues were regularly detected although concentrations tended to remain well below established MCLs and HALs. There were a few exceptions in which regulatory values were approached but never exceeded. While residue concentrations were minimal and never considered an immediate threat to human health, potential implications noted in the results of the study did generate some concern.

The raw and finished water samples were subjected to an array of pesticide analyses in which 4 to 7 compounds were investigated concurrently. The multiple compounds that were detected at raw water intakes were also found in the analogous collection of finished water samples. This occurred in every instance,

although on two occasions, four pesticides were found in raw water and only three of those were present in the correlating finished water samples.

Finished water samples frequently showed elevated levels of contaminants when samples taken from intakes also presented increased residue concentrations. Rarely was a pesticide detected in post-treated water samples and not found in the related raw water. Trends of this nature, in which results of pesticide analyses in both raw and finished waters appeared to be associated, lend support to earlier theories, that although raw and finished water collections were not timed to represent a before and after situation, samples gathered within a short time period can potentially indicate pre- and post-treatment contaminant conditions.

All concentrations detected were within legal and advisory limits and the threat to human health appeared minimal. However, at no time was there a drastic decline in contaminant concentrations following passage through treatment processes. Residue concentrations found in finished waters were similar in quantity to those values detected in raw water samples. These results were compared using paired t-tests and found to be statistically similar at each drinking water treatment plant. Therefore, it seemed as if the treatment processes had little effect on pesticide residue concentrations.

Assuming the results observed in this portion of the study were accurate representations of everyday occurrences in raw and finished water, there is a possibility of a contaminant entering, enduring, and passing out of a treatment system. Concern increases when finished water concentrations of a chemical are present in quantities that exceed regulatory limits. Surface runoff, accidental spills,

and other non-point source contaminations can transport large quantities of chemical residues. If the receiving reservoir is comprised of surface waters that serve as sources of drinking water for municipalities, the likelihood that these compounds would enter the impounding intakes and remain in post-treated drinking water increases the threat to human health.

The objective of this study was to determine if pesticide residues were present near intakes of water treatment plants and subsequently entering treatment facilities. In monitoring intakes and the correlating treatment systems, analyses revealed the presence of selected pesticides in both raw and finished waters. This furthered the concept of watershed assessment (explored in Chapter 2) in which the select areas were monitored over three years to characterize the presence of pesticide residues within these drinking water treatment plants.

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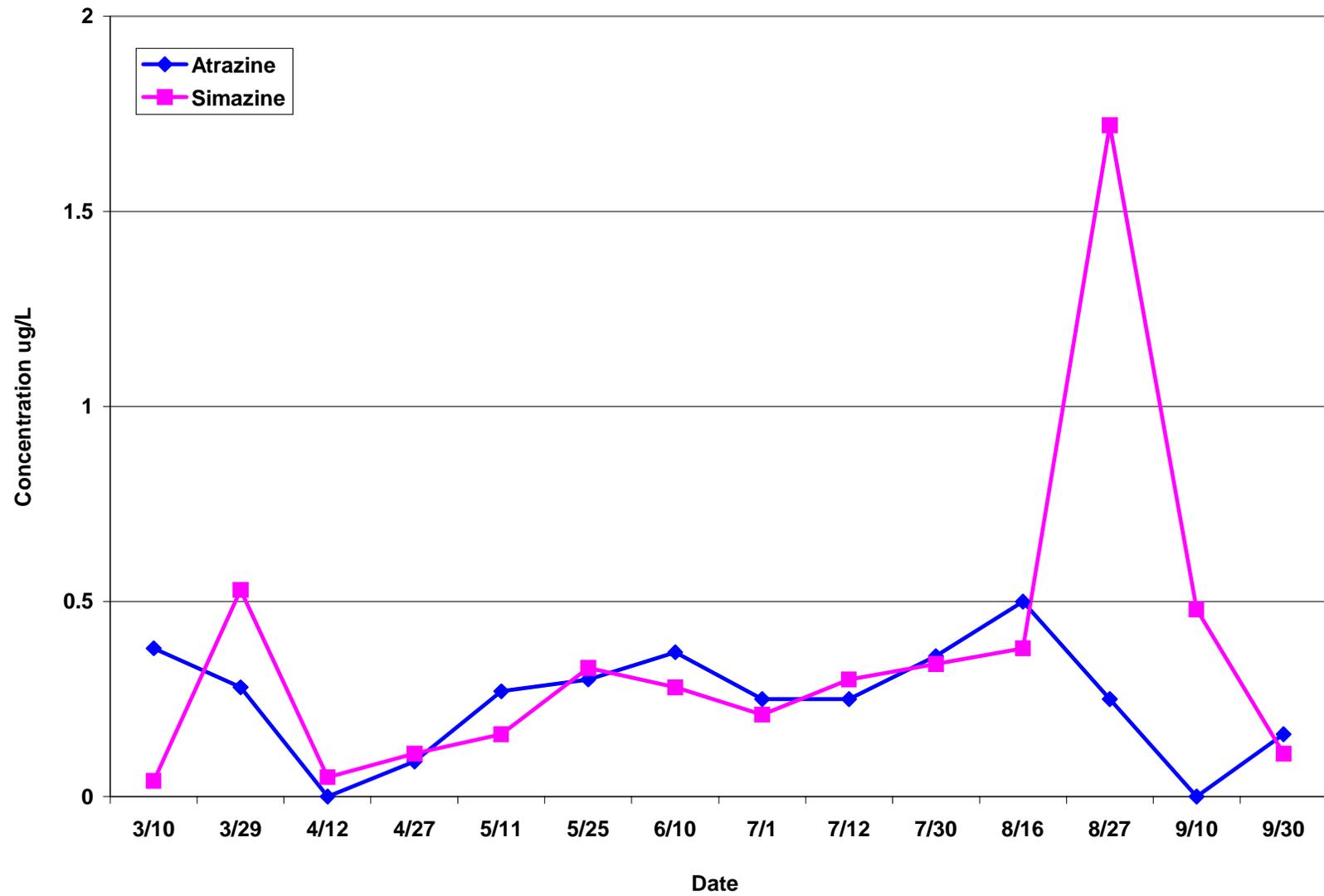


Figure 1. Raw water residue detections of atrazine and simazine from March to September of 1999 in Rural Watershed 1 (Burlington).

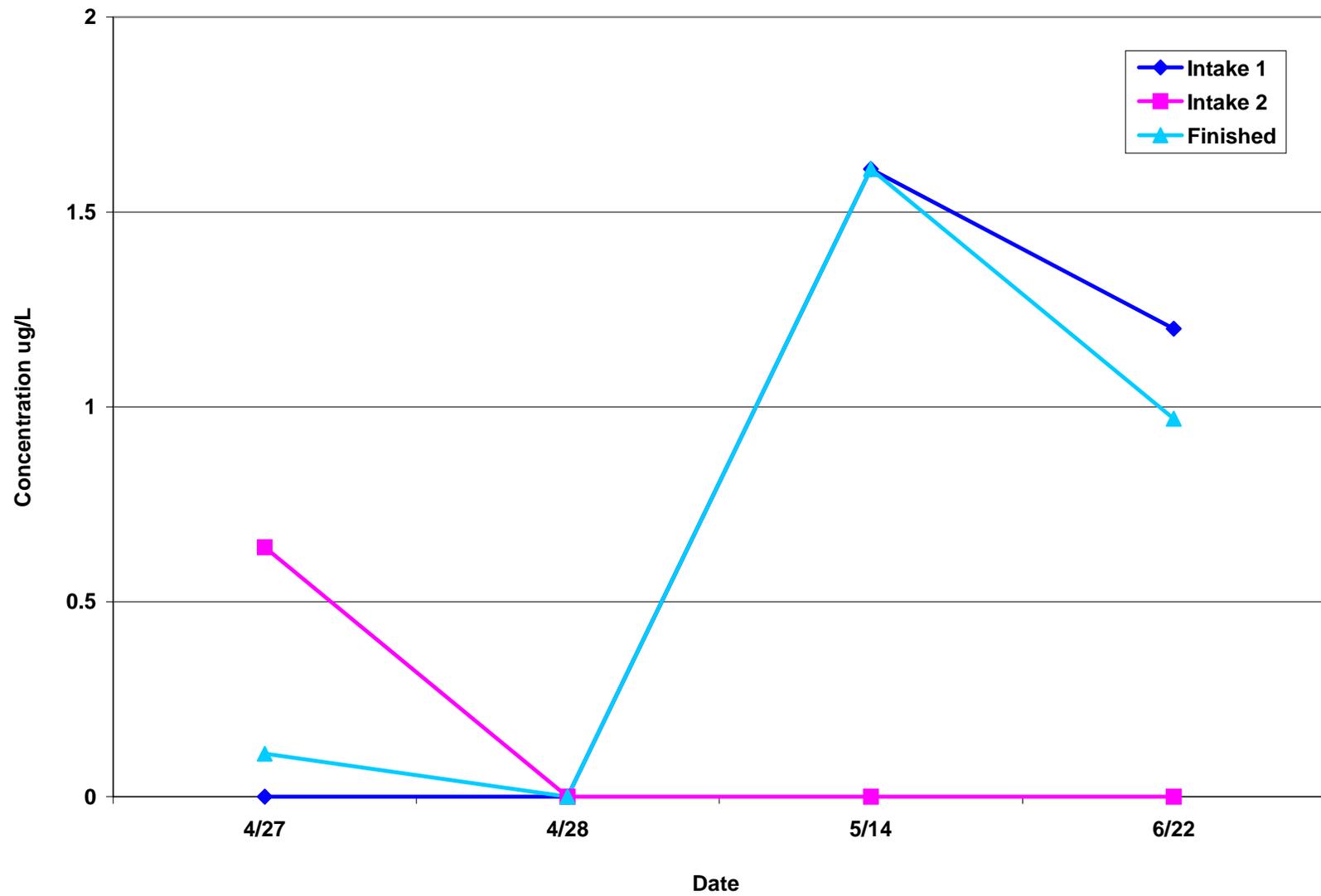


Figure 2. Raw (Intake) and finished residue detections of atrazine from April to June of 1999 in Urban Watershed 2 (High Point).

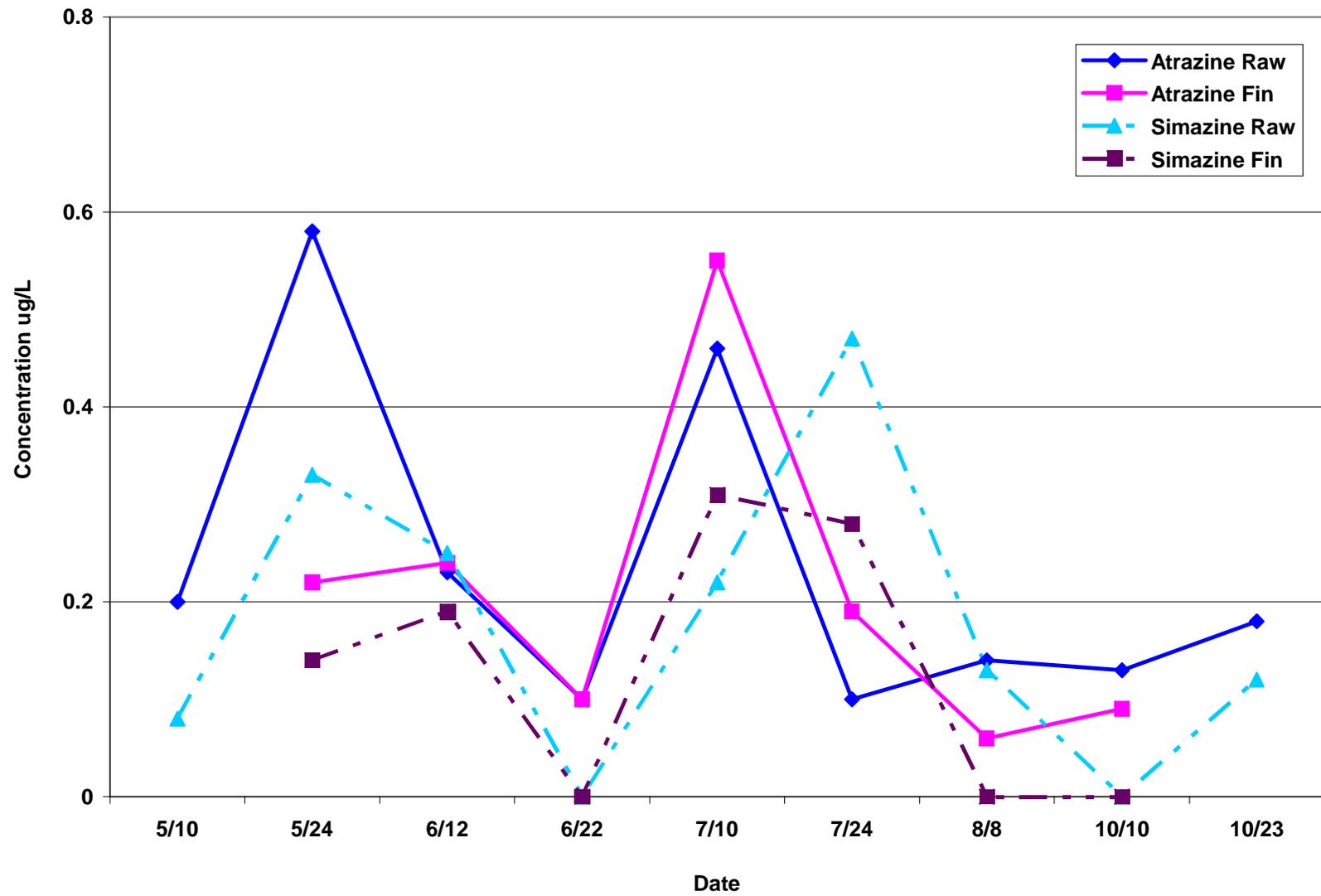


Figure 3. Raw (Intake) and finished residue detections of atrazine and simazine from May to October of 2000 in Rural Watershed 1 (Burlington).

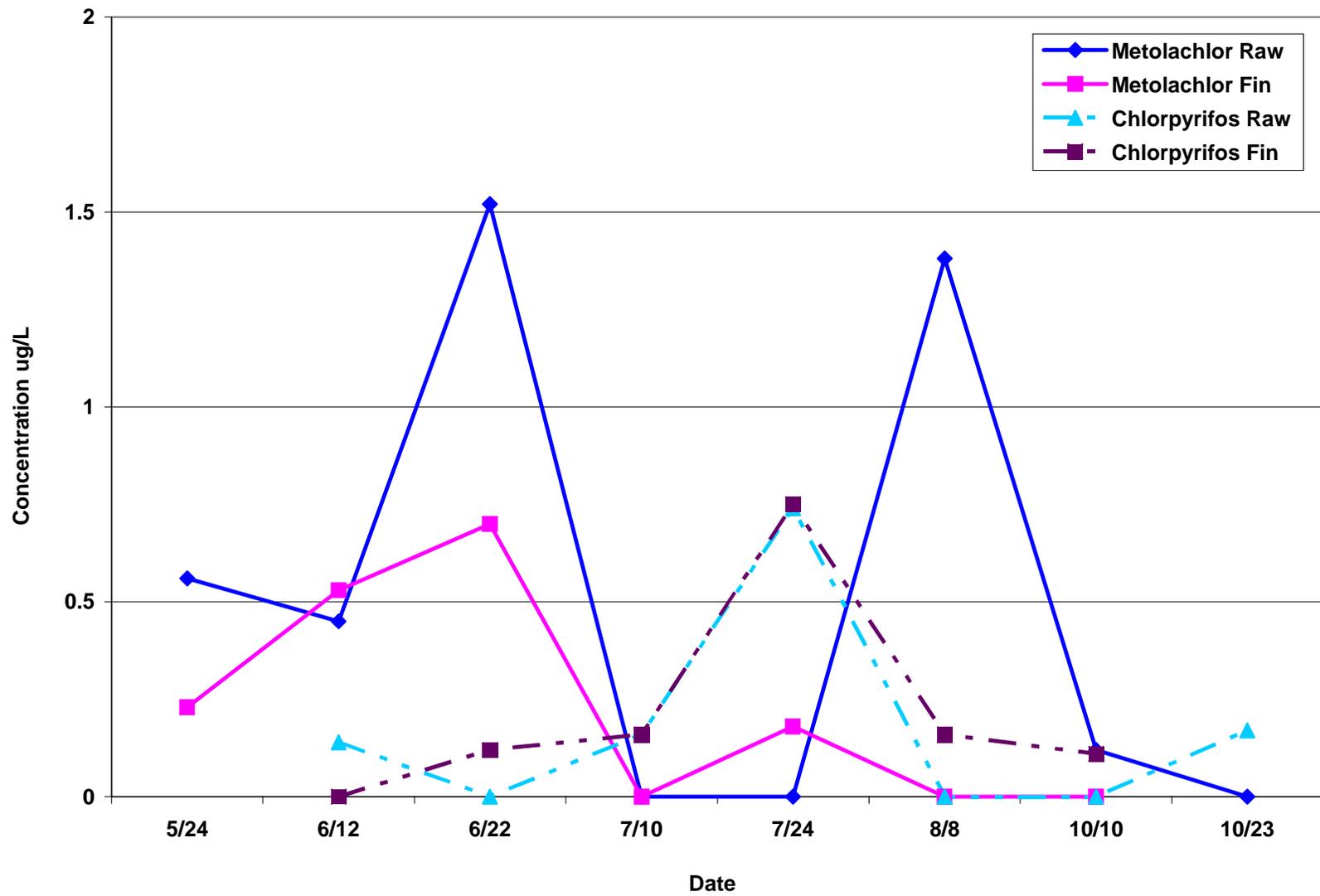


Figure 4. Raw (Intake) and finished residue detections of metolachlor and chlorpyrifos from May to October of 2000 in Rural Watershed 1 (Burlington).

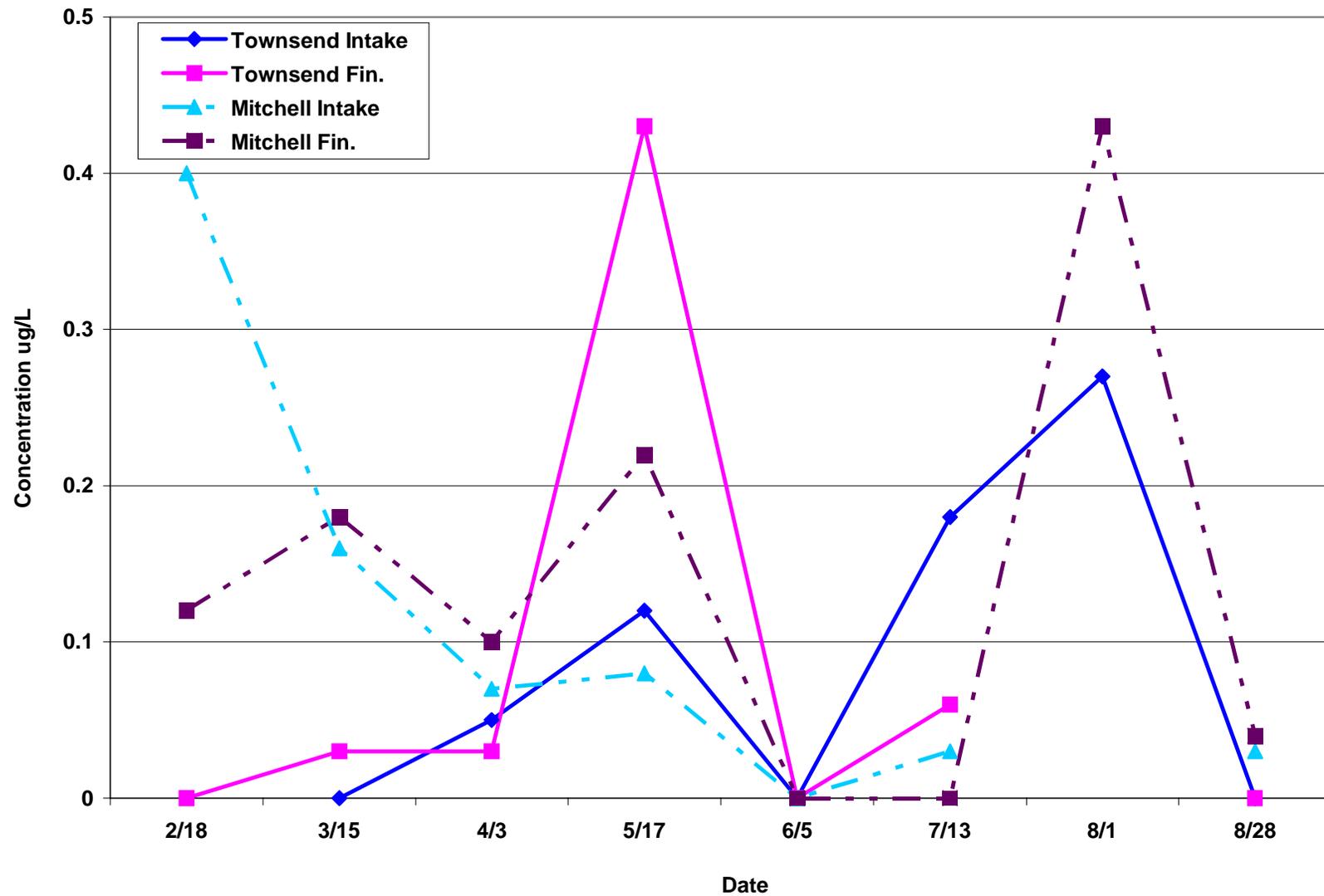


Figure 5. Raw (Intake) and finished residue detections of simazine from February to August of 2000 for Townsend and Mitchell Water Treatment Plants of Urban Watershed 1 (Greensboro).

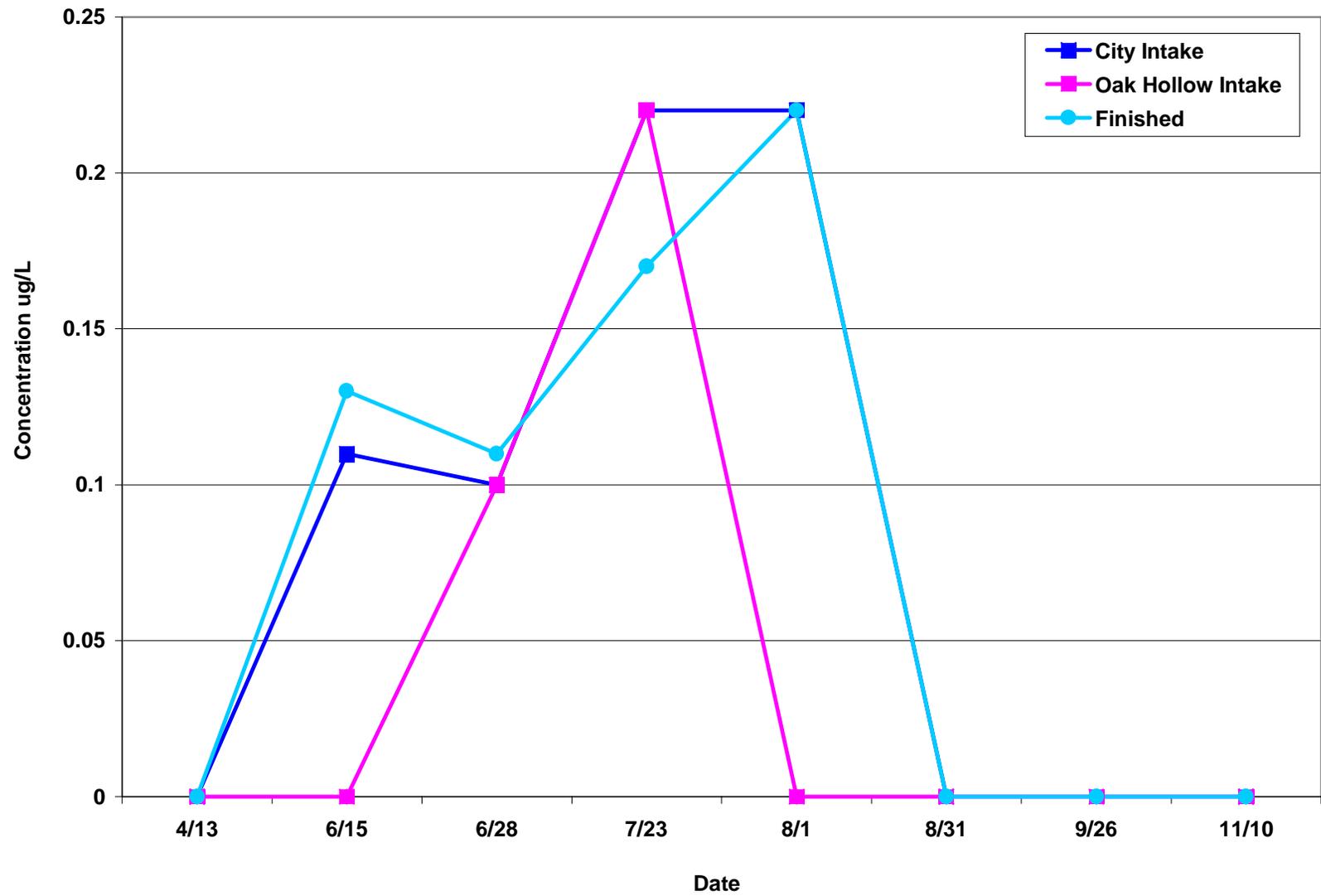


Figure 6. Raw (Intake) and finished residue detections of chlorpyrifos from April to November of 2000 in Urban Watershed 2 (High Point).

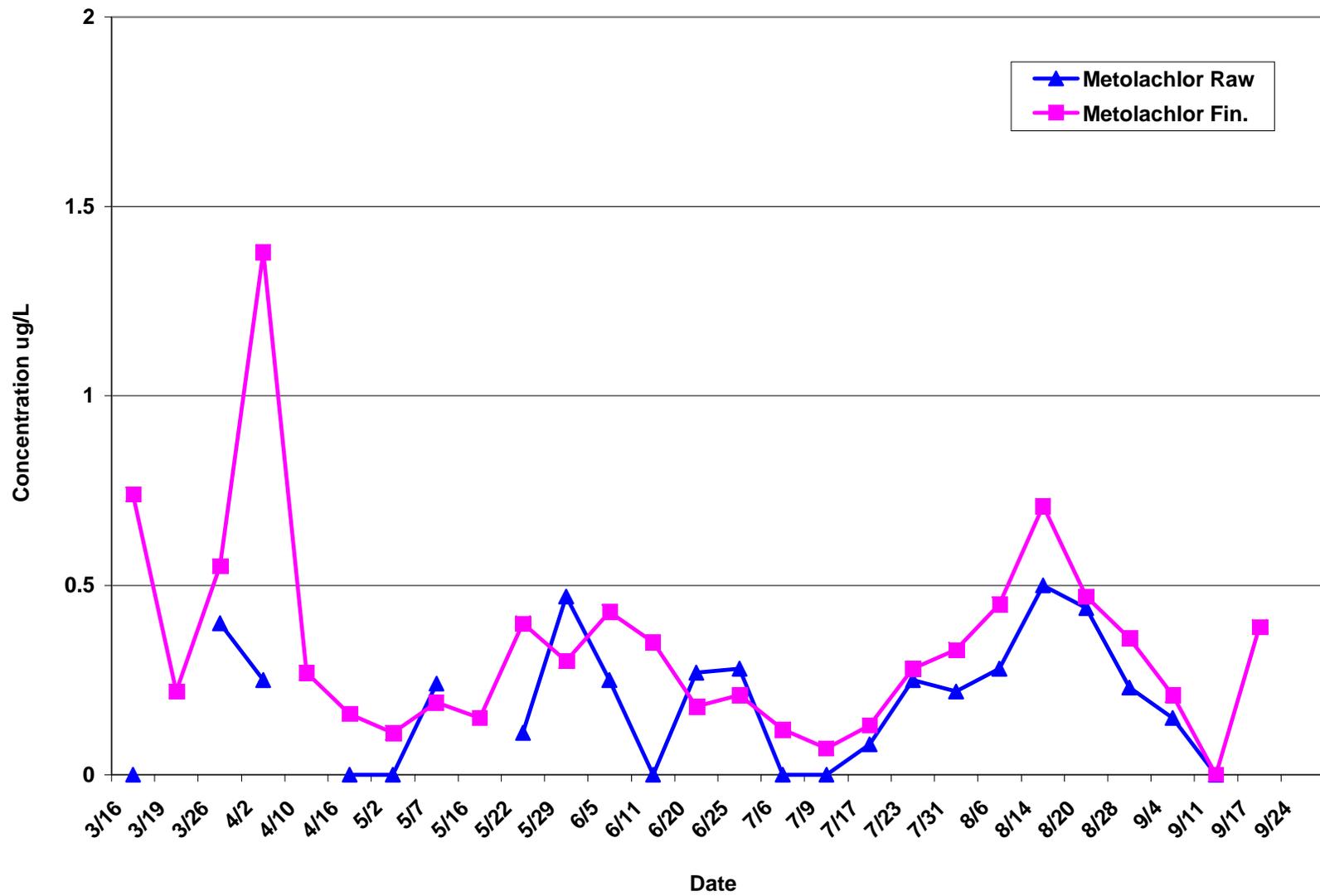


Figure 7. Raw (Intake) and finished residue detections of metolachlor from March to September of 2001 in Rural Watershed 1 (Burlington).

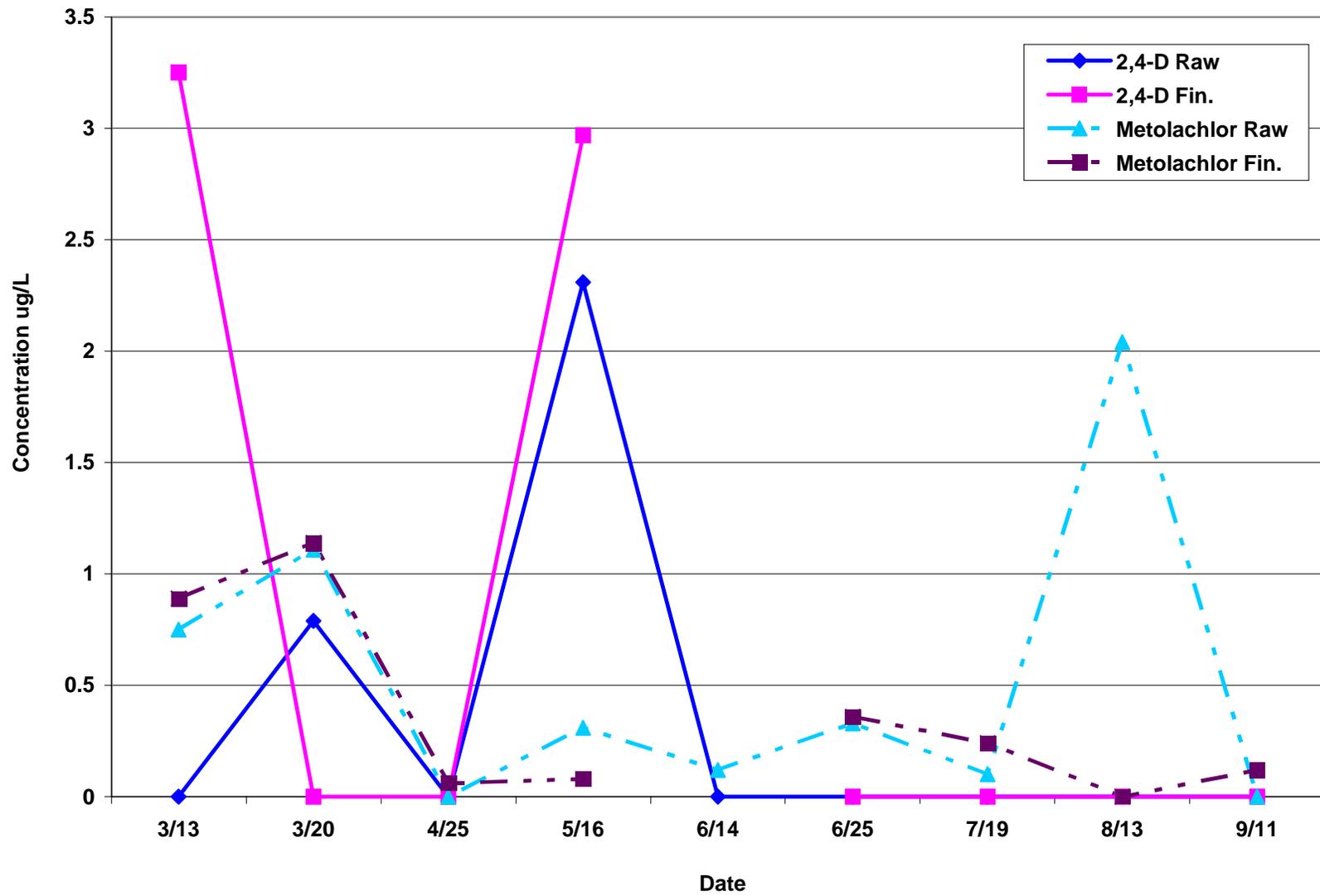


Figure 8. Raw (Intake) and finished residue detections of 2,4-D and metolachlor from March to September of 2001 in Urban Watershed 1 (Greensboro).

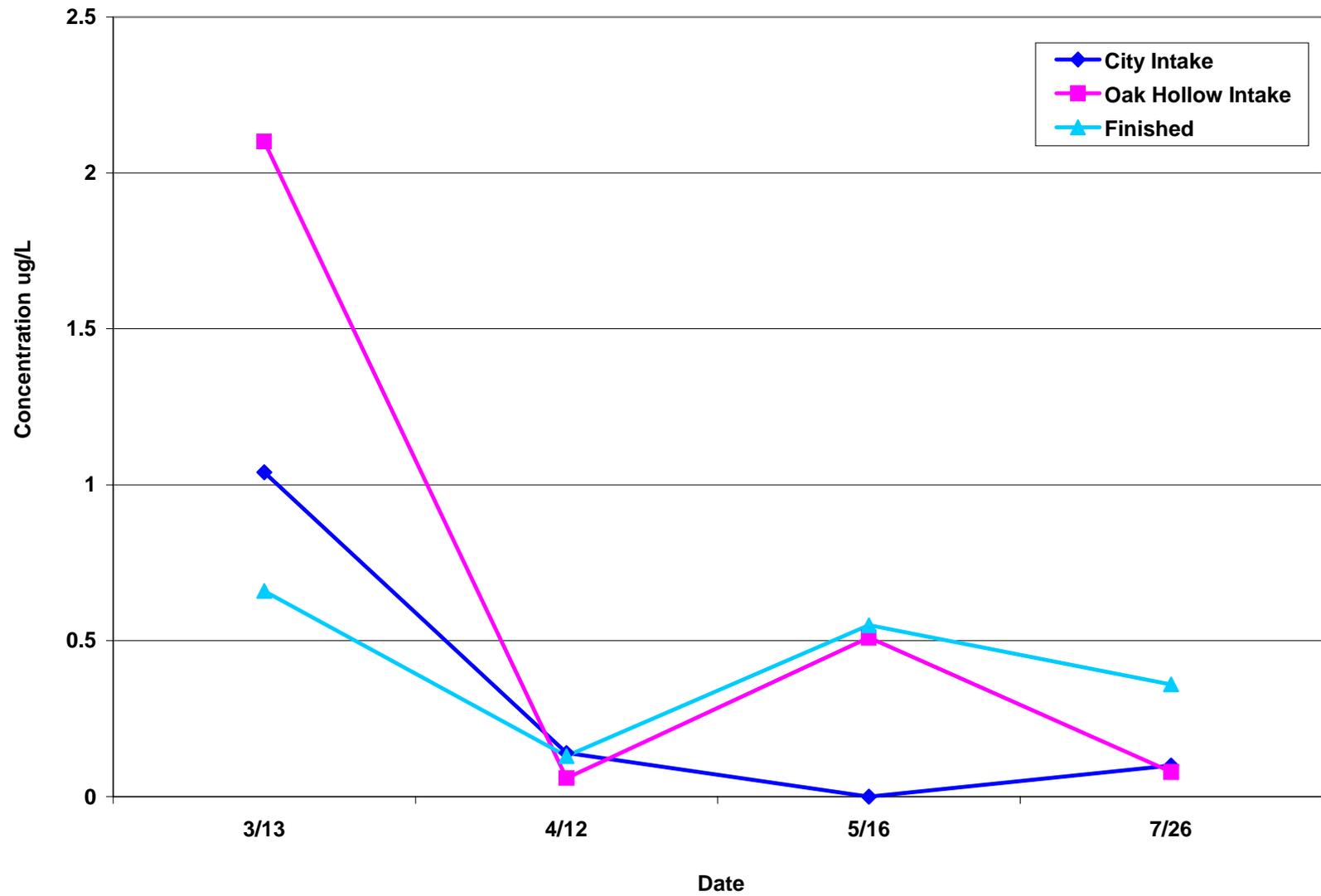


Figure 9. Raw (Intake) and finished residue detections of metolachlor from March to July of 2001 in Urban Watershed 2 (High Point).

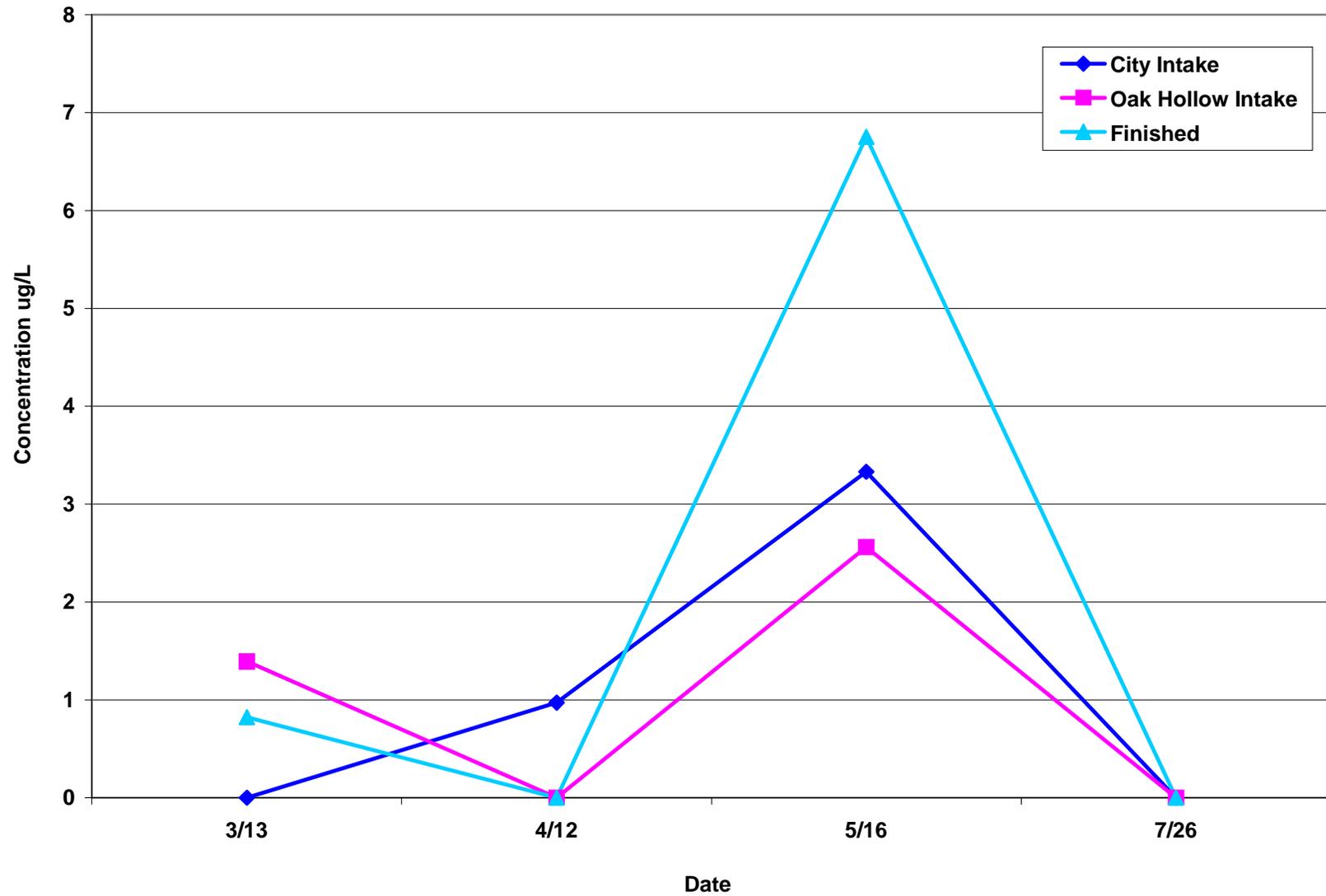


Figure 10. Raw (Intake) and finished residue detections of 2,4-D from March to July of 2001 in Urban Watershed 2 (High Point).

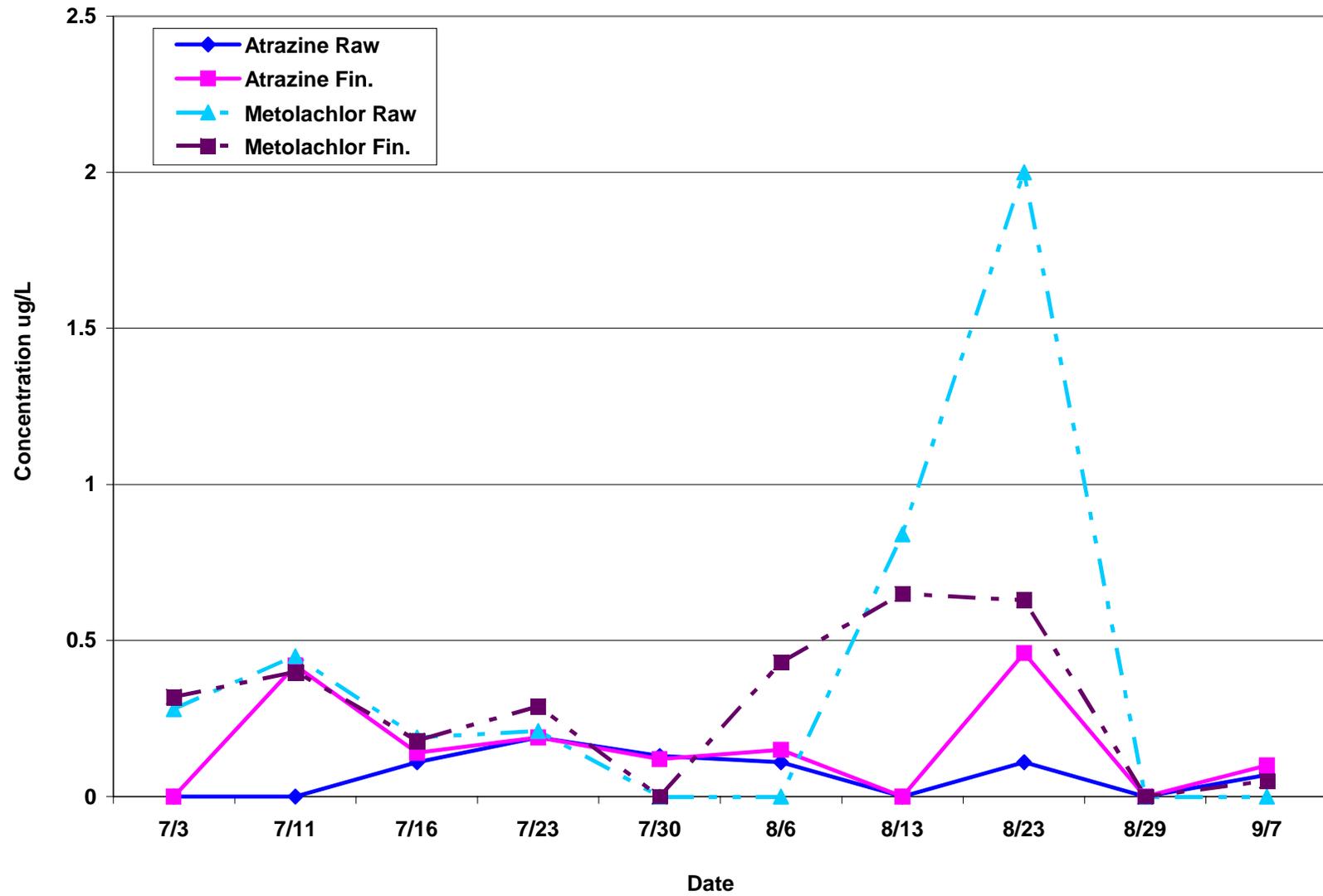


Figure 11. Raw (Intake) and finished residue detections of atrazine and metolachlor from July to September of 2001 in Rural Watershed 2 (Raleigh).

Table 1. Hazard Quotients (HQ) for yearly detections of atrazine, simazine, and 2,4-D in Burlington, Greensboro, and High Point from 1999 to 2001.

Year	City	Pesticide	Yearly Average	HQ
1999	Burlington	Atrazine	N/A	
1999	Burlington	Simazine	N/A	
1999	Burlington	2,4-D	N/A	
1999	Greensboro	Atrazine	0	0
1999	Greensboro	Simazine	0.11	0.03
1999	Greensboro	2,4-D	0	0
1999	High Point	Atrazine	0.9	0.3
1999	High Point	Simazine	1.09	0.27
1999	High Point	2,4-D	0	0
2000	Burlington	Atrazine	0.21	0.07
2000	Burlington	Simazine	0.23	0.06
2000	Burlington	2,4-D	0	0
2000	Greensboro	Atrazine	0.12	0.04
2000	Greensboro	Simazine	0.18	0.05
2000	Greensboro	2,4-D	0	0
2000	High Point	Atrazine	0.11	0.04
2000	High Point	Simazine	0.1	0.03
2000	High Point	2,4-D	0	0
2001	Burlington	Atrazine	0.11	0.04
2001	Burlington	Simazine	N/A	
2001	Burlington	2,4-D	N/A	
2001	Greensboro	Atrazine	0.06	0.02
2001	Greensboro	Simazine	0.03	0.01
2001	Greensboro	2,4-D	3.11	0.04
2001	High Point	Atrazine	0.08	0.03
2001	High Point	Simazine	0.25	0.06
2001	High Point	2,4-D	3.79	0.05

CHAPTER FIVE

POWDERED ACTIVATED CARBON AS A MEANS OF REDUCING PESTICIDE RESIDUES WITHIN SURFACE WATERS

INTRODUCTION

Investigation of pesticide contaminants in surface, intake, and finished water has noted low levels of pesticides in all three. Some efforts attempted outside of the water treatment facility were successful in reducing pesticide residues; however, the standard treatment processes were not always sufficient in always reducing contaminant levels (Miltner *et al.* 1989, Najm *et al.* 1991a). Therefore, additional remediation was developed within drinking water treatment plant facilities to assist in reducing residues to levels considered safe.

Review of the literature and resources associated with treatment in drinking water treatment facilities led to the choice of activated carbon (AC) as the subject of this study. Support for this choice was found in numerous studies including Afenya (1996) who stated: "Although there are many chemical, physical, and biological techniques of treating water contaminated with industrial and municipal wastes to produce safe and palatable drinking water none has the potential comparable to activated carbon". With this in mind, experiments were undertaken to examine activated carbon as a means of removing pesticide residues from drinking water.

Carbon can be treated in a simple two stage process to create an activated carbon product with increased adsorptive qualities. Activated carbon is initially comprised of base material containing high carbon content such as wood, lignite, coal, coconut shells, coffee beans, corncobs, and peat (Najm *et al.* 1991a, Seelig *et al.* 1992, Afenya 1996, Layton 2001). During stage one the raw material is subjected to intense heat ($\approx 400-700^{\circ}\text{C}$) in the absence of oxygen to dehydrate and volatilize lighter fractions such as carbon monoxide, carbon dioxide, and acetic acid

to produce a highly carbonaceous char (Seelig *et al.* 1992, Snoeyink and Summers 1999, Layton 2001). This first step known as carbonization creates some micropores and increases surface area. “The maximum amount of adsorption is proportional to the amount of surface area within pores that is accessible to the adsorbate” (Snoeyink and Summers 1999). Therefore, increasing the surface area will generally increase adsorption.

Stage two of the process involves activation in which the carbon char is again exposed to high heat ($\approx 700\text{-}1600^{\circ}\text{C}$) in the presence of oxidizing gases such as steam and carbon dioxide. The second heating will burn off any tar-like residues and create an internal network of pores with improved adsorptive properties. The resulting carbon particle possessing a massive surface area relative to its size is primed for adsorption (Seelig *et al.* 1992, Afenya 1996, Snoeyink and Summers 1999).

Activated carbon (AC), is adsorbent and water treatment facilities frequently use AC to remove odor and taste causing compounds (Falconer *et al.* 1989, Miltner *et al.* 1989, Najm *et al.* 1991b, Afenya 1996, Holman and Leidy 1998, Knappe *et al.* 1998, Snoeyink and Summers 1999). Compounds like 2,4-dichlorophenol, geosmin, 2-methylisoborneol (MIB), and humic substances are known to create problems with odor and taste, thereby decreasing the quality of drinking water. Several studies have focused on these compounds and activated carbon’s adsorbent ability to remove them from water supplies. Results show that activated carbon is a viable method of contaminant reduction or removal (Lalezary-Craig *et al.* 1988, Falconer *et al.* 1989, Najm *et al.* 1991a).

Removal of contaminants from drinking water may provide more benefits than improved organoleptic qualities when those compounds are considered a threat to human health. It has been shown that many organic contaminants are reduced with activated carbon (Najm *et al.* 1990, Najm *et al.* 1991b, Najm *et al.* 1991a, Vidic and Suidan 1991, Seelig *et al.* 1992, Matsui *et al.* 1994, Segar and Pevlon 1996, Knappe *et al.* 1998, Snoeyink and Summers 1999).

Nonpolar, carbon-rich compounds are preferentially adsorbed by activated carbon and it is believed that “AC filtration is most effective in removing organic contaminants from water” (Seelig *et al.* 1992). Consequently, the use of activated carbon to control organic compounds was accepted by various agencies, such as the Water Quality Association, as a method of contaminant control (Seelig *et al.* 1992). USEPA has also recognized the benefits of activated carbon and designated GAC as a part of the best available technology (BAT) in the removal of organic compounds from drinking water (Falconer *et al.* 1989).

BATs refer to technologies that best perform the treatment or function while also considering the costs and resources available. Due to high cost, the best method may not be available and a less efficient method that is available is used and deemed the best available technology (Richardson 1996, Pontius and Clark 1999, USEPA 2002).

Pesticide residue present in water at elevated concentrations has been lowered by activated carbon (Matsui *et al.* 1994, Afenya 1996). Robeck *et al.* (1965) performed studies that observed pesticide removal with water treatment processes, including powdered activated carbon. Pesticides such as lindane, parathion, and

endrin were reduced by 90% or greater in water supplies following treatment with PAC varying in concentration from 10.0 to 20.0 mg/L. One study demonstrated successful reductions of greater than 75% for residues of parathion, malathion, 2,4-D, and DDT with carbon doses of 2.0 to 20.0 mg/L (Sigworth 1965).

Knappe *et al.* (1998) reported a reduction of atrazine with various doses of carbon ranging from 1.0 to 100.0 mg/L. A study utilizing bench-scale tests of both GAC and PAC showed decreases in pesticide concentrations by AC adsorption. Several pesticide residues including alachlor, metolachlor, atrazine, cyanazine, simazine, and metribuzin were greatly reduced with filter-bed GAC adsorption. Atrazine removal was as high as 95% in Ohio River water with a PAC dose of 85.7 mg/L, while addition of 7.5 to 50.0 mg/L of PAC removed atrazine from 43 to 88% (Miltner *et al.* 1989).

Pesticide environmental studies have shown a temporal trend associated with pesticide runoff and subsequent elevated surface water contaminant residues (Goolsby *et al.* 1991, Stamer and Zelt 1994, Stamer and Wieczorek 1996, Thurman *et al.* 1996). Considering the propensity for adsorption of organic contaminants, AC has been used as an additional precaution within standard operating procedures of drinking water treatment plants to aid in controlling seasonal pesticide influxes typically associated with spring flush (Lalezary-Craig *et al.* 1988, Miltner *et al.* 1989, Najm *et al.* 1991a).

Activated carbon usage to aid in seasonal influx of pesticides might provide more than precautionary assistance considering various reports of pesticide residue breakthrough in finished drinking water. Researchers have reported that

“conventional water treatment (defined as coagulation, sand filtration, and chlorination) is ineffective in removing organonitrogen herbicides such as alachlor, atrazine, cyanazine, and metolachlor from finished drinking water” (Stamer and Wieczorek 1996) and other methods are required in addition to standard procedures (Miltner *et al.* 1989, Adams and Randtke 1992). These compounds are commonly detected in surface waters due to their frequent application, and relatively high water solubility. An example of such a situation was exemplified in a study within a Kansas River treatment plant in which levels of atrazine were found in 10 samples of finished water. Nine of these detections were greater than the 3.0 µg/L MCL and a maximum value of 16.0 µg/L was found (Stamer and Zelt 1994).

The presence of these pesticides in finished water supplies is a concern especially when residue concentrations exceed individual MCL values (Miltner *et al.* 1989, Goolsby *et al.* 1991, Adams and Randtke 1992, Stamer and Zelt 1994, Stamer and Wieczorek 1996). Results of these and other studies including Chapter Four have shown that conventional water treatment plant procedures do not remove pesticide residues and more importantly do not always reduce residue concentrations to levels required to meet legally safe drinking water standards (Miltner *et al.* 1989, Najm *et al.* 1991a, Holman and Leidy 1998, Holman and Leidy 2000, Jones and Leidy 2002).

With the threat of pesticide contamination in drinking water, even following treatment, additional methods may need to be implemented to continue to provide safe drinking water. Activated carbon has become the focus of numerous studies investigating its adsorptive qualities (Lalezary-Craig *et al.* 1988, Falconer *et al.* 1989,

Miltner *et al.* 1989, Najm *et al.* 1991a, Jack and Clark 1998, Knappe *et al.* 1998, Campos *et al.* 2000) .

There are two popular forms of activated carbon, powdered (PAC) and granular (GAC), currently available and employed in many treatment facilities within the United States. GAC is typically part of the filter bed or filter column that is fixed and remains in place for many months or years in the treatment plant. The usage rates are lower in comparison to PAC and regeneration through reactivation is possible (Najm *et al.* 1991a). However, carbon adsorption is not always needed and continuous use of GAC due to its fixed nature can result in blocked adsorption sites from a background of natural organic matter thereby reducing its effectiveness and bed-life.

Powdered activated carbon has some benefits over GAC, including lower cost, but its most important advantage is the inherent flexibility. This flexibility is valuable in addressing the seasonality of pesticide influxes. PAC can be added with little to no difficulty or expense. In avoiding installation of a GAC-fixed bed and only adding PAC when deemed necessary to control incoming contaminants, capital expenditures are greatly reduced and efficiency of adsorption is increased (Najm *et al.* 1990, Najm *et al.* 1991a).

Implementation of PAC can occur, as a dry or slurry mixture, at various points within the plant, such as the intake, rapid mix basin, coagulation chamber, sedimentation basin or filter bed (Najm *et al.* 1990, Najm *et al.* 1991a). Carbon addition at one or more of these points can increase contact time, allowing for greater adsorption and increased removal of contaminants. PAC can be used alone

or in combination with another process such as ultrafiltration (UF) (Adham *et al.* 1991, Adham *et al.* 1993, Jack and Clark 1998), floc blanket reactors (FBR), and continuous stirred tank reactors (CSTR) to increase the removal efficiency of unwanted contaminants from water supplies (Campos *et al.* 2000).

GAC and PAC perform essentially the same tasks regarding the removal of contaminants from water within the treatment plants. Practical issues of handling ease, cost, and employee experience need to be considered when choosing the best use and method of activated carbon (JH 1991, Najm *et al.* 1991a, Knappe *et al.* 1998). A plant operator must determine feasibility of treatment options while continuing to maintain regulatory requirements. In doing so, treatment facilities located throughout the country vary in methods and procedures based upon contaminant circumstances and resources available.

Supplemental powdered activated carbon addition is efficient, inexpensive, and a simple process that reduces and removes pesticide residues within water treatment facilities. PAC is especially beneficial for those cities that do not possess the inclination or capital to construct or retrofit treatment facilities. Technologically advanced equipment is not always required or preferred, as Segar and Pevlon (1996) observed, and smaller communities tend to preferentially use PAC.

Some drinking water treatment facilities currently use PAC to control seasonal influx of pesticides, but generally no explicit guidelines for PAC addition have been developed. In this project, the goal was to develop a method that would be as practical and feasible as possible while also performing at the highest level of

efficiency and develop a method that could provide guidelines for remediation efforts involving PAC within a model treatment plant.

Weaknesses associated with any procedure should be considered when designing a remediation process. Expenditures related to PAC have increased over the last few years due to rising prices of the carbon. Point of entry into the treatment train process can determine the contact time and therefore the adsorption extent and efficiency of the carbon. Ideally, a procedure would involve PAC added such that contact time was maximized.

Another potential difficulty surfaces in the disinfection stage of drinking water treatment. Chlorine or chlorine-containing disinfectants are typically used as the main form of disinfection within drinking water treatment plants. A reduction in PAC capacity as a result of the surface oxidizing reaction between powdered activated carbon and oxidants, including chlorine, chlorine-containing disinfectants, and ozone was discovered in several studies (Najm *et al.* 1990, Najm *et al.* 1991a, Snoeyink and Summers 1999). Lalezary-Craig *et al.* (1988) examined the effects chlorine and chloramines had on the adsorption efficiency of activated carbon. In the presence of these disinfectants the removal of geosmin and MIB was reduced compared to studies in which residual disinfectants were not in solution. It seems as if the carbon's capacity for adsorption was lowered upon interaction with oxidizing disinfectants (chlorine, ozone), thereby reducing the adsorption of organic compounds.

The flexible nature of PAC allows the user to circumvent the above difficulties by adding and removing the carbon prior to the disinfection stage to avoid much

interaction with other chemicals. As stated previously, treatment options are chosen with respect to individual plant resources and needs and in many cases the use of PAC is the BAT that will control pesticide contamination and meet regulatory standards for a particular plant.

EXPERIMENTAL DESIGN

Studies involving the engineering aspect of designing water treatment plant operations focus on activated carbon's adsorption and are characterized by isotherm equations. An adsorption isotherm describes a chemical's equilibrium relationship between water and an adsorbent (in this case PAC) phase. The equation quantifies the efficiency of adsorption by revealing the amount of a chemical (adsorbate) that is sorbed to the carbon (adsorbent) and the remaining water concentration of the adsorbate (Spacie 1994, Campos *et al.* 2000, Grady 2000). More specifically the adsorption isotherm is "the constant-temperature equilibrium relationship between the quantity of adsorbate per unit of adsorbent q_e and its equilibrium solution concentration C_e " (Snoeyink and Summers 1999).

There is a variety of existing isotherm equations and some of the more common include Gibbs, Brauner-Emmet-Teller (BET), Polanyi, Langmuir, and Freundlich. The latter two equations are currently the most frequently used isotherms for fitting experimental data (Corwin and Farmer 1984, Kinniburgh 1986, Adham *et al.* 1993, Spacie 1994, Knappe *et al.* 1998, Dowbiggin 1999, Snoeyink and Summers 1999, Grady 2000).

BOTTLE-POINT ISOTHERMS

A traditional beginning to activated carbon studies associated primarily with isotherms is the bottle-point technique. Described by Randtke and Snoeyink (1983), the bottle-point isotherm study entails varying concentrations of carbon in combination with constant adsorbate concentrations or keeping carbon at a constant concentration while varying the adsorbate levels. Contact between the adsorbate and adsorbent is facilitated by a jar containing a known volume of water. The bottle-point isotherm is typically performed for a time period of seven days allowing for equilibrium to be reached between pesticide residue and carbon (Miltner *et al.* 1989, Najm *et al.* 1990, Adham *et al.* 1991, Knappe *et al.* 1996, Knappe *et al.* 1998, Snoeyink and Summers 1999, Grady 2000).

During the research and designing stages of this project preliminary experiments were performed to establish background information and trends associated with reactions between varying doses of carbon and pesticides. Within this time, the activated carbon project was initiated with bottle-point isotherm experiments. The bottle-point isotherm was performed in triplicate and plotted as average percent removal including standard deviation.

MATERIALS AND METHODS

Raw water from the intake of E.M. Johnson Drinking Water Treatment Plant in Raleigh, North Carolina was fortified with a constant concentration of adsorbate (for the intents and purposes of this study the adsorbate refers to a specific pesticide or mixture of pesticides) and combined with varying concentrations of PAC in glass

amber jars. The experiment also included a jar without carbon to observe any loss from degradation. The jars were agitated for seven days to ensure adsorption equilibrium between the water and carbon phases. Analysis of the water to measure the adsorbate concentration remaining in solution indirectly indicated the amount of adsorbate that was sorbed to the carbon (adsorbent). Thereby, an adsorption curve was created that characterized the specific adsorbate and this particular type of carbon.

The more prevalent compounds detected in prior surface water environmental studies, atrazine, chlorpyrifos, metolachlor, and simazine were chosen for testing and combined to form a standard pesticide mixture. This mix was utilized in the preliminary carbon studies to determine the extent of adsorption.

Raw surface water was collected and filtered with 55 mm glass fiber (GF/B) filters (pore size 1.0 μm) (Whatman[®] International Ltd, Maidstone, England) to remove suspended organic particles. Transferred to a 950 mL amber glass jar, the ten jars each containing 900 mL of Raleigh raw water were assembled and PAC was added to each jar in varying amounts (0, 1, 3, 5, 10, 20, 25, 30, 40, and 50 mg/L). Glass beads were added as an additional mixing aid. The four pesticides were prepared at a concentration of 10 $\mu\text{g/L}$ for each compound and combined as a standard mixture. The jars were capped with a Teflon[®] lined lid and placed on a flat-bed shaker table. The bottles were left to agitate at 350 rpm for seven days.

After one week, the shaker table was stopped and a 200 mL aliquot was removed from each jar. All aliquots were then filtered with a 0.45 μm nylon membrane disk (47mm) (MSI Magna Nylon Disc Filters, Osmonics Inc., Minnetonka,

Minnesota) followed by C₁₈ Empore™ disk extraction (3M Corp., St. Paul, Minnesota). The extraction methods followed the procedures described by Mueller *et al.* (2000). The sample volumes were concentrated to 1.0 mL under a stream of dry nitrogen then transferred to a 2.0 mL GC vial for analysis.

The chosen form of chromatographic analysis required for concentrations of pesticides following adsorption by PAC was a Varian Star Model 3400 Gas Chromatograph equipped with a Model 8200 CX Autosampler and coupled with a nitrogen/phosphorous [Thermionic Specific Detector (TSD)] detector (Varian Inc., Walnut Creek, California). The 3.0 µL volumes of each sample and standard were injected onto a DB-35 fused silica column (30 m by 0.25 mm i.d.)(0.25 µm film)(J & W Scientific Inc., Folsom, California). The carrier (4.9 mL/min) and make-up (25.6 mL/min) gas was helium and detector gases were air (173.3 mL/min) and hydrogen (4.06 mL/min).

Samples with final volumes of 1.0 mL were placed on the autosampler and interspersed with the analytical standards (10 µg/L) at the start, between every five samples, and the last of the GC sample run (single level calibration). Temperatures were as follows: inlet, 175°C, detector, 300°C. The oven temperature program was as follows: initial, 160°C hold 2 minutes; to 170°C at 1°C/min, hold 2 minutes; to 280°C at 5°C /min, hold 2 minutes. Data were calculated via external standard method using peak area of standards (of known concentration) against sample peak areas. Retention times (RT) were as follows: atrazine (7.3 min), chlorpyrifos (11.5 min), metolachlor (11.2 min), and simazine (7.5 min).

RESULTS AND DISCUSSION

The bottle-point isotherm experiment revealed characteristic trends associated with the pesticides and PAC. In the first bottle-point isotherm the jars without carbon exhibited no loss in pesticide concentrations over the seven-day period. One hundred percent of the adsorbate concentration remained in the water following one week of shaking at room temperature. This was indicative of stability, lack of degradation and volatilization of pesticide mixture. A large reduction in residues was obtained with addition of 1 mg/L of carbon. Chlorpyrifos and metolachlor were reduced 85 and 46%, respectively. Atrazine residues decreased 44%, while simazine residues were reduced only 20%.

The percentage of pesticide mixture removal increased with 10 mg/L of carbon. Chlorpyrifos and metolachlor residues were reduced over 90%. Atrazine and simazine required 30 mg/L of PAC to achieve similar reductions while at this higher concentration chlorpyrifos and metolachlor were completely removed from solution. The maximum carbon dose of 50 mg/L was effective in decreasing chlorpyrifos and metolachlor 100% although residues of atrazine and simazine were reduced 97 and 96%, respectively.

In terms of regulatory values, only two of the compounds currently possess Maximum Contaminant Levels (MCLs). MCLs are the maximum legal concentrations of a contaminant allowed in finished, drinking water. Atrazine and simazine have MCLs of 3.0 and 4.0 $\mu\text{g/L}$, respectively while metolachlor and chlorpyrifos are not regulated in finished drinking water. A carbon dose of 10 mg/L was effective in greatly reducing chlorpyrifos and metolachlor residues and lowered

simazine levels below its MCL. However, 25 mg/L of carbon was required to lower atrazine residues from 10 µg/L to below 3 µg/L.

SUMMARY

Drinking water treatment plants will use PAC in concentrations ranging from 5 mg/L to 50 mg/L. This study utilized similar concentrations and resulted in adsorption of low level pesticide residues at all of the carbon levels. Most of the pesticide mixtures were removed from solution with a carbon concentration of 10 mg/L, which is a relatively low amount of PAC. The greater concentrations of carbon were effective in reducing the four pesticides and frequently the pesticide residues were completely removed from solution with the higher concentrations of PAC (e.g., 40 and 50 mg/L).

The results of the bottle-point isotherms indicated a greater potential for reduction in chlorpyrifos and metolachlor residues, especially at the lower carbon concentrations. Both of these compounds were effectively reduced with only 3 mg/L of PAC and completely removed from solution with the carbon concentration of 30 mg/L. Atrazine and simazine residues were relatively resistant to removal when compared to chlorpyrifos and metolachlor. The majority of atrazine residues were removed with 25 mg/L or greater concentrations of carbon while simazine residues were effectively reduced with 10 mg/L. Therefore, greater concentrations of carbon were required for atrazine and simazine to achieve similar removals that chlorpyrifos and metolachlor exhibited at relatively low PAC concentrations.

The cause of greater adsorptions exhibited with chlorpyrifos and metolachlor residues, when compared to atrazine and simazine, was unclear. Atrazine (2.75 log Kow) and simazine (1.96 log Kow) belong to the same class of compounds, the triazines, and are similar in structure; therefore, comparable adsorptions would be expected. Of the four pesticides, chlorpyrifos (4.96 log Kow) and metolachlor (3.45 log Kow) have slightly greater molecular weights and greater octanol:water coefficients. The greater log Kow values would drive the adsorption of chlorpyrifos and metolachlor and possibly the carbon preferentially adsorbs larger compounds due to pore sizes and distributions (Snoeyink and Summers 1999).

The pesticide residue reductions were performed with practical, commonly used concentrations of carbon; however, the removals exhibited were specific for this carbon. Other PACs might behave differently. Studies have been performed to compare the adsorption SOCs with various types of carbon. They found there were large differences in adsorptions among carbons with varying pore sizes, surface area and base materials (Najm et al. 1990, Najm et al. 1991, Afenya 1996, Campos et al. 2000). Moreover, the seven day time frame was unreasonable and impractical with respect to the laboratory and general treatment facility procedures. Ultimately, it was decided that research for this study would be restricted to a more empirical nature with hopes that results would provide viable guidelines for the treatment facility to follow.

CARBON CONTACT TIME STUDIES

Some studies have suggested that adequate contact time between activated carbon and contaminants is not provided in the time allotted for mixing within drinking water treatment plants. Adsorption kinetics can vary and the molecular size of carbon particles can influence diffusion rates and consequently require longer contact times to reach equilibrium with SOCs (Najm *et al.* 1991a). A 90-minute jar test was unsuccessful in providing ample time for alachlor and carbon to reach equilibrium (Miltner *et al.* 1989, Najm *et al.* 1991b). This study indicated that reaching equilibrium between pesticide and carbon in less than two hours was unlikely. Because this project was based on practical measures, the adsorption isotherm equations were not used in this project.

One objective of this study was to observe a relationship, other than classical adsorption isotherms, between the carbon and pesticides and reveal characteristic trends associated with adsorption and contact time. Additionally practical guidelines would be developed by identifying the shortest yet most effective contact times with carbon concentrations that reduce pesticide residues found in surface waters entering Burlington's treatment plant.

A model plant was chosen for this project in which current practices and procedures of drinking water treatment were considered when designing the activated carbon experiments. The J.D. Mackintosh Drinking Water Treatment Plant of Burlington has a treatment process with a running time of approximately eight hours (Randy Sefner 2000, personal communication). Therefore, a seven-day carbon contact time with water would be impossible within the existing parameters of

the model water treatment plant. As additional support for eliminating the seven-day bottle-point isotherms, the model plant is equipped to provide powdered activated carbon in the rapid mix basin. This basin is the point within the drinking water treatment plant that chemicals are added and water is agitated to thoroughly mix additives with water. Rapid-mix precedes the sedimentation, filtration, and disinfection steps in the treatment train. Addition of PAC in the rapid-mix basin decreases the maximum carbon contact time further and renders the seven-day time frame required in the bottle-point isotherm study impractical. Several studies were performed to determine temporal effects associated with carbon contact and specific classes of pesticides and concentrations of individual compounds and pesticide mixtures.

ONE-HOUR CARBON CONTACT TIME

The purpose of this study was to observe pesticide mixture concentrations over the course of a one-hour contact time with PAC in which samples were removed from solution every ten minutes for one hour. Most researchers agree that longer contact times yield greater carbon adsorptions and consequently improve removal of pesticides from solution. However, the author was interested in observing the reduction efficiency of PAC with minimal contact times by adsorption of the pesticide mixture. This was done to determine the lowest contact time that effectively removed sufficient levels of pesticide residues found at a typical water treatment plant in order to meet contaminant regulations.

MATERIAL AND METHODS

Water was donated by the Townsend Treatment Plant of Greensboro. A B-KER²™ (Phipps and Byrd, Richmond, Virginia) six-station mixer was used to stir the water, pesticide, and carbon solution for the requisite study time. The water (1800 mL) was fortified with the pesticide mixture to produce a concentration per pesticide of 2 µg/L. This concentration differed from earlier studies in that the initial pesticide was not 10 µg/L but the more environmentally relevant 2 µg/L. The adsorbate mixture was the same as before, with pesticides atrazine, chlorpyrifos, metolachlor, and simazine combined. A zero contact time sample was removed, before PAC addition, to measure the initial concentration of the pesticide residues and provided a background concentration to compare the solution prior to and after carbon addition. PAC was then added to yield a 2 mg/L concentration of carbon (WPX-Z, Calgon Carbon Corp., Pittsburgh, Pennsylvania).

The solution was stirred for one hour at 100 rpm. Aliquots of 200 mL were removed every ten minutes and passed through 55 mm glass fiber filters to remove organic matter and carbon. Seven samples, including the zero time point (0, 10, 20, 30, 40, 50, and 60 minute samples) were filtered and extracted as previously described; concentrated by a stream of nitrogen to a final volume of 1.0 mL and analyzed as before with GC/NPD. The temperature program, quantification of data, and retention times remained the same as before.

RESULTS AND DISCUSSION

The results of the one-hour contact time study indicated characteristics specific to each compound of the pesticide mixture (Fig. 2). Contact with carbon for 10 minutes was effective in reducing atrazine and simazine residues by approximately 50%, while chlorpyrifos and metolachlor were only reduced 7 and 3%, respectively. As stirring continued the removals of all four pesticides progressively increased albeit at varying rates.

Atrazine and simazine levels were greatly reduced within the first ten minutes and exhibited a slow decline for the remaining fifty minutes of contact time. Upon completion of mixing, 26% of the original 2 µg/L of atrazine remained in solution along with less than 0.1% of simazine. A relatively low concentration of carbon (2 mg/L) was successful in reducing the 2 µg/L concentration of triazine compounds to extremely low levels (simazine 0.21 µg/L; atrazine 1.3 µg/L).

In contrast, chlorpyrifos and metolachlor were only slightly reduced in the samples at 10, 20, and 30 minutes. At a contact time of forty minutes chlorpyrifos was reduced 17% and metolachlor only 12%. A maximum contact time of sixty minutes resulted in 26% of chlorpyrifos and 25% of metolachlor being reduced. PAC adsorption upon conclusion of the study was responsible for removals of 25% of these two compounds.

In terms of regulatory values within this study, the initial concentrations of the adsorbates were 2 µg/L, below all MCLs associated with the pesticides of the mixture. Therefore, no federal standards were exceeded in this experiment and all reductions yielded concentrations well below regulatory values.

SUMMARY

Contact times from 10 minutes to 1 hour produced variable reductions of residue concentrations. Atrazine and simazine were greatly reduced with minimal contact with PAC. Of the four pesticides studied, concentrations of simazine were reduced most significantly, and almost none of the compound remained after 60 minutes. Chlorpyrifos and metolachlor were the least successfully adsorbed. A sixty minute contact time with PAC was effective in adsorbing ca. 25% of these two compounds.

These results appeared contrary to the removals observed in the prior experiment of the seven-day isotherm. In the earlier experiment chlorpyrifos and metolachlor were greatly adsorbed with lower concentrations of carbon while atrazine and simazine seemed to require greater PAC levels for equitable removals. A carbon concentration of 1 mg/L was effective in adsorbing the majority of both chlorpyrifos and metolachlor in the previous study and the 2 mg/L of this study was successful in only removing 25% of each compound. The only variation between experiments was contact time, 168 hours (seven days) versus one hour. Possibly chlorpyrifos and metolachlor require contact times greater than one hour to achieve appreciable reductions. As mentioned before the seven-day contact time cannot be done in a water treatment plant because of time constraints. The structures of metolachlor and chlorpyrifos might have proved unfavorable for adsorption in the brief contact time. Further characterization of contact time and PAC adsorption of the mixture compounds was required.

The pesticide mixture concentration selected for this experiment was 2 µg/L; a relatively low level compared to the numerous pesticide studies existing in the literature. This lower concentration was chosen to represent the frequently minimal contaminant concentrations detected in drinking water supplies. In performing the study with a small amount of pesticide residues, the author hoped to determine the adsorption of realistic North Carolina environmental contaminant concentrations and not the elevated, infrequently detected values of pesticide residues commonly utilized in adsorption studies.

TWO-HOUR CARBON CONTACT TIME

Examination of the results of the one-hour study and bottle-point isotherms prompted some modifications for the next study. Primarily, chlorpyrifos and metolachlor seemed to require more contact time to achieved equitable removals to atrazine and simazine. A two-hour contact time was chosen to expand the potential for adsorption and subsequently lead to a greater characterization of the pesticides and PAC relationship. By retaining all of the other variables at constant values and changing only the contact times it was possible to examine the relationship between adsorbate and adsorbent.

MATERIALS AND METHODS

Flash-mix water was used at a volume of 1800 mL fortified with the pesticide mixture of earlier studies for an overall concentration of 2 µg/L. An initial 200 mL sample was removed to represent the pre-carbon, pesticide concentrations. A PAC

concentration of 2 mg/L was added to the spiked water solution in the six-station mixer and stirred for 2 hours at 100 rpm. Samples (200 mL) were removed every twenty minutes for two hours producing seven samples (0, 20, 40, 60, 80, 100, and 120 minute samples). These samples were processed as previously described.

RESULTS AND DISCUSSION

The results of the two-hour contact time (Fig. 3) showed a reduction in concentration similar to the one-hour study. Atrazine and simazine were lowered approximately 50% following contact with PAC for 20 minutes and residue levels progressively declined over the next two hours to relatively low concentrations. Approximately 73% of the atrazine was removed after 80 minutes of contact with PAC and upon completion of the study 89% was removed. After 60 minutes 97% of the simazine was removed and 99% was removed after 100 minutes of carbon contact.

Over 90% of chlorpyrifos and metolachlor continued to remain in solution after 20 minutes of mixing with carbon, and 100 minutes of PAC contact were required to reduce both pesticide residue levels 50%. Following exposure to carbon for 120 minutes, residues of chlorpyrifos and metolachlor were reduced by 62 and 60%, respectively.

SUMMARY

Adsorption of the pesticide mixture varied as before between the individual compounds with atrazine and simazine experiencing greater removals while

chlorpyrifos and metolachlor exhibited only slight reductions. The half-time point of this study was effective in significantly reducing simazine levels and lowering atrazine almost 60% of its initial concentration. Ninety-nine percent of simazine residues were adsorbed within 80 minutes of PAC contact and a concentration of 0.5 µg/L of atrazine remained at this time.

Chlorpyrifos and metolachlor were less adsorbed than the other two compounds of the mixture and approximately 0.8 µg/L of the original 2 µg/L concentrations of metolachlor and chlorpyrifos remained in solution following a carbon contact of 2 hours. The reductions exhibited by chlorpyrifos and metolachlor in this study were greater in comparison to the one-hour study. The pesticides were reduced over 40% more with 2 hours of contact with PAC than in 1 hour study.

As proposed earlier, it seemed as if chlorpyrifos and metolachlor required longer contact times. All pesticides within the mixture were removed to a greater extent in this study with longer contact times, thereby supporting the common thought that the longer the contact time the greater the absorption by PAC.

The concentration of carbon used in these studies has been 2 mg/L which is relatively low. It is possible that the longer contact time requirement might be ameliorated by an increase in carbon concentration. Elevating the level of carbon present in solution would provide more adsorption sites and subsequently would increase the potential for greater contaminant removal.

ATRAZINE AND METOLACHLOR STUDY

The preliminary studies showed that powdered activated carbon can to some extent adsorb each of the compounds within the pesticide mixture, although there was variability among the individual contaminants. The next experiment was designed to utilize the results of previous studies while continuing to characterize the relationship between these compounds and the carbon.

Attention was directed to two compounds of particular interest, atrazine and metolachlor. Residues of both pesticides were detected repeatedly in earlier surface water studies and these compounds remain two of the prominent pesticides used in North Carolina in both urban and rural areas (Holman and Leidy 1998, Holman and Leidy 2000, Leidy *et al.* 2001, Jones *et al.* 2002). Their continued presence emphasizes the likelihood that atrazine and metolachlor are potential drinking water contaminants.

Considering that one of the primary objectives of this study was to develop guidelines for the model drinking water treatment plant, raw water was collected from Burlington's J.D. Mackintosh Treatment Facilities and used in the following experiments. The experimental design was modeled after the treatment facility's procedures and its use of treatment chemicals other than carbon led to the introduction of a supplementary process involving aluminum sulfate (alum).

Generally, PAC is added in the rapid-mix basin and frequently, another chemical known as aluminum sulfate is also added. Alum acts as a coagulant to aid in the removal of organic matter from water. Through incorporation of organic matter particles floc is created, these particles bind to other particles to form flocculant that

settles to the bottom of the basin. The settled material is then removed by a mechanical rake. Remaining floc that does not settle is usually retained during the next step of treatment, filtration.

Alum has been employed for many years and multiple notions describe the interaction and relationship to activated carbon adsorption. When alum is used as a pretreatment, it can remove organic carbon from solution and increase carbon adsorption efficiency by removing the “weakly adsorbing high-molecular-weight fraction” of the organic components in solution (Semmens *et al.* 1986). Reduction of this natural organic matter that can interfere with adsorption kinetics increases the efficiency of carbon adsorption for the lower-molecular-weight organic compounds (Randtke and Jepsen 1981, Semmens *et al.* 1986).

The addition of PAC only could lead to adsorption of the organic matter removed by alum and block adsorption sites required for adequate removal of synthetic organic compounds (SOC). On the other hand, Knappe *et al.* (1996) reported that coagulation by alum that removes the high molecular weight natural organic matter might not provide the best pretreatment for carbon. This was based on a recent report that the remaining lower molecular weight compounds exhibit a greater effect on activated carbon adsorption capacity than do high molecular weight compounds. More importantly, it has been suggested that when both alum and carbon are added within a short period, residue adsorption is dampened (D Knappe 2002, personal communication).

There are two explanations for this interference. One notion being that carbon is swept up with the coagulating floc particles and consequently trapped

within the particle surrounded by natural organic matter (NOM) and alum. The “trapped” PAC would be less available to sorb the SOCs (pesticides). Another explanation involves carbon adhering to the outer surface of the flocculating particles slightly blocking some adsorption sites while remaining mostly available for contaminant adsorption and removal from solution (Najm *et al.* 1990, Najm *et al.* 1991a, D Knappe 2002, personal communication). The best methods for chemical addition involving alum and carbon remain unclear.

Thus, the atrazine and metolachlor study was designed to determine effects of alum on the carbon’s ability to adsorb the pesticide residues. Three studies were performed on each pesticide in which carbon alone, carbon and alum together, or alum alone was added to the fortified solution to discern any inhibitory effects.

MATERIALS AND METHODS

Raw water was collected and sent from J.D. Mackintosh Drinking Water Treatment Plant in Burlington and stored in amber glass bottles (4 L). The procedure performed in triplicate began with a 200 mL sample taken prior to the start of each procedure. This was filtered, extracted, and analyzed with the other samples to provide a background concentration and determine potential environmental residues of atrazine and metolachlor.

The first study added atrazine to 1500 mL of raw water at a concentration of 10 µg/L which was stirred for 1 hour with a magnetic stirrer to ensure uniform mixing. A 200 mL sample was taken to represent the zero carbon contact time. The fortified water was transferred to the B-KER²™ stirrer, and 10 mg/L of carbon (WPX-Z PAC,

Calgon Carbon Corp., Pittsburgh, Pennsylvania) slurry was added in 20 mL of deionized water. The solution was stirred rapidly (100 rpm) for one minute to account for the rapid-mix stage of the treatment plant then the mixing speed was lowered to 20 rpm. The stirrer was programmed to operate for 2 hours and paused every 30 minutes (for 0.5 minutes) for an aliquot of 200 mL to be removed. The samples were passed through a GF/B filter (Whatman[®] International Ltd., Maidstone, England) then extracted with an Empore[™] Disk (3M Corp., St. Paul, Minnesota). This process was repeated three more times totaling 2 hours of PAC contact time to yield five samples (0, 30, 60, 90, and 120 minute contact times).

Study Two repeated Study One with the exception of alum addition immediately following carbon addition. Raw water was fortified with 10.0 µg/L of atrazine one hour prior to beginning this method. A zero PAC contact time sample was removed; then the water was transferred to the six-station stirrer. The 10.0 mg/L carbon slurry and 20.0 mg/L alum were added to the solution and the mixture was stirred at 100 rpm for 1 minute then 20 rpm for 2 hours. Samples were removed as before.

Study Three involved the effects of alum added alone. Fifteen hundred milliliters of atrazine-fortified raw water (10 µg/L) were transferred to the stirrer and an alum concentration of 20 mg/L of was added. The mixture was stirred for 1 minute at 100 rpm then stirring speed was lowered to 20 rpm for 2 hours. GC/NPD parameters remained the same with the exception of retention times (atrazine, 9.1 min, metolachlor, 15.4 min).

The next portion of this study involved the same methods described above; however, metolachlor was used to fortify the raw water instead of atrazine. The metolachlor standard was prepared (10 µg/L) and added 1 hour prior to the start of the procedure to ensure uniform mixing between the water and pesticide. All of these methods were performed in triplicate (resulting in 45 samples per pesticide) and plotted as an average including standard deviation. and. All results were subjected to statistical analyses with analysis of variance (ANOVA) and paired t-test for the varying carbon contact times (SAS, Cary, North Carolina). Additional paired t-tests were performed to compare the three methods.

All materials were similar to earlier studies with the exception of the carbon slurry addition; PAC was dissolved in a small amount of deionized water (20 mL). This allowed an easier and faster transfer from beaker to solution jar. The alum was provided by the model treatment plant in a concentrated solution and according to plant procedures, a 20 mg/L solution of alum was prepared just prior to starting the procedure. The intermediate alum solution was viable for 24 hours and therefore was generated daily (Tom Murr 2001, personal communication).

Procedures of filtration and extraction were performed as described in earlier sections with the addition of 3 mL of methanol to water sample just prior to extraction. Secondary studies had shown improved recoveries with the addition of methanol as a result of the solvent maintaining the “wetness” of the C₁₈-coated Teflon[®] fiber of the extraction disk during filtration.

The results of atrazine and metolachlor in combination with carbon, carbon and alum, or alum were reported as percent of pesticide remaining in solution. This

is an indirect calculation of the amount of the pesticide adsorbed by the PAC. The values reported were an average of three data points.

RESULTS AND DISCUSSION

Atrazine with carbon and alum: Water containing 10 µg/L of atrazine was combined with 10 mg/L of PAC for two hours. Following 30 minutes of contact with carbon, levels of atrazine were reduced by 35% to 7.7 µg/L. The amount of atrazine present in solution for the remainder of the experiment was lower than the first detection but varied little. Approximately 60% was removed from solution in 60, 90, and 120 minutes.

The MCL of atrazine is 3.0 µg/L and drinking water treatment plants use this value to regulate atrazine levels, maintaining or reducing surface water concentrations of atrazine residues below this standard. In this study the initial concentration of atrazine was 10 µg/L and a contact time of 2 hours was unsuccessful in reducing this concentration below 3.0 µg/L.

Carbon (10 mg/L) and alum (20 mg/L) added together and mixed with atrazine fortified raw water showed declines in pesticide concentration over the 2 hours of the experiment. The first sample (30 min. contact time with carbon and alum) showed a 36% reduction of its initial concentration. Levels of atrazine dropped as the contact time with the chemicals increased and 50% of pesticide residue was removed from solution after 90 minutes. After 2 hours of contact the concentrations were reduced to 38%.

The initial concentration of atrazine in the experiment with carbon and alum was 10 µg/L and this value was reduced with increasing contact with the chemicals. However, the reduction did not fall below the MCL. After 2 hours of contact the amount of atrazine remaining in solution was above its MCL of 3.0 µg/L.

Raw water containing atrazine was combined with alum alone to determine if alum, like carbon, could reduce the concentration of pesticide remaining in solution. Atrazine concentrations detected in the water fluctuated slightly although reductions in concentration were not detectable. After 2 hours of contact with alum the pesticide was not reduced and 100% of the initial concentration remained in solution.

Atrazine was present at an initial concentration of 10 µg/L and in contact with alum for 0 to 120 minutes. Apparently, this was not a sufficient amount of time to reduce this concentration below its MCL of 3.0 µg/L. Thus, alum did not appear to reduce the atrazine residues to any degree.

Summary: The three procedures involved carbon and alum additions, alone or in combination, to water solutions fortified with atrazine to determine carbon adsorption effects. Differences in pesticide residue removals were demonstrated with the increasing chemical contact times. Statistical analyses of the carbon only and carbon with alum chemical addition procedures revealed significant differences between the zero-minute chemical contact and thirty-minute contact. Although, contact times of sixty minutes and greater resulted in pesticide residue concentrations significantly different from the zero time point, the variation between the other chemical contact times was not considered statistically different. The alum

alone procedure exhibited no reduction and therefore no statistically significant differences for any of the chemical contact times.

For carbon treatment alone, atrazine, at a concentration of 10 µg/L, was removed from solution to below its MCL of 3.0 µg/L. The reductions exhibited by the experiment in which both carbon and alum were added increased as the contact time increased. However, the pesticide removal in the study with carbon and alum seemed to proceed slower than the study without alum. The final results of the experiments involving carbon and carbon with alum were similar with only a 2% difference; however, this was at the completion time of 2 hours. Carbon alone produced a more effective adsorption than carbon and alum together.

The alum alone had no effect on atrazine concentration, and no reductions were observed following the 2-hour contact time. Carbon appears to be the most efficient in reducing atrazine levels based upon the concentration remaining in solution (Fig. 4). The carbon method was statistically more effective than alum at all carbon contact points (30, 60, 90, 120 minutes). The method involving both carbon and alum was also effective in reducing the atrazine concentrations but the alum might have been hindering carbon's ability to adsorb the pesticide. In comparing the three methods, statistical analyses revealed significant differences between the alum alone procedure and the others, carbon alone and the carbon/alum mixture. There was not statistical difference between the carbon and carbon/alum methods at any of the sample time points.

The results shown supported the belief that alum introduced interference in adsorption when paired with carbon. Alum alone resulted in no reduction in

pesticide concentration and reinforces the speculation that alum does not possess an immediate or strong ability to reduce or control chemical residues in drinking water supplies. The addition of these two treatment chemicals at the same time appeared to reduce the adsorption efficiency of PAC. While the carbon and carbon/alum methods were statistically similar an early time point (60 min.) exhibited some discrepancy between the two methods. This variation was not evident at 120 minutes. It is possible that alum interfered with the carbon's adsorption of atrazine briefly but was ameliorated after two hours of contact with the PAC.

Metolachlor with carbon and alum: Raw water fortified with 10 µg/L of metolachlor was combined with 10 mg/L of carbon for 2 hours. Following 30 minutes of contact time the metolachlor residues were reduced 53% to 5.5 µg/L. The longer contact times did not greatly enhance further removal of remaining pesticide; the final concentration of metolachlor that remained in solution was under 3.0 µg/L. This was a reduction from the initial concentration.

The herbicide metolachlor does not currently have an assigned MCL and no regulatory values exist that directly relate to mandated drinking water treatment values. The HAL, which is not regulated by law but used for guidance is set at 70.0 µg/L. This value far exceeded any standard concentrations used here in this study or found in North Carolina surface waters sampled over the past 7 years. Therefore, levels of metolachlor remaining in solution were acceptable with regard to drinking water.

Carbon and alum treatment resulted in reductions in the concentration of the pesticide following mixing with carbon and alum. After 1 hour, 81% of metolachlor

residues remained in solution. Reductions in concentration increased with longer contact times and 90 minutes was a sufficient amount of time for the carbon/alum combination to adsorb 49% of the metolachlor. Two hours of contact between the pesticide and treatment chemicals were adequate to reduce the original concentration of metolachlor by 65%. The levels dropped almost 5 µg/L after 90 minutes of stirring and the final concentration after 2 hours of contact was below 4 µg/L.

The third experiment involved the addition of alum to raw water fortified with metolachlor (10 µg/L) and stirred for 2 hours. There were some declines in contaminant with the addition of alum alone. A 10% reduction occurred after 30 minutes with the alum and this drop continued with the increase in contact time. Two hours of contact time was sufficient at removing some 19% of the pesticide residue with a final concentration of ca. 8 µg/L detected in the water.

Summary: The addition of alum alone, carbon and alum together, and carbon alone in three procedures with a water solution fortified with metolachlor exhibited varying adsorptions with increasing chemical contact time. There were significant differences following the first 30 minutes of chemical contact time for the carbon alone and carbon/alum combined experiments. The alum experiment exhibited some reduction in pesticide residues following 30 minutes of contact but was not considered significantly different. The remaining contact times exhibited declines in pesticide residues remaining in solution for all three experiments; however, these were not significantly different from each other.

Metolachlor levels were effectively reduced with the addition of carbon and an adequate mixing time. The longer contact times led to a greater degree of adsorption. A large percentage of metolachlor was removed at the end of the 2 hour experiment, although the majority of this reduction occurred in the first 30 minutes of contact with the carbon.

Alum and carbon together also reduced metolachlor residues to a similar extent as the carbon alone. The final percentages of residues remaining in solution after 2 hours of contact time with carbon/alum and carbon alone were 35 and 32%, respectively. The variation in reduction of pesticide levels between carbon alone versus carbon/alum was encountered in the second sample representing the 30 minute contact time. The single addition of carbon was able to adsorb 53% in 30 minutes while carbon in combination with alum reduced metolachlor residues only 30%. When 90 minutes of contact time passed the percentage of pesticide removed from solution was equal for both methods.

Alum alone reduced metolachlor concentrations a maximum of 20%. Review of the literature and previous studies indicated alum has very little capability for adsorption; it was possible a portion of the metolachlor residue adsorbed to flocculant particles and later settled out of solution onto the bottom of the mixing jar. Pesticide residues adsorbed to coagulated organic matter and flocculant particles would be retained by the filtration step and removed from the solution prior to pesticide extraction.

A comparison of the three experiments provided a representation of the adsorption abilities of the treatment chemicals (Fig. 5). Carbon was the most

effective in adsorbing metolachlor and removing the pesticide residues from the raw water. Carbon and alum together also reduced the contaminant levels although the contact time required for equitable removals was longer, and alum was the least effective in lowering the metolachlor concentration. Statistical analyses of the three methods verified these results in a comparison of the three methods in which the alum experiment was statistically the overall least effective method of the three experiments. Comparisons at each 30 and 120 minutes of contact saw the alum method varying significantly from the other methods, while carbon and carbon/alum mixture experiments were statistically similar in reductions of pesticide residues.

COMPARISONS OF PESTICIDES AND METHODS

The effects the three treatment methods had upon both atrazine and metolachlor appeared to be similar when observing the individual pesticides and the extent of adsorption upon the addition and mixing with carbon and alum. To closer examine the pesticides, the results of each method were grouped to compare atrazine and metolachlor for each individual method.

Carbon addition achieved the greatest reductions in pesticide concentrations of the three methods. Within the first 30 minutes both compounds were reduced over 35%, but metolachlor was adsorbed to a greater extent than atrazine with an 18% difference in the pesticide remaining in solution. The longer contact times exhibited reductions of comparable levels between compounds, and metolachlor was removed by 68% (8% more than atrazine) after 2 hours of contact time.

Alum paired with carbon was the second method and the more effective of the latter two treatment options. Reductions of atrazine and metolachlor residues were not as great with carbon and alum combined as with carbon alone, but a decline in pesticide concentrations was observed. While alum does appear to have an initial inhibitory effect on the carbon's ability to adsorb the pesticide residues, 2 hours of contact time appeared sufficient to reduce the inhibition. Reductions over the first hour of contact showed that atrazine was reduced to a greater degree than metolachlor at the 60 minute time point with 40% of atrazine removed compared to only 20% for metolachlor. However, upon completion of the experiment a slightly higher percentage of metolachlor was removed from solution when compared to atrazine.

The pesticides experienced minimal differences in water only containing alum. While atrazine exhibited no reduction in concentration, residues of metolachlor declined slightly when exposed to the alum. A 20% removal of metolachlor was achieved after 2 hours of contact with alum, although atrazine was not affected and 100% of the initial concentration was detected in solution upon completion of the experiment.

SUMMARY

The atrazine and metolachlor 2 hour study involved three methods of treatment to determine the most efficient method of removal with two different traditional drinking water treatment chemicals. Carbon or alum alone and carbon and alum together when mixed with pesticide fortified raw surface water produced

various results that further explained the relationships between carbon, alum, and pesticide residues.

Upon review of the results, carbon was the most effective treatment method. The studies involving carbon alone were adequate in reducing the contaminant levels below existing regulatory values. The largest relative reductions in pesticide concentrations were observed within the first 30 minutes, and levels only declined as the contact time increased.

Alum, when added simultaneously with the carbon, slowed the adsorption compared to water containing only carbon. Reductions in pesticide concentration occurred, but were not analogous to the adsorption exhibited by carbon alone. However, the 2 hour contact time appeared adequate in reducing this adsorption effect with equivalent percentages of pesticides remaining in solution at this later time.

It seemed as if the alum had a dampened effect on the carbon adsorption, initially accounting for the delayed effect seen in the first hour of contact. However, continuous mixing and extended contact time reduced this inhibitory effect, most likely due to the extensive surface area and potential for adsorption possessed by PAC.

Aside from probable trapping of the pesticide residues within flocculating particles it seemed unlikely that alum asserted any adsorption effect that was adequate in reducing pesticide residues to drinking water standards. While alum does possess the ability to aid in removing NOM from drinking water supplies (an important and necessary process) the addition of alum with PAC appeared to reduce

the ability of carbon to efficiently adsorb contaminant residues at shorter contact times.

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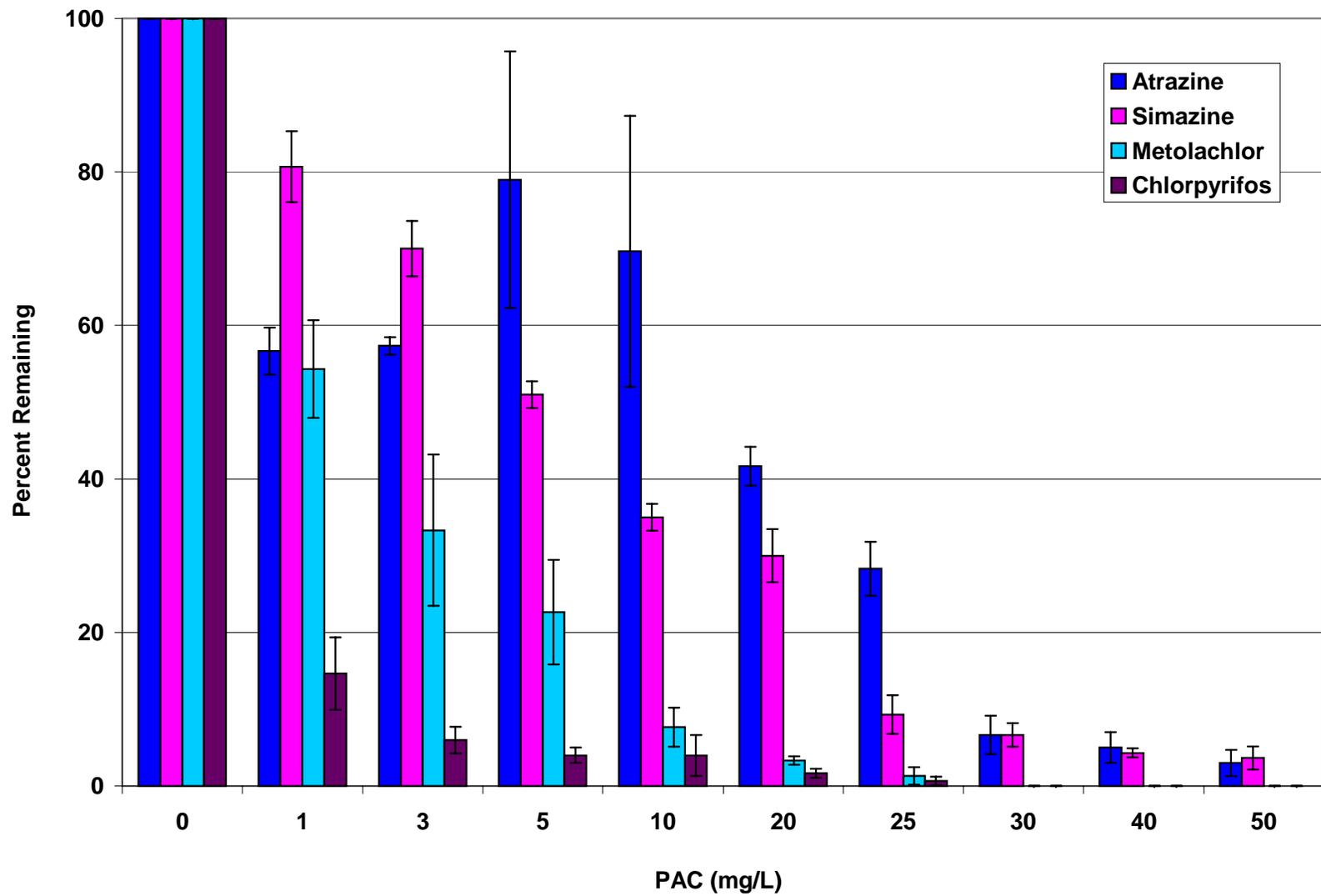


Figure 1. Bottle-Point Isotherm (1) showing reductions of atrazine, chlorpyrifos, metolachlor, and simazine residues with increasing concentrations of PAC.

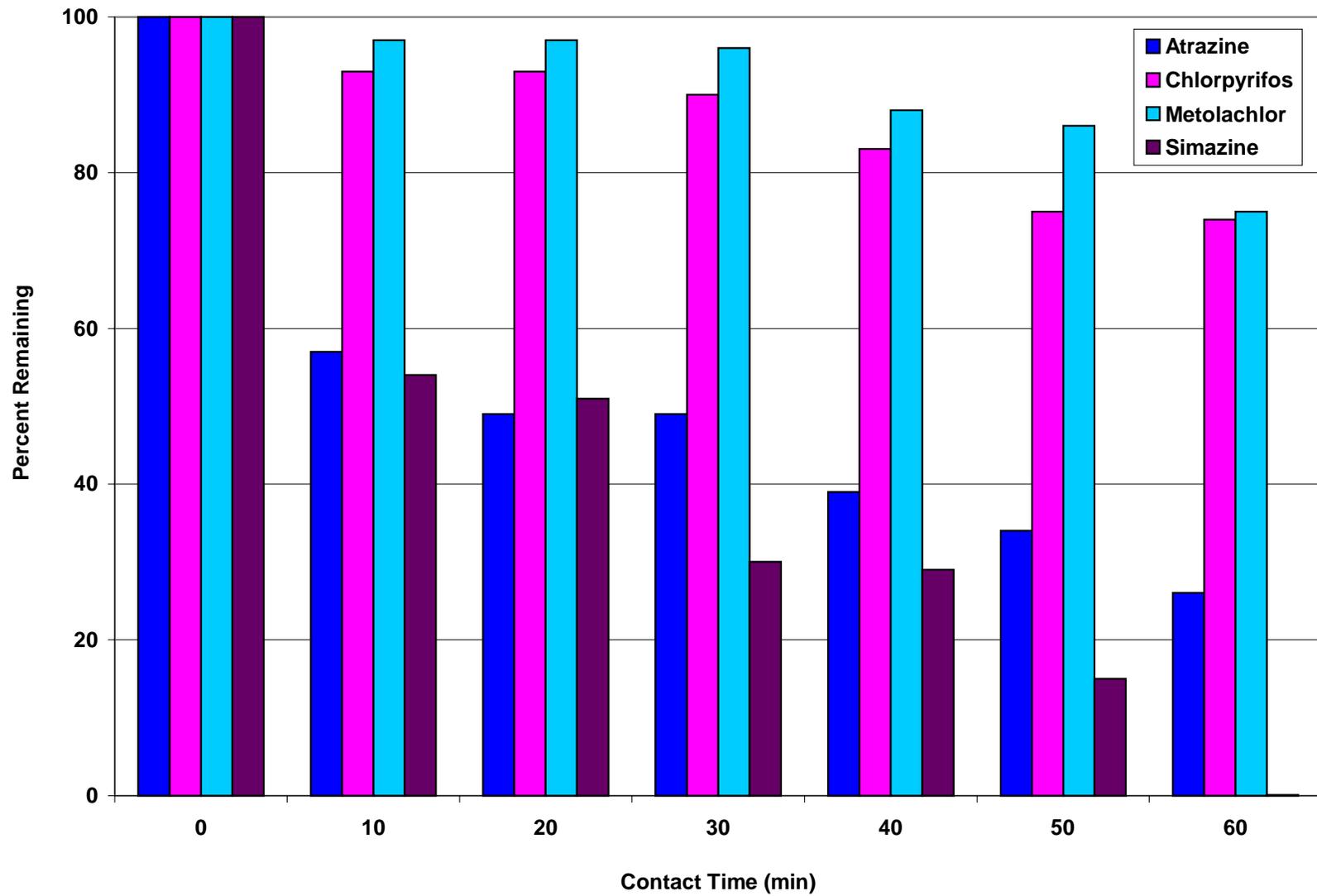


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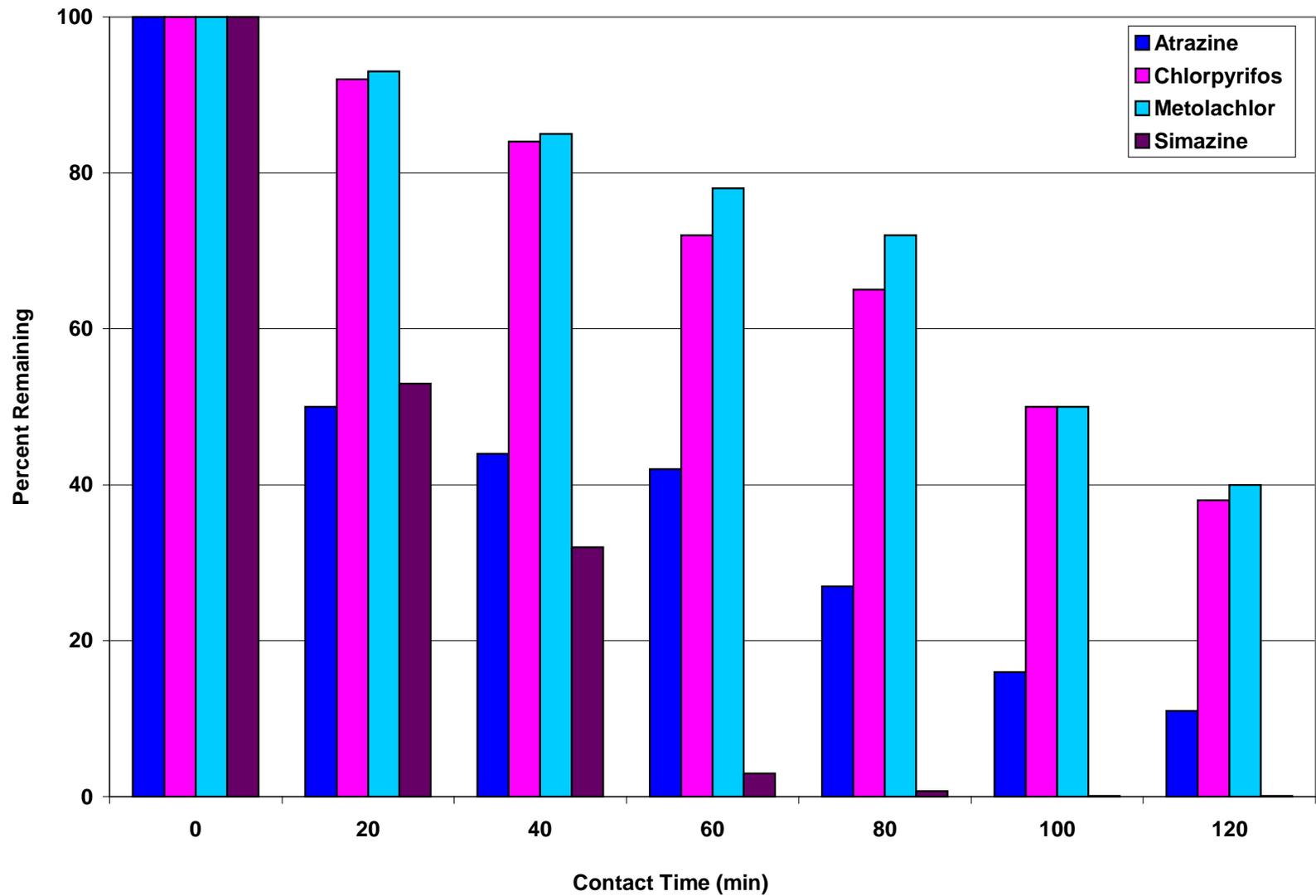


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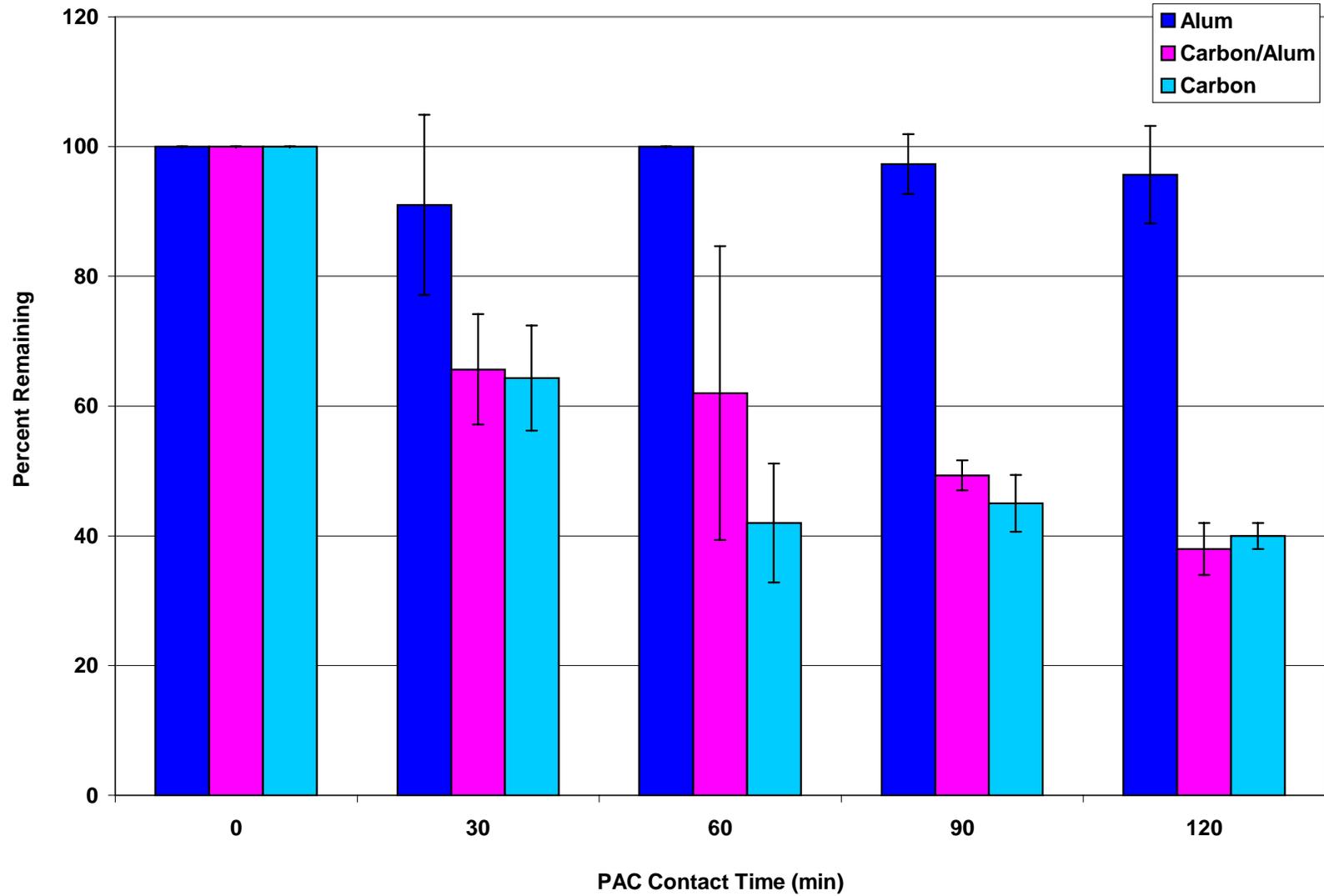


Figure 4. Reductions of atrazine residues in increments of 30 minutes for a total chemical contact time of 2 hours for the three methods of chemical addition: carbon alone, carbon/alum combined, and alum alone.

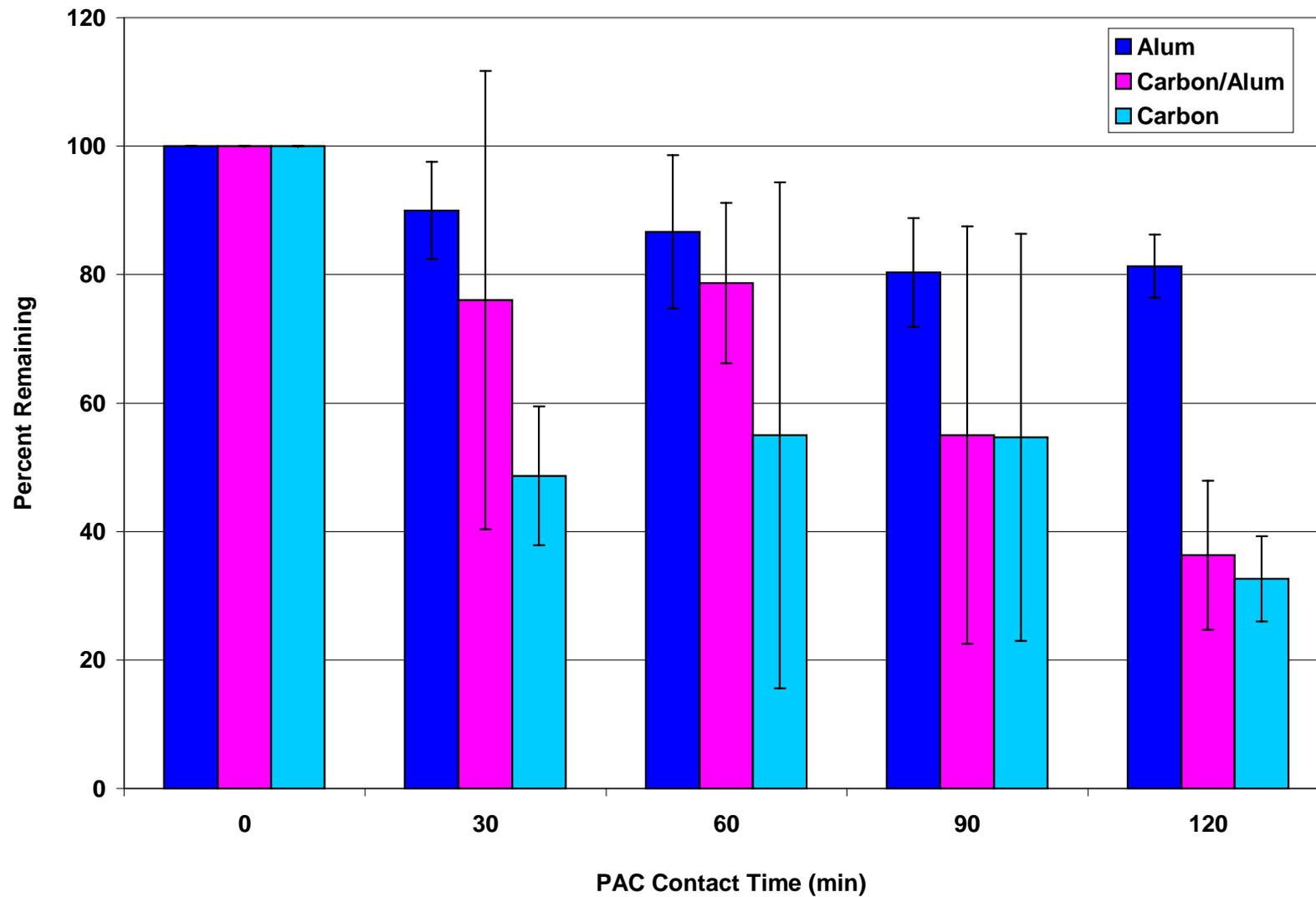


Figure 5. Reductions of metolachlor residues in increments of 30 minutes for a total chemical contact time of 2 hours for the three methods of chemical addition: carbon alone, carbon/alum combined, and alum alone.

CHAPTER SIX

THE EFFICACY OF POWDERED ACTIVATED CARBON IN REDUCING PESTICIDE RESIDUES IN A BENCH-SCALE TREATMENT PLANT STUDY

INTRODUCTION

The design of this study was influenced by preliminary studies (Chapter 5) performed by the author. Carbon use in one and two hour contact time experiments was effective in reducing pesticide concentrations. An earlier study compared treatment methods of carbon and alum and was similar to the procedures in drinking water treatment facilities. Within the treatment plant, PAC is added as a slurry in the rapid-mix basin, resulting in a maximum contact time of 30 minutes. Given that the ultimate goal of the carbon study was to develop carbon addition procedures to be used as a guideline for the J.D Mackintosh Drinking Water Treatment Plant in Burlington, the next study necessitated amendments to meet their operating requirements.

The addition of alum with the carbon resulted in pesticide removal at a slower rate than the carbon alone. The experiments without alum were most effective in removing residues of pesticides; however, treatment facilities utilize alum on a regular basis to improve taste. Considering that alum is used as part of the standard operating procedures within the model plant any future experiments with carbon should include the addition of alum.

The design of this study included all of these factors and attempted to simulate the procedures undertaken in the model treatment plant on a bench-scale. Given that both carbon and alum are used as treatment chemicals prior to filtration and disinfection, this set-up involved the portion of the treatment train that incorporated the intake, rapid-mix basin, and sedimentation basin.

The pesticides frequently detected in surface water and drinking water supplies of this watershed and near the drinking water treatment plant intake were used as the standard compounds for this study. Atrazine, alachlor, metolachlor, and simazine are four herbicides belonging to two classes of compounds, the triazines (atrazine, simazine) and chloroacetanilides (alachlor, metolachlor). This grouping of compounds allowed for comparison of carbon adsorption between as well as within classes. The individual compounds and a standard mixture of these four pesticides were used as the adsorbates in this study.

EXPERIMENTAL DESIGN

The experimental set-up was developed to encompass potential treatment methods used within the model drinking water treatment plant. Three procedures were designed to characterize carbon and alum interactions by the extent of pesticide adsorption; measured indirectly by the removal of compounds from solution with varying concentrations of PAC. The results of procedures were analyzed statistically using ANOVA and paired t-tests (SAS, Cary, North Carolina) for overall differences and using paired t-test to compare procedures at each PAC concentration.

A BKER²™ (Phipps and Byrd, Richmond, Virginia) six-station stirrer was used to model the process. Time intervals of various stirring speeds were programmed into the jar-test mixer to simulate treatment plant stations with chemical additions at the plant's intake and rapid-mix basin and also the succeeding sedimentation basin.

Najm *et al.* (1991) described various points within the treatment plant in which carbon could be added and the positive and negative aspects of these particular inputs. Viable options include addition at the intake, rapid-mix basin, and a slurry contactor installed prior to rapid mix. The addition of equipment such as a slurry contactor fell outside the realm of this study; therefore, the other input points were modeled.

Intake addition of carbon would provide for longer contact times and adequate mixing but interference from NOM normally removed with coagulation might block adsorption sites of the carbon. The rapid mix basin addition of carbon allows ample mixing and contact time but potential chemical interactions could hinder carbon adsorption. With this and suggestions from others (D Knappe 2002, personal communication) three procedures were designed to observe interaction and adsorption as a result of varied carbon additions within a drinking water treatment facility.

PROCEDURE ONE

The first method involved adding carbon at the intake and allowed for a longer contact time between the contaminants in the water and the PAC. Alum was added later in the rapid-mix basin where mixing of both carbon and alum occurred, followed by sedimentation. The point at which the pesticide concentration in solution was measured was immediately after sedimentation, just prior to filtration at the filter bed.

Based upon established theories (Randtke and Jepsen 1981, Semmens *et al.* 1986, Najm *et al.* 1990, Najm *et al.* 1991, Knappe *et al.* 1996, D Knappe 2001,

personal communication) and previous experimental results, the extra contact time between PAC and pesticide in the water prior to the addition of alum would allow for a greater degree of adsorption without interference from the alum. Once alum is introduced the carbon might become trapped within the flocculant particles and settle out of solution; aiding in carbon removal but possibly increasing inhibition of carbon adsorption. The increased contact time as a result of early carbon addition could possibly negate any inhibition from the alum.

MATERIALS AND METHODS

Raw surface water was collected by a J.D. Mackintosh Drinking Water Treatment Plant employee and transported to the NCSU Environmental and Molecular Toxicology Pesticide Residue Laboratory. The raw Burlington water was not filtered prior to the beginning of the study to more closely replicate the procedures undertaken in the treatment plant. A 200 mL sample of water was filtered (GF/B 55 mm glass fiber filter, Whatman[®] International Ltd., Maidstone, England) (pore size 1.0 μm) and extracted (C₁₈ Empore[™] extraction disk, 3M Corp., St. Paul, Minnesota) to determine if typical background concentrations of the study pesticides were present. Temperature and pH of the water was monitored in order to sustain similar conditions to the model treatment plant.

A 1200 mL volume of raw water was transferred to the jars of the Phipps and Byrd stirrer and fortified with 10 $\mu\text{g/L}$ of atrazine (in acetone), stirring for 1 minute at 100 rpm to ensure uniform mixing. Two hundred milliliters of this were removed to measure the initial pesticide concentration. The PAC (WPX-Z, Calgon Carbon

Corp., Pittsburgh, Pennsylvania) used was provided by the treatment plant and prepared as a slurry with 20 mL of deionized water to facilitate a greater degree of mixing. Carbon was added to the remaining 1000 mL of water and stirred for 10 minutes at 100 rpm to mimic the intake pipe of the water treatment plant. The carbon dose varied in concentration from 5 to 50 mg/L to yield six different concentrations of carbon (5, 10, 20, 30, 40, and 50 mg/L).

After 10 minutes of contact with the PAC, stirring was paused and 20 mg/L of alum were added to the solution. Alum was provided by the Burlington plant from their supplies and prepared immediately prior to experiment as an intermediate mixture that was stable for 24 hours. The new mixture was stirred for 1 minute at 100 rpm to fully incorporate the alum into the solution then slowed to 20 rpm for 30 minutes of agitation. The solution was allowed to settle for 20 minutes following the completion of stirring. The sedimentation step represented the actions in the treatment plant's sedimentation basin and provided time for the coagulated floc particles to settle out of solution.

The solution was passed through a 90-mm GF/B (Whatman[®] International Ltd., Maidstone, England) (pore size 1.0 μm) filter to remove the carbon and alum solid phase particles and residual atrazine was then extracted from the water using C₁₈ Empore[™] Disks (3M Corp., St. Paul, Minnesota) (Mueller *et al.* 2000). The samples were concentrated with nitrogen to a volume of 1.0 mL and transferred to a 2.0 mL GC vial (procedures described in the appendix). The analyses were performed with a Varian Star Model 3400 Gas Chromatograph equipped with a Model 8200 CX Autosampler and coupled with a nitrogen/phosphorous [Thermionic

Specific Detector (TSD)] detector (Varian Inc., Walnut Creek, California). Volumes of each sample (3.0 μ L) were injected onto a DB-5 fused silica column (30 m by 0.53 mm i.d.) (0.5 μ m film) (J & W Scientific Inc., Folsom, California). The flow rates of helium for carrier and make-up gas was 4.91 and 25.7 mL/min, respectively. Air (176.3 mL/min) and hydrogen (4.07 mL/min) flowed to the detector.

The samples (final vol. 1.0 mL) were interspersed with the analytical standards of interest (10 μ g/L) and placed on the autosampler, with standards positioned at the start, between every five samples, and at the end of the GC sample run. Temperatures were as follows: inlet, 175°C, detector, 300°C. The oven temperature program was as follows: initial, 170°C hold 2 minutes; to 200°C at 2°C/min, hold 2 minutes; to 280°C at 5°C /min, hold 2 minutes. Quantification of data was performed by comparing sample peak area against the area of standards of known concentration. Retention times (RT) were as follows: alachlor (9.6 min), atrazine (5.1 min), metolachlor (8.32 min), and simazine (4.9 min).

These procedures were repeated for all the pesticides, producing five sets of samples that included atrazine, simazine, alachlor, metolachlor, and a standard mix of these four pesticides. The pesticides were subjected to mixing with carbon and alum with varying concentrations of carbon. Triplicate runs of each were performed to increase validity and statistically reliable data. The results were averaged and plotted with standard deviation. All sets were comprised of 3 replicates of 6 doses of carbon mixed with 5 types of adsorbates and resulted in 90 samples plus the 6 standard blanks that provided an initial pesticide concentration and altogether yielded 96 samples for Procedure One.

RESULTS AND DISCUSSION

Results of background analyses showed no detectable residues of the four pesticides investigated in this study. The pesticide residues detected in Procedure One were a result of the addition of pesticide standards within a laboratory setting.

Alachlor: Raw water fortified with alachlor exhibited declines in concentration when exposed to PAC for 40 minutes and alum for 30 minutes. The drop in residue concentration increased as the concentration of carbon increased. The largest percentage of removal experienced by alachlor (< 1%) was in the presence of 50 mg/L of PAC.

In terms of reducing the pesticide contaminant to a level below its MCL when the initial concentration was 10 µg/L, the carbon concentration required to lower the alachlor concentration to its MCL of 2 µg/L was a minimum of 20 mg/L. PAC doses of higher levels reduced the alachlor residues below its MCL with both 40 and 50 mg/L of carbon adsorbing over 98% of the pesticide from solution.

Atrazine: This herbicide exhibited similar reductions and 28% of the initial pesticide concentration was lowered with 5 mg/L of PAC. Removal from solution increased as the carbon dose was elevated. A removal difference of 33% was observed when the PAC concentration was raised from 10 to 20 mg/L. Less than 20% of the initial atrazine was present in solution with 30, 40, and 50 mg/L of carbon.

The 5 and 10 mg/L carbon doses were able to adsorb some portion of the pesticide but levels of atrazine remaining in solution exceeded the regulatory value.

A PAC concentration of 20 mg/L was adequate to reduce the pesticide levels below the MCL of 3.0 µg/L.

Metolachlor: Residues of metolachlor were reduced 22% with 5 mg/L and 36% with 10 mg/L of carbon. The 20 mg/L of carbon reduced the pesticide 80% of the initial concentration. Sixty percent of metolachlor residues were removed from solution following exposure to 30 mg/L of carbon. This was 20% less that was removed with a lesser concentration of carbon (20 mg/L). The higher levels of carbon doses, 40 and 50 mg/L, reduced metolachlor concentration by 87 and 92%, respectively. Like alachlor and atrazine the 20 mg/L concentration of PAC was effective in greatly reducing the initial concentration 80% following treatment with carbon and alum.

Simazine: Reductions in simazine concentration were seen with the lowest carbon dose of 5 mg/L and 27% of the pesticide was removed from solution. The contaminant concentration was reduced as the carbon dosage increased and 10 mg/L of carbon adsorbed 51% of the simazine residues. A PAC concentration of 30 mg/L removed 88% of the pesticide and over 95% removals were experienced with the 40 and 50 mg/L of carbon.

A MCL of 4.0 µg/L is assigned to the herbicide simazine. At an initial simazine concentration of 10 µg/L, the PAC dose of 10 mg/L was successful in reducing the pesticide to sufficiently lower the concentration just above its MCL. A PAC dose of 20 mg/L reduced simazine levels below its regulatory value.

Mixture: The standard mix was comprised of the four previous compounds (alachlor, atrazine, metolachlor, and simazine) combined for a per pesticide

concentration of 10 µg/L. The reductions of all four chemicals in the standard mix experiment were similar to those in the individual studies.

The 5 mg/L of carbon removed 16% of the mixture alachlor. Standard mix alachlor was effectively reduced by some 60% with a carbon dose of 20 mg/L. Ninety percent of the compound was removed from solution following 40 minutes of contact with 50 mg/L of carbon.

Over 50% of atrazine of the standard mix was adsorbed with 10 mg/L of carbon. The larger doses of PAC reduced the pesticide concentration and over 70% was removed from solution following exposure to 20 and 30 mg/L of carbon. Atrazine residues were almost completely removed from the water with the higher levels of carbon (40 and 50 mg/L).

Standard mix metolachlor was reduced 20% by both the 5 and 10 mg/L of PAC. Greater reductions occurred with increased concentrations of carbon and 43% was removed from solution following adsorption with 20 mg/L of PAC. A concentration of 40 mg/L of carbon effectively reduced the metolachlor concentration 89%, while 100% removal was achieved with a carbon dose of 50 mg/L.

The simazine portion of the standard mix was efficiently reduced in concentration with 10 mg/L of carbon and 51% of the pesticide was removed from solution. A PAC concentration of 20 mg/L adsorbed over 73% of the initial concentration of the pesticide. Over 90% was removed from solution with the addition of 40 and 50 mg/L of carbon.

Individual reductions versus pesticides combined in the standard mixture: Alachlor as an individual contaminant was adsorbed more readily than

when combined within the mixture of pesticides. Variation between the two treatments was primarily at the 20 and 30 mg/L carbon doses. However, 50 mg/L of PAC adsorbed approximately equal percentages of alachlor alone and alachlor combined in the mixture.

Atrazine alone and standard mix atrazine were adsorbed at comparable rates; generally falling within less than 10% of each other for all concentrations of carbon. With the exceptions of 5 and 30 mg/L concentrations of PAC, standard mix levels were adsorbed more than the individual atrazine residues.

Metolachlor in the standard mix was reduced slightly more than the individual pesticide for most of the carbon doses with one exception. A 20 mg/L concentration of PAC reduced metolachlor alone by 80% and metolachlor of the mixture was reduced 63%. All other doses of carbon adsorbed more of the standard mix pesticide. A PAC concentration of 50 mg/L removed 100% of the compound while 92% of individual metolachlor was removed.

Simazine as the sole compound was reduced more than when combined with the other pesticides. A concentration of 20 mg/L of carbon showed a 4% greater adsorbance when metolachlor was in the mixture, but there were no differences at a PAC concentration of 50 mg/L (96% reduction).

Comparison of pesticide reductions: At 5 mg/L of carbon, alachlor was the least adsorbed pesticide compared to other compounds (11% vs. 25% reduction for all other pesticides) (Fig. 1). Slight variations occurred between the compounds with the different carbon concentrations. Alachlor and metolachlor were reduced over 80% with 20 mg/L of PAC while atrazine and simazine showed equivalent reductions

at a PAC concentration of 30 mg/L. As carbon dose increased alachlor and simazine were removed to a greater extent than atrazine and metolachlor.

Water solubility and molecular weight of the pesticide as well as surface chemistry of the carbon can influence adsorption. Atrazine and simazine are the least water soluble of the four pesticides which could increase their potential for adsorption. However, these two pesticides required a greater concentration of PAC to achieve similar removals to alachlor and metolachlor. Possibly structural variation among these two classes of herbicides facilitated some influence in the degree of carbon adsorption. Surface chemistry of the carbon surface likely exhibited some control in the adsorption efficiencies. These differences of adsorption between the four pesticides could be a result of any of the above factors, although the exact cause of variation was unclear.

SUMMARY

Procedure One allowed a longer carbon contact time overall and a short period where carbon was present alone before the addition of alum. The reductions in pesticide concentration increased as the contact time increased. Although declines in pesticide concentration were exhibited with the lower carbon doses of 5 and 10 mg/L, the greater adsorption of pesticides occurred with 20 mg/L of carbon.

The highest concentrations of carbon in this study, 30, 40, and 50 mg/L were effective in reducing the pesticide residues approximately 80%. However, there were a few exceptions (metolachlor added as a single component, metolachlor and alachlor in the mixture) in which reductions were slightly lower (60-75%).

For those pesticides that are regulated by law with MCLs the most effective concentration of carbon (20 mg/L) was successful in reducing the pesticide levels below their respective regulatory values. This was true in all cases except standard mix alachlor in which the concentration of pesticide following adsorption with PAC at 20 mg/L was just above its MCL of 2.0 µg/L.

No great differences were observed when comparing the adsorption of the individual pesticides and their standard mix counterparts. There was some variation between individual compounds and the mixture but no significant divergence was exhibited at the various carbon doses. When comparing the different types of pesticides there are two classes represented by the four compounds. Two triazines, atrazine and simazine, exhibited comparable results in the comparison of individual versus standard mix compounds as did the two chloroacetanilides, alachlor and metolachlor.

The differences were not extreme but some similar reductions were shared by those pesticides falling within the same class (expected as structures of compounds within the same class tend to be similar); more so than between classes. There were statistical differences from the triazines (atrazine and simazine) at carbon concentrations of 30 and 40 mg/L for metolachlor and at 50 mg/L for alachlor.

The median level carbon doses of 20 and 30 mg/L appeared to be the most efficient concentrations of carbon capable of reducing levels of pesticides; encountered individually or within a mixture of compounds. While all concentrations of carbon used in this study exhibited reductions in pesticide concentration, the lowest carbon concentrations that successfully reduced the pesticides by 80% of the

initial concentration as well as below existing MCLs were the 20 and 30 mg/L concentrations of PAC.

PROCEDURE TWO

The second procedure of the model plant simulation study involved the addition of carbon and alum simultaneously. There was equal contact time for both of the chemicals. This portion of the study would determine any counteractive effects these two would have on the adsorption of contaminants. The carbon and alum were allowed to mix sufficiently with the solution and continual stirring represented the rapid-mix basin; the stage of introduction for both treatment chemicals. Settling followed at the sedimentation basin stage and then detection of the pesticide concentrations within solution determined the extent of adsorption encountered when alum and carbon were added at the same time to drinking water supplies.

MATERIALS AND METHODS

Twelve hundred milliliters of raw water were fortified with alachlor in the six-station stirrer and stirred for 10 minutes to ensure uniform mixing. To measure the initial pesticide concentration of 10 µg/L, 200 mL of this solution were removed. The remaining 1000 mL solution received carbon at varying concentrations of 5, 10, 20, 30, 40, and 50 mg/L and alum at 20 mg/L. The mixture was stirred for 1 minute at 100 rpm to allow for sufficient incorporation into the water and pesticide solution. Stirring speed was lowered to 20 rpm and the entire mixture was stirred for 30

minutes followed by a settling stage of 20 minutes to represent the sedimentation basin step in the model treatment plant.

These procedures were repeated for the other three pesticides, atrazine, metolachlor, simazine, and the standard mixture of all four compounds. Each set was performed in triplicate for all carbon doses. A total of 96 samples, including the background concentration samples taken prior to the addition of carbon and alum, were analyzed in the second procedure of this study. All samples were extracted and analyzed as previously described in Procedure One. Results of Procedure Two were averaged and plotted with standard deviation.

RESULTS AND DISCUSSION

Results of background analyses showed no detectable residues of the four pesticides investigated in this study. The pesticide residues detected in Procedure Two were a result of the addition of pesticide standards within a laboratory setting.

Alachlor: This compound was reduced with all six concentrations of carbon. As carbon dose increased adsorption increased. A reduction of 13% was seen with 5 mg/L of carbon, and ca. 50% of alachlor residues were removed following addition of 20 mg/L of PAC. The greater levels of carbon (30, 40, and 50 mg/L) were effective at reducing alachlor residues between 67 and 72%.

Reductions in alachlor concentration by all carbon doses in Procedure Two were of a percentage range of 13 to 72%. This decline in pesticide concentration was insufficient in reducing the initial chemical concentration below its MCL of 2.0 µg/L.

Atrazine: The 5 mg/L of carbon reduced atrazine residues 4% while the next dose of 10 mg/L succeeded in lowering the initial pesticide level 30%. The greatest removal was observed following addition of the 40 (71% reduction) and 50 mg/L (58%) concentrations of PAC.

The percentage range of pesticide removal varied from 4 to 71% of the initial pesticide concentration. Five of the carbon doses were unable to reduce atrazine residues below its MCL of 3.0 µg/L. Only the greater concentration of 40 mg/L of PAC was successful in removing 70% of the original pesticide and lowering the value just below the regulatory standard.

Metolachlor: Residues were not reduced with a 5 mg/L of carbon concentration and 100% of the pesticide remained in solution after carbon and alum were added. Declines in pesticide concentration occurred with increasing levels of carbon (e.g., 20 mg/L, 30% reduction; 40 mg/L, 55% and 50 mg/L, 62%).

Reductions of the pesticide levels following addition of carbon and alum ranged from 0 to 62%. These declines in metolachlor residues were sufficient in lowering the initial concentration over 50%. However, because no MCL exists for metolachlor these values did not exceed regulations. The HAL of metolachlor is 70.0 µg/L, and the pesticide remaining in solution was well below standard values.

Simazine: Reductions in simazine concentration were observed with the varying carbon doses in Procedure Two. A small reduction occurred with 5 mg/L of PAC and 84% of the original pesticide concentration remained in solution. Larger reductions were presented with greater concentrations of carbon. The 30 and 40 mg/L of carbon reduced the initial concentration of simazine over 65%.

The MCL of simazine (4.0 µg/L) was exceeded in the experiments using 5, 10, and 20 mg/L of PAC. A PAC concentration of 30 mg/L was successful in reducing the initial simazine level below its MCL. Although 40 and 50 mg/L of PAC were effective in lowering simazine levels below the MCL, the reductions with these two higher levels of carbon were not significantly different from those observed with 30 mg/L.

Mixture: Alachlor, contained in the standard mix was slightly reduced in concentration with 5 mg/L of PAC. The greater concentrations of carbon were effective in reducing alachlor residues. A 20 mg/L concentration of carbon adsorbed 51% while the 40 and 50 mg/L concentrations of PAC reduced standard mix alachlor 68 and 75%, respectively.

The six carbon doses reduced standard mix alachlor residues from 2 to 75%. However, none were sufficient in lowering the initial concentration of the pesticide below its MCL of 2.0 µg/L. While the carbon and alum mixture reduced alachlor, the adsorption was not enough to meet regulatory values.

The atrazine portion of the standard mix was reduced by carbon and alum addition, although only a slight reduction was seen with 5 mg/L of carbon (4%). A greater reduction (38%) was observed with 10 mg/L of carbon. As concentrations of carbon increased to 40 and 50 mg/L, atrazine was reduced 71 and 79%, respectively.

With an MCL of 3.0 µg/L, the standard mix atrazine remained above this value in Procedure Two when 5, 10, and 20 mg/L concentrations of PAC were applied. Thus, while pesticide concentrations of atrazine experienced a decline with

all of the carbon concentrations, only the 40 and 50 mg/L levels were sufficient in lowering the concentration below its MCL.

Metolachlor residues in the standard mixture exhibited no reductions in concentration with the lowest concentration of carbon (5 mg/L). As PAC dose increased the amount of pesticide remaining in solution decreased. Concentrations of 20 and 30 mg/L of carbon were effective in reducing residue levels of metolachlor 48 and 54%, respectively. The greater concentrations of PAC reduced the standard mix metolachlor over 65%.

As previously mentioned the existing standard value for metolachlor is the HAL (70.0 µg/L), which is not a regulated value for drinking water. This value far exceeded any concentration of metolachlor detected in surface water samples collected in the North Carolina studies since 1995. Although no frame of reference was available for metolachlor, the reductions in pesticide concentration were comparable to other pesticides in the study that were reduced to levels near or below their MCLs.

The standard mix simazine portion was adsorbed by all six carbon doses although the larger PAC concentrations showed greater removal. Following carbon and alum addition simazine residues were reduced 57% with 20 mg/L, 71% with 40 mg/L, and 79% with 50 mg/L of carbon. The 5, 10, and 20 mg/L concentrations of carbon were inadequate to reduce the initial simazine residues below its MCL of 4.0 µg/L; therefore, concentrations of carbon 30 mg/L and greater were required.

Individual reductions versus pesticides combined in the standard mixture: The four pesticides exhibited adsorptions that differed somewhat from

their standard mix counterparts. Alachlor alone and combined showed concentration reductions within 10% of each other at all concentrations of carbon.

Atrazine alone was not adsorbed as well as the mixture atrazine. At all concentrations of carbon the standard mix atrazine was adsorbed more than when it was the sole pesticide in water. Larger discrepancies were seen with 20 and 50 mg/L of PAC, such that a 32% difference was observed with the lower concentration of PAC and 21% difference with 50 mg/L.

Metolachlor in the standard mix was adsorbed to a greater extent when tested alone at all concentrations of PAC. Differences were minimal when 5 and 10 mg/L of carbon were added, but increased as the concentration of PAC increased. There was almost a 20% difference between metolachlor added as the sole compound in water and added as a mixture for carbon concentrations of 20 and 30 mg/L. The other PAC doses adsorbed 10% more of the standard mix pesticide compared to the sole compound.

The 5 mg/L carbon dose was more effective in reducing simazine compared to the standard mixture. All other concentrations of PAC adsorbed more of the compound in the standard mix than when added as the sole compound. It seemed as if the mixture of pesticides were preferentially adsorbed more than the individual counterparts.

Comparisons of pesticides: The four pesticides were adsorbed by all concentrations of PAC with Procedure Two (Fig. 2). Overall, alachlor was reduced more efficiently than the other compounds. Atrazine was adsorbed slower than the rest until the carbon dose reached 30 mg/L. Metolachlor remained in solution at a

greater concentration than the others until 50 mg/L of PAC were added. Statistically, metolachlor was least adsorbed with 30 and 40 mg/L of carbon. The pesticide differed from simazine with 30 mg/L of PAC and from atrazine, simazine, and alachlor with 40 mg/L carbon. The pesticide residues in the standard mix were adsorbed in relatively equal percentages for all concentrations of carbon. Metolachlor, regardless of being tested individually or in the standard mixture was the overall least affected by carbon adsorption.

SUMMARY

Procedure Two involved the simultaneous addition of carbon and alum with a contact time of 30 minutes for mixing and 20 minutes for settling. The pesticides were adsorbed to some degree for most of the carbon doses. The 5 mg/L concentration of carbon sometimes had no effect on the pesticide concentrations. The most effective concentration of carbon was 30 mg/L.

The 40 and 50 mg/L carbon doses generally reduced pesticides in similar percentages to the 30.0 mg/L PAC concentration. Reductions in concentration leveled off at 30.0 mg/L and remained relatively constant as doses of PAC were increased. Concentration declines in Procedure Two ranged from 0 to 79% of the initial pesticide levels, and no less than 21% of pesticide remained in solution.

Adsorptions of individual pesticides and the standard mix counterparts were sufficient in reducing concentrations although the MCLs of alachlor, atrazine, and simazine were generally exceeded even at the higher carbon doses. The reductions

experienced with a PAC concentration of 50 mg/L were occasionally insufficient in lowering the pesticide concentrations below established regulatory values.

For the most part, the standard mix compounds were reduced to a greater extent than the individual pesticides. Although discrepancy between the two groups was minimal, it appeared the standard mix pesticides were adsorbed to a greater extent by the carbon and alum mixture. There was no explanation for these results. Few studies exist that monitor mixtures of pesticides and carbon adsorption; therefore, results of this nature were unclear.

When comparing the classes of compounds, no apparent trends were observed. The various pesticides were generally reduced as the concentration of carbon increased but residue levels of atrazine and simazine were not reduced much differently than those of alachlor and metolachlor. Except for the 20 and 50 mg/L concentrations of PAC, the presence of atrazine in solution was slightly greater. However, metolachlor was adsorbed less than the other compounds and seemed more resistant to removal. No explanation for this resistance exists; however, metolachlor is the most water soluble of the four compounds which possibly explains the lack of equitable adsorption (carbon adsorption tends to decrease as water solubility increases). Previous studies with this carbon have produced various results between the four pesticides and metolachlor was not always the least adsorbed compound. Many factors affect adsorption (e.g., carbon surface chemistry, pesticide structural configurations and functional groups, water solubility, ionization, and molecular weight) and the addition of alum introduced even more variables; therefore, the results between pesticides were difficult to explain.

PROCEDURE THREE

The third procedure of this study simulated a treatment method with alum added first in the rapid-mix basin and allowed to fully mix within the water. Later at the same stage (rapid-mix) carbon was added and stirring continued. Sedimentation permitted the settling out of the heavier solid phase matter and detection of pesticides remaining in solution determined the effects of alum addition preceding carbon addition.

The addition of alum prior to the carbon had been proposed to lead to coagulated flocculant with carbon particles adhered to the outer surfaces (Snoeyink and Summers 1999, D Knappe 2002, personal communication). If the carbon remained on the surface of the flocculated organic matter then adsorption sites would continue to be available for the pesticides, possibly negating the inhibitory effects, suspected of alum, on carbon adsorption.

MATERIALS AND METHODS

Burlington raw water (1200 mL) was fortified with individual pesticides or a pesticide mixture in concentrations of 10 µg/L. The resulting solution was stirred for 10 minutes at 100 rpm to ensure uniform mixing. A zero-time sample of 200 mL was removed to determine initial residue levels. Alum at a concentration of 20.0 mg/L was added to the 1000 mL of pesticide-fortified water and stirred for 1 minute at 100 rpm to fully mix the coagulant with the water. This mixture was stirred for 2 minutes at 20 rpm. Carbon was added at this point and the whole mixture agitated for 28

minutes at 20 rpm and allowed to settle (20 min.). Samples were prepared as previously described.

All methods were performed in triplicate to monitor effects of the 4 individual pesticides, the standard mix pesticides, and the 6 carbon doses. From this study, 96 samples were analyzed for pesticide residues as before to determine the concentration of compounds remaining in solution following addition of alum and carbon. The results of Procedure Three were averaged and plotted with standard deviation.

RESULTS AND DISCUSSION

Results of background analyses showed no detectable residues of the four pesticides investigated in this study. The pesticide residues detected in Procedure Three were a result of the addition of pesticide standards within a laboratory setting.

Alachlor: The addition of alum and carbon to the pesticide and water solution showed increased adsorption of this compound as the concentration of PAC increased. Alachlor was reduced 18% by 5 mg/L of carbon and similar reductions occurred for both 10 and 20 mg/L. The latter three concentrations of carbon adsorbed most of the alachlor residues and approximately 35% remained in solution following treatment.

Removal of pesticide residues of alachlor, facilitated by carbon, was adequate in reducing the initial concentration of the pesticide. However, the adsorptions did not reduce levels below the MCL of 2.0 µg/L. Even 50 mg/L of PAC (70% reduction) failed to lower the concentration below 2.0 µg/L.

Atrazine: This herbicide was reduced to 30% of its original concentration with a carbon level of 5 mg/L, while 20 mg/L of PAC adsorbed 70% of atrazine residues. The concentration steadily dropped with increasing carbon dose, and 40 and 50 mg/L of carbon were effective in reducing the atrazine initial concentrations 95 and 96%, respectively.

With an MCL value of 3.0 µg/L, the reductions of initial atrazine concentration must be greater than approximately 70%. While 20 mg/L of carbon left approximately 3.0 µg/L of the pesticide residue in solution, the larger doses of carbon, 30, 40, and 50 mg/L were effective in lowering the atrazine concentration well below the MCL of 3.0 µg/L.

Metolachlor: The metolachlor-fortified experiment did not show signs of adsorption with 5 mg/L of PAC. Reductions in pesticide concentration occurred with a PAC concentration of 10.0 (19% adsorbed) and 20 mg/L (50% reduction), while 30.0 mg/L were required to achieve reductions in the range of 84%. Only 4% of initial metolachlor residues remained in solution following addition of 50 mg/L of PAC.

Metolachlor does not have a MCL that must be met by drinking water treatment plants. Although if comparable reductions exhibited by other pesticides in this study were required for metolachlor, then 30 mg/L of carbon was more than adequate to effectively reduce the pesticide concentration.

Simazine: A reduction of 24% was observed with 5 mg/L of PAC and 10 mg/L adsorbed 46% of the initial pesticide concentration. The largest reduction with the lowest concentration of PAC was exhibited with 20 mg/L of carbon and only 22%

of initial simazine residues remained in solution. The carbon concentrations of 30 and 40 mg/L were effective in reducing simazine residues 93 and 98%, respectively. Simazine was not detected in solution following addition of 50 mg/L of PAC.

The MCL of simazine (4.0 µg/L) was exceeded in the experiments with the lower carbon doses of 5 and 10 mg/L. A 78% reduction after contact with 20 mg/L of PAC was adequate in lowering the concentration of simazine well below the established regulatory value. Greater concentrations of PAC also met the MCL requirement.

Mixture: The alachlor portion of the standard mix was well adsorbed by the 6 PAC doses with over 60% of the pesticide residue removed with 5 mg/L of carbon. Similar reductions occurred with 10 and 20 mg/L of PAC with removals of 60 and 70%, respectively. Only 2% of the initial alachlor concentration remained in solution following addition of 30 mg/L and carbon doses of greater concentrations, 40 and 50 mg/L, left no detectable alachlor in solution.

Alachlor in the standard mix was effectively reduced below the MCL of 2.0 µg/L with carbon doses of 30 mg/L and higher. Lower concentrations of PAC reduced alachlor residues in the mixture but these declines in concentrations were insufficient in lowering the pesticide levels below its MCL.

Standard mix atrazine was reduced 19% by 5 mg/L of carbon. Approximately 50% was removed using a PAC dose of 10.0 mg/L. Less than 20% of initial atrazine residues remained in solution following the addition of 20 and 30 mg/L of carbon, and the remaining carbon concentrations adsorbed all of the pesticide. While lower carbon doses of 5 and 10 mg/L were able to adsorb the pesticide, a carbon

concentration of 20 mg/L or greater was required to reduce the standard mix atrazine residue levels below the MCL of 3.0 µg/L.

Metolachlor in the standard mix was adsorbed by the 5 mg/L of PAC with a 12% reduction in the initial concentration of the pesticide. Over 50% of metolachlor was removed with 10 mg/L of carbon, and 20 and 30 mg/L were effective in removing standard mix metolachlor 82 and 97%, respectively. Metolachlor was not detected in solution following the addition of 40 or 50 mg/L of PAC.

As previously mentioned, the frame of reference for metolachlor was the HAL which far exceeded the concentrations used in this study. However, reductions of all pesticide residues were desired and 20 mg/L was able to reduce metolachlor residue levels over 80% of the initial pesticide concentration.

PAC doses of 5 and 10 mg/L adsorbed the simazine portion of the standard mix at 19 and 28%, respectively. A 20 mg/L concentration of PAC effectively reduced the pesticide residue in solution by 96%. The 30 mg/L concentration of PAC appeared less effective than the prior carbon dose but reduced simazine over 85%. The 40 and 50 mg/L concentrations of carbon adsorbed the standard mix simazine leaving no detectable residues in solution.

The lower doses of PAC, 5 and 10 mg/L, succeeded in reducing simazine concentrations but the remaining residue levels surpassed the regulatory value. Simazine in the standard mix was effectively adsorbed by the 20 mg/L and greater concentrations of carbon to lower the pesticide levels below the MCL of 4.0 µg/L.

Individual reductions versus pesticides combined in the standard mixture: With the exception of atrazine all of the standard mix pesticides were

adsorbed to a greater extent than the individual counterparts at all 6 carbon concentrations. The adsorption between alachlor and standard mix alachlor differed by approximately 50%, with more of the standard mix alachlor adsorbed than the individual residue.

Atrazine and standard mix atrazine were adsorbed at roughly the same percentages. The 40 and 50 mg/L of carbon were effective in fully removing the standard mix pesticide while 5% of individual atrazine remained in solution. Metolachlor of the standard mix experienced greater reductions in concentration than its individual counterpart for all of the PAC concentrations.

Simazine in the standard mix was adsorbed to a greater degree with 20 and 40 mg/L of carbon while the remaining PAC doses were more effective in reducing the individual pesticide. However, a carbon concentration of 50 mg/L was adequate in reducing both forms of simazine 100%.

Comparisons of pesticides: For the lower carbon doses metolachlor appeared to be the least adsorbed pesticide of the four compounds (Fig. 3). However, upon the addition of 20 mg/L and greater concentrations of PAC, alachlor remained in solution at higher levels than the other three pesticides. As with the results of Procedure Two and the other experiments, it was difficult to determine the exact cause of varied adsorptions between the four pesticides.

Metolachlor and alachlor possess greater molecular weights and water solubilities than atrazine and simazine and both of these qualities tend to decrease carbon adsorption. Metolachlor was found to be statistically different from the triazines for all PAC concentrations except 50 mg/L, while alachlor was adsorbed

statistically less than atrazine and simazine at 30, 40, and 50 mg/L of carbon. Both atrazine and simazine were reduced in comparable levels, never more than 8% apart in reductions, although only statistically similar at carbon concentrations 30 mg/L and less. This trend was not apparent in the comparison of pesticides in the standard mix. The four compounds were adsorbed at various rates with no relation to the other pesticides.

SUMMARY

Procedure Three involved the addition of alum followed by carbon. The adsorptions of the four pesticides and the standard mixture increased as the concentrations of the carbon increased. The PAC concentration of 5 mg/L succeeded in reducing the pesticide residues somewhat, except for metolachlor which exhibited no declines in concentration. However, larger doses of carbon removed portions of all pesticides and the PAC concentration of 30 mg/L was required to reduce pesticide levels to an appreciable extent.

The adsorption by carbon was greater for those compounds in the standard mixture than for individual pesticides. Several experiments demonstrated complete removals from solution for the larger PAC concentrations. Regardless of form, 20 mg/L of carbon generally reduced concentrations of the pesticides by approximately 50% of the initial compound concentration.

Similar removals were apparent within the class of pesticides when comparing the four chemicals. Adsorptions of atrazine and simazine were greater than those observed for metolachlor and alachlor. Although reductions in pesticide

concentrations with 30 mg/L of carbon were sufficient for comparable levels with most pesticides, alachlor was only reduced 70% at a concentration of 50 mg/L of PAC.

The standard mix of pesticides was reduced to a greater extent with lower concentrations of PAC and less than 13% of all four pesticides remained in solution following the addition of 30 mg/L. The relationship of analogous reductions between those compounds of the same class, observed with the individual pesticides, was not distinguishable in comparisons of the standard mix pesticide adsorption.

Procedure Three demonstrated more than satisfactory results with adsorption of pesticide residues; thus, the initial concentrations remaining in solution were lowered. Reductions in atrazine and simazine levels were decreased below the MCLs. Alachlor, although adsorbed by all concentrations of PAC, was not reduced to a level below its regulatory value with even 50 mg/L of carbon. The overall adsorption for both individual pesticides and the standard mix was effective with the third procedure.

COMPARISON OF THE THREE MODEL PROCEDURES

The three procedures performed to model possible treatment methods amenable to the plant's treatment train utilized carbon and alum introduction at different points of chemical addition. Divergence in adsorption among the three procedures was evident upon comparison of each pesticide. In reviewing the individual pesticides and standard mix adsorption results for each procedure it was

apparent that some procedures were better at reducing pesticide residues in solution than others.

Alachlor exhibited a greater adsorption with the first procedure which involved carbon addition 10 minutes prior to alum addition followed by 30 minutes of combined mixing (Fig. 4). Over 80% of the initial pesticide concentration was removed from solution with Procedure One at a carbon dose of 20 mg/L, while similar carbon concentrations of Procedures Two and Three reduced alachlor residues 44 and 27%, respectively.

Variations in procedural results with alachlor were evident with 20, 40, and 50 mg/L of PAC. The adsorptions of the pesticide at these concentrations of carbon were statistically greater with Procedure One compared to Procedures Two and Three. For the remaining PAC doses, the procedures were statistically similar. Statistical analyses of the alachlor residue removals from solution revealed significant differences in the overall results of Procedure One compared to both Procedures Two and Three. The most effective method of treatment involved a longer carbon contact time (Procedure One), followed by carbon and alum added simultaneously (Procedure Two) and lastly alum added to solution prior to carbon (Procedure Three).

Differences in atrazine removal indicated that Procedure Two was the least effective method in adsorbing the pesticide residues (Fig. 5). Removals by Procedures One and Three were sufficient in reducing the atrazine concentration below its MCL with 20 mg/L while Procedure Two only succeeded in lowering the pesticide residues to a level that was just above the regulatory value.

The atrazine adsorption results were subjected to statistical analyses to compare the three methods of water treatment chemical additions. Overall, Procedure Two was significantly different than the other methods in reducing the solution pesticide residues, while Procedures One and Three were similar. These differences were evident with carbon concentrations 20 mg/L and greater. Procedures one and Three exhibited similar reductions in atrazine residues for all concentrations of PAC. The least effective method of treatment involved the simultaneous addition of carbon and alum (Procedure Two) to the water solution.

Metolachlor was adsorbed similarly with the three procedures at the lower concentrations of carbon (5, 10 mg/L). With 20 mg/L of PAC, all three procedures varied with Procedure One adsorbing the most metolachlor and Procedure Two the least. The 30 mg/L carbon concentration was similar to 20 mg/L with all procedures varying in adsorption of the pesticide although Procedure Three was the most effective (Fig. 6). Procedure Two was the least successful method of treatment achieving just over 60% removal with the highest level of carbon. Procedures One and Three adsorbed over 85% of the initial metolachlor residues following the addition of 40 mg/L; however, One and Three were similar.

Statistical analyses of metolachlor residue reductions with the three methods indicated Procedure Two was significantly different from both Procedures One and Three. The overall most effective treatment method involved the longer carbon contact time (Procedure One), followed by alum addition prior to carbon (Procedure Three). Simultaneous carbon and alum chemical addition (Procedure Two) to the

water solution fortified with metolachlor was the least effective of the three procedures in reducing the pesticide residues.

Simazine was reduced below its MCL with Procedure One and Three at a carbon dose 20 mg/L (Fig. 7). Procedure Two was unable to remove significant amounts of pesticide at lower PAC concentrations (20 mg/L or less) and 30 mg/L or greater were required before substantial adsorption of simazine residues occurred. Procedure Three showed a greater degree of efficiency with PAC concentrations of 20 mg/L and higher. Procedure Two was the least effective in reducing simazine concentrations.

The adsorption results of Procedure Two were statistically least effective in adsorbing the pesticide compared to Procedures One and Three. Adding carbon and alum simultaneously (Procedure Two) was the least effective method for reducing simazine residues in solution. While extended contact time with alum (Procedure Three) was more efficient than adding the chemicals together, the addition of carbon prior to alum (Procedure One) was statistically the most effective method of chemical treatment.

The method variations for the standard mix of the pesticides were somewhat similar to the individual components. In the standard mix, alachlor was adsorbed more efficiently by the third Procedure with almost complete removal at 30 mg/L (Fig. 8). Procedure One also reduced the alachlor residues in the standard mix although greater concentrations of PAC were required to achieve removals comparable to Procedure Three. The second method demonstrated the least

amount of pesticide adsorption and only 75% of initial concentration was removed with 50 mg/L of carbon.

Standard Mix atrazine was least adsorbed by Procedure Two (Fig 9). Procedure One adsorbed slightly more atrazine than the third procedure with carbon doses of 5 and 10 mg/L. The remaining carbon concentrations exhibited the most efficient reductions with Procedure Three. At concentrations of 20 mg/L and higher, Procedures One and Two were adequate in lowering the standard mix atrazine residues, but Procedure Three was the most effective.

Metolachlor in the standard mix experienced the greatest adsorption with Procedure Three (Fig. 10). Procedure One was more efficient than Procedure Two, with the exception of the 10 mg/L carbon addition, in reducing metolachlor residues of the standard mix. Overall, the least effective method of treatment for reducing metolachlor residues was Procedure Two.

The simazine portion of the standard mix was most adsorbed by the treatment method of Procedure One at carbon doses of 5 and 10 mg/L (Fig. 11). At 20 mg/L and greater concentrations of PAC, the third procedure was most effective in removing simazine from solution. Procedure Two was overall the least effective in reducing standard mix simazine levels.

The pesticides within the standard mix exhibited similar results in the statistical analyses. Results of all three procedures were significantly different from each other for each pesticide within the mixture of compounds (atrazine, alachlor, simazine, metolachlor). Additionally, the most effective methods of treatment involved the extended contact with alum followed by carbon addition or extended

carbon contact followed by alum exemplified by Procedures Three and One, respectively. Procedure Two involved the concurrent addition of carbon and alum to the water solution fortified with the standard mixture of four pesticides and was statistically the least effective of the three procedures in reducing pesticide residues in solution.

CONCLUSION

The purpose of this study was to observe the reductions of pesticide residue concentrations in solution by adsorption with varying PAC concentrations, comparing the carbon addition time points and how alum may or may not affect carbon adsorption. There were many distinctions among the different types of pesticides and how they were present in solution (individual versus standard mix) for the select carbon doses. Variations in adsorptions were evident with the different methods of treatment, selected to represent potential chemical additions for a model drinking water treatment plant.

The consensus derived from the results of varying concentrations of carbon was that adsorption increased as the concentration of PAC increased, most likely a result of increased adsorption sites. While reductions in residue concentrations were at their maximum with a carbon concentration of 50 mg/L, the lower concentrations that were most efficient were 20 and 30 mg/L. These PAC concentrations succeeded in reducing pesticide residues of 10 µg/L below MCL values (atrazine 3.0 µg/L; simazine 4.0 µg/L).

Considering these results, a treatment plant could use between 20 and 30 mg/L to reduce pesticide residues at a concentration of 10 µg/L to levels below regulatory values. There was one pesticide, alachlor, which was not regularly reduced below its MCL with 20 mg/L of carbon. The alachlor MCL was the lowest of the regulatory values for the four pesticides in this study and required slightly greater concentrations of carbon to achieve residue levels below 2.0 µg/L. Therefore, treatment facilities encountering those pesticides with stricter regulatory values would only need to raise the carbon concentration slightly to achieve comparable adsorption results. It was evident that by slightly increasing the carbon dose (30 mg/L) the reductions of all four pesticides would meet existing drinking water requirements.

There was variation in the adsorption reactions between individual pesticides and the standard mix counterparts in which one or the other was reduced to a greater extent. This variation changed with procedure and carbon dose. For example, alachlor was adsorbed to a greater extent with Procedure One, while the standard mix alachlor residues experienced greater reductions with Procedure Three. Atrazine and the standard mix pesticide were both removed from solution at a greater rate by the third procedure. The first procedure was also effective in adsorbing atrazine although not as effective as Procedure Three.

Overall, both Procedures One and Three were the most effective treatment methods for reducing these pesticides, individual and standard mixtures, in a water solution. Procedure Three involved alum added 2 minutes prior to carbon addition and was thought to possibly produce flocculated organic matter particles that

allowed carbon particles to adhere to the outer surfaces of the coagulated masses. Therefore, the carbon's adsorption sites remained available.

Procedure One involved the addition of carbon 10 minutes before alum allowed extended contact times between the pesticide fortified water and adsorbing carbon. Considering the effects of alum reducing the adsorption capacity of carbon, the increased contact time would provide time for interaction between the pesticide and carbon; therefore, the alum addition would not be able to exert such a large effect on the adsorption.

Procedure Two was the least effective method of treatment for reducing pesticide concentrations within solution. The simultaneous addition of carbon and alum appeared to amplify the inhibitive effect of alum and reduced the adsorption capacity of the carbon. Carbon and alum together demonstrated an interference that reduced the adsorption of pesticides normally observed with similar concentrations of PAC without the alum addition. Assuming that carbon is incorporated into alum flocculant, when the two chemicals were simultaneously added to the water solution carbon could have been immediately swept up within the coagulated organic matter leaving little chance for adsorption interactions to occur between the carbon and pesticides in solution. This seemed possible considering the results of Procedure Two. Additionally, the formation of flocculant was observed immediately following the addition of alum; therefore, if carbon was incorporated within the alum then it most likely settled on the bottom of the basin with the flocculated organic matter and adsorption sites were unavailable to the pesticide residues.

In the model treatment plant PAC and alum are both used and are generally introduced into the drinking water treatment train in the rapid mix basin and allowed to mix for 30 minutes in the flocculation basin before agitation is halted and sedimentation occurs. These three procedures attempted to determine which order the two chemicals could be added in the treatment plant to facilitate a greater degree of adsorption, thereby reducing the contaminant concentrations in the water supplies.

Although the reaction between alum and carbon when these two components are combined is not fully understood, the results of this study indicated that carbon adsorption sites remained available for greater adsorptions of pesticides from solution when the alum and carbon were not added simultaneously. Therefore, the best method of treatment for reducing pesticide residues within solution for the model drinking water treatment plant is the chemical addition of alum prior to or briefly following the addition of activated carbon.

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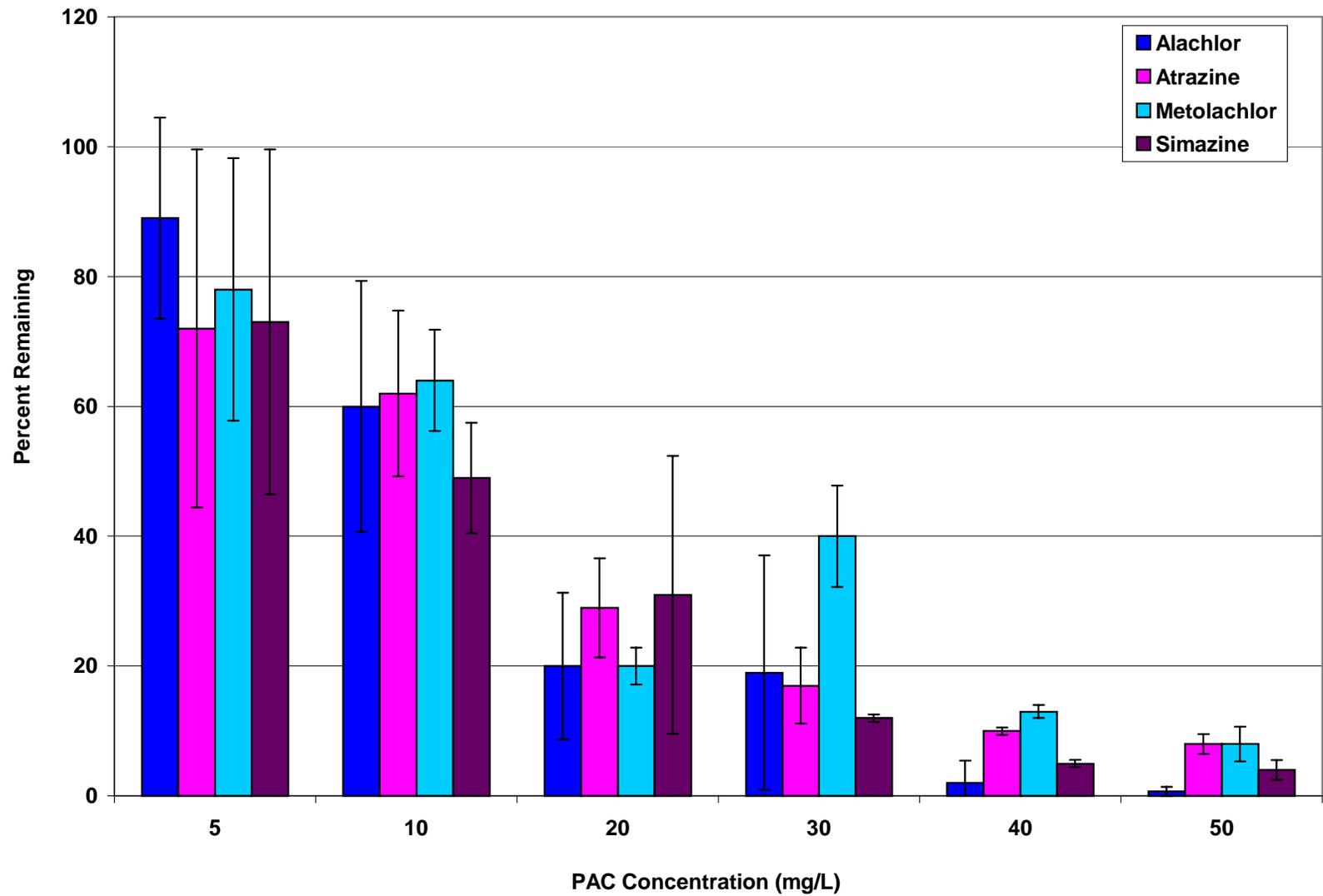


Figure 1. Procedure One comparison of residue reductions of alachlor, atrazine, metolachlor, and simazine following contact with carbon concentrations of 5 to 50 mg/L and 20 mg/L of alum.

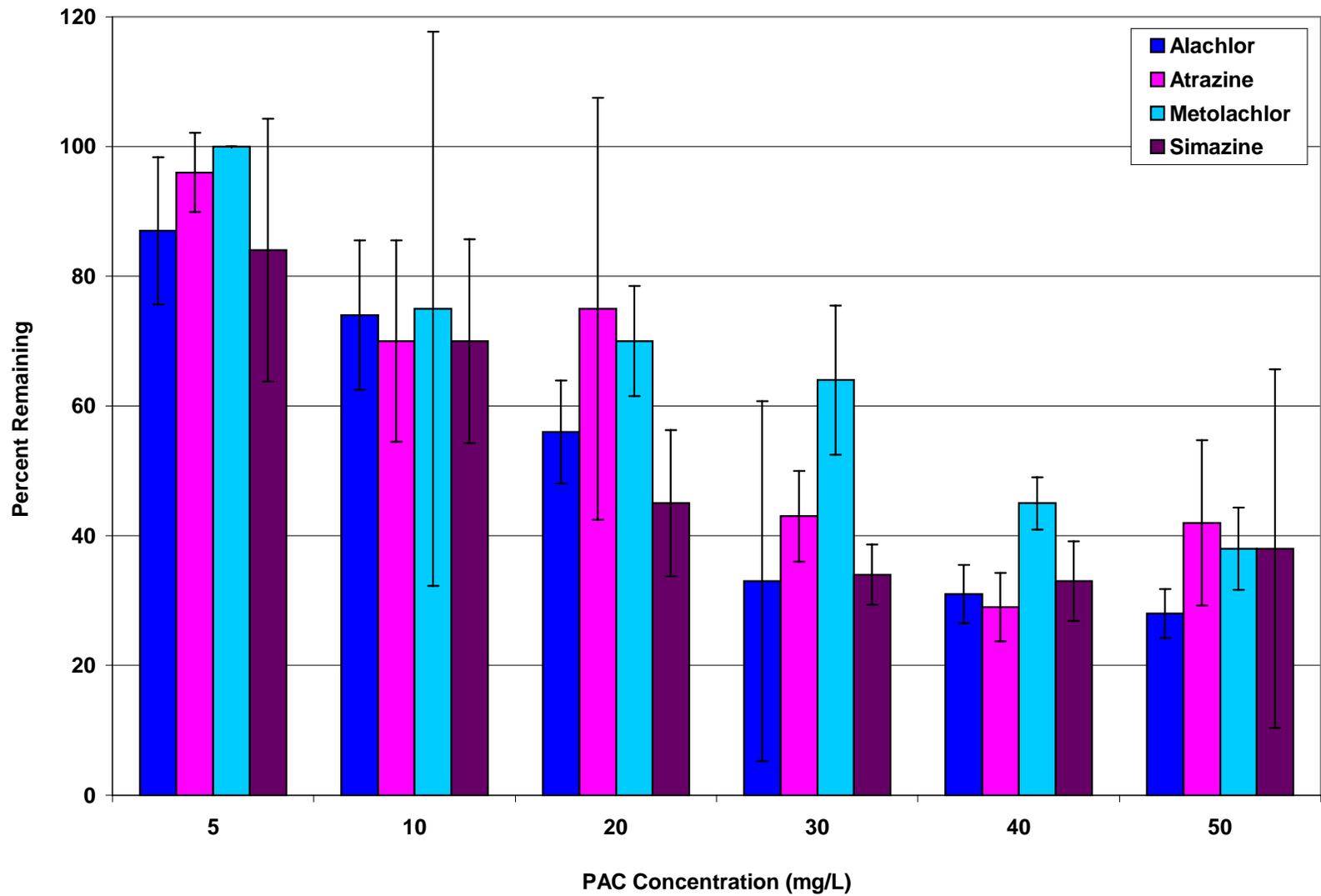


Figure 2. Procedure Two comparison of residue reductions of alachlor, atrazine, metolachlor, and simazine following contact with carbon concentrations of 5 to 50 mg/L and 20 mg/L of alum.

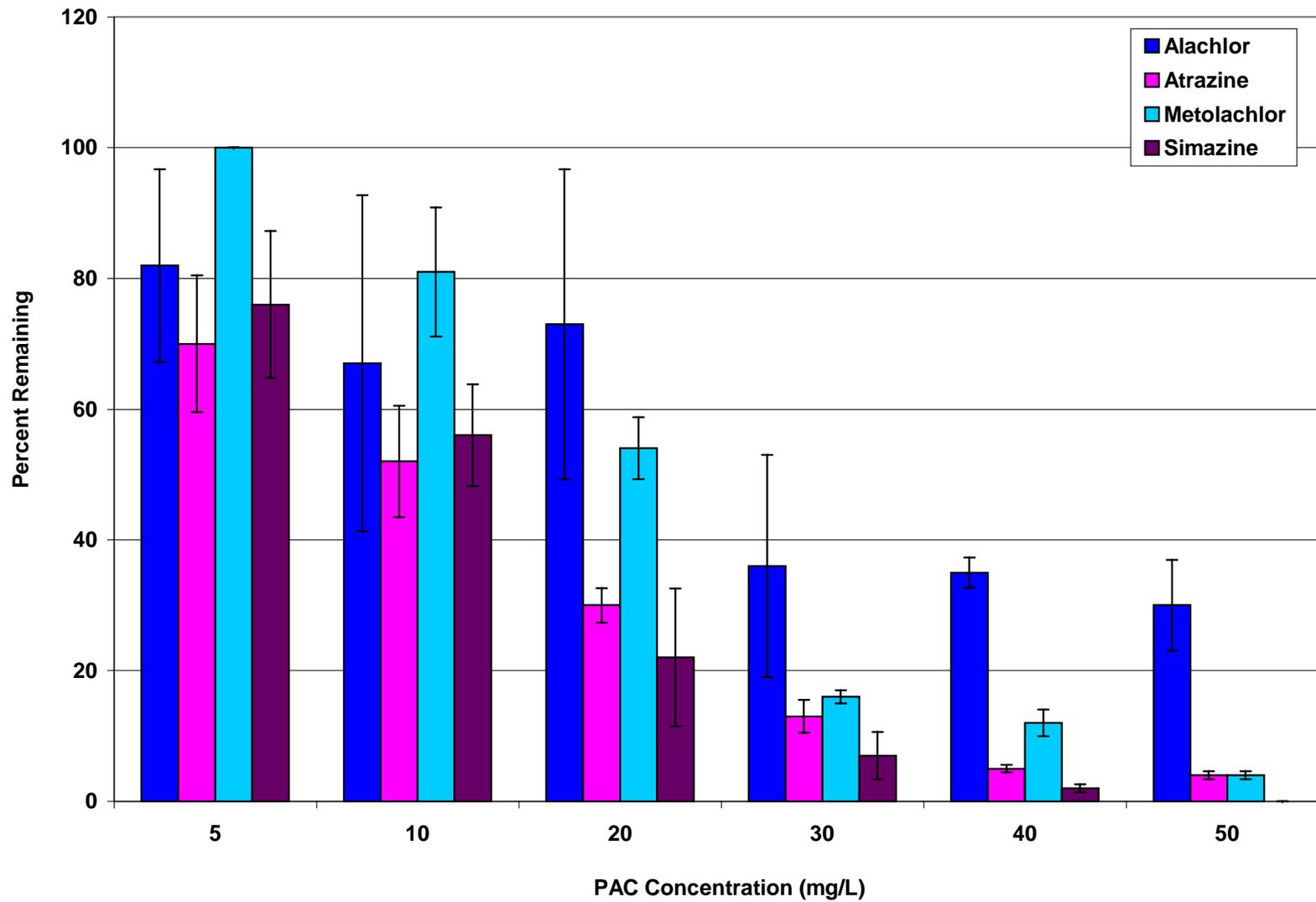


Figure 3. Procedure Three comparisons of residue reductions of alachlor, atrazine, metolachlor, and simazine following contact with carbon concentrations of 5 to 50 mg/L and 20 mg/L of alum.

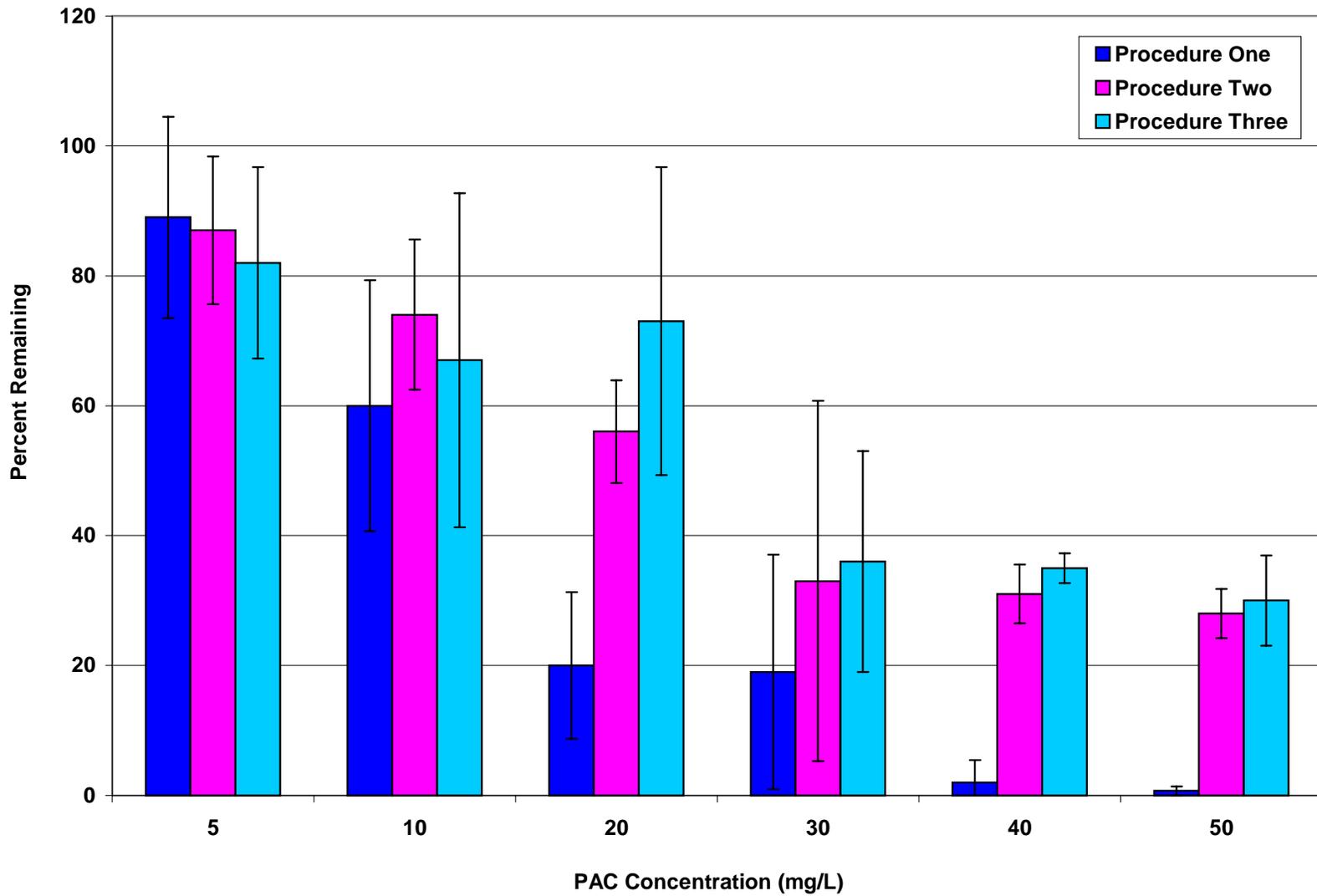


Figure 4. A comparison of the alachlor residue reductions exhibited by the three methods of chemical addition.

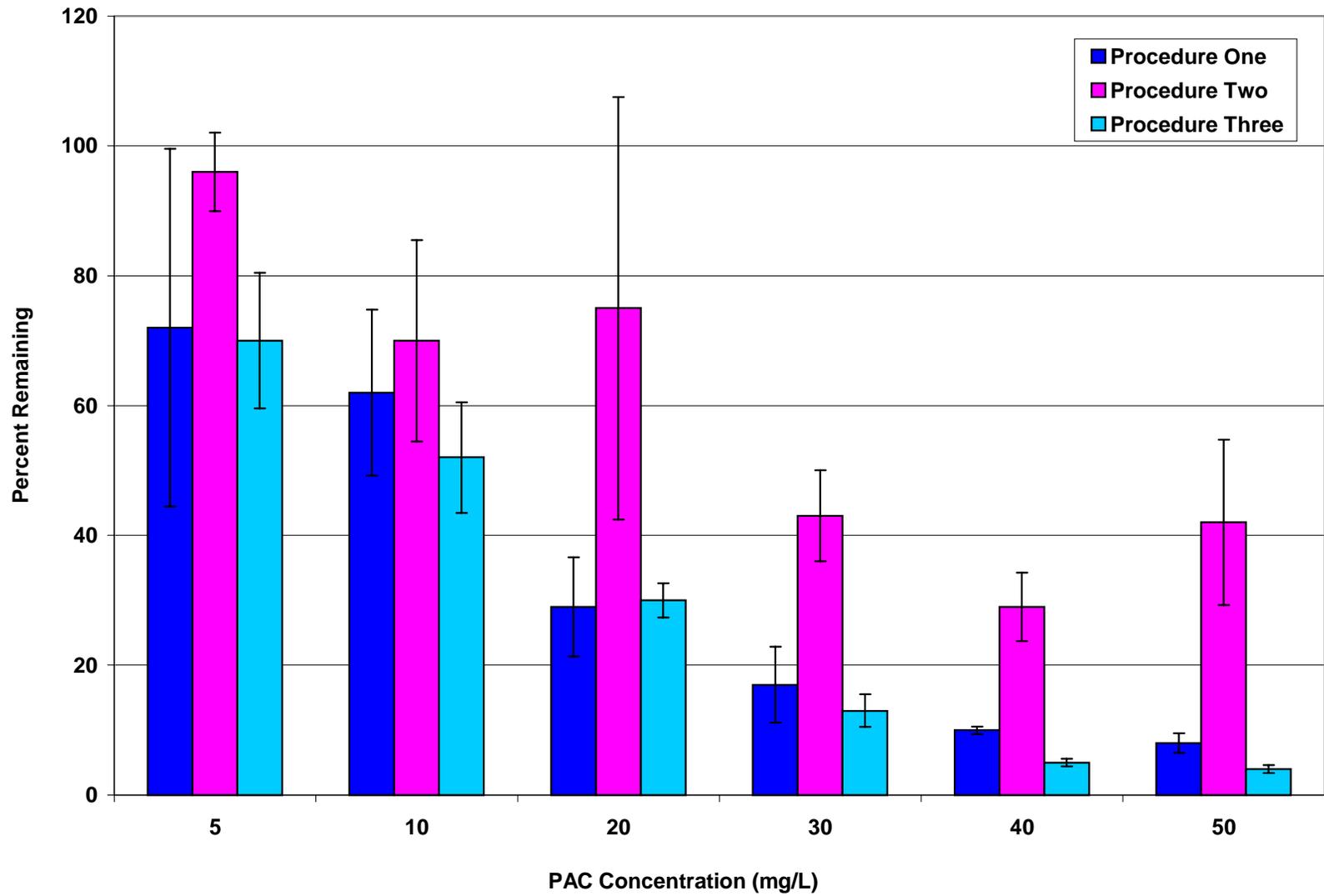


Figure 5. A comparison of the atrazine residue reductions exhibited by the three methods of chemical addition.

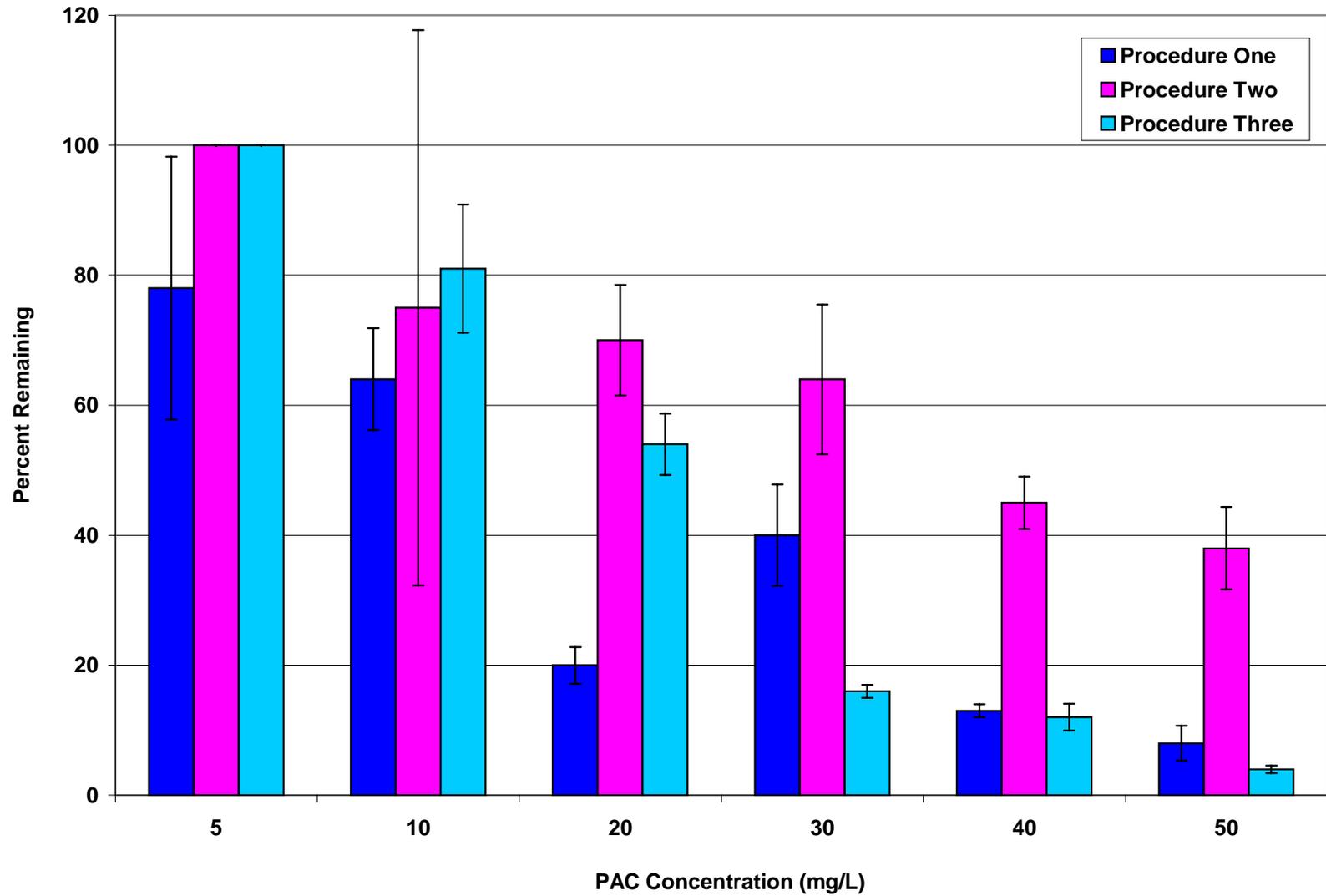


Figure 6. A comparison of the metolachlor residue reductions exhibited by the three methods of chemical addition.

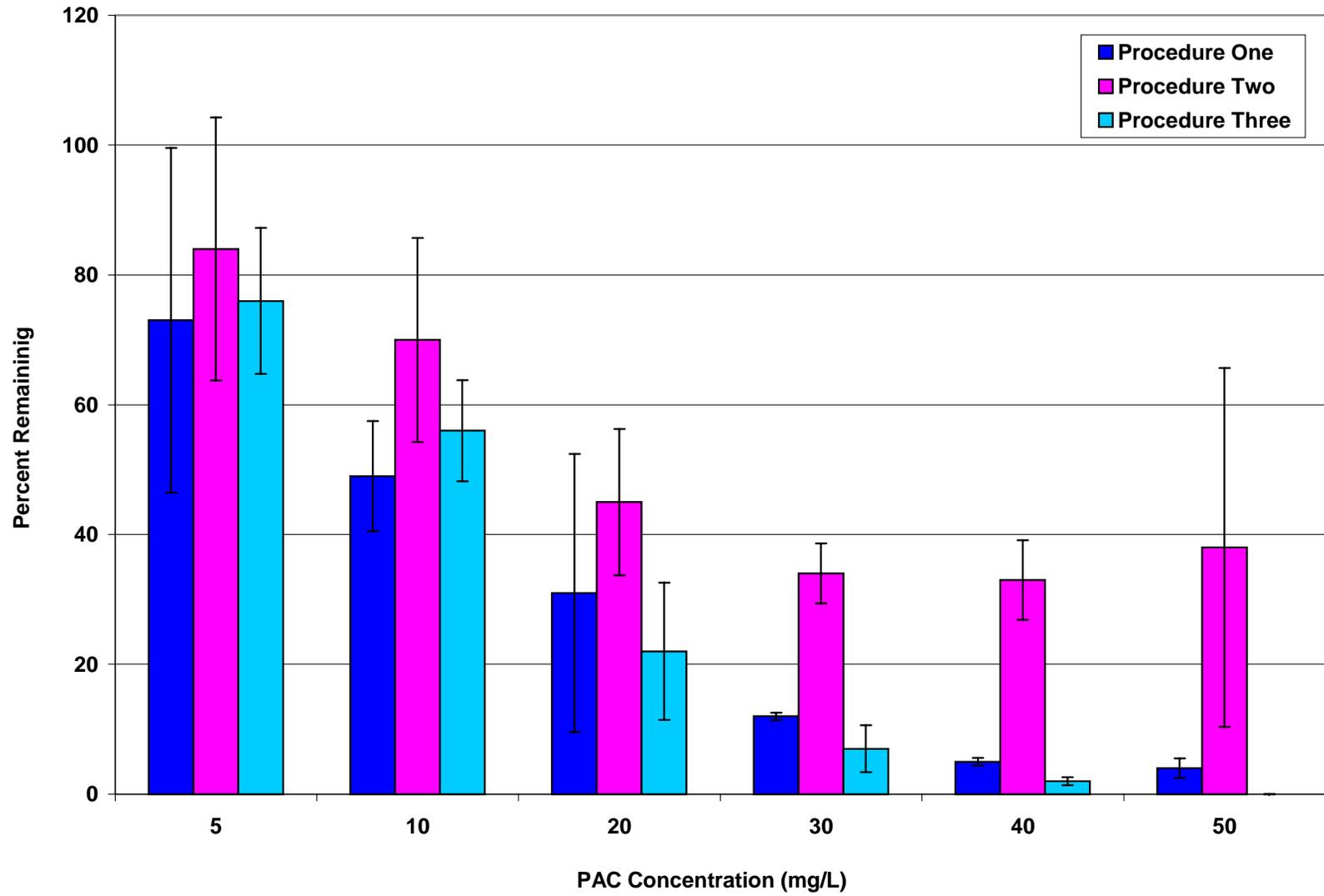


Figure 7. A comparison of the simazine residue reductions exhibited by the three methods of chemical addition.

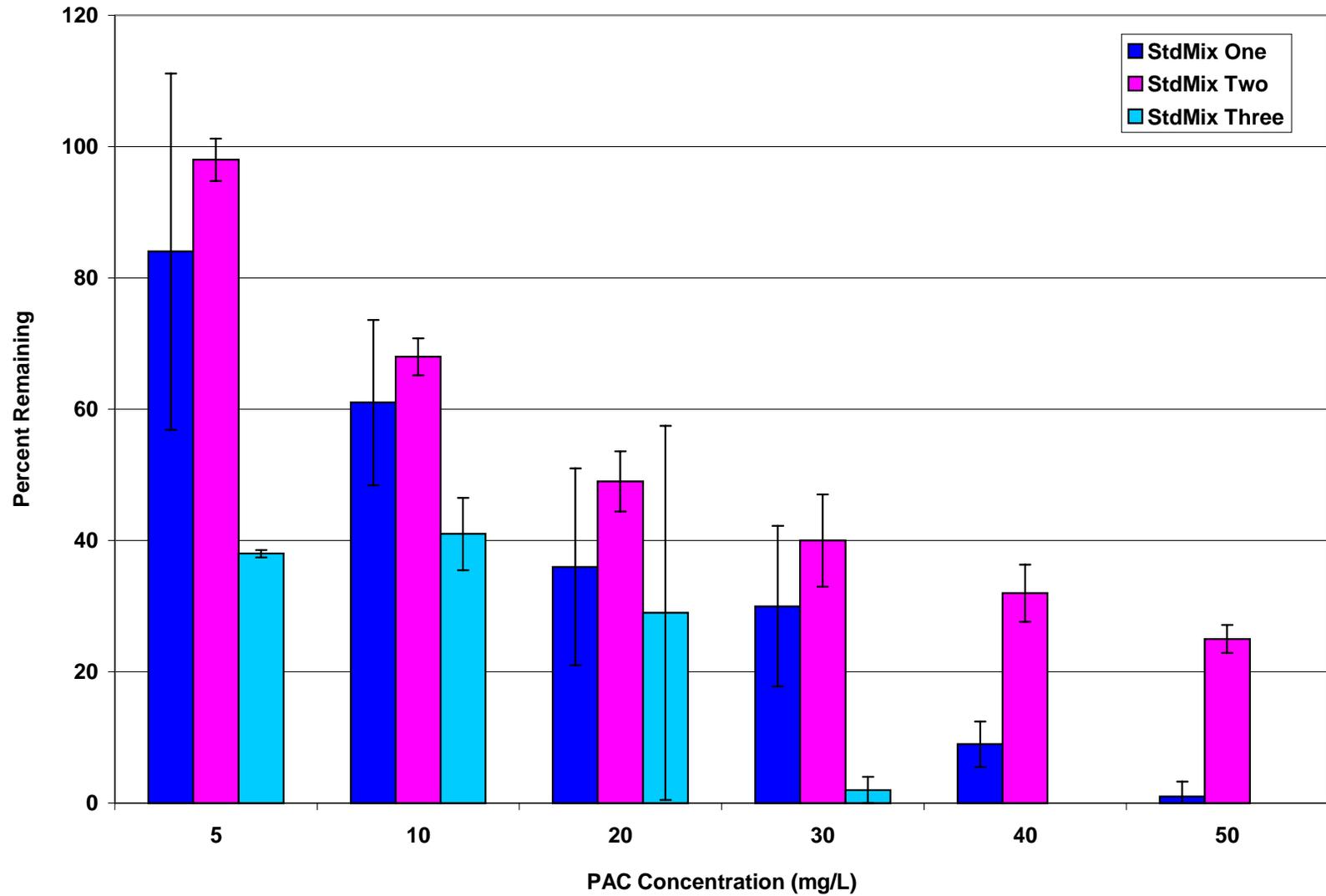


Figure 8. A comparison of the standard mixture alachlor residue reductions exhibited by the three methods of chemical addition.

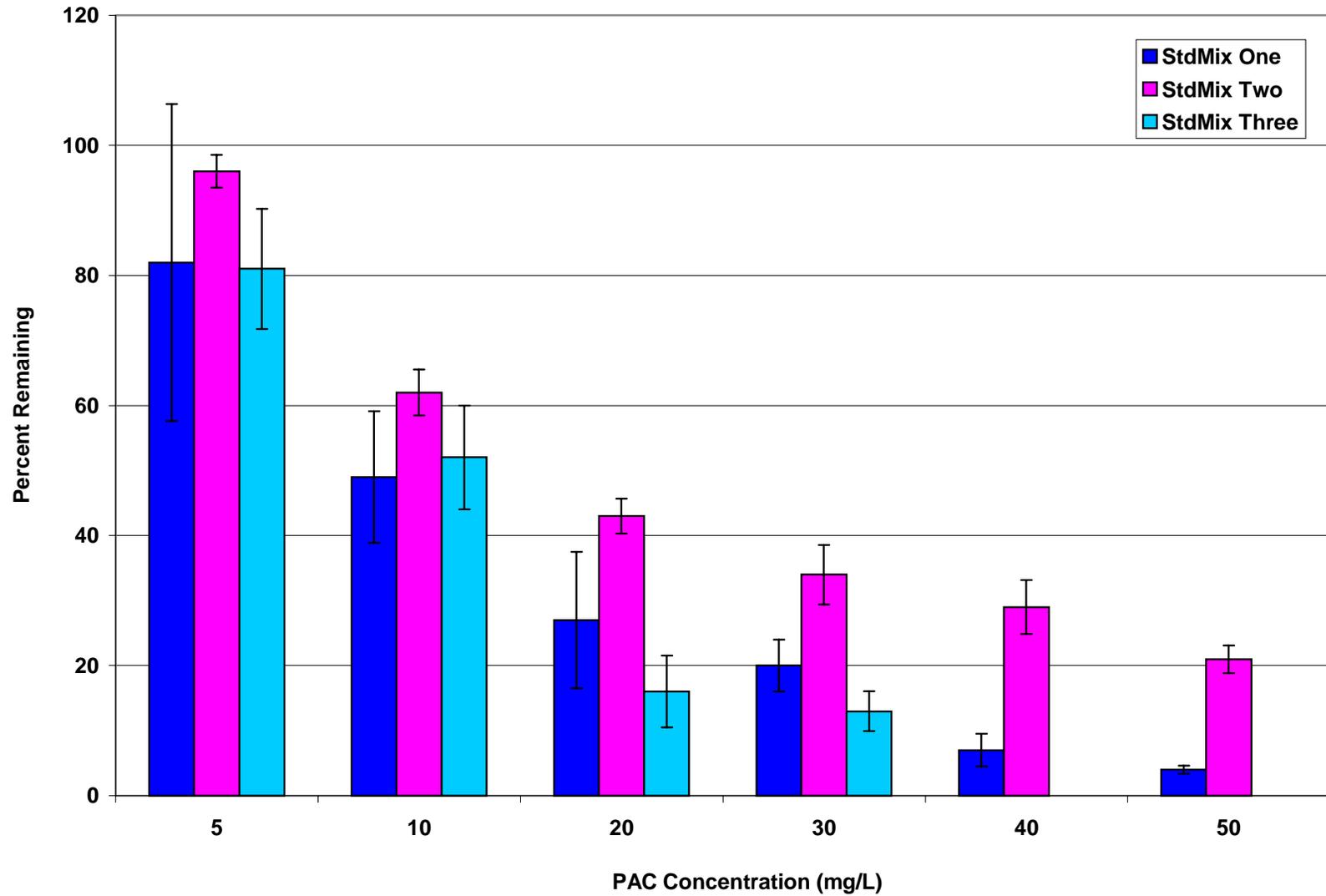


Figure 9. A comparison of the standard mixture atrazine residue reductions exhibited by the three methods of chemical addition.

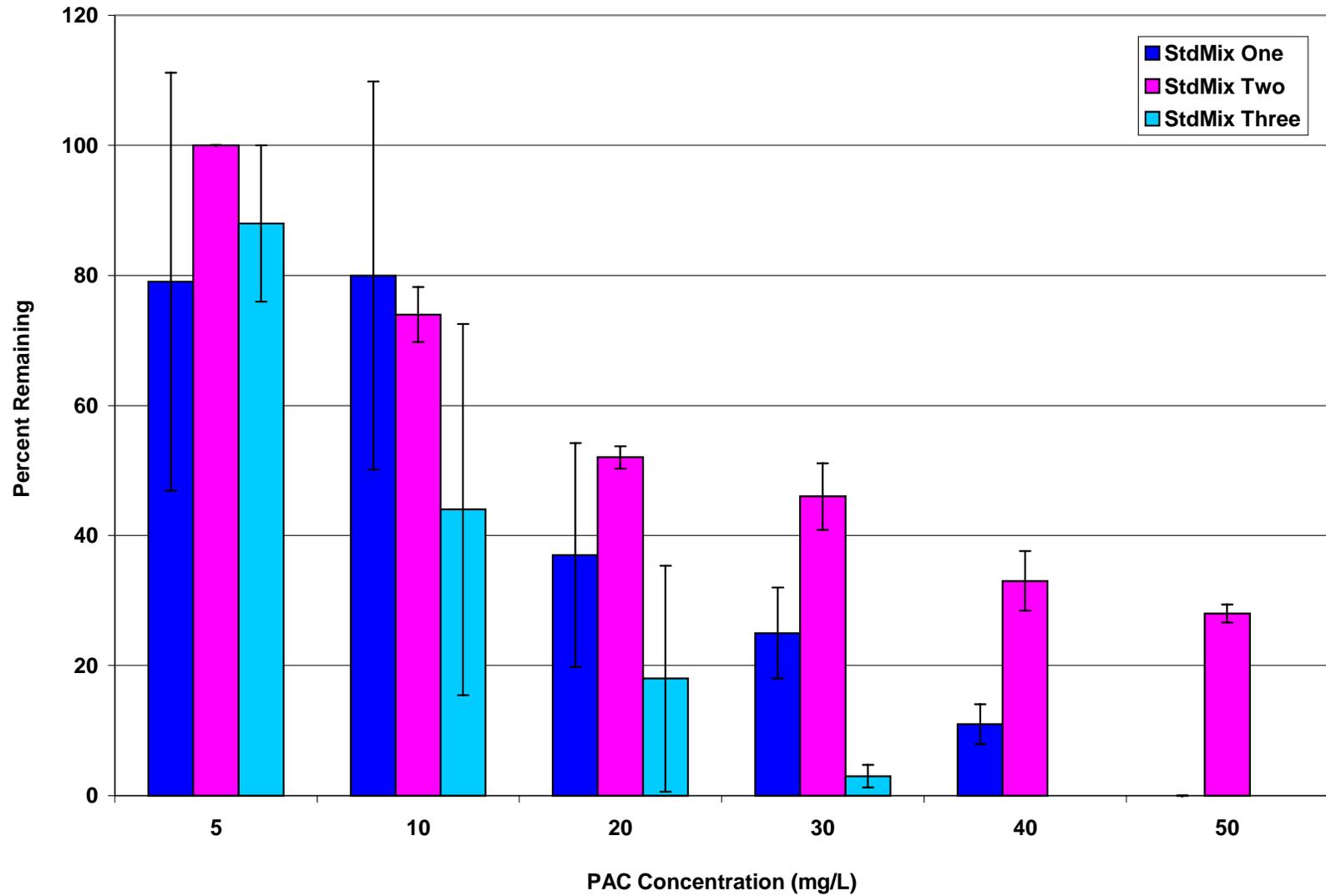


Figure 10. A comparison of the standard mixture metolachlor residue reductions exhibited by the three methods of chemical addition.

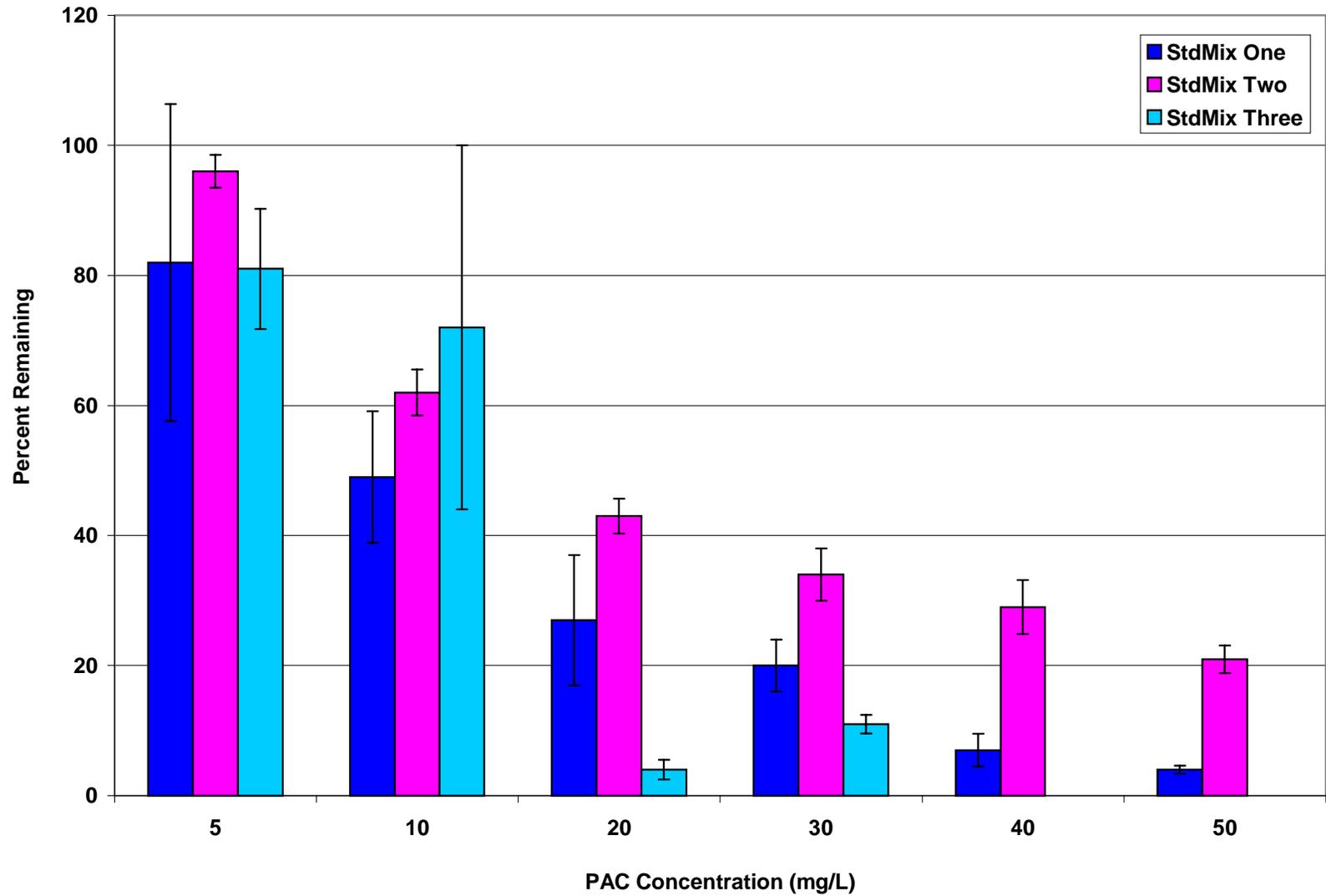


Figure 11. A comparison of the standard mixture simazine residue reductions exhibited by the three methods of chemical addition.

EXECUTIVE SUMMARY

Watershed management often encompasses the characterization of a watershed through risk assessment with consideration of competing resources and the practicality of implementing efforts to maintain a safe and healthy environment within the watershed. Watershed assessment in this study began with identification and quantification of seven pesticides (atrazine, alachlor, chlorpyrifos, chlorothalonil, metolachlor, simazine, and 2,4-D) within surface waters of three rural and two urban watersheds in North Carolina that serve as source for drinking water.

The analysis of sites of suspected contamination helped to pinpoint those areas receiving pesticide residues from runoff and discovered that all seven compounds were present in most of the samples collected from 1999 to 2001. Pesticide residues of rural and urban watersheds were similar in concentrations, although the chief compounds found varied somewhat between the two types of watersheds. Atrazine, simazine, and 2,4-D were found most often and in greater concentrations in rural areas, while urban watersheds exhibited 2,4-D and metolachlor residues at elevated concentrations. Seasonal patterns were observed in rural watersheds and loosely followed in urban detections.

Occasionally, pesticide residues approached and exceeded MCL values, although the majority of detections were well below regulatory levels. However, there was a presence of multiple pesticides (potential synergistic effects) providing for chronic exposure to aquatic organisms. There are limited resources available on these effects that culminate in potential contaminations that are obscured if focus is only on those pesticide detections that exceeded MCL values.

Contribution to watershed management involved the source prevention study that was an innovative approach where several points-of-view were taken into account to design, implement, and verify a remediation effort that focused on the non-point sources of atrazine within a watershed to reduce surface water contamination from runoff containing these residues. Atrazine residues were reduced and occasionally eliminated as a result of the preventative/reduction measures; substitution of less persistent, alternate pesticides or genetically-modified seed for atrazine applications.

Furthermore, drinking water treatment plants and the intakes impounding surface waters to these plants were monitored for the presence of the seven pesticides. Residues of these compounds were found frequently throughout the three years of the analysis of raw and finished water. Concentrations found in finished waters were similar to those values detected in raw water samples, although levels generally remained well below established Maximum Contaminant Levels (MCL) and Health Advisory Levels (HAL). For most samples the treatment processes had little effect on pesticide residue concentrations and pesticide residues found in finished water were similar in concentration to those found in raw water. Therefore, additional remediation was required within the drinking water treatment plant facilities.

Preliminary carbon studies using bottle-point isotherm experiments characterized adsorption of a mixture of four pesticides (atrazine, chlorpyrifos, metolachlor, and simazine) in which most of the chlorpyrifos and metolachlor

(>90 %) residues were reduced with a PAC concentration of 10 mg/L. Comparable adsorptions for atrazine and simazine were achieved 30 mg/L. Carbon contact time studies were performed to evoke a descriptive relationship, other than classical adsorption isotherms, between PAC and pesticides. The one-hour and two-hour carbon contact studies exhibited similar adsorption results in which atrazine and simazine experienced greater removals (75-100%) while chlorpyrifos and metolachlor exhibited less significant reductions (25-60%). The reductions in concentration increased with carbon contact time.

Further carbon studies utilized alum in addition to PAC as treatment methods for reducing pesticide residues in drinking water. Atrazine and metolachlor were most effectively adsorbed in experiments with carbon alone and atrazine residues were reduced to levels below its MCL of 3.0 µg/L. Carbon and alum together also reduced the contaminant levels although longer contact times were required for reductions similar to carbon alone. The adsorptions exhibited when both carbon and alum were added together seemed to proceed slower than in the study without alum. Alum alone was the least effective in lowering the pesticide concentrations and results seemed to indicate that alum interfered with carbon adsorption.

Three procedures were designed to characterize carbon and alum interactions and determine which order these two chemicals could be added in the treatment plant to facilitate a greater degree of adsorption while also comparing carbon addition points and how alum might affect carbon adsorption. With the objective of reducing pesticide residues in water supplies, three procedures involving

carbon added prior to alum, alum added prior to carbon, and alum and carbon added simultaneously were developed.

All three methods exhibited reductions in residue concentrations at a maximum with a PAC concentration of 50 mg/L. The median doses (20 and 30 mg/L) of carbon greatly reduced the pesticide residues in solution and also lowered compound concentrations below respective MCL values. Overall, adsorptions of the pesticides (atrazine, metolachlor, simazine, alachlor, and mixture of these four compounds) were greatest with alum added prior to or briefly following the carbon and least affected by the simultaneous addition of the two chemicals. Although the reaction between alum and carbon when these two components are combined is not fully understood, the results of this study indicated that carbon adsorption sites remained available for greater adsorption of pesticides from solution when the alum and carbon were not added together.

Working with stakeholders in the areas (farmers, county extension, and city representatives) provided a variety of information and resources otherwise unavailable that allowed the foundation of watershed assessment in these select watersheds to take shape. Results of the surface, raw and finished water studies, and source prevention and carbon studies provided an understanding of some of the environmental effects of pesticide usage and the means to develop a management plan to maintain a safe and healthy watershed.

APPENDIX

STEPS FOR ELISA

1. Label test tubes for 4 standards, 1 control, and n samples.
2. Add 200 μL (or 250 μL depending upon pesticide) of the appropriate standard, control, or sample.
3. Add 250 μL of Pesticide Enzyme Conjugate to each tube.
4. Mix the Pesticide Antibody Coupled Paramagnetic Particles thoroughly and add 500 μL to each tube.
5. Vortex for 1 to 2 seconds minimizing foaming.
6. Incubate for 15 minutes (or 30 minutes depending upon pesticide) at room temperature.
7. Separate in the Magnetic Separation Rack for 2 minutes.
8. Decant and gently blot all tubes briefly in a consistent manner.
9. Add 1 mL of Washing Solution to each tube and allow them to remain in the magnetic separation rack unit for 2 minutes.
10. Decant and gently blot all tubes briefly in a consistent manner.
11. Repeat Steps 9 and 10 an additional time.
12. Remove the rack from the separator and add 500 μL of Color Solution to each tube.
13. Vortex for 1 to 2 seconds minimizing foaming.
14. Incubate for 20 minutes at room temperature.
15. Add 500 μL of Stopping Solution to each tube.
16. Add 1 mL of Washing Solution to a test tube. Use as blank in Step 17.

17. Read results with RaPID Analyzer at 450 nm within 15 minutes after adding the Stopping Solution.

STEPS FOR SPE DISK PREPARATION AND EXTRACTION

1. Assemble glass filtration apparatus to accommodate the 47 mm C18 Empore™ disk.
2. Condition the disk with 10 mL of ethyl acetate pulling the solvent through by vacuum until disk is dry, allowing vacuum to continue pulling for 2 minutes.
3. Remove vacuum, add 10 mL of methanol.
4. Pull a small volume through with the vacuum and leaving a thin film on the surface of the disk.
5. Remove vacuum, add 10 mL of deionized water repeating step 4.
6. Remove vacuum, add 10 mL more of deionized water, repeating step 4.
7. Disk is now appropriately conditioned and ready for sample.
8. Add approximately 3 mL of methanol to sample then add sample to extraction manifold pulling with vacuum and taking care to not let the disk go dry.
9. Once the whole of the sample has passed through the disk allow vacuum to continue pulling for 5 minutes to dry the disk.
10. Transfer the disk to a test tube with 15 mL of ethyl acetate.
11. Place tubes containing disks and solvent on shaker table at medium speed.
12. Remove tubes after 20 minutes.
13. Decant solvent into a second tube containing approximately 3 grams of anhydrous sodium sulfate.
14. Transfer dried solvent into a third calibrated tube.
15. Add 5 mL of ethyl acetate to first tube still containing disk and place on shaker table once again at medium speed.

16. Remove tubes after 5 minutes and repeat steps 13 and 14.
17. Place final calibrated tubes with dried solvent now containing extracted analytes under a nitrogen evaporator (Meyer N-Evap, Organomation Associates, Inc., Berlin, Massachusetts).
18. Create a steady stream of nitrogen and hot water bath of approximate 30°C to evaporate solvent and concentrate pesticide residues.
19. Once sample has been reduced to 1 mL this volume is transferred to a 2 mL GC vial and capped to await analysis.

Pesticide	Class	Toxicity Class	Description	Use	MCL/*HAL µg/L	ELISA MDL µg/L	H2O Sol mg/L	Crops
Alachlor	Herbicide	III	Slightly Toxic	Restricted	2.0	0.05	242.0	corn, soybeans, cotton, ornamentals, turf
Atrazine	Herbicide	III	Slightly Toxic	Restricted	3.0	0.05	215.7	corn, sorghum, non-cropland, rangeland, turf
Chlorothalonil	Fungicide	II	Moderately Toxic	General	*150.0	0.07	0.6	fruits, vegetables, turf, ornamentals, soybeans
Chlorpyrifos	Insecticide	II	Moderately Toxic	General	*20.0	0.10	350.6	cotton, soybeans, corn, fruit trees, turf
Metolachlor	Herbicide	III	Slightly Toxic	General/ Restricted	*70.0	0.05	530.0	corn, cotton, soybeans, fruits, nuts, ornamentals
Simazine	Herbicide	IV	Practically Non-Toxic	General	4.0	0.03	5.0	aquatic weeds, non-cropland, turf, fruit crops, corn
2,4-D	Herbicide	III	Slightly Toxic	General	70.0	0.70	900.0	lawns, orchards, rice, corn, grains

Table 1. Descriptive properties of the seven pesticides involved in the study, including classification, toxicity class and descriptions, regulatory values, method detection limits of ELISA, water solubility values and common recipients of these pesticide applications

Year	Sampling Date	City	Type	Alachlor	Atrazine	Chlorothalonil	Chlorpyrifos	Metolachlor	Simazine	2,4-D
1999	3/10--9/30	Burlington	Rural		X		X		X	X
1999	4/1--12/14	Greensboro	Urban		X	X	X		X	X
1999	4/27--6/22	High Point	Urban		X	X	X		X	X
2000	3/13--10/23	Burlington	Rural	X	X		X	X ^a	X	X
2000	2/18--10/19	Greensboro	Urban		X	X	X	X ^b	X	X
2000	4/13--11/10	High Point	Urban		X	X	X	X ^c	X	X
2001	3/16--9/24	Burlington	Rural		X			X		
2001	5/2--9/7	Raleigh	Rural		X			X		
2001	3/13--9/20	Greensboro	Urban	X	X			X	X	X
2001	3/13--7/26	High Point	Urban	X	X			X	X	X

^a sampled from 6/12-10/23

^b sampled from 9/19-10/19

^c sampled from 10/19-11/10

Table 2. Pesticides analyzed in rural and urban watersheds from 1999 to 2001.

Procedure One (1): Carbon added at the intake
Procedure Two (2): Carbon added at start of rapid-mix
Procedure Three (3): Carbon added shortly after start of rapid-mix

Alum: added at the start of rapid-mix

Samples removed at
this point



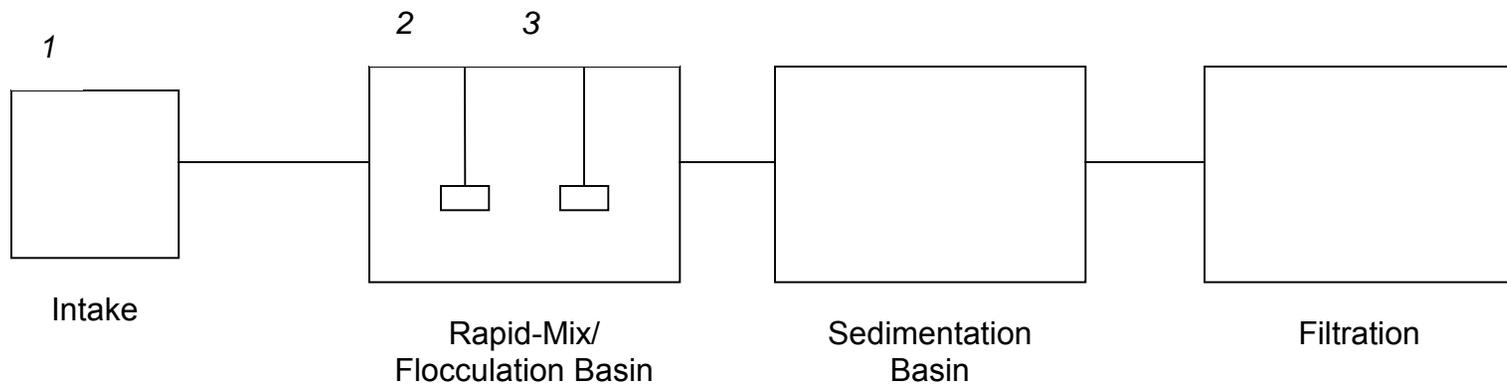


Figure 1. Schematic of partial treatment train for J.D. Mackintosh Drinking Water Treatment Plant showing the points of chemical addition and sample removal utilized in the carbon adsorption and alum studies.