12-2003

Determination of Residential-Use Turf Pesticides in Surface and Ground Water by HPLC/DAD

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DETERMINATION OF RESIDENTIAL – USE TURF PESTICIDES IN SURFACE AND GROUND WATER BY HPLC/DAD

By

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B.S. Hefei United University, 1984

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Food Science and Human Nutrition)

The Graduate School

The University of Maine

December, 2003

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By Danyun Zhu

Thesis Co-Advisor: Dr. Rodney J. Bushway and Dr. L. Brian Perkins

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
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A simple, relatively fast, and efficient method has been developed for the simultaneous detection of residual levels of the pesticides dithiopyr, fenoxaprop-P-ethyl, halofenozide, and oryzalin in surface and ground water. This method involves solid phase (SPE) extraction/clean-up of these pesticides from water, followed by detection and quantification by a high performance liquid chromatograph (HPLC) equipped with a photo diode array detector (DAD). The recoveries for dithiopyr, fenoxaprop-P-ethyl, halofenozide, and oryzalin were performed by fortifying ground water from 0.1 ppb to 100 ppb, and surface water from 0.2 ppb to 100 ppb. For ground water, percent recoveries ranged from 89 to 122 with an average percent coefficient of variation (%CV) of 8.1 for dithiopyr, 82 to 94 with an average %CV of 6.6 for fenoxaprop-P-ethyl, 98 to 115 with an average %CV of 6.9 for halofenozide, and 95 to 110 with an average %CV of 5.7 for oryzalin. For surface water, percent recoveries ranged from 82 to 93 with an average %CV of 5.5 for dithiopyr, 78 to 98 with an average %CV of 4.8 for fenoxaprop-P-ethyl, 91 to 102 with an average %CV of 3.2 for halofenozide, and 91 to 100 with an

average %CV of 5.6 for oryzalin. The limit of quantitation for dithiopyr, fenoxaprop-P-ethyl, halofenozide, and oryzalin were 0.50 ppb, 0.15 ppb, 0.10 ppb, and 0.10 ppb for ground water; 0.50 ppb, 0.30 ppb, 0.20 ppb, and 0.20 ppb for surface water. Reproducibility studies showed that for ground water, %CVs ranged from 2.6 to 25 for dithiopyr, 2.5 to 24 for fenoxaprop-P-ethyl, 1.0 to 9.3 for halofenozide, and 2.0 to 14 for oryzalin. For surface water, the %CVs ranged from 2.2 to 17 for dithopyr, 2.3 to 12 for fenoxaprop-P-ethyl, 0.80 to 9.9 for halofenozide, and 3.9 to 12 for oryzalin.

ACKNOWLEDGMENTS

First, I would like to express my sincere gratitude and deep appreciation to my advisors, Dr. Rodney J. Bushway and Dr. L. Brian Perkins, for their encouragement, guidance and direction throughout my graduate career and during the completion of this thesis, as well as their enduring patience and advice. Their help smoothed my work very much and their immense patience was essential to the completion of this thesis.

Thanks also to the member of my thesis committee, Dr. Alfred A. Bushway, for his willingness to serve on my thesis committee, for his counsel and assistance. His advise, comments, and suggestions provided significant support and impact on the overall effectiveness of this thesis.

I sincerely thank Dr. Mary Ellen Camire and Dr. Denise I. Skonberg for their support and encouragement during my graduate studies. Thanks also to Kelly Guthrie for her friendly help. She was always there to answer any questions.

I also would like to take this opportunity to extend my thanks to each one of my friends, here in the U.S. and back home, for their truthful and sincere helping me get through two years of graduate school.

Finally, I would like to thank my family for their understanding and support throughout my graduate years.

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LIST OF ABBREVIATIONS

AI	Active ingredient
BCF	Bioconcentration vector
CV	Coefficient of variation
DAD	Diode array detector
DT_{50}	Chemical half-life in water (days)
EC_{50}	Effective concentration at which the desired response is present for 50 % of the population
ECD	Electron capture detector
GC	Gas chromatography
H	Henry's Law Constant
HPLC	High performance liquid chromatography
Koc/K_d	Sorption coefficient
K_{ow}	Octanol/water partition coefficient
LC_{50}	Lethal concentration of a compound for 50 % of a test population
LD_{50}	Lethal dose of a compound for 50 % of a test population
LLE	Liquid – liquid extraction
LOD	Limit of detection
LOQ	Limit of quantitation
MRL	Limit of maximum residue
MS	Mass spectrometry
MTBE	Methyl tert butyl ether
NPD	Nitrogen – phosphorous detector
PAN	Pesticide Action Network
PPB	Parts per billion
PPM	Parts per million
R^2	Coefficient of determination
S	Solubility
SPE	Solid phase extraction
$T_{1/2}$	Half – life
THF	Tetrahydrofuran
UV	Ultraviolet

INTRODUCTION

As urban areas expand, turf areas have been increased rapidly throughout the United States since the 1960s, and now they cover more than 30 million acres, including 50 million home lawns, golf courses, parks, athletic fields, cemeteries, sod farms, and other sites (Walston et al., 2001). Color, uniformity, and density of the turfgrass will be affected adversely by incursions of weeds, disease, and insects. The public demand for high quality and uniform turf often requires the use of intensive management strategies to maximize pest control and nutrient availability (Walston et al., 2001). The use of pesticides has significantly contributed to the overall aesthetic quality of turfgrasses.

The major concern for the impact of pesticides on the environment is their potential entrance into drinking water sources which is facilitated by movement in surface water and groundwater from the treated site (Gilliom et al., 1999). Studies in urban watersheds from the U.S. Geological Survey National Water Quality Assessment indicated widespread presence of pesticides typically used in lawns, gardens, and golf courses (USGS, 1999). Other studies also detected many pesticides in surface and ground waters on or near golf courses, including nine pesticides that exceeded maximum allowable concentrations based on protection of aquatic species (Cohen et al, 1999).

Winters in the Maine can be long and cold. Soils are generally frozen during this period (December-March). Significant runoff can occur in the winter due to snowmelt or rainfall on frozen soils, which can contain and transport unused or unbound pesticides from turfgrass despite the fact that no compounds were applied in the winter (Easton,

2003). Furthermore when the temperature is below freezing, the time needed to break down a pesticide increases.

Because of these factors, information is needed concerning pesticides' pollution potential, its fate in agricultural runoff and other aquatic environments. Analytical methodology is, therefore, needed for the determination of pesticides in surface and ground water.

The purpose of this thesis was to develop a method to reduce sample handing while providing reproducible and sensitivity results for the determination of pesticides in surface and ground water using a high performance liquid chromatograph (HPLC) equipped with a photo diode array detector (DAD). To obtain efficient pre-concentration with good precision and recovery, a Styrene-divinylbenzene copolymer was selected as the solid phase for the extraction of pesticides from water. Finally, the proposed method was validated. The parameters involved in the validation were linearity, limits of detection (LOD) and quantification (LOQ), precision (reproducibility), and recovery. The pesticides were dithiopyr, fenoxaprop-P-ethyl, halofenozide, and oryzalin. These pesticides are commonly used on turfgrasses in Maine.

LITERATURE REVIEW

Pesticides Runoff and Leaching

Runoff and leaching are two major ways that pesticides can reach surface and ground water. Runoff will occur if the chemical does not adsorb onto soil. Leaching will occur if the chemical is weakly adsorbed by soil and can easily move through the soil profile. Amounts of leaching and runoff are largely affected by two major groups factors – compound related factors and environmental factors.

Compound Related Factors

Initial levels. The larger the initial levels, the greater the potential for runoff and leaching. Larger initial levels of chemicals (e.g., > 2-3 lb/A active ingredient) generally take more time to break down than smaller levels (e.g., < 2 lb/A a.i.) (Deubert, 1990). Precipitation or sprinkler irrigation may wash more material into the ground or surface water after the application of a heavy dose as compared to a light dose.

Solubility in water. Solubility is a measure of the amount of chemical that can dissolve in water. Water solubility is an important factor in determining a pesticide's tendency to move through the soil profile with infiltrating water, and over the soil with runoff. As a rule of thumb, highly water-soluble pesticides leach or runoff faster than the less-soluble ones. Pesticides with > 30 ppm solubility may be considered mobile in sandy soil when their persistence is high and their adsorption is low (Deubert, 1990). Polar

chemicals tend to dissolve in water and non-polar chemicals tend to partition in non-polar organisms or soil since these are made up of molecules comprising of non-polar C-H bonds. Salts and acids tend to remain dissolved in water until degraded through photolysis or hydrolysis. Esters will often adsorb to the suspended matter in water, and precipitate to the sediments. Once in the sediments, esters can remain adsorbed to soil particles or be degraded through microbial metabolism. Highly acidic or alkaline waters can chemically alter an herbicide and change its behavior in water. The average pH oftypical surface waters is between five and nine (Hutzinger 1981).

Persistence. Persistence is reported as half-life, i.e., the time it takes for 50% of a given substance to break down. Compounds with a half-life of > 3-4 months are considered persistent, while those with a half-life of < 1 month are considered non-persistent (Deubert, 1990). Chemicals are usually more persistent in dry, compacted, cold soil than in moist, warm, well-aerated soil. Dry spells after an application may extend the persistence of a chemical in the ground (Deubert, 1990).

Adsorption: Adsorption describes the tendancy of a pesticide to bind soil particles and is reported as the adsorption coefficient (Koc), whereby Koc < 300-500 is considered low adsorption. Adsorbed chemicals do not move with the soil water but remain adsorbed while the water moves towards the ground or surface water (Van Es, 1990). A polar pesticide is very water soluble and tends not to be adsorbed onto soil. Pesticides that are non-polar tend to leave water and be adsorbed onto soil especially soils contain high

concentrations of non-polar carbon material. Table 1 lists where a chemical is likely to end up depending on its Koc value and its persistence in the environment.

Table 1. Factors Affecting the Pathway of Potential Water Contamination (Rao et al., 1983)

Koc	Half-life	Pathway of loss	Potential contaminating
Low	Long	Leaching	Ground water
Low	Short	Leaching	Ground water*
High	Long	Runoff	Surface water
High	Short	Runoff	Surface water*

* if only heavy rains or irrigation occur soon after pesticide application

Environmental Factors

Interception by leaves and thatch. Leaves and thatch are rich in organic carbon. High organic carbon can increase sorption of pesticides and increase microbial degradation, and therefore attenuate movement of pesticides in soil (OSU, 2003).

Photodegradation. In the atmosphere, there are two major degradation pathways that occur. The first is photochemical reactions caused by sunlight and the second is free radical reactions. The products formed may or may not be more toxic than the parent chemical. Sunlight may break down a chemical deposited on a leaf surface. Photochemical reactions can take place in air or water when sunlight is present.

Precipitation. Precipitation up to several days after an application washes residues off the leaves and moves them into the ground or surface water. This can be significant for soluble chemicals (> 30 ppm) in sandy soil containing small amounts of organic matter. The farther apart the rainfall events and the less precipitation, the less the potential for leaching (Deubert, 1990).

Topography (slope). The topography of an area may affect the distribution of a chemical through surface runoff, provided the conditions are favorable. Dry formulations as well as residues adsorbed on soil particles are affected. Residues may accumulate in low spots, thus increasing the residue load of an area. This can be significant where the groundwater table is high (1-2 ft.) (Deubert, 1990).

Soil properties. Soil properties are also important, as each soil has a characteristic ability to adsorb pesticides. Soils high in clay or organic matter adsorb pesticides better than sandy soils low in organic matter. In addition, organic matter serves as nutrient substrate for microorganisms active in the breakdown of residues. The more organic matter there is, the more adsorption and breakdown occur, and the likelihood of leaching is greatly reduced (Deubert, 1990). Soil structure determines the infiltration rate. Rapidly infiltrating water may move pesticides on the surface deeper into the soil as they have less time for sorption. Soils that weakly adsorb pesticides and have a rapid infiltration rate are more sensitive to groundwater pollution than soils that strongly adsorb pesticides and have a slow infiltration rate. Soil sorption and infiltration rate also determine pesticide loss in runoff. Soils with slow infiltration rate may be more prone to runoff, as

more water will remain on the surface. Pesticides adsorbed to soil will not be lost to runoff. However, if runoff results in soil erosion, pesticides adsorbed to surface soil will also move with runoff. Soil texture affects the movement of water as the carrier of the pesticide, and indirectly the adsorption of the chemical on soil particles. Sandy soils retain less water and pesticides than clay soils or organic soils. The heavier the soil, the lower the potential for leaching. Soil moisture is essential for soil microorganisms activity in the breakdown of pesticide residues. Obviously, residues are more persistent in dry than in moist soils.

Root density. The root zone is the most active part of the topsoil for the break down of pesticide residues due to aeration and activity of microorganisms. The healthier and the denser the root system, the more break down takes place and the lower the potential is for leaching.

Table 2 summarizes the factors that contribute to the potential of ground and surface water contamination.

Table 2. Factors Influencing Water Contamination (Modified from Kenna, 1995)

Factor	Values
Water solubility	> 300 ppm
Soil adsorption coefficient (Koc)	< 300 - 500
Hydrolysis (half - life)	> 25 weeks
Photolysis (half - life)	> 1 week
Field dissipation (half - life)	> 3 weeks
Aerobic soil metabolism (half - life)	> 3 weeks
Anaerobic soil metabolism (half - life)	> 3 weeks

Selected Turfgrass Pesticides

The turfgrass pesticides are chemicals that are applied to lawns and gardens to control weeds, bugs, fungus and other unwanted living organisms. Some commonly used turfgrass pesticides in Maine include dithiopyr, fenoxaprop-P-ethyl, halofenozide, and oryzalin. The following sections represent a review of the chemical and usage, fate and behavior, toxicity, and analytical methods of these turfgrass pesticides.

Chemical and Usage

Dithiopyr. The scientific name of dithiopyr (CAS # 97886-45-8) is S,S-Dimethyl-2-(difluoromethyl)-4-(2methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarbothioic acid (Figure 1). The trade name is Dimension. It is also known by the development code number MON 7200. The major physical/chemical properties are listed in Table 3.

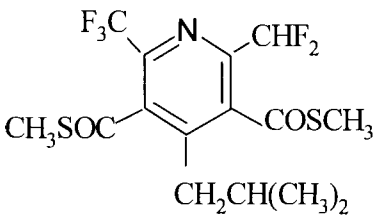
Dithiopyr is a member of pyridine family. It was introduced by Monsanto and subsequently sold to Rohm and Haas in 1994. It is a pre-emergence and early post-emergence herbicide used to control of annual grass and selected broad-leaved weeds in turf at 0.25 to 1.0 lb/a. Its mode of action is to inhibit cell division by disrupting spindle microtubule formation (British Crop Protection Council, 2000).

Fenoxaprop-P-ethyl. Fenoxaprop-P-ethyl (CAS # 71283-80-2) is the proposed common name for (+)-ethyl 2-(4-(6-chloro-2-benzoxazolyloxy)-phenoxy)-propanoate (Figure 1). The trade names are Acclaim Super and Excel Super. It is also known by the Hoechst code number HOE 046360. Its major physical/chemical properties are listed in Table 3. Fenoxaprop-P-ethyl is a member of the phenoxy chemical group. It was discovered by H.P. Huff et al. (1989) and introduced by Hoechst AG (now AgrEvo GmbH). The product is used for post-emergence control of annual and perennial grass weeds in potatoes, beans, beets, vegetables, peanuts, flax, oilseed rape, and cotton; and (when applied with the herbicide Safener mefenpyr-diethyl) annual and perennial grass weeds and wild oats in wheat, rye, triticale, and in some barley varieties (British Crop Protection Council, 2000). Fenoxaprop-P-ethyl is a selective and systemic herbicide primarily absorbed through the leaves of plants and is translocated in the xylem and phloem, where it is changed to the free phenoxy acid to inhibit the biosynthesis of fatty acid (Food and EPA, 1985).

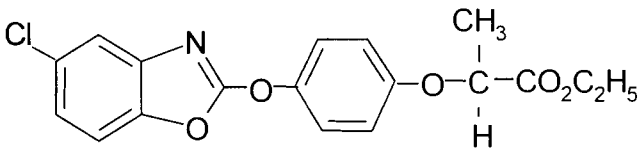
Halofenozide. Halofenozide (CAS # 112226-61-6) is the proposed common name for 4-chlorobenzoic acid 2-benzoyl-2-(1,1-dimethylethyl)hydrazide (Figure 1). The trade name is Mach 2. It is also known by the development code number RH-0345. The major

physical/chemical properties are listed in Table 3. Halofenozide is a member of the new diacylhydrazine class of insecticides. It is a joint venture between Rohm and Haas and Americal Cyanamid, and is registered for control of Coleoptera and Lepidoptera in turf and ornamentals at 0.5-2.0 lb/a (British Crop Protection Council, 2000). Halofenozide is a systemic, ingested insecticide. Its mode of action is to inhibit insect by binding the receptor site of the hormone ecdysone. The result is premature molting, resulting in a loss of hemolymph and molting fluid, which causes desiccation, and death of the larvae (Gardner et al., 2001).

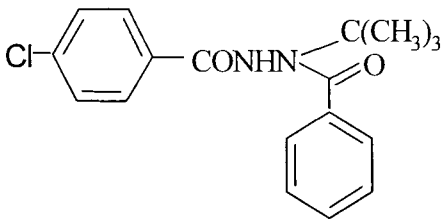
Oryzalin. Oryzalin (CAS # 19044-88-3) is the proposed name for 4-(dipropylamino)-3,5-dinitrobenzenesulfonamide (Figure 1). It is also known by the development code number EL-119 and is available in aqueous suspension, dry flowable, and wettable powder formulations. The major physical/chemical properties are listed in Table 3. Oryzalin is a dinitroaniline sulfonamide herbicide. It was first reported by Gramlich et al. (1969), introduced in Bulgaria by Eli Lilly & Co. (now DowElanco) in 1973, and was first registered by the U.S. Environmental Protection Agency (EPA) in 1974. Oryzalin is a selective, pre-emergence, surface-applied herbicide used for control of annual grasses and broadleaf weeds in fruit trees, nut trees, vineyards, established bermudagrass turf, and established ornamentals. It inhibits the growth of germinating weed seeds by blocking cell division in the meristems (Meister, 1992).



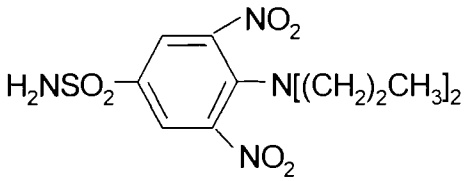
Dithiopyr



Fenoxaprop-P-ethyl



Halofenozide



Oryzalin

Figure 1. The Chemical Structures of Four Pesticides

Table 3. The Major Physical Chemical Properties of Dithiopyr, Fenoxaprop-P-ethyl, Halofenozide, and Oryzalin

Name	Mol. WT.	Form	M.P.	V.P.	Solubility	Stability	PH	Koc
Dithiopyr	401.4	Colorless crystals	65 °C	0.53 mPa (25 °C)	1.4 ppm (water, 20 °C)	Stable (normal storage conditions)	4.1 (aqueous solution)	1920
Fenoxaprop-P-ethyl	361.8	White odorless solid	89-91 °C	5.3×10^{-4} mPa (20 °C)	0.7 ppm (water, pH 5.8, 20 °C)	Not light- sensitive	7 - 9 (emulsion in water)	No data
Halofenozide	330.8	White crystalline powder	> 200 °C	$< 1.3 \times 10^{-2}$ mPa (20 °C)	12.3 ppm (water)	Stable to heat, light, water	7 -10 (2 % dispersion)	1.78
Oryzalin	346.4	Yellow-orange crystals	141-142 °C	< 0.0013 mPa (25 °C)	2.6 ppm (pH 7, 25 °C)	Stable (normal storage conditions)	No data	600

Fate and Behavior

When a pesticide is used in the environment, it becomes distributed among four major compartments: water, air, soil, and biota (living organisms). The fraction of the chemical that will move into each compartment is governed by the physio-chemical properties of that chemical (Linde, 1994). Figure 2 illustrates the flow for the major routs of travel for pesticides in the environment. Pesticides are distributed in the environment by physical processes such as sedimentation, adsorption, and volatilization. They can then be degraded by chemical and / or biological processes. Chemical processes generally occur in water or the atmosphere and follow one of four reactions: oxidation, reduction, hydrolysis, and photolysis. Biological mechanisms in soil and living organisms utilize oxidation, reduction, hydrolysis and conjugation to degrade chemicals (Linde, 1994). Chemicals that have high solubility will remain in water. A pesticide reacts with water to form degradation products that can be distributed in the environment. Chemicals that are non-polar tend to be pushed out of water and onto soils which contain non-polar carbon material. Bioconcentration factor (BCF) is an indicator of how much a chemical will accumulate in living organisms (linde, 1994). Polar chemicals are soluble in water (polar) and not very soluble in tissues (non-polar), whereas non-polar chemicals will accumulate in fatty tissues. Henry's law constant (H') is a measure of the concentration of a chemical in air over its concentration in water (Linde, 1994). A pesticide with a high H' will volatilize from water into air and be distributed over a large area. Chemicals with a low H' tend to persist in water and may be adsorbed onto soil. Pesticides with high vapor pressures may become environmental problems because they can volatilize and disperse over a large area.

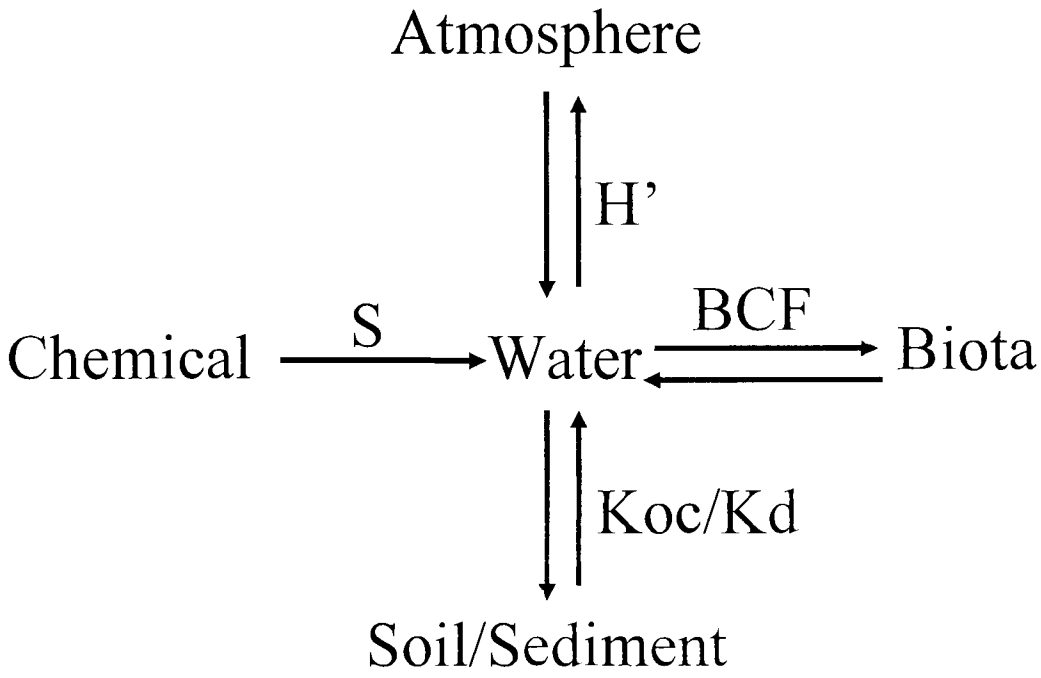


Figure 2. Fate of Pesticides in the Environment

Concerns associated with pesticides use include environmental contamination and nonselectivity. Contamination of the water supply can have toxic effects on plants and wildlife in the area of administration. Contamination of the food being produced can have widespread effects, as well. Pesticides may pose threats to nontarget organisms. Whether these nontarget organisms are humans, wildlife, or plant life; the use of pesticides may pose a threat to the environment that should be considered carefully.

Dithiopyr. When dithiopyr is released to the sod and soil surface, it metabolizes rapidly by photodegradation and volatilization. Upon entry into the root media, biotic and abiotic mediated degradation occurs at a much slower rate compared to loss by volatilization. When exiting the golf course greens in the solution, the compound can be further degraded by UV light, as well as by biological and abiotic mediated processes (Hong, 1996). The half-life in soil is 17-61 days depending on the formulation type. The major soil metabolites are the di-acid, the normal mono-acid and the reverse mono-acid. These metabolites, dissipate almost completely within one year. (British Crop Protection Council, 2000). When dithiopyr is fed to rats, it is rapidly absorbed, extensively metabolized and rapidly excreted. Transformation of dithiopyr by rat liver enzymes "in vitro" produces the monoacids as the predominant metabolites (Feng, 1991). The low water solubility (1.38 ppm), high octanol-water partition coefficient (Kow = 56,250), and organic carbon partition coefficient (Koc = 1920) suggest a high potential of dithiopyr retention within the thatch, mat, and surface soil (Schleicher, 1995). Modeling results and calculations (based upon field studies) performed by the Department of Health

(NYSDEC, 1993) indicate that groundwater concentrations of dithiopyr and its metabolites could approach or exceed the potential groundwater standard of 25 ppm (dithiopyr) and 50 ppm (each metabolite).

Fenoxaprop-P-ethyl. Fenoxaprop-P-ethyl is stable for 90 days at 50 °C. It is not sensitive to light, but can be decomposed by acids and alkalis. At 20 °C, the DT 50 > 1000 days at pH 5, 100 days at pH 7, and 2.4 days at pH 9 (British Crop Protection Council, 2000). When fenoxaprop-P-ethyl is released to the soil, it breaks down rapidly to the free acid, which is subsequently degraded by 90% within 13 to 38 days with partial mineralisation can also taking place. Studies show that parent compounds and major metabolites are unlikely to leach from soil (Food & EPA, 1985). No data has been submitted for the behaviour of fenoxaprop-P-ethyl in water, therefore, extrapolation from the studies on fenoxaprop-P-ethyl should be made. The metabolism and degradation of fenoxaprop-P-ethyl in plants is first hydrolyzed to 2-(4-(6-chloro-2-benzoxazoloxy)-phenoxy)-propionic acid 'B' HOE 053022. Fenoxaprop-P-ethyl also hydrolyzes to the D+ form of this acid 'P' HOE 088406. In wheat these acids undergo cleavage of the benzoxazolyloxy-linkage to form 6-chloro-2,3-dihidro-benzoxazol-2-one HOE 054014. Further degradation takes place to form polar conjugates and bound residues (Food & EPA, 1985). When fenoxaprop-P-ethyl is fed to rats, it is rapidly adsorbed and excreted. The metabolism of fenoxaprop-P-ethyl proceeds via identical pathways to those determined for the racemate (Food & EPA, 1985).

Halofenozide. Halofenozide is stable to heat, light, and water. The hydrolysis DT 50 is 310 days at pH 5, 481 days at pH 7, and 226 days at pH 9. When halofenozide is applied to soil, the half-life, under aerobic laboratory conditions is 68-72 days in silt loam, 653-818 days in sandy loam; soil dissipation half-life is 46-267 day in the field; turf half-life is 3-7 days; the half-life for soil photolysis is 129 days. When halofenozide is released to surface water, the pond water photolysis half-life is 10 days (British Crop Protection Council, 2000). According to the PAN Pesticides Database, halofenozide has a related high water solubility (12.3 ppm) with the hydrolysis half-life of 30 days. Aerobic soil half-life is 218.9 days, anaerobic soil half-life is 60 days, the adsorption coefficient (Koc) is 1.78. Therefore halofenozide has the potential to contaminate water. No data has been found for the fate behaviour of halofenozide in animals.

Oryzalin. When oryzalin is released to the atmosphere, it will degrade rapidly in the vapor-phase by reacting with photochemically produced hydroxyl radicals (half-life of about 3.7 hr) (Spectrum Laboratories). When released to soil or water, oryzalin may degrade through microbial degradation and photodecomposition. Oryzalin has a water solubility of 2.5 ug/ml, and it does not have a strong tendency to adsorb to soil particles (USDA, 1990). These properties indicate a potential for offsite movement by runoff and percolation. It leaches downward to a limited extent with rainfall (WSSA, 1989) and has a moderate potential to contaminate groundwater (USDA, 1990). Its soil half – life is estimated to be 20 days (USDA, 1990). Microbial degradation may be responsible for the breakdown of oryzalin in soils. It is subject to photodecomposition, but not volatilization at the soil surface (WSSA, 1989). Oryzalin has a low solubility in water. No hydrolysis of

oryzalin was observed at pH 5, 7, and 9 (WSDOT, 1993). It has a high potential of runoff (Koc = 600 cm^3/g, $T_{1/2}$ = 42 day) and to contaminate surface water (Guo, 2000). Plant metabolism of oryzalin is minimal. Unmetabolized oryzalin is rarely detected (WSDOT, 1993). When used at the recommended level, damage to plants in the following year is not expected (The Royal Society of Chemistry, 1983). When it was administered to male rats, 40% of the dose was excreted in the urine and 40% in the feces within 3 days. Similar results were obtained from tests with rabbits, a 400 pound steer, and with Rhesus monkeys (USEPA, 1987).

Toxicity

Dithiopyr. Dithiopyr has low acute mammalian toxicity following oral, dermal or inhalation exposure. The toxicity category established by WHO is III, which means the acute toxicity rating is slightly toxic. The summary of acute toxicity data is listed in Table 4. Repeated exposure to dithiopyr may cause kidney, liver, blood, and adrenal effects, as well as thyroid damage. Subchronic and chronic exposure produces primarily liver and kidney toxicity. Dithiopyr did not produce any tumors in long-term animal studies. No birth defects were observed in rabbit and rat given dithiopyr during pregnancy (Dow AgroSciences Inc., 2001). Dithiopyr is considered toxic to bees and fish, and somewhat toxic to aquatic invertebrates. Dithiopyr shows a slight acute toxic to birds but no chronic toxicity. Bio-concentration data is not available (Dow AgroSciences Inc., 2001). Dithiopyr is not genotoxic or oncogenic and does not interfere with normal reproduction and development. (Ward, 1993)

Table 4. Acute Toxicity Data for Dithiopyr (Dow AgroSciences Inc., 2000)

Test	Results
Oral LD_{50} (rat)	3600 mg/kg
Dermal LD_{50} (rabbit)	> 5000 mg/kg
Inhalation LC_{50} (rat)	11 mg/L for 4 hr
Eye Irritation (rabbit)	Substantial irritation
Skin Absorption LD_{50} (rat and rabbit)	> 5000 mg/kg
Skin Irritation (rabbit)	Severe irritation
Skin Sensitization (sensitive individuals)	Positive

Fenoxaprop-P-ethyl. Fenoxaprop-P-ethyl demonstrates low acute mammalian toxicity following acute oral, dermal or inhalation exposure. The summary of acute toxicity data is listed in Table 5. The toxicity to birds was generally low with a oral LD_{50} > 2000 mg/kg. Whereas the toxicity to the aquatic organisms is high. The LC_{50} for rainbow trout is 0.57 mg/l for 96 hours and EC_{50} for daphnia magna is 0.56 mg/l for 48 hours. Fenoxaprop-P-ethyl shows a low toxicity to bees (Bayer CropScience, 2002). Fenoxaprop-P-ethyl is a slight to moderate skin irritant, depending on the contact time. Sub-chronic studies in rats and mice shows reduced blood lipids and cholesterol and increased liver weights, but these changes are reversible. These findings were not apparent in lifetime feeding studies in rats and mice, confirming their transient nature.

Birth defects studies were performed in mice, rats, rabbits and monkeys by both oral and dermal exposure. No embryotoxic or fetotoxic effects were seen at doses non-toxic to the mothers. Reduced pup body weight gain during lactation was observed at high doses in a two generation reproduction study in rats. There were no effects on fertility in this study. A variety of mutagenicity studies conducted in bacterial and mammalian cells "in vitro" and "in vivo" have shown fenoxaprop-P-ethyl to be non-mutagenic (AgrEvo USA Co., 1996).

Table 5. Acute Toxicity Data for Fenoxaprop-P-ethyl (Bayer CropScience, 2002)

Test	Results
Oral LD_{50} (rat)	> 5000 mg/kg
Dermal LD_{50} (rat)	> 4000 mg/kg
Inhalation LC_{50} (rat)	> 10.74 mg/L for 4 hr
Eye Irritation (rabbit)	Slightly irritation
Sensitisation (guinea pig)	None sensitizing
Skin Irritation (rabbit)	Slightly irritation

Halofenozide. There is no available cancer, endocrine disruption, reproductive, or developmental toxicity information. The toxicity category established by EPA is III, which means the acute toxicity rating is "slightly toxic". Halofenozide has a low

mammalian toxicity. The summary of acute toxicity data is presented in Table 6. Based on physical property data, halofenozide is considered to have a high potential to pollute water (Orme et al., 2002). Based on results from standard laboratory studies, halofenozide was shown to be toxic to fish, very toxic to aquatic invertebrates, and harmless to algae and adult honeybees (MSDS, 2003). Halofenozide is slightly toxic to birds, the acute oral half-life for quail is greater than 2250 mg/kg, the acute dietary half-life is 4522 mg/kg for quail, and greater than 5000 ppm for mallard ducks (British Crop Protection Council, 2000). Study from a turfPQ model, which is a pesticide runoff model developed exclusively for turf, simulating the runoff of halofenozide from turf found that the concentration of halofenozide runoff from turf was well below LC_{50} levels (Haith et al., 2003).

Table 6. Acute Toxicity Data for Halofenozide (British Crop Protection Council, 2000)

Test	Results
Oral LD_{50} (rat)	2850 mg/kg
(mice)	2214 mg/kg
Inhalation LC_{50} (rat)	> 2.7 mg/l
Eye Irritation	Moderately irritation
Skin Sensitize (guinea pig)	Positive
Skin Irritation (rabbit)	Negative
NOEL 90 d (dog)	3.8 mg/kg daily
(rat)	5.7 mg/kg daily

Orizalin. Orizalin demonstrates low acute toxicity to mammals. The toxicity class established by EPA and WHO is III. The summary of acute toxicity data is presented in Table 7. Large oral doses cause nausea and vomiting in dogs and cats (WSSA, 1994). Long-term exposure to oryzalin has found to cause blood changes and tumors in animals (WSSA, 1994). When oryzalin was fed to rats at a dose of 135 mg/kg for 2 years, there was an increase in the incidence of thyroid, mammary and skin tumors. Repeated ingestion of large doses led to adverse changes in blood cell formation in dogs (OHS Inc., 1992). Rats fed a dietary level of 45 mg/kg for two years exhibited blood changes, increased liver and kidney weights, inhibition of growth, and decreased survival (OHS Inc., 1992). Mice given dietary doses of 1,350 ppm for one year exhibited decreased uterine and ovarian weight (OHS Inc., 1992) (USEPA, 1990). Rats fed 45 mg/kg or 135 mg/kg, the highest dose tested, for one year showed minimal signs of toxicity (USEPA, 1987). There were no adverse effects on reproduction in a 3- generation study where rats were fed the highest dose testing (OHS Inc., 1992) (USEPA, 1990). There were no birth defects in the offspring of pregnant rats fed dietary concentration as high as 112 mg/kg/day for 3 generations, nor in the offspring of pregnant rabbits given doses of 125 mg/kg/day (WSSA, 1994) (USEPA, 1990). The EPA reports that oryzalin was not mutagenic in several tests, including tests on live rats and mice and on bacterial cell cultures (USEPA, 1990). Oryzalin did not produce tumors in more than one test species, did not produce tumors in more than one experiment, and did not produce an unusual degree of tumors, so the EPA has classified oryzalin as a possible human carcinogen (USEPA, 1990). Oryzalin is not hazardous to birds. Its oral LD_{50} in bobwhite quail and mallard ducks is > 500 mg/kg (BCPC, 2000), and > 1,000 mg/kg in hens (Meister, 1992).

The 5-day dietary LD_{50} for oryzalin in quail and ducks is 5,000 mg/kg (WSSA, 1994). Oryzalin is moderately toxic to fish. Direct contamination of a body of water with oryzalin from a wettable power formulations may kill fish, the 96-hour LC_{50} for oryzalin in bluegill sunfish is 2.88 mg/l, 3.26 mg/l in rainbow trout (Meister, 1992; WSSA, 1994), and > 1.4 mg/l in goldfish finglings (BCPC, 2000).

Table 7. Acute Toxicity Data for Oryzalin (Modified from British Crop Protection Council, 2000 and WSSA, 1994)

Test	Results
Oral LD_{50} (rat and gerbil)	> 10,000 mg/kg
(cat and dog)	> 1000 mg/kg
Dermal LD_{50} (rabbit)	> 2000 mg/kg
Inhalation LC_{50} (rat)	> 3.1 mg/l for 4 hr
Eye Irritation (rabbit)	None
Skin Irritation (rabbit)	Mild irritation
NOEL 2 y (rat)	300 mg/kg diet
(mice)	1350 mg/kg diet

Analysis Methods

There are several approaches to pesticide analysis. These methodological approaches vary on their degree of complexity; in the time, effort, and analytical instrumentation required to complete them; and in the degree of confidence that can be placed in the final results. Typically, one would use the least demanding procedure that will provide a level of confidence in the final results sufficient to answer the questions being posed (Nielsen, 1998).

High performance liquid chromatography (HPLC) and gas chromatography (GC) are good options for the determination of pesticides. Each analytical method has advantages and disadvantages.

GC is the technique of choice because of its ability to resolve a single member of a chemical class and individual analytes in suitable prepared extracts containing potential interferences. However, GC is not capable of determining thermally labile and nonvolatile pesticides. Compared with the GC, HPLC is very effective in separating non-volatile and thermally labile compounds. Recently developed pesticides together with their degradation products are representative candidates for HPLC separations because of their thermolability and/or low volatility (Pico, 2000). However, HPLC has some limitation with its selectivity and sensitivity because of the variety and complexity of matrix and small amount of pesticides present.

The sample preparation process has a direct impact on accuracy, precision, and quantitation limits and is often the rate determining step for many analytical methods. Analytical chemists continue to search for sample preparation procedures that are faster,

easier, safer, and less expensive to perform, yet provide accurate and precise data with reasonable quantitation limits.

Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are the methods most commonly used to purify analytes from interfering substances in different sample matrices. Such purification is based on the differences of polarity between components. LLE method has been widely used in the past for extraction of pesticides from different matrices. This procedure has several disadvantages, including: the use of large quantities of organic solvent which may be flammable or toxic, requiring hazardous waste disposal; processes are generally time consuming, laborious and difficult to automate; emulsion may form between the two liquid phases; glassware and distillation apparatus are required; and LLE methods are not easily conducted in the field. SPE is a liquid-solid separation. It was developed commercially by the Waters Co. in 1978 and is sold as cartridges called as Sep-Pak. Since then, others have entered the field. It offered an alternative to LLE (Font et al., 1993; Simpson, 1992). SPE cartridges and disks are now available from many suppliers and represent a variety of matrix chemistries. These matrices can be polar, non-polar, or ionic with numerous examples including octadecyl (C_{18}), octyl (C_8), ethyl (C_2), cyclohexyl, diol, silica, cyanlpropyl, aminopropyl, phehyl, and Florisil (Font, 1993). Of the sorbent materials available for SPE of pesticides from water, C_{18} has become by far the most popular (Nollet, 2000). However, there is an increasing awareness, supported by experimental data, that C_{18} cartridges are inadequate to solve the problems of isolating polar contaminants from large water volumes. This failure has led to alternative sorbent material, such as styrene divinylbenzene copolymer (PRP-1) and highly crosslinked styrene-divinylbenzene copolymers (PS-DVB) (Nollet,

2000). These SPE is exhibited better performance for retaining medium - and high - polar pesticides. The polymer SPE columns have advantages over the silica – based C_{18} SPE columns. These include excellent pH stability (pH 1 - 13), higher percentage recoveries, and improved reproducibility. Also, many analytes are less likely to irreversibly bind to the polystyrene divinylbenzene polymer resin than to the C_{18} coated silica matrix. (Posyniak et al., 1999). SPE and LLE both involve a partitioning of the analyte between two phases. SPE methods have several advantages over conventional LLE when trace components are of interest. It is faster, requires less organic solvent per extraction, eliminates solvent immiscibility, is easily automated for multiple sample extractions, and can be conducted in the field. EPA methods are currently being tested, and some have been approved using SPE methodology to replace LLE methods (Federal Register, 1995; USGPO, 1995).

The following sections represent a review of the published methods for analysis of dithiopyr, fenoxaprop-P-ethyl, halofenozide, and Oryzalin. The summaries are listed in Table 8, 9, 10, and 11, respectively.

Dithiopyr. The determination of dithiopyr is accomplished by GC equipped with different detectors. The concentration of dithiopyr in soil and plant can be determined by GC equipped with an electron capture detector (ECD) (Hong et al., 1994; Saikia et al., 1999; and Monsanto Co., 1991 and 1997). The dithopyr is extracted from soil by liquid-liquid extraction, followed by methylation with diazomethane and purified by liquid-liquid partitioning or Florisil column. The methods are very time- and labor-consuming. The concentration of dithiopyr in water can be determined by GC/MS (Tanabe et al., 1996 and Kiguchi et al., 2000). The dithiopyr is extracted form water with SPE, then

determined by GC/MS. The introduction of MS detection has enabled the chromatographer to simultaneously determine and confirm dithiopyr in water. While there is no published information about determination of dithiopyr by HPLC.

Halofenozide. There is very little information available on methods for the analysis of halofenozide. The determination of halofenozide in soil can be accomplished by GC with a nitrogen-phosphorous detector (NPD) (American Cyanamid Co., 1996). Halofenozide is extracted from soil with methanol-HCl, and purified by liquid-liquid partitioning. Following a Aluminum oxide column clean up. Extracted analytes need further derivitization prior to GC/NPD analysis. Determination of halofenozide in turfgrass and soil can be accomplished by HPLC with a ultraviolet detector (UV). Halofenozide has been extracted with ethyl acetate liquid-liquid extraction following by reversed-phase HPLC/UV (American Cyanamid Co., 1996).

Fenoxaprop-P-ethyl. There is little literature available on methods for the analysis of fenoxaprop-P-ethyl. Fenoxaprop-P-ethyl can be determinated by GC (Food & EPA, 1985). The disadvantage of the GC method determination for this compound is that the extracted analytes need derivatization prior to GC analysis. The derivatization process is rather time consuming and requires a 130 ^{0}C oil bath. The effective compounds are easily volatilize and can be lose. Li et al. (2003) developed a HPLC with DAD procedure for the determination of fenoxaprop-P-ethyl in rape seed and soil. Fenoxaprop-P-ethyl is extracted in rape seed and soil by soxhlet with ether, and cleaned up with a C18 column.

Oryzalin. The concentration of oryzalin in technical and formulated products can be determinated by spectrophometry (Decker et al., 1976) or by reversed-phase HPLC with ultraviolet detection (HPLC/UV) (Kennedy, 1977). Oryzalin can not be quantitatively estimated directly by GC. Under a wide range of operating conditions, the gas chromatographic peaks are broad and exhibit considerable tailing, making quantitative assessment uncertain. This is most probably associated with the greater polarity and hydrogen bonding potential of the sulfonamide group (Sieck et al., 1976). The reported methods for the determination of oryzalin in crops and soil are based on an overnight chemical derivatization followed by gas chromatography (FDA, 1985; Sieck, 1976). Oryzalin is extracted from the crops by blending with methanol and derivatized to a N,N-dimethyl derivative with methyl iodide after filtration. The N,N-dimethyl derivative is purified by alumina column chromatography and finally determined by electron capture gas chromatography. The disadvantages of derivatization methods are that extra time is required for the derivative formation, the derivatization step is usually not quantitative, and the probability of error increases because of the extra sample manipulation. An HPLC method has been reported for determination of oryzalin in soil (Macy et al., 1980). The method requires no derivatization. Oryzalin is extracted with methanol following by purification and separated by liquid-liquid partitioning and Florisil column chromatography to clean up the samples before reverse-phase HPLC analysis with UV detection. HPLC equipped with a mass spectrometry (MS) detector has also been reported for determination of oryzalin in fruits and vegetables (Liu et al., 1991). This method involves the extraction of pesticides with acetone followed by purification by liquid-liquid partitioning prior to HPLC/MS analysis. The EPA (1993) method for the

determination of oryzalin in industrial and municipal wastewaters involves the extraction of oryzalin with methylene chloride by liquid-liquid extraction and Florisil column clean-up the sample before HPLC analysis with UV detection.

Table 8. Methods for Analysis of Dithiopyr

Analyte Matrix	Separation/ Detection	Extraction	Clean-up	LOQ	Spike Level	Recovery	Reference
Soil leachate	GC/ECD	LLE (hexane+ethyl acetate) SPE(C18)	None	6.25 ppb 1.0 ppb	6.25-125 ppb 1.0-100 ppb	56 % 87 %	Hong et al., 1994
River water	GC/MS	Water: SPE(SDB-L) Suspended substances: ultrasonic extr.(acetone)	None	Water: 0.01 ppb Suspended substances: 0.05 ppb	0.5 ppb None	81-128 % 80-110 %	Tanabe et al., 1996
Soil	GC/ECD	Acetonitrile-0.2 M HCl (95:5) and petroleum ether	Diethyl ether partitioning and Florisil column	10 ppb	10 ppb, 100 ppb	94.3 %	Monsanto Co., 1997
Soil, wheat grain and straw	GC/ECD	Acetone-0.2 M HCl (95:5)	Partitioning (hexane)	50 ppb	Soil: 1000-5000 ppb Wheat and straw: 200-2000ppb	80-99 %	Saikia et al., 1999
Water	GC/MS	SPE (SDB-XD Empore disk + Carbon Empore disk	None	None	0.2-2.0 ppb	70-120 %	Kignchi et al., 2000

Table 9. Methods for Analysis of Fenoxaprop-P-ethyl

Analyte Matrix	Separation/ Detection	Extraction	Clean-up	LOQ	Spike Level	Recovery	Reference
Formulations	HPLC/UV	None	None	None	None	None	Henriet, 1985
Biological material and soil	GC/ECD	Unknown	Unknown	20 ppb	20 - 500 ppb	75-90 %	Food & EPA, 1985
Rape and Soil	HPLC/DAD	Soxhlet Extraction (ethylnitrile/ 6MHCl, 9:1)	Cyclohexane, ether partitioning and SPE (C_{18})	Rape: 25 ppb Soil: 13 ppb	100-500 ppb	75-108 %	Li et al., 2003

Table 10. Methods for Analysis of Halofenozide

Analyte Matrix	Separation/ Detection	Extraction	Clean-up	LOQ	Spike Level	Recovery	Reference
Soil	GC/NPD	Methanol/HCl (70:30)	Methylene chloride partitioning and Aluminum oxide column	10 ppb	10 ppb	> 80 %	Americal Cyanamid Co., 1996
Turfgrass and soil	HPLC/UV	Ethyl acetate LLE	Methylene chloride	10 ppb	1000 ppb	96 %	Gardner et al., 2001

Table 11. Methods for Analysis of Oryzalin

Analyte Matrix	Separation/ Detection	Extraction	Clean-up	LOQ	Spike level	Recovery	Reference
Crop and soil	GC/ECD	Methanol	LLE and alumina column	10 ppb	Crop: 50 ppb Soil: 100 ppb	72 % 92 %	Sieck et al., 1976
Water/sediment	GC/ECD	Benzene-methanol (3:1-9:1)	None	1.0 ppb	1.0 ppb	95 %	Communication, 1978
Soil	HPLC/UV	Methanol	LLE and Florisil column	20 ppb	20-160 ppb	80-108 %	Macy et al., 1980
Crop, soil and water	GC/ECD or NPD	Soil and crop: Methanol Water: Benzene Methanol (3:1)	Multiple Liquid-liquid partitioning	ECD: 1.0-10ppb NPD: 5.0-50 ppb	80-500 ppb	80-90 %	Bardalaye et al., 1984
Crop	GC/ECD	Methanol	Alumina column	None	None	None	FDA, 1985

Table 11. Cont.

Soil	GC/FID or LC/DAD	Methano Acetone (ultrasonic extr.)	None	None	10,000 ppb	103 %	Taylor, 1991 Liu et al., 1991
Crop	HPLC/MS	Acetone	Multiple Liquid Liquid partitioning	50 ppb	500 ppb	78-96 %	Mattern et al., 1991
Wastewater	HPLC/UV	Methylen chloride	Florisil column	0.5 ppb	10 ppb 200 ppb	106 % 100 %	EPA, 1993
Wine	GC/MS	SPE (Oasis cartridge)	SPE (Aminopropyl cartridge)	10 ppb	100 ppb 10 ppb	45 % Nd	Wong et al., 2003

MATERIALS AND METHODS

Sample Collection

Surface water was collected from the Stillwater River in Orono, ME. The water was collected in a 4 L jar and stored under refrigeration at 5 ^{o}C . Samples were processed within 2 days of collection.

Ground water was collected from 439 Wing Road in Hermon, ME. The water was collected in 4 L jars and stored under refrigeration at 5 ^{o}C. Samples were processed within 4 days of collection.

Pesticides

Dithiopyr (99.9% pure), halofenozide (96.9% pure), fenoxaprop-P-ethyl (99.5% pure), and oryzalin (99.9% pure) standards were obtained from the EPA repository, Fort Mead, MD.

Solvents

All solvents were HPLC grade and obtained from the Fisher Scientific Company, Fair lawn, NY.

HPLC System and Operating Conditions

The HPLC system consisted of a Hewlett Packed model 1050 isocratic pump and auto sampler equipped with upgraded 1040 diode array detector (DAD). The analytical

column was a Columbus C-18, 5 um, 50 x 4.6 mm. Data was collected using a HP Chemstation (version A03.01) software.

Operating conditions: The injection volume of standards and sample were 50 ul. The flow rate was set at 1.0 ml/min. The analytical column was operated at ambient temperature. The UV spectra was collected from 200 to 350 nm. The quantification was carried out with 250 nm for dithiopyr, 240 nm for fenoxaprop-P-ethyl, 237 nm for halofemozide, and 288 nm for oryzalin. The selected mobile phase was a mixture of acetonitrile-water-phosphoric acid (325 + 175 + 0.1, V/V/V).

Quantification of pesticides was accomplished by comparing the peak area response for samples with peak area of the standards. Confirmation for water samples showing positive response for pesticides was accomplished by comparing the sample UV spectra with standard UV spectra.

Preparation of Standard Solution

Standard stock solutions were prepared by accurately weighing a known amount of pesticide (approximately 25 mg) analytical standard into a 25 ml volumetric flask. The stock solutions were diluted to the volume with acetonitrile. A mixed working standard solution was prepared by diluting an appropriate aliquot of stock solution in 25 ml of the acetonitrile.

Sample Preparation

Ground and surface water samples were prepared by passing a 500 ml of water through the styrene-divinylbenzene copolymer (SDB-L) cartridge at a flow-rate of 10

ml/min. The cartridge was conditioned by passing consecutively 5 ml methanol and 5 ml volume of deionized water. After the entire sample volume was passed through, the SPE cartridges was washed with 10 ml of deionized water and dried under vacuum for 30 min. The pesticides collected on the cartridges were eluted with 20 ml ethyl acetate at a flow-rate of 10 ml/min. The elutes were dried using a rotary evaporation at 40^{0}C and residues were re-dissolved in 1 ml acetonitrile prior to injection into the HPLC system.

Standard Curves

Calibration standards of the four pesticides were prepared by dilution with the acetonitrile, in concentrations of 0.02, 1.0, 5.0, 10.0, 25.0, 50.0 ppm for halofenozide, 0.05, 1.0, 5.0, 10.0, 25.0, 50.0 ppm for fenoxaprop-P-ethyl and oryzalin, 0.1, 1.0, 5.0, 10.0, 25.0, 50.0 ppm for dithiopyr.

Recovery Studies

Recovery studies were carried out by spiking 500 ml ground and surface water samples with a mixed standard of known amounts. The spiked samples were then extracted and cleaned up with SPE, and analyzed by HPLC as previously described. Six different spiking levels of the pesticides were prepared for HPLC analysis. For ground water, the spiking levels were 0.50, 2.0, 12, 25, 50, and 100 ppb for dithiopyr, 0.15, 2.0, 12, 25, 50, and 100 ppb for fenoxaprop-P-ethyl, 0.10, 2.0, 12, 25, 50, and 100 ppb for halofenozide and oryzalin. For surface water, the spiking levels were 0.50, 2.0, 12, 25, 50, and 100 ppb for dithiopyr, 0.30, 2.0, 12, 25, 50, and 100 ppb for fenoxaprop-P-ethyl,

0.20, 2.0, 12, 25, 50, and 100 ppb for halofenozide and oryzalin. These samples were then extracted and analyzed by HPLC.

Reproducibility Studies

Samples from six different spiking levels were extracted and analyzed once a day for six different days. The lowest spike levels in ground water were 0.50 ppb for dithiopyr, 0.15 ppb for fenoxaprop-P-ethyl, 0.10 ppb for halofenozide and oryzalin, respectively. The other spike levels in ground water were 2.0, 12, 25, 50, and 100 ppb for these pesticides. The lowest spike levels for surface water were 0.50 ppb for dithiopyr, 0.30 ppb for fenoxaprop-P-ethyl, 0.10 ppb for halofenozide and oryzalin, respectively. The other spike levels in surface water were same as those used for ground water.

RESULTS AND DISCUSSION

HPLC-DAD is an excellent analytical system for the analysis of compounds that contain aromatic rings, carbonyl groups, nitro groups, or sulphur because of its sensitivity and specificity. The chemical structures of dithiopyr, fenoxaprop-P-ethyl, halofenozide, and oryzalin (Figure 1) contain at least one of groups, witch listed above, makes make them very ideal candidates for HPLC-DAD determination. The HPLC-DAD method has the advantage that the identification of the pesticides based on the retention time is confirmed by the UV spectrum.

The surface water contains relatively high concentrations of anions as well as humic and fulvic acids that produce a high UV response because of their high percentage of aromaticity (Peuravuori et al., 1997). This response is often produced in the early part of the chromatogram and interferes with early-eluting peaks from the most polar analytes. These humic substances can be removed by pre-column, chemical treatment of sample, or adjustment of solvent concentrations in the mobile phase (Peuravuori et al., 1997). In this study, these humic substances were eluted within the first 5 minutes, and no interfering peaks were observed for the quantification of the four pesticides.

Optimum Conditions

Wavelength. The choice of wavelength was based on where the compounds of interest have the best response and interfering compounds have the lowest response. One of the advantages of the DAD detector is that it can simultaneously collect different

chromatograms at different wavelengths during a single run. The choice of maximum absorbing wavelengths of dithiopyr, fenoxaprop-P-ethyl, halofenozide, and oryzalin in this study were 250 nm, 240 nm, 237 nm, and 288 nm, respectively.

Mobile Phase. Different mobile phases were tested in order to optimize the separation of pesticides from the matrix substances of the water samples. There was an overlapping pair of compounds (dithiopyr and fenoxaprop-P-ethyl) and peak shapes were not good when using acetonitrile and water mixture alone. These problems were be overcome by adding of 0.1 ml phosphoric acid in 500 ml acetonitrile and water mixture. It is often essential to acidify the mobile phase to control selectivity and to achieve reproducible separations with acceptable peak shape (Tindall et al., 2003). Therefore, the optimal mobile phase in this study was a mixture of acetonitrile-water-phosphoric acid (325 + 175 + 0.1, V/V/V).

HPLC Columns. Five different HPLC columns were tested in order to find the best separation and peak shapes of the detection responses of the four pesticides. Table 12 shows the results of the separation and peak shapes with different HPLC columns. With Nucleosil and Prontosil columns, there were two overlapping pair of pesticides (halofenozide and oryzalin, fenoxaprop-P-ethyl and dithiopyr). With Luna and Columbus columns, base-line separation for all four pesticides was achieved. However, the peaks were non-gaussian when using the Luna column. Therefore, the best column was the Columbus C-18, 5 um, 50 **x** 4.6 mm.

Table 12. Separation Results from Different HPLC Columns

Column	Non-gaussian peaks	Peaks separation problems
Luna 3 u C18 (2) (150 x 4.60 mm)	Dithiopyr, fenoxaprop-P-ethyl, and oryzalin	None
Nucleosil 5 u C18 100 R (150 x 4.60 mm)	Unknown	Halofenozide and oryzalin partly overlapped, fenoxaprop-P-ethyl and dithiopyr mostly overlapped
Prontosil 120-5-C18-ace-EPS 5.0 um (150 x 4.60 mm)	Unknown	Halofenozide and oryzalin partly overlapped, fenoxaprop-P-ethyl and dithiopyr mostly overlapped
Spherex 5 C18 (250 x 4.60 mm)	Unknown	Halofenozide and oryzalin partly overlapped, fenoxaprop-P-ethyl and dithiopyr completely overlapped
Columbus 5 u C18 (150 x 4.60 mm)	None	None

Elution Solvents and Solvent Volume for SPE. Acetonitrile, ethyl acetate, MTBE, MTBE:THF (90+10, V/V), and acetone were evaluated as elution solvents for the SPE cartridges. The recoveries of dithiopyr, fenoxaprop-P-ethyl, halofenozide, and oryzalin for each of these elution solvents were tested. The results demonstrated ethyl acetate and acetonitrile had the best recoveries. Ethyl acetate was chosen as the elution solvent because ethyl acetate dissolves less interfering compounds and its lower boiling point madeit faster to condense. To determine the elution solvent volume, 500 ml water samples were spiked with 2.0 ug (2.0 ppm x 1 ml) standard mixture before passed through the cartridge. The cartridge was eluted with 5 ml of ethyl acetate for four times. The recoveries of the different steps of eluent were evaluated. The results of HPLC-DAD analysis showed that most of the analytes were eluted with the first 5 ml of the ethyl acetate solvent (Table 13). The second 5 ml elutes further improved the recoveries of four pesticides, but the third 5 ml elutes only improve halofenozide and fenoxaprop-P-thyl recoveries. The final 5 ml eluted all four pesticides at a satisfactory level. Therefore, the selected eluting solvent was 20 ml of ethyl acetate.

Table 13. Recoveries from Different Eluate Solvent Volumes

Pesticides	Elute step	Recovery (%)	Total recovery (%)
Dithiopyr	First 5 ml	91.7	97.0
	Second 5 ml	5.3	
	Third 5 ml	0	
	Forth 5 ml	0	
Fenoxaprop-P-ethyl	First 5 ml	82.3	95.6
	Second 5 ml	9.1	
	Third 5 ml	3.1	
	Forth 5 ml	1.1	
Halofenozide	First 5 ml	97.2	99.9
	Second 5 ml	2.6	
	Third 5 ml	0.1	
	Forth 5 ml	0	
Oryzalin	First 5 ml	97.9	100.4
	Second 5 ml	2.5	
	Third 5 ml	0	
	Forth 5 ml	0	

Retention Time

The retention times under the above mentioned HPLC conditions for halofenozide, oryzalin, fenoxaprop-P-ethyl and dithiopyr were 5.1, 7.0, 16.1, and 18.6 min, respectively.

Limit of Detection (LOD) and Limit of Quantitation (LOQ)

The LOD and LOQ of dithiopyr, fenoxaprop-P-ethyl, hanofenozide, and oryzalin in ground and surface water are summarized in Table 14. The comparison of the response with the baseline noise, the LOD for the dithiopyr, fenoxaprop-P-ethyl, halofenozide, and oryzalin were 0.10, 0.050, 0.020 and 0.050 ppm, respectively. The effective LOQ after the pre-concentration step for dithiopyr, fenoxaprop-P-ethyl, halofenozide, and oryzalin was 0.50, 0.15, 0.10, and 0.10 ppb in the ground water, 0.50, 0.30, 0.20, and 0.20 ppb in the surface water. Although there is no regulations for the limits of maximum residues (MRL) of these pesticides, the LOQ in here are well below the maximum contaminant level in drinking water set by the Environmental Protection Agency for herbicides (USEPA Office of Drinking Water, 1990)

Linearity Studies

Results of the linearity study using peak area are shown in Figures 3, 4, 5 and 6. The photo diode array detector demonstrated linearity over the range from 0.020 to 50 ppm for halofenozide, from 0.10 to 50 ppm for dithiopyr, from 0.050 to 50 ppm for fenoxaprop-P-ethyl, and oryzalin, with a correlation coefficient (r^2) of 1.000. Thus, the linearity values and correlation coefficient are excellent for this analytical method.

Table 14. The LOD and LOQ of Dithiopyr, Fenoxaprop-P-ethyl, Halofenozide, and Oryzalin in Ground and Surface Water

	LOD (ppm)	LOQ (ppb)	
Dithiopyr	0.10	0.50	0.50
Fenoxaprop-P-ethyl	0.050	0.15	0.30
Halofenozide	0.020	0.10	0.20
Oryzalin	0.050	0.10	0.20

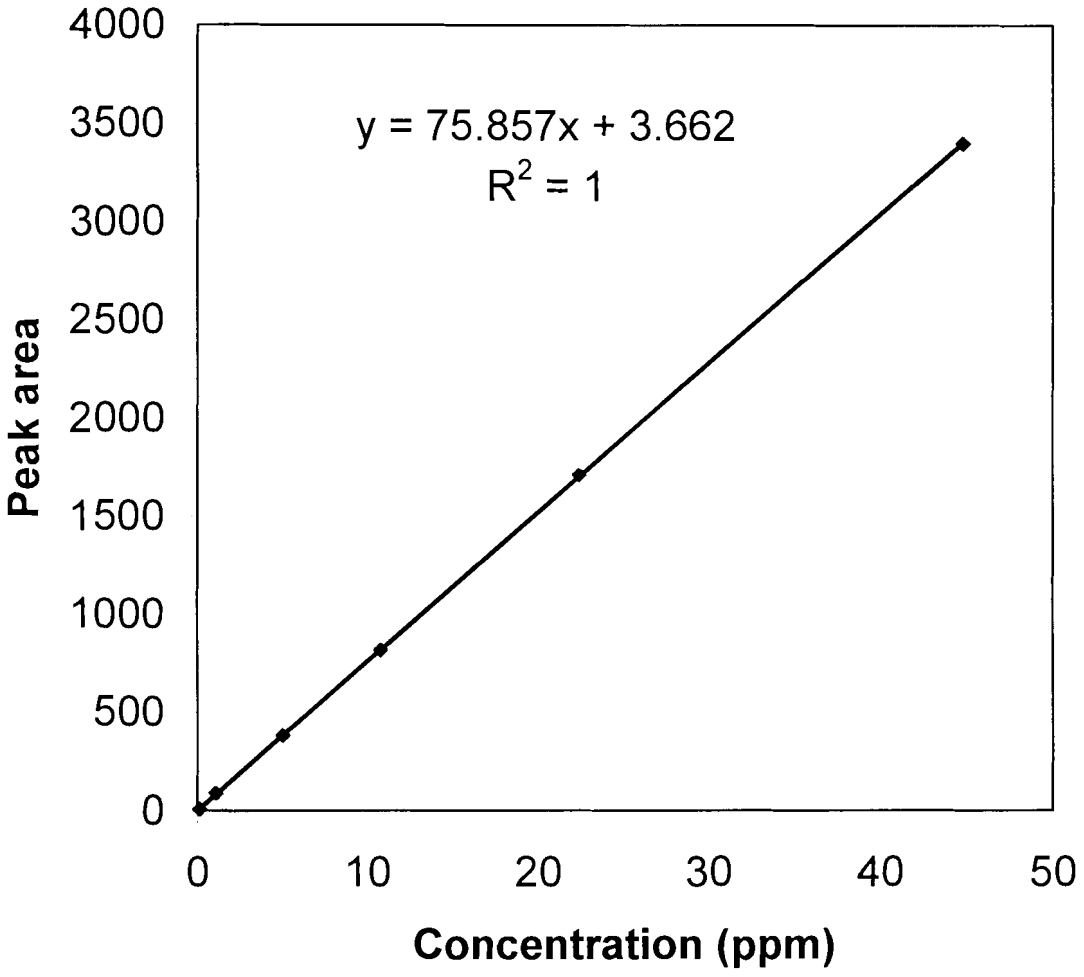


Figure 3. Standard Curve of Dithiopyr

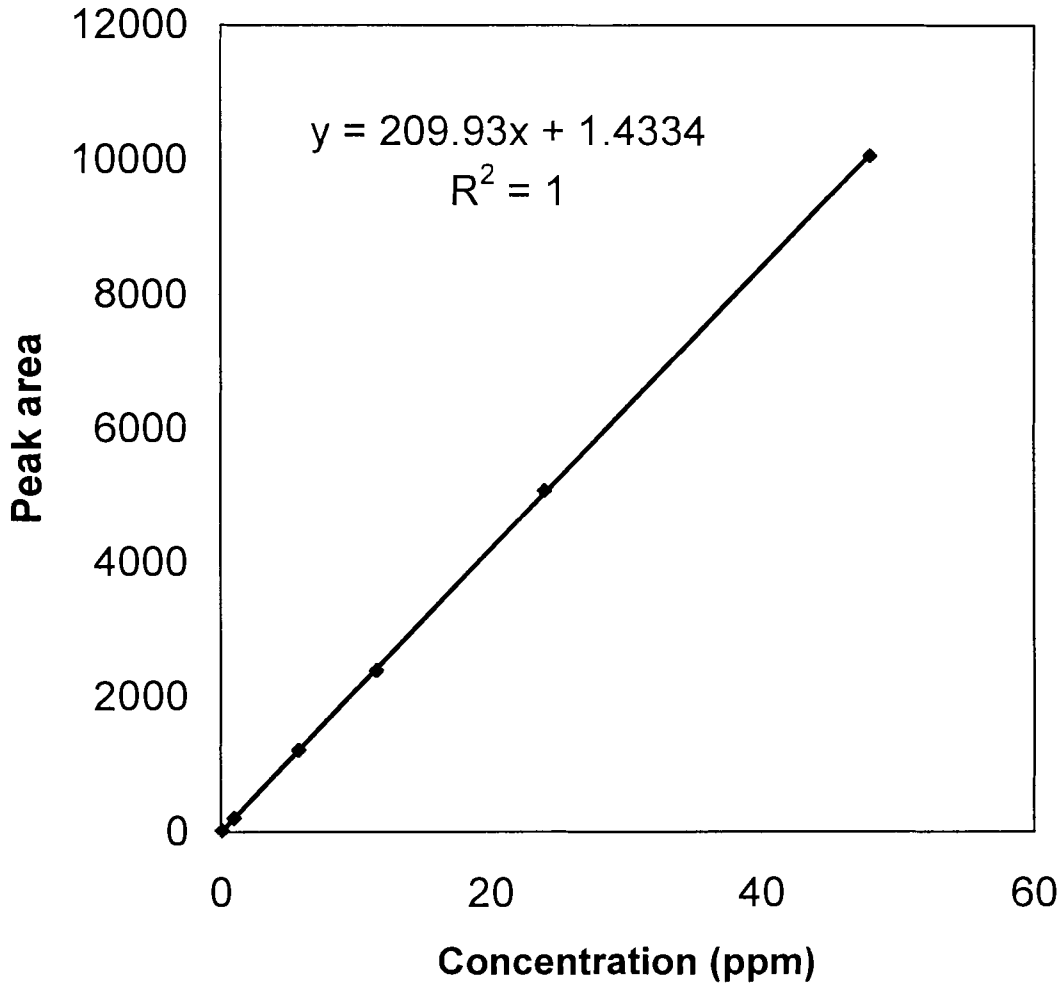


Figure 4. Standard Curve of Fenoxaprop-P-ethyl

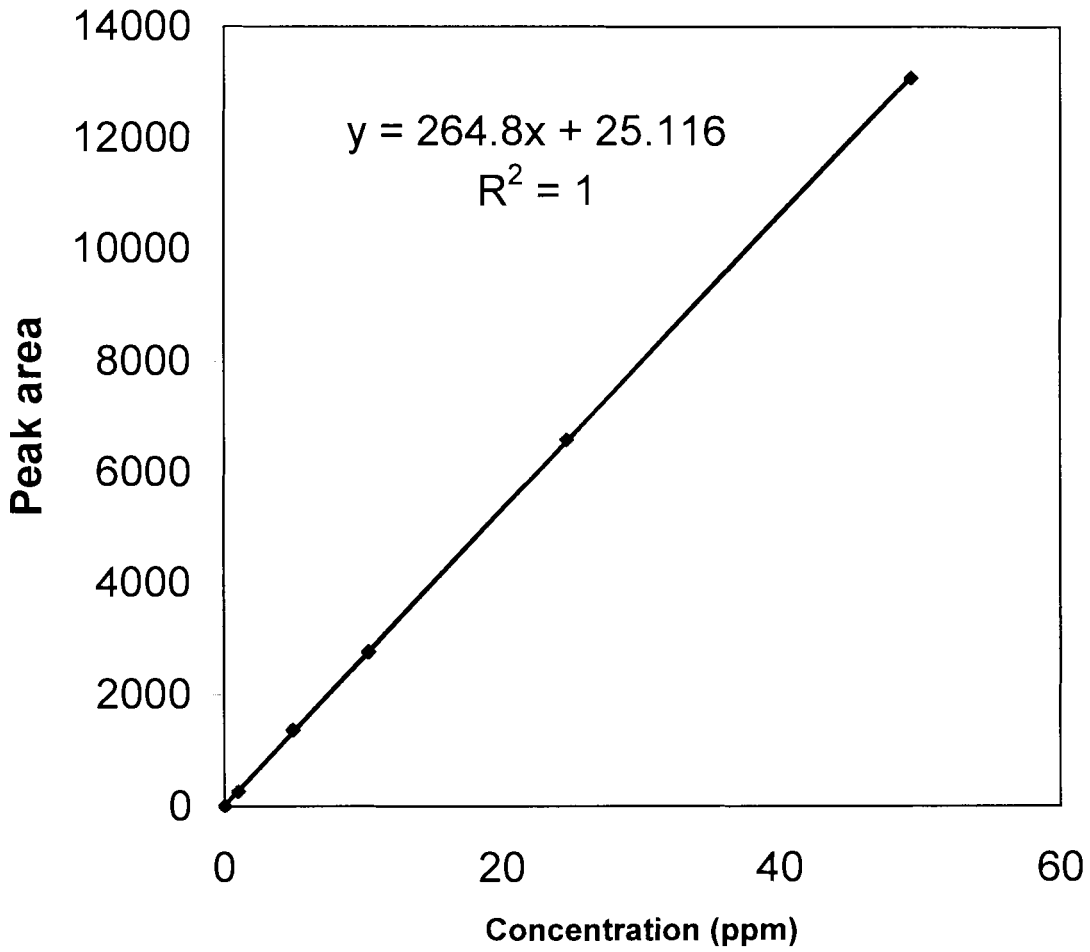


Figure 5. Standard Curve of Halofenozide

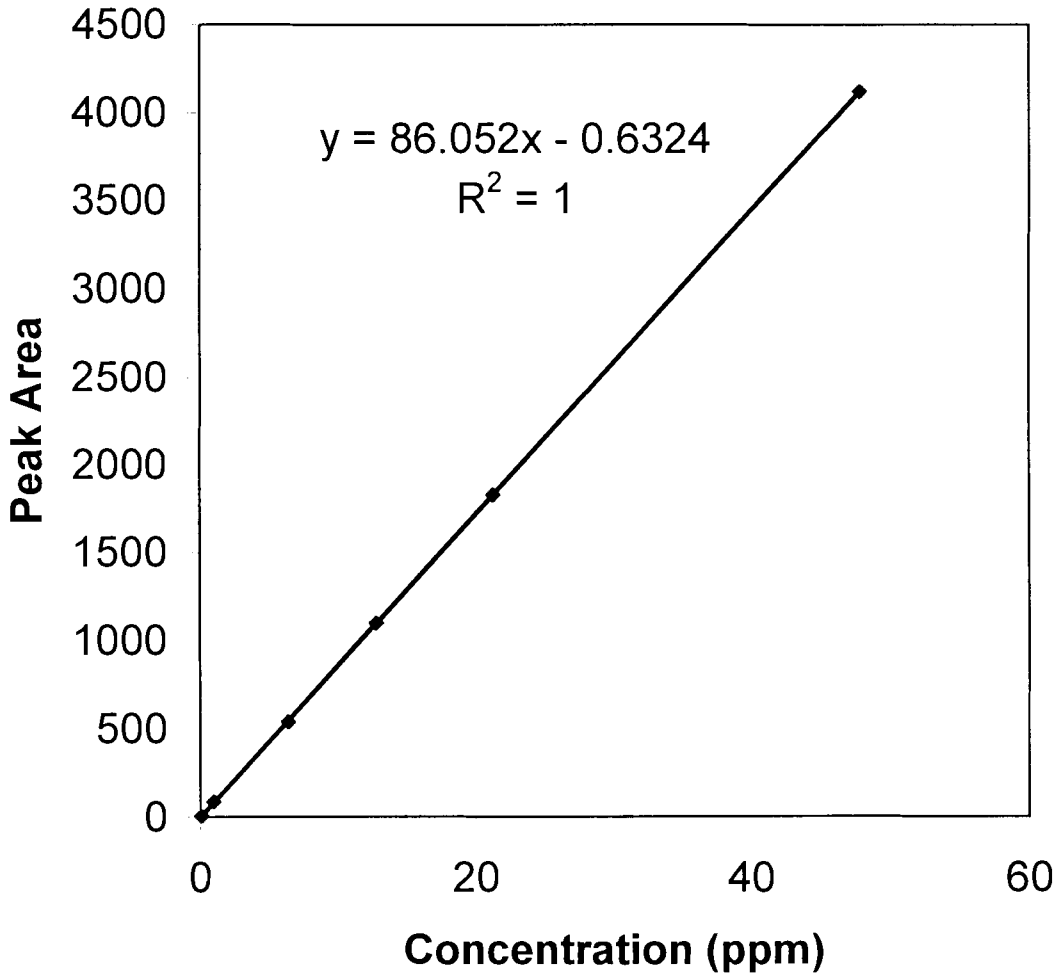


Figure 6. Standard Curve of Oryzalin

Recovery Studies

The accuracy of the analytical method is estimated based on measuring of recoveries of fortified ground and surface water samples. The results of the recovery studies are shown in Tables 15 and 16, respectively. The chromatogram of the separation of standard mixture under the above mentioned HPLC conditions is shown in Figure 7. The chromatograms of ground and surface water samples are shown in Figures 8 and 10, respectively. The chromatograms of spiked ground and surface water samples are shown in Figures 9 and 11, respectively.

For ground water, the mean percent recoveries ranged from 89 to 122 with percent coefficients of variation (%CV) varying from 1.0 to 20 for dithiopyr, from 82 to 96 with %CV from 1.7 to 18 for fenoxaprop-P-ethyl, from 98 to 115 with %CV 2.2 to 15 for halofenozide, and from 92 to 110 with %CV 2.3 to 19 for oryzalin. For surface water, the mean percent recoveries ranged from 82 to 93 with %CV varying from 1.2 to 19 for dithiopyr, from 78 to 98 with %CV 2.1 to 8.5 for fenoxaprop-P-ethyl, from 91 to 102 with %CV 1.0 to 9.3 for halofenozide, and from 91 to 100 with %CV 2.0 to 14 for oryzalin. Recoveries for both water samples were considered satisfactory. Thus, Styrene-divinylbenzene copolymer as a solid-phase extractor with ethyl acetate as elution solvent was a very effective procedure for extraction, pre-concentration, and clean-up water samples.

Table 15. Percent Recovery of Fortified Samples from Ground Water

Pesticides	Spiked Level (ppb)	Mean Percent[a] Recovery (%)	CV(%)
Dithiopyr	0.5	122	20
	2.0	105	14
	12	89	3.7
	25	92	1.0
	50	91	4.9
	100	95	5.1
Fenoxaprop-P-ethyl	0.15	82	18
	2.0	96	6.1
	12	88	5.8
	25	87	6.0
	50	91	1.7
	100	94	1.9
Halofenozide	0.10	115	15
	2.0	104	6.4
	12	101	8.8
	25	100	5.6
	50	98	2.2
	100	98	3.4
Oryzalin	0.10	110	19
	2.0	97	2.6
	12	98	3.5
	25	95	2.7
	50	92	2.3
	100	95	4.1

[a] Mean percent recovery based on four determinations

Table 16. Percent Recovery of Fortified Samples from Surface Water

Pesticides	Spiked Level (ppb)	Mean Percent Recovery[a] (%)	CV(%)
Dithiopyr	0.50	82	19
	2.0	89	3.2
	12	86	2.6
	25	91	1.2
	50	92	4.3
	100	93	2.5
Fenoxaprop-P-ethyl	0.30	78	4.0
	2.0	98	2.1
	12	86	4.8
	25	91	5.7
	50	91	8.5
	100	94	3.4
Halofenozide	0.20	91	9.3
	2.0	102	3.5
	12	98	1.8
	25	98	1.0
	50	98	2.5
	100	97	1.1
Oryzalin	0.20	92	14
	2.0	100	4.3
	12	94	2.0
	25	91	6.9
	50	95	3.6
	100	95	3.0

[a] Mean percent recovery based on four determinations

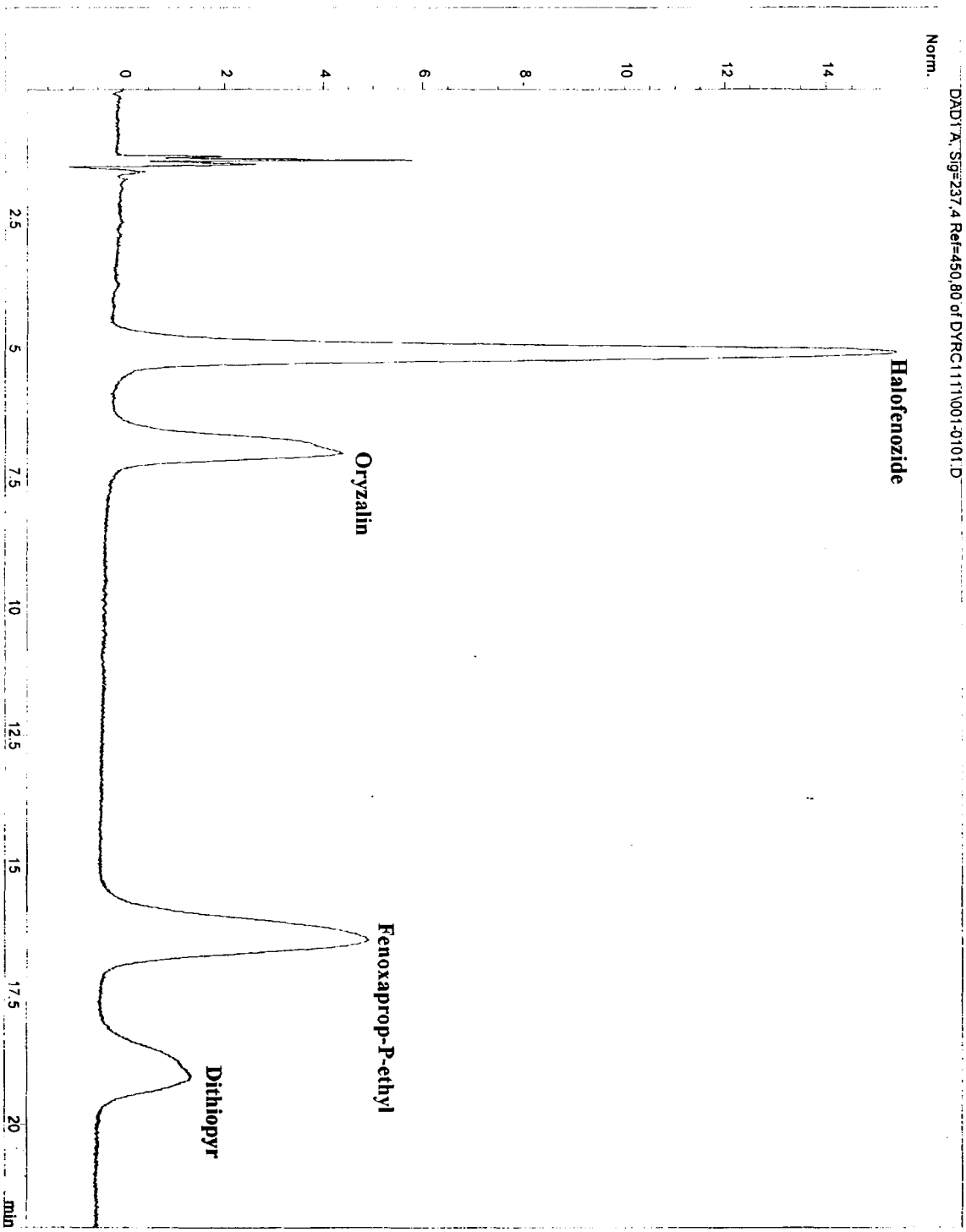


Figure 7. HPLC-DAD Chromatogram of Standard Mixture

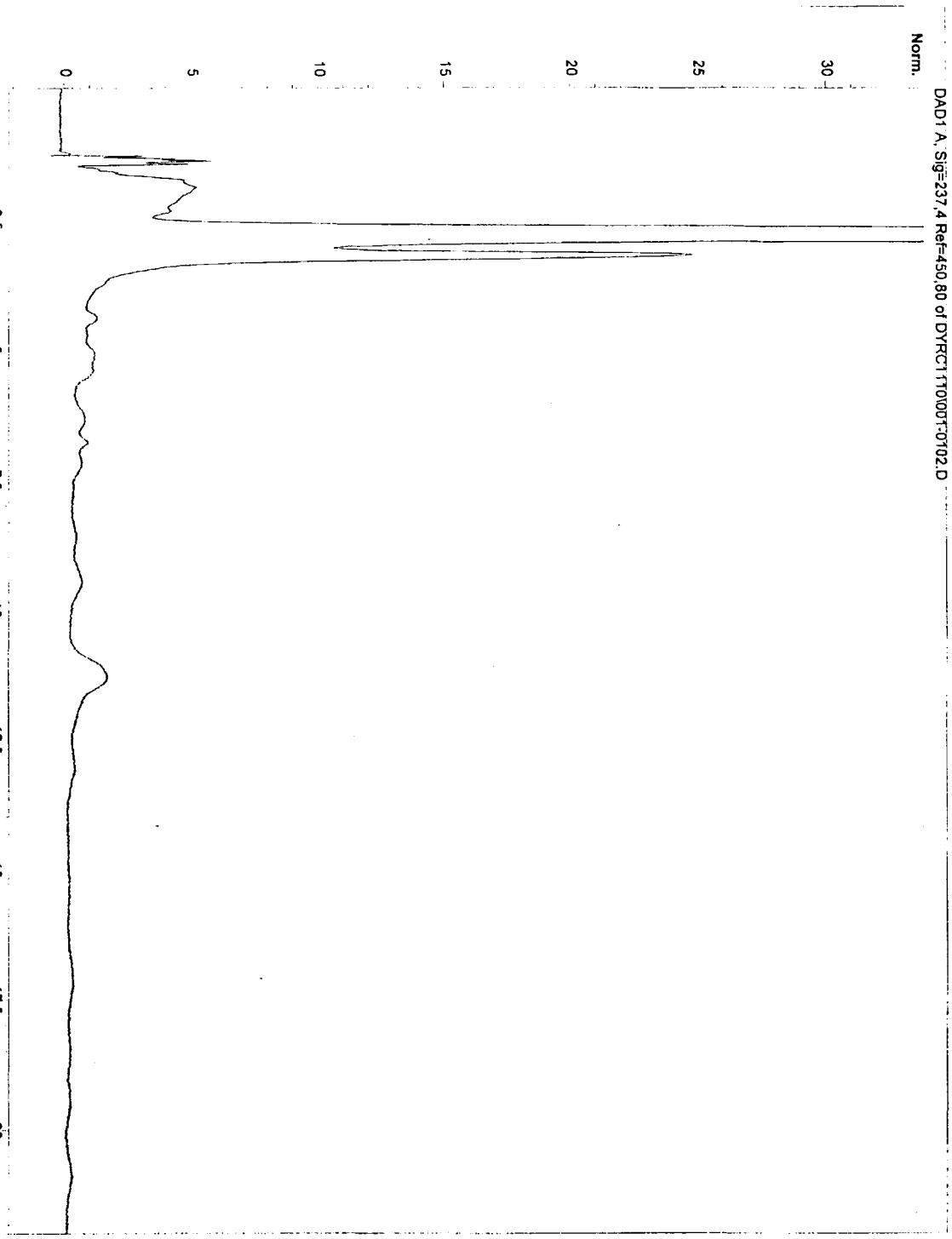


Figure 8. HPLC-DAD Chromatogram of Ground Water

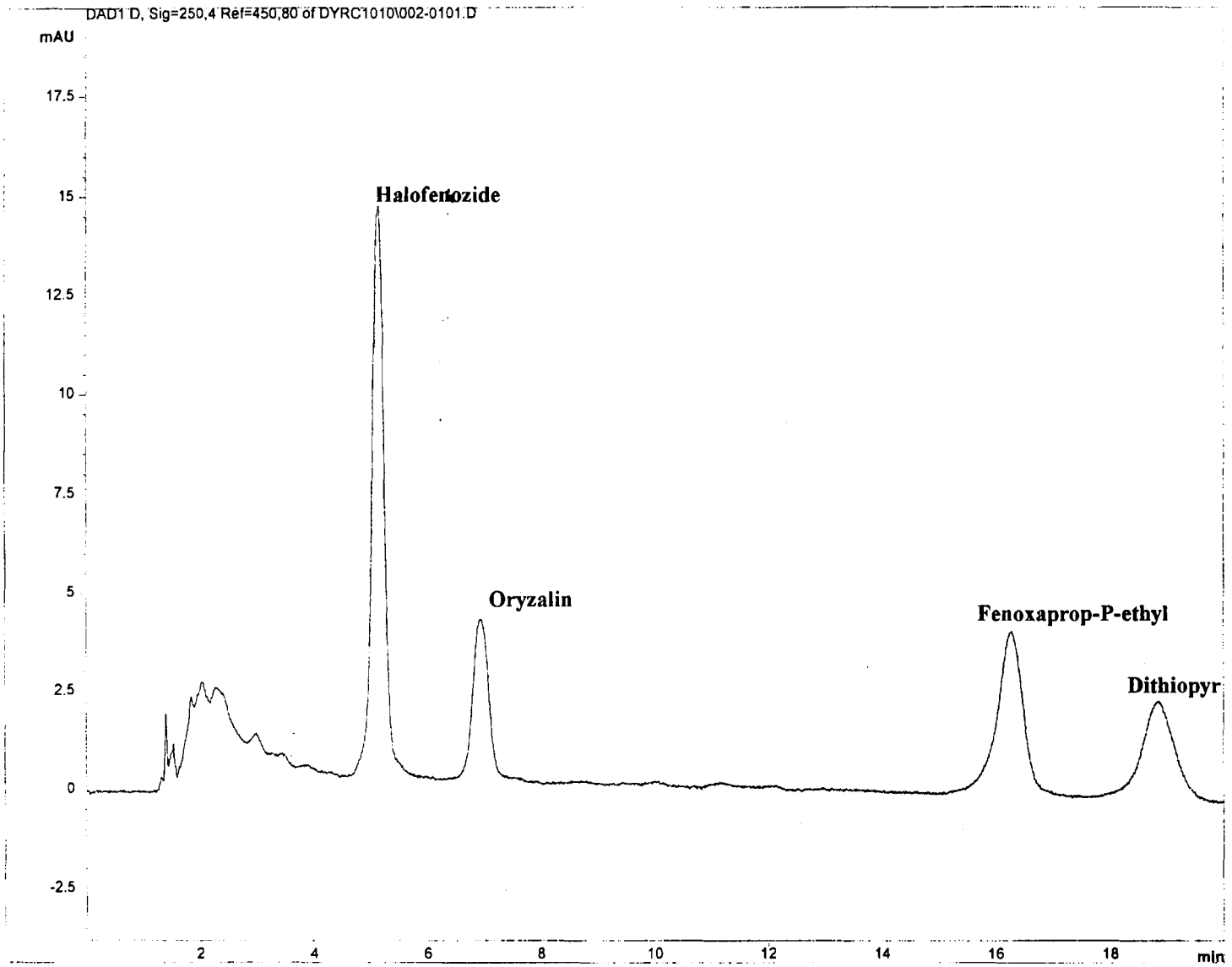


Figure 9. HPLC-DAD Chromatogram of Spiked Ground Water

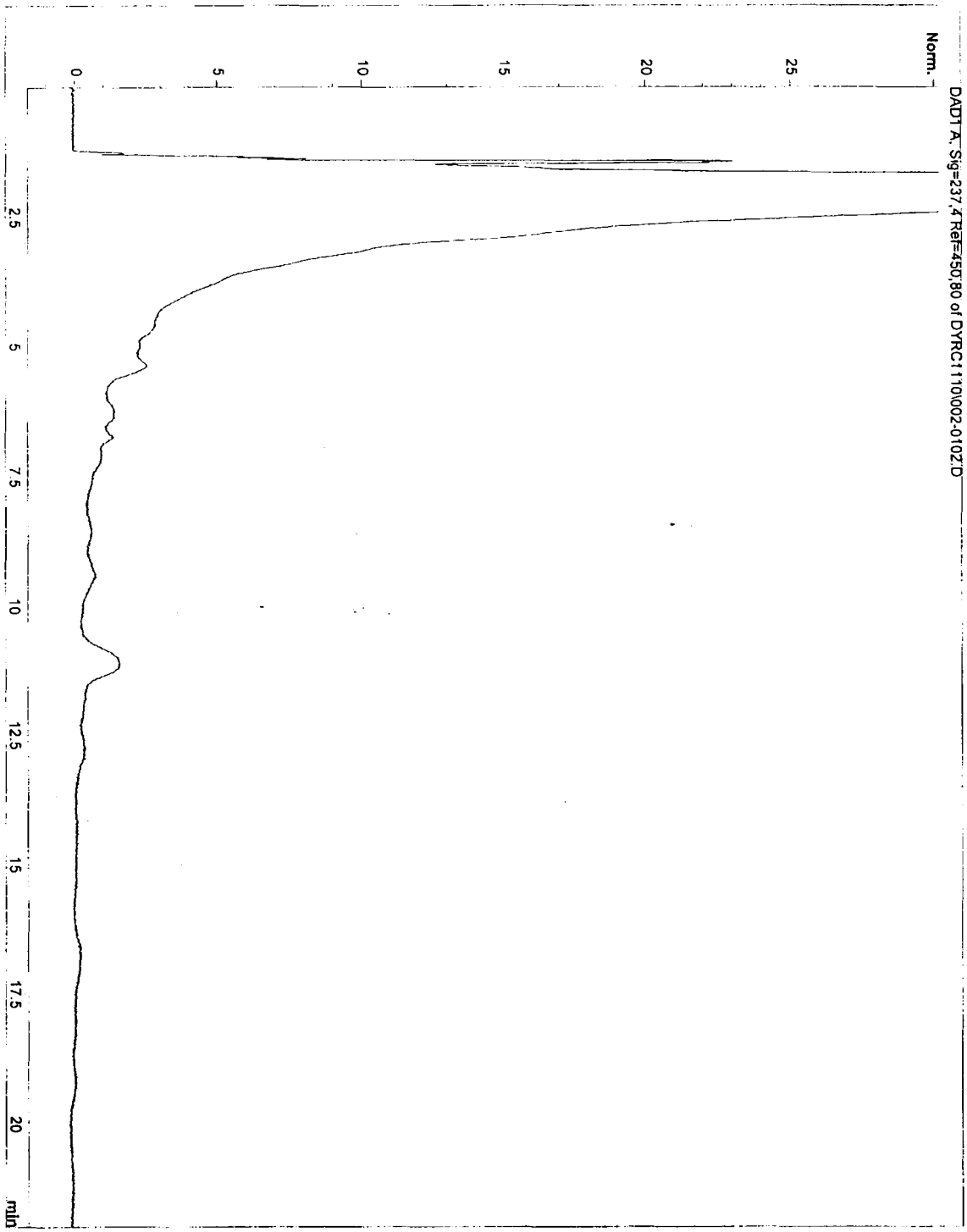


Figure 10. HPLC-DAD Chromatogram of Surface Water

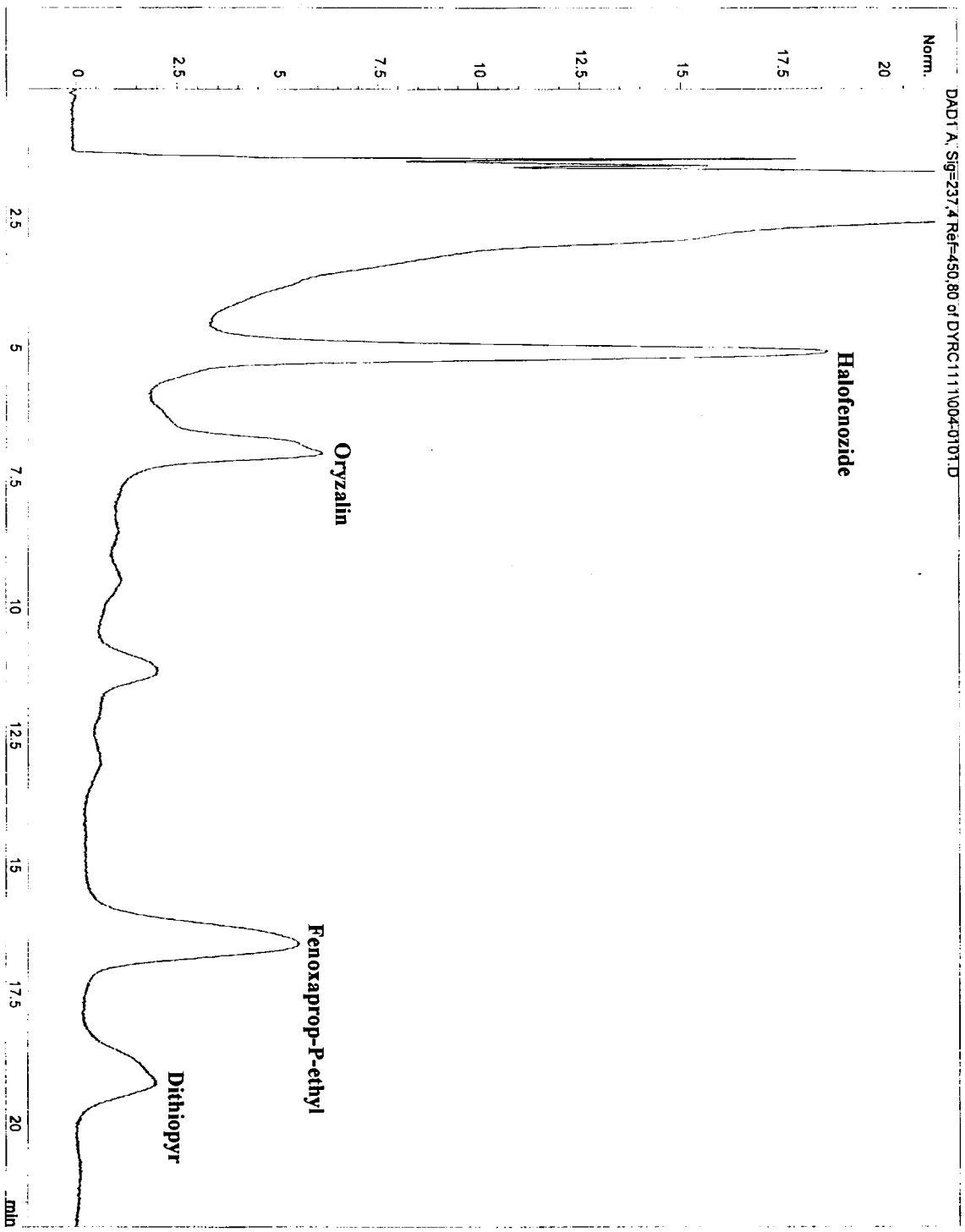


Figure 11. HPLC-DAD Chromatogram of Spiked Surface Water

Reproducibility Studies

The precision of the analytical method was estimated based on spiking water samples with six different levels, and determinations were conducted over a period of six different days indicated the procedure was reproducible. The reproducibility results of ground and surface water are given in Tables 17 and 18, respectively.

For ground water, the ranges of %CV values were from 2.6 to 25 for dithiopyr, 2.5 to 24 for fenoxaprop-P-ethyl, 2.1 to 19 for halofenozide, and 2.4 to 14 for oryzalin. For surface water, the ranges of %CV values were from 2.2 to 17 for dithiopyr, 2.3 to 12 for fenoxaprop-P-ethyl, 0.80 to 9.9 for halofenozide, and 3.9 to 12 for oryzalin. Overall the reproducibility for six different days was good with an average %CV of 8.4 for dithiopyr, 7.5 for fenoxaprop-P-ethyl, 7.5 for halofenozide, and 5.6 for oryzalin in ground water; with an average %CV of 5.5 for dithiopyr, 5.6 for fenoxaprop-P-ethyl, 3.3 for halofenozide, and 6.6 for oryzalin in surface water. With the exception of lowest levels of spiked samples, the most of %CVs were below 5. The generally high %CVs of the lowest level of spiked sample may result from the integration error associated with the small peaks. Also, high concentrated matrix may have interfered with the analytes.

Table 17. Reproducibility of Fortified Samples from Ground Water

Pesticides	Spiked Level (ppb)	Mean Recovered Value[a] (ppb)	CV (%)
Dithiopyr	0.50	0.54	25
	2.0	2.2	12
	12	11	3.1
	25	23	2.6
	50	46	4.1
	100	95	3.3
Fenoxaporp-P-ethyl	0.15	0.16	24
	2.0	1.9	4.1
	12	10	6.6
	25	22	4.7
	50	46	3.1
	100	93	2.5
Halofenozide	0.10	0.11	19
	2.0	2.1	8.6
	12	12	7.3
	25	24	5.0
	50	49	2.1
	100	98	2.9
Oryzalin	0.10	0.11	14
	2.0	2.0	6.8
	12	12	4.1
	25	24	3.1
	50	47	2.4
	100	95	3.3

[a] Mean recovered value based on six determinations performed on six different days

Table 18. Reproducibility of Fortified Samples from Surface Water

Pesticides	Spiked Level (ppb)	Mean Recovered Value[a] (ppb)	CV (%)
Dithiopyr	0.50	0.45	17
	2.0	1.8	2.2
	12	10	2.7
	25	22	3.3
	50	45	5.8
	100	92	2.2
Fenoxaporp-P-ethyl	0.30	0.25	12
	2.0	2.0	2.3
	12	11	4.3
	25	23	4.3
	50	46	6.0
	100	92	4.8
Halofenozide	0.20	0.19	9.9
	2.0	2.0	3.8
	12	12	1.3
	25	24	0.80
	50	48	3.4
	100	96	1.6
Oryzalin	0.20	0.19	12
	2.0	2.0	3.9
	12	11	5.2
	25	23	6.1
	50	46	6.6
	100	92	5.7

[a] Mean recovered value based on six determinations performed on six different days

CONCLUSION

A simple, relatively fast, and efficient HPLC method has been developed for the simultaneous determination of dithiopyr, fanoxaprop-P-ethyl, halofenozide, and oryzalin in ground and surface water. The results of the linearity, sensitivity, recovery and reproducibility studies indicate the method presented here is a successful, acceptable technique.

Compared with the existing methods, the method discussed in this thesis has several advantages over previous methods. First no derivatization step is required as compared to current official methods. Second the styrene divinylbenzene polymer SPE has shown to be an efficient tool for extracting pesticides from water samples and reducing the matrix effects as observed in control samples. SPE procedure makes unnecessary the cleanup steps in presently used procedures. Although some of the methods using GC may provide better sensitivity for some of the target pesticides than this method described, they are very time-and labor-consuming due to the complex extraction procedure and derivatization process. Finally, in terms of sensitivity, this method permits determination of pesticide residues in surface and ground waters at levels of around 0.1 ppb. Method detection limits were adequate for environmental monitoring and can satisfy the requirements set by EPA and international regulations for the limits of maximum residues (MRL), which are usually at the ppm level for the majority of pesticides and ppb for some others.

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