Padden Creek Pesticide Monitoring Project

Quality Assurance Project Plan

Prepared by

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March 26, 2001

Washington State Department of Ecology
Environmental Assessment Program
Olympia, Washington

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Errata to:

Padden Creek Pesticide Monitoring Project:
Quality Assurance Project Plan.
March 26, 2001.

<u>Page 4, paragraph 2, last sentence:</u>

The correct spelling for Bob's last name is "Carrell".

<u>Page 8, Table 2</u>:

The preservative for TOC samples is HCl, not H2SO4.

<u>Page 8, paragraph 2, last sentence should read:</u>

Water samples will be stored at MEL at $4 \pm 2°C$, until they are extracted and analyzed.

<u>Page 8, paragraph 1, last sentence should read:</u>

After collection, samples will be stored in a refrigerator at Ecology facilities then transported to the Ecology/EPA Manchester Environmental Laboratory (MEL) on the next business day.

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Project Description

Recent water quality studies in the Puget Sound region have raised concern about the impacts that residential use of pesticides are having on the aquatic environment (Bortelson and Davis, 1997; Voss et al., 1997). Because homeowners receive very little training and education in the use of pesticides, these products are often over-used and misapplied, presenting a considerable risk to aquatic life.

Several groups are cooperating to minimize pollution from residential sources to urban streams in Bellingham, WA. They include: Bellingham Field Office of the Department of Ecology; Western Washington University; City of Bellingham, and RESources – an environmental education group. These participants cooperate under the umbrella of the "Whatcom Watersheds Pledge" program. The program provides educational materials and technical assistance to residents living in various watersheds around Bellingham to help them identify and implement specific actions they can take to reduce water pollution.

The Padden Creek watershed in Bellingham provides an excellent opportunity to study the effects of residentially-used pesticides on an urban stream and the effectiveness of targeted educational outreach to change the behavior of residents with regard to their use of pesticides. Padden Creek is one of the three major urban streams running through the City of Bellingham. The Padden Creek watershed is different from the two other major watersheds in the area (Whatcom Creek and Squalicum Creek) in that most of its length it is surrounded almost entirely by residential development.

A study of Padden Creek will involve monitoring pesticides, general water quality, and benthic macroinvertebrates in Padden Creek before and after basin residents are educated about the use of pesticides. Ecology's Environmental Assessment Program will characterize pesticide levels in the stream. This Quality Assurance Project Plan (QAPP) describes how the pesticide monitoring component of the study will be performed. Western Washington University (WWU) will assess general water quality conditions and benthic macroinvertbrates. Details of WWU's water quality monitoring efforts are described in a separate document (Matthews,2000). The benthic macroinvertebrate component of the project will be coordinated by BFO and performed according to a standardized protocol developed by Ecology (Plotnikoff, 1994).

Study Objectives

The objectives of this pesticide monitoring program are to:

- Characterize pesticide concentrations in the Padden Creek watershed during the spring season of two consecutive years.
- Compare pesticide concentrations in Padden Creek before and after implementation of an education outreach program.
- Evaluate if differences in pesticide concentrations, if present, can be attributed to the education efforts in the basin.

The goal of the WWU monitoring effort is to evaluate water quality conditions in the Padden Creek watershed and identify areas of greatest concern in order to educate the public and focus efforts in pollution controls.

Responsibilities

Ecology, Bellingham Field Office (BFO), Project Managers
Bruce Barbour (360) 738-6249 and David Laws (360) 676-6573 are responsible for the overall study design, coordination, and the overall project final report. The BFO will also coordinate the IPM program and characterize the extent of the education efforts in order to help determine their potential effect on improving water quality.

Institute for Watershed Studies – Western Washington University
Joan Vandersypen (360) 650-7384 is the contact for WWU's role in elements of the broader study. These elements include conducting general water quality monitoring and associated laboratory analysis, benthic macroinvertebrate sampling and identification. This program and results will be reported to the BFO.

Ecology Manchester Environmental Laboratory (MEL)
Stuart Magoon (360) 871-8801 is the director of the MEL and is responsible for coordinating pesticide analysis services for the project at MEL. Norm Olson and Bob Carrol (360) 871-8820/8804 are senior chemists who will conduct the pesticide analyses.

Ecology Quality Assurance
Cliff Kirchmer (360) 407-6455 is the quality assurance officer for Ecology. He will review this QAPP to ensure that it meets Ecology quality standards and be available to provide assistance with the evaluation of QA/QC data for the project.

Ecology Contaminant Studies Unit

Keith Seiders (360) 407-6689 will prepare and finalize the QAPP, conduct the pesticide sampling, and prepare a report that describes results from the pesticide sampling effort.

Schedule

QAPP Finalized and Approved	March, 2001
Baseline Pesticide Monitoring	April to May, 2001
Baseline Progress Report	October, 2001
Post-Education Pesticide Monitoring	April to May, 2002
Draft Report	October, 2002
Final Report	November, 2002
Data Entered into EIM System	by November, 2002

Study Design

Pesticide sampling will occur in the spring of 2001 prior to implementation of the education program and again in the spring of 2002 after implementation of the education program. Results from the two seasons of sampling will be characterized and compared for differences in mean pesticide concentrations using the Student's t-test and a paired-comparison test as described in Lombard and Kirchmer (2001). The nonparametric Mann-Whitney test may also be used.

The months of April and May are targeted for sampling because this is the period when surface runoff follows peak application of residential pesticides. This is also the period when the highest pesticide levels have traditionally been detected in the Washington State Pesticide Monitoring Program (WSPMP) administered by Ecology since 1991.

Water samples for pesticide analysis will be collected from three sites in Padden Creek and one tributary stream (Connelly Creek) on a total of ten occasions between April 2001 and May 2002 (Figure 1). Five collections will occur in the spring of 2001 and five during the spring of 2002. Sites were selected to bracket neighborhoods targeted for educational programs. Sample site locations are described below in Table 1.

Table 1. Sample site descriptions.

Site	Location	Ecology pesticides	WWU water quality and macro-invertebrates
PC-1	Padden Cr. at Marine View Park		X
PC-2	Padden Cr. at Fairhaven Park	X	X
PC-3	Connelly Cr. Just upstream of confluence with Padden Cr.	X	X
PC-4	Padden Cr. Upstream of confluence with Connelly Cr.	X	X
PC-5	Padden Cr. Below outlet of Lake Padden	X	X
PC-6	Unnamed Cr. Above Lake Padden		X

Water samples will be analyzed for three classes of pesticides: nitrogen, organophosphorous, and chlorophenoxy (herbicides). This suite of pesticide analyses was chosen on the basis of previous detection during Ecology's WSPMP and the potential for residential use. Samples will also be analyzed for total suspended solids (TSS) and total organic carbon (TOC) to aid the interpretation of pesticide data. Measurements of flow, pH, temperature, and specific conductance will be made in the field. The estimated laboratory cost for the project is shown in Appendix A.

Sample collection will be attempted during periods when pesticide transport is likely to occur through runoff processes. The criteria for sampling are several days of dry weather followed by precipitation that causes an increase in streamflow at sample sites. A recent study in the nearby Whatcom Creek basin suggests that a rainfall event of about 0.15 inch will generate an increase in streamflow (Serdar, et.al., 1999). These criteria may be modified based on observed responses in streamflow from rainfall and the ability to mobilize sampling crews and meet available lab capacity. Review of precipitation data compiled by Perrich (1988) indicates that April and May will likely present enough storm events with desirable characteristics for sampling (e.g. mean storm duration of about ten hours, mean total storm precipitation of about 0.35 inch, and about five days between storms).

Meteorological forecasts and information from the National Weather Service will be used to help select rainfall events to sample. Five rainfall events will be targeted for sampling each season. A single sample at each site will be collected during the event. Efforts will not be made to sample the entire stream hydrograph because of the logistical challenges and limited resources associated with this effort.

Expectations for relying on water quality data to demonstrate the success of this IPM education program may need to be tempered. Evaluating the effectiveness of nonpoint pollution control efforts in general is a challenging task because of the need to account for so many variables that affect the generation, transport, and detection of target pollutants (EPA, 1997). The ability to discern differences in pesticide concentrations from one year to the next in this study will be confounded by a various factors such as sampling and analytical variability and seasonal use patterns of pesticides by area residents. These and other factors will also contribute to the difficulty in attributing differences in pesticide concentrations solely to the IPM education efforts. These challenges could be examined more closely after reviewing results from the first year's sampling effort.

Data Quality: Objectives and Assessment

Bias from interference of matrix effects will be assessed through analysis of matrix spikes. The data quality objective for bias is 50% - 150% recoveries of matrix spikes. Surrogate recoveries will provide estimates of accuracy for the entire analytical procedure. Transport and equipment rinsate blanks will be used to assess bias. ***Precision*** of the data will be assessed through the analysis of matrix spike duplicates and field replicate samples. The data quality objective for precision is a relative percent difference (RPD) that is <25%. Matrix spike/spike duplicate and field replicate data from recent pesticide projects (e.g. Davis, 1998; Serdar *et al*., 1999) indicate that these objectives for bias and precision are achievable. Should field duplicate results for some compounds exceed the target RPD, a closer examination of the sampling and analytical circumstances associated with such results will be done.

Representativeness will be achieved by sampling multiple times each spring and by obtaining a composite sample at each site on each sampling event for analysis of target compounds. Samples will be collected on five separate occasions during both spring sampling periods, thus representing of a range of hydrologic and pesticide application conditions. Pollutant concentrations in surface water can exhibit high variability throughout a runoff event and this variability may confound the ability to determine if differences in pesticide concentrations between years is due to this variability or is due to changes in pesticide use resulting from the education efforts. Sampling variability will be examined using sample results, field replicate results, and literature reviews.

The probability of attaining 100% ***completeness*** will be improved by detailed field preparation, following sample collection methods outlined previously, and using care in transporting samples. The laboratory and the laboratory courier will be notified in advance of a sampling event to ensure recommended holding times be met.

The ***comparability*** of pesticide data from the 2001 and 2002 sampling events, and with pesticide data from other studies should be adequate for comparing these data sets to one another. Sample collection and field procedures will be the same for each year's sampling effort and are consistent with current and historic methods used by the WSPMP. However, the comparability of the pesticide results between the two seasons of sampling could be negated by other factors such as stream flow, precipitation, and seasonal characteristics. These factors will be examined to determine their potential effect on the comparability of the pesticide data.

Sampling Methods

Samples will be collected using a U.S. Geological Survey depth-integrating sampler for depths greater than one foot. A hand held bottle will be used to collect samples where the water depth is less than one foot. The depth-integrating sampler consists of a DH-81 adapter with a D-77 cap and one-liter jar assembled so that water contacts only Teflon or glass. Samples will be collected by slowly lowering the sampler to the bottom and immediately raising the sampler at the same rate to fill the sampler bottle. Three points (quarter-point transects) across the stream at each site will be sampled to create a composite sample. The sub-samples will be split into one-gallon glass sample containers, filling each container one-third full from each quarter-point.

The depth-integrating samplers and other sampling equipment will be cleaned prior to sampling by scrubbing with Liquinox® detergent followed by sequential rinses with tap water, deionized water, pesticide-grade acetone, and spectro-grade hexane. All cleaned sampling equipment will be wrapped in aluminum foil to prevent contamination.

Temperature, pH, conductivity, TSS, TOC, and streamflow will be measured each time water is sampled for as described in Cusimano (1993) and Ecology (1999). Recommended sample bottles, preservatives, and holding times are listed in Table 2. Temperature will be measured with a thermometer. The measurement of pH will be done using an Orion Model 250 temperature-compensating pH meter. Specific conductance will be measured using a YSI Model 33 S-C-T meter. Sample location coordinates will be determined in the field by using a Magellan GPS 320 global positioning receiver. Stream flow will be measured using a Swoffer Model 2100 TSR or a Marsh-McBirney, Inc. Model 201 flow meter.

Table 2. Recommended Sample Containers and Preservation.

Parameter	Sample Container	Preservation	Holding Time
Pesticides	Glass/teflon lid liner, 1 gal.	4°C	7 days
Total Suspended Solids	Polyethylene, 1 L	4 °C	7 days
Total Organic Carbon	Polyethylene, 60 mL	4°C, H_2SO_4, <pH 2	28 days

Sample containers will be placed into coolers and cooled with ice. Glass sample containers will be protected from breakage by wrapping each in bubble-wrap. The cooler will then be sealed with a chain-of-custody seal. Chain-of-custody procedures will be used for all samples. After collection, samples will be stored in a refrigerator at the Ecology Bellingham Field Office building then transported to the Ecology/EPA Manchester Environmental Laboratory (MEL) the next business day morning by Ecology's sample courier.

MEL personnel will observe the condition of the shipped water samples, and make note of any samples that are leaking, not cold or with other problems. Upon receipt of water samples, laboratory personnel will complete all paperwork required to track the shipment and log-in the samples. Water samples will be stored at MEL at 4 ± 1°C, until they are extracted and analyzed.

Laboratory Methods

Analytical methods and target detection limits for pesticides and conventional parameters are summarized in Table 3 below. All classes of pesticides will be analyzed using gas chromatography with atomic emission detection (GC/AED). Total suspended solids and TOC will be analyzed using standard EPA methods. Sample analyses will be conducted MEL.

Table 3. Analytical Methods and Expected Detection Limits.

Parameter	Practical Quantitation Limit (1)	Expected Range of Results	Method	Lab
Total Suspended Solids	1.0 mg/L	1-2,000 mg/L	Gravimetric – EPA 160.2	MEL
Total Organic Carbon	1.0 mg/L	1-20 mg/L	Combustion IR – EPA 415.1	MEL
Nitrogen Pesticides	0.01-1.0 µg/L	0.01-0.5 µg/L	GC/AED – EPA 8085	MEL
Organophosphorous Pesticides	0.01-1.0 µg/L	0.01-0.2 µg/L	GC/AED – EPA 8085	MEL
Chlorophenoxy Herbicides	0.01-1.0 µg/L	0.01-1.0 µg/L	GC/AED – EPA 8085	MEL

(1) The PQL varies among target pesticide compounds and should be within the stated range.

The target detection limits and expected range of results are derived from WSPMP data. Historically, most of the pesticides detected by WSPMP in water samples are below quantitation limits. Appendix B shows target pesticides for analysis at MEL.

Quality Assurance and Quality Control

Laboratory quality control procedures routinely used by MEL will be sufficient for this project. Should problems with samples or analyses arise, MEL will confer with the project lead about the nature and need for corrective actions.

Several field procedures will help assess the quality of sample data. Procedures include the use of: field replicates; rinsate blanks for sampling equipment; transport blanks; and spike and duplicate spike samples. The use of field instruments will follow manufacturer's calibration and operating procedures. Commercial standards will be used for calibrating pH and conductivity instruments. The field thermometer will be checked against a laboratory reference thermometer.

Data Reduction, Review, and Reporting

Project data generated in the field or received from the laboratory will be tabulated and then verified. Field measurements will be reviewed by the project lead for quality and the results summarized in narrative form. Water quality data received from MEL will be accompanied by written quality assurance reviews done my MEL staff. Results from field and laboratory measurements will be entered into the Ecology Environmental Information Management (EIM) database.

A report for the pesticide monitoring component of the overall project will be prepared for the project manager at Ecology's BFO. The pesticide monitoring report will contain the following elements:

- Description of the project.
- Summary of the findings.
- Detailed description of the sampling methods and sampling stations.
- Map and coordinates (latitude/longitude) of the sampling stations.
- Discussion of the analytical methods and data quality.
- Tables of all chemical data.
- Discussion of pesticide results:
    1. Comparison of pre- and post-education results and testing for significant differences between them using appropriate statistical analysis such as the Student's t-test, the paired-comparison test, and the Mann-Whitney test.
    2. Discussion of the variability of pesticide concentrations and ability to discern sampling

variability from changes in pesticide loading to streams as a result of education efforts.

3. Comparison of results to water quality criteria, guidelines, and recommended maximum concentrations to protect aquatic life, wildlife, and human health.
4. Comparison of results to WSPMP and other applicable pesticide data.

- Recommendations for further action (if warranted)

References

Bortleson, G. and Davis, D. 1997. Pesticides in Selected Small Streams in the Puget Sound Basin, 1987 – 1995. U.S. Dept. of Interior – U.S. Geological Survey National Water Quality Assessment Program, and the Washington State Department of Ecology, USGS Fact Sheet 067-97.

Cusimano, B., 1993. Field Sampling and Measurement Protocols for the Watershed Assessments Section. Publication No. 93-e04. Washington State Department of Ecology, Environmental Assessment Program, Olympia, WA.

Davis, D., 1998. Washington State Pesticide Monitoring Program: 1996 Surface Water Sampling Report. Publication No. 98-305. Washington State Department of Ecology, Environmental Investigations and Laboratory Services Program, Olympia, Washington.

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USEPA, 1997. Monitoring Guidance for Determining the Effectiveness of Nonpoint Source Controls. Publication No. EPA 841-B-96-004. U.S. Environmental Protection Agency, Office of Water - Nonpoint Source Control Branch, Washington D.C.

Lombard, S. and C. Kirchmer. 2001. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Publication No.01-03-003. Washington State Department of Ecology, Environmental Assessment Program, Department of Ecology, Olympia, WA.

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Serdar, D., D. Davis, and J. Hirsch. 1999. Lake Whatcom Watershed Cooperative Drinking Water Protection Project: Results of 1998 Water, Sediment and Fish Tissue Sampling. Publication No. 99-337. Washington State Department of Ecology, Environmental Assessments Program, Olympia, Washington.

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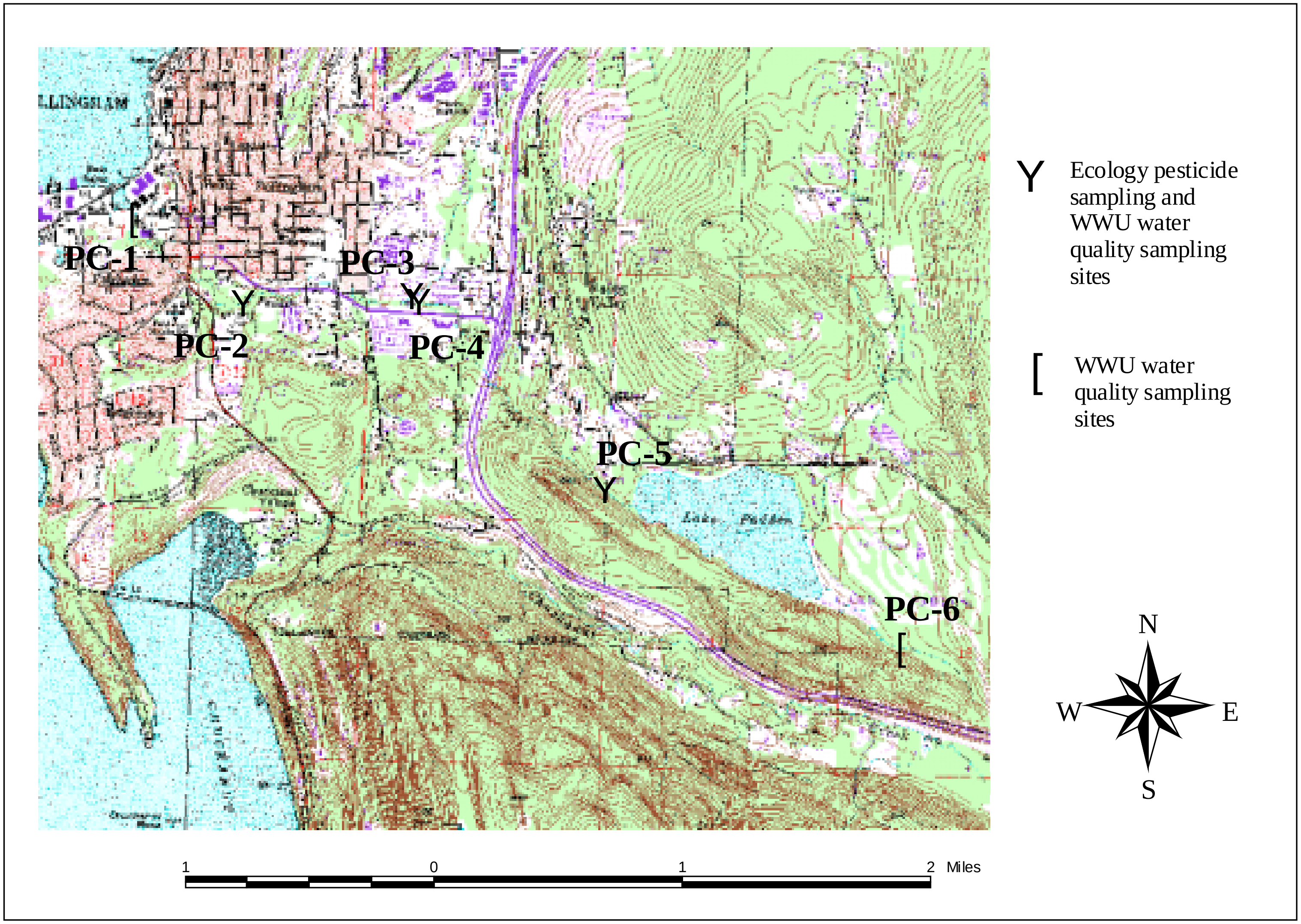

Figure 1. Padden Creek water quality study sample sites.

Appendix A. Estimated Ecology Lab Costs for the Padden Creek Water Quality Study.

Analyte	Laboratory	Method	No. WQ Samples	No. QA Samples	No. Total Samples	Cost per Sample ($)	Subtotal Cost ($)
Conventionals							
pH	Field	Field meter	40	10	50	0	0
Specific Conductance	Field	Field meter	40	10	50	0	0
Temperature	Field	Thermometer	40	10	50	0	0
Dissolved Oxygen	Field	SM 19 4500OB	40	10	50	0	0
Flow	Field	Marsh-McBirney	40	10	50	0	0
Total Suspended Solids	MEL	EPA160.2	40	10	50	10	500
Total Organic Carbon	MEL	EPA415.1	40	10	50	29	1450
Organics							
N-Pesticides	MEL	GC/AED (EPA8085)	40	20	60	184	11040
OP-Pest	MEL	GC/AED (EPA8085)	40	20	60	184	11040
Dual scan discount					56	-55	-3080
Herbicides	MEL	GC/AED (EPA8085)	40	20	60	184	11040

Cost for 1 season = 15,995

Cost for 2 seasons = 31,990

Quality Assurance Samples:

Conventionals: 1 field replicate per sample outing; study total = 10

Organics: 1 field replicate per sample outing; study total = 10
3 equipment blanks per season; study total = 6
2 matrix spike/matrix spike duplicates per season; study total = 4
(the dual scan discount does not apply to MS/MSDs)

Appendix B. Target Pesticides for the Padden Creek Water Quality Study.

<u>Nitrogen Compounds</u>

Alachlor
Ametryn
Atraton
Atrazine
Benefin
Bromacil
Butachlor
Butylate
Carboxin
Chlorothalonil (Daconil)
Chlorpropham
Cyanazine
Cycloate
Di-allate (Avadex)
Diphenamid
Dichlobenil
Eptam
Ethalfluralin (Sonalan)
Fenarimol
Fluridone
Hexazinone
Metalaxyl
Metolachlor
Metribuzin
MGK264
Molinate
Napropamide
Norflurazon
Oxyfluorfen
Pebulate
Pendimethalin
Profluaralin
Prometon (Pramitol 5p)
Prometryn
Pronamide (Kerb)
Propachlor (Ramrod)
Propazine
Simazine
Tebuthiuron
Terbacil
Terbutryn (Igran)
Treflan (Trifluralin)
Triadimefon
Triallate
Vernolate

<u>Surrogate</u>

1,3-Dimethyl-2-nitrobenzene

<u>Organophosphorus Compounds</u>

Abate (Temephos)
Azinphos (Guthion)
Bolstar (Sulprofos)
Carbophenothion
Chlorpyrifos
Coumaphos
Demeton-O
Demeton-S
Diazinon
Dichlorvos (DDVP)
Dimethoate
Dioxathion
Disulfoton (Di-Syston)
EPN
Ethion
Ethoprop
Azinphos Ethyl (Ethyl Guthion)
Fenamiphos
Fenitrothion
Fensulfothion
Fenthion
Fonofos
Imidan
Malathion
Merphos (1 & 2)
Methyl Chlorpyrifos
Methyl Paraoxon
Methyl Parathion
Mevinphos
Parathion
Phorate
Phosphamidan
Propetamphos
Ronnel
Sulfotepp
Tribufos (DEF)
Tetrachlorvinphos (Gardona)

<u>Surrogate</u>

Triphenyl Phosphate

<u>Chlorophenoxy Herbicides</u>

Acifluorfen (Blazer)
Bentazon
Bromoxynil
2,4-D
Dacthal (DCPA)
2,4-DB
Dicamba I
3,5-Dichlorobenzoic Acid
Dichlorprop
Diclofop-Methyl
Dinoseb
Ioxynil
MCPA
MCPP (Mecoprop)
4-Nitrophenol
Pentachlorophenol
Picloram
2,4,5-T
2,4,5-TB
2,3,4,5-Tetrachlorophenol
2,3,4,6-Tetrachlorophenol
2,4,5-TP (Silvex)
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Trichlopyr

<u>Surrogate</u>

2,4,6-Tribromophenol