WASHINGTON STATE DEPARTMENT OF ECOLOGY

Potholes Reservoir Pesticide Survey, 1998

Abstract

There has been a recent decline in the fisheries in the Potholes Reservoir. In an attempt to determine a possible cause, water samples were collected from the reservoir during the peak application period for agricultural pesticides in 1998. Much of the water entering the Potholes Reservoir is irrigation-return water.

Four herbicides were detected in every sample: 2,4-D, eptam (EPTC), atrazine, and atrazine desethyl (a breakdown component of atrazine). Other pesticides detected were the herbicides, 4-nitrophenol, MCPP (Mecoprop), MCPA, bentazon, simazine, bromacil, hexazinone, as well as the insecticide, azinphos-methyl (Guthion®). Levels of pesticides detected in the reservoir were lower than found in previous studies that sampled surrounding irrigation-return water, but the detection frequency was higher (Embrey and Block 1995, Wagner et al. 1996, Williamson et al. 1998).

Water quality criteria exist for only six of the 12 pesticides detected. Of these six, azinphos-methyl was detected at levels that exceeded EPA (U.S. Environmental Protection Agency) chronic water quality criteria for the protection of aquatic organisms. This occurred at two sites in the northwest part of the reservoir in May. This study does not definitively link pesticides to declining fish levels; however, pesticides may play a part.

Recommendations

- Monitor water quality in the reservoir and inflows for pesticide levels.
- Consider using bioassays to determine if the combination of pesticides detected in the reservoir is having a direct affect on aquatic organisms.
- Consider adding the Potholes Reservoir to the Washington State Pesticide Monitoring Program.
- Consider listing the Potholes Reservoir on the state 303(d) list for impacted water bodies for exceeding the water quality criterion for azinphos-methyl.

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August 1999

Ecology Report No. 99-331
Waterbody No.1193444470140

Introduction

Background

The fisheries in many of the lakes and reservoirs in the Mid-Columbia Basin have been declining for several years (Corth 1998). The Washington State Department of Fish and Wildlife (WSDFW) is assessing fish populations in Potholes Reservoir in an attempt to identify the cause of the declines. Poor water quality may be a contributing factor, but little information is available to perform an evaluation.

Pesticides are heavily used in the Mid-Columbia Basin for crop protection. Studies show that irrigation-return water from these crops carries high concentrations of several pesticides (Embrey and Block 1995, Wagner et al. 1996, Davis et al. 1998). Much of the water entering Potholes Reservoir is from irrigation-return by way of the Frenchman Hills Wasteway, Winchester Wasteway, and Lind Coulee.

The possibility that pesticides in Potholes Reservoir are causing a decline of the fisheries was identified during the needs assessment for the Mid-Columbia Watershed (Knight 1997).

Objectives

In May and June of 1998, Ecology collected water samples from the Potholes Reservoir during the peak application period for agricultural pesticides. This study is part of an effort to identify the cause of recent declines in the fisheries in the reservoir. Ecology's Ambient Monitoring Section measured conventional water quality parameters in the reservoir during the summer of 1998 (Hallock 1998), and the WSDFW will assess fish populations as part of an ongoing study (Corth 1998). Results from the three studies will be combined with information from a literature search to produce a comprehensive assessment.

The objectives of this study were to:

1. Screen water samples from the reservoir for pesticides during the peak pesticide application period.
2. Assess the types and concentrations of pesticides detected to determine their potential for impacting fauna in the reservoir and contributing to the decline of the fisheries.

Pesticides detected were compared to available water quality criteria designed to protect aquatic life. Aquatic criteria indicate concentrations that, when exceeded, can adversely affect aquatic organisms. The criteria used were obtained from

- *Canadian Water Quality Guidelines, Freshwater Aquatic Life Criterion* – maximum concentrations that should not be exceeded (Environment Canada 1999)
- EPA chronic water-quality criteria for the protection of aquatic organisms

- If available, the EPA Maximum Contaminant Level (MCL) – the maximum permissible level of a contaminant in water that is delivered to any user of a public water system

Potholes Reservoir

Potholes Reservoir is located in north central Grant County within the South Columbia Basin Irrigation District. Agriculture in Grant County is primarily wheat, hay (alfalfa/other, wild, silage), corn, and potatoes (Washington Agricultural Statistics Service 1997).

Potholes Reservoir collects excess canal water and return-flow water from irrigated land in the northern part of the Columbia Basin Project for reuse in the southern part. It is managed by the Bureau of Reclamation. Potholes Reservoir receives irrigation-return water and wastewater from the Winchester and Frenchman Hills Wasteways, and Lind Coulee. The Winchester and Frenchman Hills Wasteways drain much of the irrigated agricultural land south of the Beezley Hills and north of the Frenchman Hills on the west side of the reservoir. Lind Coulee drains irrigated agriculture land east of the reservoir, and receives water from Weber Coulee and Weber Wasteway. Water also enters the reservoir from Moses Lake. Peak water withdrawal (irrigation deliveries) in 1998 occurred from June through August (Smith 1999).

The northern half of the reservoir, particularly the western side, is shallow. The southern end is deepest near the dam on the east side at about 70 feet. The shallow area in the northwest corner is very productive and is the rearing grounds for juvenile fish (Corth 1998). These rearing grounds are likely to be the most sensitive area in the reservoir to pesticide contamination.

Methods

Sampling sites are shown in Figure 1. Sites 1 and 2 are in the northwest shallow area (9 and 17 feet deep), Site 3 is near the center of the reservoir, Site 4 is in the cove in the southwest corner, and Site 5 is in the deepest part of the reservoir near the outlet (91 feet deep). Appendix A lists specific site locations. All of the sites were located away from the direct influence of discharges into the reservoir, and are intended to represent general pesticide concentrations.

Samples were collected May 19 and again on June 15-16, 1998. May and June are the months of peak pesticide use in the Mid-Columbia Basin (Ebbert 1995). One depth-integrated sample was collected from Sites 1 through 4 during each sampling event. A thermocline (surface temperature of 16° C, bottom temperature 9.2° C) was present at Site 5 in June; as a result, separate surface and bottom samples were collected.

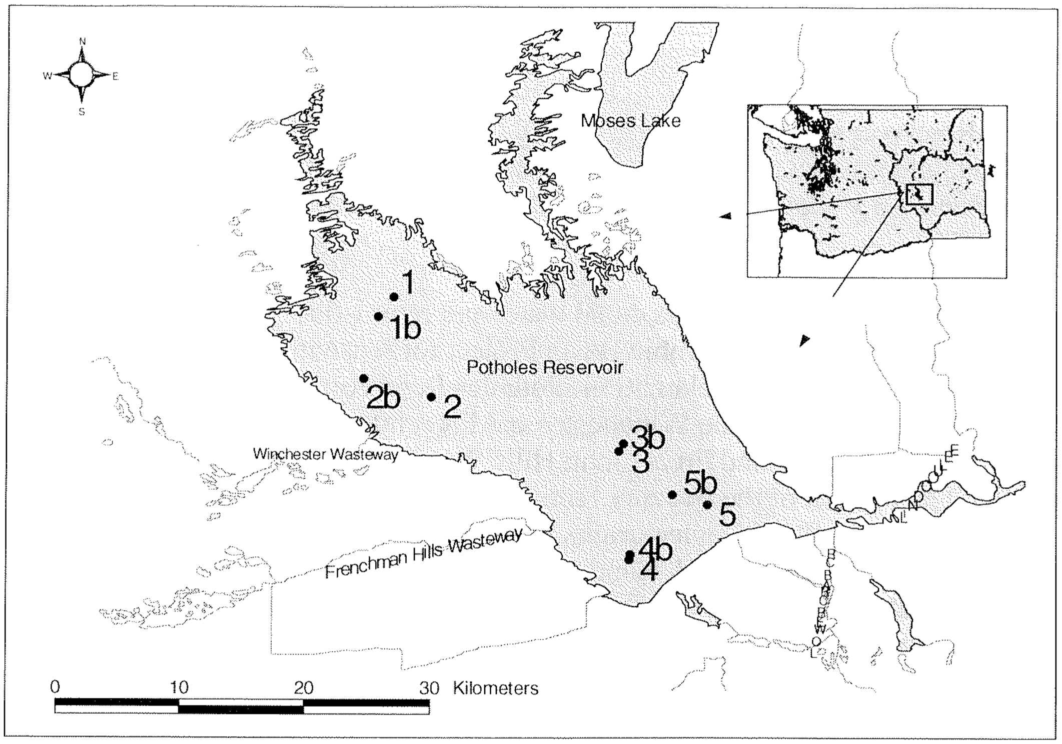

Figure 1. Potholes Reservoir and sampling sites.

b sites are June samples

A DH-76 hand line sampler, modified so sample water contacts only Teflon or glass, was used to collect depth-integrated samples. A hand-held bottle was used to collect surface samples. The bottom samples were collected with a 10-liter, Go-Flo water-sampling bottle.

Depth integrated samples were collected by slowly lowering the sampler to the bottom and immediately raising the sampler at the same rate; care was taken to keep the sampler from touching the bottom to prevent sediment disturbance. Water depth was measured with a weighted line or the boat's depth sounder. The hand line sampler collects one quart of water, which required nine samples to fill two one-gallon bottles and one 125ml bottle. The Go-Flo sampler was lowered to the bottom, but positioned on the line about five feet above the weight to avoid collecting sediment disturbed by the sampler hitting the bottom. Only one bottom sample was needed to fill all the sample bottles. Samples were stored on ice until delivery to the laboratory.

All samples for pesticide analyses were placed in pre-cleaned sample containers. The sampler bottles for water collection were also precleaned. The depth-integrating sampler was decontaminated prior to field work and between samples in the field by washing with laboratory-grade detergent (Liquinox), rinsing with de-ionized water, and rinsing with pesticide-grade acetone. The Go-Flo sampler is made of PVC (the inside is Teflon coated), so acetone cannot be used to clean it. This sampler was used at one site per sampling event, so field cleaning was not necessary. The Go-Flo sampler was cleaned prior to fieldwork by carefully washing it with Liquinox, rinsing with de-ionized water and organic-free water, and finally rinsing with pesticide-grade methanol.

Quality Assurance/Quality Control

Samples were analyzed for 157 pesticides and breakdown products (Appendix B). All samples were analyzed at the Ecology/EPA Manchester Laboratory. Analytical methods are listed in Table 1.

Table 1. Pesticide compounds and analytical method.

COMPOUND	METHOD
Chlorinated	EPA Method 8085
Organophosphorous	EPA Method 8085
Nitrogen-containing	EPA Method 8085
Carbamates	EPA Method 531.1 (modified)

A sample from Site 1 was duplicated (split) to estimate analytical precision. Each cast from the depth-integrated sampler was hand split into the sample bottles, which required 17 casts to fill four one-gallon bottles and two 125-ml bottles. The relative percent difference (RPD) between sample one and its duplicate is presented in the Table 2. There were three instances in which a pesticide was detected in one sample and not the other. Only pesticides that were detected in both samples were used to calculate the overall RPD.

Table 2. Relative percent difference between duplicate samples (µg/l).

Pesticide	A	B	Average	Difference	RPD
4-Nitrophenol	0.033	0.015	0.024	0.018	75
MCPP	0.017	ND	0.0085	0.017	
2,4-D	0.031	0.034	0.0325	0.003	9.2
Simazine	ND	0.002	0.001	0.002	
Atrazine	0.005	0.005	0.005	0	0
Bromacil	0.004	0.005	0.0045	0.001	22.2
Eptam	0.068	0.071	0.0695	0.003	4.3
Hexazinone	0.002	ND	0.001	0.002	
Atrazine Desethyl	0.005	0.006	0.0055	0.001	18.2
Azinphos-methyl	0.014	0.013	0.0135	0.001	7.4
Dicamba	ND	0.015	0.0075	0.015	
			Average RPD		**19.5**

ND - not detected

Data packages and analytical QA/QC results were reviewed and assessed by Manchester Laboratory personnel. Case narratives are included in Appendix C. All data are useable as qualified. All analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection limit. If a target analyte is detected and its identification is unambiguously confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate, 'J' qualifier. Approximately 84% of the detected pesticide concentrations were qualified as estimates.

Although most concentration levels are qualified as an estimate (J), the analytes were positively detected. Most of the pesticides detected were present in multiple samples, and no target compounds were detected in laboratory blanks.

Results

Of the 157 pesticides and breakdown products analyzed in the samples from the Potholes Reservoir, 12 were consistently detected at or above the detection limit (Table 3 and 4). Over 50 percent of the pesticides detected were below 0.01 µg/l. Only one of the 12 pesticides detected exceeded aquatic life criteria: Azinphos-methyl (Guthion®). Four pesticides were detected at every site and sampling event: 2,4-D, eptam (EPTC), atrazine and atrazine desethyl. There was one unidentified compound found in three samples: a nitrogen containing pesticide. In one sample (Site 5, May 19, 1998) caffeine was identified.

Although this study was not specifically designed to test for differences between the northern and southern areas of the reservoir, some statistical analyses were conducted. A Bonferroni adjustment was applied to all tests to maintain an overall alpha level of 0.05.

Statistically there was no discernable difference in the number of pesticides detected between the two sampling events in May and June (Table 5, t-test, $p = 0.111$) or between the northern sites (1, 2) and the southern sites (3, 4, 5) ($p = 0.85$). Of the six pesticides most frequently detected (Table 6), there was no difference in pesticide levels between the two sampling events or between the northern sites and the southern sites. MCPA was detected in only the southern sites, and predominantly in June. Simazine was detected only once in the northwest sites and in all samples collected from the southern sites.

The 12 pesticides detected in the Potholes Reservoir are discussed in further detail in the following paragraphs. Usage information is primarily derived from the Farm Chemicals Handbook 1996 (Meister and Sine 1996).

4-Nitrophenol, a chlorophenoxy herbicide, was detected at all sites, but not in every sample. 4-Nitrophenol is primarily a breakdown component of parathion and flouridifen; it is also used to make fungicides. There is no water quality criterion for this chemical.

MCPP (Mecoprop), a chlorophenoxy herbicide, was detected at two sites (1 & 2) in the May samples. MCPP (potassium salt) is used to control clover, chickweed, plantain, and other broadleaf weeds in grasses such as fescue, bluegrass, ryegrass, bentgrass, and

Table 3. Pesticides detected in Potholes Reservoir May 19, and June 15-16, 1998 (µg/l).

Pesticides	Sample Sites					
May 19, 1998	**1**	**2**	**3**	**4**	**5[a]**	**5[b]**
4-Nitrophenol	0.033 NJ	0.012 NJ	0.023 J	0.027 J	0.014 J	0.021 J
MCPP	0.017 NJ	0.01 NJ	---	---	---	---
MCPA	---	---	0.007 NJ	---	---	---
2,4-D	0.031 J	0.024 J	0.031 J	0.035 J	0.038 J	0.043
Bentazon	---	---	---	---	---	---
Simazine	---	0.001 NJ	0.003 NJ	0.003 J	0.003 J	0.003 J
Atrazine	0.005 J	0.009 J	0.006 J	0.007 J	0.007 J	0.007 J
Bromacil	0.004	---	---	---	---	0.01 J
Eptam	0.068	0.084	0.054	0.061	0.065	0.015 J
Hexazinone	0.002	0.005 J	0.004 NJ	0.005 NJ	0.005 NJ	---
Atrazine Desethyl	0.005 J	0.008 J	0.004 J	0.006 J	0.006 J	0.007 J
Azinphos-methyl	0.014 J	0.014 J	0.004 NJ	0.005 NJ	0.004 NJ	---
Caffeine	---	---	---	---	---	0.041 NJ
Unknown	---	---	---	---	---	---
June 15-16, 1998						
4-Nitrophenol	0.035 NJ	0.039 J	---	---	0.047 NJ	0.026 NJ
MCPP	---	---	---	---	---	---
MCPA	---	---	0.022 NJ	0.018 NJ	---	0.018 NJ
2,4-D	0.023 J	0.025	0.072	0.077	0.039	0.068
Bentazon	---	---	---	---	0.031 J	---
Simazine	---	---	0.003 NJ	0.003 NJ	0.004 NJ	0.003 NJ
Atrazine	0.008 J	0.011 J	0.006 J	0.006 J	0.007 J	0.007 J
Bromacil	---	---	---	---	0.009 J	---
Eptam	0.053	0.056	0.095	0.1	0.03 J	0.11
Hexazinone	0.006 NJ	0.013 J	0.011 J	0.007 J	0.006 J	0.005 NJ
Atrazine Desethyl	0.009 J	0.008 J	0.008 J	0.007 J	0.007 J	0.007 J
Azinphos-methyl	0.006 NJ	0.007 NJ	---	---	---	---
Caffeine	---	---	---	---	---	---
Unknown	---	---	1 J	1.1 J	---	1 J

J - Analyte was positively identified. The value is an estimate.
NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.
--- - Analyte is below detection limits.

Table 4. Maximum and median concentrations, and aquatic criteria, of pesticides detected in water samples collected May 19 and June 15-16, 1998 from the Potholes Reservoir.

Pesticide	Maximum (µg/l)	Median of Detects (µg/l)	Aquatic-life Criterion (µg/l)
2,4-D	0.077	0.037	4.0[ae], 70.0[c]
Atrazine	0.011	0.007	1.8[a], 3.0[c]
Eptam (EPTC)	0.110	0.063	NA
Atrazine Desethyl	0.009	0.007	NA
Hexazinone	0.011	0.005	NA
4-Nitrophenol	0.047	0.027	NA
Simazine	0.005	0.003	10[a,e], 4.0[c]
Azinphos-methyl (Guthion®)	**0.014**	0.006	0.01[b]
MCPA[d]	0.022	0.018	2.6[a]
Unknown	1.1	1.0	NA
Bromacil	0.010	0.009	5.0[a]
MCPP (Mecoprop)	0.017	0.014	NA
Bentazon	0.031	0.031	NA

a - Canadian Water Quality Guidelines,Freshwater Aquatic Life Criterion – maximum concentrations that should not be exceeded; some are interim levels (Environment Canada 1999)
b - EPA chronic water-quality criteria for the protection of aquatic life (EPA 1986)
c - EPA Maximum Contaminant Level (MCL) – the maximum permissible level of a contaminant in water that is delivered to any user of a public water system
d - Value applies to all forms of MCPA, and all transformation products
e - National Academy of Sciences and National Academy of Engineering 1973
NA - not available

Table 5. Number of pesticides detected in Potholes Reservoir during two sampling events by site location.

Site	Number of Pesticides	
	Detected May 19, 1998	Detected June 15-16, 1998
1	9	7
2	9	7
3	9	7
4	8	7
5 (surface)[a]	8	9
5 (bottom)[a]	7	8

a - Because the reservoir was stratified, two samples were collected at Site 5: a surface and a bottom sample.

bermuda grass. MCPP is used on ornamentals and sports turf for selective control of surface-creeping broadleaf weeds such as red, white clovers, and chickweed. There is no water quality criterion for this chemical.

MCPA is a systemic postemergence chlorophenoxy herbicide. It was detected at three sites (3, 4, and 5). MCPA is a growth regulating selective herbicide used as a translocated herbicide in small grains, peas, grassland, tree crops, turf and non-crop areas for control of many annual and perennial weeds. Canada has an Interim freshwater aquatic criterion of 2.6 μg/l for MCPA. This was not exceeded.

2,4-D was detected in every sample at every site. It is a selective hormone-type, translocated phenoxy compound used mainly as a post-emergence herbicide. It is used for grasses, wheat, barley, oats, rye, hay, rangeland, pasture, asparagus, fallow land, turf, and non-crop areas for control of Canada thistle, dandelion, ragweed and others. The Canadian aquatic criterion for 2,4-D at 4 μg/l is more stringent than the EPA chronic water-quality criterion for the protection of aquatic organisms at 70.0 μg/l. The levels of 2,4-D detected in the Potholes Reservoir were well below these criteria, ranging from 0.023-0.077 μg/l.

Bentazon was detected in only one sample (0.031 μg/l); this was at Site 5 collected June 16, 1998. Bentazon is a selective post-emergence herbicide used to control many broadleaf weeds and sedges in alfalfa, asparagus, cereals, clovers, dry beans, dry peas, and grasses. There is no water quality criterion for this chemical.

Simazine was detected in nine samples. Simazine is a selective triazine herbicide used to control most annual grasses and broadleaf weeds in corn, established alfalfa, established bermudagrass, cherries, peaches, certain nuts, in turf grass sod production, fairways, lawns, and similar areas. Before 1992, simazine was used to control submerged weeds and algae in large aquariums, farm ponds, fish hatcheries, swimming pools, ornamental ponds, and cooling towers (EXTOXNET 1998). The *Canadian Water Quality Guidelines, Freshwater Aquatic Life Criterion* for simazine is 10 μg/l. The EPA maximum contaminant level (MCL) for simazine is 4.0 μg/l; the levels detected in the Potholes Reservoir ranged from 0.001-0.004 μg/l.

Atrazine was detected at every site and every sample. It is a herbicide used as a season-long weed control in corn, sorghum, and certain other crops. It is not commonly used in agricultural fields in the Central Columbia Plateau (Wagner et al. 1996). It is more widely used to control the growth of weeds along the irrigation canals and roads (Greene et al. 1996). The *Canadian Water Quality Guidelines, Freshwater Aquatic Life Criterion* for atrazine is 1.8 μg/l. The MCL for atrazine is 3.0 μg/l; the levels detected in the Potholes Reservoir ranged from 0.005-0.011 μg/l.

Bromacil is a general herbicide used to control weeds and brush in non-crop areas, especially for perennial grasses. This herbicide was detected at Sites 1 and 5 with a concentration range of 0.004-0.010 μg/l. The interim *Canadian Water Quality Guidelines, Freshwater Aquatic Life Criterion* for bromacil is 5.0 μg/l.

Eptam (EPTC) was detected at every site and in every sample. EPTC is a selective thiocarbamate herbicide used for annual grassy weeds, perennial weeds, some broadleaf weeds in beans forage legumes, and potatoes. There is no water quality criterion for this chemical. Levels detected ranged from 0.015-0.11 μg/l.

Hexazinone is a contact and residual herbicide that was detected at every sampling site. It is used when plants are actively growing, to control many annual, biennial and perennial weeds and woody plants on non-crop areas. There is no water quality criterion for this chemical. Levels detected ranged from 0.002-0.013 μg/l.

Atrazine desethyl is a breakdown product of the popular herbicide atrazine. This breakdown product was detected at every site and in every sample. Values detected ranged from 0.004 to 0.009 μg/l. There is no water quality criterion for this chemical.

Azinphos-methyl (Guthion®) is an organophosphorus broad spectrum insecticide registered for use on apples and pome fruit, citrus, stone fruit and roses. It is used for the control of beetles, caterpillars and their larvae, aphids, spiders and mites. This insecticide was detected at all sites. Values detected ranged from 0.004 to 0.014 μg/l. Two samples collected in May, from Site 1 and 2, exceeded the EPA chronic water-quality criteria for the protection of aquatic organisms of 0.01 μg/l.

Caffeine was detected in one of the samples. Caffeine has been detected in water bodies receiving effluent from wastewater treatment plants, and also in urban runoff. It is not believed that any treatment plants directly discharge into Potholes Reservoir.

Discussion

The types of pesticides detected were similar to those found in surface water streams in the Central Columbia Plateau (Williamson et al. 1998) and in the National Water Quality Assessment Pesticide National Synthesis Project Summary (USGS 1998). Of the 12 pesticides detected, there was one insecticide, azinphos-methyl; the remainder were herbicides. The predominance of herbicides over insecticides is typical in agricultural areas (Bortleson and Davis 1997).

This was not a comprehensive pesticide study. A number of commonly used pesticides were not included in the analysis: for example, acrolein and glyphosate (Roundup®). Acrolein is a herbicide used to control vegetation in irrigation canals. Glyphosate is a common general herbicide sold for home use, and applied to winter wheat and other crops. According to the U.S. Department of Agriculture (USDA 1999) approximately 177,000 pounds of glyphosate were applied to winter wheat crops in Washington State in 1998.

The National Agricultural Statistical Service (NASS) and the USDA periodically surveys farmers for chemical usage on certain crops. A quick review of these data reveals a number of pesticides commonly applied to wheat, apples or cherries in Washington that were not included in this pesticide screening survey. Some of the pesticides not included for analysis were clopyralid, thifensulfuron, triasulfuron, methamidophos, esfenvalerate (USDA 1998, 1999), and clofentizine (NASS 1998).

Twelve pesticides or breakdown products were detected in the Potholes Reservoir: 4-nitrophenol, MCPP (Mecoprop), MCPA, 2,4-D, bentazone, simazine, atrazine, bromacil, eptam (EPTC), hexazinone, atrazine desethyl (a breakdown component of atrazine), and azinphos-methyl (Guthion®). Only six of these chemicals have a water quality criterion. The insecticide, azinphos-methyl, was the only chemical detected that exceeded water quality criteria. This occurred at Sites 1 and 2 during the May sampling.

Pesticide levels detected in the Potholes Reservoir were lower than those found in a study (USGS 1999) of the Central Columbia Plateau (CCP), but were found at a greater frequency (Table 6). The difference between the two studies can be primarily attributed to the samples from the CCP being collected from streams that received direct runoff from agricultural areas. The CCP samples were in the upper range of pesticides levels detected in the National Water Quality Assessment Program nationwide. In addition the CCP samples were collected throughout the year, which in part accounts for the lower frequency of detection. Samples for this 1998 study were collected during the peak pesticide application period, which would account for the greater frequency of detects in the samples. However for this study, samples were collected away from direct inflows to provide a more general representation of pesticide levels in the reservoir. It is anticipated that levels of pesticides would be greater in areas around inflows that received direct agricultural runoff.

Although atrazine is not a major herbicide used in agriculture in the Central Columbia Plateau, it and its breakdown product atrazine desethyl were among the most commonly detected compounds in this and other studies (Wagner et al. 1996). This herbicide is widely used in non-agricultural practices such as roadside vegetation control and in turfgrass (EXTOXNET 1998, Greene et al. 1996). Atrazine also has a relatively long half-life in reservoirs, approximately 1-2 years (Goolsby et al. 1993). There is some evidence that groundwater is a source for atrazine to surface waters in the Columbia Basin (Williamson et al. 1998).

2,4-D was detected in all twelve samples. A July 1992 USGS pesticide study detected 2,4-D in water samples from the Potholes Reservoir (Embrey and Block 1995). Samples collected in the east and the west arm of the reservoir in 1992 both had 0.04 μg/l of 2,4-D. These results are similar to the median level (0.037 μg/l) of 2,4-D detected in this 1998 study. Other pesticides that were detected in this 1998 study were not included in the analyses conducted in the 1992 USGS study.

There is some concern about the levels of pesticides in the northern shallow end of the reservoir. These shallow areas are the rearing grounds for many fish and are likely to be the most sensitive area in the reservoir to pesticide contamination. There was no difference in the number of pesticides detected between the northern and southern samples, nor was there a difference in concentrations of the six most frequently detected pesticides (Table 6.). Also, there was no difference in the number of pesticides detected between the two sampling events (May and June), nor was there a difference in concentrations of the six most frequently detected pesticides. Despite these results, some differences between the distribution of pesticides were observed.

Table 6. Comparison of pesticides detected in Potholes Reservoir with streams in the Central Columbia Plateau NWAQP study (USGS 1999).

Potholes Reservoir (present 1998 study)				Streams in the Central Columbia Plateau			
Pesticide	Median of Detects µg/l	Number Detected	Percent Detected	Median of Detects µg/l	Number Detected	Samples	Percent Detected
2,4-D	0.037	12	100	0.13	56	211	27
Atrazine	0.007	12	100	0.017	201	231	87
Eptam	0.063	12	100	0.025	119	231	52
Atrazine Desethyl	0.007	12	100	0.006	136	231	59
Hexazinone	0.005	11	92	NA	NA	NA	NA
4-Nitrophenol	0.027	10	83	NA	NA	NA	NA
Simazine	0.003	9	75	0.011	178	231	77
Azinphos-methyl	0.006	7	58	0.045	28	231	12
MCPA	0.018	4	33	0.125	8	211	4
Bromacil	0.009 [a]	3	25	ND [b]	0	213	0
MCPP	0.014	2	17	NA	NA	NA	NA

[a] - detection limit for Potholes Reservoir was 0.080 µg/l.
[b] - detection limit for the Central Columbia Plateau was 0.035 µg/l.
NA - samples were not analyzed for these pesticides.
ND - non detect; samples were below the analytical detection limit.

Two pesticides, MCPA and simazine, were detected at a greater frequency in the southern sites than in the northern sites. Three of the four detections of MCPA occurred in June. The water quality criterion for azinphos-methyl was exceeded in May at Sites 1 and 2 in the northern half of the reservoir.

Pesticide concentrations can be affected by many things. Pesticide use, pathways, migration, residence time, degradation processes, and circulation patterns in the reservoir all can affect pesticide concentrations within the reservoir. Based on the few samples collected in this study, it is not known how these processes affected the differences in distribution of the pesticides detected.

Conclusions

This is not a comprehensive pesticide study of the Potholes reservoir. It is merely a screening survey of pesticides in the water column. Although 157 pesticides were included in the sample analysis, there are a variety of commonly used pesticides that were not included in the analysis. The only conclusions that can be drawn from this study are those based on the pesticides that were or were not detected.

Of the 157 pesticides and breakdown products analyzed, twelve were detected in the Potholes Reservoir. Seven to nine pesticides were detected in each sample. One insecticide, azinphos-methyl (Guthion®), was detected; the remainder were herbicides.

Little is known about the effects of many of these chemicals on aquatic organisms. There are no available water quality criteria for half of the pesticides detected. Water quality criteria are based on individual chemicals and do not take into account mixtures. This study was too limited in scope to definitively link pesticides to declining fish levels; however, pesticides may play a part.

There is an indication that current levels of pesticides may be harming aquatic life. One pesticide, azinphos-methyl (Guthion®), was detected at levels that exceeded water quality criteria. This is a level at which aquatic organisms may be adversely affected. As a result, Potholes Reservoir should be considered for listing as "water quality limited" for azinphos-methyl under section 303(d) of the Clean Water Act. Potholes Reservoir is currently listed for dieldrin concentrations above the criterion for edible fish tissues (Serdar et al. 1994). Although dieldrin was not detected in the water column in this study, it and other persistent bioaccumulative chemicals may be present in sediment and organisms.

Pesticide analysis of tissue and sediments may provide additional data to help determine pesticide exposures to aquatic life in the Potholes Reservoir. Bioassays may also help determine if pesticides detected in the reservoir are having a direct effect on aquatic organisms.

This study was designed to provide a general view of pesticides in the reservoir and to avoid potential *hotspots*, i.e., near the inflows. One would expect higher levels of pesticides in the agricultural returns entering the reservoir: Frenchman Hills Wasteway, Winchester Wasteway, and Lind Coulee.

More directed pesticide monitoring of the Potholes Reservoir and surrounding irrigation-return waterways is recommended. This monitoring should target those pesticides that are commonly used in the area. Monitoring should include pesticides that are used on crops and in irrigation canals, as well as pesticides used for roadside and railroad vegetation control. This would help to define the sources and levels of pesticides entering the Potholes Reservoir.

References

Bortleson, G.C. and D.A. Davis, 1997. Pesticides in selected small streams in the Puget Sound Basin, 1987-1995. U.S. Geological Survey Fact Sheet 067-97.

Corth, J., 1998. Personal communication, April 24. Washington State Department of Fish and Wildlife, Ephrata, Washington.

Davis, D., A. Johnson, and D. Serdar, 1998. Washington State Pesticide Monitoring Program – 1995 Surface Water Sampling Report. Environmental Investigations and Laboratory Services Program, Olympia, Washington. Publication No. 98-300.

Ebbert, J., 1995. Written communication, October 24. U.S. Geological Survey, Water Resources Division, Tacoma, Washington.

Embrey, S. and E. Block, 1995. Reconnaissance Investigation of Water Quality, Bottom Sediment, and Biota Associated with Irrigation Drainage in the Columbia Basin Project, Washington, 1991-92. U.S. Geological Survey, Water Resources Investigation Report 95-4007, Tacoma, Washington.

Environment Canada, 1999. Canadian Water Quality Guidelines - Freshwater Aquatic Life Criterion: Summary table. 7 pp. http://www.ec.gc.ca.ceqg%2drcqe/wattbl%sfe.doc. Accessed 4/15/1999.

EPA, 1986. Quality Criteria for Water. U.S. Environmental Protection Agency, Office of Regulations and Standards, Washington D.C.

EXTOXNET, 1998. University of California, Davis, Oregon State University, Michigan State University, Cornell University, and the University of Idaho. The EXTOXNET InfoBase is accessible via the World Wide Web (WWW). URL http://ace.orst.edu/info/extoxnet/ Accessed 9/24/1998.

Goolsby, D.A., W.A. Battaglin, J.D. Fallon, et al., 1993. Persistence of Herbicides in Selected Reservoirs in the Midwestern United States - Some Preliminary Results, in D.A. Goolsby, L.L. Boyer, G.E. Mallard, eds. Selected papers on Agricultural Chemicals in Water Resources of the Midcontinental United States: U.S. Geological Survey Open-File Report 93-418, p. 51-63.

Greene, K.E., J.C. Ebbert, and M.D. Munn, 1996. Nutrients, Suspended Sediment, and Pesticides in Streams and Irrigation systems in the Central Columbia Plateau in Washington and Idaho, 1959-1991. U.S.Geological Survey Water-Resources Investigations Report 94-4215.

Hallock, D., 1998. Personal communication, April 29. Washington State Department of Ecology, Environmental Investigations and Laboratory Services Program, Ambient Monitoring Section, Olympia, Washington.

References

Bortleson, G.C. and D.A. Davis., 1997. Pesticides in selected small streams in the Puget Sound Basin, 1987-1995. U.S. Geological Survey Fact Sheet 067-97.

Corth, J., 1998. Personal communication, April 24. Washington State Department of Fish and Wildlife, Ephrata, Washington.

Davis, D., A. Johnson, and D. Serdar, 1998. Washington State Pesticide Monitoring Program – 1995 Surface Water Sampling Report. Environmental Investigations and Laboratory Services Program, Olympia, Washington. Publication No. 98-300.

Ebbert, J., 1995. Written communication, October 24. U.S. Geological Survey, Water Resources Division, Tacoma, Washington.

Embrey, S. and E. Block, 1995. Reconnaissance Investigation of Water Quality, Bottom Sediment, and Biota Associated with Irrigation Drainage in the Columbia Basin Project, Washington, 1991-92. U.S. Geological Survey, Water Resources Investigation Report 95-4007, Tacoma, Washington.

Environment Canada, 1999. Canadian Water Quality Guidelines - Freshwater Aquatic Life Criterion: Summary table. 7 pp. http://www.ec.gc.ca.ceqg%2drcqe/wattbl%sfe.doc. Accessed 4/15/1999.

EPA, 1986. Quality Criteria for Water. U.S. Environmental Protection Agency, Office of Regulations and Standards, Washington D.C.

EXTOXNET, 1998. University of California, Davis, Oregon State University, Michigan State University, Cornell University, and the University of Idaho. The EXTOXNET InfoBase is accessible via the World Wide Web (WWW). URL http://ace.orst.edu/info/extoxnet/ Accessed 9/24/1998.

Goolsby, D.A., W.A. Battaglin, J.D. Fallon, et al., 1993. Persistence of Herbicides in Selected Reservoirs in the Midwestern United States - Some Preliminary Results, in D.A. Goolsby, L.L. Boyer, G.E. Mallard, eds. Selected papers on Agricultural Chemicals in Water Resources of the Midcontinental United States: U.S. Geological Survey Open-File Report 93-418, p. 51-63.

Greene, K.E., J.C. Ebbert, and M.D. Munn, 1996. Nutrients, Suspended Sediment, and Pesticides in Streams and Irrigation systems in the Central Columbia Plateau in Washington and Idaho, 1959-1991. U.S.Geological Survey Water-Resources Investigations Report 94-4215.

Hallock, D., 1998. Personal communication, April 29. Washington State Department of Ecology, Environmental Investigations and Laboratory Services Program, Ambient Monitoring Section, Olympia, Washington.

Knight, D., 1997. Watershed Approach to Water Quality Management – Needs Assessment for the Mid-Columbia Watershed. Washington State Department of Ecology, Water Quality Program, Eastern Regional Office, Spokane, Washington.

Meister R.T., and C. Sine (ed.), 1996. Farm Chemicals Handbook '96. Meister Publishing Co., Willoughby, Ohio.

NASS, 1998. Washington Agricultural Chemical Usage: Apples, 1997 Crop. National Agricultural Statistical Service. http://www.nass.usda.gov/wa/appchem.htm.

National Academy of Sciences and National Academy of Engineering, 1973. Water Quality Criteria, 1972, a report of the committee on water quality criteria: Washington D.C., Environmental studies Board, National Academy of Sciences, National Academy of Engineering. 594 pp.

Serdar, D., A. Johnson, D. Davis, 1994. Survey of chemical contaminants in ten Washington lakes. Washington State Department of Ecology Publication #94-154. 25 pp.

Smith, R., 1999. Personal correspondence. Electronic mail of Potholes Reservoir irrigation deliveries for the entire year, 1998. United States Bureau of Reclamation.

USDA, 1998. Agricultural Chemical Usage. 1997 Restricted Use Pesticides Summary, December 1998 National Agricultural Statistics Service Economic Research Service. U.S. Department of Agriculture. Ag Ch 1(98). 1997 Agricultural Chemical Use Estimates for Restricted Use Pesticides. http://usda.mannlib.cornell.edu/reports/nassr/other/pcu-bb/agricultural_chemical_usage_1997_restricted_use_pesticides_summary_12.18.98. Accessed 7/6/1999

USDA, 1999. Agricultural Chemical Usage. 1998 Field Crops Summary. May 1999 National Agricultural Statistics Service Economic Research Service Ag Ch 1(99). U.S. Department of Agriculture. http://usda.mannlib.cornell.edu/reports/nassr/other/pcu-bb/agch0599.txt. Accessed 7/6/1999. http://www.usda.gov/nass/.

USGS, 1998. Pesticides in Surface and Ground Water of the United States: Summary of Results of the National Water Quality Assessment Program (NAWQA). July 22, 1998 Record of Revisions. Pesticides National Synthesis Project National Water-Quality Assessment U.S. Geological Survey. http://water.wr.usgs.gov/pnsp/allsum/ Last modified: Wed Sep 02 09:30:59 98. Accessed 9/14/1998.

USGS, 1999. Water Quality in the Central Columbia Plateau raw data accessed 6/8/1999 from http://wa.water.usgs.gov/ccpt/pns_data/data/ccpt_rsw <http://wa.water.usgs.gov/ccpt/pns_data/data.html.

Washington Agricultural Statistics Service, 1997. Washington Agricultural County Data 1997. URL: http://www.nass.usda.gov/wa/homepage.htm.

Wagner, R., J. Ebbert, L. Roberts, and S. Ryker, 1996. Agricultural Pesticide Applications and Observed Concentrations in Surface Waters from Four Drainage Basins in the Central Columbia Plateau, Washington and Idaho, 1993-94. U.S. Geological Survey, Water Resources Investigation Report 95-4285. 52 pp.

Williamson, A.K., M.D. Munn, S.J. Ryker, R.J. Wagner, J.C. Ebbert, and A.M. Vanderpool, 1998. Water quality in the Central Columbia Plateau, Washington and Idaho, 1992-95. USGS Circular 1144. 35 pp.

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Appendix A. Potholes Reservoir sample location and date of collection.

May Sampling, Event One

Site	Latitude	Longitude	Date	Depth (m)	Depth (ft)
1[a]	47 02 08 N [a]	119 23 50 W [a]	05/19/1998	2.8	9.2
2	47 00 48 N	119 23 07 W	05/19/1998	5.2	17
3	47 00 03 N	119 19 34 W	05/19/1998	11.9	39
4	46 58 37 N	119 19 25 W	05/19/1998	13.7	45
5 (surface)[b]	46 59 20 N	117 17 54 W	05/19/1998	--	--
5 (bottom)[b]	46 59 20 N	117 17 54 W	05/19/1998	27.7	91

a - Estimated position.

June Sampling, Event Two

Site	Latitude	Longitude	Date	Depth (m)	Depth (ft)
1	47 01 04 N	119 24 25 W	06/15/1998	2.1	7
2	47 01 53 N	119 24 08 W	06/15/1998	1.8	6
3	47 00 09 N	119 19 29 W	06/16/1998	10.6	35
4	47 58 41 N	119 19 24 W	06/16/1998	12.2	40
5 (surface)[b]	46 59 28 N	119 18 35 W	06/16/1998	--	--
5 (bottom)[b]	46 59 28 N	119 18 35 W	06/16/1998	NA	NA

b - Because the reservoir was stratified, two samples were collected at Site 5: a surface and a bottom sample.

NA - Not available; depth was not recorded at this location.

Appendix B. Pesticides analyzed in water samples from the Potholes Reservoir, May 19 and June 15, 16, 1998.

Chlorophenoxy Herbicides	Nitrogen-Containing Pesticides		Organophosphorous Pesticides
2,4,6-Trichlorophenol	Dichlobenil	Molinate	Demeton-O
3,5-Dichlorobenzoic Acid	Tebuthiuron	Chlorpropham	Sulfotepp
4-Nitrophenol	Propachlor (Ramrod)	Atraton	Demeton-S
2,4,5-Trichlorophenol	Ethalfluralin (Sonalan)	Triadimefon	Fonofos
Dicamba I	Treflan (Trifluralin)	MGK264	Disulfoton (Di-Syston)
2,3,4,6-Tetrachlorophenol	Simazine	Butachlor	Methyl Chlorpyrifos
MCPP (Mecoprop)	Atrazine	Carboxin	Fenitrothion
MCPA	Pronamide (Kerb)	Fenarimol	Malathion
Dichloroprop	Terbacil	Diuron	Chlorpyriphos
Bromoxynil	Metribuzin	Di-allate (Avadex)	Merphos (1&2)
2,4-D	Alachlor	Profluralin	Ethion
2,3,4,5-Tetrachlorophenol	Prometryn	Metalaxyl	Carbophenothion
Trichlopyr	Bromacil	Cyanazine	EPN
Pentachlorophenol	Metolachlor	Atrazine Desethyl	Azinphos Ethyl
2,4,5-TP (Silvex)	Diphenamid		Ethoprop
2,4,5,-T	Pendimethalin		Phorate
2,4-DB	Napropamide		Dimethoate
Dinoseb	Oxyfluorfen		Diazinon
Bentazon	Norflurazon		Methyl Parathion
Ioxynil	Fluridone		Ronnel
Picloram	Eptam		Fenthion
Dacthal (DCPA)	Butylate		Parathion
2,4,5-TB	Vernolate		Fensulfothion
Acifluorfen (Blazer)	Cycloate		Bolstar (Sulprofos)
Diclofop-Methyl	Benefin		Imidan
	Prometon (Pramitol 5p)		Azinphos-methyl (Guthion®)
	Propazine		Coumaphos
	Chlorothalonil (Daconil)		Dichlorovos (DDVP)
	Triallate		Mevinphos
	Ametryn		Dioxathion
	Terbutryn (Igran)		Propetamphos
	Hexazinone		Methyl Paraoxon
	Pebulate		Phosphamidan
			Tetrachlorvinphos (Gardona)
			Fenamiphos
			Butifos (DEF)
			Abate (Temephos)

Appendix B (cont.). Pesticides analyzed in water samples from the Potholes Reservoir, May 19 and June 15-16, 1998.

Carbamate Pesticides	Chlorinated Pesticides
Aldicarb Sulfone	Alpha-BHC
Aldicarb Sulfoxide	Beta-BHC
Oxamyl (Vydate)	Gamma-BHC (Lindane)
Methomly	Delta-BHC
3-Hydroxycarbofuran	Heptachlor
Aldicarb	Aldrin
Baygon (Propoxur)	Heptachlor Epoxide
Carbofuran	Trans-Chlordane (Gamma)
1-Naphthol	Endosulfan I
Carbaryl	Dieldrin
Methiocarb	4,4'-DDE
	Endrin
	Endosulfan II
	4.4'-DDD
	Endrin Aldehyde
	Endosulfan Sulfate
	4, 4'-DDT
	Endrin Ketone
	Methoxychlor
	Alpha-Chlordene
	Gamma-Chlordene
	Oxychlordane
	DDMU
	Cis-Chlordane (Alpha-Chlordane)
	Cis-Nonachlor
	Kelthane
	Captan
	2,4'-DDE
	Trans-Nonachlor
	2,4'-DDD
	2,4'-DDT
	Captafol
	Mirex
	Toxaphene

Appendix C. Analytical case narrative for Potholes Reservoir samples.

July 21, 1998

MEMORANDUM

SUBJECT: WSPMP Weeks 21 and 25 for Carbamates

S. H. Reimer, Chemist

Sample numbers 98218020 through 98218026 and 98258020 through 98258025.

Analysis of the samples by the WSPMP Method.

I. Holding Times:

The samples were collected on the 19th of May for week 21 samples and the 15th and 16th of June for week 25. They were extracted on the 4th and 24th of June. Analysis was completed by the 7th of July. Holding times were met for extraction and analysis for all samples. No qualifiers assigned based on holding times.

II. Instrument Performance:
Instrument performance was acceptable.

III. Calibration:

Initial Calibration: acceptable
The instrument was calibrated using a five point curve for 531.1 components.

All calibrated components had a coefficient of variation of .995 or better except propoxur and carbofuran. All components were detectable at the 0.12 μg/L level except for 1-naphthol and methiocarb.

Continuing Calibration: acceptable
No qualifiers assigned based on calibration.

IV. Method Blank Analysis:

No targets were present in any of the blanks.

V. Surrogate Recoveries:

One surrogate, BDMC, is used in this method. Recoveries for all samples except 98218024 were acceptable. The recovery for 98218024 was 47%. Sensitivity was good enough to not alter the reporting limit.
During the initial analysis run the retention time for BDMC drifted outside of the data collection window. All samples affected were rerun.

VI. Matrix Spike Analysis:

Matrix spikes and duplicates were run on sample number 98218022. Recoveries were within the expected range for all analytes present in the spike mix.

VII. Compound Identification/Quantitation:

No targets were found in any of the samples.

Data is usable without qualification.

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

August 25, 1998

Subject: Potholes (weeks 21 and 25)

Samples: 98218020-26 and 98258020-25

Officer(s): Dale Davis

By: Norman Olson NO
Organics Analysis Unit

NEUTRAL PESTICIDE ANALYSIS

ANALYTICAL METHODS: (EPA SW846 Method 8085 (proposed status)) All water samples were analyzed for nitrogen-containing, chlorinated and organophosphorous pesticides. A stir-bar extraction with methylene chloride followed by solvent exchange to iso-octane is Manchester Laboratory's standard operating procedure that was used for the extraction of pesticides. Extract analyses by capillary Gas Chromatography and Atomic Emission Detection (GC/AED) yielded compound detection and quantitation. Confirmation of detected pesticides was performed by Gas Chromatography and Ion-Trap mass spectrometry (GC/ITD) or comparisons of elemental ratios of heteroatoms to empirical formulas.

Analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection level (MDL). If a target analyte is detected and confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate, ' J' qualifier. This procedure also applies to the method blanks.

NITROGEN-CONTAINING PESTICIDE ANALYSIS

BLANKS: No nitrogen-containing target compounds were detected in the laboratory blanks at or above the associated reporting level. Hence, the blanks demonstrate the system was free from this type of contamination.

HOLDING TIMES: All samples were extracted within seven days of sampling and analyzed within 40 days of extraction.

SURROGATES: All 1,3-Dimethyl-2-nitrobenzene (DMNB) recoveries were acceptable ranging from 66% to 100%.

MATRIX SPIKING: Recoveries of the spiked target compounds was acceptable ranging from 64% to 147%. Precision between spike recoveries was also acceptable with relative percent differences (RPDs) not more than 50%.

COMMENTS: One unknown nitrogen-containing compound was detected at relatively large concentrations in three samples: 98258022, 23 & 25. It has been reported as "Unknown 01" on the sample data reports. The molecular weight (MW) of the compound detected is 147 amu and it probably contains only one nitrogen atom in it's structure. However, it is possible that this detected compound is a breakdown product due to the sample analysis. Some effort to elucidate the structure yielded possibilities such as a substituted phenyl-urea (if the detected compound is a breakdown product) or a phenyl-akylamine (if the detected compound is not a breakdown product). However, more investigation would be required if a complete compound identification is desired.

Data is useable as qualified.

ORGANOPHOSPHOROUS PESTICIDE ANALYSIS

BLANKS: No organophosphorous target compounds were detected in the laboratory blanks at or above the associated reporting level. Hence, the blanks demonstrate the system was free from this type of contamination.

HOLDING TIMES: All samples were extracted within seven days of sampling and analyzed within 40 days of extraction.

SURROGATES: Triphenylphosphate recoveries were acceptable ranging from 53% to 111%.

MATRIX SPIKING: Recoveries of the spiked target compounds was acceptable ranging from 80% to 103%. Precision between spike recoveries was also acceptable with RPDs not more than 50%.

COMMENTS: The data is useable as qualified

ORGANOCHLORINE PESTICIDE ANALYSIS

BLANKS: No organochlorine target compounds were detected in the laboratory blanks at or above the associated reporting level. Hence, the blanks demonstrate the system was free from this type of contamination.

HOLDING TIMES: All samples were extracted within seven days of sampling and analyzed within 40 days of extraction.

SURROGATES: Decachlorobiphenyl recoveries were acceptable ranging from 62% to 120%.

MATRIX SPIKING: Recoveries of the spiked target compounds was acceptable ranging from 65% to 83%. However, only one matrix spike sample is reported because the duplicate was lost. Therefore, no precision between spike recoveries is available.

COMMENTS: The data is useable as qualified.

DATA QUALIFIER CODES:

U	-	The analyte was not detected at or above the reported result.
J	-	The analyte was positively identified. The associated numerical result is an estimate.
UJ	-	The analyte was not detected at or above the reported estimated result.
REJ	-	The data are unusable for all purposes.
NAF	-	Not analyzed for.
N	-	For organic analytes there is evidence the analyte is present in this sample.
NJ	-	There is evidence that the analyte is present. The associated numerical result is an estimate.

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

September 3, 1998

Subject: Potholes Reservoir Project

Sample(s): 98258020-25

Officer(s): Dale Davis

By: Bob Carrell
Organics Analysis Unit

ACID HERBICIDE ANALYSIS

ANALYTICAL METHOD(S): (Draft EPA Method 8085)

The water samples for acid herbicides were extracted following Manchester Laboratory's standard operating procedure for the extraction of herbicides. The herbicide samples were hydrolyzed at pH > 12, extracted with methylene chloride at pH < 2, solvent exchanged and derivatized along with two method blanks. These extracts were analyzed by capillary Gas Chromatography and Atomic Emission Detection (GC/AED). Confirmation of herbicides is performed by Gas Chromatography and Ion-Trap mass spectrometry (GC/ITD) or comparisons of elemental ratios of hetero-atoms to empirical formulas.

The method utilizes compound independent calibration (CIC) for quantitation of detected compounds. A calibration validation is performed each time CIC is used for target compounds. This is done by comparison of CIC to a single point calibration (SPC) of the target analyte being quantitated.

All analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection limit (MDL). If a target analyte is detected and its identification is unambiguously confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate, ' J' qualifier.

BLANKS:

No target compounds were detected in the laboratory blanks. Hence, the blanks demonstrate the system was free from contamination.

HOLDING TIMES:

All samples were extracted and analyzed within the method holding times.

SURROGATES:

The 2,4,6-tribromophenol surrogate recoveries were acceptable, ranging from 69% to 100%

MATRIX SPIKING:

Not applicable.

COMMENTS:

The target analyte picloram received the 'UJ' qualifier because we traditionally experience highly variable recoveries for this compound.

The data is useable as qualified.

DATA QUALIFIER CODES

U	-	The analyte was not detected at or above the reported result.
J	-	The analyte was positively identified. The associated numerical result is an estimate.
UJ	-	The analyte was not detected at or above the reported estimated result.
REJ	-	The data are unusable for all purposes.
NAF	-	Not analyzed for.
N	-	For organic analytes there is evidence the analyte is present in this sample.
NJ	-	There is evidence that the analyte is present. The associated numerical result is an estimate.
NC	-	Not Calculated
E	-	This qualifier is used when the concentration of the associated value exceeds the known calibration range.

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

August 28, 1998

Subject: Potholes Reservoir Project

Sample(s): 98218020-26

Officer(s): Dale Davis

By: Bob Carrell
Organics Analysis Unit

ACID HERBICIDE ANALYSIS

ANALYTICAL METHOD(S): (Draft EPA Method 8085)

The water samples for acid herbicides were extracted following Manchester Laboratory's standard operating procedure for the extraction of herbicides. The herbicide samples were hydrolyzed at pH > 12, extracted with methylene chloride at pH < 2, solvent exchanged and derivatized along with two method blanks. These extracts were analyzed by capillary Gas Chromatography and Atomic Emission Detection (GC/AED). Confirmation of herbicides is performed by Gas Chromatography and Ion-Trap mass spectrometry (GC/ITD) or comparisons of elemental ratios of hetero-atoms to empirical formulas.

The method utilizes compound independent calibration (CIC) for quantitation of detected compounds. A calibration validation is performed each time CIC is used for target compounds. This is done by comparison of CIC to a single point calibration (SPC) of the target analyte being quantitated.

All analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection limit (MDL). If a target analyte is detected and its identification is unambiguously confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate, ' J' qualifier.

BLANKS:

No target compounds were detected in the laboratory blanks. Hence, the blanks demonstrate the system was free from contamination.

HOLDING TIMES:

All samples were extracted and analyzed within the method holding times.

SURROGATES:

The 2,4,6-tribromophenol surrogate recoveries were acceptable, ranging from 56% to 92%

MATRIX SPIKING:

The percent recovery of all target analytes was acceptable, ranging from a low of 22% (picloram) to 134% (PCP). The relative percent difference (RPD) between the two spike recoveries was also acceptable (<50%), ranging from 0.1% (2,4,5-trichlorophenol) to 22% (picloram).

COMMENTS:

The target analyte picloram received the 'UJ' qualifier because we traditionally experience highly variable recoveries for this compound.

The data is useable as qualified.

DATA QUALIFIER CODES

U	-	The analyte was not detected at or above the reported result.
J	-	The analyte was positively identified. The associated numerical result is an estimate.
UJ	-	The analyte was not detected at or above the reported estimated result.
REJ	-	The data are unusable for all purposes.
NAF	-	Not analyzed for.
N	-	For organic analytes there is evidence the analyte is present in this sample.
NJ	-	There is evidence that the analyte is present. The associated numerical result is an estimate.
NC	-	Not Calculated
E	-	This qualifier is used when the concentration of the associated value exceeds the known calibration range.