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CHRISTINE O. GREGOIRE
Director

Waterway Segment 01-01-04

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STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY
7272 Cleanwater Lane, LU-11 • Olympia, Washington 98504-6811 • (206) 753-2353

TO: Kevin Fitzpatrick

FROM: Jim Cubbage, Toxics and Ground Water Investigations Section

SUBJECT: Metals Concentrations in Fish Caught in Claypit Pond, Whatcom County, WA

DATE: October 11, 1988

INTRODUCTION

Heavy metal contamination is a concern in Claypit Pond, a small (12 acre) lake 200 feet directly downstream from the Thermal Reduction Company, a municipal-scale incineration facility in Whatcom County. Ash from incineration is deposited on site. Claypit Pond was the site of a purported fish kill in 1979 (an age class of fish was missing from a sample taken in 1980) and relatively high heavy metal concentrations in water (Kittle 1980). These problems were addressed by the installation of a leachate interceptor in 1981 and the runoff from the site is now piped to the Ferndale sewage treatment plant. In 1987, due to reports of high concentrations of metals at one site in waters upstream from Claypit Pond (Douglas 1987), the Washington Department of Wildlife, the owner of the pond, closed the pond to all fishing. At the request of the Northwest Regional Office (Department of Ecology) to preliminarily assess the potential health risk in ingesting fish caught from the pond, Toxics Investigation Section (Ecology) conducted this study of metals concentration in the tissues of fish caught from Claypit Pond by the Department of Wildlife. This memorandum reports results of these analyses. A subsequent report will document and interpret sediment data collected during this study.

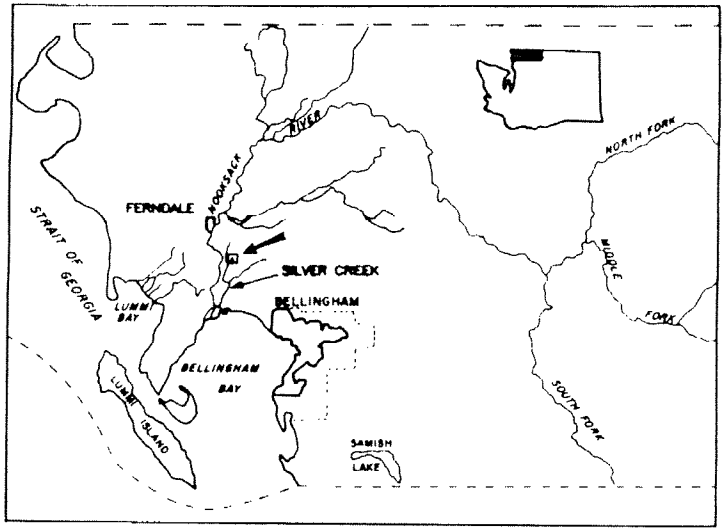
METHODS

Sampling Methods

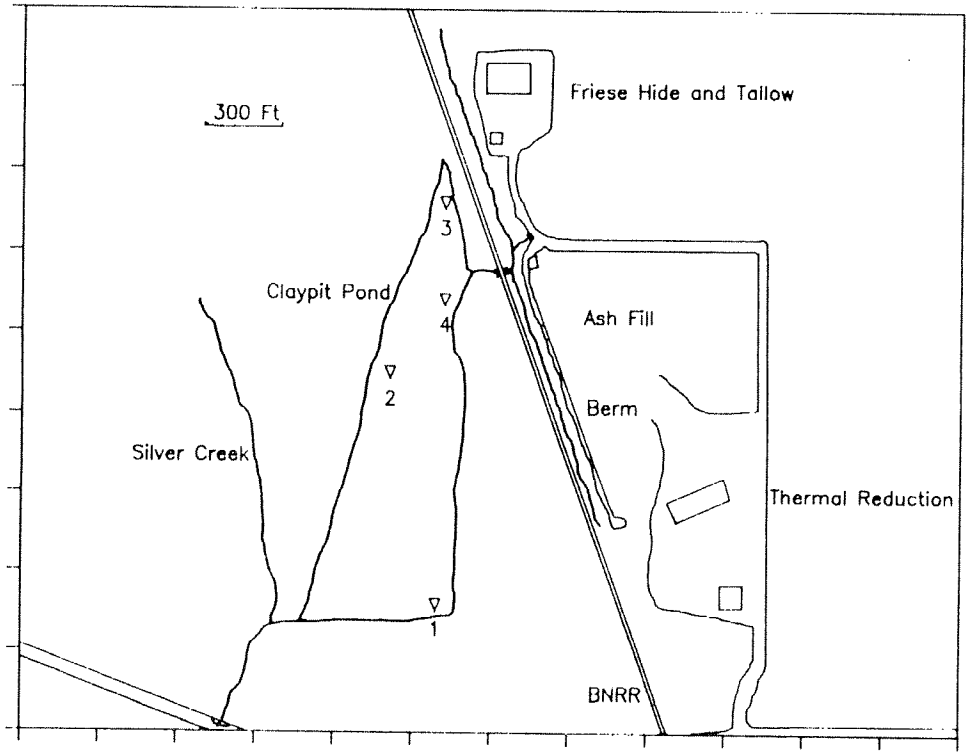
Fish were caught with four 60 ft gill nets each composed of four panels of differing mesh size (.5, 1.0, 1.5, 2.0 inches) set overnight for 20 hours between the 15th and 16th of June. Figure 1 shows the location of Claypit Pond and the gill net sets. All fish were measured and scales or otoliths taken for age determination. (The age determination has not been conducted yet.) A subsample of caught fish was taken for metals analysis. These fish were wrapped in aluminum foil and frozen whole within 8 hours of collection.

Laboratory Methods

Fish were fileted using acid-rinsed stainless steel knives at the Department of Ecology/EPA Laboratory at Manchester, Washington. Skin was left on the filets. Samples were homogenized in acid-rinsed Waring blenders and stored in pesticide/metals clean glass jars with teflon lid liners (I-Chem series 300, Hayward, California). Samples were analyzed at the Manchester laboratory.



a. Nooksak River Drainage



b. Claypit Pond, Thermal Reduction and vicinity

▽ NETS (6/16/88)

Figure 1. Study Area

Tissue samples were digested using nitric acid and hydrogen peroxide as specified by EPA Method 3050 (EPA, 1984). All metals except arsenic and mercury were analyzed by EPA Method 200.7 (inductively coupled plasma; EPA, 1983). Arsenic was analyzed by graphite furnace/ atomic absorption (EPA Method 206.2) while mercury was analyzed using cold vapor/ atomic absorption EPA Method 245.5 (EPA, 1983).

Quality Assurance

To assess precision and accuracy of the analytical methods one sample was homogenized and split. These split duplicates were spiked with the target metals. In addition, reference material (freeze-dried fish) that has been analyzed by 5-7 EPA referee laboratories, was analyzed twice in the same run as these fish samples.

Table 1 reviews tests of precision of analytical methods. Precision was measured using relative percent difference (RPD: the difference between two measurements divided by their mean) of replicate analyses. For the spiked samples, the RPD's are acceptably low for all metals (<35% [based on EPA Contract Lab Program (CLP) requirements for tissues]). However, replicates of reference material show high RPD's for arsenic and copper (nickel has a high RPD but the concentrations reported are near the apparent quantitation limit and thus are not a good measure of RPD). Based on these results, the concentrations of arsenic and copper may be considered estimates and are flagged with a "E".

Results of tests of accuracy are also presented in Table 1. Recovery of metals from spiked samples show acceptable recovery (EPA CLP requires 75 to 125% recovery) for all metals except arsenic and mercury. Arsenic and mercury recoveries were between 41 and 52%. These metals are also flagged with an "E".

The recovery performance from reference material compared to other laboratories' analyses of the same material is more difficult to interpret. The metals concentrations associated with the reference materials were the mean of the values determined through three replicate analyses by 5-7 EPA referee laboratories and the standard deviation of the mean represents the variation in results between these EPA labs. Only after these analyses were made was it discovered that the reference material was last produced in 1981 with the most recent checks made in 1984. EPA warrants the concentrations for a period of two years and has recently removed the material from distribution (pers. comm. Jim Longbottom, EPA Cincinnati). Thus, current concentrations in reference materials may differ from earlier values obtained from EPA referee laboratories. The extent of this possible variation is unknown.

During the present study, analyses of the reference samples showed only copper and zinc falling within the 95% confidence interval on both replicate analyses. Analytical accuracy for cadmium, chromium, and lead could not be calculated from these analyses because reference sample contractions were below the Manchester Laboratory's reported detection limits for these metals. Arsenic was within these bounds on one of two replicates. Note the recovery of mercury and arsenic in the spiked samples is very similar to the recovery concentrations in the reference materials. Thus, the lab methods used at Manchester Laboratory recovered a fairly consistent 40-50% of arsenic and mercury in the samples. Concentrations reported here have not been corrected for these recoveries.

Table 1. Measures of accuracy and precision of metals analysis tissue samples.

Type of measure	Metals - Total							
	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn
Spike								
CP2 Spike recovery %	52	90	92	94	42	88	86	130
CP2 Spike recovery %	42	101	106	98	49	75	94	98
Relative % difference (RPD)	21%	12%	14%	4%	15%	16%	9%	28%
Reference Material								
Reference value[1] ug/g dry	2.43	0.16	0.58	2.21	2.52	0.26	0.54	43.6
95% CI[2] ug/g dry	0.8-4.1	0.0-3.2	0.0-1.3	0.9-3.4	1.2-3.8	0.0-0.6	0.0-1.1	35 - 51
Reference analysis[3] ug/g dry	1.6	1.0U[4]	2.0U	3.4	1.08X[5]	4.0U	3.9X	48.2
Reference analysis ug/g dry	0.8	1.0U	2.0U	2.3	0.98X	4.0U	2.0U	38.6
Avg recovery	49%	-	-	129%	41%	-	722%	99%
Relative % difference (RPD)	67%	-	-	39%	10%	-	64%	22%

[1] Mean value of reference material (freeze-dried fish) reported by 5-7 referee labs (From EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio). Concentrations reported as reference are not certified. Reference material prepared in 1981 and not validated since 1984. These reference values are may be incorrect.

[2] 95% confidence interval of the population of reference values reported by labs above.

[3] Analysis of reference material conducted in same batch as Claypit Pond fish.

[4] U = Quantitation limit above 95% confidence interval

[5] X = Outside of 95% confidence interval

RESULTS AND DISCUSSION

Metals Concentrations in Fish

Fish caught with 4 gill nets and composited for analysis are summarized in Table 2. The predominant fish caught was yellow perch (Perca flavescens). Two samples were composited from these fish, one composed of whole bodies of subadults and the other filets of adult fish. Whole fish were analyzed to give an indication of overall contamination in all tissues (including muscle) as well as to provide a comparison to literature values that often report whole fish concentrations. Filets from cutthroat trout (Salmo clarkii) also were composited into one sample. All filet samples (with skin attached) were taken primarily to assess possible adverse health effects of consumption of fish caught in Claypit Pond.

Table 2. Weight and length of fish taken from Claypit Pond, June 15-16, 1988, for heavy metals analysis.

Net#[1]	Species	Weight (gm)	Fork Length (cm)	Sample No.	Sample Tissue
1	S. clarkii	148.5	22.5	CC3	Filet
1	S. clarkii	221.2	24.0	CC3	Filet
2	S. clarkii	621.0	36.5	CC3	Filet
3	P. flavescens	34.9	12.0	CP2	Whole fish
3	P. flavescens	44.0	14.0	CP2	Whole fish
4	P. flavescens	42.0	13.0	CP2	Whole fish
4	P. flavescens	55.9	15.0	CP2	Whole fish
4	P. flavescens	34.9	13.5	CP2	Whole fish
4	P. flavescens	217.2	21.0	CP1	Filet
4	P. flavescens	135.8	19.0	CP1	Filet
4	P. flavescens	137.8	18.0	CP1	Filet
4	P. flavescens	109.6	17.5	CP1	Filet
3	I. nebulosus	531.1	30.5	F4	Filet

S. clarkii = cutthroat trout,
P. flavescens = yellow perch,
I. nebulosus = brown bullhead.

[1]Position 1 on south shore,
2 on middle western shore,
3 on northernmost shore,
4 on 3/4 up north on east shore just off inlet.

Concentrations of metals (As, Cd, Cr, Cu, Hg, Pb, Ni, Zn) found in the four fish samples are shown in Table 3. All concentrations are reported on a wet weight basis. Neither cadmium nor lead was detected. With the exception of arsenic, the cutthroat had lower metals concentrations than the other samples. These cutthroat were sea-run and may reflect exposure from other habitats (marine waters). The resident catfish presumably is exposed to the highest concentrations of contaminants near the sediments owing to its near-benthic habitat. The concentrations of nickel and arsenic were highest in catfish. However with these small sample sizes, little significance can be placed on differences in interspecies concentrations.

Table 3. Metals concentrations in fish caught in Claypit Pond. All values ug/g wet weight basis.

Sample #	Fish	Tissue	Metals - Total							
			As	Cd	Cr	Cu	Hg	Pb	Ni	Zn
CP1	Perch	filet	0.04UE	0.1U	0.8	1.6E	0.064E	0.4U	1.7	13.2
CC3	Cutthroat	filet	0.40E	0.1U	0.3	0.7E	0.049E	0.4U	0.9	4.0
F4	Catfish	filet	0.52E	0.1U	0.2U	0.8E	0.034E	0.4U	3.5	5.7
CP2	Perch	whole	0.12E	0.1U	1.0	2.1E	0.058E	0.4U	1.2	11.5

U = Detection limit (contaminant not found at or above this concentration)
E = Considered estimate because quality control bounds were exceeded (see text for complete explanation).

Comparison of Concentrations in Fish

Table 4 compares concentrations of selected metals found in whole yellow perch in several river systems in Washington and California. Concentrations found in Claypit Pond fish do not appear elevated above fish tissue from these other drainages. Unfortunately, the studies referenced in this table (Lowe *et al.*, 1985, and May and McKinney, 1981) did not include nickel and chromium analyses.

Table 4. Comparison of metals concentrations found in whole yellow perch (*Perca flavescens*) in Washington and California. Concentrations are ug/g wet weight.

Location	Year	N	Length (avg) cm	As	Cd	Cu	Hg	Pb	Zn
Columbia, Pasco	1980	1	7.3	0.05	0.01	0.5	0.030	0.1	22.1
Columbia, Pasco	1978	1	7.6	0.05	0.01	0.6	0.040	0.1	26.1
Grand Coulee	1978	1	9.3	0.05	0.07	0.3	0.050	0.1	28.5
Grand Coulee	1976	5	20.1	<0.25	<0.05		0.030	0.2	
Klamath River	1981	1	7.8	0.05	0.01	0.3	0.120	0.1	17.9
Klamath River	1976	5	23.4	<0.05	<0.01		0.090	<0.1	
Claypit pond	1988	5	13.5	0.12	<0.10	2.1	0.058	<0.4	11.5

1978 and 1980 data from Lowe *et al.*, 1985
1976 data from May and McKinney (1981)
"<" = less than

Table 5 shows the concentrations of mercury found in yellow perch in 1980 and in 1988 in Claypit Pond. Although the concentrations appear to have increased since 1980, the sample size is too small to appraise significance. Mercury concentrations in both years appear low.

Table 5. Comparison of concentrations of mercury in whole perch caught in Claypit Pond. (ug/g wet weight)

Year	Sample #	Hg	Reference
1980	80-6-466	0.030	Kittle 1980
1980	80-6-467	0.025	Kittle 1980
1980	80-6-468	0.022	Kittle 1980
1988	CP2	0.058	This study, 1988

Table 6 shows concentrations of metals in freshwater fish reviewed by Moore and Ramamoorthy (1984). The concentrations found in Claypit Pond fish generally fall below concentrations that these authors characterize as high. Chromium, copper, and arsenic may be slightly elevated in several tissue samples. Interpretation of the arsenic concentration in the cutthroat trout is somewhat difficult as these fish were sea-run and marine fishes often show naturally elevated arsenic concentrations: e.g. Johnson (1988) found 0.6 to 0.9 ug/g arsenic (wet weight) in the muscle of Atlantic salmon near Port Townsend, WA. The levels of chromium and copper may also be marginally elevated. The chromium result is consistent with the high levels of chromium found in the sediment of Claypit Pond and will be reviewed in a separate report (Cubbage, in prep).

Table 6. Summaries of literature review on concentrations of metals in fish by Moore and Ramamoorthy (1984). All concentrations wet weight in muscle or whole body.

Metal	"High level"1 ug/g	"Low level"2 ug/g	Tissue3	Claypit Pond ug/g	Comment
As	0.5-2.0	<0.1-0.4	W	<0.04-0.52	Toxic inorganic forms converted in fish to easily excretable organic forms depuration rapid
Cd	2.5	<0.5	M	<0.1	Accumulates in organs, not generally in muscle.
Cr	1-1.7	<0.25	M	<0.2-1.0	Residues decline with age, rapid elimination
Cu	2-6	<1.0	M	0.7-2.1	May accumulate with age in liver
Pb	>0.7	<0.7	M	<0.4	No variation in tissues
Hg	1-3	<1	W	0.03-0.06	Consumption limits assume all in methylated form
Ni	9.5-13.6	<1	W	0.9-3.5	Slightly higher in organs than muscle
Zn	16-100	<3-9	M	4.0-13.2	Concentrates in organs.

1 "High level" = Cited by Moore and Ramamoorthy (1984) as high concentration usually found near industrial areas

2 "Low level" = Cited by Moore and Ramamoorthy (1984) as typical or common concentration found away from industrial areas.

3 Tissue = Basis for "high level" determination. W: whole body basis, M: muscle basis.

Legal Limits of Metals Contamination

One of the major concerns that originated this study was the possible threat to human health posed by consumption of fish caught in Claypit Pond. Table 7 shows legal limits of metals for USFDA and Canada as well as median limits from other countries reported by Nauen (1983). The FDA only regulates mercury concentrations in fish.

Table 7. Legal limits for metals concentrations in fish sold commercially for human consumption compared to levels found in Claypit Pond fish muscle. Units - ug/g wet wt.

	Hg	As	Pb	Cu	Cd	Zn
USFDA "Action Level"	1.0	--	--	--	--	--
Canadian limits	0.5	3.5	0.5	--	--	--
Median International Legal Limits	0.5	1.5	2.0	20	0.3	45
Claypit Pond fish	0.03-0.06	<0.04-0.52	<0.4	0.7-1.6	<0.1	4.0-13

The FDA limit is for methylmercury, is set at 1.0 ug/g and represents a judgement by FDA to balance the potential risk of consumption against economic considerations. This FDA "action level" is the threshold above which a product can be removed from market. Some states (e.g., Wisconsin and California) have adopted 0.5 ug/g as a guideline for health advisories in consumption of sport fish based on potential adverse effects on pregnant women and their fetuses, children, and people consuming fish at a higher rate than assumed by the FDA (Wisconsin: Anderson and Olson 1986, California: Stratton et al., 1987). FDA formerly had an action level of 0.5 ug/g, but raised it to 1.0 in 1979 (FDA 1979). Johnson et al., (1988) suggests the FDA faces a regulatory problem at the 0.5 ug/g level because some commercial species commonly exceed this concentration.

Table 7 shows none of the concentrations in Claypit Pond fish exceed limits posted by the Canadian or US governments. If mercury concentrations in Claypit Pond fish are corrected for consistent analytical recovery problems noted earlier, then the concentrations in all samples are at least an order of 3 lower than limits in Canada, Wisconsin, and California. Canada's limit for arsenic is 3.5 ug/g, a concentration again about three times higher than the highest similarly corrected value for Claypit Pond fish. The limit for lead in Canada is 0.5 ug/g and no lead was found in any samples at the 0.4 ug/g detection limit. Thus the concentrations of regulated metals in fish in Claypit Pond are below legal limits set by the US and Canada and below the median limits for up to 29 countries reviewed by Nauen (1983).

SUMMARY AND CONCLUSIONS

- The laboratory consistently recovered 41-52% of the known amounts of mercury and arsenic. Recoveries of spike concentrations in other metals were acceptable. Recoveries of concentrations in a reference material were variable, in part, possibly owing to the age of the reference material.

- Concentrations of mercury in fish caught in Claypit Pond were below legal limits for the USA and Canada. Arsenic and lead concentrations in fish were below limits posted by Canada. When these concentrations were corrected for recovery they are still all below legal limits for fish. Thus if legal limits of Canada, the US and advisory limits from California and Wisconsin are the criteria for delineating health risk then fish at Claypit Pond apparently pose no significant health risk from elevated levels of metals examined in this study.

- Other metals concentrations in fish are comparable to those found in fish at other sites.

- The metals with the greatest potential for bioaccumulation are mercury and cadmium. Mercury concentrations were low and cadmium was below the detection limit (0.1 ug/g).

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