### **Mercury Concentrations in Fish from Brush Hollow Reservoir**

Water Quality Control Division Colorado Department of Public Health and Environment

**March 2006** 

#### Mercury Concentrations in Fish from Brush Hollow Reservoir

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This report is also available on the CDPHE website at: www.cdphe.state.co.us/wq/wqhom.asp

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Water Body Identification (WBID): COARUA27

Brush Hollow Reservoir

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### Summary

The Colorado Department of Public Health and Environment's Water Quality Control Division (Division) investigated the concentrations of mercury in edible portion (fillets) of fish collected in Brush Hollow Reservoir. The Division collected 60 walleye, 10 yellow perch, 18 black crappie, and 8 catfish, with the assistance of the Colorado Division of Wildlife, in October of 2004. Composite samples of fillets from each species were analyzed by the Department of Public Health and Environment's laboratory.

The Division analyzed 10 composited samples of walleye, 5 composited samples of yellow perch, 3 composited samples of black crappie and 4 composited samples of catfish. All sample concentrations for yellow perch, black crappie and catfish were below the Department's current action level for mercury of 0.5 mg/kg (wet weight). Two walleye sample concentrations were higher than 0.5 mg/kg, 3 were higher than 0.4 mg/kg and 1 was higher than 0.3 mg/kg.

The information gathered from this study was used to assess the potential health risk from mercury to the public consuming those fish. At this time, the Division is recommending that restrictions be issued on the consumption of walleye caught in this lake, due to mercury.

#### Introduction

Mercury enters the environment as a result of natural events such as erosion of soils, volcanoes, fires and surface degassing and from anthropogenic sources such as industrial processes, commercial products and the combustion of fuels. It is found everywhere, transported in the atmosphere, deposited over land and water surfaces, and eventually finds its way into rivers and lakes. Since the 19<sup>th</sup> century, the total amount of mercury in the environment has increased by a factor of two to five above pre-industrial levels. (EPA Mercury Research Strategy, Sept. 2000)

Because mercury and its compounds are persistent and bioaccumulative, they pose risks of mercury poisoning to humans and animals. The organic form of mercury, methylmercury, is the most toxic form and most readily bioaccumulates in the tissues of animals and humans. Inorganic mercury, which is less efficiently absorbed and more readily eliminated from the body than methylmercury, does not tend to bioaccumulate.

Mercury bioaccumulates most efficiently in the aquatic food web, especially in fish, which bioaccumulate high concentrations of mercury. Nearly all of the mercury that accumulates in fish tissue is methylmercury. Because consumption of fish is the major source of mercury to humans, the monitoring of mercury in fish can provide the most direct indication of the potential risks.

This study of Brush Hollow Reservoir is part of a larger Water Quality Control Division (Division) study that started in 2004 to quantify the levels of mercury in fish in selected reservoirs throughout the state. Brush Hollow Reservoir was selected for evaluation because of the high angler use and the abundance of species that are known to bioaccumulate mercury at levels that pose health risks and are harvested by the public.

Brush Hollow Reservoir is a 461 surface acre waterbody located in Fremont County, near Penrose, on County Road 123, at an altitude of 5,600 feet. It is a combination warm water and cold water reservoir, and it holds several fish species that are sought after by the angler population, such as largemouth bass, bluegill, black crappie, walleye, channel catfish, cutthroat trout and rainbow trout.

The objective of this study is to assess whether concentrations of mercury in fish found in Brush Hollow Reservoir are above the Department's action level of 0.5 mg of mercury per kilogram of fish (wet weight). Based on the assessment, the Department can decide whether to take further action, including conduct targeted studies (as time and resources allow), or issue fish consumption advisories. The assessment may also help in evaluating the potential risk that these contaminants may pose to wildlife that consume these fish.

This study targeted fish that are most likely to be caught and consumed by the public. The selection of the target fish species in a reservoir is a site-specific decision based on the Division of Wildlife biologist's knowledge of the relative abundance of species and angler harvest. For Brush Hollow Reservoir, the target species was walleye (*Stizostedion vitreum*); yellow perch (*Perca flavescens*), black crappie (*Pomoxis nigromaculatos*) and

channel catfish (*Ictalurus punctatus*) were collected as ancillary data because they are very abundant in this reservoir and also highly desirable to anglers.

#### Methods

#### Sampling Strategy

#### Lake Selection

The Division developed a monitoring and assessment plan to investigate levels of mercury in fish in almost 100 lakes, reservoirs and rivers in Colorado, over a five-year period, starting in 2004. Waterbodies to be sampled were chosen from among the entire population in the state based on the following criteria:

- If there are no historical data on contaminants in fish tissue;
- A high harvest of fish from the waterbody
- The need to update existing fish consumption advisories;
- Any on-going collaborative studies of contaminants in any media, with other entities such as the U.S. Geological Survey, U.S. Fish and Wildlife Service, universities, etc. and
- If there are concerns or questions about health risks for a specific lake or reservoir.

Brush Hollow Reservoir was included in the monitoring plan because of the lack of information about mercury levels in the fish, the abundance of certain types of sport fish that are likely caught, and the high levels of angler use.

#### Fish Collection

Fish were collected during the Division of Wildlife's regularly scheduled fish population survey of Brush Hollow Reservoir, in October of 2004. Fish were captured by gillnets. The Division coordinated its fish collection with the Division of Wildlife's survey in order to minimize negative impacts on the fish populations that could result from multiple sampling events and to optimize resources. Fish collection and field processing followed the Division's Standard Operating Procedures. Fish contamination was minimized by not allowing fish slated for inclusion in the sample to rest on the bottom of the boat, or to be handled by the person operating the boat. Fish were kept in buckets with water until brought on shore. They were then killed and placed in plastic bags; packed in ice and immediately transported to the laboratory where they were placed in freezers for subsequent processing. Once at the laboratory, the fish were measured to the nearest 1mm.

Table 1 lists the species collected, the total numbers collected and the range in lengths. Walleye were selected as target species principally because they are found in this lake in large numbers and are highly desirable by anglers. They are also at the top of the food web, which makes them good indicators of mercury bioaccumulation. Other fish species that were analyzed for mercury provide valuable supplemental data about mercury bioaccumulation in the lake. Appendix 1 presents the data about all fish specimens sampled from the reservoir and used in the study. The table includes the unique identifier

number for each fish specimen, the species abbreviation and the length. The unique identifier number was later used to create the table of composited samples (see Appendix 2).

Table 1. Fish collected from Brush Hollow Reservoir in October 2004.

Species	Number	Length Range (mm)
	collected	
Walleye (Stizostedion vitreum)	60	222 to 504
Yellow perch (Perca flavescens)	10	193 to 271
Black crappie (Pomoxis nigromaculatos)	18	147 to 229
Channel catfish (Ictalurus punctatus)	8	213 to 440

#### Tissue Type

Because the main objective of this study is to evaluate potential risks associated with consuming potentially contaminated fish, the edible portion or fish fillets were used for analyses. Skinless fillets from each fish were collected according to the Division's Standard Operating Procedures. Skin was removed from the fillets to provide the most conservative (highest concentrations) assessment of mercury.

#### Sample Composition

One of the first issues addressed in the statewide sampling plan was whether to analyze tissue samples from individual fish or to analyze composite samples of tissues from several fish. This is an important study consideration that requires the balancing of the desire for precise estimates of variability in tissue concentration with the analytical costs. The Division followed the EPA (2000) recommendation to use composite samples of the edible portion (fillets) when evaluating the mean concentration of mercury in the target population of fish. Composite samples are homogeneous mixtures of samples from two or more individual organisms, analyzed as a single sample. The main advantage of using composite samples is the reduced analytical costs, as compared to the costs of acquiring and handling the samples. The disadvantage of using composite samples is that individual extreme concentrations are lost in the mix of the composite.

Composite samples in this study met the following criteria:

- All specimens in a composite are of the same species;
- The smallest specimen in the composite is not smaller than 85 percent of the length of the largest specimen in the composite;
- And the fish are collected during the same sampling event.

Composite tables were generated by ranking all fish specimens per species by length, from the largest to the smallest. Then, they were grouped according to the statistical design, as calculated for each waterbody, which depends on how many fish specimens are actually captured per sampling event.

Appendix 2 presents the table of composite samples, which was created using the fish specimens' unique identifier numbers.

#### Sample Design

The Division's objective in the statewide monitoring plan is to collect sufficient samples to estimate the mean mercury concentration in each population of fish with a known statistical certainty and to statistically test whether the mercury concentration of the samples for each species and size group exceeded the action level of 0.5 mg/kg. The Division followed the statistical sampling design, rationale, and calculations recommended in EPA (2000) for an optimal monitoring design. Optimal designs require prior information about population standard deviation and the actual difference between the mean mercury concentrations and the action level. For situations where this information is lacking, EPA (2000) provides guidance in Table 6.1 and 6.2 for estimating sufficient sample size. The Division consulted these tables and selected the following specifications in its sampling design:

- A detectable difference of 50 percent between the site-specific mean mercury concentrations and the action level;
- A probability of detecting a true difference between the mean and the action level of 70 to 80 percent (statistical power);
- A level of statistical significance of 0.05 (commonly used in biological sampling);
- The need to minimize the costs associated with analysis of the samples because of a fixed analytical budget;
- The decision to assign a maximum estimated population standard deviation of 0.024 as the target for attaining the desired statistical power.

The resultant design is conservative in that it likely requires more samples to be collected than actually are required to achieve the desired statistical power. It calls for the collection of 120 fish per waterbody with 60 fish collected per species from two different species and 30 fish collected for each of 2 size classes within each species. The desired number of fish per composite is 6 and the number of replicate composite samples is 5. When it is not possible to collect this combination of fish for a particular waterbody, sample size is modified by adjusting the number of fish per composite and the number of composites so that the estimated standard error remains less than or equal to 0.024. For these situations, the new estimated standard error is calculated and supplied with the results.

For Brush Hollow, walleye were composited in 10 samples of six fish each. This combination generated an estimated standard error of 0.008, which provides a greater level of precision when compared to the goal of 0.024. The other fish species collected were composited and analyzed, but the data were used as supplemental information only, not for decision-making.

#### Tissue Analysis

#### Fish Processing

Fish specimens were prepared for mercury analysis at the state's laboratory in accordance with the Division's Standard Operating Procedures. In the laboratory, all fish specimens were held frozen prior to processing and were processed as soon as possible after collection, depending on staff time availability.

Fish were processed in two steps. First, all fish fillets were removed from the foil wraps that were prepared in the field, inserted in labeled containers and frozen. Fish were only partially thawed during processing to preserve the integrity of the tissue and the cells. Second, the sample compositing scheme was generated (see Appendix 2) and the composite samples were made up.

Prior to use, all fish processing equipment was washed with detergent and rinsed with tap water. Fish were placed on plastic cutting boards and whole fillets or a significant portion of a fillet were removed with high quality stainless steel knives. The skin was removed from the underlying muscle tissue after filleting. Sufficient mass of tissue was removed to meet the analytical detection requirements and the remainder saved as archived material. Fish tissue was transferred to unused 50 ml Nalgene vials, which were labeled individually and kept frozen as archived material.

After the sample compositing scheme was generated, it was used to allocate fillets that make up each composite, using the same fish processing equipment that was used for fish filleting. The vials containing fish tissue were taken from the freezer and grouped according to the prepared compositing scheme. A small portion of tissue was extracted from each fillet and placed in another unused and labeled 50 ml Nalgene vial. Each small portion extracted from the fillets was of approximate equal size. The vial was first weighed empty and then with the fish material and the net weight of the fish sample was calculated. All the information was captured on a laboratory sheet form that was submitted to the state laboratory, accompanying the samples and with the chain of custody document. Samples were analyzed within the recommended holding time for mercury of 6 months.

#### Mercury Analysis

All samples were analyzed for total mercury using US EPA Method 245.6 for cold vapor atomic absorption spectrometry. Total mercury was the analytical method chosen because it provides a comparable estimate of methylmercury, which is the main form of mercury accumulated in fish and it is much less costly to analyze than methylmercury. This is consistent with the EPA (1995a) that recommends that fish contaminant monitoring programs measure total mercury and make the conservative assumption that all mercury is present as methylmercury in order to be most protective of human health. In addition to mercury, the concentrations of selenium and arsenic in fish tissue were determined as part of this study, but are not reported here.

The concentration of total mercury was expressed in units of mg/kg (wet weight). The method detection limit (MDL) for mercury analysis in fish tissue for the state laboratory was 0.1 mg/kg for the 2004 analyses, and the reporting limit was also 0.1 mg/kg.

#### Data Validation and Verification

Several quality assurance steps were taken to ensure that data quality and data integrity met the data objectives for the study. Fish collection, processing and compositing were done following Division protocols. The compositing scheme was created taking in consideration the range of fish lengths, so that the composite was made with fish of comparable sizes. Proper documentation was prepared to document all the steps in the process, to include chain of custody documentation. The results of the laboratory analysis and all field data are stored in an Access database. A complete set of field and laboratory data can be found in Appendix 3.

Data results and chain of custody documentation were received and reviewed for completeness by the project manager. All data documentation was complete, and there were no apparent problems or anomalies.

#### Results

Five yellow perch samples were submitted for analysis and all had mercury concentrations less than 0.12 mg/kg. Four black crappie samples were submitted for analysis and all had mercury concentrations less than 0.21 mg/kg. Four channel catfish were submitted for analysis and all had mercury concentrations less than 0.12 mg/kg. Ten walleye samples were submitted for analysis; two samples had mercury concentrations higher than 0.5 mg/kg, two samples were higher than 0.4 mg/kg and one was higher than 0.3 mg/kg.

Based on laboratory results from each waterbody, the Department makes a decision to either issue or rescind a fish consumption advisory or do nothing. Because there are so many data results from each waterbody, the decision was made that just **one sample** exceedance (above the action level of 0.5 mg/kg) provided sufficient information to cause the waterbody to be under consumption restrictions.

Please consult Appendix 3 for detailed laboratory results.

#### Mercury Concentrations in Fish Fillets from Brush Hollow Reservoir

(some values, although depicted as 0.00, actually represent less than method detection limits)

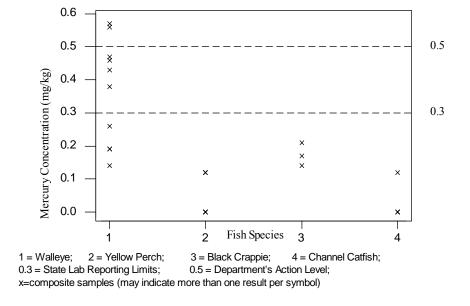


Figure 1

#### Discussion

Brush Hollow Reservoir was sampled in order to evaluate the potential risk to the public from consuming fish that may be potentially contaminated with mercury. Mercury bioaccumulates as it moves up the food web and in the case of Brush Hollow Reservoir, walleye are at the top of the food web. By investigating walleye, this study looked at not only the very desirable species, but also took in consideration the greatest opportunity for mercury to be found in fish in the lake.

The mercury results indicate that the lake does have a mercury problem. This statement is made based on two important indicators: first, because a top predator species was used for the study and second because several data results were above the action level. This action level was used by the state as the threshold for issuing fish consumption advisories at four other waterbodies in the Colorado. The lake might be re-sampled during the next 5-year cycle, depending on available resources.

#### Conclusion

Mercury was found at levels above the Department's action level of 0.5 mg/kg in several fish collected and analyzed from Brush Hollow Reservoir. At this time, the Division is recommending that restrictions be placed on the consumption of walleye caught in this lake due to mercury.

### Acknowledgments

The Division appreciates the assistance of Gary Dowler and his crew from the Colorado Division of Wildlife who conducted fish sampling for this study. Thanks to James Dominguez, a staff member for the Division, who participated in sampling, processing and, in general, handling every step of the study.

#### References

U.S.EPA's Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume I: Fish Sampling and Analysis, Third Edition (USEPA 2000).

U.S.EPA Office of Research and Development: *Mercury Research Strategy*, EPA/600/R-00/073, September 2000.

# Appendix 1

Fish Field Data

#### Brush Hollow Reservoir

#### Field Data Sheet -10/08/2004 - Gillnets

Sample ID	Species	Total Length (mm)
BHOL001	WAL	408
BHOL002	WAL	311
BHOL003	WAL	326
BHOL004	WAL	316
BHOL005	WAL	330
BHOL006	WAL	318
BHOL007	WAL	413
BHOL008	WAL	390
BHOL009	WAL	222
BHOL010	WAL	355
BHOL011	WAL	367
BHOL012	WAL	309
BHOL013	WAL	371
BHOL014	WAL	431
BHOL015	WAL	413
BHOL016	WAL	413
BHOL017	WAL	383
BHOL018	WAL	353
BHOL019	WAL	421
BHOL020	WAL	395
BHOL021	WAL	325
BHOL022	YPP	240
BHOL023	YPP	212
BHOL024	YPP	194
BHOL025	YPP	271
BHOL026	YPP	205
BHOL027	YPP	193
BHOL028	YPP	198
BHOL029	YPP	196
BHOL030	YPP	155
BHOL031	YPP	195
BHOL032	BCR	205
BHOL033	BCR	229
BHOL034	BCR	211
BHOL035	BCR	213
BHOL036	BCR	213
BHOL037	BCR	205
BHOL038	BCR	147
BHOL039	BCR	201
BHOL040	BCR	220

BHOL041	BCR	227
BHOL042	BCR	208
BHOL043	BCR	200
BHOL044	BCR	208
BHOL045	BCR	221
BHOL046	BCR	215
BHOL047	BCR	226
BHOL048	BCR	219
BHOL049	BCR	212
BHOL050	CAT	266
BHOL051	CAT	357
BHOL052	CAT	303
BHOL053	CAT	340
BHOL054	CAT	397
BHOL055	CAT	440
BHOL056	CAT	213
BHOL057	CAT	338
BHOL058	WAL	
BHOL059	WAL	395
		453
BHOL060	WAL	382
BHOL061	WAL	404
BHOL062	WAL	390
BHOL063	WAL	358
BHOL064	WAL	395
BHOL065	WAL	399
BHOL066	WAL	421
BHOL067	WAL	460
BHOL068	WAL	413
BHOL069	WAL	405
BHOL070	WAL	417
BHOL071	WAL	403
BHOL072	WAL	318
BHOL073	WAL	410
BHOL074	WAL	449
BHOL075	WAL	301
BHOL076	WAL	371
BHOL077	WAL	370
BHOL078	WAL	333
BHOL079	WAL	397
BHOL080	WAL	378
BHOL081	WAL	377
BHOL082	WAL	343
BHOL083	WAL	403
BHOL084	WAL	410
BHOL085	WAL	397
BHOL086	WAL	420
DITOLUOU	WAL	720

BHOL087	WAL	400
BHOL088	WAL	397
BHOL089	WAL	361
BHOL090	WAL	404
BHOL091	WAL	410
BHOL092	WAL	504
BHOL093	WAL	412
BHOL094	WAL	361
BHOL095	WAL	418
BHOL096	WAL	421

#### Abbreviations:

WAL = Walleye YPP = Yellow Perch BCR = Black Crappie CAT = Channel Catfish

## Appendix 2

**Table of Composite Samples** 

## Table of Composite Samples for Brush Hollow Reservoir

Composite	In	divid	ual									
Sample ID	Fi	sh ID.	S									
BHOLWAL01	=	092	+	067	+	059	+	074	+	014	+	019
BHOLWAL02	=	066	+	096	+	086	+	095	+	070	+	007
BHOLWAL03	=	015	+	016	+	068	+	093	+	073	+	084
BHOLWAL04	=	091	+	001	+	069	+	061	+	090	+	071
BHOLWAL05	=	083	+	087	+	065	+	079	+	085	+	088
BHOLWAL06	=	020	+	064	+	058	+	008	+	062	+	017
BHOLWAL07	=	060	+	080	+	081	+	013	+	076	+	077
BHOLWAL08	=	011	+	089	+	094	+	063	+	010	+	018
BHOLWAL09	=	082	+	078	+	005	+	003	+	021	+	006
BHOLWAL10	=	072	+	004	+	002	+	012	+	075	+	009
BHOLYPE11	=	025	+	022								
BHOLYPE12	=	023	+	026								
BHOLYPE13	=	028	+	029								
BHOLYPE14	=	031	+	024								
BHOLYPE15	=	027	+	030								
BHOLBCR16	=	033	+	041	+	047	+	045	+	040	+	048
BHOLBCR17	=	046	+	035	+	036	+	049	+	034	+	042
BHOLBCR18	=	044	+	032	+	037	+	039	+	043	+	038
BHOLYPE19	=	055	+	054								
BHOLYPE20	=	051	+	053								
BHOLYPE21	=	057	+	052								
BHOLYPE22	=	050	+	056								

## Appendix 3

**Table of Laboratory Results** 

#### Table of Laboratory Results for Brush Hollow Reservoir Mercury Concentrations in mg/kg (wet weight)

Composite	LSD Analyzed in June 2004
Sample ID	ın June 2004
1004BHOLWAL01	0.43
1004BHOLWAL02	0.38
1004BHOLWAL03	0.47
1004BHOLWAL04	0.46
1004BHOLWAL05	0.56
1004BHOLWAL06	0.57
1004BHOLWAL07	0.19
1004BHOLWAL08	0.26
1004BHOLWAL09	0.19
1004BHOLWAL10	0.14
1004BHOLYPE11	< 0.1
1004BHOLYPE12	< 0.1
1004BHOLYPE13	0.12
1004BHOLYPE14	0.12
1004BHOLYPE15	< 0.1
1004BHOLBCR16	0.21
1004BHOLBCR17	0.14
1004BHOLBCR18	0.17
1004BHOLCCT19	0.12
1004BHOLCCT20	< 0.1
1004BHOLCCT21	< 0.1
1004BHOLCCT22	< 0.1

#### Fish Species Abbreviations:

WAL = Walleye

YPE = Yellow Perch

BCR = Black Crappie

CCT = Channel Catfish