Mercury Concentrations in Fish from Vallecito Reservoir

Water Quality Control Division
Colorado Department of Public Health and Environment

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Water Body Identification (WBID): COSJPN03
Vallecito 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 Vallecito Reservoir. The Division collected 30 northern pike and 12 walleye with the assistance of the Colorado Division of Wildlife, in April 2004. Composite samples of fillets from each species were analyzed by the Department of Public Health and Environment's laboratory.

The Division analyzed 15 composited samples of northern pike and 6 composited samples of walleye. Of the northern pike, 2 had mercury concentration higher than 0.3 mg/kg, 1 higher than 0.4 mg/kg and 1 higher than 0.5 mg/kg. Of the walleye, 1 had mercury concentrations higher than 0.3 mg/kg, 1 higher than 0.5 mg/kg, 1 higher than 0.6 mg/kg and 1 higher than 0.7 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 northern pike and 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 19th 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 Vallecito 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. Vallecito 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.

Vallecito Reservoir is located about 18 miles northeast of Durango and is part of the Pine River Irrigation District. The construction of the dam and reservoir was completed in 1941, and the reservoir has a maximum surface area of 2,720 acres. Rainbow, brown trout, kokanee salmon, walleye and northern pike can be found in the reservoir.

The objective of this study is to assess whether concentrations of mercury in fish found in the 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. In the case of Vallecito Reservoir, the target species were northern pike (*Esox lucius)* and walleye *(Stizostedion vitreum).*

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.

Vallecito 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 Vallecito Reservoir in April 2004. Fish were captured with 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, measured to the nearest 1mm and filleted. Each fillet was individually labeled and wrapped in aluminum foil. Fish fillets were placed in ice for immediate transportation to the laboratory where they were placed in freezers for subsequent processing.

Table 1 lists the species collected, the total numbers collected and the range in lengths. Northern pike and 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 may have been 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 Vallecito Reservoir in April 2004.

Species	Number collected	Length Range (mm)
Northern pike (*Esox lucius*)	30	325 to 901.7
Walleye *(Stizostedion vitreum).*	12	298 to 570

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. Fish were ranked by species, from the largest in length to the smallest. They were then grouped according to how many individual specimens were in each composite, and put together in order from largest to smallest.

Sample Design

The Division's objectives in the statewide monitoring plan are 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 that help estimate sufficient sample size to ensure statistical certainty. 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 Vallecito Reservoir, northern pike were composited in 15 samples of two fish each. This combination generated an estimated standard error of 0.013, which provides a greater level of precision, compared to the goal of 0.024. Walleye were composited in 6 samples of two fish each. This combination generated an estimated standard error of 0.053, which provides a lesser level of precision, compared to the goal of 0.024.

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 wrapping that was done 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, with 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 fillet 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 with 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 0.0001 mg/kg for the 2004 analyses, but the reporting limit was 0.3 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

Fifteen composited samples of northern pike were submitted for analysis to the state laboratory; 2 had mercury concentration higher than 0.3 mg/kg, 1 higher than 0.4 mg/kg and 1 higher than 0.5 mg/kg. Six composited samples of walleye were submitted for analysis to the state laboratory; 1 had mercury concentrations higher than 0.3 mg/kg, 1 higher than 0.5 mg/kg, 1 higher than 0.6 mg/kg and 1 higher than 0.7 mg/kg. Please consult Appendix 3 for detailed laboratory results.

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 about each waterbody, the decision was made that just **one sample** exceedance (above the action level of 0.5 mg/kg) was sufficient information to cause the waterbody to be under consumption restrictions.

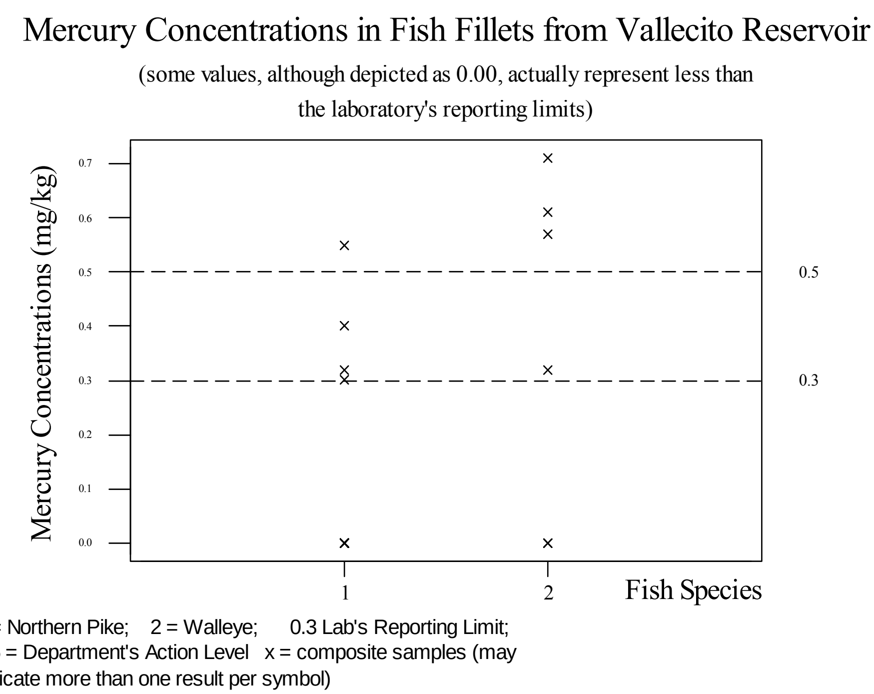

Figure 1

Discussion

Vallecito 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 Vallecito Reservoir, northern pike and walleye are at the top of the food web. By investigating both species, 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 top predator species were used for the study, and second because several data results were above the action level of 0.5 mg/kg. 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 Vallecito Reservoir. At this time, the Division is recommending that restrictions be placed on the consumption of northern pike and walleye caught in this lake due to mercury.

Acknowledgments

The Division appreciates the assistance of Mike Japhet 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

Vallecito Reservoir

Field Data Sheet – 04/21/2004 – Gillnets

Sample ID	*Species*	*Total Length (mm)*
P01	NPK	720
P02	NPK	780
P03	NPK	730
P04	NPK	590
P05	NPK	633
P06	NPK	514
P07	NPK	902
P08	NPK	704
P09	NPK	701
P10	NPK	575
P11	NPK	740
P12	NPK	715
P13	NPK	605
P14	NPK	500
P15	NPK	857
P16	NPK	825
P17	NPK	604
P18	NPK	654
P19	NPK	563
P20	NPK	550
P21	NPK	523
P22	NPK	604
P23	NPK	585
P24	NPK	718
P25	NPK	675
P26	NPK	669
P27	NPK	697
P28	NPK	715
P29	NPK	605
P30	NPK	530
W01	WAL	540
W02	WAL	496
W04	WAL	515
W05	WAL	450
W06	WAL	570
W07	WAL	547
W08	WAL	425
W09	WAL	430
W10	WAL	475
W11	WAL	441

W12	WAL	336
W13	WAL	298

Fish Species Abbreviations:

NPK = Northern pike
WAL = Walleye

Appendix 2

Table of Composite Samples

Table of Composite Samples for Vallecito Reservoir

Composite Sample ID		*Individual Fish IDs*		
VALLNPK001F	=	P07	+	P15
VALLNPK002F	=	P16	+	P02
VALLNPK003F	=	P03	+	P11
VALLNPK004F	=	P01	+	P24
VALLNPK005F	=	P28	+	P12
VALLNPK006F	=	P08	+	P09
VALLNPK007F	=	P27	+	P26
VALLNPK008F	=	P25	+	P18
VALLNPK009F	=	P05	+	P29
VALLNPK010F	=	P17	+	P22
VALLNPK011F	=	P13	+	P04
VALLNPK012F	=	P23	+	P10
VALLNPK013F	=	P19	+	P20
VALLNPK014F	=	P30	+	P21
VALLNPK015F	=	P06	+	P14
VALLWLL016F	=	W06	+	W07
VALLWLL017F	=	W01	+	W04
VALLWLL018F	=	W02	+	W10
VALLWLL019F	=	W05	+	W11
VALLWLL020F	=	W09	+	W08
VALLWLL021F	=	W12	+	W13

Appendix 3

Table of Laboratory Results

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

Composite Sample ID	*LSD Analyzed in June 2004*
VALLNPK001F	0.40
VALLNPK002F	0.32
VALLNPK003F	0.55
VALLNPK004F	<0.3
VALLNPK005F	<0.3
VALLNPK006F	0.30
VALLNPK007F	<0.3
VALLNPK008F	<0.3
VALLNPK009F	<0.3
VALLNPK010F	<0.3
VALLNPK011F	<0.3
VALLNPK012F	<0.3
VALLNPK013F	<0.3
VALLNPK014F	<0.3
VALLNPK015F	<0.3
VALLWLL016F	0.71
VALLWLL017F	0.57
VALLWLL018F	0.61
VALLWLL019F	0.32
VALLWLL020F	<0.3
VALLWLL021F	<0.3

Fish Species Abbreviations:

NPK = Northern pike
WLL = Walleye