

From: <Kozelka.Peter@epamail.epa.gov>
To: <John.Zastrow@tetrattech-ffx.com>
Date: 9/30/04 10:40AM
Subject: NBay arsenic fish tissue data

942

see table XX for raw data of total and inorganic arsenic results for subset of fish bioaccumulation study completed by Jim Allen, SCCWRP, for RB8.

(See attached file: NBay TMDL_Arsenic analysis.doc)(See attached file: Appendix XX_arsenic fish tissue.doc)

Melenee--this fish tissue data should be part of Admin. Record for 2004 list. I believe you already have it but I wanted to be sure. Call if I've confused you.

CC: Melenee Emanuel <emanm@dwq.swrcb.ca.gov>

VIII. Arsenic Analysis (from Newport Bay Toxics TMDLs)

EPA has concluded that an arsenic TMDL is not required because available data indicate that applicable numeric water quality standards, and the best available screening guidelines used to interpret narrative standards, are not being exceeded. Although the State and EPA initially concluded that arsenic TMDLs were needed based on comparisons with older recommended screening values, we have revised our conclusions based on an updated data set and new information concerning arsenic toxicity and consumption risk. This section explains the basis for EPA's revised assessment of the need for arsenic TMDLs.

EPA's initial assessment of fish tissue monitoring results was based on comparisons with two screening values. Total arsenic concentrations in fish tissue were compared to the California OEHHA screening value (1.0 mg/kg wet for total arsenic). This screening value was developed from a human health study for chemical contaminants in sportfish from two California freshwater lakes (OEHHA 1999). OEHHA recognized that inorganic arsenic is the preferred contaminant to evaluate for potential human health risk; however, analytical methods to measure inorganic arsenic were not available during that study. OEHHA developed a plan to a) evaluate total arsenic fish tissue results against the screening value for freshwater species and b) delay further decisions about water quality impairment or potential health risk until they had actually measured inorganic arsenic in popular sportfish (pers. commun. B. Brodberg). Furthermore, OEHHA recognizes its total arsenic screening value is ill-suited for saltwater systems. EPA Region 9 has reconsidered using this *freshwater* total arsenic tissue screening value and has determined that it would be inappropriate to make final decisions based only on comparison of total arsenic in tissues with this screening value.

EPA's initial assessment also considered another fish tissue screening value, (0.026 mg/kg wet for inorganic arsenic); however no monitoring data exists for measurements of inorganic arsenic in Newport Bay fish. To enable a comparison of available data to the inorganic arsenic screening value, EPA estimated levels of inorganic arsenic present in Newport Bay fish as a percentage of total arsenic for finfish (4% of total) and for shellfish (60% of total). These percentages were based on information obtained from a literature search (for finfish, Donohue and Abernathy 1999) or discussion with analytical chemists (for shellfish, pers. commun. J. Creed). Upon further review of the screening values cited in recent EPA guidance for assessing fish advisories (USEPA 2000d), EPA has determined the 0.026 mg/kg wet inorganic screening value is incorrect and that 1.2 mg/kg wet inorganic arsenic is a more reliable risk-based screening value. Preferably this screening value should be compared to measurements of inorganic arsenic in local fish, although calculation of inorganic arsenic as a percentage of total arsenic is still acceptable.

In the process of developing these TMDLs, EPA reevaluated local fish tissue data in comparison with the new EPA screening value of 1.2 mg/kg wet inorganic arsenic based on EPA's fish advisory guidance. The most recently available set of fish tissue monitoring results was compiled from Toxics Substances Monitoring program (1995-1998), California Fish Contamination Study (1999-2000) Southern California Coastal Water Research Project (2001b) and State Mussel Watch program (1995-2000). We evaluated results from both San Diego Creek and saltwater bodies of Newport Bay but focused more on saltwater results since those results showed some exceedances with respect to the OEHHA screening value applied in EPA's earlier assessment. To be conservative and consistent with other agencies (e.g., FDA), EPA assumed that inorganic arsenic comprised 10% of total arsenic for finfish and 60% of total for shellfish. We used only one screening value, 1.2 mg/kg wet for inorganic arsenic, which is consistent with both State and Federal agencies' determination that human health risk from arsenic exposure is attributed to inorganic arsenic exposures.

The final assessment of saltwater tissue results (using calculated values of inorganic arsenic) shows no exceedances of the EPA inorganic screening value (1.2 mg/kg wet). This is true for both finfish (0%, n = 80) and shellfish (0%, n = 24). There are also no exceedances of freshwater tissue results. Table 8-1 summarizes arsenic tissue concentrations for Newport Bay. Table 8-2 provides a perspective of arsenic tissue concentrations for Newport Bay and other saltwater bodies. The raw data and calculated results for this reassessment are provided in Appendix B at the end of this summary document. Therefore, based on this revised assessment, EPA concludes that San Diego Creek and Newport Bay are not exceeding water quality standards for arsenic and that no TMDLs are needed. This result is consistent with local ambient water column data for arsenic, which indicate that Bay arsenic

levels are about the same as average sea water arsenic levels.

Table 8-1. Total Arsenic results in fish tissue in Newport Bay waterbodies (mg/kg wet)

Waterbody	Collection dates	Org.	n	Min	Max	Mean	Median
San Diego Creek	1995 -- 98	TSMP	15	0.06	0.88	0.18	0.13
Newport Bay (finfish)	1995 -- 98	TSMP*	4	0.4	8.6	2.93	1.3
	1999 -- 00	CFCS	26	0.2	4.0	1.29	0.79
	2000 - 01	SCCWRP	50	0.22	8.6	1.64	0.68
(shellfish)	1995 - 00	SMW	24	0.8	2.5	1.28	1.25

*these TSMP results for individual samples, all other results are tissue composites

Table 8-2. Total Arsenic results in marine waterbodies (mg/kg wet)

Tissue	Study	n	Range	Mean	Median
Finfish	Newport Bay	80	0.2 – 8.6	1.5	0.7
	Wash State	12	0.15 – 10.7	3.5	0.9
	Donohue	77	0.2 – 65	5.1	2.1
	Great Britain	720	0.9 – 30.1	5.6	4.3
Shellfish	Newport Bay	24	0.8 – 2.5	1.3	1.3
	Wash State	10	1.0 – 6.9	2.4	2.2
	Donohue	57	0.2 – 126	15.9	4.2

Newport Bay results compiled from Table 8-1

Washington State results from Yilmazer et al. 2000

Donohue results from various North American waterbodies (1996)

Great Britain results from Collins et al. 1996

Post note: attached below are arsenic speciation results finalized on March 2003, after the NBay Toxics TMDLs were promulgated on June 14, 2002. They provide further verification of very low inorganic arsenic values found in fin fish tissue and these observed results are all below the appropriate screening value (1.2 ppm inorganic As).

Table XX. Arsenic speciation concentrations found in sport fish muscle tissue collected during the summer of 2001 from Newport Bay, California, with quality control (QC) duplicates and matrix spike sample recoveries.

Sample ID	Fish type	Total Arsenic			Inorganic Arsenic		
		dry wt. total	% solids	wet wt. ug/g	dry wt. inorg.	% solids	wet wt. ug/g
DTOUW01-01-3	diamond turbot	5.461	0.2399	1.310	0.021	0.2399	0.005
DTOLW01-01-2	diamond turbot	10.814	0.2432	2.630	0.012	0.2432	0.003
CSOLW01-01-1	C-O sole	30.766	0.2181	6.710	0.046	0.2181	0.010
CSOLW01-01-2	C-O sole	31.369	0.2206	6.920	0.023	0.2206	0.005
CHOLW01-01-2	California halibut	1.883	0.2264	0.426	0.013	0.2264	0.003
CHOUW01-01-1	California halibut	3.276	0.2375	0.778	0.013	0.2375	0.003
BPOLW01-01-1	Black perch	3.164	0.2102	0.665	0.019	0.2102	0.004
SSBOUW01-01-1	spotted sand bass	2.110	0.2317	0.489	0.026	0.2317	0.006
SSBOLW01-01-1	spotted sand bass	2.871	0.217	0.623	0.014	0.217	0.003
STOLW01-01-1	spotted turbot	28.952	0.21	6.080	0.095	0.21	0.020

Quality Control (QC) samples		analysis	% recovery
DORM-2	Standard reference material	As-total	98.4
LCS (corn oil)	Standard reference material	As-inorganic	98.6

Avg. Spike Recovery		analysis	% recovery
CHOUW01-01-1	California halibut	As-total	112
STOLW01-01-1	spotted turbot	As-inorganic	73.6

Minimum detection limits = 0.015 µg/g ww As-total; 0.005 µg/g ww As-inorganic.
 QC control limits are expected ranges which spike sample recoveries should meet.
 % R = average percent recovery (expected range 70-130%)

Sampling locations: IU = inner upper bay; OU = outer upper bay; IL = inner lower bay; OL = outer lower bay.

Sample Processing--Sport fish

Sport (or recreational) fish were processed from August 8-23, 2001. Chemistry composite sizes of 3 to 10 fish per composite were adjusted following rules suggested in USEPA (1995). To maximize the number of samples across species, composite size was held constant within species but varied, as needed, between species. Within a given composite, the smallest fish selected was within 75% of the largest fish. This criterion sometimes reduced the size of the composite from that expected from field data. In addition, we used the same composite size for a given species in both winter and summer sampling periods.

Sport fish tissues were prioritized by project importance for selected chemical analyses. Tier I represented the bulk of the analysis. These were skin-off muscle tissue samples analyzed for organic compounds and selected trace metals. Our priorities (with sample aliquot size) were as follows: Immediate use for chemical analysis (skin-off); organics analysis (50 g); metals analysis (10 g).

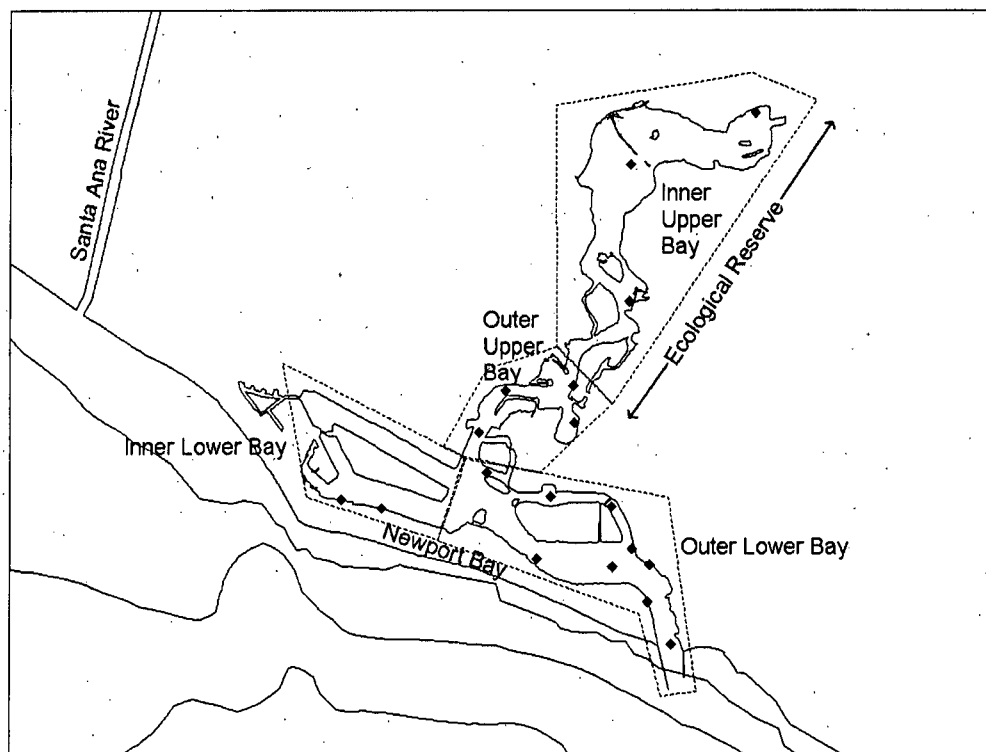


Figure 1. Map of Newport Bay, California, divided into subregions for this study. Black diamonds indicate collection sites of fish. Sampling locations: IU = inner upper bay; OU = outer upper bay; IL = inner lower bay; OL = outer lower bay.

Appendix XX

Table 8. Arsenic speciation concentrations found in sport fish muscle tissue collected during the summer of 2001 from Newport Bay, California, with quality control (QC) duplicates and matrix spike sample recoveries.

Sample ID	Fish type	Total Arsenic			Inorganic Arsenic		
		dry wt. total	% solids	wet wt. ug/g	dry wt inorg.	% solids	wet wt. ug/g
DTOUW01-01-3	diamond turbot	5.461	0.2399	1.310	0.021	0.2399	0.005
DTOLW01-01-2	diamond turbot	10.814	0.2432	2.630	0.012	0.2432	0.003
CSOLW01-01-1	C-O sole	30.766	0.2181	6.710	0.046	0.2181	0.010
CSOLW01-01-2	C-O sole	31.369	0.2206	6.920	0.023	0.2206	0.005
CHOLW01-01-2	California halibut	1.883	0.2264	0.426	0.013	0.2264	0.003
CHOUW01-01-1	California halibut	3.276	0.2375	0.778	0.013	0.2375	0.003
BPOLW01-01-1	Black perch	3.164	0.2102	0.665	0.019	0.2102	0.004
SSBOUW01-01-1	spotted sand bass	2.110	0.2317	0.489	0.026	0.2317	0.006
SSBOLW01-01-1	spotted sand bass	2.871	0.217	0.623	0.014	0.217	0.003
STOLW01-01-1	spotted turbot	28.952	0.21	6.080	0.095	0.21	0.020

Quality Control (QC) samples		analysis	% recovery
DORM-2	Standard reference material	As-total	98.4
LCS (corn oil)	Standard reference material	As-inorganic	98.6
Avg. Spike Recovery		analysis	% recovery
CHOUW01-01-1	California halibut	As-total	112
STOLW01-01-1	spotted turbot	As-inorganic	73.6

Minimum detection limits = 0.015 µg/g ww As-total; 0.005 µg/g ww As-inorganic.

QC control limits are expected ranges which spike sample recoveries should meet.

% R = average percent recovery (expected range 70-130%)

Sampling locations: IU = inner upper bay; OU = outer upper bay; IL = inner lower bay; OL = outer lower bay.

Sample Processing--Sport fish

Sport (or recreational) fish were processed from August 8-23, 2001. Chemistry composite sizes of 3 to 10 fish per composite were adjusted following rules suggested in USEPA (1995). To maximize the number of samples across species, composite size was held constant within species but varied, as needed, between species. Within a given composite, the smallest fish selected was within 75% of the largest fish. This criterion sometimes reduced the size of the composite from that expected from field data. In addition, we used the same composite size for a given species in both winter and summer sampling periods.

Sport fish tissues were prioritized by project importance for selected chemical analyses. Tier I represented the bulk of the analysis. These were skin-off muscle tissue samples analyzed for organic compounds and selected trace metals. Our priorities (with sample aliquot size) were as follows: Immediate use for chemical analysis (skin-off); organics analysis (50 g); metals analysis (10 g).

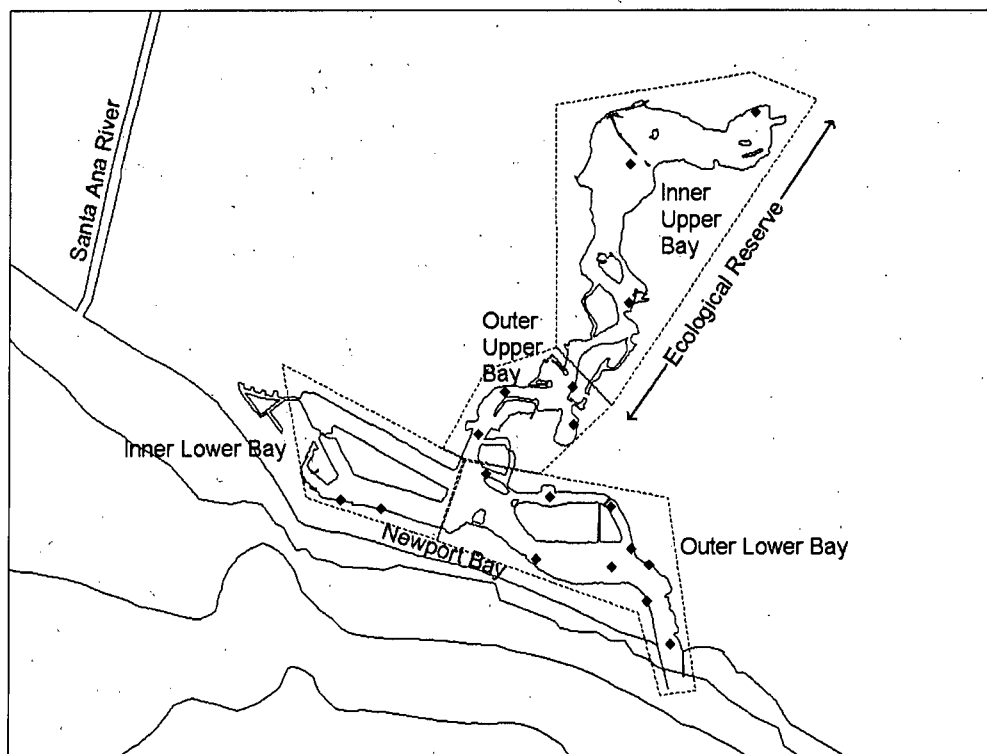


Figure 1. Map of Newport Bay, California, divided into subregions for this study. Black diamonds indicate collection sites of fish. Sampling locations: IU = inner upper bay; OU = outer upper bay; IL = inner lower bay; OL = outer lower bay.

Peter ~~Kozelko~~
Kozelko
5/1/2004

Arsenic Overview—using the appropriate tissue screening value

Here is an overview of using the appropriate tissue screening values for Arsenic (As) assessments. Information in bullets below is designed to give succinct details regarding this topic. Some recommendations for assessment methodologies using various reported data are also provided. Additional information and references are provided in the attached documents.

Briefly, water quality evaluations using fish tissue results should use the inorganic As screening value of 1.2 ppm wet weight. If the tissue results are reported in total arsenic concentrations, then the final assessment should be delayed until further analyses of As speciation are available or else each total concentration should be converted to inorganic via calculation. Assessments based on the total As screening value of 1.0 ppm wet weight are likely to be inaccurate and yield false positive result.

1. For arsenic, the risk exposure is associated with inorganic As species; whereas, organoarsenic species are not toxic and thus the total arsenic concentration is not optimal means of assessing risk. This is well documented in scientific literature. (see Eisler, 1994, Donohue and Abernathy 1996, Yilmazer et al. 2001)
2. In fish tissue, the most appropriate screening value is 1.2 ppm wet weight for inorganic Arsenic. This is supported by EPA scientists and policy makers. (see excerpt from EPA Guidance for Fish Advisories, 2000 and Newport Bay Toxics TMDLs, 2002)
3. The more common fish tissue screening value, 1.0 ppm for total As, is not effective for final assessment purposes. Water quality assessors should not use this value or else use it for preliminary evaluation and then require further inorganic As speciation analyses prior to final assessment. (see B. Brodberg, pers. commun.)
4. Analytical measurements of arsenic in fish tissue are typically reported in total arsenic concentrations (wet weight); however, these results do not provide a viable means of assessment. Preferably, fish tissue samples are also analyzed for inorganic species (or for organic species and thereby indirectly yielding the inorganic levels) and these inorganic results are compared with the 1.2 ppm wet weight inorganic As tissue screening value. (see Newport Bay Toxics TMDLs—Arsenic Analysis and post-note Table XX, both attached)
5. For finfish, inorganic As levels are often reported at 100 to 1000 fold less than the total As concentrations. For shellfish, inorganic As levels range from 10 to 60% of the total As concentration. (see Donohue and Abernathy, 1996)
6. Scientists have explored the build up of total As levels in fish. It appears to be a nature process whereby, arsenic is ingested by fish and internally converted to arsenobetaine and other organoarsenic species preferentially. Complete synthetic pathways have been proposed but not confirmed. This is true for freshwater and saltwater finfish. (see Francesconi and Edmonds, 1994; Geiszinger, Goessler and Francesconi, 2002)

Pathways for completing assessments of As levels in fish tissue:

- a. Demand/await study results that provide wet weight measurements of inorganic As and compare with EPA tissue screening value: recreational fishers = 1.2 ppm and subsistence fishers = 0.147 ppm.
- b. If study results provide only wet weight measurements of total As, then use either of two options:
 - i. Delay assessment decision until further analyses of inorganic As species are provided, then see item a above.
 - ii. Convert (via calculation) total arsenic results into inorganic estimates by assuming that inorganic As is between 4 or 10% of total As concentration. Use these inorganic estimates and compare with inorganic As tissue screening value in item a above.

Phone conversation between Peter Kozelka, EPA Region 9 Water Div., and Robert Brodberg, Ph.D., chief of Pesticide and Environmental Toxicology section, Office of Environmental Health Hazard Assessment, California EPA, Sacramento, CA

Date: Jan. 22, 2002

Topic: OEHHA fish tissue screening value for total arsenic

At my request, Bob and I discussed the OEHHA screening value for arsenic in fish tissue. I wanted to learn more about how the fish tissue was derived as well as the OEHHA policy for using screening values to determine fish consumption advisories.

From my notes —

Bob stated the total arsenic screening value (1.0 ppm) was developed during study of contaminants in sportfish for two freshwater lakes in California. Bob said this was OEHHA's first attempt at developing screening values and that he and his colleagues wanted to follow guidelines recommended by EPA scientists and policymakers. (EPA has recommended using an inorganic arsenic tissue screening value, and making comparisons of actual measurements of inorganic arsenic in sample fish.) However, Cal EPA did not have analytical support in-house to accommodate this request for inorganic arsenic measurements in fish tissue. Thus, they decided to develop the total arsenic screening value and if there were many exceedances then they would request inorganic analyses (via outside lab in necessary) to further evaluate the extent of the problem. Bob said the report actually states this preference but few people read the report, rather they use the screening values and cite it.

Bob didn't say definitively that using this freshwater screening value for saltwater fish tissue was inappropriate, but he did recognize that elevated arsenic in saltwater tissue is common phenomenon.

Bob said there is no general policy or set of guidelines for determining if waterbody requires fish consumption advisory. He believes it is important to get an adequate representation of fish, especially those species that people consume, before assessment. Another factor is whether people eat lots of the heavily contaminated fish types. So sample size is important, as is fish species and human consumption of that (contaminated) fish type.

References:

- Donohue, JM and CO Abernathy 1996 *Exposure to Inorganic Arsenic (As) from Fish and Shellfish*. Proceedings of International Arsenic conf.
- Eisler, R. 1994 A review of arsenic hazards to plants and animals with emphasis on fishery and wildlife resources. In: *Arsenic in the Environment. Part II Human Health and Ecosystem effects*. JO Nriagu, Ed. John Wiley & Sons, Inc. NY. pp185—251.
- Francesconi, KA and JS Edmonds 1994 *Biotransformations of Arsenic in the Marine Environment*. in Arsenic in the Environment, Part 1: Cycling and Characterization. J.O. Nriagu, editor. pp. 221-262.
- Geislinger, AE; W Goessler and KA Francesconi. 2002 The marine polychaete *Arenicola marina*: its unusual arsenic compound pattern and its uptake of arsenate from seawater. *Mar. Env. Res.* **53**, 37-50.
- OEHHA 1999 *Prevalence of Selected Target Chemical Contaminants in Sport Fish from Two California Lakes: Public Health Designed Screening Study*. June 1999, RK Brodberg and GA Pollack, Pesticide and Environ. Toxic. Sctn, Office of Environmental Health Hazard Assessment, Calif. EPA, Sacramento, Calif.
- USEPA 2002 *Total Maximum Daily Loads for Toxic Pollutants in San Diego Creek and Newport Bay, California*. U.S. Environmental Protection Agency, Region 9, Water Division, San Francisco CA.
<http://www.epa.gov/region09/water/tmdl/final.html>
- USEPA 2000 *Guidance for Assessing Chemical Contaminant Data for Use in Fish Consumption Advisories, Vol. 1: Fish Sampling and Analysis*, 3rd ed. EPA-823-B-00-007. U.S. Environmental Protection Agency, Office of Water, Wash. DC.
- US Fish & Wildlife Service 1998 *Guidelines for Interpretation of the Biological Effect of Selected Constituents in Biota, Water, and Sediment*. US Department of Interior report.
- Yilmazer, M and S Shawky, RN Sanga, RM Lorenzana 2001 Concurrent Exposure Evaluations Arsenic MCL Options and Arsenic in seafood. *Toxicol. Sci.* **60**(1): p90.