U.S. Fish and Wildlife Service
Region 2
Contaminants Program

ENVIRONMENTAL CONTAMINANTS IN DUCKS COLLECTED FROM WASTEWATER TREATMENT PLANT PONDS, NOGALES, ARIZONA 1996

by

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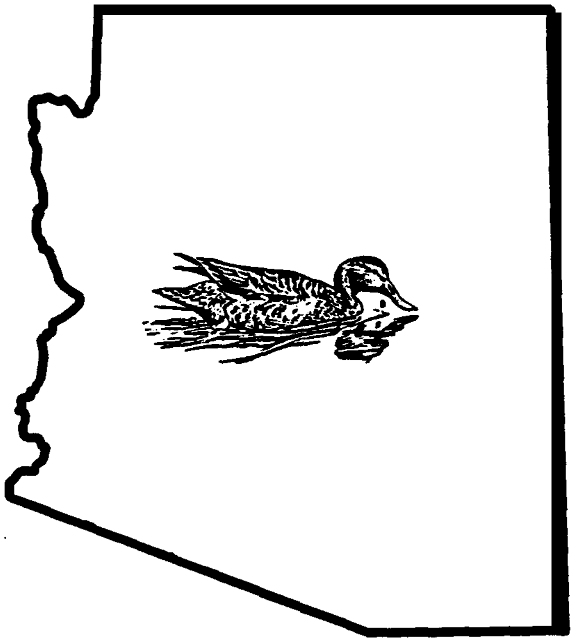

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ABSTRACT

Five gadwalls and five northern shovelers collected from the Nogales International Wastewater Plant ponds in February 1996 contained low residues of organochlorine pesticides and PCBs in carcass tissues. Concentrations were below those known to adversely affect adult survival and reproduction.

Arsenic, beryllium, lead, selenium, and zinc were either not detected or concentrations in liver tissues were within the normal background range and below levels associated with reproductive failure. Cadmium concentrations in one shoveler and chromium in one gadwall were above background levels but below concentrations known to be toxic. Nickel was present in one sample at about 25-times the normal background level; the remaining samples contained low levels of nickel. Average mercury concentrations were significantly higher in shovelers than gadwalls. Mercury concentrations in shovelers approached levels associated with toxic effects in other bird species.

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INTRODUCTION

The Santa Cruz River in south-central Arizona sustains one of the richest, most diverse riparian areas in southwestern United States. Several endangered and proposed endangered species including the Gila topminnow (*Poeciliopsis occidentalis),* cactus ferruginous pygmy-owl (*Glaucidium brasilianum cactorum*), and Sonora tiger salamander (*Ambystoma tigrinum stebbinsi*) are found along the Santa Cruz River riparian corridor. Historically the Santa Cruz River supported seven species of native fish, but only two species are currently present, the Gila topminnow and longfin dace (*Agosia chrysogaster*) (Minckley 1979, Lawson 1995).

The Nogales International Wastewater Plant (treatment plant) is located on the west bank of the Santa Cruz River just north of the city of Nogales, Arizona. The treatment plant treats wastewater from both Nogales, Arizona and Nogales, Sonora, Mexico. Effluent from the plant is a major source of water for the Santa Cruz River downstream from Nogales. More than 50% of the fish collected in 1994 immediately downstream of the treatment plant had physical anomalies such as lesions or skeletal deformities (Lawson 1995). Fish diversity, density and age structure varied considerably among collection locations with a general improvement at sites further from the treatment plant (Lawson 1995). Macroinvertebrate population diversity and density also improved with increasing distance downstream from treatment plant (Lawson 1995).

Bioaccumulation of contaminants in fish from the Santa Cruz River was documented in recent Environmental Protection Agency (EPA) sampling programs (Rector 1994, Rector 1997). Elevated concentrations of arsenic, cadmium, and zinc were recorded in all fish collected from four locations on the river. In addition, fish from one or more locations also contained elevated levels of mercury, selenium, and DDE.

The occurrence of fish with anomalies and associated high levels of contaminants is a source for concern for the entire Santa Cruz ecosystem. The objective of our study was to document the levels and potential effects of contaminants on waterfowl wintering on the Nogales International Wastewater Treatment Plant ponds.

STUDY AREA AND METHODS

<u>Sample collections</u>:

Five adult gadwalls (*Anas strepera)* and five adult northern shoveler (*A. clypeata*) were collected from the treatment ponds on February 9, 1996, using shotguns loaded with steel shotshells and with a .22 caliber rifle. Whole bodies were weighed then plucked and bills, feet, wingtips and gastrointestinal tract were removed and discarded. Carcass remainders and liver tissues were individually wrapped in aluminum foil and placed in a cooler on wet ice until they were transferred to a commercial freezer later that day. Samples were stored frozen until chemical analyses.

Chemical analvses:

Duck carcasses were analyzed for organochlorine compounds including o,p'-and p,p'-DDE, o,p'-and p,p'-DDD, o,p'-and p,p'-DDT, dieldrin, heptachlor epoxide, hexachlorobenzene (HCB), alpha, beta, delta, and gamma BHC, alpha and gamma chlordane, oxychlordane, *trans*-nonachlor, cis-nonachlor, endrin, toxaphene, mirex, and polychlorinated biphenyls (PCB) at the U.S. Fish and Wildlife Service's Patuxent Analytical Control Facility (PACF), Laurel, Maryland. The analytical methods, including preparation, Soxhlet extraction, and lipid removal are described by Cromartie et al. (1975). Glass extraction thimbles were used. The silica gel separation of the pesticides from PCBs was different from the above reference in that four fractions were used instead of three to enable the separation of dieldrin and endrin from the rest of the pesticides. Pesticides in each fraction were quantified with a gas-liquid chromatograph (GLC), equipped with a 63Ni electron capture detector. The GLC column used was a 30m megabore coated with a 1 .O micron film of 7% cyanopropyl7 % phenyl polysiloxane. Residues in 10% of the samples were confirmed by gas chromatography/mass spectrometry (GC/MS). The lower limit of quantification was 0.01 parts per million (ppm) for most organochlorine pesticides and 0.05 ppm for toxaphene and PCBs. Organochlorine compounds are expressed in ppm wet weight.

Liver samples were analyzed at PACF for aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, manganese, mercury, molybdenum, nickel, selenium, strontium, vanadium, and zinc. Atomic absorption spectroscopy hydride generation was used to quantitate selenium and arsenic. Mercury concentrations were determined by cold vapor atomic absorption. All other elements were analyzed by inductively coupled plasma atomic emission spectroscopy. Blanks, duplicates, and spiked samples were used to maintain laboratory quality assurance and quality control (QA/QC). Analytical methodology and reports met or exceeded PACF QA/QC standards.

To interpret our data, we compared our findings to normal background levels in ducks as reported by other authors. Many authors reported metal concentrations in ppm dry weight while others, especially authors of earlier papers, reported results in ppm wet weight. To facilitate comparison of our findings with those in published reports, we tabularized our data in both ppm dry weight and ppm wet weight. The lower limits of quantification varied by element and by sample mass and are listed in the appropriate tables.

We recognize that not all the elements listed in this report are "heavy metals" or even true metals. But for convenience, and to avoid often ambiguous terms such as "trace elements, metalloids, and heavy metals", we refer to all elements simply as metals.

RESULTS AND DISCUSSION

Ducks were collected in February so that contaminant levels in tissues would reflect maximum over-winter bioaccumulation burdens. One problem inherent in collecting birds as biological samples is that feeding areas (i.e. contaminant exposure areas) cannot be precisely determined. Since relatively large numbers of both gadwall and northern shoveler were present on the treatment ponds throughout the winter, the treatment ponds are likely a major feeding as well as resting area. Also, in this region of the desert southwest, there are few alternate waterfowl habitats that could support large numbers of ducks. It is highly likely that the contaminant profile of the ducks reflects bioaccumulation of compounds and elements primarily from the treatment ponds.

Organochlorines: DDE and PCBs were the only organochlorines detected and these compounds were present at relatively low (< 1.0 ppm) levels (Table 1). DDE residues in duck carcasses were similar to the concentrations detected in control birds in dietary experiments. When mallards ***(A. platyrhynchos)*** were fed diets containing 40 ppm DDE for 96 days, DDE residues in skinned carcasses averaged 33 ppm wet weight 42 days after cessation of treated food (Haegele and Hudson 1974). Eleven months after DDE exposure ceased, carcass residues averaged 9.6 ppm in treated birds and 0.5 ppm in control birds. DDE residues in plucked carcasses of black ducks ***(A. rubripes)*** fed 10 ppm DDE for 7 months averaged 155 ppm wet weight and residues in control group ducks averaged about 0.3 ppm (Longcore and Stendell 1977). Two years after the DDE treatment was terminated, DDE residues in carcasses averaged 12.2 ppm in males and 3.4 ppm in females. Gadwalls and northern shovelers collected from the treatment ponds reflect exposure to low environmental levels of DDE since residues in their carcasses were far lower than those in ducks fed DDE in laboratory studies and were similar to levels in experimental controls.

PCBs were detected in all duck carcasses. Residues ranged from 0.20 to 0.92 ppm wet weight. Average residues were low compared to levels reported in other species of birds collected from known PCB contaminated areas. PCBs in canvasback ducks ***(Aythya valisineria)*** from Chesapeake Bay, Maryland averaged 1.5 and 2.7 ppm wet weight (White et al. 1979). Adult ruddy duck (*Oxyura jamaicensis*) carcasses collected from the highly industrialized Delaware River area contained from 2.8 to 10 ppm wet weight (White and Raiser 1976). Two great blue heron ***(Ardea herodias)*** carcasses from PCB contaminated portions of the Sheboygan River, Wisconsin contained 23 and 36 ppm wet weight (Heinz et al. 1984). PCBs in four adult belted kingfishers (*Ceryle alcyon*) from the same area ranged from 23 to 218 ppm wet weight (Heinz et al. 1984). Cormorants collected from highly contaminated habitats in the Netherlands contained up to 460 ppm wet weight PCBs (Koeman 1973). In contrast to these high concentrations in birds from contaminated habitats, PCBs in northern shovelers from uncontaminated California areas ranged from 0.11 ppm in females to 0.33 ppm in males (Ohlendorf and Miller 1984); levels similar to those in shovelers from treatment ponds. PCBs in gadwalls and shovelers collected from treatment ponds may represent background levels; at least in comparison to those in birds from highly contaminated areas.

Metals: Of 20 metals known to be toxic, 14 are of particular concern because of their widespread production and use, as well as their subsequent discharge and persistence in the environment (Jenkins 1981). Eleven of those 14 metals are quantified in this report: arsenic, beryllium, boron, cadmium, chromium, copper, lead, mercury, nickel, selenium, and vanadium. When ingested in sufficient quantities, arsenic, beryllium, cadmium, chromium, lead, mercury, and selenium are toxic. Arsenic, cadmium, lead, and mercury are cumulative poisons. Arsenic and beryllium are known carcinogens.

The liver is the single most useful tissue for quantifying most elements when recent exposure of a bird is being assessed. Cadmium, mercury, and selenium should be measured in both liver and kidneys, because the ratio of concentrations between these two tissues helps assess environmental exposure (Ohlendorf 1993). Unfortunately, we did not have sufficient funds to analyze both liver and kidney tissues. Concentrations of 18 metals were detected in liver tissues (Tables 2 and 3). The following discussion is limited to nine EPA priority pollutants (arsenic, beryllium, cadmium, chromium, copper, lead, nickel, selenium, and zinc) as these are the elements of greatest ecological concern.

Arsenic and beryllium- Arsenic and beryllium were not detected in any liver samples and therefore, pose little potential problem for ducks wintering on the treatment ponds. Fish collected from the Santa Cruz River had elevated levels of arsenic, therefore; arsenic concentrations may be of concern for fish-eating birds.

Cadmium- Cadmium threshold concentrations for effects in wildlife are relatively high. Adult female mallards fed 200 ppm cadmium for 13 weeks accumulated up to 110 ppm wet weight ($\approx$ 367 ppm dry weight) in their livers and ceased egg laying, but no other gross effects were observed (White and Finley 1978). Mallard ducklings fed 20 ppm cadmium for 12 weeks accumulated 42 ppm wet weight ($\approx$ 140 ppm dry weight) in the liver and developed mild to severe kidney lesions (Cam et al. 1983). Background levels of cadmium in liver tissues of birds are considered to be 3 ppm dry weight or less (Ohlendorf 1993). Cadmium concentrations in vertebrate liver tissues that exceed 10 ppm wet weight ($\approx$ 33 ppm dry weight) should be viewed as evidence of probable cadmium contamination (Eisler 1985). The highest cadmium concentration in treatment pond ducks, 6.88 ppm dry weight, was higher than background concentrations but below those known to be toxic to birds.

Chromium- Levels of chromium in 9 of 10 samples was $\leq$ 0.82 ppm dry weight. One sample contained an anomalously high concentration of 35.71 ppm dry weight. Reanalysis of this sample confirmed earlier results. Chromium is an essential trace element in humans and some laboratory animals, but the data are incomplete for birds (Eisler 1986). At high environmental concentrations, chromium is a mutagen and teratogen. Concentrations are usually elevated in waters of municipal water treatment plants (Eisler 1986). We were unable to locate any scientific literature containing data that linked concentrations of chromium in bird livers with adverse biological effects.

Copper- Copper concentrations ranged from 30 to 230 ppm dry weight in duck livers from treatment ponds. Livers of gadwalls and shovelers collected from relatively unpolluted areas in England contained mean copper concentrations in livers of 100.4 and 77.3 ppm dry weight, respectively (Parslow et al. 1982). Copper in livers of canvasbacks from Chesapeake Bay, Maryland averaged 59 ppm wet weight ($\approx$ 197 ppm dry weight, White et al. 1979). Copper averaged 114.7 ppm dry weight in 15 species of waterfowl from Chesapeake Bay as reported by DiGuilio and Scanlon (1984). The mean liver copper concentration in greater scaup (*Aythya fuligula*) from British Columbia was 55.1 ppm dry weight (Vermeer and Peakall 1979). From 56 to 97 ppm wet weight copper ($\approx$ 187 to 323 ppm dry weight) in immature Canada *goose (Branta canadensis)* liver tissues was associated with acute copper toxicosis (Henderson and Winterfield 1974). Because there was a slight overlap in the range of copper concentrations in healthy birds (5 1.1-197 ppm dry weight) and concentrations associated with mortality (187-323 ppm dry weight), additional work is needed to determine "normal background" concentrations of copper in waterfowl. We were unable to interpret copper concentrations observed in gadwalls and shovelers collected from the treatment ponds.

Lead- Lead poisoning has long been recognized as a serious problem for waterfowl (Ohlendorf et al. 1978, Jordan and Bellrose 1951, Belrose 1959), but mortality was usually associated with the ingestion of lead shot as opposed to bioaccumulation of environmental lead. Normal background concentrations of lead in tissues of adult birds living in relatively uncontaminated environments are 0.5 to 5.0 ppm dry weight in liver (Scheuhammer 1987). Ohlendorf (1993) considered levels greater than 5 ppm in liver tissues to be toxic to birds. The highest concentration of lead in livers of ducks collected from the treatment ponds was 3.01 ppm dry weight (Table 2); which suggests that ducks wintering on the treatment ponds were not exposed to potentially harmful levels of lead.

Mercury- Reproductive effects usually occur at lower doses than required to produce other pathological effects (Scheuhammer 1987). Liver concentrations of about 2 ppm dry weight mercury were associated with decreased hatchability due to early embryonic mortality and an increased number of unfertilized eggs. Mortality was associated with 30 to 130 ppm mercury in the liver (Scheuhammer 1987). Mean mercury concentrations were significantly ($P = 0.0001$, t-test) higher in treatment pond shovelers (1.79 ppm dry weight) than gadwalls (0.53 ppm). Mercury concentrations in shovelers approached levels associated with toxic effects in other duck species. It is not known for certain why average levels of mercury were nearly three times higher in shovelers than gadwalls. Differences may be related to different food habits, different bioaccumulation rates on the treatment ponds, or differences in exposure on the nesting grounds.

Nickel- Nickel was detected in only 1 of 10 liver samples. The single sample in which nickel was detected contained an anomalously high level, 24.79 ppm dry weight. Background levels of nickel in livers of waterfowl are usually less than 1 ppm dry weight (Fleming 1981). We are at a loss to explain why nickel was detected at nearly 25 ppm in one gadwall liver but not detected in the remaining samples. Reanalysis of this sample confirmed earlier results.

Selenium- In livers of birds from selenium normal environments, selenium usually averages less than 10 ppm dry weight (Schroeder et al. 1988, Ohlendorf 1993, Skorupa et al. in review). In game-farm mallards fed selenomethionine, the threshold mean liver concentration associated with reproductive impairment was 3.5 ppm wet weight ($\approx$ 11.7 ppm dry weight) (Heinz et al. 1989). The highest concentration of selenium detected in duck livers from treatment ponds was 4.59 ppm dry weight; well within the normal background range and below concentrations associated with reproductive failure.

Zinc- Two independent studies of metals in livers of canvasbacks from Chesapeake Bay, Maryland revealed that zinc concentrations ranged from 41 ppm wet weight ($\approx$ 137 ppm dry weight) to 170 ppm dry weight (White et al. 1979, DiGuilio and Scanlon 1984). Gadwalls and shovelers collected from an unpolluted area in England contained mean zinc concentrations of 113 and 111.5 ppm dry weight, respectively (Parslow et al. 1982). Surf scoters (*Melanitta perspicillata*) and greater scaup from British Columbia averaged 100 and 123 ppm dry weight zinc (Vermeer and Peakall 1979). Zinc in gadwalls and shovelers from the treatment ponds ranged from 104 to 174 ppm dry weight, which is similar to zinc concentrations in waterfowl from other locations. Zinc does not pose a potential problem to ducks over-wintering at the treatment ponds.

RECOMMENDATIONS

Elevated concentrations of mercury, and possibly cadmium, chromium and nickel, in the Santa Cruz River ecosystem may originate in effluent from the treatment plant. Other sources for these contaminants should also be investigated. Untreated waters from Nogales Wash, which originates in Nogales, Sonora, Mexico enter the Santa Cruz River just upstream of the treatment plant discharge point. Nogales Wash receives wastes from numerous border maquiladora industries and discharges are largely unregulated. Periodic storm flow events may exacerbate the problem by flushing contaminants from upland urban and industrial areas into Nogales Wash. Contaminant levels in Santa Cruz River fish are likely influenced by perennial and stormwater runoff discharges from Nogales Wash. Future studies should focus on Nogales Wash and other tributaries as sources of contamination in the Santa Cruz River ecosystem. The levels and effects of ammonia and chlorine, two chemicals often associated with deformities in fish and reduced invertebrate diversity in wastewater receiving streams, should also be investigated.

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Table 1. Organochlorine residues in individual whole body gadwalls and northern shovelers collected at the Nogales International Wastewater Treatment Plant ponds, February 9, 1996

Sample	Weight (g)	Prcnt lipid	Ptcnt moist	ppm wet wt.[1] PIP' DDE	PCB 1254
Gadwall					
Sample 1	573	17.9	62.7	0.19	0.39
Sample 2	600	13.0	67.2	0.20	0.20
Sample 3	647	18.2	61.4	0.06	0.20
Sample 4	628	23.1	56.7	0.07	0.29
Sample 5	579	22.6	60.1	0.24	0.50
Shoveler					
Sample 1	390	10.5	67.6	0.34	0.27
Sample 2	407	14.6	59.8	0.49	0.41
Sample 3	414	15.1	61.2	0.44	0.54
Sample 4	425	25.1	55.7	0.49	0.92
Sample 5	382	10.6	69.2	0.45	0.35

[1]The following compounds were not detected in any samples: HCB, alpha chlordane, cis-nonachlor, dieldrin, endrin, gamma chlordane, heptachlor epoxide, mirex, o,p'-DDD, o,p'-DDE, o,p'-DDT, oxychlordane, p,p'-DDD, p,p'-DDT, trans-nonachlor, and alpha, beta, and gamma BHC. The lower limit of detection was 0.05 ppm wet weight for toxaphene and PCB and 0.01 ppm for all other compounds.

Table 2. Metal concentrations (ppm dry weight) in livers of gadwalls and northern shovelers collected at Nogales International Wastewater Treatment Plant ponds, February 9, 1996

Sample	Element concentration, ppm dry weight'													
	Al	B	cd	Cr	cu	Hg	Mg	Mn	MO	Pb	Se	Sr	V	Zn
Gadwall														
Sample 1	9.28	3.17	2.62	0.74	230	0.47	646	11.5	12.55	2.52	4.59	19.30	1.11	174
Sample 2	9.29	3.61	1.53	35.71	69	0.61	611	15.2	4.47	0.91	4.16	4.52	0.59	117
Sample 3	48.88	6.74	2.60	x1.22	115	0.60	751	14.8	7.17	3.01	3.08	7.60	0.87	146
Sample 4	8.79	2.30	1.78	0.57	76	0.52	647	17.5	3.97	2.43	3.08	1.98	0.75	118
Sample 5	9.30	<12.66	1.48	<3.17	149	0.45	520	13.4	4.12	2.15	3.35	3.45	0.77	104
Shoveler														
Sample 1	8.34	<1.58	2.43	0.70	83	1.70	583	10.7	7.62	1.49	4.22	10.55	<O.40	118
Sample 2	22.15	2.17	1.37	0.82	79	1.70	823	13.2	3.30	1.38	4.45	4.13	CO.54	154
Sample 3	10.47	<1.6O	6.88	0.79	67	1.70	695	12.0	3.41	2.43	4.05	12.85	CO.40	147
Sample 4	7.90	<1.48	1.02	0.38	47	2.00	591	13.9	2.88	1.20	3.10	6.33	<O.35	120
Sample 5	10.66	<1.76	1.38	0.51	30	1.87	741	10.9	5.61	1.59	4.48	15.82	CO.41	104

Chemical abbreviations: Al= aluminum, B= boron, Cd= cadmium, Cr= chromium, Cu = copper, Hg = mercury, Mg = magnesium, Mn= manganese, Mo= molybdenum, Pb = lead, Se= selenium, Sr= strontium, V= vanadium, Zn= zinc. Arsenic, barium, and beryllium were not detected in any samples. Nickel was recorded in one gadwall sample (No. 2) at 24.79 ppm dry weight.

Table 3. Wet weight metal concentrations in livers of gadwalls and northern shovelers collected at Nogales International Wastewater Treatment Plant ponds, February 9, 1996

Sample	Element concentration, ppm wet weight'													
	Al	B	Cd	Cr	Cu	Hg	Mg	Mn	MO	Pb	Se	Sr	V	Zn
Gadwall														
Sample 1	2.55	0.87	0.92	0.20	63	0.13	177	3.15	3.44	0.69	1.26	5.29	0.30	48
Sample 2	2.59	1.01	0.43	9.96	19	0.17	170	4.25	1.25	0.25	1.16	1.26	0.16	33
Sample 3	13.98	1.93	0.74	<0.35	33	0.17	215	4.23	2.05	0.86	0.88	2.17	0.25	42
Sample 4	2.96	0.77	0.60	0.19	26	0.18	218	5.91	1.34	0.82	1.04	0.67	0.25	40
Sample 5	2.83	<3.85	0.45	<0.96	45	0.14	158	4.07	1.25	0.65	1.02	1.05	0.23	31
Shoveler														
Sample 1	2.58	co.49	0.75	0.22	26	0.52	180	3.30	2.36	0.46	1.31	3.27	<0.12	36
Sample 2	5.11	0.50	0.32	0.19	18	0.39	190	3.04	0.70	0.32	1.03	1.64	<0.12	36
Sample 3	3.23	co.49	2.12	0.24	21	0.52	214	3.70	1.05	0.75	1.25	3.96	<0.12	45
Sample 4	2.82	co.53	0.36	0.14	17	0.71	211	4.96	1.03	0.43	1.10	2.26	<0.12	43
Sample 5	3.20	co.53	0.41	0.15	9	0.56	222	3.27	1.69	0.48	1.35	4.75	so.12	31

Chemical abbreviations: Al = aluminum, B= boron, Cd= cadmium, Cr= chromium, Cu= copper, Hg= mercury, Mg = magnesium, Mn= manganese, Mo= molybdenum, Pb= lead, Se= selenium, Sr= strontium, V= vanadium, Zn= zinc. Arsenic, barium, and beryllium were not detected in any samples. Nickel was recorded in one gadwall sample (No. 2) at 6.91 ppm wet weight.