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Water quality in a reservoir used for carp production

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RESUMEN

El estudio de calidad del agua fue realizado en el Reservorio Guadalupe, situado en la comunidad de San Sebastián Lerdo de Tejada (Toluca, estado de México). Está sobre el río San Cayetano, el cual se une al río Lerma cerca del km 18 al norte del estado.

El 9 de agosto de 1995 más de 6000 carpas Israeli (*Cyprinus carpio* v. *specularis* and *rubrofruscus*) murieron en menos de una semana en este reservorio. El propósito de este estudio fue investigar la causa por la que murieron las carpas, así como determinar el tiempo en que este reservorio puede ser de nuevo utilizado para el cultivo de este pez.

Cinco días después del accidente se encontraron, en el reservorio, evidencias de la presencia de cloro residual, el cual fue cuatro veces mayor al límite máximo permisible. También se encontraron concentraciones arriba de los niveles recomendados de nitrógeno amoniacal, demanda bioquímica de oxígeno (DBO) y demanda química de oxígeno (DQO).

Seis meses más tarde, ya no se detectó cloro. Sin embargo, otros como el amonio, DBO y DQO se encontraron en concentraciones más bajas, pero siempre mayores a los niveles recomendados. Lo más probable es que el cloro residual haya sido la causa de la muerte de las carpas debido a que su concentración fue muy alta en la época en que murieron los peces.

PALABRAS CLAVE: Agua, contaminación, carpa, cloro residual.

ABSTRACT

Guadalupe Reservoir, on the San Cayetano river, feeds into the Lerma river about 18 km north of Toluca in the State of Mexico, Mexico. On August 9, 1995, more than 6000 Israeli carp (*Cyprinus carpio* v. *specularis* and *rubrofruscus*) died within a week in this reservoir. We investigated the cause of the fish mortality and we determined whether the reservoir could be used again for carp culture. Five days after the accident the residual chlorine was 4 times higher than the maximum permissible amount. Ammonia nitrogen, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were also above the recommended levels. Six months later, the amount of some contaminants in the water, such as chlorine, were back to normal ranges of water quality criteria for aquaculture. Ammonia, BOD and COD concentrations were lower to those found in the previous analyses but remained higher than the recommended levels. Most probably, residual chlorine was the cause of carp mortality as the chlorine level was very high when the fishes died.

KEYWORDS: Water, pollution, carp, ammonia, free-residual chlorine.

1. INTRODUCTION

Guadalupe Reservoir is located in the San Cayetano river watershed, on the left bank of the river, about 18 km north of Toluca in the State of Mexico. San Cayetano river, a subbasin of the Lerma river, is situated in Central Mexico (Figure 1). This watershed has a C(w2)(w) climate according to the Köeppen climatic classification (Miller, 1982). The average annual rainfall is approximately 920 mm year^{-1}, with a peak occurring in July and a distinct dry season from October to April. The mean annual temperature is 15-18 °C, the mean temperature of the coldest month (January) is 11-12 °C while that of the hottest month is 20-24 °C. The zone covers an area of about 132 km^2, and the surface elevation at the site ranges from 2630 m at the southwestern corner to 2570 m at the northeastern corner. The topography of the area is a flat land, and the economy of the region is based on agriculture. The principal crop is maize, which is grown on 90% of cultivable land (CCRECRL, 1993).

The surface area of the reservoir is approximately 0.08 km^2, with a mean annual water volume of approximately 150 000 m^3, which originates from the Tejalpa river. The storage volume is almost constant throughout the year, because of the existence of canals for water recharge and discharge control. Besides, this reservoir provides water for agricultural demands via a distribution canal. The water remains stagnant from September to March (non-irrigation period) but is often renewed from April to August during the rainy season.

The Guadalupe Reservoir is used to satisfy the demand for fish in the surrounding region; however, on August 9, 1995,

and on the following five days, about 6000 Israeli carp (*Cyprinus carpio* v. *Specularis* and *rubrofruscus*) died in that small water reservoir.

The main aim of the present study was to investigate the cause of the fish death and to determine whether the reservoir could be used again for carp culture and the specific objective was to evaluate the chemical, physical and bacteriological characteristics of the water after the death of the carp.

2. EXPERIMENTAL

2.1. Sampling

From August 14, 1995 to February 1, 1996, temperature, pH, alkalinity, carbon dioxide, total hardness and free residual chlorine, have been analysed in the water samples.

Sampling locations were: site A at the influent end of the canal, site B in the central area and site C in the effluent end of the canal (Figure 1). Each of water samples drawn from the reservoir with a grab sampler, was assayed for different contaminants. Mixed water samples were collected from the bottom of the pond up to the surface.

All sample containers for trace metals analyses were made of high-density clean polyethylene; they were washed with ultrapure nitric acid (2N), prior to use. Samples destined for bacteriological analyses and determination of the chemical and biochemical oxygen demands were collected in sterile bottles, which were hermetically sealed at 4 ºC in the dark and double-bagged in the field for transport to the laboratory.

The details of sampling are shown in Table 1.

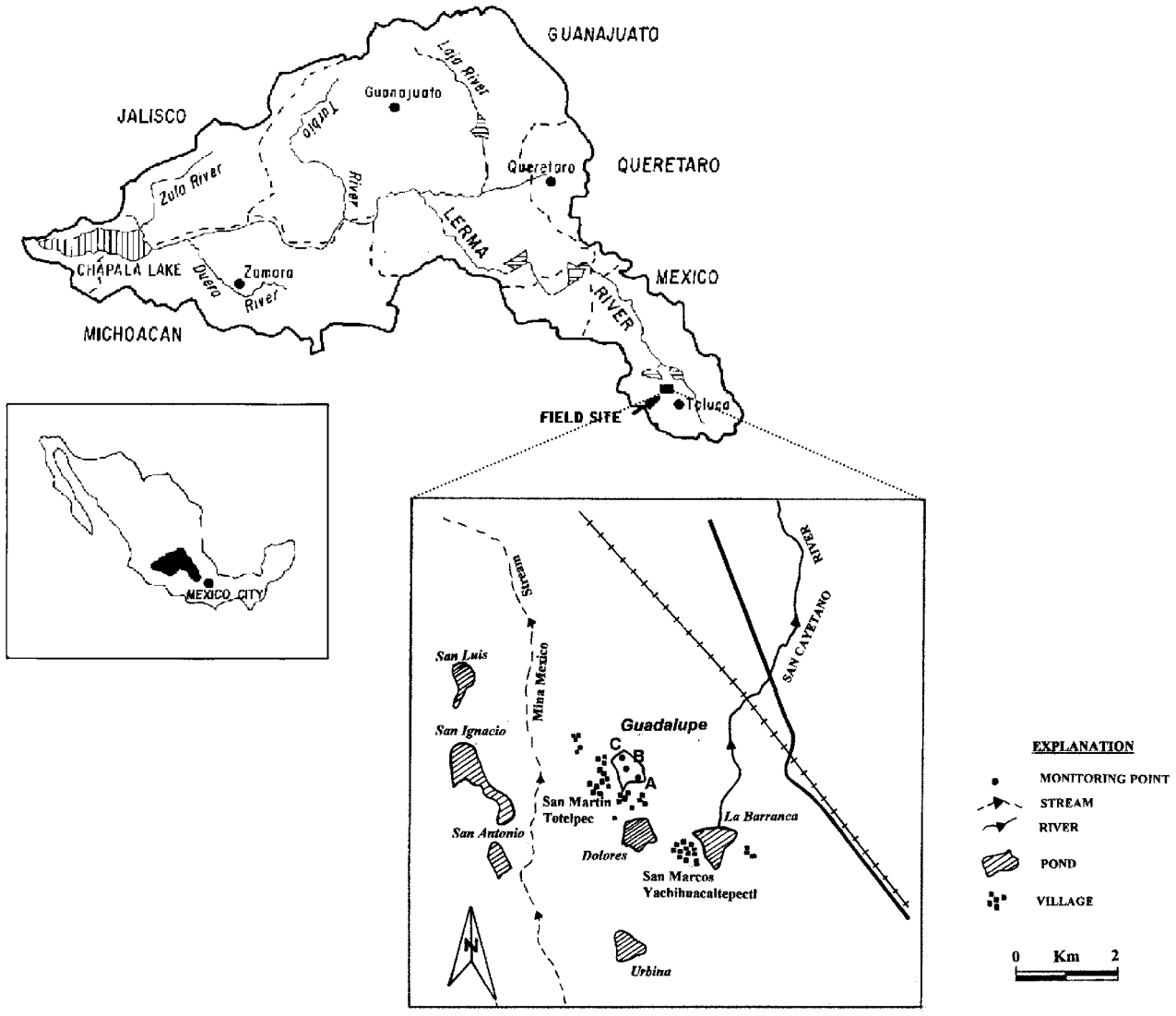

Fig. 1. Location of the Lerma watershed and the field site in the San Cayetano subbasin.

Table 1

Sampling of the water and dead carp

SAMPLE	DATE	DAYS AFTER THE ACCIDENT	SITE
Water	8/14/1995	5	C
Water	8/25/1995	16	A,B,C
Water	2/1/1996	175	A,B,C
Dead carp	8/14/1995	5	C

2.2. Analytical determinations

La Motte, model AQ-23633-01 field portable laboratory for fresh water analyses, was utilized to determine the following physicochemical parameters: temperature, pH, alkalinity, carbon dioxide, total hardness, dissolved oxygen and free residual chlorine. Free residual chlorine was analyzed by the titration method (N-N-diethyl-p-phenilendiamine-Fe^{2+}), DFD. Alkalinity, carbon dioxide, total hardness and dissolved oxygen were determined by using titration methods (APHA-AWWA-WPCF, 1995; DOF, 1992).

An Inductively Coupled Plasma - Atomic Emission Spectrometer with an ARL 3500 ICP equipment was utilized to determine As, Ca, Cd, Cr, Cu, Fe, Pb, Sn, Sr and Zn cations. A Hach DREL/ 5 Spectrophotometer DR/3 was used to analyze ammonia nitrogen, nitrite and chloride. Gas chromatography was used to analyze organophosphates, organochlorines and acid herbicides and liquid chromatography to determine carbamates (APHA-AWWA-WPCF, 1995; DOF, 1992).

Biochemical oxygen demand (BOD) was determined by the 5-day method. An airtight bottle, once filled with the samples to overflowing, was incubated at 20°C for 5 days. Dissolved oxygen (DO) produced by organic material descomposition was measured before and after incubation, and the BOD was computed from the difference between the initial and the final DO.

Chemical oxygen demand (COD) was determined by a titration method. Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. A sample was refluxed in a strongly acid solution with a known excess of potassium dichromate ($K_2Cr_20_7$). After digestion, the remaining unreduced $K_2Cr_20_7$ was titrated with ferrous ammonium sulfate to determine the amount of $K_2Cr_20_7$ consumed and the oxidizable organic matter was calculated in terms of oxygen equivalent (APHA-AWWA-WPCF, 1995; DOF, 1981).

Total and fecal coliforms were determined by the standard total coliform fermentation techniques at 35 ±0.5 and 44.5±0.2 °C, respectively for 24 h (APHA-AWWA-WPCF, 1995; DOF, 1987).

Bacteriological analyses to determine *E. Coli*, *Salmonella-shigela* and *V. Cholerae* were performed on a recently dead carp (DOF, 1993).

2.3. Calculation of the chlorine concentration

If we take into consideration the large concentration of chlorine atoms in the water $\boldsymbol{C_o}$, we may then take the fraction remaining unchanged after time $\boldsymbol{t}$ to be:

$$\boldsymbol{C/C_o = e^{-Kt}} \quad , \qquad (1)$$

where $\boldsymbol{C}$ is the concentration of chlorine atoms remaining unchanged at time $\boldsymbol{t}$; $\boldsymbol{K}$ is the proportionality constant given by $\boldsymbol{K=ln2/t_{1/2}}$, $\boldsymbol{t_{1/2}}$ is the half life of chlorine in water and t is the time required for an initial large number of chlorine atoms in water to be reduced to half that number. Using expression (1), we can determine the concentration, $\boldsymbol{C_o}$, at time $\boldsymbol{t_o} = 0$, the day of the accident (Friedlander *et al.,* 1981).

3. RESULTS AND DISCUSSION

All analyses were performed after the death of the fish. We grouped the results in three parts: ***A)*** the presence of contaminants that were lower than the water quality criteria for carp, which, therefore, could not have been the cause of their death, ***B)*** the evaluations of some parameters that indicate changes in the water quality and ***C)*** the presence of contaminants that were above the water quality criteria for carp.

A) The temperature, pH, total alkalinity, carbon dioxide and total hardness were found within the normal range of water quality criteria for aquaculture (Table 2). The only pesticides observed were 2,4-D (2,4-dichlorophenoxyacetic diamine) in a very low concentration (0.63 μgL^{-1}) and traces of acridin, which was not quantified.

B) In general, the presence of nitrites in water indicates biochemical and bacterial contamination. In the present case, the very low quantity of nitrites (Table 3) found in the Guadalupe Reservoir on August, 1995 showed that there was low bacterial contamination (Droste, 1995) during that period. This result concurs with the very low amount of coliform found in the water (Table 4). The absence of bacterial activity in the water shows that the water was subjected to a very

Table 2

In situ physicochemical analyses of the water samples. Sampling dates: August 14 and 25, 1995 and February 1st, 1996

PARAMETERS		INPUT SITE A		CENTRAL SITE B		OUTPUT SITE C					WATER QUALITY CRITERIA FOR AQUACULTURE
						SURFACE	BOTTOM	OUTPUT			
		8/25/95	2/1/96	8/25/95	2/1/96	8/14/95	8/14/95	8/14/95	8/25/95	2/1/96	
Temperature	°C	24	15.0	22	14				20	14.5	6-30 (DOF, 1989; Arrignon, 1984)
pH		6.8	6.8	7.8	7.4	7.18	7.40	7.11	8.0	7.6	6.5-8.5 (Roberts, 1978)
Total alkalinity ($CaCO_3$)	mgL^{-1}	84	95	84	101	87.5	82.5	80	84	92	100 (Max) (DOF, 1989)
Carbon dioxide	mgL^{-1}	40	32	40	16				40	28	
Total hardness ($CaCO_3$)	mgL^{-1}	84	63	72	64	30.38	34.3	27.44	74	84	300 (Max) (DOF, 1989)
Dissolved oxygen	$mgL^{-1}O_2$	10.80	5.6	10.8	7.6	ND	ND	ND	10.8	5.4	5.0 (Min) (DOF, 1989)
Free residual chlorine	mgL^{-1}	0.011	ND	0.009	ND	0.04	0.02	0.04	ND	ND	0.01 (Max) (DOF, 1989)

Max: Maximum permissible level
Min: Minimum permissible level
ND: Not detectable

Table 3

Chemical analyses of water samples (mgL^{-1}). Sampling dates: August 25, 1995 and February, 1st, 1996

PARAMETERS	INPUT (SITE A)		CENTRAL (SITE B)		OUTPUT (SITE C)		WATER QUALITY CRITERIA
mgL^{-1}	8/28/95	2/1/96	8/28/95	2/1/96	8/28/95	2/1/96	FOR AQUACULTURE
As	<0.12	<0.30	<0.12	<0.30	<0.12	<0.30	1.0
Ca	16.13±0.26	15.80±0.20	16.34±0.22	14.60±0.05	16.44±0.32	15.40±0.20	2.5 (min) (DOF, 1989)
Cd	0.030±0.002	<0.01	0.040±0.002	<0.01	0.040±0.002	0.15±0.01	0.2 (Environment Canada, 1979)
Cr	0.10±0.01	<0.02	0.057±0.002	<0.02	0.067±0.005	<0.02	0.1 (Rogers and Klemetson,
Cu	0.014±0.001	<0.02	0.043±0.001	<0.02	0.042±0.003	<0.02	0.5 (Nightingale, J. W., 1976)
Fe	0.9±0.02	0.6±0.03	3.05±0.05	0.03±0.01	2.62±0.1	0.48±0.010	0.5
Pb	0.097±0.005	<0.05	0.11±0.01	<0.05	0.11±0.02	<0.05	0.1
Zn	0.070±0.010	0.10±0.03	0.031±0.003	<0.01	0.030±0.002	0.02±0.02	0.1 (Nightingale, J. W., 1976)
Cl^-	0.5	2.0	0.5	1.5	4	1.5	250 (DOF, 1989)
NH_4^+	1.3	0.5	0.2	0.25	1.1	0.25	0.06 (DOF, 1989)
NO^-_2	< 0.01	< 0.02	< 0.01	<0.02	< 0.01	<0.02	0.1 (Brocksen et al., 1992)
NO^-_3	3.0	3.0	2.0	2.0	1.8	3.0	5.0 (DOF, 1989)

strong bactericide effect. However, when the total coliforms increased in the dry season (February 1, 1996) the nitrites remained at very low concentrations, probably because of the very low dissolved oxygen (DO) present during this period, which did not allow the oxidation of the very high amount of ammonia nitrogen present.

As mentioned, bacteriological analyses in the water (Table 4) showed a minimal presence of fecal coliforms and total coliforms (3.6 most probable number, MPN) 16 days after the accident on August 25th; 1995. In the sampling taken in the dry season, February 1, 1996, an increase of total coliforms in the influent end of canal (9.1 MPN) and in the central Site B (28 MPN) was observed, showing that the bactericide effect had disappeared (Nielsen, 1991).

A lower DO was observed in February, when water temperature was 14-15 °C, than in August 1995, when the water temperature was higher, 20-24°C (Table 2). This was probably due, first, to the oxidation process of organic material during the period when the reservoir was closed because contaminants that induce an oxygen demand in water would

reduce the DO (Nielsen; 1991), second to the low sun stroke as the photosynthetic process is delayed, and third to the nule aquatic flux velocity, which does not permit the oxygenation of water (Eckenfelder, 1989; Barcelo, 2000).

BOD and COD values, on August 25, 1995 were higher, 33 mgL^{-1} and 98 mgL^{-1} respectively, than in samples taken in February 1, 1996, 16 mgL^{-1} and 55 mgL^{-1} respectively, 175 days after the accident (Table 4), probably because of the decomposition of organic matter from aquatic plants in the water.

C) The presence of contaminants, in higher concentrations than the maximum permissible amount, can be explained as follows: either they were formed as a consequence of the death of the carp and plants or they were present before, possibly causing the death of the carp.

In the first group, we can consider that ammonia nitrogen was high, 1.3 mg L^{-1}, in the samples taken on August 25,1995 (Table 3), probably due to the contamination produced by the dead carp and the decomposition of the organic matter from aquatic plants. This contaminant is highly toxic (Biro, 1995). However, ammonia nitrogen concentration was reduced to 0.5 mg L^{-1} in the samples collected during the dry season (February, 1,1996), therefore, the presence of ammonia nitrogen was probably not the cause of the fish death but rather its consequence.

In the second group, we can consider that some metals such as Cd, Cr, and Fe were concentrated in the first samples taken on August 25, 1995, but in the samples collected on February 1, 1996 they were found to be within the normal range of water quality criteria for aquaculture (Table 3). High metal concentrations in water was probably due to metals present in the water input during the rainy season. In the following period (from 25 August, 1995 to February 1, 1996) no water entered the reservoir, thus reducing the concentrations of metals in the water. Hence, the presence of the high concentrations of these metals in the water did not last long enough to produce the fishes death.

Also in the third group, we find chlorine. Chemical analyses showed the presence of free residual chlorine on August 14, 1995 in a concentration of 0.04 mgL^{-1} (five days after the accident) (Table 2). This amount is 4 times higher than the maximum permissible amount for aquaculture purposes (DOF, 1989). It was reduced to 0.011 mgL^{-1} on the analyses performed on August 25, (9 days after the accident) and was not detected on February 1, 1996, (175 days after the accident)

Since in our case, the half life of total residual chlorine in the reservoir was 5.4 days, calculated from equation 1, the actual concentration on the day the fish were killed was probably 0.062 mgL^{-1}. However, with all the dead fish and plants the chlorine levels would be decreasing more rapidly during the first days due to all the oxidation material present. It is possible then that the chlorine levels would have been much higher than 0.062 mgL^{-1}. This free residual chlorine concentration is highly toxic for aquatic environments. In fact, for rainbow trout the lethal concentration ranges from 0.03 to 0.08 mgL^{-1} (Van de Leedene *et al.,* 1990). Free residual chlorine has a very strong bactericide effect and causes death of aquatic plants. Since we can not explain the presence of chlorine by natural reasons, we consider that its presence was due to an accidental input and that the presence of this element in the water was the probable cause of the death of the fish.

Although the water quality was improved from August 14, 1995 to February 1, 1996, the ammonia nitrogen, COD and the BOD were still too high and the DO too low. Therefore, it was necessary to wait longer to use the reservoir for carp culture.

Table 4

BOD, COD and bacteriological analyses of the water samples. Sampling dates: August 25, 1995 and February, 1st, 1996. (MPN: most probable number).

PARAMETERS	INPUT (SITE A)		CENTRAL (SITE B)		OUTPUT (SITE C)		WATER QUALITY CRITERIA
	8/25/95	2/1/96	8/25/95	2/1/96	8/25/95	2/1/96	FOR AQUACULTURE
Total Coliform MPN	Negative	9.1	3.6	28	Negative	Negative	14 (Rogers and Klemetson, 1985)
Fecal Coliform MPN	Negative	Negative	Negative	Negative	Negative	Negative	-
Dissolved oxygen mgL^{-1}	10.80	5.6	10.8	7.6	10.8	5.4	5.0 minimum (Rogers and Klemetson, 1985)
BOD mgL^{-1}	21	15	17	15	33	16	> 6 situation anormal (Arrignon, 1984)
COD mgL^{-1}	83	46	83	55	98	48	-

On the other hand, the bacteriological analyses showed only *E. Coli* on the recently dead carp, neither *Salmonela-shigela* nor *V. cholerae* were found, thus indicating only fecal contamination.

5. CONCLUSIONS

The main findings of this research study in the Guadalupe Reservoir are the following:

Pesticides and most metals in the water reservoir were in lower concentrations than those recommended by the water quality criteria for aquaculture; therefore, they could not have been the cause for the death of the carp.

Although iron was present in concentrations higher than the recommended values, it could not produce the death of the carp because its duration in the water was very short.

Ammonia nitrogen was found in very high concentration a few days after the accident, probably due to the high level of contamination produced by the death of the carp and the decomposition of organic matter from aquatic plants. Therefore, its presence was not the cause of the fish death but rather its consequence.

Most probable residual chlorine was the cause of the sudden death of the carp as the chlorine levels were very high in the water when the fish died. This conclusion is supported by the high biological and chemical oxygen demands and by the disinfectant effects observed in the sampling performed 16 days after the accident. The source of the chlorine is unknown.

The condition of the water six months after the accident was found to be still not adequate for fish production mainly because of the high concentration of ammonia nitrogen.

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