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Heavy Metals in Wet Method Coffee Processing Wastewater in Soconusco, Chiapas, Mexico

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Abstract One of the driving forces of the economy in southeast Mexico is agriculture. In Soconusco, Chiapas, coffee is one of the main agricultural products and is traded on the international market. Coffee grown in this region is processed using the wet method in order to be commercialized as green coffee. In the *beneficio* (coffee processing plant) water is an essential resource which is required in great quantities (Matuk et al., 1997; Sokolov, 2002) as it is used to separate good coffee berries from defective ones, as a method of transporting the coffee berries to the processing machinery, in the elimination of the berry husk from the coffee grains (pulping) and finally in the post-fermentation washing process. This process gives rise to one of the smoothest, high-quality coffees available (Zuluaga, 1989; Herrera, 2002). Currently, many producers in Soconusco are opting for ecological coffee production, which has, among its many criteria, human health and environmental protection (Pohlan, 2005). Furthermore, increasing concern during the past few years regarding the production of food that is free from contaminants such as heavy metals, and recent environmental policies in relation to aquatic ecosystem protection, have given rise to questions concerning the quality of water used in coffee processing, as well as pollutants produced by this agroindustry. Water used in the coffee processing plants originates from the main regional rivers whose hydrological basins stretch from the Sierra Madre mountain range down to the coastal plain. As well as providing water, these rivers also receive the wastewater produced during coffee processing (Sokolov, 2002).

There are no previous studies pertaining to heavy-metal pollution in these rivers, however, the presence of these elements in river water could be related to the comparatively recent geology of the region (Müllerried, 1957). Heavy metals could also be a result of the coffee agroindustry as the metals considered in this study; lead (Pb), copper (Cu), iron (Fe), zinc (Zn), manganese (Mn) and arsenic (As), are regarded as part of the residual compounds produced by agroindustrial activities (Adriano, 1986; Metcalf and Eddy, 1996). These metals are classified as priority and Pb, Cd and As are regarded by the World Health Organization as possible causes of cancer in humans. The aim of this study is to determine the concentration of Pb, Cu, Cd, Mn, Zn, Fe, Ni, As, the pH, conductivity, turbidity, dissolved oxygen, chlorides, hardness, phosphorous, nitrates and total nitrogen in the water that is used and discharged in wet method coffee processing.

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Materials and Methods

This study was carried out in three wet method processing plants located in the Santa Fé, Eduviges and Chinicé coffee *fincas* (plantations) in the Soconusco region of Chiapas, Mexico. The Santa Fe processing plant is supplied by water from the Comaltitlán River, whilst the Eduviges and Chinicé plantations use water from the Huehuetán River.

Two samples were taken at each processing plant during the 2005 coffee-harvesting season. Three sampling sites

Table 1 Condition of equipment used for heavy metal detection

Element	Method	Wave length/slit (nm)	Lamp current (mA)	Detection limit
Pb	Graphite furnace	228.8 / 0.7	6	0.113 μg/L
Cu	Graphite furnace	324.8 / 0.7	6–15	0.014 μg/L
Cd	Graphite furnace	283.3 / 0.7	10–12	0.25 μg/L
Mn	Graphite furnace	279.5 / 0.2	20–25	0.025 μg/L
Zn	Flame	213.9 / 1	5	0.1 mg/L
Ni	Flame	232 / 0.2	5	0.7 mg/L
Fe	Flame	248.3 / 0.2	25–40	0.03 mg/L
As	Hydride Generation	193.7 / 0.7	10	0.1 μg/L

The results were analyzed using analysis of variation (ANOVA with a $p < 0.05$ significance level by means of the JMP statistic program

were selected at each plant: where water enters the processing plant (inflow), at the pulping process stage, and finally at the point of wastewater discharge into the river (outflow). Two samples were taken at each site, one in order to analyze heavy metals, collected in 250 ml VWR Trace Clean polyethylene bottles and the other to determine chemical parameters, collected in one liter Nalgen bottles. The samples were conserved at 4°C before being transported to the laboratory. The samples that were to be used for heavy metal analysis were conserved in nitric acid at pH 2.

In situ pH (pH meter, HI98127 Hanna USA), conductivity, turbidity (Electrode Water Checker U10 Horiba USA) and dissolved oxygen (oxygen meter HQ10 HACH LDU, USA) were all determined using selective electrodes. In the laboratory, chloride concentration was determined using the argentometric method, water hardness by ethylenediaminetetracetic acid (EDTA) titrimetric, total phosphorous using the tin chloride method, nitrates by spectrophotometer and total nitrogen using the Kjeldal method (APHA, 1995).

In order to determine heavy metal measurements, the pulping process and discharge water samples were filtered as they presented high organic matter content. The samples taken at the entrance to the processing plant were analyzed without any previous treatment. The analysis of Pb, Cu, Cd and Mn was carried out using a 3110 atomic absorption spectrometer with a HGA-600 graphite furnace and an AS-60 Perkin Elmer autosampler. Zn, Fe and Ni were determined in a SpectrAA 220 vanian flame atomic absorption spectrometer. Arsenic was measured in a Perkin Elmer Precisely A Analyst 200 atomic absorption spectrometer coupled with a FIAS 100 flow injection analysis system and a AS 90 Perkin Elmer autosampler. Calibration curves with 1000 mg/L SIGMA standards were elaborated for each metal analyzed and 0.2% HNO3 was used as a dilutant. Intensitron Perkin Elmer and Varian hollow cathode lamps were used. The general specifications of the equipment used for the detection of each element are given in Table 1.

Results and Discussion

The physical and chemical characteristics of the water that entered the coffee processing system were notably modified in the pulping stage (Table 2), pH and dissolved oxygen levels were markedly reduced and the water was acidified by the chemical composition of the coffee berry pulp (Zuluaga, 1989).The mean pH value for the evaluated coffee processing plants was five. Sokolov (2002) and Mejia (2006) report values ranging from 4.5 to 5.5 in pulping process water. The high organic matter content saturates the water, reducing the dissolved oxygen concentration. The chemical components of the coffee berry pulp were dissolved; thus, values of conductivity, turbidity, salinity, chlorides, hardness, nitrates, phosphorous and nitrogen all increased.

Water contaminated by coffee components is discharged directly into the rivers; Matuk et al. (1997) and Sokolov (2002) mention that these wastewaters cause serious desequilibrium in aquatic ecosystems. In this study, all the wastewater physicochemical parameters were below the maximum permitted limits established by the official Mexican environmental regulations (1996) regarding water discharged into rivers. In general, wastewaters originating from coffee processing plants present high organic matter concentrations (Zuluaga, 1989). It is worth pointing out that due to hurricane Stan in 2005, coffee producers suffered huge losses and were harvesting mainly defective, damaged coffee berries. Mejia (2006) states that wastewaters generated from the processing of defective berries present lower concentrations of nitrogen, phosphorous and total suspended solids (40, 30 and 110 mg/L, respectively). With the exception of Zn and Ni, all the identified heavy metals (Pb, Cd, As, Cu, Mn and Fe) were detected in the water entering the coffee processing plant, as all these elements are found naturally in the river water that supplies these plants. The concentrations detected were below the maximum permitted limits for water for general use and human consumption established by the Official Mexican Environmental Regulations (1994). All the identified heavy

Table 2 Physicochemical characteristics of water in wet method coffee processing plants at the Santa Fe, Eduviges and Chinice coffee plantations

Physicochemical parameters	Water entering processing plant (inflow)	Pulping-stage water	Discharge wastewater (outflow)	Maximum permitted limits	
				*NOM-127-SSA 1–1994	**NOM-001-ECOL-1996
pH (units)	6.7–7.1	4.3–5.4	5.3–5.7	6.5–8.5	5–10
Conductivity (μS/cm)	50–263	400–1,600	429–578	NA	NA
Turbidity (NTU)	8- 117	584–927	309–685	5	NA
Dissolved oxygen (mg/L)	7.4–7.7	2.2–4.3	3.0	NA	NA
Salinity (‰)	0.0	0.01–0.07	0.01–0.02	NA	NA
Chlorides (mg/L)	3.0–4.2	3.5–5.2	3.0–4.2	250	NA
Hardness (mg/L)	20–152	59–206	59–206	500	NA
Nitrates (mg/L)	0.4–3.8	3.3–4.4	3.8–5.9	10	NA
Phosphorous (mg/L)	0.4–1.3	11–70	5–25	NA	30
Nitrogen (mg/L)	0.6–3.0	37–64	25–64	NA	60

NA = not applicable, *water for general use and human consumption, **water discharged in rivers

Table 3 Mean heavy metal concentrations (μg/L) detected in water from wet method coffee processing plants of Soconusco, Chiapas, Mexico

Heavy metals (μg/L)	Water entering processing plant (inflow)	Pulping-stage water	Discharge wastewater (outflow)	Maximum permitted limits	
				*NOM-127-SSA1–1994	**NOM-001-ECOL-1996
Pb	2.5[a]	0.8[b]	0.8[b]	10	400
As	2.9[a]	6.4[b]	4.5[a]	50	200
Cd	0.25[a]	0.35[a]	0.39[a]	5	200
Zn	ND	6.7[a]	13.7[a]	5,000	20,000
Cu	10[a]	113[b]	36[c]	2,000	6,000
Mn	63[a]	200[b]	420[c]	150	NA
Fe	212[a]	1,013[b]	1,872[b]	300	NA
Ni	ND	ND	23	NA	4,000

ND = not detected, NA = not applicable, *water for general use and human consumption **water discharged into rivers; [a,b,c]statistical differences ($p < 0.05$)

metals, except for Pb, increased during the coffee pulping process (Table 3). Pb is regarded as one of the most toxic heavy metals (ATSDR, 2005), characterized by a lack of mobility and a tendency to be absorbed by organic matter (Moore and Ramamoorthy, 1984). Therefore, the reduction in Pb concentration in the pulping process and discharge water is probably due to some Pb remaining in the coffee pulp.

Cadmium was the least concentrated metal found in the processing waters of the three coffee processing plants; however, in the pulping process and discharge water the concentrations increase when compared with the water entering the processing plant. The same pattern is displayed with As (Fig. 1). Furthermore, notable differences are observed between the three coffee processing plants. The concentration of As in the water entering each plant was different due to variations in natural occurring elements in each river. The increase in Cd and As detected in the pulping-stage water in the studied processing plants is probably due to the type of machinery which is used during the process; Cd and As are typical residual elements produced in agroindustrial activities as Cd forms part of the machinery enamel and red paint, while As is used as an additive in metal alloys such as the lead and copper ones used for making machinery (Metcalf and Eddy, 1996; Valdés, 1999). Friction between the coffee berries and the machinery, and the acidity of the pulping water, could have provoked a modification of the machinery enamel and paint. In the pulping water from the Santa Fe plantation processing plant there was a higher concentration of As (9.1 μg/L). This could be due to the pulping water in this plant having the most acidic pH values (4.3), which could result in greater machinery corrosion. The concentrations of Cd and As in the discharge water in the three processing plants were less than those measured in the pulping-process water but higher than in the water entering the processing system. Fortunately these concentrations were below the maximum permitted limits established for discharge waters, since these elements are considered by the World Health Organization as toxic contaminants and have carcinogenic effects in humans (Hernández et al., 1999).

The presence of Zn in wet method processing was observed only in the pulping water from the Eduviges coffee processing plant and in the discharge water from all three

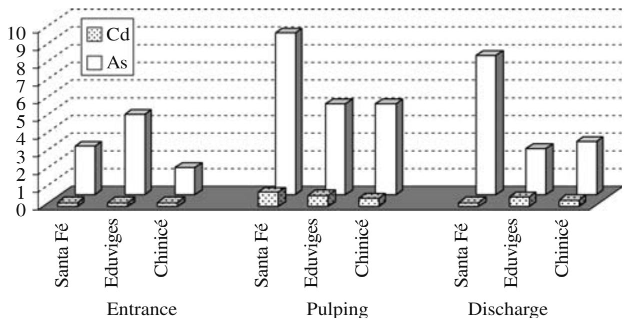

Fig. 1 Concentrations of cadmium and arsenic (μg/L) detected in the water of wet method coffee processing plants at Soconusco, Chiapas, Mexico

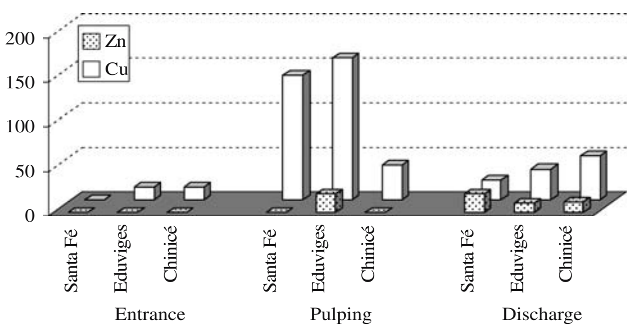

Fig. 2 Concentrations of zinc and copper (μg/L) detected in the water of wet method coffee processing plants at Soconusco, Chiapas, Mexico

plants. This could indicate that the Zn originated in fertilizers or chemical formulas used for pest control such as Zn sulphate applied to coffee plants before the harvest (Martinez, 2004). In addition, a soil analysis of the Santa Fé plantation reveals that there is an excess of Zn in the soil.

Copper concentrations differ greatly between sampling sites and the three processing plants (Fig. 2).In the pulping-process water in the Santa Fe and Eduviges processing plants, copper concentrations increased to 140 and 160 μg/L respectively and although in the Chinicé plant these concentrations were not reached, higher values were measured than in the entrance water. This is probably due to the wearing of the machinery that is made mainly from copper; Klein et al. (1974) report high copper concentrations in wastewater from non-metallic industrial systems such as those in the food industry. Although the copper concentrations in the discharge water decrease they are still greater than in the entrance water. In the Chinicé coffee processing plant, higher concentrations of copper (50 μg/L) are discharged than in the other two processing plants; however, these values are below the maximum permitted limits for wastewater discharge into rivers (Official Mexican Environmental Regulations, 1996).

The concentrations of Mn and Fe in the three coffee processing plants showed notable differences but all followed the same pattern; the discharge-waters contained a greater concentration of Mn and Fe than the water entering the plant and the water in the pulping process. (Figure 3). In Santa Fe the water entering the plant displayed a higher concentration of manganese (90 μg/L) than in the other plants due to the nature of the Comaltitlán River which supplies the water for coffee processing. Iron was the metal detected in the greatest concentrations, moreover, in the Chinicé coffee plantation it exceeded the maximum permitted limits (300 μg/L) for general use and human consumption established by the Mexican Environmental Regulations (1994). Whilst iron is not harmful to human health, this element, which is found in soluble form, is easily oxidized, damaging water pipes, pumps and other machinery. In the pulping process manganese and iron concentrations increased in all the coffee processing plants, probably because these metals are natural minerals found in coffee. Zuluaga (1989) reports iron concentrations in coffee pulp, however, the extremely high amounts of iron in the pulping water (1,500 μg/L) are the result of corrosion and wearing of the machinery, which is made of iron and copper.

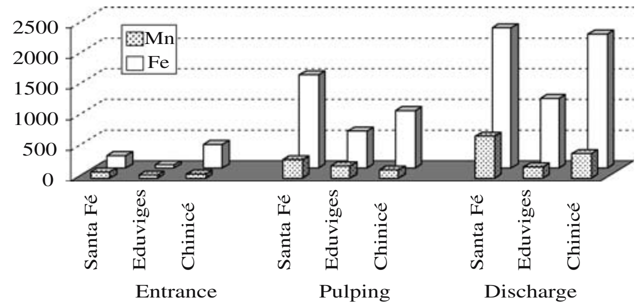

Fig. 3 Concentrations of manganese and iron (μg/L) detected in the water of wet method coffee processing plants at Soconusco, Chiapas, Mexico

In the case of the Santa Fé coffee processing plant the discharge wastewater presented the highest Mn and Fe concentrations, reaching values of 290 and 2,295 μg/L, respectively. This could be due to the high levels of Mn (14,600 μg/L) and Fe (132,533 μg/L) found in the soil (Martínez, 2004). Although the official Mexican environmental regulations do not stipulate maximum permitted limits for these elements in discharge systems, and there are no records of harmful effects on human health, these elements can oxidize easily, causing problems such as staining of clothes, blocking of pipes, pumps and other machinery related to water supply systems in communities downstream that are supplied by the river water. Furthermore, the elevated concentrations of Mn can accelerate biological growth in water distribution systems, contributing to problems of the taste and smell of the water (RIPDA, 2003).

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