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# Estimation of potential pollution from mine tailings on the San Pedro River (1993-2005), Mexico-U.S. border.

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## ABSTRACT

The accumulation and distribution of heavy metals in surface water from the San Pedro River (Mexico-U.S. border) was evaluated from 1993 to 2005. Total concentrations of Cd, Cu, Fe, Mn, Pb y Zn are above maximum permissible levels in sampling sites near the mine tailings. A gradual decrease of heavy metals values in surface water was observed from 1993 to 2005. $SO_4^{2-}$ and Fe contents in water close to the mine tailings were 7180 mg/L and 1600 mg/L in 1994 and the values decrease to 460.39 mg/L ($SO_4$) and 9.51 mg/L (Fe) in 2005. Approximately 2.3 kilometers downstream the mine tailings, heavy metal contents in water drop quickly following an increase in pH values due to wastewater discharge in the river. Attenuation mechanisms of heavy metals include precipitation, co-precipitation, sorption and dilution. Determining the concentration of heavy metals enabled the conclusion that the Cananea Mining area and the San Pedro River is an ecosystem impacted by the mining industry and untreated wastewater discharges coming from the city of Cananea, Sonora, México.

Keywords: heavy metals, mine tailings, water pollution, copper mining, Mexico-U.S. border.

## Introduction

Various heavy metals have been reported to be dangerous to the health of humans and wildlife when they occur in the environment at some high concentrations. The vicinities of many mining sites are particularly liable to such high levels of toxic heavy metals that are derived from the discharge of poorly treated liquid effluents to land. The presence of heavy metals in such high concentrations above their normal distribution in soil generally reflects the contamination of soil in the study area. Heavy metal introduced on the soil surface, undergo downward transportation, which does not occur to any greater extent unless the metal retention capacity of the soil is overloaded or metal interaction with associated waste matrix enhances mobility. There are many different sources of heavy metal contaminants including deposition, wastewater leachate and surface runoff. Mine tailings contain high levels of Pb, Cd, Zn, As, Cu, Fe and other metals of environmental concern and may be the most important sources of toxic metal pollution on earth. Tailings are dumped frequently along streams near mines, where interaction with air and rainfall oxidizes sulphides, particularly pyrite, thus generating acid mine drainage (AMD). Effluent streams transport high contents of Fe and $SO_4$ , and potentially toxic trace elements such as As, Cd, Pb, Zn, Cu, Hg, Sb, Se, etc. (Fernández et al. 1986; Ritchie 1994; Monterroso and Macías 1998; Williams and Smith 2000; Dinelli et al. 2001). These elements can be leached into the surface water or groundwater, taken up by plants, bond semi-permanently by soil components such as clay or organic matter, which later effect human health. Very small quantities of copper and zinc are required for a normal metabolism, but when the quantities of these oligoelements increase they become toxic and could produce damage and malfunctioning of human organs (Stoica et al. 2000).

The San Pedro River (SPR) flows mainly in southeastern Arizona, U.S.A. It is a tributary to the Gila River, which flows into the Colorado River. Upstream of the SPR, in Sonora, Mexico, flow is perennial through much of the region. Agricultural use in Mexico has depleted the stream, but not dewatered it for the most part. Long stretches of the SPR are dry. However, recent mitigation efforts have been undertaken to rewater some portions of the lower reaches through the purchase of irrigated riparian farmland followed by the cessation of ground-water pumping from the stream aquifer (Haney 2002). The SPR area provides habitat for many plants and animals, including the federally endangered Huachuca water umbel (*Lilaesopsis schaffneriana*), and sustains regionally rare biotic communities including Sonoran cottonwood-willow gallery forest, Wright sacaton grasslands, and cienegas (mid-elevation marshlands) (Arias 2000). The riparian corridor provides a migratory route for neotropical songbirds (Skagen et al. 1998).

The Cananea mine site is located in Mexico, approximately 100 miles southeast of the Tucson city in Arizona, U.S.A. The current mine site, including a large open pit and mine dumps, may encompass approximately 3,000 to 4,000 acres (1,215 to 1,620 hectares). The associated mine tailings likely cover another 2,500 acres (1,000 hectares). Stream waters spring up from the mine tailings, so the quality of waters can be directly linked to the pollution sources.

The present study has focused on a 53 km long segment of the San Pedro River comprised between the area of the Cananea Copper Mine and the Mexico-U.S. border (Fig. 1). While the Cananea town contains one of the largest copper mining activities in Mexico, no work, to our knowledge, has been undertaken to investigate the heavy metal accumulation in this area. In contrast to metalliferous mine pollution in temperate regions, the environmental impact of mining activities in arid and semi-arid regions has received little study (Wray 1998). Where such studies have taken place, work has generally concentrated on the contamination of perennial streams (for example, Rampe and Runnells, 1989). Despite the semi-arid nature of the Cananea area, visual inspection of tailings indicates that considerable fluvial erosion occurs during rainfall events. Therefore, the present work is an earnest effort as to provide a common picture of the common load of pollutants into the ecosystem in semi-arid region. The objectives of the present investigation were to perform a general survey distribution of heavy metals in surface waters and to evaluate time and spatial variations along the studied segment.

## Methodology

### *Study area*

The San Pedro groundwater basin (SPB) is located in Sonora in the northern part of Mexico and southeastern Arizona (Fig. 1). It is characterized as a predominantly rural landscape with small scattered settlements. The SPB is drained by two major waterways: the Gila River and the San Pedro River. The San Pedro River, perennial in stretches, flows north through the center axis of the basin in Sonora, Mexico to the confluence with the Gila River (U.S.A.). Mining is the most important economic activity as several large copper mining and milling operations are located in the area. Limited areas of irrigated farmland are scattered along stretches of floodplain. Upland areas have been utilized by ranches for livestock grazing. The climate is semi-arid with sparse vegetation. Mean annual maximum, minimum, and mean temperatures in the area are 25 °C, 10 °C and 18 °C (Tombstone station, U.S.A.). Average annual precipitation is 36 cm, 53% of which occurs during the monsoon season (July-September). Evaporation exceeds calculated monthly and annual precipitation (Fig. 2). Floods occur mainly during three seasons: late summer, winter and fall. Mean annual flow in the river is 1.5 $m^3/s$. The study was carried out in surface water near a mine tailings. The mine tailings were generated by residues produced from the concentration operations of a copper mine located 1 km south of the mine tailings.

### *Sample collection*

Surface water was sampled at five sites along a major tributary and three sites along the course of the San Pedro River over a distance of 53 km downstream of the mining area (Fig. 1). Reported data in Tables 1 to 5 resulted from sampling during November 1993; April and August

1994; February, May, August and November 1997; April and August, 1999 and August, 2005. Recommended sampling procedures from the Mexican Agency of Water Management (CNA 1993), Handbook for Sampling and Sample Preparation of Water and Wastewater (EPA 1982) and Field Manual for Water Quality Sampling (AWRRC y ADEQ 1995) were followed.

Surface flow measurements were performed using Global Flor Prob EP101 equipment (Linsley et al. 1984). Water samples were collected from the middle of the water column from a depth of 30 cm, through the manual introduction of decontaminated plastic bottles. Duplicate samples and field blanks were taken for quality control (CNA 1993; AWRRC and ADEQ 1995). Before water sample collection, hydrogen potential (pH), electric conductivity (EC), dissolved oxygen (OD) and bicarbonates ($HCO_3^-$) of water samples were determined. Total metal contents were obtained from acid-preserved samples (pH<2). Nitrate (as $N\text{-}NO_3$) contents were obtained from water samples preserved with sulphuric acid (pH<2). For chloride and sulphates, non preservative was added to the sample. Samples were packaged in ice and transported in sealed coolers to the laboratory in the subsequent 24 hours. Prior to water sample collection, the plastic bottles were soaked using detergent, DI water, 20% (v/v) nitric acid for 3 days and finally with DI water once again (Moody and Lindstrom 1977). The research involved field work consisting of visual observation of the area, measurements of the distance between the samples sites, and sample collection.

*Analytical procedures*

Laboratory analytical methodologies from the CNA Methods and Analysis Manual (CNA 1995), the Methods for Chemical Analysis of Water and Wastes (EPA 1983) and Methods and Guidance for Analysis of Water (EPA 1999), were used for field parameters, chlorides, sulfates, nitrates (as $N\text{-}NO_3^-$) and heavy metals. Water samples were analyzed by AAS for Cd, Cu, Fe, Mn, Pb and Zn. Analyses were performed using an AAS Perkin-Elmer 3110 equipment with the following detection limits: Cd (0.01 mg/l), Cu (0.02 mg/l), Fe (0.04 mg/l), Mn (0.02 mg/l), Pb

(0.07 mg/l), and Zn (0.01 mg/l). Precision and accuracy were evaluated by using fortified high-purity standards, the following recovery values were obtained: Cd (98-100%), Cu (99-101%), Fe (93-100%), Mn (92-100%), Pb (97-101%), and Zn (95-101%). Sulfates, chlorides and nitrates (as $N\text{-}NO_3^-$) were analyzed by gravimetric, volumetric and spectrophotometric methods, with the following detection limits: 5, 2, and 0.10 mg/L respectively. Precision and accuracy were evaluated by using fortified high-purity standards; the following recovery values were obtained: sulfates (94-101%), chlorides (97-101%), and nitrates (93-98%). Additionally, water samples were characterized by their specific charge balance; accepted values are less than 10%.

## Results and discussion

Concentration levels and distribution of total metals (Cd, Fe, Mn, Pb, and Zn) in surface water from the San Pedro River were monitored from 1993 to 2005. Results of the physical and chemical analyses are listed in Tables 1 to 5. E1 sampling point corresponds to leaking acid drainage fluids released from the mine tailings. Between sampling points E1 and E2 there is a contention dike built by the mining company in order to recover and recycle leaking acid drainage fluids. This dike was built in the beginning of year 2000. The dike can be used as a deposit for acid drainage settlement, thus reducing the levels of heavy metals by oxidation and precipitation. As a result, the levels of heavy metals in the surface water were observed to decrease during sampling of 2005, compared to previous years. City waste-water is discharged into the stream at sampling point E2 and it mixes with the acid mine drainage. Minimum pH-values are reported for E1, E2, and E3 (2.44 to 6.78), these sampling points eventually received infiltrations from Fe-Cu rich acid waters. Acid mine drainage coming from the tailings contains high levels of Cu, Fe, Mn, Zn and sulfates (Gómez et al. 1994, 1996). Highest pH-values are reported for E7 and E8 (7.79 to 9.25), which are located around 53 km away from the mine tailings.

The strong pH contrast between the mine effluent E1 (pH 2.44-3.95) and the E2 sampling point (pH 7.6-7.72), is caused by a mixing of acid (acid mine drainage) and alkaline waters (untreated waste-water). In the stations nearby the pollution sources the pH is acid. In acid solution the iron (as ferric sulfate) is highly soluble. However, when the acid and alkaline waters (E1 and E2) are mixed an increase of pH (>3) is observed. This produce the formation of Fe as hydroxide and Fe oxyhydroxysulphate precipitates (Dang et al. 2002) along with precipitation and or-adsorption of other metals, and reducing the levels of metals in all the other stations. This will cause the formation of a plume of ochreous to whitish precipitates which are settled and accumulated in low-flow segments and/or transported downstream as particulate load. This interpretation is corroborated by the presence of thick layers of ochreous material in sediments on sampling points E2 and E3. The oxidation of ferrous iron to ferric iron causes precipitation of iron hydroxides (III) along with precipitation and/or adsorption of other metals (Cidu et al. 1997) (Fig. 3). In the stations (E4 to E8) the pH was increased (>7) because of the contribution of clean water from the major tributaries. There are not other pollution sources nearby the sampling stations (E4 to E8). This could explain the difference in spread of pH values at sampling points 2,3,4,5 versus 6, 7, and 8. In this study, excepting Mn, the rest of analyzed metals (Cd, Cu, Pb, and Zn) also diminish their contents; it could be assumed that such metals could be eliminated from water column by co-precipitation and/or adsorption, along with Fe-precipitation (Herr and Gray 1997). Mn persists in water along studied segment. Fe-hydroxides precipitate following neutralization of pH, however, because Mn (II) is more resistant to oxidation than Fe, at atmospheric conditions, Mn will precipitate at higher pH as manganese oxide (IV). It has been established that metals sorbed onto Fe-oxyhydroxides are highly sensitive to pH-Eh changes in the water column and that metals can be easily liberated along hydraulic gradient several kilometers from the source point, consequently becoming a permanent source of toxic metals. However, aside described precipitation processes, dilution caused by rain could attenuate metal contents in surface waters which are affected by acid drainage (Chapman et al. 1983).

Electric conductivity values for studies conducted from 1993 to 1997 are within a range from 7030 to 11000 µS/cm with the highest value reported for E1 (11000 µS/cm). Such high values are presumably caused by high activity of hydrogen ions (low pH) from iron-copper acid wastes from tailings dam (Gómez et al. 2004). Characteristics of such wastes include acidity, metal toxicity and sedimentation (Gray 1997). Additionally, acid conditions solubilize metals which are deposited in sediment causing an increment in electric conductivity values. Sampling points E1, E2, E3 and E4 are characterized by high electric conductivity values for all studied years. Lowest levels of electric conductivity values were observed in sampling points located far from the tailings dam.

Dissolved oxygen values for E1, E2, and E3 sampling points are within the range from 0.17 to 6.0 mg/L. These sampling points receive a mixture of acid waste infiltrations from the mine tailings and untreated waste-water discharges from the Cananea city. Organic contents in waste-waters from domestic and industrial activities can significantly reduce the dissolved oxygen content in water. The presence of organic matter also has an influence on the sediment-water interface, since the reducing conditions caused by the exhausted dissolved oxygen favours the migration of a significant number of metals from the sediment substrate to the water column (Förstner 1986). Additionally, Fe-rich acid-wastes are considered strong reducing agents which eliminate dissolved oxygen contents in a water body (Klein 1973). Iron-content values from 1099.9 to 3680 mg/L have been registered for E1 to E3 sampling points. Sampling points located away from the tailings dam show high dissolved oxygen values (7.5 to 12.35 mg/L) for most studied sampling years (1993-2005). Chloride values are highly variable (3.95 o 200.83 mg/L) for all studied samples.

Sulfide minerals have been reported in chimney breccias, limestones and disseminated in porphyry copper deposits, and volcanic rocks from the Cananea mining site (Cendejas et al. 1998). Copper and iron sulfates have been reported in sediments collected from the river (Gomez et al. 1994, 1996). Samples from E2 and E3 sites contain high concentrations of sulfates for all studied years. Sulfates levels significantly drop in farther sampling points (e.g. E8 sampling point, 38.02-68 mg/L). High levels of Cd (0.03-0.60 mg/L), Cu (2.08-136 mg/L), Fe (15.23-3680 mg/L), Mn (5.37-787.5), Pb (0.05-0.87 mg/L) and Zn (2.42-84 mg/L) have been reported for sampling points E1, E2 and E3 from 1993 to 2005. Such values exceeded the maximum permissible levels by mexican legislation. In 2005, Cd-, Pb-, and Zn-values considerably drop in the same sampling points as a consequence of a containment dike built by the mining company to recover leaking acid-drainage. The presence of such dike causes the reduction of heavy metal levels in water by oxidation and precipitation. However, iron content was highly variable and above the regulatory limit at E1 to E5 sites for all studied years. At near neutral sites (E4 to E8), iron content was below 1 mg/L, whereas at the acidic site E1, Fe ranged from 9.51 to 3680 mg/L (Fig. 4).

Pb and Cd were below the detection limit for most taken samples. In acidic samples, Pb can range from 0.1 to 0.3 mg/L. The acidic site E1 (pollution source) exceeded the maximum regulatory levels for $SO_4^{2-}$, Cu and Fe during all sampling periods. Lead concentrations were below the detection limit at all sites for most sampling periods except for sites E1 to E5 in 1997 (range from 0.1 to 0.3 mg/L), sites E1 to E8 in August 1994 (range from 0.03 to 0.87 mg/L) and sites E1 to E3 in 1993 (range 0.01 to 0.5 mg/L). Some samples contained significant levels of Pb, which exceed the Mexican Legislation Regulatory Level (0.05 mg/L). Zn-values were below maximum permissible level (5 mg/L) for most sampling periods, excepting E1 sampling site in 1993, 1994 and 1997 (range from 26.7 to 84 mg/L), sampling sites E2 and E3 in 1993 (range 5.4-55.4 mg/L).

Elevated total concentrations of Fe and Cu were found in sampling points E1, E2, E3 and E4 (Fig. 4). The oxidation of sulphide minerals within the mine tailings releases $H^+$, $SO_4^{2-}$, $Fe^{2+}$, and trace metals into the surface water. Samples E2, E3, E4, and E5 were collected within a segment of the river affected by the discharge of domestic waste waters from the Cananea City, such discharge provokes a S-N trend of the water alkalinity, which varies from the upstream stations (lower pH) to the downstream stations (higher pH, higher alkalinity). Sampling stations E6, E7, and E8 are located within the San Pedro River which receives water from other tributaries along its course. Such water input causes a dilution effect in metal contents and a spread of pH values at sampling points E2 to E5 versus E6 to E8. These data indicate a limited acid neutralizing capacity for the stream waters of the area (Fig. 4). Average concentrations of Cu, Fe and Zn in water samples were within the accepted world-wide normal value. In general, there exists a tendency of water samples to contain lower metal and $SO_4^{2-}$ in water samples from sites located farther away from the mine tailings (Fig. 4). Pearson´s correlation coefficients above 0.95 were determined for Fe-Cu and $SO_4^{2-}$-Zn, thus reflecting the influence of the mine tailings on the water chemistry of the river (Fig. 5).

The iron precipitates formed by the neutralization of acid drainage and alkaline waters (E1 to E2), include some mineral phases. X-ray powder diffraction studies of the sediments confirmed the presence of jarosite. Some of the relatively insoluble minerals may become unstable, however, if environmental conditions change or if remedial measures such as raising river pH are implemented. Jarosite can transform to Fe oxides or hydroxides by hydrolysis or simple dissolution and re-precipitation, although this is likely to be a slow process. The transformation of jarosite to ferric oxyhydroxide occurs above pH 5.89, but the mechanism of redistribution of associated contaminant metals is not known.

The precipitation of jarosite ($K_2Fe_6^{3+}(SO_4)_4(OH)_{12}$) would account for the further removal of heavy metals and the presence of dissolved metals in most samples suggest the potential for the Cananea mine tailings to release metals to the environment. The high metal content measured in sites E1 to E5 in 1997, sites E1 to E8 in August 1994, and sites E1 to E3 in 1993 indicates that significant amounts of metals are mobilized from tailings by a simple interaction with meteoric water during rainfall events. In climates where evaporation exceeds precipitation, as in the case of San Pedro River, the water-flow direction is upwards via capillary forces. This phenomenon transfers mobilized elements to the top of tailings under oxidant conditions so they can be turned into water soluble form and move to the downstream during seasonally strong rainfalls (Dold and Fontobotè 2001). Subsequent precipitation and adsorption processes considerably reduce the metal load from leachates. Near neutral leachates contain lower concentrations of metals, but they are high enough to be an easily available source of toxic metal. Iron content was high close to the mine tailings (acidic sampling point E1, 3680 to 9.6 mg/L). At near neutral sites (E2 to E6), Fe significantly decreases (75.9 to 5 mg/L). Seasonal variation in three sampling points of the studied segment is shown in Fig. 6. Summer rains are more abundant (85-90% of the total yearly volume) than winter rains. In summer season rapid evaporation cause random variations in major cations contained in surface water near mine tailings (Fig. 6a). $SO_4^{2-}$ concentration in water increases significantly with the autumm-winter rains in middle of the studied segment. This could be because the amount of precipitates that are carried as sediments downstream decreases in the river and re-dissolves, and they are incorporated into the water column (Fig. 6b). Values significantly decrease in the river segment located close to the U.S.-México border and major cations and anions content in water do not show seasonal variations (Fig. 6c).

The presence of thick layers of ochreous material in sediments on sampling points E2 and E3 indicates a precipitation of metals. These sediments may become a potential source of bioavailable heavy metals, since some of the metals bound to the sediment can remobilize and be again released into water when environmental conditions change, thus producing adverse effects on living organisms (Xiangdong et al. 2001) and acting as a significant metal contamination source. The pollution caused by untreated waste water should be evaluated since it could represent a significant source of pollution for surface water. Connell and Miller (1984) report that domestic effluents containing products such as soap and detergents could contribute with significant amounts of Cu, Cd, Cr, Pb and Zn. Villalba et al. (2000), have reported the presence of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) on wastewaters coming from Cananea City, but in much lower concentrations than those detected in the acid wastes coming from mining activity.

## Conclusions

Results of this work show high values of heavy metals (Cd, Cu, Fe, Mn, Pb, and Zn), electric conductivity, and sulfates, as well as low pH-values in the samples collected from the San Pedro River in Cananea, México. A strong attenuation was observed from 1993 to 2005, but sampling stations E1, E2, and E3 currently show acidic conditions. Attenuation mechanisms include precipitation, co-precipitation, sorption and dilution. Some metals like iron are strongly affected by pH and redox potential. Oxidation from ferrous iron to ferric iron causes precipitation of Fe-oxides and –hydroxides along with precipitation of other metals. This could explain the lowering of Fe-content in sampling points E5 to E8. Excepting Mn, the rest of the metals (Cd, Cu, Pb, and Zn) also diminish their concentration in water after Fe-precipitation.

The presences of high levels of heavy metals (Cd, Cu, Fe, Mn, Pb, and Zn) in surface water from the San Pedro River were higher than maximum permissible levels according to Mexican legislation. These results are important because the San Pedro River represents the main water source for towns located along the river course, including agriculture and cattle activities along the U.S.-Mexico border. The studied area is part of the habitat for native fish considered in danger and for a great variety of bird species hibernating in Mexico and reproducing during summer in U.S. Mining actives were found to be the main source of pollution of the surface water in the San Pedro River. Wastewater discharges of untreated raw sewage coming from the city of Cananea were found to be the second most important source of pollution for the river. Further studies regarding bioavailability and chemical speciation of heavy metals in sediments should be conducted.

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## Figure Captions

Figure 1. Map of water drainage and sampling sites.

Figure 2. Precipitation and evapotranspiration in the Cananea, Sonora area.

Figure 3. pH against heavy metal contents in water samples.

Figure 4. Spatial and time-scale variation in Cu, pH, Fe and $SO_4^{2-}$-concentrations in surface water samples. Dashed line represent the confluence of wastewater into the river.

Figure 5. Fe-Cu and Zn- $SO4^{2-}$ plots showing Pearson´s correlation coefficients

Figure 6. Time-variation in major metals and anions for three segments of the studied river.

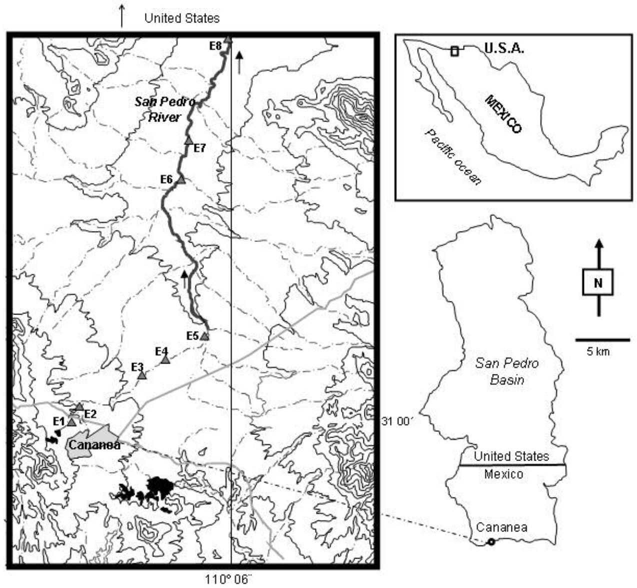

**Figure 1. Map of water drainage and sampling sites.**
254x190mm (96 x 96 DPI)

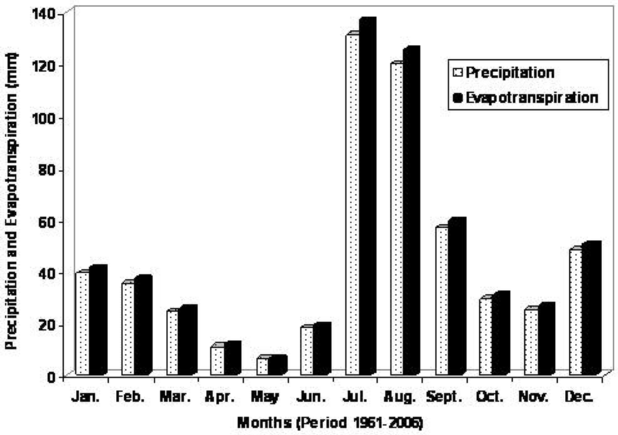

**Figure 2. Precipitation and evapotranspiration in the Cananea, Sonora area.**
190x254mm (96 x 96 DPI)

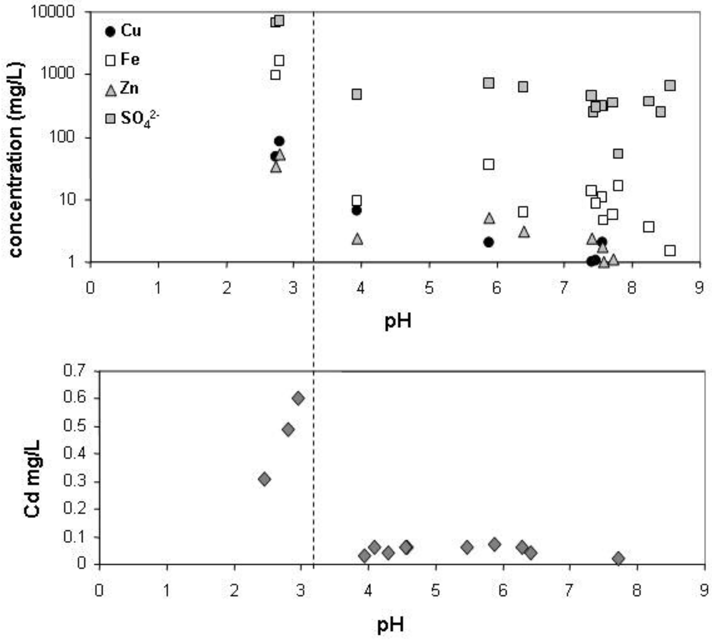

**Figure 3. pH against heavy metal contents in water samples.**
190x254mm (96 x 96 DPI)

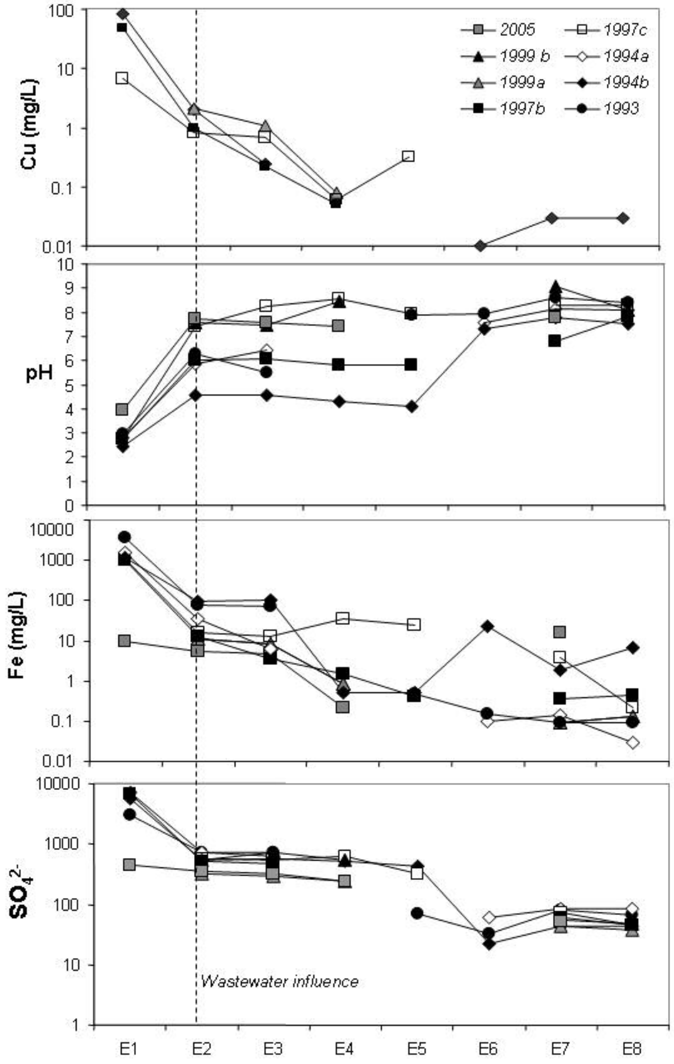

**Figure 4. Spatial and time-scale variation in Cu, pH, Fe and SO42--concentrations in surface water samples. Dashed line represent the confluence of wastewater into the river.**
190x254mm (96 x 96 DPI)

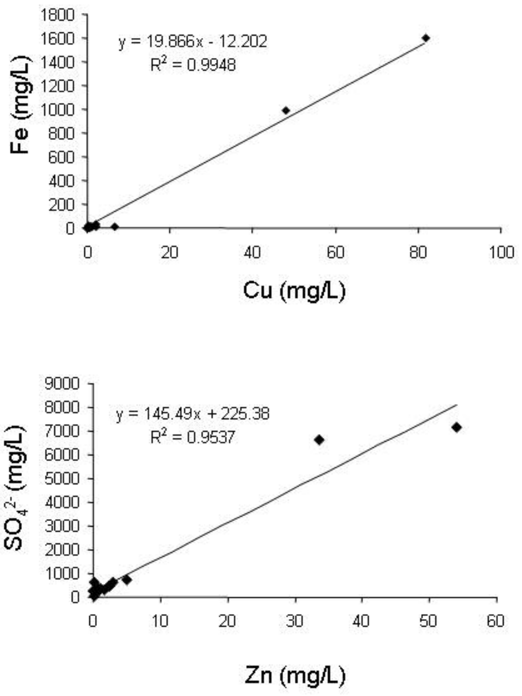

**Figure 5. Fe-Cu and Zn- SO42- plots showing Pearson´s correlation coefficients**
190x254mm (96 x 96 DPI)

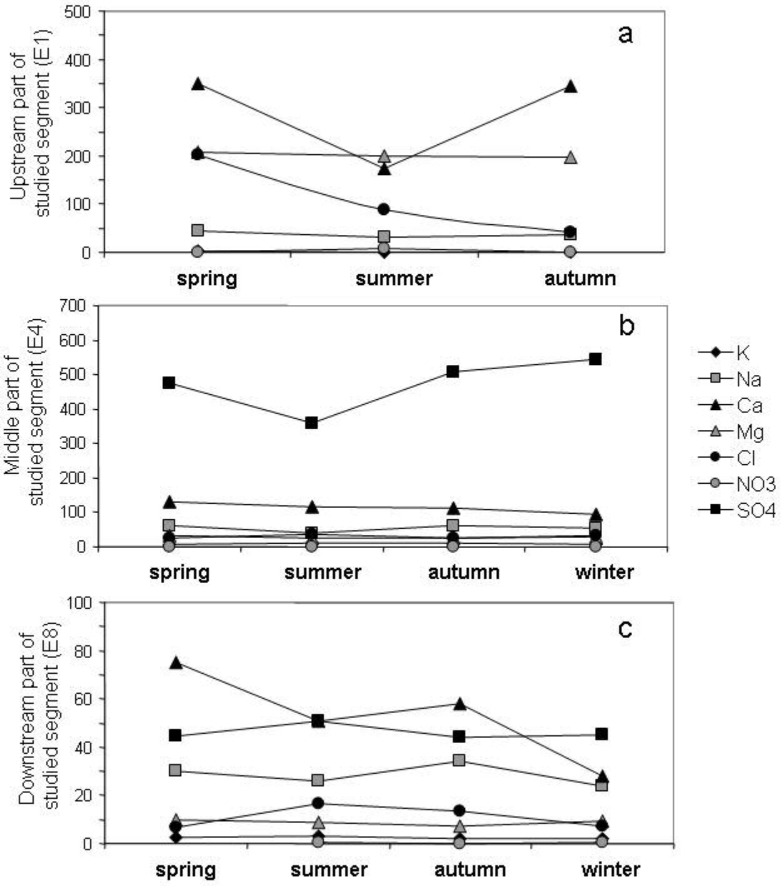

**Figure 6. Time-variation in major metals and anions for three segments of the studied river.**
190x254mm (96 x 96 DPI)

Table 1. Basic characteristics and heavy metal concentrations of surface water from the San Pedro River, 1993.

| Sample | pH | EC | DO | $Cl^-$ | $N\text{-}NO_3^-$ | $SO_4^{2-}$ | $HCO_3^-$ | Cd | Cu | Fe | Mn | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| units |  | µS cm$^{-1}$ | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| E1 | 2.9 | 11000 | 1 | 1072 | NA | 3060 | ND | 0.60 | 136 | 3680 | 788 | 0.54 | 84 |
| E2 | 6.3 | 1292 | 1 | 24.2 | NA | 710 | ND | 0.06 | 1.87 | 76 | 18 | <DL | 55 |
| E3 | 5.5 | 1269 | 3 | 25.2 | NA | 710 | ND | 0.06 | 1.91 | 70 | 18 | <DL | 5 |
| E4 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E5 | 7.9 | 338 | NA | 3.9 | NA | 70 | 64 | NA | <DL | 0.49 | 0.11 | NA | NA |
| E6 | 7.9 | 542 | 5 | 6.9 | NA | 33 | 255 | <DL | <DL | 0.15 | 0.21 | <DL | <DL |
| E7 | 8.6 | 529 | 8 | 7.9 | NA | 81 | 128 | <DL | 0.02 | 0.09 | 0.04 | <DL | <DL |
| E8 | 8.4 | 484 | 12 | 9.9 | NA | 68 | 191 | <DL | <DL | 0.09 | 0.03 | <DL | <DL |

ND: not detected. DL: detection limit. NA: not analyzed.

Table 2. Basic characteristics and heavy metal concentrations of surface water from the San Pedro River, 1994.

| Sample<br>units | pH | EC<br>µS $cm^{-1}$ | DO<br>mg/L | $Cl^-$<br>mg/L | N-$NO_3^-$<br>mg/L | $SO_4^{2-}$<br>mg/L | $HCO_3^-$<br>mg/L | Cd<br>mg/L | Cu<br>mg/L | Fe<br>mg/L | Mn<br>mg/L | Pb<br>mg/L | Zn<br>mg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *April 1994* | | | | | | | | | | | | | |
| E1 | 3 | 7760 | 0.17 | 26.7 | NA | 7180 | ND | 0.49 | 82 | 1600 | 245 | 0.31 | 54 |
| E2 | 6 | 1460 | 0.17 | 67 | NA | 721 | 66.29 | 0.07 | 2 | 36 | 18 | <DL | 5 |
| E3 | 6 | 1270 | 1 | 53 | NA | 617 | 33.14 | 0.04 | 0.24 | 6.1 | 13 | 0.03 | 3 |
| E4 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E5 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E6 | 7.6 | 470 | 7 | 20 | NA | 59.8 | 265.17 | <DL | <DL | 0.1 | 0.15 | <DL | <DL |
| E7 | 8 | 490 | 8.8 | 20 | NA | 85.64 | 165.73 | <DL | <DL | 0.14 | 0.02 | <DL | <DL |
| E8 | 8 | 490 | 12.4 | 20 | NA | 85.64 | 198.88 | <DL | <DL | <DL | <DL | <DL | <DL |
| *August 1994* | | | | | | | | | | | | | |
| E1 | 2.5 | 7500 | 4.3 | NA | 5540 | <DL | 0.31 | 63.95 | 1200 | 120 | 0.22 | 75 | NA |
| E2 | 4.6 | 1060 | 5.4 | NA | 545 | 33.35 | 0.06 | 6.75 | 98 | 8.5 | 0.87 | 9.19 | NA |
| E3 | 4.6 | 1170 | 4.6 | NA | 578 | 33.35 | 0.06 | 8.55 | 106 | 9.5 | 0.84 | 9.44 | NA |
| E4 | 4.3 | 1050 | 6.6 | NA | 507 | 13.42 | 0.04 | 4.65 | 0.51 | 9.8 | 0.07 | 4.84 | NA |
| E5 | 4 | 930 | 3.9 | NA | 425 | 13.42 | 0.06 | 4.55 | 0.52 | 9.6 | 0.05 | 5.44 | NA |
| E6 | 7 | 160 | 4.8 | NA | 22 | 136 | ND | 0.10 | 22 | 0.59 | 0.06 | 0.09 | NA |
| E7 | 7.8 | 500 | 6.6 | NA | 43 | 272 | ND | <DL | 1.88 | <DL | 0.03 | <DL | NA |
| E8 | 7.5 | 420 | 5 | NA | 43 | 272 | ND | <DL | 6.84 | 0.36 | 0.05 | 0.07 | NA |

ND: not detected. DL: detection limit. NA: not analyzed.

Table 3. Basic characteristics and heavy metal concentrations of surface water from the San Pedro River, 1997.

| Sample | pH | EC | DO | $Cl^-$ | $N\text{-}NO_3^-$ | $SO_4^{2-}$ | $HCO_3^-$ | Cd | Cu | Fe | Mn | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| units | | $\mu S\ cm^{-1}$ | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| | | | | | | *February 1997* | | | | | | | |
| E1 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E2 | 6.72 | 1000 | 8.3 | 48.41 | 3.4 | 571.16 | NA | 0.01 | 1.17 | 18.05 | 6.5 | <DL | 2.05 |
| E3 | 7.13 | 1000 | 7.80 | 34.07 | 0.65 | 544.82 | NA | 0.01 | 0.78 | 11.95 | 6.0 | <DL | 1.46 |
| E4 | 9.25 | 910 | 9.0 | 39.45 | 0.45 | 613.95 | NA | <DL | 0.10 | 0.26 | 0.49 | <DL | 0.07 |
| E5 | 7.68 | 830 | 9.30 | 35.86 | 1.70 | 323.43 | NA | <DL | 0.28 | 2.45 | 1.50 | <DL | 0.40 |
| E6 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E7 | 7.40 | 434 | 9.10 | 7.17 | 0.15 | 74.48 | NA | <DL | 0.06 | 0.21 | 0.11 | <DL | 0.02 |
| E8 | 7.10 | 432 | 9.60 | 7.17 | 0.36 | 45.26 | NA | <DL | <DL | 0.21 | 0.11 | <DL | <DL |
| | | | | | | *May 1997* | | | | | | | |
| E1 | 2.44 | 6680 | 4.0 | 200.83 | 0.156 | 6724 | NA | 0.30 | 47.8 | 905 | 104 | <DL | 26.7 |
| E2 | 6.76 | 1120 | 8.2 | 26.9 | 0.473 | 513.83 | NA | 0.03 | 1.29 | 17.58 | 8.1 | <DL | 2.47 |
| E3 | 7.59 | 1060 | 8.6 | 26 | 0.304 | 474.2 | NA | 0.02 | 0.55 | 7.68 | 7.6 | <DL | 1.59 |
| E4 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E5 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E6 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E7 | 8.37 | 460 | 7.4 | 7.17 | 0.156 | 61.51 | NA | <DL | <DL | 0.63 | <DL | <DL | 0.055 |
| E8 | 8.26 | 480 | 8.6 | 6.72 | <DL | 44.52 | NA | <DL | <DL | 0.04 | <DL | <DL | 0.045 |
| | | | | | | *August 1997* | | | | | | | |
| E1 | 2.73 | 6640 | 6.2 | 88.09 | 6.73 | 6625.35 | NA | 0.33 | 48 | 985 | 85 | 0.3 | 33.55 |
| E2 | 7.4 | 1110 | 6.8 | 34.64 | 0.14 | 451.99 | NA | 0.03 | 1 | 13.2 | 6.5 | 0.1 | 2.4 |
| E3 | 8.25 | 1120 | 12 | 37.61 | 0.29 | 360.01 | NA | 0.01 | 0.22 | 3.5 | 5.5 | 0.1 | 0.69 |
| E4 | 8.56 | 1080 | 7.8 | 42.56 | 0.84 | 635.95 | NA | <DL | 0.05 | 1.5 | 0.47 | 0.1 | 0.17 |
| E5 | 7.95 | 1130 | 7.8 | 28.70 | 1.20 | 653.19 | NA | <DL | <DL | 0.41 | 1.34 | 0.1 | 0.16 |
| E6 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E7 | 8.3 | 410 | 8.1 | 14.35 | <DL | 50.15 | NA | <DL | <DL | 0.37 | 0.09 | <DL | <DL |
| E8 | 8.29 | 440 | 7.2 | 16.83 | 0.42 | 50.95 | NA | <DL | <DL | 0.44 | 0.15 | <DL | <DL |
| | | | | | | *November 1997* | | | | | | | |
| E1 | 2.75 | 7030 | 6.2 | 41.87 | 0.23 | NA | NA | 0.38 | 50 | 1099.9 | 90 | 0.3 | 31.5 |
| E2 | 6 | 1130 | 9.0 | 28.24 | 0.82 | 534.15 | NA | 0.05 | 5 | 16.18 | 6.7 | 0.2 | 3.40 |
| E3 | 6.04 | 1000 | 9.2 | 25.32 | 1.02 | 505.68 | NA | 0.04 | 2 | 12.68 | 6.4 | 0.2 | 2.89 |
| E4 | 5.8 | 780 | 10.2 | 16.55 | 0.76 | 312.03 | NA | 0.04 | 3.4 | 34.88 | 5.7 | 0.3 | 3.30 |
| E5 | 5.8 | 690 | 10.0 | 14.61 | 0.92 | 289.25 | NA | 0.03 | 2.2 | 23.63 | 5.3 | 0.1 | 2.80 |
| E6 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E7 | 6.8 | 520 | 7.6 | 9.74 | 0.23 | 120.5 | NA | <DL | 0.02 | 3.68 | 0.16 | <DL | 0.04 |
| E8 | 7.8 | 480 | 9.0 | 13.63 | 0.11 | 44.3 | NA | <DL | <DL | 0.21 | <DL | <DL | 0.01 |

ND: not detected. DL: detection limit. NA: not analyzed.

Table 4. Basic characteristics and heavy metal concentrations of surface water from the San Pedro River, 1999.

| Sample<br>units | pH | EC<br>µS $cm^{-1}$ | DO<br>mg/L | $Cl^-$<br>mg/L | N-$NO_3^-$<br>mg/L | $SO_4^{2-}$<br>mg/L | $HCO_3^=$<br>mg/L | Cd<br>mg/L | Cu<br>mg/L | Fe<br>mg/L | Mn<br>mg/L | Pb<br>mg/L | Zn<br>mg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *April 1999* | | | | | | | |
| E1 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E2 | 7.56 | 1040 | 9.2 | 26.92 | 0.39 | 317.8 | 183.96 | <DL | 2.08 | 11 | 4.1 | <DL | 1.71 |
| E3 | 7.47 | 1000 | 6 | 30.41 | 0.33 | 291.1 | 196.22 | <DL | 1.06 | 8.27 | 2.84 | <DL | 0.95 |
| E4 | 8.42 | 970 | 8.4 | 35.4 | 4.53 | 237.7 | 191.32 | <DL | 0.08 | 0.83 | 0.13 | <DL | 0.06 |
| E5 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E6 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E7 | 9.07 | 430 | 10.8 | 10.97 | <DL | 42.5 | 220.75 | <DL | <DL | 0.09 | 0.25 | <DL | 0.01 |
| E8 | 8.07 | 520 | 7.2 | 8.22 | <DL | 38.02 | 255.09 | <DL | <DL | 0.13 | 0.19 | <DL | 0.01 |
| | | | | | | *August 1999* | | | | | | | |
| E1 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E2 | 6.78 | 1180 | 5.9 | 26.29 | 0.53 | 541.73 | 153.85 | <DL | 1.1 | 15.23 | 5.37 | <DL | 2.62 |
| E3 | 6.78 | 1297 | 7.1 | 22.53 | 0.818 | 740.09 | 79.49 | <DL | 1.74 | 9.64 | 6.23 | <DL | 3.19 |
| E4 | 8.72 | 1160 | 7.5 | 26.29 | 1.48 | 541.73 | 46.15 | <DL | 0.21 | 0.60 | 1.78 | <DL | 0.26 |
| E5 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E6 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E7 | 8.17 | 400 | 8.17 | 7.01 | <DL | 54.62 | 200 | <DL | <DL | 0.31 | 0.043 | <DL | 0.07 |
| E8 | 7.2 | 485 | 7.2 | 8.51 | 0.216 | 48.76 | 261.54 | <DL | <DL | 0.29 | 0.023 | <DL | 0.05 |

ND: not detected. DL: detection limit; NA: not analyzed.

Table 5. Basic characteristics and heavy metal concentrations of surface water from the San Pedro River, 2005.

| Sample units | pH | EC µS $cm^{-1}$ | DO mg/L | $Cl^-$ mg/L | $N\text{-}NO_3^-$ mg/L | $SO_4^{2-}$ mg/L | $HCO_3^=$ mg/L | Cd mg/L | Cu mg/L | Fe mg/L | Mn mg/L | Pb mg/L | Zn mg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| E1 | 3.94 | 1016 | 6.1 | 50 | 2.07 | 460.39 | <1.0 | 0.03 | 6.60 | 9.51 | 6.30 | <DL | 2.42 |
| E2 | 7.72 | 833 | 6.8 | 28.22 | 1.02 | 352.75 | 80.52 | 0.02 | 0.83 | 5.62 | 2.67 | <DL | 1.10 |
| E3 | 7.58 | 803 | 6.5 | 12.08 | 0.96 | 321.28 | 70.76 | <DL | 0.67 | 4.62 | 2.87 | 0.09 | 1.02 |
| E4 | 7.42 | 743 | 4.4 | 14.23 | 1.11 | 237.65 | 136.64 | <DL | 0.06 | 0.21 | 0.43 | <DL | 0.12 |
| E5 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E6 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| E7 | 7.79 | 294 | 7.5 | 31.45 | 0.61 | 52.33 | 112.24 | <DL | 0.32 | 16.3 | 0.34 | <DL | 0.22 |
| E8 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |

ND: not detected. DL: detection limit.