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# Long-range effect of cyanide on mercury methylation in a gold mining area in southern Ecuador

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ABSTRACT

Small-scale gold mining in Portovelo–Zaruma, Southern Equador, performed by mercury amalgamation and cyanidation, yields 9–10 t of gold/annum, resulting in annual releases of around 0.65 t of inorganic mercury and 6000 t of sodium cyanide in the local river system. The release of sediments, cyanide, mercury, and other metals present in the ore such as lead, manganese and arsenic significantly reduces biodiversity downstream the processing plants and enriches metals in bottom sediments and biota. However, methylmercury concentrations in sediments downstream the mining area were recently found to be one order of magnitude lower than upstream or in small tributaries. In this study we investigated cyanide, bacterial activity in water and sediment and mercury methylation potentials in sediments along the Puyango river watershed, measured respectively by in-situ spectrophotometry and incubation with $^{3}$H-leucine and $^{203}Hg^{2+}$.
Free cyanide was undetectable (<1 $\mu g \cdot L^{-1}$) upstream mining activities, reached 280 $\mu g \cdot L^{-1}$ a few km downstream the processing plants area and was still detectable about 100 km downstream. At stations with detectable free cyanide in unfiltered water, 50% of it was dissolved and 50% associated to suspended particles. Bacterial activity and mercury methylation in sediment showed a similar spatial pattern, inverse to the one found for free cyanide in water, i.e. with significant values in pristine upstream sampling points (respectively 6.4 to 22 $\mu gC \cdot mg$ wet weight$^{-1} \cdot h^{-1}$ and 1.2 to 19% of total $^{203}Hg \cdot g$ dry weight$^{-1} \cdot day^{-1}$) and undetectable downstream the processing plants, returning to upstream values only in the most distant downstream stations. The data suggest that free cyanide oxidation was slower than would be expected from the high water turbulence, resulting in a long-range inhibition of bacterial activity and hence mercury methylation. The important mercury fluxes resultant from mining activities raise concerns about its biomethylation in coastal areas where many mangrove areas have been converted to shrimp farming.


## 1. Introduction

The Puyango River basin is situated in South Western Ecuador, near the border with Peru and has been a site of gold and silver mining since pre-colonial times, leading to the present name of the province, El Oro. In the Portovelo–Zaruma region, upper Puyango basin, larger scale mining by foreign companies produced 1000 t of Au, 500 t of Ag and 1500 t of Cu during the first half of the 20th century (Astudillo, 2007). In the 1980s, an economic crisis combined with a sharp increase in gold prices led to the invasion of abandoned mines, resulting in a boom of small-scale mining. Today, over 110 small riverside processing plants operate in the region, extracting approximately 9–10 t of gold per annum by a combination of amalgamation with Hg and cyanide leaching from ore coming from over 400 mines. This combination of extraction processes is not exclusive to Ecuador and is used in other developing countries for the same reason, namely the low gold recovery when using Hg amalgamation alone. Velasquez-Lopez et al. (2010, 2011) described in close detail the extraction processes used by the miners from Portovelo–Zaruma and, more important, the inventory of the resultant Hg and cyanide emissions in each step of the process. Besides gold, the sulfur-rich polymetallic ore they process contains high concentrations of Mn, Cd, Pb, As, Cu and Zn and inadequate management of mine tailings results in the discharge of toxic cyanide effluents and of sediments highly enriched with Hg and other metals, and the signature of mining activity in sediments and suspended particles is detectable far downstream (Tarras-Wahlberg et al., 2001; Betancourt et al., 2005). In the 2000 dry season Hg in suspended sediments 100 km downstream the processing plants was ~400 $ng \cdot g^{-1} \cdot$ dry weight and it increased by one order of magnitude in the wet season, while for lead the concentrations were 250 and 2600 $\mu g \cdot g^{-1}$ in the dry and wet season respectively.

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The cyanidation plants operate in a hilly region and due to the scarcity of flat areas the mining facilities and cyanidation plants are built directly on the river banks and as a consequence cyanidation plants respond for ±80% of the sediment slurry laden by mining activities to the river (Prodeminca, 1998). In May 2011, over 110 cyanidation plants were operating in the region, releasing estimated 880.000 t/a of tailings into the river (Veiga, 2011). The Puyango river flows into the Tumbes River that reaches the Pacific Ocean, transporting mining-derived metals to the coastal areas, affecting mangroves and large shrimp farms. Studies in the 70s and 80s have estimated that about 289 kg of Hg was annually discharged into the Calera River in Portovelo–Zaruma (Prodeminca, 1998) and recently Velasquez-Lopez et al. (2010) estimated an annual discharge of 430 kg of Hg.

Betancourt et al. (2005) studied the impact of mining on environment and human health along the Puyango river basin, documenting the occupational exposure to Pb and Hg in the upper basin, where the intake of fish and river water are low, and the high exposure to lead in the semi-arid lower basin, where the population relies heavily on the river for fish and water supply. They found very low suspended particle loads upstream the mining area, ranging from 1.6 to 3.0 $mg \cdot L^{-1}$ depending on the season, while near the processing plants, levels ranged 132–328 $mg \cdot L^{-1}$, and similar profiles were found for metals in river sediments, with maximum mercury concentrations of 0.061 $\mu g \cdot g^{-1}$ upstream mining activities and 0.730 $\mu g \cdot g^{-1}$ downstream.

However, Roulet et al., 2006 found that methylmercury was at least one order of magnitude lower in sediments downstream the mining area when compared to levels upstream or in small tributaries unaffected by mining activities, both as absolute concentrations or as % of total mercury and raised the hypothesis that gold mining could be reducing methylmercury. Mercury is converted from Hg (II) to methylmercury by microbiological activity and such low methylmercury concentrations and percentages suggest a very low availability of mercury, possibly due to its binding to sulfur, abundant in the processed ore and hence in the mining effluents, and/or a strong inhibition of microbiological activity due to the very high cyanide concentrations in these effluents. For the present study we returned to the region in 2009 to test the second hypothesis, measuring cyanide and bacterial activity in water along the Puyango river basin, as well as bacterial activity and mercury net methylation potentials in bottom sediments, in three reference stations upstream the mining area and four stations downstream.

## 2. Materials and methods

### 2.1. Study area and sampling sites

The Puyango River crosses southern Ecuador from NE to SW from the Andes' western foothills to the border with Peru, where it changes its name to Tumbes River, before finally reaching the Pacific Ocean (Fig. 1).

The Upper Basin of the Puyango includes the Zaruma and Portovelo mining and urban centers (stations 4) and the reference sampling stations upstream (stations 1 to 3): it is a temperate humid region. The Middle Basin includes Puyango Viejo and Marcabelí and it is a sub-tropical humid region, while the Lower Basin (Gramadal-Las Vegas and Chaguarhuaycu) is a tropical semi-arid region. The Upper Basin has around 42,000 inhabitants while the middle and lower parts of the Basin are scarcely populated. The river is an important source of fish and drinking water for communities living in the semi-arid Lower Basin while the towns of Zaruma and Portovelo in the upper basin draw their drinking water from small Puyango tributaries. Agriculture and cattle are the predominant economic activities in the Lower and Middle Basin, aside from gold mining. The reference stations 1 to 3 are almost pristine and range 1550 to 1820 m in altitude with little or no agriculture upstream. The waters carry very little suspended particulate matter and support a varied fauna of birds, macroinvertebrates and fish. In contrast, stations 4 and 5 are under the direct influence of untreated urban sewage and of mining effluents, showing very high levels of particulate matter and cyanide, Pb, Cd, Mn and Hg among other metals, leading to a severe reduction in the density and diversity of the aquatic fauna. The latter parameters

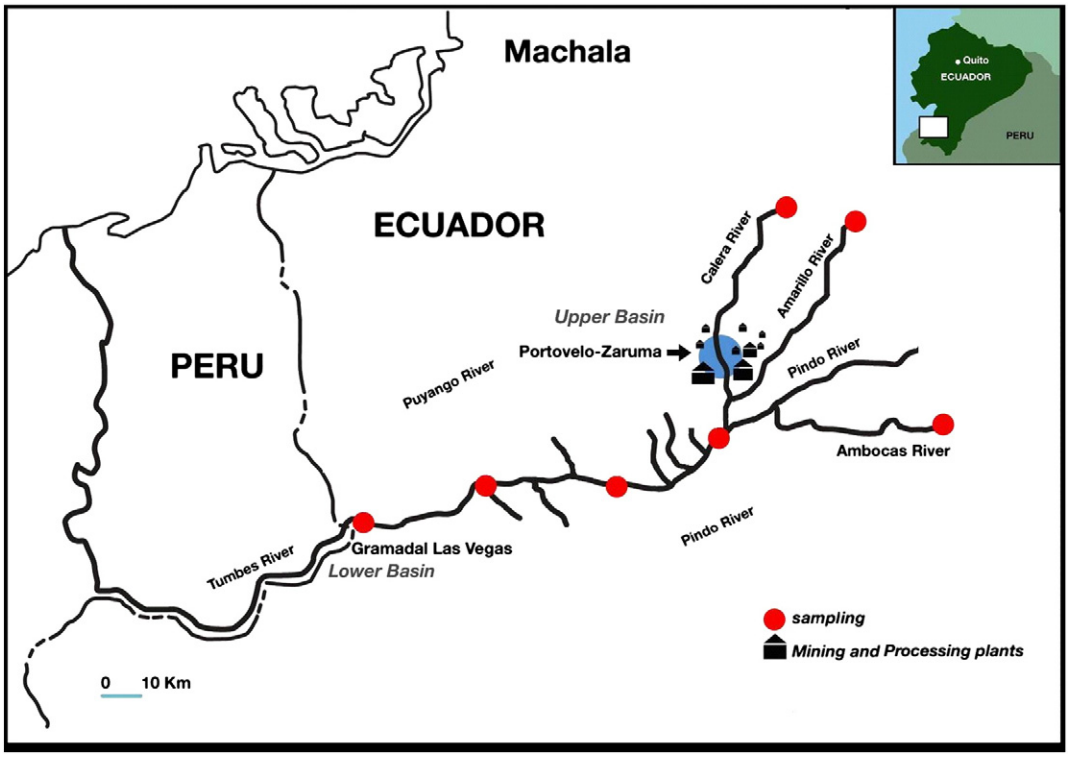


**Fig. 1.** Map of the study area and sampling stations, Puyango river basin, Ecuador.