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Evaluation of Water Quality Information and Potential Environmental Effects of Informal Gold Mining in Northern Esmeraldas Province, Ecuador

(Spanish summary/English Report)

16 August 2013

Resumen

Por la solicitud del Centro de Investigación y Desarrollo, Pontificia Universidad Católica del Ecuador Sede Esmeraldas (CID-PUCESE), E-Tech International has revisado informes y resultados de muestreo ambiental relacionados con los efectos de la minería informal de oro en la provincia norteña ecuatoriana de Esmeraldas. Nuestro análisis inicial se enfoca en los parámetros de muestras en los estudios y sobre la calidad de agua para el consumo humano y para la protección de biótica acuática. Nuestro análisis preliminar indica que los diseños de los estudios y los enfoques analíticos necesitan mejoramientos importantes antes de poder conocer definitivamente la calidad del agua.

Nuestra evaluación encontró varios problemas con el diseño del estudio, que hace difícil determinar si la actividad minera está causando impactos ambientales en la zona. Estas preocupaciones son las siguientes: 1) falta de información ambiental que forme una línea de base para la condición de los ríos; 2) identificación inadecuada de contaminantes de preocupación y falta de muestreo de fuentes de contaminación relacionado con la minería informal; 3) problemas analíticos, específicamente sobreestimación de contaminantes y límites de detección inadecuados cuando se utilizaba el método Potalab; 4) falta de evaluación de las condiciones hidrológicas y meteorológicas. Aunque la información de métodos de análisis estaba bastante limitada en los informes, parece que se utilizaron los métodos portables Potolab que utiliza resultados colorimétricos, y también los servicios de unos laboratorios acreditados. Los métodos de los laboratorios acreditados no estaban especificados en los informes pero parece que los límites de detección eran aceptables y en general más sensibles de lo requerido para los estándares de calidad de agua.

Muchas excedencias de contaminantes se encontraron utilizando el método de Potolab, incluyendo hiero, aluminio, cromo, cobre, cianuro, níquel, fluoruro, y bacterias coliformes. Sin embargo, los límites de detección, en general, eran demasiados altos para los estándares relevantes, y cuando se analizaban los mismos contaminantes con los dos métodos, los niveles encontrados con el método Potalab eran mucho más altos. Por eso, muchos resultados del método Potalab no se consideran confiables. La mayoría de resultados de laboratorios acreditados estaban debajo de los límites de detección, pero si se encontraron algunas excedencias como aluminio, cobre (para vida acuática), hiero, manganeso, cromo, y zinc (para vida acuática), plomo, y vanadio. El sitio con la mayor cantidad de excedencias encontradas en laboratorios acreditados era el estero Zapatillo en el sector Juan Montalvo. Concentraciones de mercurio y cianuro rara vez se encontraban sobre los niveles permisibles.

En los últimos dos informes, solo se compararon las concentraciones para la protección de salud humana. Sin embargo, las concentraciones permisibles para la protección de vida acuática son más bajas para varios contaminantes como cianuro, cadmio, cromo, cobre, mercurio, plomo, y zinc. Todos estos pudieran ser contaminantes de preocupación en zonas de actividad minera. En general, el nivel muy bajo de dureza en muchos de los ríos implica que la vida biótica está muy susceptible a impactos negativos por metales. La preocupación más grande para el consumo humano son los niveles muy altos de bacterias coliformes.

En lo que avanzan los estudios, se requieren los siguientes mejoramientos en la metodología: 1) tomar muestras aguas arriba de cualquier efecto de la actividad minera; 2) tomar muestras en más tajos mineros y desechos directos de la actividad minera para identificar claramente los contaminantes de preocupación; 3) mejorar la calidad de datos haciendo un plan global de muestras y análisis, haciendo análisis duplicados de la misma muestra utilizando los métodos de Potolab y laboratorio acreditado para una comparación directa de resultados, y asegurando que los límites de detección son suficientemente bajos (sensibles) para hacer comparación con estándares de agua establecidos; y 4) estimar el volumen de flujo de los ríos en el momento de muestreo.

Summary

At the request of the Centro de Investigación y Desarrollo, Pontificia Universidad Católica del Ecuador Sede Esmeraldas (CID-PUCESE), E-Tech International has reviewed reports and environmental sampling data related to the effects of unlicensed gold mining in northern Esmeraldas Province in Ecuador. Our initial review is focused on the parameters of the study design and the suitability of water for human consumption and the health of aquatic biota. Our preliminary findings indicate that the overall study design and analytical approaches need substantial improvement before definitive results on water quality can be determined.

Our evaluation found several issues with the design of the study that make it difficult to know if mining activity is causing adverse environmental effects: 1) lack of baseline environmental information; 2) inadequate identification of contaminants of concern and sampling of contaminant sources related to informal mining; 3) analytical issues, especially related to high detection limits and overestimation of concentrations by the Potalab method; and 4) lack of evaluation of hydrologic/meteorological conditions. Although only limited information on analytical methods was included in the reports, it appears that two types of laboratories were used: a portable instrument called a Potolab that uses colorimeric analysis, and an accredited laboratory (more than one accredited laboratory could have been used). We could find no

information on the analytical methods used at the accredited laboratory, but the detection limits were generally acceptable and lower than the most sensitive water quality standards.

Many exceedences of water quality standards were found for water samples analyzed by the Potalab approach, including exceedences of iron, aluminum, chromium, copper, cyanide, nickel, fecal and total coliform bacteria, and fluoride. However, the detection limits were generally higher than the most sensitive relevant standards, and, where samples were analyzed for the same constituents by both laboratories, the Potalab results were substantially higher. Therefore, most results from the Potalab are considered to be unreliable. The majority of the results from the accredited laboratory for contaminants of concern were below detection, but some exceedences were found for aluminum, copper (for aquatic life), iron, manganese, chromium, zinc (for aquatic life), lead, and vanadium. The location with the most exceedences, as measured by the accredited laboratory, was Estero Zapallito in the sector Juan Montalvo. Concentrations of cyanide and mercury rarely exceeded water quality standards at any location.

In the two most recent reports, measured stream concentrations were only compared to human health (drinking water) standards. However, water quality standards for protection of aquatic life are even lower (in terms of concentrations) for cyanide and for metals including cadmium, chromium, copper, mercury, lead, and zinc – all of which could be mining-related contaminants of concern. The general water quality results do suggest that a number of the locations are especially susceptible to adverse impacts to fish and other aquatic biota from metal pollution because of the low stream hardness values. The greatest concern for human consumption of the water in most locations is the high levels of coliform bacteria.

As the studies move forward, the following improvements should be instituted to resolve the analytical and study design issues: 1) sample water and sediment quality in upstream or tributary reaches that are not affected by mining activity; 2) sample more pits and direct discharges from illegal mining operations and clearly identify contaminants of concern associated with mining; 3) improve data quality by preparing a detailed overall sampling and analysis plan, analyzing split samples for all contaminants of concern using the Potalab and the accredited laboratory, and ensuring that detection limits are substantially lower than the most sensitive water quality standards; and 4) measure or approximate stream flow at each location during each sampling event.

1. Introduction

E-Tech International is pleased to submit this initial review of environmental conditions in an area affected by informal mining activity in northern Esmeraldas Province, Ecuador. The primary reports reviewed for our analysis included:

1. Ministerio del Ambiente (MAE), Secretaria Nacional del Agua (SENAGUA), y Pontifica Universidad Católica de Esmeraldas (PUCESE), 2011. Evaluación Ambiental de los Cantones Eloy Alfaro y San Lorenzo (Cuenca del Rio Santiago y Bogotá). Junio. (MAE, SENAGUA Y PUCESE, 2011)
2. MAE – Programa de Reparación Ambiental y Social (PRAS) and Centro de Investigación y Desarrollo (CID) – PUCESE, 2011. Documento preliminar de daños Sociales y ambientales y descripción de la actividad minera ilegal en el norte de la Provincia de Esmeraldas. Diciembre. (MAE-PRAS y CID-PUCESE, 2011)
3. CID-PUCESE – MAE-PRAS, 2012a. Monitoreo de calidad ambiental de ríos de la cuenca del Santiago afectados por la actividad minera aurífera ilegal en el norte de Esmeraldas durante el periodo Febrero Marzo del 2012. 5 de Abril. (CID-PUCESE y MAE-PRAS, 2012a)
4. CID-PUCESE – MAE-PRAS, 2012b. Informe final de monitoreo de calidad ambiental de ríos de la cuenca del Santiago afectados por la actividad minera aurífera entre el periodo Noviembre del 2011 a Noviembre del 2012. 14 de Noviembre. (CID-PUCESE y MAE-PRAS, 2012b).

Although some comments are provided on sediment quality, biodiversity, and the effects on fish, the primary focus of this review is water quality and the associated potential adverse effects on human health and aquatic biota.

2. Issues with Study Design

To evaluate whether the observed effects are related to illegal mining activity or other causes, certain scientific elements are needed that appear to be missing in the reports we reviewed. Because our report is an initial review, it is possible that other reports address these elements that E-Tech has not received or reviewed. We discuss four scientific elements related to study design that make it difficult to say definitively that mining activity has caused adverse effects to the environment in the northern Esmeraldas area: 1) lack of baseline environmental information; 2) inadequate identification of contaminants of concern and sampling of contaminant sources related to informal mining; 3) analytical issues, especially related to high detection limits and overestimation of concentrations by the Potalab method; and 4) lack of evaluation of hydrologic/meteorological conditions.

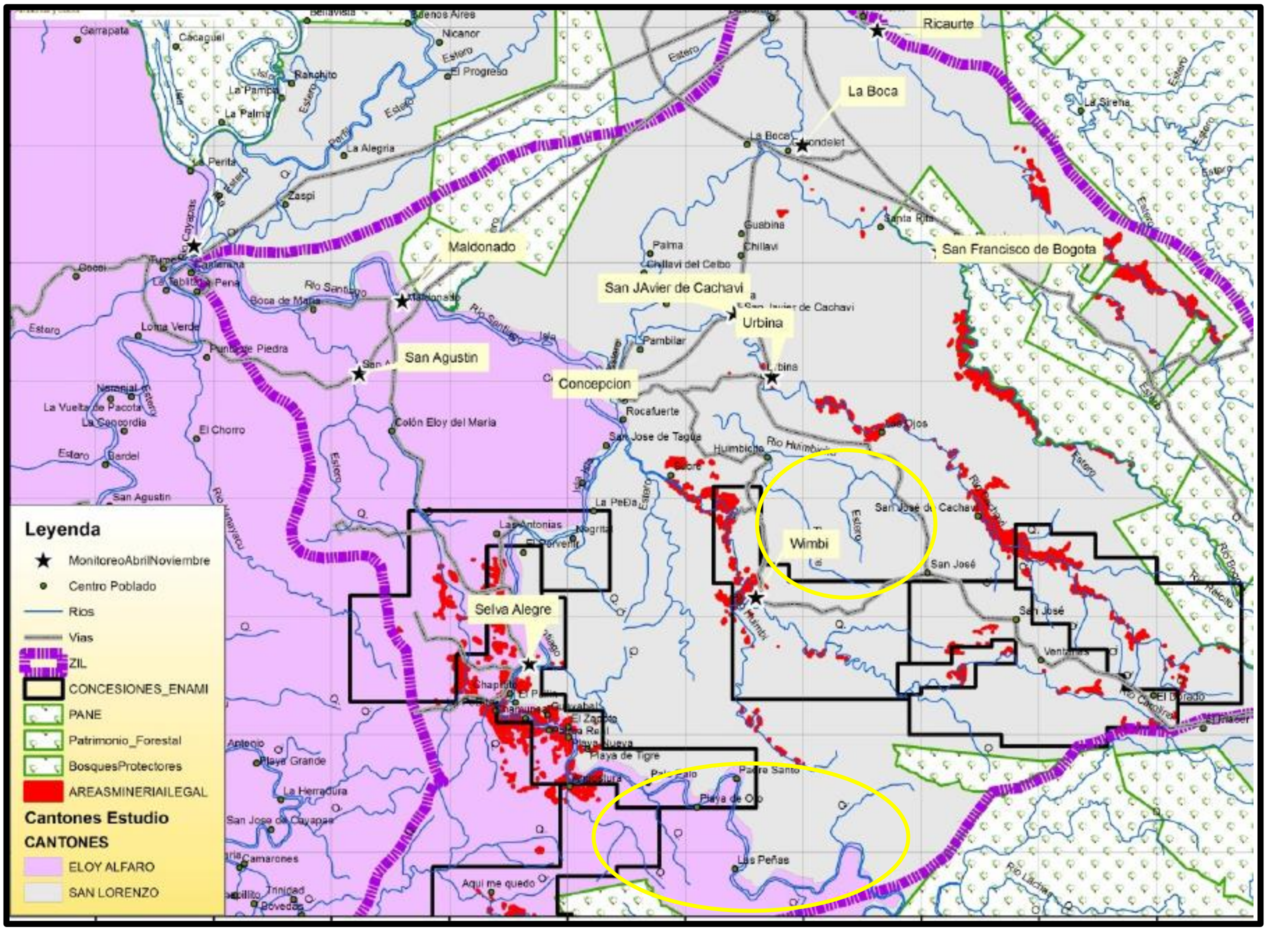
2.1 Lack of baseline environmental information

Based on our initial review, baseline water and sediment quality have not been adequately evaluated. Baseline conditions are defined as those that would exist absent the release of contaminants under investigation. In the case of Esmeraldas, the release of contaminants under investigation is associated with informal mining activity. The reports reviewed mention baseline water and sediment quality conditions but conclude that no sampling occurred before mining began, so no baseline analysis is possible – that the only type of evaluation possible would be investigating the evolution of waters over time (MAE, SENAGUA Y PUCESE, 2011 y MAE-PRAS y CID-PUCESE, 2011). Some examples of statements in the second joint report (MAE-PRAS y CID-PUCESE, 2011) that demonstrate the lack of baseline analysis for water and sediment quality include:

- "No se dispone de antecedentes sobre parámetros de calidad de agua previos de los ríos afectados por la actividad minera en la actualidad, por lo que los datos de calidad de agua obtenidos por SENAGUA13 durante Noviembre y Diciembre del 2010 y durante la primera semana de Mayo del 2011, los se constituyen en una línea base del nivel de afectaciones que deberán monitorearse en el tiempo para observar la evolución de parámetros físico químicos en la columna de agua." (p. 35)
- "No se dispone hasta la fecha de estudios relativos a la calidad previa del suelo, aunque la misma puede desprenderse de la evolución de la cobertura vegetal existente y que se analiza en el capitulo 3. Cobertura vegetal." (p. 60).

The maps provided show upstream areas or tributaries that are not affected by informal mining activity and that could be sampled for baseline conditions (see yellow circled area in Figure 1). MAE-PRAS y CID-PUCESE (2011) mention in the Introduction that such locations exist but are likely influenced by other types of polluting activities, such as palm plantations. If no areas exist that are outside the influence of all industrial activity, baseline sampling locations should be selected in areas that exclude informal mining but include other polluting activities. The evaluations of fish (for shrimp populations, see MAE-PRAS y CID-PUCESE, 2011, p. 86) and macroinvertebrate diversity and health (see CID-PUCESE y MAE-PRAS, 2012b, Tables CXLI and CXLII) did include some baseline analysis, and the effects were generally worse in areas known

Figure 1. Map showing areas of "illegal" mining (in red) and sampling locations (stars). Yellow circles show potential baseline sampling areas.



Fuente: Adapted From CID-PUCESE y MAE-PRAS, 2012a, Figure 2.

to be impacted by illegal mining activity. The macroinvertebrate sampling locations that were considered to have no mining impact were Wimbicito, El Parto, Palabi, Las Antonias, and Estero Limpio San Francisco (CID-PUCESE y MAE-PRAS, 2012b, Table CXLI). Two of these locations, Palabi and Wimbicito, also had depressed macroinvertebrate populations, possibly related to upstream clothes washing and detergent use (CID-PUCESE y MAE-PRAS, 2012b).

Another approach that could be used to demonstrate that mining activity is the cause of the observed impacts would be to analyze water and sediment quality near the downstream end of mining activity and at a number of more downstream locations in areas that are not subjected to mining. If concentrations of contaminants associated with mining activity decrease in a downstream direction, it is likely that cleaner inputs of water and sediment have diluted mining-related contaminant concentrations.

2.2 Inadequate identification of contaminants of concern from informal mining sources

The sources of contamination (e.g., pits, active discharge) should have been sampled more extensively and analyzed for a full list of constituents to determine the contaminants of concern that are specifically associated with information mining. The list of contaminants of concern should be the focus of future analytical efforts. Contaminants typically associated with informal gold mining operations include cyanide and mercury. However, many metals can be dissolved from the mined material and could also be contaminants of concern, including arsenic, cadmium, lead, copper, and zinc. For the recirculation pits that were sampled, the concentrations of contaminants in the water were not particularly high or of concern (MAE-PRAS y CID-PUCESE, 2012b, Tabla VIII and XLIV). However, concentrations of certain metals (barium, chromium, cobalt, copper, vanadium, and zinc) in sediment were higher in the recirculation pit than in nearby stream sediment (MAE-PRAS y CID-PUCESE, 2012b, Tabla XLV). Cyanide was not measured in either pit water sample, and concentrations of mercury were below detection at 0.0001 mg/l. Concentrations of mercury were below detection in the pit sediment sample, as shown in Tabla XLV. The process of informal gold mining involves the use of large amounts of cyanide and mercury (MAE-PRAS y CID-PUCESE, 2011, p. 4). Therefore, the sources, if properly identified and sampled, should contain measureable amounts of cyanide and/or mercury.

Cyanide and mercury can change chemical form and move from one environmental medium to another (e.g., from sediment to water) as they are transported through the environment. Cyanide can degrade readily in surface water from exposure to sunlight, but it can persist in groundwater (Filipek 1999; Smith and Mudder, 1999; Tarras-Wahlberg et al., 2000). Elevated concentrations of nitrate can result from the degradation of cyanide, so nitrate may also be a contaminant of concern. Mercury can become methylated and more toxic (U.S. EPA, 2001). Contaminants can move from sources (e.g., pits) into groundwater and then into springs or stream. Depending on the sources found and their locations relative to streams, alluvial groundwater should possibly also be sampled so that the contaminants can be tracked through the environment.

2.3 Sampling and analytical issues

E-Tech could not find a sampling and analysis plan for the project in the materials that we received. The only mention of methods used that we could find was for biodiversity, in which the rapid biological assessment methodology (Evaluación Rápida de Recursos Bioacuáticos (AQUARAP)) was used, and references to the approach were provided (MAE-PRAS y CID-PUCESE, 2011, p. 67). A sampling and analysis plan should include the study objectives; a sampling and analysis schedule; the types, numbers, and locations of samples to be collected; sample identification and labeling; field sampling protocols (including whether samples will be filtered, measurement of field parameters, preparation of field and equipment blanks); field documentation; sample preservation, storage, shipping, and chain-of-custody; and information on analytical measurements (including parameters, methods of detection, holding times, and detection limits). For example, sediment samples should be sieved, retaining the fraction <63 μm for analysis. In this way, concentrations can be compared across sites with wide ranges of sediment sizes. Manuals for the collection of water quality information are available online from the U.S. Geological Survey (2007). A field safety plan should also be created for the protection of the samplers.

Although only limited information on analytical methods was included in the reports, it appears that two types of laboratories were used for water quality: a portable instrument called a Potalab that uses colorimeric analysis with spectrophotometric detection, and an accredited laboratory (more than one accredited laboratory could have been used). The Potalab was used for chemical analysis in the two most recent reports (CID-PUCESE y MAE-PRAS, 2012a and b). We believe that the Laboratorio OSP de la Facultad de Ciencias Químicas de la Universidad Central del Ecuador en Quito was used for the first two reports, or at least for the May 2011 sampling (MAE, SENAGUA Y PUCESE, 2011). We could find no information on the analytical methods used at the accredited laboratory, but the detection limits were generally acceptable and lower than those for the Potalab.

In the second report (MAE-PRAS y CID-PUCESE, 2011), many of the detection limits for water and soil were higher than relevant standards, including aluminum, arsenic, mercury, and barium for soils (p. 60 and 113), and aluminum, lead, Cr(VI), mercury, fecal coliform, and cyanide in water (p. 50 and 53). Ideally, detection limits should be five to ten times lower than the lowest (most protective) relevant standard.

In the most recent report (CID-PUCESE y MAE-PRAS, 2012b), water samples were analyzed by Potalab and at an accredited laboratory. For several important heavy metals (e.g., cadmium, copper, zinc), aquatic life standards/criteria values are much lower than those for protection of human health and drinking water. Table 1 shows the relevant water quality standards for Ecuador and the United States for drinking water and protection of aquatic life. None of the reports that we read included a list of detection limits for the Potalab instrument. However, E-Tech contacted the company that makes the Potalab and the field spectrophotometer and obtained the detection limits (Appendix A). Table 1 also includes some of the Potalab detection limits, several of which are close to or higher than the most sensitive relevant standards.

One of the most important analytical issues is that it appears that the Potalab overestimates concentrations of many potential contaminants of concern. In many cases, the most important analytes were not determined by both methods (especially arsenic and mercury), so a full comparison between the methods for important contaminants typically associated with artisanal mining cannot be made (see, e.g., CID-PUCESE y MAE-PRAS, 2012b, Tablas VII and VIII for Rio Bogotá, sector Valle de la Virgen. Al, As, and Hg were determined at an accredited laboratory but not by POTALAB).

Our finding that the Potalab overestimates concentrations assumes that samples we compared are splits collected at same location and at approximately the same time, and that the accredited laboratory results are more reliable than those of the Potalab because they have lower detection limits. With these assumptions, as shown in Table 2, the Potalab overestimated concentrations of cobre, cromo, fosforo, hierro, magnesio, niquel, potasio, and zinc. Many of the constituents that commonly exceeded water quality standards (cromo, hierro, and niquel), using the Potalab results, are those with overestimated concentrations. Therefore, if the Potalab results indicate an exceedence of a water quality standard, and the results are for a contaminant of concern, a split sample should be sent to an accredited laboratory for further analysis. In the longer run, a detailed study of the reliability of the Potalab, using split samples and standard reference samples (samples with known concentrations of constituents, available from the U.S. Geological Survey and other sources), should be conducted.

Tabla 1. Normas de Calidad del Agua, Ecuador y los EE.UU., Posibles Efectos Adversos, y la Comparación de Potalab Límites de Detección

Parámetros	Unidad	Limites Maximos Permisibles (LMP) TULAS (Tablas 1 o 2)	US EPA - Consumo Humano[a]	Los Posibles Efectos Adversos para la Salud Humana en Concentraciones Superiores a los Niveles Máximos de Contaminantes (NMC)[a]	LMP TULAS - Preservacion de flora y fauna (Tabla 3, agua calida)	US EPA - Protección de la vida acuática (Dureza = 25 mg/L as $CaCO_3$)[d]	US EPA - Protección de la vida acuática (Dureza = 100 mg/L as $CaCO_3$)[d]	Potalab Límite de Detección
pH	UE	de 6 a 9	6,5 - 8,5*	No es un NMC	6,5-9	--/6,5-9	no depende en la dureza	6,8-8,4
Aluminio	mg/l	0,1	0,05 - 0,2*	No es un NMC	0,1	0,750/0,087	no depende en la dureza	0,02
Arsenico	mg/l	0,05	0,010	Daño en la piel o problemas con sistemas circulatorios, posible mayor riesgo de cáncer	0,05	0,340/0,150	no depende en la dureza	NA
Cadmio	mg/l	0,001	0,005	Daño renal	0,001	0.0005/0.0001	0,0021/0,0003	NA
Cianuro	mg/l	0,01 (total)	0,2 (como cianuro libre)	Daño en los nervios o problemas de la tiroides	0,01 (como cianuro libre)	0,022/0,0052	no depende en la dureza	2 (ácido cianúrico)
Cobre	mg/l	1	1,0*, 1,3	Corto plazo: molestias gastrointestinales, Largo plazo: Daño renal o hepático	0,02	0,004/0,0029	0,014/0,0093	0,03
Cromo	mg/l	0,05	0,1 (total)	Dermatitis alérgica	0,05 (total)	0,579/0,028 (CrIII)	1,803/0,086 (CrIII)	0,02
Fluoruro	mg/l	1,5	2,0*, 4	Enfermedades óseas (dolor y sensibilidad de los huesos), dientes moteados posibles (niños)	--	--	--	0,1
Hierro	mg/l	0,3	0,3	No es un NMC	0,3	--/1000	no depende en la dureza	0,02
Mercurio	mg/l	0,001	0,002	Daño renal	0,0002	0,0014/0,00077	no depende en la dureza	NA
Níquel	mg/l	0,025	0,1**	No es un NMC	0,025	0,145/0,016	0,469/0,052	0,12
Nitrato	mg/l como N	10	10	Los bebés menores de seis meses se pueden enfermar seriamente y, si no se trata, pueden morir. Los síntomas incluyen dificultad para respirar y el síndrome del bebé azul.	--	10 (salud humana para el consumo de agua y el organismo)	no depende en la dureza	0,2
Plomo	mg/l	0,05	0,015	Bebés y niños: Retrasos en el desarrollo físico o mental, los niños pueden mostrar leve déficit de capacidad de atención y la capacidad de aprendizaje. Adultos: problemas renales, hipertensión	--	0,014/0,0005	0,082/0,0032	NA
Sulfato	mg/l	250	250*	No es un NMC	--	--	--	5
Zinc	mg/l	5	5*/2**	No es un NMC	0,18	0,037/0,037	0,120/0,120	0,02
Coliformes Fecal	npm/100 ml	100	[b]	Diarrea, calambres, náuseas, dolores de cabeza u otros síntomas; pueden presentar un riesgo epecial para bebés, niños pequeños, y personas con sistemas inmunológicos severamente debilitados	200	--	--	NA
Coliformes Totales	npm/100 ml	600	5%[c]	Véase arriba	--	--	--	NA

npm = numero posible maximo

a Los valores son los Niveles Máximos de Contaminantes (NMC) para la protección de la salud humana a menos que se indique de otra manera. http://water.epa.gov/drink/contaminants/index.cfm#Inorganic, and http://www.epa.gov/waterscience

* El valor es un Reglamento Nacional de Agua Potable secundarios (RNAPs o normas secundarias). RNAPSs son pautas no obligatorias sobre niveles de contaminantes que pueden causar efectos cosméticos (como decoloración de la piel o de los dientes) o efectos estéticos (como el sabor, olor o color) en el agua potable. EPA recomienda normas secundarias a los sistemas de agua, pero no requiere que los sistemas cumplan. Sin embargo, los estados pueden elegir adoptar como normas exigibles

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b Cada muestra con coliformes totales debe analizarse ya sea para coliformes fecales o E. coli; si dos muestras consecutivas son TC-positivo y uno también es positivo para E. coli coliformes fecales, el sistema tiene una violación grave de NMC

c más de 5,0% de las muestras son positivas para coliformes totales en un mes. (Para los sistemas de agua que recogen menos de 40 muestras rutina por mes, no más de una muestra puede ser coliformes totales positiva al mes.)

d Los criterios son para los metales totales recuperables, el primer valor es el criterio de concentración máxima (CMC), un promedio de "corto plazo" que no debe ser superarse más de una vez en 3 años ("aguda"); el segundo valor es el criterio de concentración continua (CCC), el promedio de 96 h que no debe ser superarse más de una vez en 3 años ("crónica"); http://www.epa.gov/waterscience/criteria/wqctable/

NA =muestras no analizadas por Potalab para este constituyente, no límite de detección disponible

(amarillo) Límite de detección para el Potalab demasiado cerca del o más alto que el estándar más sensible

Tabla 2. Comparación de los resultados por Potalab y el laboratorio acreditado por tres muestras recogidas en julio de 2012.

Lugar del Muestreo			Union rios Bogota y Tululbi		Rio Tululbi		Rio Palabi	
Laboratorio/Metodo			Potalab	Acreditado	Potalab	Acreditado	Potalab	Acreditado
Fecha del Muestreo			21/07/2012	Julio 2012	20/07/2012	Julio 2012	20/07/2012	Julio 2012
Parámetros	**Unidad**	**LMP TULAS**						
Aluminio	mg/l	0,1	0,03	0,1	0,020	0,1	0,020	0,1
Cobre	mg/l	1	0,140	<0.005	0,080	<0,005	0,000	<0,005
Cromo	mg/l	0,05	0,090	0,0006	0,040	0,0006	0,110	0,001
Fósforo	mg/l		0,650	<0,02	0,410	<0,02	0,680	<0,02
Hierro	mg/l	0,3	0,500	0,3	0,300	0,2	0,220	0,1
Magnesio	mg/l		5,000	1,5	8,000	1,7	8,000	1,2
Níquel	mg/l	0,025	0,150	<0,001	0,200	<0,001	0,050	<0,001
Potasio	mg/l		2,000	0,9	>>12	0,8	1,800	0,6
Zinc	mg/l	5	0,010	<0,005	0,010	<0,005	0,000	<0,005

(amarillo)	El resultado sobrepasa el limite maximo permisible (LMP) TULAS
(verde)	No es un numero de confianza - se debe ser menos que un limite de deteccion real

Fuente de información: CID-PUCESE y MAE-PRAS, 2012b.

2.4 Lack of evaluation of hydrologic/meteorological conditions

The first two reports (MAE, SENAGUA Y PUCESE, 2011 and MAE-PRAS y CID-PUCESE, 2011) presented results from May 2011. The May sampling event took place after a rainstorm, and concentrations were diluted compared to results from the December sampling:

> "En este punto es imprescindible mencionar que este tipo de análisis debe ser continuo, pues a simple vista parecería que los rios se "arreglaron" de acuerdo a los muestreos de mayo del 2011, lo que representa un engaño pues se debe tener en cuenta el nivel de pluviosidad de la zona, habiendo sido "diluidas" las muestras obtenidas por el aumento del caudal del agua…" (MAE-PRAS y CID-PUCESE, 2011, p. 47).

The summary table in the second report (Tabla XXX) uses only the results from the May 2011 sampling event. With only two samples, the results should not be averaged because they were likely collected under very different flow conditions. It is likely that even higher (and lower) concentrations exist, and as a precautionary measure, the highest concentrations from the two dates should have been compared to relevant standards to approximate concerns that could exist during "normal," non-rainy times. Some examples of the differences in concentration are shown in Table 3.

Tabla 3. Comparación de los resultados para diciembre de 2010 y mayo de 2011 (MAE-PRAS y CID-PUCESE, 2011).

Localidad		Estero Maria en San Agustin		Estero Maria union estero Sabaleta		Rio Bogotá Localidad San Francisco	
Parametro	**Unidades**	**Dic. 2010**	**Mayo 2011**	**Dic. 2010**	**Mayo 2011**	**Dic. 2010**	**Mayo 2011**
Conductividad	mS/cm	96,3	31	60,3	24,4	37,5	22,1
Arsénico	µg/L	1,625	0,0003	3,69	0,0002	0,36	0,0002
Aluminio	mg/L	18,095	1,08	70,35	<0,40	2,365	<0,40
Mercurio	µg/L	0,26	0,0005	<0,26	0,0004	<0,26	0,0011
	El resulto sobrepase el limite maximo permisible (LMP) TULAS						
	Límite de detección es más alto que el estándar						

The results indicate that rain events change concentrations in the streams. In this case, samples were collected at some time after a rain storm when stream flows were likely higher, and concentrations were diluted. However, during or immediately following a rainstorm, it is possible that contaminants could move into streams from sources under lower flow conditions, and concentrations could be higher than "normal." Stream flows should be measured or approximated at each location sampled during each water quality sampling event. To accomplish this, gages could be established for key locations, especially for larger river reaches that would be dangerous to measure under higher flow conditions. Rating curves would need to be established at these locations (see USGS, 2007).

3. Comments on Water Quality and Environmental Effects

3.1 General comments on water quality

The waters sampled for the studies are generally of low ionic strength, near neutral or slightly acidic, with low hardness and high color.

The conductivity, which is a measure of the saltiness of the water, is quite low at most of the stations. This suggests that the streams are not highly contaminated with natural or anthropogenic inorganic contaminants, such as sulfates or chlorides.

The pH values are generally slightly acidic. This could result from contaminants, but it might just as likely reflect the natural chemistry of the water – and could be a result of high amounts of dissolved organic matter in the streams. Such a condition is relatively common in the tropics. The elevated color values could also be a result of naturally high amounts of dissolved organic matter. Dissolved organic matter can also protect fish from dissolved metals effects.

A number of the locations have very low hardness values (as measured by Potalab: see (CID-Pucese y PRAS-MAE, 2012a and b). Hardness (a measure of the amount of divalent cations – calcium, magnesium, and iron) and alkalinity can protect aquatic biota from the adverse effects of metals. Where values are low, fish can be more susceptible to metals toxicity (especially copper, cadmium, lead, zinc, silver, and chromium). The only locations that did not have low hardness values were in the Estero Maria (sector Selva Alegre and Sector San Agustin). Sampling locations with at least one hardness measurement ≤25 mg/L as $CaCO_3$ from the most recent report (CID-PUCESE y MAE-PRAS, 2012b) include:

- Rio Bogota (sector Valle de la Virgen, sector San Francisco; union rios bogota y Tululbi, sector La Boca)
- Rio Tullulbi (sector Minas Viejas, sector Ricaurte)
- Rio Palabi (sector Ricaurte)
- Rio Cachavi (sector San Antonio, sector la Union, sector Los Ajos, sector Urbina, sector San Javier)
- Rio Wimbi (sector Wimbi)
- Estero Zapallito (sector Juan Montalvo)
- Estero Angostura (sector Angostura)
- Estero El Muerto (sector cruce de la via Selva Alegre-Palma real)
- Estero Las Antonias (sector Las Antonias)
- Rio Santiago (sector Playa de Oro, sector Playa Nueva, sector Selva Alegre, sector Conception, sector Maldonado; Rio Santiago-Rio Cayapas, sector Borbon)
- Estero San Antonio (sector Campamento).

There is a need to do site-specific background sediment quality and toxicity studies on the aquatic biological species living in the streams that are potentially affected, especially if the native species were not used to develop the standards for protection of aquatic life.

3.2 Water quality exceedences

Many exceedences of water quality standards were found for water samples analyzed by the Potalab approach, including exceedences of iron, aluminum, chromium, copper, cyanide, nickel, fecal and total coliform bacteria, and fluoride. However, the detection limits were generally higher than the most sensitive relevant standards, and, where samples were analyzed for the same constituents by both laboratories, the Potalab results were substantially higher. Therefore, most results from the Potalab are considered to be unreliable.

The majority of the results from the accredited laboratory for contaminants of concern were below detection, but some exceedences were found for aluminum, copper (for aquatic life), iron, manganese, chromium, zinc (for aquatic life), lead, and vanadium. The location with the most exceedences, as measured by the accredited laboratory, was Estero Zapallito in the sector Juan Montalvo. Concentrations of cyanide and mercury rarely exceeded water quality standards at any location.

In the two most recent reports, neither arsenic nor mercury were exceeded in accredited lab results for water samples. In the two most recent reports, measured stream concentrations were only compared to human health (drinking water) standards. However, water quality standards for protection of aquatic life are even lower (in terms of concentrations) for cyanide and for metals including cadmium, chromium, copper, mercury, lead, and zinc – all of which could be mining-related contaminants of concern. The general water quality results do suggest that a number of the locations are especially susceptible to adverse impacts to fish and other aquatic biota from metal pollution because of the low stream hardness values. The greatest concern for human consumption of the water in most locations is the high levels of coliform bacteria.

A summary of the sampling efforts and exceedences of water quality standards in the four reviewed reports follows.

<u>MAE, SENAGUA Y PUCESE, 2011:</u>

- **Sample dates and number of locations:** May 2011 (same as below – results are the same); 14 locations
- **Laboratory:** Laboratorio OSP de la Facultad de Ciencias Químicas de la Universidad Central del Ecuador en Quito
- **Summary of water quality exceedences:** Mercury at 8 locations (but can't read the majority of the results because they are covered with red blocks); for ones that are legible, exceedences of drinking water standards are not great.
- **Additional comments:** Samples not analyzed for cyanide; cadmium, copper, and zinc concentrations were all below detection, but detection limit too high to compare to relevant standards (20 µg/l for Cd, 50 µg/l for Cu, 100 µg/l for Zn). Fe exceeded 1 mg/L at 5 locations. Total coliform exceeded at 5 locations.

<u>MAE-PRAS y CID-PUCESE, 2011:</u>

- **Sample dates and number of locations:** Dec 2010 and May 2011; 18 locations
- **Laboratory:** Did not use Potalab, but no mention of laboratory used
- **Summary of water quality exceedences:** Turbidity, DB05, color, arsenic (1), aluminum, mercury (1), iron, low pH, total and fecal coliform
- **Additional comments:** Highest concentrations were in December 2010; rain diluted values in May 2011. Only arsenic and mercury are of potential concern for human consumption. Results were compared to aquatic life criteria in TULAS. A few samples were analyzed for cyanide, but the detection limit was too high (0,007 mg/l) to compare to more protective aquatic life criterion (0,005 mg/l); units for arsenic and mercury are confusing – some in mg/L, others in µg/L.

<u>CID-PUCESE y MAE-PRAS, 2012a:</u>

- **Sample dates and number of locations:** February and March 2012; 15 locations.
- **Laboratory:** Potalab only

- **Summary of water quality exceedences:** Iron (drinking water and aquatic life), chromium (drinking water), aluminum, fecal and total coliform, copper (aquatic life), nickel (drinking water and aquatic life), turbidity
- **Additional comments:** Too much uncertainty with Potalab to know if exceedences are meaningful; did not compare to aquatic life criteria; did not measure cyanide.

CID-PUCESE y MAE-PRAS, 2012b:

- **Sample dates and number of locations:** November and December 2011 (not sure of year), January to May, July September, November 2012 (Potalab); November 2011, June and July 2012 (accredited laboratory); 24 locations (not all locations were sampled on all dates)
- **Laboratory:** Used Potalab and accredited laboratory – uncertain if samples were splits; detection limits for accredited lab generally good, but no information on methods used
- **Summary of water quality exceedences:** Potalab: Fe, Cr (drinking water and aquatic life), copper (drinking water and aquatic life), cyanide, nickel (drinking water and aquatic life), fecal and total coliforms, fluoride. Accredited laboratory: aluminum, copper (aquatic life), iron (drinking water and aquatic life), manganese (drinking water, barely), chromium, zinc (aquatic life), lead, vanadium.
- **Additional comments:** Zapalito had the worst water quality (using results from accredited lab); results were not compared to aquatic life criteria; the only exceedences (using accredited lab) of concern are copper (for aquatic life only) at several locations, and chromium, lead, and zinc for aquatic life at Zapalito.
-

4. Recommendations

As the studies move forward, the following improvements should be instituted to resolve the analytical and study design issues: 1) sample water and sediment quality in upstream or tributary reaches that are not affected by mining activity; 2) sample more pits and direct discharges from informal mining operations and clearly identify contaminants of concern associated with mining; 3) improve data quality by preparing a detailed overall sampling and analysis plan, analyzing split samples for all contaminants of concern using the Potalab and the accredited laboratory, and ensuring that detection limits are substantially lower than the most sensitive water quality standards; and 4) measure or approximate stream flow at each location during each sampling event. In addition, the water quality, sediment quality, fish, and macroinvertebrate data collected for the studies should be assembled into an electronic database that is easily accessible to the public.

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Appendix A: Potalab Detection Limits

Palintest®

Leaders in Water Analysis Technology

The Photometer 7100 offers a precise means of water analysis Using an advanced solid-state digital readout colorimeter.

Photometer 7100

The new Photometer 7100 is fully integrated with the Palintest system of water analysis. It offers great value instrumental analysis for an extensive range of water tests.

NEW Test DEHA from 0.01 - 0.500 mg/l

NEW Test Boron from 0 - 2.5 mg/l

- Fully Waterproof with IP67 rating: It even floats
- Rugged, portable design with no moving parts
- Automatic method set up for each parameter
- Unique adaptive cell holder

The Photometer 7100 accurately assesses the colour formed in the test sample and displays the readings directly in concentration units on its large LCD screen – no more inaccurate results due to variation in operator eyesight or lighting conditions.

Not only does the Photometer 7100 have the whole range of Palintest tests available, it is also easily portable, and rugged in design. Its IP67 rating means it is fully waterproof- ideal for on-site testing in any application.

The unique adaptive cell holder automatically adjusts to the tube size, and accommodates any size vial with no adapter needed. The instrument interface comes with five languages built-in, and a large easy to read backlit display with easy to navigate menu.

The Photometer 7100 is part of the successful and versatile Palintest water test system. It is supplied in a carrying case designed to carry the instrument and reagents/accessories.

PT 740 **Standard Photometer 7100 Kit**
The Standard Photometer 7100 kit comprises a Photometer 7100 instrument, six glass test tubes and a dilution tube all contained in a moulded plastic carrying case. There is space to hold up to four reagent starter packs. Reagents sold separately

PT 742 **Engineers Photometer 7100 Kit**
The Engineers Photometer 7100 kit contains a Photometer 7100 instrument, eight glass test tubes, De-ion pack (de ionised water maker), dilution tube and sample container. Supplied in an aluminium reinforced carrying case with space to hold up to 15 different reagent starter packs. Reagents sold separately.

PT 804 **Check Standards for Photometer 7100**

PT 595/5 **Round Test Tubes, 10ml, pack of 5**

Technical Specifications

Instrument Type	Direct-reading colorimeter with automatic set-up and reading
Operating Wavelengths	450 nm, 500 nm, 550 nm, 570 nm, 600 nm and 650 nm
Display	Large Backlit graphic LCD screen
Accuracy	± 0.5% at 4% transmittance ± 0.005 at 0.3 AU
Resolution	0.001 AU
User Selectable Options	Display language (French, German, Spanish, English and Italian)Test units
Internal Memory	500 sample results stored with selective recall
Test Cells	Automatic adjustment for round test tubes from 12 - 20 mm diameter
Power	Battery power (3 x 'AA')
Size	W146 x D275 x H75 mm
Weight	975g
Instrument Rating	Waterproof IP67

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Reagents

TEST	RANGE (mg/l)	REAGENT STARTER PACKS (50 TESTS)	REAGENT REFILL PACKS (250 TESTS)
Alkalinity Total (Alkaphot)	10-500 ($CaCO_3$)	PM 188	AP 188
Alkalinity M (Alkaphot M)	10-500 ($CaCO_3$)	PM 250	AP 250
Alkalinity P (Alkaphot P)	10-500 ($CaCO_3$)	PM 251	AP 251
Aluminium	0.02-0.5	PM 166	AP 166
Ammonia	0.01-1.0 (N)	PM 152	AP 152
Boron	0-2.5 (B)	PM 190	AP 190-
Bromine	0.04-10.0	PM 060	AP 060
Calcium Hardness (Calcicol)	5-500 ($CaCO_3$)	PM 252	AP 252
Chloride (Chloridol)	0.5-50 (NaCl)	PM 268	AP 268
Chlorine DPD 1	0.01-5.0	PM 011	AP 011
Chlorine DPD 2	0.01-5.0	PM 021	AP 021
Chlorine DPD 1 & 3	0.01-5.0	PM 031	AP 031
Chlorine DPD 4	0.01-5.0	PM 041	AP 041
Chlorine HR (High Range)	1-250	PM 162	AP 162
Chlorine Dioxide (DPD)	0.2-9.5	PM 052	AP 052
Chlorine Dioxide LR (Low Range)	0.03-2.5	PM 064	AP 064
Chlorine Dioxide HR (High Range)	0.45-20	PM 065	AP 065
Chromium (VI) (Chromicol)	0.02-1.0	PM 281	AP 281
Copper (Coppercol) (free, combined, and total)	0.03-5.0	PM 186	AP 186
Copper (free)	0.03-5.0	-	AP 187
Colour/Turbidity	10-500 (Hazen units)	PM 269	-
Cyanuric Acid	2-200	PM 087	AP 087
DEHA	0.01-0.500	PM 275	AP 275
Dissolved Oxygen (0.8/vials)	0.02-0.8	PL 553†	PL 553/R†
Dissolved Oxygen (2.0/vials)	0.05-2.0	PL 503†	PL 503/R†
Dissolved Oxygen (20/vials)	0.2-20	PL 513†	PL 513/R†
Fluoride	0.1-1.5	PM 179	AP 179*
Hardness (Hardicol)	5-500 ($CaCO_3$)	PM 254	AP 254
Hydrazine	0.05-0.5	PM 103†	AP 103 •
Hydrogen Peroxide LR	0.02-2.0	PM 104	AP 104
Hydrogen Peroxide HR	1-100	PM 105	AP 105
Iron LR	0.01-1.0	-	AP 155
Iron HR	0.05-10	PM 156	AP 156
Iron MR	0.02-5.0	PM 292	AP 292
Magnesium (Magnecol)	2-100	PM 193	AP 193
Manganese	0.001-0.03	PM 173	AP 173
Manganese HR	0.02-5.0	PM 174	AP 174
Molybdate LR	0.2-15	PM 258	AP 258*
Molybdate HR	0.5-100	PM 175	AP 175
Nickel (Nickeltest)	0.12-10	PM 284	AP 284*
Nitrate (Nitratest)	0.2-20 N	PM 163	AP 163*
Nitrite (Nitricol)	0.01-0.5 N	PM 109	AP 109
Nitrite (Nitriphot)	10-1500 ($NaNO_2$)	PM 260	AP 260
Organophosphonate (OP)	0.2-20 (PO_4)	PM 262	AP 262
Ozone	0.01-2.0	PM 056	AP 056
pH (phenol red)	6.8-8.4	PM 130	AP 130
Phenol (Phenoltest)	0.07-5.0	PM 287	AP 287*
PHMB	2-100	PM 272	AP 272
Phosphate LR	0.03-4.0	PM 177	AP 177*
Phosphate HR	1-100	PM 114	AP 114
Potassium	0.5-12	PM 189	AP 189
Silica	0.02-4.0	PM 181	AP 181*
Silica HR	0.5-150	PM 290	AP 290*
Sulphate	5-200	PM 154	AP 154
Sulphide	0.01-0.5	PM 168	AP 168*
Sulphite (Sulphitest)	5-500 (Na_2SO_3)	PM 266	AP 266
Zinc	0.02-4.0	PM 148	AP 148

*200 tests - 160 tests • 150 tests † 30 tests