UNIVERSIDAD AUTÓNOMA DE MADRID

FACULTAD DE CIENCIAS

PROGRAMA DE DOCTORADO EN QUÍMICA AGRÍCOLA

# IMPACTO AMBIENTAL SOBRE SUELOS Y PLANTAS POR ACTIVIDADES EXTRACTIVAS EN LOS CONTENIDOS DE METALES PESADOS Y CIANURO EN LA ZONA MINERA DE REMANCE, PANAMÁ

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Tesis Doctoral Madrid, 13 de diciembre de 2021

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**Tesis Doctoral 2021**

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CERTIFICAN:

Que el trabajo presentado por Doña ANA CRISTINA GONZÁLEZ VALOYS, Licenciada en Tecnología Química Industrial y Magister en Ciencias con Especialización en Ingeniería Ambiental, constituye un trabajo original de investigación y que ha sido realizado bajo nuestra dirección.

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La presente tesis doctoral se ha realizado bajo el auspicio de la Secretaría Nacional de Ciencias, Tecnología e Innovación (SENACYT) y del Instituto para la Formación y Aprovechamiento de los Recursos Humanos (IFARHU) de la República de Panamá, bajo el Programa de Doctorado y Postdoctorado de Investigación, código BIDP-II-2018-002, contrato n° 270-2019-109. Al igual que con la colaboración de la Universidad Tecnológica de Panamá, de la Universidad Autónoma de Madrid, de la Escuela Técnica Superior de Ingenieros Agrónomos (ETSIA) de Ciudad Real, y del Instituto de Geología Aplicada (IGeA) de la Universidad de Castilla - La Mancha.

Para realizar el trabajo de la presente tesis se han disfrutado estancias en la Universidad Tecnológica de Panamá (UTP), quienes han colaborado con el trabajo de campo en la zona minera de Remance, Veraguas, y también con la colaboración del uso de laboratorios para el desarrollo de ensayos, estos son:  Laboratorio de Suelos de la Facultad de Ingeniería Civil, Laboratorio de Ciencias Ambientales y Análisis Industriales (LABAICA), Laboratorio de Geotecnia (LABGEO) del Centro Experimental de Ingeniería (CEI), y la colaboración del Centro de Investigaciones Hidráulicas e Hidrotécnicas (CIHH).

Las estancias en la UTP se fecharon del 17 de mayo al 13 septiembre de 2019 (primera fase del muestreo y de análisis fisicoquímicos), y del 13 de enero al 28 de febrero de 2020 (segunda fase del muestreo y de análisis fisicoquímicos). Así mismo se efectuaron estancias de investigación en la Universidad de Castilla - La Mancha para la realización de ensayos geoquímicos desde el 24 de septiembre al 13 de diciembre de 2019, y desde el 9 de marzo de 2020 hasta el presente, en la Escuela Técnica Superior de Ingenieros Agrónomos de Ciudad Real (Laboratorios de Química Agrícola y de Edafología) y en el Instituto de Geología Aplicada (IGeA) de Almadén (Laboratorio de Biogeoquímica Ambiental).

## DEDICATORIA

A Dios quien me ha dado las fuerzas para afrontar este reto, sin Él nada soy, ha sido mi fiel compañero en todo momento, especialmente en los más difíciles.

A mis padres, Ana y Marcial, que han sido mi sostén físico, moral y espiritual, dándome su respaldo incondicional.

A mis amados hijos Cristhine Mariam y Efraín Samuel, quienes han sido comprensivos en el sacrificio del tiempo juntos, y son mis compañeros de viaje.

A mis hermanos Laura, Félix, Miriam, mis sobrinos Daybeth, Luis, Laura, Reyna y Miriam que han sido mi equipo de trabajo, todos colaborando para lo que ha sido necesario.

A Jonatha que aún a la distancia está pendiente de mí, y ha colaborado en lo que ha tenido a su alcance.

A todos aquellos amigos y familiares que siempre me han dado ánimos de continuar.

# AGRADECIMIENTOS

Mis agradecimientos a la Secretaría Nacional de Ciencias, Tecnología e Innovación (SENACYT) y al Instituto para la Formación y Aprovechamiento de los Recursos Humanos (IFARHU) de la República de Panamá, quienes me han otorgado la beca para realizar los estudios de doctorado en Química Agrícola en la Universidad Autónoma de Madrid (UAM), a la UAM por aceptarme dentro del programa de doctorado.

Al Dr. Raimundo Jiménez Ballesta, quien aceptó ser mi tutor, por todos sus ánimos, confianza y consejos, que siempre me instaron a avanzar y culminar. Quien a pesar de haberse acogido a su jubilación ha seguido su tutoría para conmigo, y colaboración en la preparación de publicaciones científicas.

A la Dra. Rosario García Giménez, quien ante la jubilación del Dr. Raimundo en el año 2020, aceptó ser mi tutora a petición de él, y ha estado siempre dispuesta a colaborar y a resolver mis dudas.

Al Dr. Francisco Jesús García Navarro, co-director de tesis, y de quien nunca me ha faltado su apoyo, palabras de ánimo, y colaboración en el proyecto de tesis.

Al Dr. Pablo Higueras, mi director de tesis, quien me acogió en mi estancia en la Universidad de Castilla La Mancha, siempre está atento a cualquier consulta, y a compartir sus conocimientos. También me ha hecho parte del Instituto de Geología Aplicada (IGeA), Institución que él dirige. Y ha sido un excelente director de tesis para conmigo, con todo su conocimiento y experiencia, por lo cual me siento honrada.

A la Universidad de Castilla La Mancha (UCLM), y a todos los que han contribuido en mi formación y aprendizaje. Al Dr. José María Esbrí por su guía en la conceptualización de los manuscritos y enseñanza en el tratamiento de la data, a la Dra. Eva María García Noguero por todo el apoyo en la parte química del laboratorio, al Dr. Juan Antonio Campos y al Dr. Jesús Peco por toda la colaboración con los ensayos de actividad enzimática del suelo, a la Dra. Sandra Bravo por sus enseñanzas en edafología y ensayos de laboratorio, a Sofía Rivera, Sandra Viso y todos aquellos que de alguna manera han contribuido a este trabajo de tesis doctoral, o dado su empatía durante mi estancia en la UCLM.

Al Dr. Efrén Garcia Ordiales de la Universidad de Oviedo por su colaboración al proyecto de tesis, y que con su experiencia siempre nos orienta.

A la Universidad Tecnológica de Panamá (UTP) por ser la Institución de respaldo de la Investigación en Panamá, al Vicerrector de Investigación, Posgrado y Extensión, Dr. Alexis Tejedor por todas sus gestiones para el proyecto de tesis ante las autoridades. Al Dr. Miguel

Vargas “profesor escalera” que creyó en mí, ha sido mi mentor en este camino de estudiar el doctorado y me dio las primeras clases de escritura de un artículo científico, preparación base que me ha sido de mucha utilidad. A la Profesora Dra. Tisla de Destro quién me acogió dentro de su equipo de investigación “Propuesta de Geoparque Puente De Las Américas” abriendo así las puertas de los laboratorios de la UTP y todo lo que ha sido necesario para este proyecto de tesis dentro de la UTP. A los Ingenieros Rita Rodríguez y Ernesto Martínez, miembros del grupo de investigación Propuesta de Geoparque Puente De Las Américas, que junto al Profesor Dr. Eric Gutiérrez me ayudaron en el proceso de lograr el acceso a la Mina de Remance, planificar la logística del trabajo de campo y ejecutarlo en Remance. Al Magister José Ulises Jiménez por su colaboración con la parte botánica para identificar las plantas de la Mina de Remance. Al Lic. Jonatha Arrocha por su colaboración con el trabajo de campo y de laboratorio para procesar las muestras. Y a todas aquellas personas dentro de la UTP que no dudaron en brindarme su apoyo.

A la Dirección Nacional de Recursos Minerales del Ministerio de Comercio e Industrias (MICI), por otorgarnos el acceso a la zona de reserva minera de Remance. Dentro de esta institución agradecemos a su director el Ing. Jaime Pashalles, al Ing. Temístocles Velarde y la Dra. Xenia Ríos, por sus gestiones para otorgarnos el permiso de acceso a la mina. A la Lic. Dania Franco y al Técnico José Rangel por el apoyo brindado para el trabajo de campo en la mina de Remance.

A mi familia que participaron del trabajo de campo, a Félix González, Luis González, Marcial González, Daybeth González y Dayra Sánchez. A la Ing. Eufemia Lam que nos acompañó al campo. A la comunidad de Remance y la Utiria que nos acogieron durante el tiempo del trabajo de campo, de manera especial al señor Doroteo Concepción y Francisco Hernández, que fueron nuestros guías en la zona de la mina, y a la señora Mariana Cruz Pardo que nos acogió en su hogar.

A todos muchas gracias.

# RESUMEN

La mina de oro de Remance, ubicada en la Provincia de Veraguas, en Panamá, ha sido explotada de manera intermitente desde los años 1800, por diversas compañías (Nelson y Ganoza, 1999). La última compañía en disfrutar la concesión minera fue Minera Remance S.A., quien la operó durante los años 1989 a 1999 (Nelson y Ganoza, 1999), empleando el proceso de cianuración para extraer el precioso metal (Gómez, 2008). Producto de la última actividad minera han quedado expuestos al medio ambiente tres relaves conteniendo desechos mineros con elementos potencialmente tóxicos (EPTs) y cianuro, y una bocamina que mana agua subterránea y aporta sedimentos (González-Valoys et al., 2021a). En la zona de actividad minera y sus alrededores viven actualmente campesinos, quienes también desarrollan actividades de subsistencia como la agricultura y la ganadería, además de desarrollarse actividades recreativas (González-Valoys et al., 2021b).

El objetivo del presente estudio como trabajo de Tesis Doctoral ha sido evaluar el grado de afectación del suelo por la actividad minera en relación a la concentración de metales pesados y de cianuro en la zona de la mina de oro de Remance. Para ello se caracterizaron los parámetros fisicoquímicos relativos al laboreo minero y sus alrededores; se determinó la concentración de elementos potencialmente tóxicos y de cianuro; se midieron parámetros biogeoquímicos relacionados con la calidad y salud del suelo; y se recolectaron plantas comestibles y no comestibles para determinar la afectación de la flora del lugar, y la biodisponibilidad de los elementos potencialmente tóxicos. Con los datos obtenidos se determinó el grado de contaminación de la zona, el potencial riesgo ecológico para la biota, y se evaluó el riesgo a la salud humana no carcinogénico y carcinogénico, levantándose mapas temáticos que servirán como base de información para el plan de restauración y remediación que se recomienda establecer en toda la región.

El estudio muestra que los relaves y la bocamina de la zona de Remance, a más de 20 años del cese de operaciones de la actividad minera y por su contenido en elementos potencialmente tóxicos (EPTs) como Cu, Zn, As, Sb, Ba y Hg, y su contenido en cianuro total, constituyen un foco de contaminación para el entorno, llegando a representar un riesgo ecológico para la biota local.

Las zonas descritas son un foco de contaminación para el área del entorno, siendo mayormente afectados los sedimentos y terrazas de arroyos, ya que sobre ellos descargan los relaves, y los sedimentos de la bocamina. Le siguen en grado de afectación los suelos de labores mineras, los sedimentos de las lagunas de cianuración y los suelos de las zonas cercanas; lo cual es corroborado con el indicador de la salud del suelo, donde el suelo tiene mayor actividad enzimática por deshidrogenasa (DHA) que los sedimentos de arroyos y terrazas. Estas zonas representan riesgos ecológicos para la biota y efectos nocivos a la salud humana por su riesgo no carcinogénico y carcinogénico. Desde el punto de vista sanitario, el

As es el principal contaminante para el riesgo no carcinogénico, y As y Cu para el riesgo carcinogénico, en ambos casos por ingesta accidental y contacto dérmico. Siendo más afectados los niños que los adultos, y el peor escenario, el relativo a la zona residencial para niños, y para los adultos el residencial y el agrícola (González-Valoys et al., 2021b). El As es el contaminante de mayor relevancia, debido a su potencial riesgo de generar cáncer de piel, hígado y pulmón (Bini y Wahsha, 2014).

El estudio de la flora muestra que las plantas están absorbiendo del suelo elementos potencialmente tóxicos (EPTs) como As, Hg, Cu y Zn en grado que varía de débil a fuerte absorción. Los elementos que se encontraron en mayor concentración total en el suelo son As y Cu, siendo el Cu más biodisponible y más absorbido por las plantas, mientras que las plantas parecen poseer mecanismos para excluir el As, aunque el mismo aumente su biodisponibilidad. El Zn y Cu existentes en el pasto (*Poaceae morfoespecie*) y plantas de Remance sobrepasan los requerimientos recomendados para la nutrición animal de rumiantes. Desde el punto de vista de la afectación a la salud humana y las plantas comestibles, el Sb es el elemento potencialmente tóxico que representa riesgo no carcinogénico, mientras que el Cu y As se relacionan como el principal riesgo carcinogénico en las plantas comestibles como arroz, maíz, yuca y hojas de té, las cuales forman parte de la dieta diaria de los campesinos locales (González-Valoys et al., 2021c).

Del compendio del estudio y las publicaciones científicas, se hace notorio que la zona de la mina de Remance requiere de un plan de remediación, para minimizar la contaminación, los riesgos ecológicos sobre la biota, y sobre la salud humana, siendo este estudio la base y caracterización para futuras acciones de remediación de la zona.

## ABSTRACT

The Remance gold mine, located in the Province of Veraguas in Panama, has been operated intermittently since the 1800s by several mining companies (Nelson and Ganoza, 1999). The last company to enjoy the mining concession was Minera Remance S.A., which operated it from 1989 to 1999 (Nelson and Ganoza, 1999), using the cyanidation process to extract the precious metal (Gómez, 2008). As a result of the last mining activity, three tailings containing mining waste with potentially toxic elements (PTEs) and cyanide, and a mine pithead that leaks groundwater and contributes sediments have been exposed to the environment (González-Valoys et al., 2021a). The mining area and its surroundings are currently inhabited by farmers, who also carry out subsistence activities such as agriculture and cattle ranching, as well as recreational activities (González-Valoys et al., 2021b).

The objective of the present study as a Doctoral Thesis work has been to evaluate the degree of soil affectation by the mining activity in relation to the concentration of heavy metals and cyanide in the area of the Remance gold mine, Panama. For this purpose, the physicochemical parameters related to the mine workings and its surroundings were characterized; the concentration of potentially toxic elements (PTEs) and cyanide were determined; biogeochemical parameters related to soil quality and health were measured; and edible and non-edible plants were collected to determine the impact on the local flora and the bioavailability of potentially toxic elements (PTEs). The data obtained were used to determine the degree of contamination of the area, the potential ecological risk to biota, and to evaluate the non-carcinogenic and carcinogenic risk to human health, creating thematic maps that will serve as the basis of information for the restoration and remediation plan recommended for the entire region.

The study shows that the tailings and pithead sediments the Remance area's, more than 20 years after the cessation of mining operations and due to their content of potentially toxic elements (PTEs) such as Cu, Zn, As, Sb, Ba and Hg, and their total cyanide content, constitute a source of contamination for the environment, representing a serious ecological risk for local biota.

The areas described are a source of contamination for the surrounding area, with the stream sediments and terrace sediments being the most affected, as the tailings and pithead sediments are discharged on them. It is followed in degree of affectation by the soils of mining areas, the sediments of the cyanidation ponds and the soils of the surrounding areas; this is corroborated by the soil health indicator, where the soil has higher enzymatic activity by dehydrogenase (DHA) than the stream sediments and terrace sediments. These areas represent ecological risks to biota and harmful effects to human health due to their non-carcinogenic and carcinogenic risk. From the health point of view, As is the main contaminant for the non-carcinogenic risk, and As and Cu for the carcinogenic risk, in both cases by

accidental ingestion and dermal contact. Children are more affected than adults, and the worst-case scenario is the residential area for children, and for adults the residential and agricultural areas (González-Valoys et al., 2021b). As is the contaminant of greatest relevance, due to its potential risk of generating skin, liver and lung cancer (Bini and Wahsha, 2014).

The study of the flora shows that plants are absorbing potentially toxic elements (PTEs) such as As, Hg, Cu and Zn from the soil to a degree varying from weak to strong absorption. The elements that were found in higher total concentration in the soil are As and Cu, with Cu being more bioavailable and more absorbed by plants, while plants seem to possess mechanisms to exclude As, even though As increases its bioavailability. The Zn and Cu in the grass (Poaceae morphospecies) and plants of Remance exceed the recommended requirements for animal nutrition of ruminants. From the point of view of human health and edible plants, Sb is the potentially toxic element that represents a non-carcinogenic risk, while Cu and As are related as the main carcinogenic risk in edible plants such as rice, corn, cassava and tea leaves, which are part of the daily diet of local farmers (González-Valoys et al., 2021c).

From the compendium of the study and scientific publications, it is clear that the Remance mine area requires a remediation plan to minimize contamination, ecological risks to biota and human health, and this study will be the basis and characterization for future remediation actions in the area.

## INDICE GENERAL

# INTRODUCCIÓN

# 1 INTRODUCCIÓN

La minería se hace necesaria para el desarrollo de la sociedad actual, aún las tecnologías limpias o verdes que se proponen como alternativa para reemplazar las fuentes de combustibles fósiles y disminuir el calentamiento global hacen uso de metales (Swann, 2021). Todas estas tecnologías, tales como paneles solares, aerogeneradores, automóviles eléctricos, y otras que se han vuelto indispensables para la vida moderna (teléfonos inteligentes, tabletas y dispositivos médicos), requieren del servicio de la minería (Swann, 2021). El problema lo constituye la minería desarrollada de manera no sustentable, y/o donde la etapa de cierre y remediación del área es deficiente o nula (O'Faircheallaigh & Corbett, 2016), creando con esto un foco de contaminación para el medio ambiente, que implica riesgos ecológicos y sanitarios (González-Valoys et al., 2021b).

## 1.1. La Mina de oro de Remance y los riesgos ambientales asociados a la actividad minera

La existencia de metales preciosos y su mineralización está frecuentemente ligada a la presencia de metales pesados como As, Hg, Cu, Zn, entre otros (Nordstrom, 2015), exponiéndose al medioambiente al ser explotados. Influye también el tipo de procesado empleado, con la exposición de contaminantes y residuos que se hacen presentes en suelo, agua, sedimentos y aire (Higueras et al., 2004; Bueno et al., 2009; García-Giménez & Jiménez-Ballesta, 2017; Pavoni et al., 2018). Por lo cual pueden tener efectos nocivos sobre el medio ambiente y la salud humana (Lillo et al., 2015), según la concentración en que se encuentren.

La Mina de Remance ha producido oro de manera intermitente desde los años 1800 (Nelson & Ganoza, 1999). La extracción y beneficio de oro en Remance en el último periodo (1989-1999) se realizó de manera híbrida por métodos subterráneos y a cielo abierto, a través del proceso de cianuración (Nelson & Ganoza, 1999). En la zona existen tres relaves expuestos a las condiciones ambientales, como el viento y la escorrentía, y que desembocan a la red hídrica que atraviesa el área. En la mina y sus alrededores viven campesinos que desarrollan actividades de subsistencia, como la agricultura y la ganadería. Si la zona no ha sido remediada adecuadamente, los elementos potencialmente tóxicos y los complejos cianurados formados en los relaves pueden contaminar suelos cercanos (Jaszczak, 2017). Ante esta situación se hace necesaria la caracterización geoquímica de la zona de labores mineras y sus alrededores, de la red hídrica que recorre la zona, y de la flora local, para determinar la concentración de los elementos potencialmente tóxicos y de cianuro, y así evaluar el grado de contaminación de cada zona, la salud del suelo, los potenciales riesgos ecológicos que representan a la biota, y sanitarios, a más de 20 años del cese de las actividades mineras.

Este tipo de estudio no se había realizado en la zona, y será de utilidad para futuros planes de remediación sobre el área donde viven campesinos y se desarrollan labores agrícolas. Por otra parte, el modelo de estudio puede ser replicable en otras regiones de laboreo minero dentro del país, que han sido abandonadas y carentes de las medidas adecuadas de cierre o remediación. La metodología empleada para el estudio es replicable también para el levantamiento de una línea base antes de desarrollar la actividad minera, y establecer estándares para labores de remediación. Este es un tema de gran interés para la sociedad panameña, ya que recientemente el Gobierno de Panamá ha reactivado la concesión minera sobre la Mina de Remance, y se encuentra en negociación de otras concesiones mineras en el país. La comunidad de Remance y grupos cívicos del país están alerta, no queriendo que se repita el escenario del mal manejo de los desechos mineros.

## 1.2. Objetivos y planteamiento del estudio

El Objetivo de la investigación es desarrollar un estudio de suelo de la mina abandonada de Remance, que arrojará una caracterización del sitio que permitirá evaluar el grado de afectación de los suelos por la actividad minera, y valorar las medidas de control y/o restauración que eventualmente consideren adecuadas para minimizar efectos indeseados en los ecosistemas de la zona.

**Objetivo General:**
Analizar la concentración de metales pesados en la zona de la mina de Remance y sus alrededores, en suelos y sedimentos; y evaluar el grado de afectación de los suelos del área de estudio por la actividad minera. También se determinará la calidad del suelo, mediante la medida de parámetros biogeoquímicos.

**Objetivos Específicos**:
a) Caracterizar los parámetros edáficos del área de la Mina de Remance, y sus alrededores.
b) Determinar la concentración de metales mayoritarios, minoritarios y trazas en la zona de la Mina de Remance.
c) Determinar parámetros biogeoquímicos relacionados con la calidad del suelo del área afectada por la actividad minera.
d) Elaborar mapas temáticos de la zona en el Sistema de Información Geográfica (SIG) sobre los parámetros analizados.

## 1.3. Publicaciones derivadas de la tesis y otras publicaciones

A raíz de este proyecto de Tesis Doctoral, y para cubrir los objetivos planteados en el plan de investigación se realizó el trabajo de campo en la zona de la mina de oro de Remance, y los ensayos de laboratorio necesarios, de manera que hemos producido tres publicaciones científicas en revistas científicas de alto impacto, cuartil Q1, siendo las siguientes:

- González-Valoys, A.C., Arrocha, J., Monteza-Destro, T., Vargas-Lombardo, M., Esbrí, J.M., Garcia-Ordiales, E., Jimenez-Ballesta, R., García-Navarro, F.J., Higueras, P., 2021. Environmental challenges related to cyanidation in Central American gold mining; the Remance mine (Panama). Journal of Environmental Management, 302 (2022) 113979. https://doi.org/10.1016/j.jenvman.2021.113979
  En esta primera publicación se caracterizaron los parámetros fisicoquímicos, los elementos potencialmente tóxicos, y el cianuro total, sobre las zonas de los relaves, los sedimentos de la bocamina, las lagunas de cianuración y suelos cercanos a estas lagunas, para determinar el grado de contaminación de cada una y el potencial riesgo ecológico que representa para la biota. A la vez que se estableció el orden de prioridad de las zonas a tratar para un futuro plan de remediación.
- González-Valoys, A.C., Esbrí, J.M., Campos, J.A., Arrocha, J., García-Noguero, E.M., Monteza-Destro, T., Martínez, E., Jiménez-Ballesta, R., Gutiérrez, E., Vargas-Lombardo, M., et al., 2021. Ecological and Health Risk Assessments of an Abandoned Gold Mine (Remance, Panama): Complex Scenarios Need a Combination of Indices. Int. J. Environ. Res. Public Health 2021, 18, 9369. https://doi.org/10.3390/ijerph18179369
  En esta segunda publicación se complementa el primer estudio, ampliándolo a los suelos de labores mineras, suelos alrededor de la mina, y los sedimentos de los arroyos y de las terrazas, para determinar el grado de afectación de estos. Además de determinar la salud del suelo y zonas del entorno, con esta data se generaron mapas temáticos de la concentración de elementos potencialmente tóxicos, mapas de contaminación, de potencial riesgo ecológico, y de riesgos sanitarios no carcinogénico y carcinogénico en niños y adultos dentro de la zona de estudio.
- González-Valoys, A.C., Jiménez Salgado, J.U., Rodríguez, R., Monteza-Destro, T., Vargas-Lombardo, M., García-Noguero, E.M., Esbrí, J.M., Jiménez-Ballesta, R., García-Navarro, F.J., Higueras, P., 2021. An approach for evaluating the bioavailability and risk assessment of potentially toxic elements using edible and inedible plants – the Remance (Panama) mining area as a model. Environmental Geochemistry and Health, Environ Geochem Health, https://doi.org/10.1007/s10653-021-01086-8
  En esta tercera publicación se estudió la flora del lugar, en plantas no comestibles y comestibles, se determinó la biodisponibilidad de los elementos potencialmente tóxicos mayoritarios, el grado de absorción en las plantas, y sobre las plantas comestibles se determinó el riesgo a la salud humana no carcinogénico y

carcinogénico por el consumo de dichos alimentos.

Resultados parciales del estudio fueron presentados en congresos y encuentros de investigación, generando las siguientes publicaciones:

- González-Valoys, A., Garcia-Ordiales, E., Vargas-Lombardo, M., Arrocha, J., Monteza-Destro, T., Esbrí, J.M., Jiménez-Ballesta, R., García-Navarro, F.J., Higueras, P., 2021. Riesgos ambientales asociados a la gestión inadecuada de residuos mineros en una explotación minera de oro, Remance, Panamá. Revista de la Sociedad Española de Mineralogía, MACLA, 2021, 25, 36-37, ISSN 2659-9864.
- González Valoys, A.C., Monteza-Destro, T., Esbrí, J.M., Vargas-Lombardo, M., Garcia-Ordiales, E., Arrocha, J., Jiménez-Ballesta, R., Garcia-Navarro, F.J., Higueras, P., 2021. Risks associated with the presence of cyanide in waste materials in an abandoned gold mine, Panama. EGU General Assembly 2021, EGU21-8236, DOI: 10.5194/egusphere-egu21-8236

A su vez que se desarrollaba la Tesis Doctoral, junto a mis directores y primer tutor, trabajamos las siguientes publicaciones científicas con un trabajo de investigación previo:

- González-Valoys, A.C., Vargas-Lombardo, M., Higueras, P., García-Navarro, F.J., Garcia-Ordiales, E., Jiménez-Ballesta, R., 2021. Hydrochemistry of groundwater from Tocumen sector, Panamá city: an assessment of its possible usage during emergency events. Environmental Earth Sciences 80, 176 (2021). https://doi.org/10.1007/s12665-021-09497-7
- González-Valoys, A.C., Vargas-Lombardo, M., Jiménez-Ballesta, R., Arrocha, J., Gutiérrez, E., Garcia-Ordiales, E., Cienfuegos, P., García-Navarro, F.J., Higueras, P., 2021. Characterization of Soil and Rock Hosting an Aquifer in Southeast Panama City using Geotechnical, Geophysical and Geochemical Parameters. Environmental Earth Sciences, 2021, bajo revisión, en fase de resolución de revisión menor.

# ENVIRONMENTAL CHALLENGES RELATED TO CYANIDATION IN CENTRAL AMERICAN GOLD MINING; THE REMANCE MINE (PANAMA)

Journal of Environmental Management 302 (2022) 113979

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

# Environmental challenges related to cyanidation in Central American gold mining; the Remance mine (Panama)

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ARTICLE INFO

*Keywords:*
Tailings
Potentially toxic elements (PTEs)
Total cyanide
Environmental assessment
Gold mine
Panama

ABSTRACT

Mine tailings are a potential source of environmental pollution because they typically contain potentially toxic elements (PTEs) and the residue of chemical compounds used during extraction processes. The Remance gold mine (NW Panama) is a decommissioned mine with mining activity records dating from the 1800s and several periods of abandonment. Very little remediation work has been performed, and waste is exposed to climatic conditions. This study aimed to evaluate the PTEs and cyanide contents in mine waste after mining operations ceased some 20 years ago, and to evaluate the degree of pollution and the environmental risks they pose with the use of the Pollution Load Index (PLI) and the Ecological Risk Index (RI). Although the total cyanide (T-CN) concentration (1.4–1.9 mg kg$^{-1}$) found in most of the study area falls within the limits of gold mining tailing values for American sites (1.5–23 mg kg$^{-1}$), it is worth noting that the values of the tailings of the last used mining operation exceed it (25.2–518 mg kg$^{-1}$) and persist at the site. The PLI and RI suggest that the tailings from the mine and mine gallery sediments represent a source of pollution for soils and surrounding areas given their high content of PTEs (As, Cu, Sb, Hg) and T-CN, which pose serious ecological risks for biota. Therefore, it is necessary to draw up a remediation plan for this area.

## 1. Introduction

Gold mining is perhaps the most widespread and most practiced mining type in the world, performed by large mining companies and small groups of miners. These mining operations work with very low mineral/waste ratios and produce large volumes of waste after concentration processes. These concentration processes often employ compounds with a high toxic environment potential, such as cyanide compounds or Hg, which are also used inefficiently in Indonesia, Colombia, Brazil, Ecuador, Ghana, among other countries (Velásquez-López et al., 2011; Seccatore et al., 2014; García et al., 2015; Clifford, 2017). Gold mining production depends on mining technology and efficiency, and the highest levels are mined in South America, with intermediate levels in Asia and Central America, and low levels in Africa (Seccatore et al., 2014). The degree of pollution produced by a gold mining operation depends on the nature and composition of the extracted minerals (Kyle et al., 2011, 2012; Luque-Almagro et al., 2016), the extraction process (Higueras et al., 2004; Olobatoke and Mathuthu, 2016) and the taken remediation measures, which are often inadequate or insufficient (O'Faircheallaigh and Corbett, 2016). Gold appears in

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https://doi.org/10.1016/j.jenvman.2021.113979
Received 15 June 2021; Received in revised form 22 September 2021; Accepted 17 October 2021

# 2 ENVIRONMENTAL CHALLENGES RELATED TO CYANIDATION IN CENTRAL AMERICAN GOLD MINING; THE REMANCE MINE (PANAMA)

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## Abstract

Mine tailings are a potential source of environmental pollution because they typically contain potentially toxic elements (PTEs) and the residue of chemical compounds used during extraction processes. The Remance gold mine (NW Panama) is a decommissioned mine with mining activity records dating from the 1800s and several periods of abandonment. Very little remediation work has been performed, and waste is exposed to climatic conditions. This study aimed to evaluate the PTEs and cyanide contents in mine waste after mining operations ceased some 20 years ago, and to evaluate the degree of pollution and the environmental risks they pose with the use of the Pollution Load Index (PLI) and the Ecological Risk Index (RI). Although the total cyanide (T-CN) concentration (1.4 - 1.9 mg kg$^{-1}$) found in most of the study area falls within the limits of gold mining tailing values for American sites (1.5- 23 mg kg$^{-1}$), it is worth noting that the values of the tailings of the last used mining operation exceed it (25.2-518 mg $kg^{-1}$) and persist at the site. The PLI and RI suggest that the tailings from the mine and mine gallery sediments represent a source of pollution for soils and surrounding areas given their high content of PTEs (As, Cu, Sb, Hg) and T-CN, which pose serious ecological risks for biota. Therefore, it is necessary to draw up a remediation plan for this area.

**Keywords**: Tailings, potentially toxic elements (PTEs), total cyanide, environmental assessment, gold mine, Panama.

## 2.1. Introduction

Gold mining is perhaps the most widespread and most practiced mining type in the world, performed by large mining companies and small groups of miners. These mining operations work with very low mineral/waste ratios and produce large volumes of waste after concentration processes. These concentration processes often employ compounds with a high toxic environment potential, such as cyanide compounds or Hg, which are also used inefficiently in Indonesia, Colombia, Brazil, Ecuador, Ghana, among other countries (Velásquez-López et al. , 2011; Seccatore et al., 2014; García et al., 2015; Clifford, 2017). Gold mining production depends on mining technology and efficiency, and the highest levels are mined in South America, with intermediate levels in Asia and Central America, and low levels in Africa (Seccatore et al., 2014). The degree of pollution produced by a gold mining operation depends on the nature and composition of the extracted minerals (Kyle et. al, 2011; Kyle et al. 2012; Luque-Almagro et al. 2016), the extraction process (Higueras et al., 2004; Olobatoke & Mathuthu, 2016) and the taken remediation measures, which are often inadequate or insufficient (O'Faircheallaigh & Corbett, 2016). Gold appears in ores with other elements like metals and metalloids, which can be an environmental concern when mining operations spread them in the environment (Drace et al., 2016; Pavoni et al., 2018; García-Lorenzo et al., 2019; Elmayel et al., 2020).

Mine tailings are focal pollution points for surroundings, and often contain high levels of metals and metalloids, e.g., Fe, Cu, Zn, As, Sb, Cd, Hg, Pb (Eisler & Wiemeyer, 2004; Shaw et al., 2006; Donato et al., 2007; Veiga et al.,2014; García-Lorenzo et al., 2019; Basri et al., 2020). They are generally considered to be potentially toxic elements (PTEs) (Hooda 2010), and environmental factors like rain, wind and erosion lead to the mobilisation of metals and waste (Meeussen et al., 1992; Hilson & Murck, 2001; García-Giménez & Jiménez-Ballesta, 2017; Ramappa & Muniswamy, 2018). Soil and sediment properties, such as pH, texture, clay minerals, Fe and Al oxyhydroxides, among others, play a crucial role in the geochemical mobility of toxic metals in areas affected by gold mining (Palansooriya et al., 2020). This problem is combined with the fact that most ore-processing companies use one of the most toxic chemical products, cyanide, to leach out the valuable elements contained in mined ore (Shaw et al., 2006; Donato et al., 2008; Ramappa & Muniswamy, 2018; Anning et al., 2019). These mines require solution-processing ponds that contain alkaline waters, and high concentrations of sodium cyanide, free cyanide and metal-cyanide complexes (Donato et al., 2008). Given their cyanide content, these water bodies are an environmental risk, which is compounded in the event of accidental spillages in rivers and streams because cyanide volatilises at a high rate and releases hydrogen cyanide to air (Brüger et al., 2018). This process potentially affects agricultural areas, plants and groundwater, and also poses a risk for human and animal health (Khan et al., 2020).

The cyanide types typically found in gold mine tailings are free cyanide ($HCN$, $CN^-$), which is easily released, weak acid dissociable (WAD) cyanide (Cu, Ni, Zn) (these complexes are unstable and break up, and free cyanide is released into the environment) and stronger cyanide complexes (Au, Co, Fe), which do not release cyanide, but decompose slowly and are stabler than WAD cyanides in sunlight and under strongly acid conditions (Meeussen et al., 1992; Anning et al., 2019). Cyanide at low concentrations in soil can biodegrade in the presence of nitrifying bacteria, but higher concentrations caused by anthropogenic activities, such as manufacturing industries, the application of herbicides and mining operations, impact both soil and the environment (ATSDR, 2006). Cyanide is harmful for human health, even at low concentrations, and over long periods. The workers who breathe in small amounts of hydrogen cyanide, i.e., between 6 and 10 mg $m^{-3}$, for a lengthy period can have breathing difficulties, chest pains, vomiting, changes in blood, headaches and enlarged thyroid gland. Breathing high concentrations causes death, and skin that comes into contact with hydrogen cyanide and cyanide salts can be irritated with sores (ATSDR, 2006).

In light of all this, the present study aimed to assess the implications of the contents of PTEs and total cyanide that remain in Remance gold mine tailings in Panama more than 20 years after the mining company shut down its operations. The obtained information was used to evaluate the pollution risks for the environment, which were evaluated with the use of the Pollution Load Index (PLI) and the Ecological Risk Index (RI). It was hypothesized that the remaining amounts of these pollutants still pose risks for both human health and the environment. Therefore, this study lays the basis to establish remediation plans in the area.

## 2.2. Materials and Methods

### 2.2.1. Study Area

The Remance mine belongs to the gold-rich strip of the Veraguas province in Panama and corresponds to an epithermal gold deposit hosted on a bed of pyroclastic rocks. The hydrothermal alteration covers an area of 10 $km^2$, and gold is found in veins as either small inclusions in pyrite and marcasite ($FeS_2$) or free gold disseminated within quartz, with small amounts of accessory minerals in the form of chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS) and arsenopyrite (FeAsS) (Nelson & Ganoza, 1999). The geochemical surveys conducted by the company Minera Remance S.A. have revealed high levels of PTEs in the area, including Au, Ag and As, as well as localised Hg and anomalous amounts of Sb (Nelson & Ganoza, 1999). The deposit comprises a system of veins, in which the principal vein contains the biggst ore quantities, along with minor, but important, veins like Santa Rosa and Consuelo, which are subterranean and have sporadic outcrops (Nelson & Ganoza, 1999). The mine was mainly operated on a subterranean basis during intermittent periods between 1800 and 1999 by three different companies (Nelson & Ganoza, 1999), and the relatively rudimentary technology employed in the process, at least by the last company, resulted in low production levels and major environmental problems (Hughes-Ortega, 1998). The features that are still visible in the mine area are two mine galleries and one mine shaft, as well as accumulated waste, which includes mine sterile rock (dumps) and dams that, in turn, include cyanidation process waste. These waste types have been exposed to local environmental effects related to the local tropical climate for at least the last two decades.

According to the Köppen climate classification map (Dirección de Hidrometeorología de ETESA, 2007), the local climate is the Ami type, a humid tropical climate with a monsoon influence, annual rainfall of > 2,250 mm, a dry season lasting 5 months and a lengthy rainy season. The study area presents a mountainous physiography with average slopes between 35-50% in the central elevated area, where the presence of loose materials from mineral processing with insufficient plant cover can increase the risk of these materials' erosion, and cause their transport to lower topographically areas during torrential rain periods.

While the company Minera Remance S.A. ran its operations between 1989 and 1999 (Nelson & Ganoza, 1999), the cyanidation process was used to extract the precious metal. It stated neutralising the sodium cyanide employed during the process with sodium hypochlorite. Over the years, three tailings ponds were utilised to contain the corresponding mine waste:

- Tailings Pond 1 (TP1): used from April 1990 to March 1992. This pond is located NW of the mining concession to one side of the so-called Veneno (poison in Spanish) stream, and stored approximately 75,000 tonnes of tailings, with a front wall measuring 27 m high (Gómez, 2008). The area has a plain relief and is now employed as a football ground

- Tailings Pond 2 (TP2): it is located NE of the mining concession at the head of the *Chitreca* stream and it stored 100,000 m$^3$ of waste material. This pond was employed from April 1992 to October 1994, when it was ordered to be closed as a result of a wall collapsing following an extreme precipitation event during the rainy season, which led to the *Chitreca* stream being polluted with mine waste material (Gómez, 2008).
- Tailings Pond 3 (TP3): it was built as a replacement following the collapse of TP2. This pond is located in the centre of the mining concession on the eastern hill slope where the '*Principal'* vein is found, and the area has a less pronounced slope than that of TP2. This pond was employed from October 1994 until operation shyt down (Gómez, 2008). Unlike the previous tailing points, TP3 was not positioned directly in a natural basin and, following treatment in sedimentation ponds, the tailings wash water was discharged to the *Agustina* stream, which flows into the mid course of the *Chitreca* stream which, in turn, flows into the River Santa María (Delgado, 1994).
- Secondary Ponds SP1 and SP2: the use of these ponds is unclear in terms of the local mining and mineral processing works; SP1 is located between TP2 and TP3, and SP2 is located between TP2 and the *Paisana* stream.

All three tailings ponds, along with one of the two aforementioned mine galleries, was allowed to allow uncontrollable discharges into local streams. This circumstance led to frequent complaints being made against the company, which was accused of polluting the water in streams and, hence, the River Santa María (Gómez, 2008). There were also complaints by local inhabitants about deforestation and the pollution of soil, flora and fauna (Hughes-Ortega, 1998). Given this mechanical instability scenario of tailing points and the wet tropical climate in the area, there is a real possibility of an extreme climatic rainfall event causing tailing materials to enter the local hydrological system. Such a discharge would affect the soil and groundwater in the area and would, thus, increase pressure on the River Santa María and pose a risk for the peasant population living in the region and its surroundings, who engage in subsistence agriculture and livestock farming activities. Currently, the Panamanian government has plans to reactivate the Remance mining concession, which has led to protests by residents in the area against mining because they fear that the pollution history in the region will be repeated.

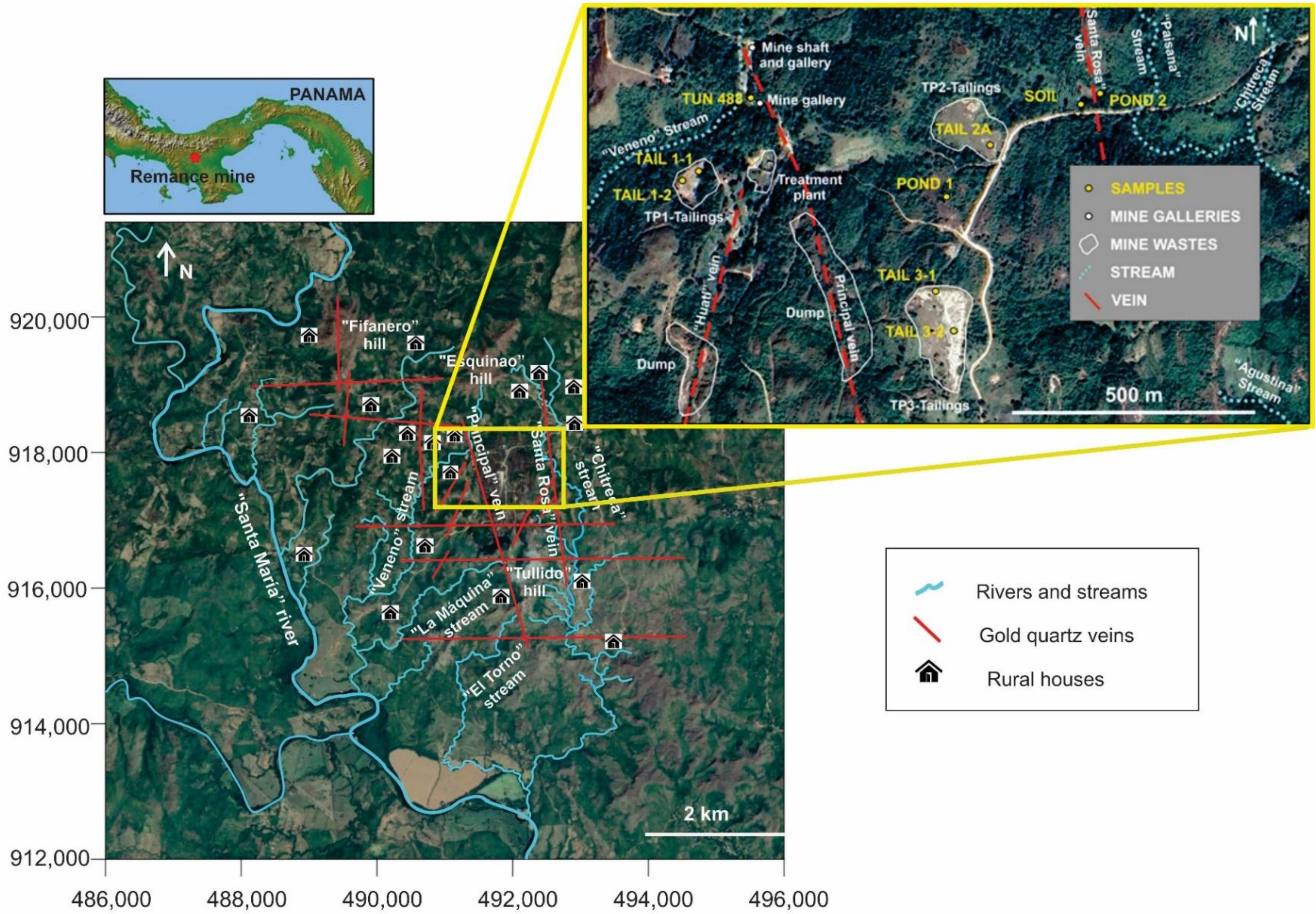

**Figure 2.1.** Remance mine, locations of tailings, ponds and taken samples.

### 2.2.2. Sampling of tailings

Sampling was performed between May and June 2019 during the rainy season. The location map of the taken samples is presented in Figure 2.1.

The survey included 13 samples (seven from tailing ponds, six from secondary ponds and their surroundings) and one corresponding to the sediments from the mouth of a mine gallery, which actively released water to a local stream. Samples TP1 (2) corresponded to the surface samples (0–15 cm depth) taken from two locations in this accumulation of tailings; samples TP2 (3) corresponded to a single site, but at two depths (0–15 cm and 15–30 cm) near the SE border of this pond; samples TP3 (3) corresponded to two sites, with a surface sample (0–15 cm) and two samples at different depths (0–15 cm and 15–30 cm); samples SP1 and SP2 included one taken from the button of each site and three samples from adjacent soils: one in SP1 (0–15 cm) and two in SP2 (at two depths, 0–15 and 15–30 cm). A reference sample was taken outside the mining area at the El Naranjal community, which located approximately 4 km away from the mining area.

Samples were collected with PVC tubes, which were jacked into the materials to obtain samples. The material was placed inside a plastic bag using a plastic shovel. The sediment samples (including those taken from the bottom of secondary ponds, which were flooded during sampling) were directly collected with a plastic shovel. Each sample was stored in a hermetic plastic bag, which contained approximately 3 kg of sample, to be stored at ambient temperature.

### 2.2.3. Laboratory analysis

Samples were taken to the laboratory, dried at ambient temperature, broken up with a wooden rolling pin and passed through a 2 mm sieve (Soiltest). The physicochemical analyses were conducted on the sieved sample, particularly pH, electrical conductivity (EC) and oxidation-reduction potential (ORP), which were determined in a 1:5 suspension (w/V) (ASTM D 4972) with a multiparameter benchtop Orion Versa Star Pro device. Moisture was determined by weight loss at 105°C in an oven (P Selecta 2000200) and on an OHAUS Adventurer Pro AV264C balance. Organic matter (OM) was established by weight loss at 455°C (ASTM D 2974) in a Hobersal HD150 furnace. Cationic exchange capacity (CEC) was determined by the potentiometer method (Weaver et al. 1991). Colour when wet was measured by Munsell soil charts. The sample texture classification was assigned by the Unified Soil Classification System (USCS), which is a soil classification system employed in engineering and geology to describe the texture and size of the particles of a given soil. To classify soil, it is necessary to previously perform soil granulometry by sieving. Then close to the Atterberg limits, the corresponding group was classified (ASTM D 2487) (ASTM, 2004). All the sieved samples were sent to Activations Laboratories Ltd. (Canada), where they were processed to determine total cyanide and PTEs. Metals were determined by partial digestion with aqua regia using a microprocessor hotbox to analyse pseudo-total concentrations (Melaku et al., 2005; Higueras et al., 2017). Extracts were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with certified reference materials Oreas 45d and Oreas 520, which were also digested and analysed in triplicate. Recovery percentages were 90-100%. Total cyanide was measured by NaOH leaching for 16 h in the dark. A diluted portion of the solution was analysed by a SAN Plus Segmented Flow Analyzer. For the quality control, blanks, controls and duplicates were also analysed in all the analyses.

### 2.2.4. Methods

#### 2.2.4.1. Pollution Index and Pollution Load Index

A site polluted by a certain element can be assessed by the Pollution Index (PI) (Equation 1), and the same, but with more than one element, can be determined by the Pollution Load Index (PLI) (Tomlinson et al., 1980; Pan et al., 2019) using Equation 2.

$$PI= C_{soil}/C_{background} \qquad (1)$$

$$PLI = (PI_1 \times PI_2 \times . . . \times PI_n)^{1/n} \qquad (2)$$

where $C_{soil}$ and $C_{background}$ are the concentrations of the particular PTE in the soil and background samples, respectively (mg $kg^{-1}$). The PLI is the Pollution Load Index of several elements, and the PI is the single Pollution Index for a certain element. Table **1** presents the evaluation criteria for both the PI and PLI (Pan et al., 2019).

#### 2.2.4.2. Toxicity response coefficient and the Potential Ecological Risk Index

Hakanson (1980) defined RI as an index that combines environmental effects and element toxicity to consider the general ecological migration and transformation trends of these elements in soils and sediments. Pan et al. (2019) defined the toxicity response coefficient (Er) as the single potential ecological risk for a certain element (Equation 3), which is used to obtain RI (Equation 4):

$$Er^i= PI \times Tr^i \qquad (3)$$

$$RI= Er_1 + Er_2 + … + Er_n \qquad (4)$$

where $Er^i$ is the single RI, the PI is the single Pollution Index for a certain element and $Tr^i$ is the toxicity response coefficient of element i. The Er calculation is based on Hakanson's element toxicity response coefficient standards (Hakanson, 1980), which can be given as follows: Hg=40, As=10, Cu=5, Zn=1, and Sb=7 (wang et al., 2018). Table 2.1 summarises the evaluation thresholds for these indices based on the respective proposers.

**Table 2.1.** Evaluation criteria for the Pollution Index (PI), the Pollution Load Index (PLI), the toxicity response coefficient (Er) and the Potential Ecological Risk Index (RI).

| Index | Not polluted | Slightly polluted | Moderately polluted | Considerably polluted | Seriously polluted | Extremely polluted |
|---|---|---|---|---|---|---|
| PLI/ PI | < 1 | 1< PLI< 2 | 2< PLI< 3 | PLI > 3 | - | - |
| Er | < 10 | < 40 | 40 < Er < 80 | 80 < Er < 160 | 160 < Er < 320 | Er > 320 |
| RI | < 50 | < 150 | 150< RI <300 | 300 < RI < 600 | 600 < RI < 1200 | RI > 1200 |

### 2.2.5. Statistical analysis

Microsoft Excel spreadsheets were used to manage the results and the programme Minitab 15 was employed to analyse the statistical parameters of the analytical results. A multivariate analysis was performed by applying a factor analysis and a principal component analysis (PCA). Both were applied to search for the influence of factors, or group of factors, using "Varimax" orthogonal rotation. The map figure was generated with the Surfer 9 software and was edited in CorelDraw 2020 licensed by the UCLM.

## 2.3. Results

### 2.3.1. Total cyanide and correlations with edaphic parameters and PTEs

Regarding cyanide and its changes over time, the Remance gold mine, where the cyanidation process was used to extract Au and other precious metals during the last mining extraction (20 years ago since mining operations shut down), presented higher total cyanide values than those reported for uncontaminated sites in America (<0.005 - 0.5 mg $kg^{-1}$ T-CN) (Kjeldsen, 1999), which were similar to those reported in gold mine tailings at American sites (1.5-23 mg $kg^{-1}$ T-CN) (Kjeldsen, 1999) in TP1, TP2, mine gallery sediments, secondary ponds and nearby soil (1.8, 1.6, 1.4, 1.9 and 1.7 mg $kg^{-1}$, respectively). However, TP3 had higher T-CN values (25.2-518.0 mg $kg^{-1}$ T-CN) than these, and those reported in gold tailing 6, closed in Quebec, Canada (4.8 mg $kg^{-1}$ T-CN) (Zagury et al., 2004). A statistical analysis was performed to seek any correlations between pollution in the area and the presence of T-CN.

The description of the taken samples, together with their colour and texture characteristics, are presented in Table 2.2. The colour and texture of the samples in tailings 1 (TP1), tailings 2 (TP2) and tailings 3 (TP3) were the same: yellowish brown with mainly a silty sand texture. The sediments of secondary pond 1 (SP1) and secondary pond 2 (SP2) had the same silt texture, but different colours. The soil near SP1 was silt in texture and olive brown in colour, while the soil near SP2 was sandy silt in texture. The sediment in the mine gallery differed from the rest, with a yellowish red colour and a high plasticity clay texture.

**Table 2.2.** Description of the taken samples, Munsell colour and USCS soil classification.

| **ID** | **Location/ Sample type** | **Depth (cm)** | **Munsell colour** | **Sample texture (USCS name group)** |
|---|---|---|---|---|
| Tail 1-1 | TP1/tailing | 0- 15 | Yellowish brown, 10 YR 5/6 | Silty sand |
| Tail 1-2 | TP1/tailing | 0- 15 | Yellowish brown, 10 YR 5/8 | Silty sand |
| Tail 2 A | TP2/tailing | 0- 15 | Yellowish brown, 10 YR 5/8 | Silty sand |
| Tail 2 B | TP2/tailing | 15- 30 | Yellowish brown, 10 YR 5/8 | Silty sand |
| Tail 3-1 A | TP3/tailing | 0- 15 | Yellowish brown, 10 YR 5/8 | Silty sand with gravel |
| Tail 3-1 B | TP3/tailing | 15- 30 | Yellowish brown, 10 YR 6/8 | Silty clayey sand |
| Tail 3-2 | TP3/tailing | 0- 15 | Yellowish brown, 10 YR 5/8 | Silt with sand |
| Pond 1-sed | SP1/sediment | Surface | Light yellowish brown, 2.5 YR 6/4 | Silt |
| Pond 1- T | Close to SP1/soil | 0- 15 | Olive brown, 2.5 Y 4/4 | Silt |
| Pond 2-sed | SP2/sediment | Surface | Olive brown, 2.5 Y 4/4 | Silt |
| Pond 2- T A | Close to SP2/soil | 0- 15 | Dark grey, 5 Y 4/1 | Sandy silt with gravel |
| Pond 2- T B | Close to SP2/soil | 15- 30 | Dark brown, 7.5 YR 4/6 | Sandy silt |
| Tun 488 | Mine gallery/sediment | Surface | Yellowish red, 5 YR 5/8 | High plasticity clay |

The average and standard deviation values of the physicochemical parameters and elements of interest are found in Table 2.3, while all of those obtained results appear in S1. The samples taken from each tailing, the sediment samples from secondary ponds, the soil samples close to SP1 and SP2, and the mine gallery sediments were grouped. Values of pH ranged between 3.9 and 5.0. The most acidic pH corresponded to the mine gallery sediments, and the highest to the sediments of secondary ponds. The EC ranged between 0.03 and 0.52 dS $m^{-1}$, and TP1 and TP2 had the lowest value, with the highest value for the mine gallery sediments. The ORP values ranged from 281.5 to 686.7 mV, with the lowest in the sediments of secondary ponds and the highest in TP3. Humidity was between 14.0% and

**Table 2.3.** Average values and standard deviations of the physicochemical parameters and PTEs (mg $kg^{-1}$) in the different material types in the sampled areas. Abbreviations: EC, electrical conductivity; ORP, oxidation reduction potential; OM, organic matter; CEC, cationic exchange capacity; T-CN, total cyanide.

| Location | Sample type | pH | EC dS $m^{-1}$ | ORP mV | Humidity % | OM % | CEC cmol $kg^{-1}$ | Fe % | Au ng $g^{-1}$ | Ag mg $kg^{-1}$ | T-CN mg $kg^{-1}$ | As mg $kg^{-1}$ | Hg mg $kg^{-1}$ | Sb mg $kg^{-1}$ | Cu mg $kg^{-1}$ | Ba mg $kg^{-1}$ | Zn mg $kg^{-1}$ | Pb mg $kg^{-1}$ | Co mg $kg^{-1}$ | Cr mg $kg^{-1}$ | V mg $kg^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TP1 | Tailing | 4.5 ± 0.4 | 0.03 ± 0.01 | 612.6 ± 23.1 | 14.0 ± 4.9 | 0.8 ± 0.2 | 4.8 ± 0.2 | 3.4 ± 1.7 | 617.5 ± 190.2 | 1.2 ± 0.2 | 1.8 ± 0.1 | 658.0 ± 410.1 | 1.1 ± 0.7 | 18.4 ± 10.1 | 34.4 ± 17.1 | 407.0 ± 227.7 | 18.0 ± 8.5 | 13.4 ± 6.7 | 1.3 ± 0.1 | 3.5 ± 0.7 | 18.0 ± 4.2 |
| TP2 | Tailing | 4.5 ± 0.3 | 0.03 ± 0.01 | 505.5 ± 76.3 | 14.5 ± 1.0 | 0.6 ± 0.1 | 4.5 ± 0.1 | 2.5 ± 0.2 | 507.0 ± 26.9 | 1.9 ± 0.3 | 1.6 ± 0.1 | 465.5 ± 37.5 | 1.0 ± 0.3 | 20.7 ± 2.5 | 21.5 ± 1.1 | 514.5 ± 135.1 | 14.5 ± 2.1 | 11.7 ± 1.6 | 0.9 ± 0.1 | 6.5 ± 0.7 | 14.5 ± 0.7 |
| TP3 | Tailing | 3.6 ± 0.7 | 0.49 ± 0.71 | 686.7 ± 66.2 | 19.5 ± 2.8 | 1.0 ± 0.4 | 3.5 ± 0.5 | 3.6 ± 1.5 | 464.7 ± 217.8 | 5.7 ± 8.7 | 187.9 ± 285.9 | 633.0 ± 96.6 | 1.4 ± 1.6 | 15.2 ± 2.3 | 109.1 ± 138.5 | 305.7 ± 102.7 | 40.3 ± 6.8 | 24.9 ± 22.8 | 1.4 ± 0.3 | 6.0 ± 2.6 | 16.3 ± 1.5 |
| SP1, SP2 | Sediment | 5.0 ± 0.4 | 0.08 ± 0.03 | 281.5 ± 6.6 | 40.7 ± 8.4 | 5.4 ± 2.9 | 10.2 ± 2.1 | 1.0 ± 0.3 | 86.4 ± 53.2 | 0.4 ± 0.4 | 1.9 ± 0.1 | 25.0 ± 10.8 | 0.2 ± 0.1 | 1.7 ± 0.8 | 12.8 ± 10.4 | 298.5 ± 40.3 | 23.5 ± 2.1 | 7.4 ± 0.0 | 2.4 ± 2.7 | 2.0 ± 0.0 | 19.0 ± 1.4 |
| Soil close to SP1, SP2 | Soil | 4.8 ± 0.2 | 0.11 ± 0.06 | 453.8 ± 153.3 | 26.5 ± 8.1 | 5.3 ± 1.2 | 9.6 ± 0.3 | 2.3 ± 0.7 | 29.9 ± 19.3 | 0.1 ± 0.1 | 1.7 ± 0.2 | 56.0 ± 4.2 | 0.1 ± 0.1 | 0.9 ± 0.6 | 10.4 ± 4.3 | 196.3 ± 45.4 | 44.0 ± 23.4 | 5.5 ± 1.9 | 1.7 ± 1.1 | 2.7 ± 0.6 | 26.7 ± 8.5 |
| Mine gallery | Sediment | 3.9 | 0.52 | 542.3 | 63.9 | 12.9 | 10.9 | > 30.0 | > 1000 | 0.7 | 1.4 | 5030.0 | 0.6 | 2.2 | 403.0 | 55.4 | 153.0 | 1.7 | 13.7 | 2.0 | 27.0 |

**Table 2.4.** Soil guidelines for the PTEs for Panama and Costa Rica (all the values are expressed as mg $kg^{-1}$).

| Soil Guidelines | Uses | Ag | As | Hg | Sb | Cu | Ba | Zn | Pb | Co | Cr | V | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Panama** | Others (agricultural) | | 4 | 1.4 | | | 10 | 3 | | | 10 | | Gaceta Oficial Digital (2009) |
| Maximum permissible limits of soil contaminants for human health | Residential | | 20 | 14 | | | 100 | 30 | | | 100 | | |
| | Industrial | | 30 | 140 | | | 1000 | 300 | | | 1000 | | |
| **Costa Rica** | Prevention Value | 2 | 5 | 0.5 | 2 | 20 | 150 | 300 | 72 | 25 | 2 | 52 | Ministerio de Salud (2010) |
| Intervention Value | Agricultural | 25 | 35 | 12 | 5 | 20 | 300 | 450 | 180 | 35 | 40 | 250 | |
| (Concentration above which there are potential direct or in direct risks for human health) | Residential | 50 | 55 | 36 | 10 | 50 | 500 | 1000 | 300 | 65 | 270 | 250 | |
| | Industrial | 100 | 150 | 70 | 25 | 100 | 750 | 2000 | 400 | 90 | 270 | 250 | |

63.9%, with the lowest value in TP1 and the highest in the mine gallery sediments. Organic matter ranged from 0.6 to 12.9%, with the lowest value in TP2 and the highest in the mine gallery sediments. CEC went from 3.5 to 10.9 cmol kg$^{-1}$, with the lowest in TP3 and the highest in the mine gallery sediments.

The Fe concentration varied between 1.0 and > 30.0%, and that of As was between 25.0 and 5,030.0 mg kg$^{-1}$, with the lowest values in the sediments of secondary ponds and the highest in the mine gallery sediments. The Au concentration varied from 29.9 to > 1,000.0 ng g$^{-1}$, and that of Cu between 10.4 to 403.0 mg kg$^{-1}$, with the lowest values in the soils close to the secondary ponds and the highest in the mine gallery sediments. The Zn concentration Ranged from 14.5 to 153.0 mg kg$^{-1}$, that of Co from 0.9 to 13.7 mg kg$^{-1}$ and that of V from 14.5 to 27.0 mg kg$^{-1}$, with the lowest values in TP2 and the highest in the mine gallery sediments. The average Ag concentration varied between 0.7 and 5.7 mg kg$^{-1}$, and that of Hg between 0.6 and 1.4 mg kg$^{-1}$, with the lowest concentration in the soils near secondary ponds and the highest in TP3. The average total cyanide (T-CN) concentration varied from 1.4 to 187.9 mg kg$^{-1}$, and that of Pb from 1.7 to 24.9 mg kg$^{-1}$, with the lowest concentration in the mine gallery sediments and the highest in TP3. The average Ba concentration ranged between 55.4 and 514.5 mg kg$^{-1}$, and that of Cr between 2.0 and 6.5 mg kg$^{-1}$, with a low concentration in the mine gallery sediments and the highest in TP2. The Sb range went from 0.9 to 20.7 mg kg$^{-1}$, with a low concentration in the soils near secondary ponds and the highest in TP2. The gallery mine sediments corresponded to the sediments that left a tunnel located in the ´Principal´ vein, where an underground water current flows and discharges into the ´Veneno´ stream. TP3 corresponded to the last tailings used until 1999, when mining operations ceased. Although the use of secondary ponds is unclear, they may have acted as a stage prior to downloading in streams (González Valoys et al. 2021).

According to the Panama Soil Standard (Gaceta Oficial Digital, 2009) (Table 2.4), the soils near secondary ponds exceeded the limit that the standard sets out for industrial use for As, and also for residential use for Ba and Zn.

Although tailings are not soil, their behaviour with the climatic conditions is similar and also, they can disperse pollutants to surrounding soils and water bodies is favoured (González-Valoys et al., 2021, Rodríguez-Hernández et al., 2021). This is why the study materials relating to mining operations were compared to a soil standard, either from Panama or Costa Rica (Table 4), which gave the following PTEs of interest: As, Hg, Ba, Zn (Gaceta Oficial Digital, 2009), Cu, Sb (Ministerio de Salud, 2010), for exceeding the limit for some agricultural, residential or industrial uses. Local residents employ tailings, one as a football ground (TP1) and another to graze animals on, e.g. horses

(TP3). Hence the need to study and compare them to regulations, and to evaluate their degree of pollution and the ecological risk they pose.

### 2.3.2. Statistical analysis

Figure 2.2 presents the multivariate PCA performed of the samples studied for the T-CN physicochemical parameters, the precious elements that were the object of the mining process (Au, Ag), Fe, and the PTEs of interest (Cu, Zn, As, Sb, Ba, Hg). According to the strengths of the relations (Table 5), the most significant relations were: for the first principal component (PC1), a positive relation was observed among T-CN (0.310), Ag (0.322), Cu (0.316), Au (0.313), Hg (0.343), EC (0.337) and ORP (0.282), and a negative relation to pH (-0.371). The second principal component (PC2) was positively related to Ba (0.316) and Sb (0.313), and negatively to OM (-0.396), texture (-0.364), Zn (-0.342), CEC (-0.330), Fe (-0.307) and As (-0.274).

The PCA diagram also revealed how samples were grouped according to their nature, the tailings in the upper zone, the sediments of secondary ponds and the soils close to them on the left, and the mine gallery sediments far from the two previous groups (at the bottom) and to the right point Tail 3-2 of TP3, whose values were higher than the other tailings samples. This point had the highest T-CN concentration (518.0 mg $kg^{-1}$).

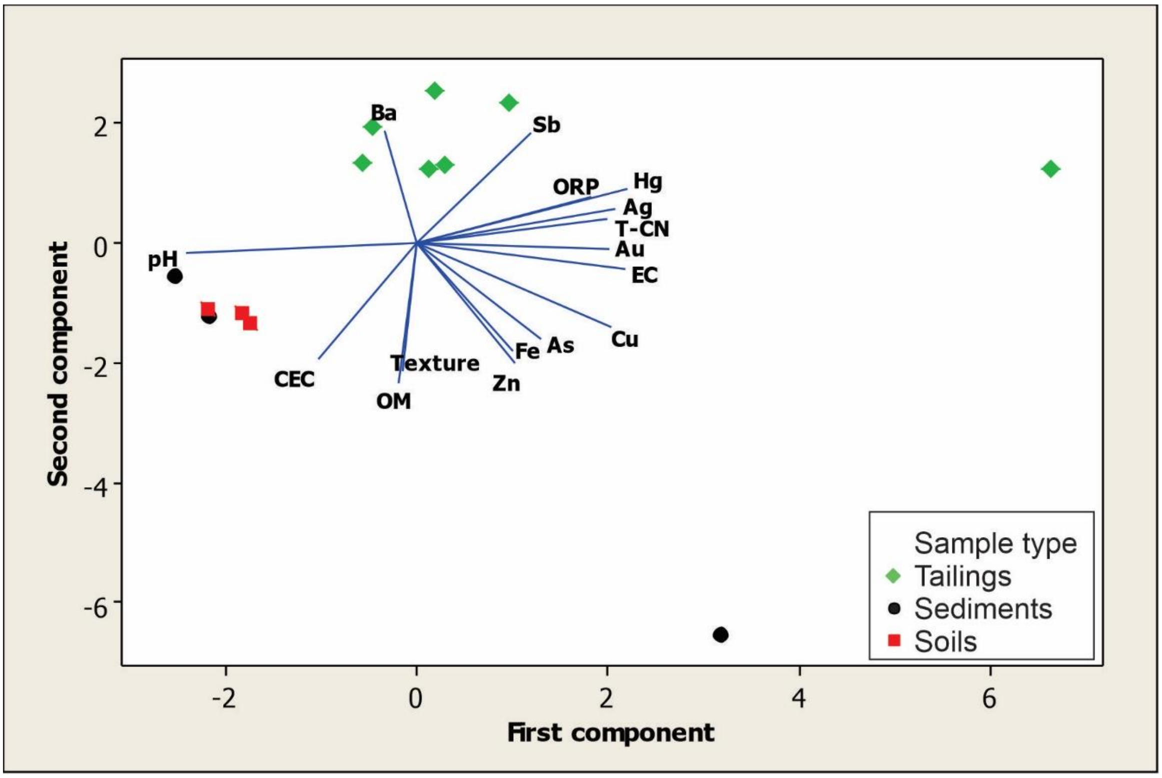

**Figure 2.2.** PCA of the relations among T-CN, the main parameters and the PTEs concentrations. Generated with the data from tailings, sediments and soils.

**Table 2.5.** Principal component analysis matrix for the relation between T-CN (total cyanide) and the physicochemical parameters. Numbers in bold correspond to PC1 or PC2 and are more significant.

| Variable | PC1 | PC2 |
|---|---|---|
| pH | **-0.371** | -0.026 |
| EC | **0.337** | -0.075 |
| ORP | **0.282** | 0.130 |
| OM | -0.028 | **-0.396** |
| CEC | -0.157 | **-0.330** |
| Fe | 0.158 | **-0.307** |
| Au | **0.313** | -0.016 |
| Ag | **0.322** | 0.096 |
| T-CN | **0.310** | 0.069 |
| As | 0.203 | **-0.274** |
| Hg | **0.343** | 0.153 |
| Sb | 0.184 | **0.313** |
| Cu | **0.316** | -0.237 |
| Ba | -0.049 | **0.316** |
| Zn | 0.159 | **-0.342** |
| Texture | -0.021 | **-0.364** |

### 2.3.3. Pollution Index (PI) and Pollution Load Index (PLI)

Table 2.6 presents the PI and PLI values. According to the evaluation criteria for the PI and PLI in Table 1, the PI indicated considerable pollution (PI>3) by T-CN, As, Hg, Sb and Cu, with the highest values in the tailings and the mine gallery sediments, followed in order of affect by secondary ponds and the soils near them. It is worth noting the very marked T-CN pollution that TP3 presented, and the mine gallery sediments with As.

The PLI came in the following order: TP3> mine gallery sediments> TP1> TP2> secondary pond sediments> soil close to secondary ponds. These findings indicated that the gallery mine and tailings were sources of pollution for the surrounding area.

### 2.3.4. Toxicity response coefficient (Er) and the Potential Ecological Risk Index (RI)

The values calculated for Er and RI of Cu, Zn, As, Sb and Hg are shown in Table 2.7. According to the evaluation criteria in Table 1 for Er and toxicity according to each element, the Er values suggests that TP1, TP2 and TP3 pose a serious risk for their As, Hg and Sb contents, and also for mine gallery sediments given their As, Hg and Cu contents. The extreme risk of the mine gallery sediments is highlighted for their high As content.

The average RI value presented the following order of potential ecological risk: mine gallery sediments (extreme risk); TP3, TP1, TP2 (serious risk); secondary pond sediments and nearby soils (considerable risk). This means that the gallery mine and tailings are sources of pollution for the surrounding area and represent a high ecological risk.

**Table 2.6.** The average values and standard deviations of the Pollution Index (PI) and the Pollution Load Index (PLI) calculated for the different sample types.

| | Sample type | PI T-CN | PI As | PI Hg | PI Sb | PI Cu | PI Ba | PI Zn | PLI |
|---|---|---|---|---|---|---|---|---|---|
| TP 1 | Tailing | 3.5 ± 0.1 | 35.4 ± 22.0 | 7.1 ± 4.7 | 61.2 ± 33.7 | 4.9 ± 2.4 | 1.7 ± 1.0 | 0.6 ± 0.3 | 6.0 ± 2.9 |
| TP 2 | Tailing | 3.2 ± 0.3 | 25.0 ± 2.0 | 6.7 ± 1.7 | 68.8 ± 8.2 | 3.1 ± 0.2 | 2.2 ± 0.6 | 0.5 ± 0.1 | 5.3 ± 0.6 |
| TP 3 | Tailing | 375.9 ± 571.7 | 34.0 ± 5.2 | 9.4 ± 10.5 | 50.6 ± 7.5 | 15.6 ± 19.8 | 1.3 ± 0.4 | 1.4 ± 0.2 | 12.6 ± 8.2 |
| SP1, SP2 | Sediment | 3.7 ± 0.1 | 1.3 ± 0.6 | 1.4 ± 0.5 | 5.7 ± 2.8 | 1.8 ± 1.5 | 1.2 ± 0.2 | 0.8 ± 0.1 | 1.8 ± 0.4 |
| Soil close to SP1, SP2 | Soil | 3.3 ± 0.3 | 3.0 ± 0.2 | 0.7 ± 0.3 | 3.1 ± 1.9 | 1.5 ± 0.6 | 0.8 ± 0.2 | 1.6 ± 0.8 | 1.6 ± 0.3 |
| Mine gallery | Sediment | 2.8 | 270.4 | 4.1 | 7.3 | 57.6 | 0.2 | 5.5 | 7.7 |

**Table 2.7.** Average values and standard deviations of the toxicity response coefficient (Er) and the Potential Ecological Risk Index (RI) for the different sample types.

| | Sample type | Er As | Er Hg | Er Sb | Er Cu | Er Zn | RI |
|---|---|---|---|---|---|---|---|
| TP 1 | Tailing | 353.8 ± 220.5 | 284.0 ± 186.7 | 428.2 ± 235.9 | 24.6 ± 12.2 | 0.6 ± 0.3 | 1091 ± 656 |
| TP 2 | Tailing | 250.3 ± 20.1 | 266.7 ± 67.9 | 481.8 ± 57.7 | 15.3 ± 0.8 | 0.5 ± 0.1 | 1015 ± 145 |
| TP 3 | Tailing | 340.3 ± 51.9 | 376.0 ± 421.0 | 353.9 ± 52.5 | 77.9 ± 98.9 | 1.4 ± 0.2 | 1150 ± 592 |
| SP1, SP2 | Sediment | 13.4 ± 5.8 | 56.0 ± 18.9 | 39.7 ± 19.8 | 9.1 ± 7.4 | 0.8 ± 0.1 | 119 ± 40 |
| Soil close to SP1, SP2 | Soil | 30.1 ± 2.2 | 29.3 ± 13.9 | 21.8 ± 13.5 | 7.4 ± 3.1 | 1.6 ± 0.8 | 90 ± 27 |
| Mine gallery | Sediment | 2704.3 | 165.3 | 51.3 | 287.9 | 5.5 | 3214 |

## 2.4. Discussion

Remance mine tailings still contain large amounts of PTEs and, together with the mine gallery sediments, they pose a source of environmental pollution given their total As, Cu, Sb, Ba, Hg and Zn contents, as verified by the presence of these PTEs in nearby soils and the sediments of the water network in the study area (González-Valoys et al., 2021). All these pollutants can cause several health problems: As can cause skin, liver and lung cancers; Cu can provoke abnormalities to the nervous system; Sb can harm the respiratory system; Ba can favor muscle paralysis; Hg produces neurological damage; Zn can weaken the immune system (Bini & Wahsha, 2014).

Although the T-CN concentrations found in most of the studied area fell within the ranges reported for gold mine tailings at American sites (Kjeldsen, 1999), T-CN at TP3 was higher than that reported in the literature for closed gold tailings in Canada (Zagury et al., 2004). Although we would expect cyanide to have evaporated as free cyanide 20 years after mining operations ceased, its concentrations should be similar to those in other areas, but it persists in TP3. The high T-CN concentration at TP3 did not seem to be linked with sample texture as the texture and colour of the three tailings were similar, and they also had similar Fe, As, Hg and Sb concentrations. Nevertheless, the pH at TP3 was more acidic, both EC and ORP were higher, as were the Cu, Zn and Ag concentrations. The PCA showed a close relation between T-CN and Au, Ag, Hg and Cu, with which it would seem complexed and favoured by today's EC and ORP conditions. These cyanide complexes formed under certain conditions like sunlight and a strongly acidic medium slowly decompose (Meeussen et al., 1992; Anning et al., 2019) and are released to the environment, a phenomenon that has been reported by the study of Johnson et al. (2002), as photochemical changes in cyanide in tailing piles. The presence of T-CN and complexed cyanide was found in surrounding soils, stream sediments and the terrace sediments near the Remance mine tailings, while easily released cyanide was below the detection limit (González-Valoys et al., 2021), which demonstrates that cyanide complexes affect soils and water bodies, favoured by the slope at the site and by runoff. All this suggests that the cyanides at TP1 and TP2 were treated after mining closed. However, high T-CN concentrations persist at TP3, which is the largest of the three and the last to be used, due to inappropriate abandonment and no residual cyanide decomposition.

In turn, T-CN is slowly released to the environment, and favours the release of other pollutants, such as Cu and Hg, with which it travels complexed. They have also been found in nearby soils, streams and terrace sediments (González-Valoys et al., 2021). Ba in the PCA analysis did not appear to be bound to T-CN, but to a second factor, Ba, which was inert, and could be bound due to its relations with Au-Sb in mineralisation as inert Ba.

The acidic pH at certain points like TP3 (pH 3.6), and the mine gallery sediments (pH 3.9), which are potential acid mine drainage (AMD) generators, could be due to their content of pyrite and marcasite ($FeS_2$), chalcopyrite ($CuFeS_2$) and arsenopyrite (FeAsS), minerals, as reported in the mining by the company Remance S.A. (Nelson & Ganoza, 1999). AMD is produced as a result of abiotic and biotic reactions that involve water and air, and with sulphide minerals present in mine wastes (e.g., pyrite). These reactions produce acidic effluents that tend to be loaded with several heavy metals and metalloids (e.g., Fe, Cu, As, Hg) (Nadeif et al., 2019).

As came at high concentrations (5,030.0 mg $kg^{-1}$) in the mine gallery sediments, and had to take an inorganic form after being released from minerals, such as arsenopyrite (FeAsS) from the ´Principal vein´, from which the underground water stream came. The mine gallery sediments were characterised for their clay texture composition, acidic pH (3.9) and high CEC (10.9). The high concentration of these PTEs (As, Cu, Zn) at this point could be associated with clay fractions, such as kaolinite and illite (Palansooriyaa et al., 2020), which were detected in the soil and sediment samples taken from streams near the area (González-Valoys et al., 2021), for which the best explanation would be the absorption/adsorption of PTEs by clays (González-Valoys et al., 2021).

The PI and PLI allowed a comparison to be made of the pollution level in an area to background areas. Thus the PI of T-CN showed marked pollution (PI> 3) in the tailings area and its surroundings, and TP3 obtained the highest value (PI 375.9) and, therefore, poses a source of pollution for the surroundings given its T-CN, As, Hg, Sb and Cu contents, which can have adverse health effects. For the PLI, TP3 was also the area with the most pollution, followed by the mine gallery sediments, TP1 and TP2 This would be the order to be followed to recover areas in a recovery management plan for this area. To evaluate the possible effect of PTEs on the biota, the RI and Er were used, which complement information about the PLI. They revealed that the mine gallery sediments and tailings posed a serious ecological risk for the biota in this place, as well as a considerable ecological risk for the surrounding area.

Tailings with high Au and Ag contents must be reprocessed to extract the amount of remaining precious metals, which should then be properly remediated to avoid them becoming a source of pollution for the community via polluting soils, stream sediments and terrace sediments, which pose a risk for the ecology and human health of its inhabitants (González-Valoys et al., 2021). Longer-term remediation should be implemented using the measures proposed in the literature, such as chemical degradation of residual cyanide (Ebbs, 2004), covering tailing ponds (Henny et al., 1994) and the bioremediation (Vieira & Stefenon, 2017) of not only surrounding soils, but also of stream sediments and sediments.

The problem of improperly abandoned mines is a latent problem in Panama and other countries. For this reason, there is a dire need to implement some type of economic surety for mining companies to raise funds with which to remedy the area if the company goes bankrupt. It is also necessary to reinforce measures to monitor proper compliance with environmental regulations and to promote scientific research in this field.

## 2.5. Conclusions

The tailings from the Remance gold mine and mine gallery sediments present a high degree of pollution given their PTEs (As, Hg, Sb, Cu) and T-CN contents. The highest PLI went to tailings 3 due to their high T-CN content. Hence, they represent a source of pollution for the surrounding areas and pose a serious ecological risk (RI) for the biota in this place.

Total cyanide content is similar to that of gold mine tailings at American sites in most of this area, but the last used tailings from mining operations contained a highest T-CN concentration. This clearly demonstrates that this pollutant persists more than 20 years after closing mining operations. This finding suggests that in later tailings, cyanide contents were not chemically treated before shutting down mining operations.

T-CN under certain specific pH, EC and ORP conditions is slowly released to the environment, which favours the release of other pollutants like Cu and Hg, with which it travels in a complexed manner. The pollutants that were also found in nearby soils, streams and terrace sediments also pose a risk to both the environment and human health of Remance community inhabitants (González-Valoys et al., 2021).

The Remance mine is an abandoned area with no environmental control. An environmental monitoring plan should be set up to avoid undesirable water, soil and plant uses by the local population. We recommend remediating the tailings ponds and mine works areas because they pose a serious environmental risk. We also recommend conducting bioavailability and bioaccessibility studies on these materials.

## 2.6. Declarations

**Funding information**: Open Access funding provided thanks to the CRUE- CSIC agreement with Elsevier. This study was funded by the Secretaría Nacional de Ciencia, Tecnología e Innovación (SENACYT) and the Instituto para la Formación y Aprovechamiento del Recurso Humano (IFARHU) of Panama (270-2019-109), Universidad Tecnológica de Panamá (UTP); and Fondos para Grupos de Investigación UCLM (2020-GRIN-27011).

**Conflicts of Interest/Competing interest:** The authors declare no conflict of interest.
**Availability of data and material**: Not applicable.

**Code availability**: Not applicable.

**Authors´ Contributions**: The paper was written by Ana González, Pablo Higueras, Raimundo Jimenez Ballesta, Francisco Jesús García Navarro, José María Esbrí, Efrén García Ordiales, Jonatha Arrocha, Miguel Vargas Lombardo and Tisla de Destro. The field and laboratory work by Ana González and Jonatha Arrocha.

**Animal research**: Not applicable.

**Ethics approval**: Not applicable.

**Consent to participate**: Not applicable.

**Consent for publication**: Not applicable.

**Acknowledgements**: We would like to thank the Secretaría Nacional de Ciencia Tecnología e Innovación (SENACYT), the Instituto para la Formación y Aprovechamiento del Recurso Humano (IFARHU) of Panama, the Sistema Nacional de Investigación de Panamá (SNI), the Universidad Tecnológica de Panamá (UTP), the University of Castilla-La Mancha (UCLM), the University of Oviedo and the Autonomous University of Madrid (UAM) for their support in this research, as well as the Dirección Nacional de Recursos Minerales of the Ministerio de Comercio e Industria (MICI) of Panama for granting access to the Remance mine. Thanks also go to Neil Thompson (PhD in Chemistry, Scientific English) and Helen Warburton (Scientific English) for reviewing the English style of this manuscript.

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## 2.8. Supplementary Materials

S1. Supplementary Table. Results of all samples

| **ID** | **pH** | **EC dS m$^{-1}$** | **ORP mV** | **Humidity %** | **OM %** | **CEC cmol kg$^{-1}$** | **Au ng g$^{-1}$** | **Ag mg kg$^{-1}$** | **T-CN mg kg$^{-1}$** | **As mg kg$^{-1}$** | **Hg mg kg$^{-1}$** | **Sb mg kg$^{-1}$** | **Fe %** | **Cu mg kg$^{-1}$** | **Ba mg kg$^{-1}$** | **Zn mg kg$^{-1}$** | **Pb mg kg$^{-1}$** | **Co mg kg$^{-1}$** | **Cr mg kg$^{-1}$** | **V mg kg$^{-1}$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tail 1-1 | 4.8 | 0.02 | 596.2 | 17.5 | 0.7 | 4.9 | 483.0 | 1.0 | 1.8 | 368.0 | 0.6 | 11.2 | 2.2 | 22.3 | 246.0 | 12.0 | 8.6 | 1.4 | 3.0 | 15.0 |
| Tail 1-2 | 4.2 | 0.03 | 628.9 | 10.5 | 0.9 | 4.7 | 752.0 | 1.3 | 1.7 | 948.0 | 1.6 | 25.5 | 4.5 | 46.5 | 568.0 | 24.0 | 18.1 | 1.2 | 4.0 | 21.0 |
| Tail 2 A | 4.7 | 0.03 | 451.5 | 15.2 | 0.6 | 4.4 | 488.0 | 1.7 | 1.7 | 439.0 | 0.8 | 18.9 | 2.4 | 22.2 | 419.0 | 13.0 | 10.6 | 0.9 | 7.0 | 14.0 |
| Tail 2 B | 4.3 | 0.03 | 559.4 | 13.8 | 0.6 | 4.6 | 526.0 | 2.1 | 1.5 | 492.0 | 1.2 | 22.4 | 2.7 | 20.7 | 610.0 | 16.0 | 12.8 | 0.8 | 6.0 | 15.0 |
| Tail 3-1 A | 3.9 | 0.08 | 646.8 | 22.6 | 1.4 | 3.5 | 276.0 | 0.5 | 25.2 | 698.0 | 0.4 | 13.4 | 4.7 | 31.0 | 377.0 | 38.0 | 10.4 | 1.2 | 4.0 | 16.0 |
| Tail 3-1 B | 4.0 | 0.07 | 650.3 | 17.2 | 0.9 | 3.0 | 415.0 | 0.9 | 20.6 | 522.0 | 0.6 | 14.4 | 4.3 | 27.3 | 352.0 | 35.0 | 13.2 | 1.2 | 5.0 | 15.0 |
| Tail 3-2 | 2.8 | 1.31 | 763.1 | 18.7 | 0.7 | 4.0 | 703.0 | 15.7 | 518.0 | 679.0 | 3.2 | 17.7 | 1.9 | 269.0 | 188.0 | 48.0 | 51.2 | 1.7 | 9.0 | 18.0 |
| Pond 1-sed | 5.2 | 0.06 | 276.8 | 34.7 | 3.3 | 8.7 | 48.7 | 0.1 | 1.9 | 32.6 | 0.2 | 1.1 | 1.3 | 5.4 | 270.0 | 22.0 | 7.4 | 0.5 | 2.0 | 18.0 |
| Pond 1- T | 5.0 | 0.10 | 277.2 | 35.8 | 4.6 | 9.4 | 51.9 | 0.2 | 1.8 | 60.0 | 0.2 | 1.6 | 1.5 | 5.4 | 248.0 | 71.0 | 7.7 | 0.4 | 2.0 | 17.0 |
| Pond 2- sed | 4.7 | 0.10 | 286.1 | 46.6 | 7.5 | 11.7 | 124.0 | 0.6 | 1.8 | 17.3 | 0.3 | 2.3 | 0.8 | 20.1 | 327.0 | 25.0 | 7.4 | 4.3 | 2.0 | 20.0 |
| Pond 2- T A | 4.7 | 0.18 | 532.0 | 22.5 | 6.6 | 10.0 | 15.8 | 0.1 | 1.7 | 51.7 | 0.1 | 0.6 | 2.6 | 12.3 | 163.0 | 29.0 | 4.4 | 2.4 | 3.0 | 30.0 |
| Pond 2- T B | 4.8 | 0.06 | 552.3 | 21.1 | 4.5 | 9.6 | 21.9 | < 0.1 | 1.5 | 56.4 | 0.1 | 0.6 | 2.9 | 13.4 | 178.0 | 32.0 | 4.4 | 2.3 | 3.0 | 33.0 |
| Tun 488 | 3.9 | 0.52 | 542.3 | 63.9 | 12.9 | 10.9 | > 1000 | 0.7 | 1.4 | 5030.0 | 0.6 | 2.2 | > 30.0 | 403.0 | 55.4 | 153.0 | 1.7 | 13.7 | 2.0 | 27.0 |

# ECOLOGICAL AND HEALTH RISK ASSESSMENTS OF AN ABANDONED GOLD MINE (REMANCE, PANAMA): COMPLEX SCENARIOS NEED A COMBINATION OF INDICES

International Journal of
*Environmental Research and Public Health*

MDPI

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# Ecological and Health Risk Assessments of an Abandoned Gold Mine (Remance, Panama): Complex Scenarios Need a Combination of Indices

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**Citation:** González-Valoys, A.C.; Esbrí, J.M.; Campos, J.A.; Arrocha, J.; García-Noguero, E.M.; Monteza-Destro, T.; Martínez, E.; Jiménez-Ballesta, R.; Gutiérrez, E.; Vargas-Lombardo, M.; et al. Ecological and Health Risk Assessments of an Abandoned Gold Mine (Remance, Panama): Complex Scenarios Need a Combination of Indices. *Int. J. Environ. Res. Public Health* **2021**, *18*, 9369. https://doi.org/10.3390/ijerph18179369

Academic Editor: Paul B. Tchounwou

Received: 18 July 2021
Accepted: 31 August 2021
Published: 5 September 2021

**Abstract:** The derelict Remance gold mine is a possible source of pollution with potentially toxic elements (PTEs). In the study area, diverse mine waste has been left behind and exposed to weather conditions, and poses risks for soil, plants and water bodies, and also for the health of local inhabitants. This study sought to perform an ecological and health risk assessment of derelict gold mining areas with incomplete remediation, including: (i) characterizing the geochemical distribution of PTEs; (ii) assessing ecological risk by estimating the pollution load index (PLI) and potential ecological risk index (RI); (iii) assessing soil health by dehydrogenase activity; and iv) establishing non-carcinogenic (HI) and carcinogenic risks (CR) for local inhabitants. Soil health seems to depend on not only PTE concentrations, but also on organic matter (OM). Both indexes (PLI and RI) ranged from high to extreme near mining and waste accumulation sites. As indicated by both the HI and CR results, the mining area poses a health risk for local inhabitants and particularly for children. For this reason, it will be necessary to set up environmental management programs in the areas that are most affected (tailings and surrounding areas) and accordingly establish the best remediation strategies to minimize risks for the local population.

**Keywords:** potentially toxic elements (PTEs); pollution load index (PLI); potential ecological risk index (RI); dehydrogenase activity (DHA); human risks; Panama

# 3 ECOLOGICAL AND HEALTH RISK ASSESSMENTS OF AN ABANDONED GOLD MINE (REMANCE, PANAMA): COMPLEX SCENARIOS NEED A COMBINATION OF INDICES

Ana Cristina González-Valoys [1,2,3]*, José María Esbrí [2], Juan Antonio Campos [4], Jonatha Arrocha [1], Eva María García-Noguero [2], Tisla Monteza-Destro [5], Ernesto Martínez [6], Raimundo Jiménez-Ballesta [3], Eric Gutiérrez [5], Miguel Vargas-Lombardo [7,8], Efrén Garcia-Ordiales [9], Rosario García-Giménez [3], Francisco Jesús García-Navarro [4] and Pablo Higueras [2]

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## 3.1. Introduction

Mining activities can potentially pollute the environment, especially when tailing materials are left exposed to weather conditions, which favor the release and dispersion of pollutants to the surrounding soil, plants, water bodies and humans [1–4]. The dispersion of potentially toxic elements (PTEs) can be primarily assessed by edaphological characterization and geochemical quantification of pollutants. However, assessing the possible impact on biota requires that certain indices be determined, such as the pollution load index (PLI) to evaluate the degree of contamination; the potential ecological risk index (RI) to evaluate the ecological risk that mine materials can pose [5]. Soil health is the capacity of the soil to function as a vital living ecosystem to sustain plants, animals, and humans [6]. Indicators of soil health provide information about how the soil is functioning with respect to a particular management goal or ecological role [7]. A specific soil function may involve several processes, and each process may be associated with a combination of soil chemical, physical, and biological properties [7]. In this sense, dehydrogenase activity (DHA) is a biological indicator that, added to the rest of the physical and chemical properties measured in this study, allows us to evaluate the health of the soil. Dehydrogenase activity (DHA), as an indicator of "soil health" [8], acts as a monitor of microbiological redox systems and is considered an adequate measure of microbial oxidative activities in soil [9]. DHA also plays a significant role in the biological oxidation of organic matter (OM) by transferring hydrogen from organic substrates to inorganic acceptors [10] and is affected by several factors such as soil moisture, oxidation reduction potential (ORP), reactivity (pH), OM, soil profile depth and concentrations of PTEs [4,9,11]. Thus, it is important to measure these factors and to analyze their relation to DHA.

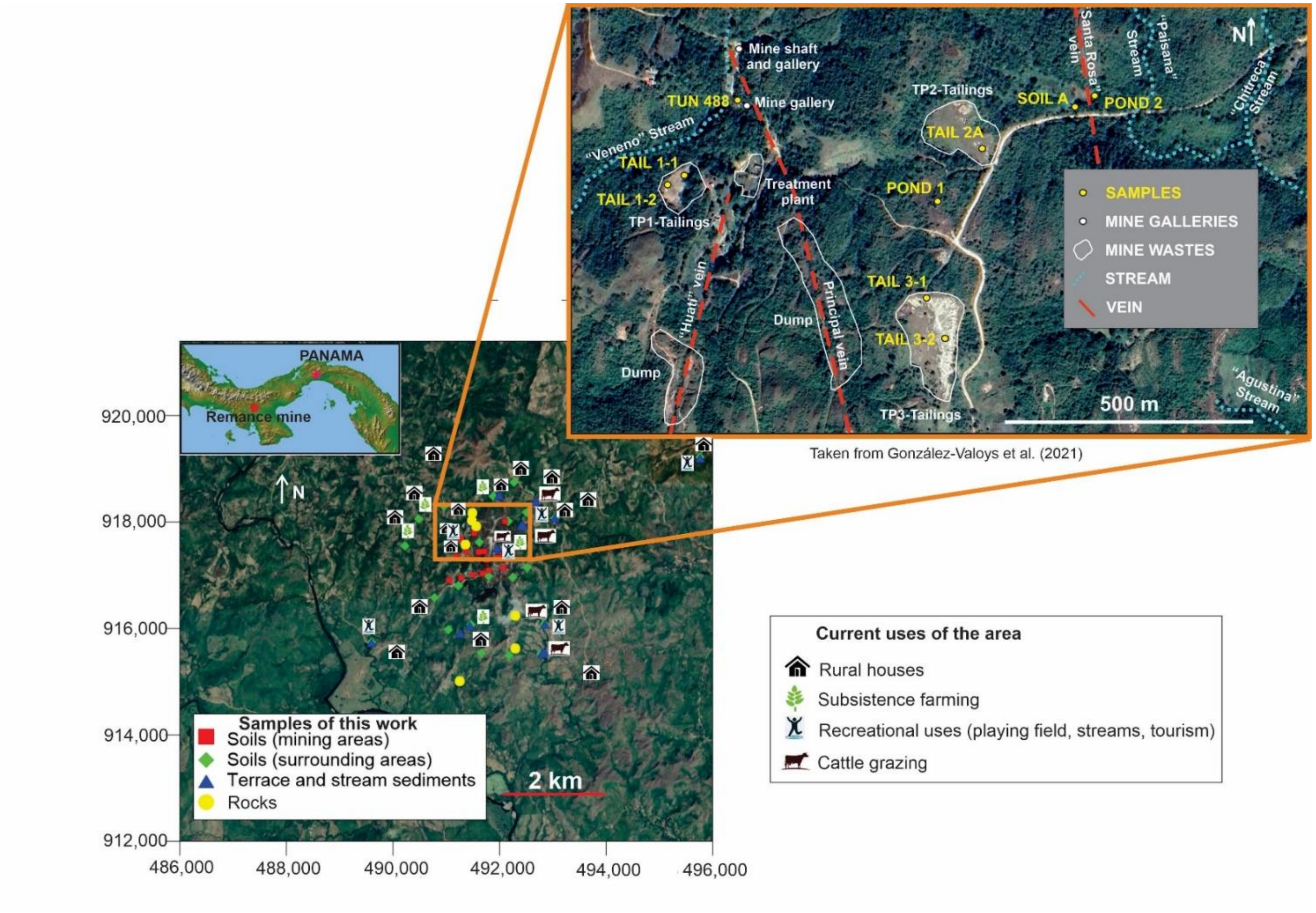
PTEs in mining areas can be of natural origin because they are components of rocks and ore minerals, whether the area has been exploited or not [12]. Mining activity can promote the distribution of these PTEs (Cu, Zn, As, Sb, Ba, Hg) on the surface and increase their concentrations as a result of mineral weathering, which would increase their potential toxicity [13]. It is necessary to recognize that some PTEs released through mining activity (e.g., Cu, Zn) are also essential elements for life, but are toxic in excess, while even low concentrations of other non-essential (e.g., Hg, Pb) elements are toxic for the environment [14,15]. Some of the pollutants found at high concentrations in the Remance area (As, Hg, Zn, Cu, Ba, Sb and cyanide) are on the priority list of the Agency for Toxic Substances and Disease Registry because these substances can potentially affect human health depending on their toxicity, frequency and exposure at polluted sites [16]. All of these pollutants can cause various health problems: arsenic (As) can cause skin, liver and lung cancers; mercury (Hg) produces neurological damage; zinc (Zn) can weaken the immune system; copper (Cu) can cause abnormalities to the nervous system; barium (Ba) can favor muscle paralysis; antimony can harm the respiratory system [17]; and cyanide can cause headaches and enlarge the thyroid gland, even at low concentrations [18]. Other possible effects of PTEs include carcinogenic and non-carcinogenic ones [1,19].

The objective of this study was to characterize the geochemical distribution of these pollutants in soil and fluvial sediment (including active channel stream sediments and terrace sediments). An ecological and health risk assessment was performed by estimating the PLI and RI indices. Besides DHA, an edaphological characterization was used to provide soil health information. The ultimate objective was to gain complete insights to assess the local risks for human health in this area.

## 3.2. Materials and Methods

### 3.2.1. Study Area

The Remance gold mine is located in the province of Veraguas in central Panama. The weather in this area is AMI type according to the Köppen-Geiger classification: a humid tropical climate, with the influence of monsoons and annual rainfall >2250 mm, concentrated (60%) in the four wettest months (August–November). Dry months (January–March) have rainfall rates below 60 mm, and the average temperature of the coolest month is >18 °C [20,21]. The topography in the area is quite irregular, with an altitudinal range between 150 and 266 m.a.s.l. that corresponds to the Veneno stream mouth and the maximum height of hills Principal and Tullido, respectively. The stream is called the Veneno (Poison) because the waters from the first tailings facility used by the Minera Remance company are discharged into it along with the water that flows from the



Taken from González-Valoys et al. (2021)

**Figure 3.1.** Location map of the samples taken at the Remance gold mine site and use of the area.

pithead. Plant cover corresponds mostly to bushes, with areas delimited for small-scale agriculture, with rotary burning for crop cultivation and cattle farming [22].

The exploited mineralization corresponds to epithermal gold hosted in pyroclastic rocks, which include several veins distributed in an area covering approximately 10 $km^2$ [23] (Figure 3.1). Mining exploitation has occurred there intermittently since 1800, but we were unable to find details on its extraction processes. The Veraguas Mining Company produced 15,500 tons with 10.5 g of gold extracted per ton from the Remance mine during the 1800s; the Panama Corporation produced another 70,000 tons with 12 g of gold extracted per ton between the years 1923 and 1932 [23]. The last company to operate the site using the cyanidation process [22] was Minera Remance S.A., between 1989 and 1999 [23]; for this period, it reported cumulative production of 53,480 ounces of gold [24]. During this period, many complaints were filed regarding pollution of local water bodies and the Santa María River [22,24]. Presently (June 2021), there is a plan to reinitiate mining activity, which has led to local discord [25].

A drainage network runs through the area, and includes the Veneno stream, the Chitreca stream and the La Máquina stream on the slopes of Hill Tullido, excavated to exploit a quartz stockwork [23]. Possible sources of pollution in the area include mine excavations, which correspond mostly to surface trenches following mineralized veins. Au occurs as small inclusions within pyrite and marcasite, as well as free gold, disseminated within quartz, together with other accessory minerals in small quantities such as chalcopyrite, sphalerite, galena and arsenopyrite. Ag and As are found with Au, along with anomalous amounts of Sb and locally Hg [23]. Other polluting sources are represented by a mine gallery with its continuous water flow, a number of scattered dumps as a result of excavating trenches that evidently contain some proportions of exploited ore minerals and three tailing dams used to concentrate gold ore by means of cyanidation and containing high concentrations of PTEs (Cu, Zn, As, Sb, Ba, Hg, T-CN) according to studies carried out by González-Valoys et al. (2021) [26]. They are all currently exposed to local tropical climate conditions, such as rain (more than 2200 mm/year) and high temperatures, which favor chemical changes in ore and gangue minerals [4], and wind, which favors the aerial dispersion of pollutants [27]. The area is inhabited by peasants, who engage in subsistence activities such as agriculture and livestock farming [22,28]. Hence, the Remance area can be considered a rural, agricultural and recreational site (Tailing 2 is used as a soccer field by inhabitants, and people visit the area to see the old mine; in rural areas, streams are often used for recreational purposes and for water intake for livestock).

### 3.2.2. Sampling

Samples were collected between May–June 2019 (wet season) and January 2020 (dry season), and included the following the types:

- 43 soil samples, including 19 samples collected in the mining area around the tailings and excavations of the mine's veins and tunnels, and 24 samples collected within the perimeter of the mine and its surroundings;
- 39 sediment samples, including 19 fluvial active channel stream sediments and 20 fluvial terrace sediment samples taken from the banks of water bodies;
- 7 rock samples collected from outcrops to acquire data about the general lithology in the area.

In order to make a comparison to the regional base level, a background sample for each material type (soil, terrace sediment and stream sediment) was taken approximately 4 km from the mining area, near the town of El Naranjal. Figure 1 shows the locations of samples, mine structures and waste accumulation areas [26]. Table S1 displays the sample codes and typology, along with geographic coordinates.

Soil samples were taken using a PVC tube at a depth of 0–30 cm from the potentially most affected zone. Sediment samples were collected with plastic shovels from the top 5–10 cm. All of the samples weighed about 3 kg each and were stored in plastic bags at room temperature prior to sample preparation.

### 3.2.3. Sample Preparation and Analysis

All of the samples were dried at room temperature in the laboratory, disaggregated and passed through a 2 mm sieve. Afterward, some representative aliquots were extracted according to different analytical determinations. The subsamples taken to determine DHA were transported in hermetically sealed bags and were cold-stored. An aliquot of the samples taken at <2 mm (50 g) was crushed in an agate mortar to a <100 µm grain size to determine the concentrations of PTEs (Cu, Zn, As, Sb, Ba, Hg) and for mineralogy identification purposes. Another aliquot was used to determine certain edaphic parameters: pH, electrical conductivity (EC), ORP. The methodology to perform these analyses included a 1:5 suspension (*w*/*v*) (ASTM D 4972) [29], and determination was performed using a multi-parameter benchtop Orion Versa Star Pro device. Other established edaphological parameters included OM, quantified by weight loss at 455 °C (ASTM D 2974) [29], and cationic exchange capacity (CEC), established by the potentiometer method [30]. Color when wet was measured by Munsell soil charts. The soil texture classification was determined by the Bouyoucos method described by Porta [31].

The concentrations of Cu, Zn, As, Sb and Ba were analyzed by energy dispersive X-ray fluorescence spectroscopy (ED-XRF) with Epsilon1 equipment (Panalytical brand) [4]. Total Hg (THg) was determined by Zeeman atomic absorption spectroscopy with high-frequency modulation of light polarization (ZAAS-HFM) using commercial equipment Lumex RA-915 M with a pyrolytic attachment (PYRO-915+) [32]. Certified reference material was employed to check both precision and accuracy: NIST 2710A (Montana soil), with recovery percentages between 95–105%. The analysis of total cyanide, cyanide complexes and easily leachable cyanide was performed by the ALS Global laboratory using the cyanide (CN) complexes according to Standard UNE-EN ISO 14403-2 [33].

DHA was determined by the triphenyltetrazolium chloride (TTC) method [34–36] on samples selected after considering variabilities in As and Cu to assess the influence of the concentrations of these PTEs on this enzymatic activity. Dehydrogenase converts 2,3,5-TTC into triphenyl formazan (TPF) [36]. The homogenized soil samples (1.5 g) were placed inside test tubes (15 × 120 mm) and were mixed with 1.5 mL of deionized water, 0.015 g of $CaCO_3$ and 0.250 mL of TTC (3% *v*/*w*) to be vortexed (2 min) and incubated (Memmert In 30) at 37 °C for 24 h. Next, samples were vortexed (4 min) with methanol used as the extractor agent (5 mL). Tubes were centrifuged (Ortoalresa, Unicen 21) at 4000 rpm for 10 min, and the supernatant was obtained and analyzed in a UV visible spectrophotometer (Biochrom, Libra S60) at 485 nm. The results were expressed as µg TPF $d^{-1}$ $g^{-1}$.

Mineralogy was analyzed by X-ray powder diffraction (XRD) using a PAN analytical X-Pert PRO X-ray diffractometer fitted with a Cu anode. The operating conditions were 40 mA, 45 kV, 0.5° divergence slit and 0.5 mm reception slits. Samples were scanned with a step size of 0.0167° (2θ) and 150 ms per step. Characterization of samples was performed by the powder method between 5 and 55° (2θ). The Match v.3 and Fullprof software for the Rietveld analysis were used for the quantification [37–39]. The Crystallography Open Database (COD) reference patterns were utilized to identify mineral phases.

### 3.2.4. Methods

#### 3.2.4.1. Pollution Index and Pollution Load Index

Soil quality can be estimated by various indices [40]. A site polluted by a certain element can be assessed by the pollution index (PI) (Equation (1)), and the same, but with more than one element, can be determined by the pollution load index (PLI) [5,41] using Equation (2).

$$PI = C_{soil}/C_{background} \quad (1)$$

$$PLI = (PI_1 \times PI_2 \times \ldots \times PI_n)^{1/n} \quad (2)$$

where $C_{soil}$ and $C_{background}$ are the concentrations of the particular PTE in the soil and background samples, respectively (mg $kg^{-1}$). The PLI is the pollution load index of several elements, and the PI is the single pollution index for a certain element. Table 3.1 presents the evaluation criteria for the PLI [5].

**Table 3.1.** Evaluation criteria for the pollution index (PI), the pollution load index (PLI), the toxicity response coefficient (Er) and the potential ecological risk index (RI).

| **Index** | **No Polluted** | **Slightly Polluted** | **Moderately Polluted** | **Considerably Polluted** | **Seriously Polluted** | **Extremely Polluted** |
|---|---|---|---|---|---|---|
| PLI/PI | <1 | 1 < PLI < 2 | 2 < PLI < 3 | PLI > 3 | - | - |
| Er | <10 | <40 | 40 < Er < 80 | 80 < Er < 160 | 160 < Er < 320 | Er > 320 |
| RI | <50 | <150 | 150 < RI < 300 | 300 < RI < 600 | 600 < RI < 1200 | RI > 1200 |

### 3.2.4.2. Toxicity Response Coefficient and the Potential Ecological Risk Index

Hakanson [42] defined RI as an index that combines environmental effects and element toxicity with the aim of considering the general ecological migration and transformation trends of these elements in soils and sediments. Pan et al. (2019) [5] defined the toxicity response coefficient (Er) as the single potential ecological risk for a certain element (Equation (3)), which is used to obtain RI (Equation (4)):

$$Er^i = PI \times Tr^i \quad (3)$$

$$RI = Er_1 + Er_2 + \ldots + Er_n \quad (4)$$

where $Er^i$ is the single RI, PI is the single pollution index for a certain element and $Tr^i$ is the toxicity response coefficient of element i. The Er calculation is based on Hakanson's element toxicity response coefficient standards [42], which can be given as follows: Hg = 40, As = 10, Cu = 5, Zn = 1 and Sb = 7 [43]. Table 3.1 summarizes the evaluation thresholds for these indices based on the respective proposers.

### 3.2.4.3. Human Health Risk Assessment

Some PTEs released from mining waste and incorporated into different environmental compartments can have an immediate effect on human health. The assessment was performed by using the average daily doses (ADD) through three pathways: accidental soil

ingestion (ADD soil ingestion); skin contact (ADD dermal contact) [19,44–46]; and soil dust inhalation (ADD inhalation) [1,47]. Additionally, both the HI and CR risks were assessed in different scenarios: residential, agricultural and recreational [19,48].
ADDs were calculated as mg kg$^{-1}$ day$^{-1}$ as follows (Equations (5)–(7)):

$$\text{ADD soil ingestion} = (C_{soil} \times CF \times IR_{ing} \times FI \times EF \times ED \times RBA)/(BW \times AT) \tag{5}$$

$$\text{ADD dermal contact} = (C_{soil} \times CF \times AF \times ABS_{d} \times EF \times ED \times EV \times SA)/(BW \times AT) \tag{6}$$

$$\text{ADD inhalation} = (C_{soil} \times IR_{air} \times EF \times ED)/(BW \times AT \times PEF) \tag{7}$$

where $C_{soil}$ is the concentration of PTEs in soil in mg kg$^{-1}$; CF is the conversion factor ($1 \times 10^{-6}$ kg mg$^{-1}$); BW is body weight (70 kg in an adult, 15 kg in a child); $IR_{ing}$ is the ingestion rate in soil; FI is fraction ingested; EF is exposure frequency; ED is exposure duration; RBA is the relative bioavailability factor (unitless); AT is the averaging time; AF is the adherence factor; $ABS_{d}$ is the dermal absorption factor (unitless); EV is event frequency; SA is the skin surface area; $IR_{air}$ is the inhalation rate; and PEF is the soil-to-air particulate emission factor (m$^{3}$ kg$^{-1}$). All of these parameters are presented in Table 3.2 for the three exposure pathways in three scenarios. The constants for the PTEs used in the study appear in Table 3.

**Table 3.2.** The exposure parameters used for the study calculations.

| Parameter | Unit | Residential | | Recreational | | Agricultural |
|---|---|---|---|---|---|---|
| | | Adult | Child | Adult | Child | Adult |
| Exposure frequency (EF) | day year$^{-1}$ | 365 | 365 | 96 | 96 | 250 |
| Exposure duration (ED) | year | 30 [a] | 6 | 30 [a] | 6 | 40 |
| Averaging time (AT) | | | | | | |
| Non carcinogenic | year day | ED × EF | ED × EF | ED × EF | ED × EF | ED × EF |
| Carcinogenic | | 70 x EF | 70 x EF | 70 x EF | 70 x EF | 70 x EF |
| Ingestion | | | | | | |
| Ingestion rate in soil ($IR_{ing}$) | mg kg$^{-1}$ | 100 | 200 | 100 | 200 | 100 |
| Fraction ingested (FI) | unitless | 1 | 1 | 1 | 1 | 1 |
| Dermal contact | | | | | | |
| Adherence factor (AF) | mg (cm$^{2}$ event)$^{-1}$ | 0.07 | 0.2 | 0.07 | 0.2 | 0.07 |
| Event frequency (EV) | events day$^{-1}$ | 1 | 1 | 1 | 1 | 1 |
| Skin surface area contact (SA) | cm$^{2}$ | 6032 | 2373 | 6032 | 2373 | 6032 [b] |
| Inhalation | | | | | | |
| Inhalation rate ($IR_{air}$)[a] | m$^{3}$ day$^{-1}$ | 20 | 10 | 20 | 10 | 20 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Particulate emission factor (PEF) | $m^3 kg^{-1}$ | $1.36 \times 10^9$ | $1.36 \times 10^9$ | $1.36 \times 10^9$ | $1.36 \times 10^9$ | $1.36 \times 10^9$ |

[a] Values taken from Department of Environmental Affairs [47]. [b] Value equaling exposure of an adult who engages in agricultural work in the same rural environment. The other values were taken from Gruszecka-Kosowska et al. (2020) [19].

### Non-Carcinogenic Risk

The HI risk was calculated with the hazard quotient (HQ) as follows (Equation (8)):

$$HQ = ADD/RfD \qquad (8)$$

where ADD is the average daily dose for soil ingestion, dermal contact or inhalation as mg $kg^{-1}$ $day^{-1}$, and RfD is the reference dose for oral, dermal or inhalation as mg $kg^{-1}$ $day^{-1}$. Table 3.3 presents the RfD values for the three exposure pathways: RfDo (oral reference doses), RfDd (dermal reference doses) and RfDinh (inhalation reference doses). RfDd was calculated according to Wcislo et al. (2016) [49] and Gruszecka-Kosowska et al. (2020) [19].

The total HI risk of PTEs was determined by the hazard index (HIt) [48], as Equation (9) shows:

$$HIt = HQ1 + HQ2 + \ldots + HQn \qquad (9)$$

where HQs are the hazard quotient values for the 1–n PTEs herein investigated.

**Table 3.3.** The toxicological parameters used for the calculations in this study. Abbreviations: RBA, relative bioavailability factor; ABSd, dermal absorption factor; GIABS, fraction of contaminant absorbed in the gastrointestinal tract; RfDo, oral reference doses; RfDd, dermal reference doses; RfDinh, inhalation reference doses; SFo, slope factor for oral; SFd, slope factor for dermal; SFinh, slope factor for inhalation. RBA, ABS and GIABS are unitless, Reference doses (RfD) in mg $kg^{-1}$ $day^{-1}$ and slope factors (SF) in (mg $kg^{-1}$ $day^{-1})^{-1}$.

| **Element** | **(Unitless)** | | | **RfD (mg $kg^{-1}$ $day^{-1}$)** | | | **SF (mg $kg^{-1}$ $day^{-1})^{-1}$** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **RBA** [a] | **ABSd** [a] | **GIABS** [b] | **RfDo** [b] | **RfDd** [c] | **RfDinh** [d] | **Sfo** [e] | **SFd** [c] | **Sfinh** [d] |
| Cu | 1 | 0.01 | 1 | $4.0 \times 10^{-2}$ | $4.0 \times 10^{-2}$ | - | 1.7 | 1.7 | - |
| Zn | 1 | 0.01 | 1 | $3.0 \times 10^{-1}$ | $3.0 \times 10^{-1}$ | - | - | - | - |
| As | 0.6 | 0.03 | 1 | $3.0 \times 10^{-4}$ | $3.0 \times 10^{-4}$ | $3.0 \times 10^{-4}$ | 1.5 | 1.5 | 15 |
| Sb | 1 | 0.01 | 0.15 | $4.0 \times 10^{-4}$ | $2.7 \times 10^{-3}$ | - | - | - | - |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Ba | 1 | 0.01 | 0.07 | $2.0 \times 10^{-1}$ | $2.9 \times 10^{0}$ | - | - | - | - |
| Hg | 1 | 0.01 | 0.07 | $3.0 \times 10^{-4}$ | $4.3 \times 10^{-3}$ | $8.6 \times 10^{-5}$ | - | - | - |

[a] Values taken from Gruszecka-Kosowska et al. (2020) [17]. [b] Values taken from USEPA [50]. [c] Values calculated according to Wcislo et al. (2016) [49] and Gruszecka-Kosowska et al. (2020) [19]. [d] Values taken from Kamunda et al. (2016) [1]. [e] Values taken from Pan et al. (2019) [5].

**Carcinogenic Risk**

CR risks were calculated as follows (Equation (10)):

$$CR = ADD \times SF \qquad (10)$$

where ADD is the average daily dose for soil ingestion, dermal contact or inhalation as mg $kg^{-1}$ $day^{-1}$ and SF is the slope factor for oral, dermal or inhalation over a lifetime for a particular PTE that plays a key role in daily toxin intake and results in an increased risk of an individual developing cancer [1,5]. Table 3 presents the SF values for the three exposure pathways. SFd was calculated according to Wcislo et al. (2016) [49] and Gruszecka-Kosowska et al. (2020) [19].

The total CR risks of PTEs were determined according to the CRt values [48] as follows (Equation (11)):

$$CRt = CR1 + CR2 + \ldots + CRn \qquad (11)$$

where CRt are the CR risk values for the 1–n PTEs investigated in this study.

The total risk for both the HI and CR risks was calculated by the sum of the risks for the different exposure pathways: (Equation (12)):

$$\text{Risk (total)} = \text{Risk (ingestion)} + \text{Risk (dermal)} + \text{Risk (inhalation)} \qquad (12)$$

### 3.2.4.4. Statistical Analyses

Microsoft Excel spreadsheets were used to manage the results. Minitab 15 was employed to analyze the statistical parameters of the analytical results. A multivariate analysis was performed by applying Ward's linkage to obtain significant dendrograms. A factor analysis and a principal component analysis (PCA) were applied to search for the influence of factors, or group of factors, using "Varimax" orthogonal rotation.

The distribution maps of PTEs, PLI, RI, HI and CR were generated with the Surfer 9 software, licensed by the UCLM, using the option "inverse distance to a power (2)" to generate the corresponding distribution maps.

## 3.3. Results

### 3.3.1. Total Contents

The average concentrations of the PTEs from the different material types in the sampled Remance gold mine areas are presented in Table 3.4, while all of the obtained results appear in S2. pH ranged between 3.9 and 5.9. The most acidic value was found in pithead sediments and the most neutral one in the mining work areas. EC ranged between 0.03 to 0.52 dS m$^{-1}$, with the lowest value in the mining area and the highest value in pithead sediments. OM varied between 0.8% and 12.9%, with the smallest amount in tailings and the largest amount in pithead sediments.

**Table 3.4.** Average values and standard deviation of the physicochemical parameters and PTEs (mg kg$^{-1}$) in the different material types in the sampled areas.

| **Sample Type** | **N** | **pH** | **EC (dS m$^{-1}$)** | **OM (%)** | **Cu** | **Zn** | **As** | **Sb** | **Ba** | **Hg** |
|---|---|---|---|---|---|---|---|---|---|---|
| Soils (mining area) [a] | 19 | 5.9 ± 0.5 | 0.03 ± 0.03 | 8.2 ± 3.8 | 61.3 ± 51.8 | 46.9 ± 23.9 | 56.4 ± 54.4 | 13.7 ± 2.6 | 200.6 ± 123.5 | 0.11 ± 0.16 |
| Soils (surrounding areas) [a] | 24 | 5.2 ± 0.4 | 0.05 ± 0.04 | 5.1 ± 2.0 | 93.5 ± 85.6 | 62.8 ± 35.9 | 35.5 ± 44.2 | 16.4 ± 5.4 | 349.7 ± 198.0 | 0.06 ± 0.06 |
| Terrace sediments [a] | 20 | 5.3 ± 1.0 | 0.14 ± 0.22 | 4.3 ± 2.2 | 65.2 ± 32.7 | 55.3 ± 18.8 | 152.7 ± 210.3 | 19.8 ± 8.9 | 355.7 ± 115.0 | 0.62 ± 1.48 |
| Stream sediments [a] | 19 | 5.8 ± 0.5 | 0.07 ± 0.08 | 3.4 ± 2.7 | 74.5 ± 40.0 | 66.3 ± 34.1 | 143.4 ± 131.7 | 23.2 ± 12.5 | 398.7 ± 125.5 | 0.21 ± 0.25 |
| Tailings [b] | 5 | 4.1 ± 0.8 | 0.29 ± 0.57 | 0.8 ± 0.2 | 77.7 ± 107.4 | 27.0 ± 15.2 | 614.1 ± 222.7 | 17.8 ± 5.6 | 376.2 ± 164.6 | 1.37 ± 1.12 |
| Cyanidation ponds [b] | 4 | 4.9 ± 0.2 | 0.09 ± 0.02 | 5.3 ± 1.7 | 10.9 ± 7.0 | 37.1 ± 22.9 | 41.0 ± 19.7 | 1.4 ± 0.7 | 253.9 ± 64.8 | 0.17 ± 0.07 |
| Pithead sediments [b] | 1 | 3.9 | 0.52 | 12.9 | 403.0 | 153.0 | 5030.0 | 2.2 | 55.4 | 0.62 |

[a] This work. [b] Values according to González-Valoys et al. (2021) [26].

The concentrations of Cu varied between 10.9 and 403.0 mg kg$^{-1}$, and those of As from 41.0 to 5030.0 mg kg$^{-1}$, with the lowest concentration in cyanidation ponds and the highest in pithead sediments. Cyanidation ponds are the final part of the process, and then join the streams [22]; these have been exposed to rain currents for more than 20 years. Pithead sediments are sediments that come out of the galleries of the mine, located in the "principal" vein, where underground water flows; this water current is then incorporated into a "Veneno" stream. Zn concentrations varied between 27.0 and 153.0 mg kg$^{-1}$, with the lowest in mine tailings and the highest in pithead sediments. Sb concentrations ranged from 1.4 to

23.2 mg kg$^{-1}$, and those of Ba between 55.4 and 398.7 mg kg$^{-1}$, with the lowest in cyanidation ponds and the highest in stream sediments for both elements. Hg concentrations ranged from 0.06 to 1.37 mg kg$^{-1}$, with the lowest in soils from the surrounding areas and the highest in mine tailings. The last tailings were from mining operations in 1999. Mercury is one of the elements present in mineralization in small amounts [23], which is why it can be present in tailings after mining.

The order of the average concentration of PTEs was: Ba>As>Cu>Zn>Sb>Hg in stream sediments and terrace sediments, Ba>Cu> As> Zn> Sb> Hg in the soils from the mining area and Ba>Cu>Zn>As>Sb>Hg in the soils from the surrounding area.

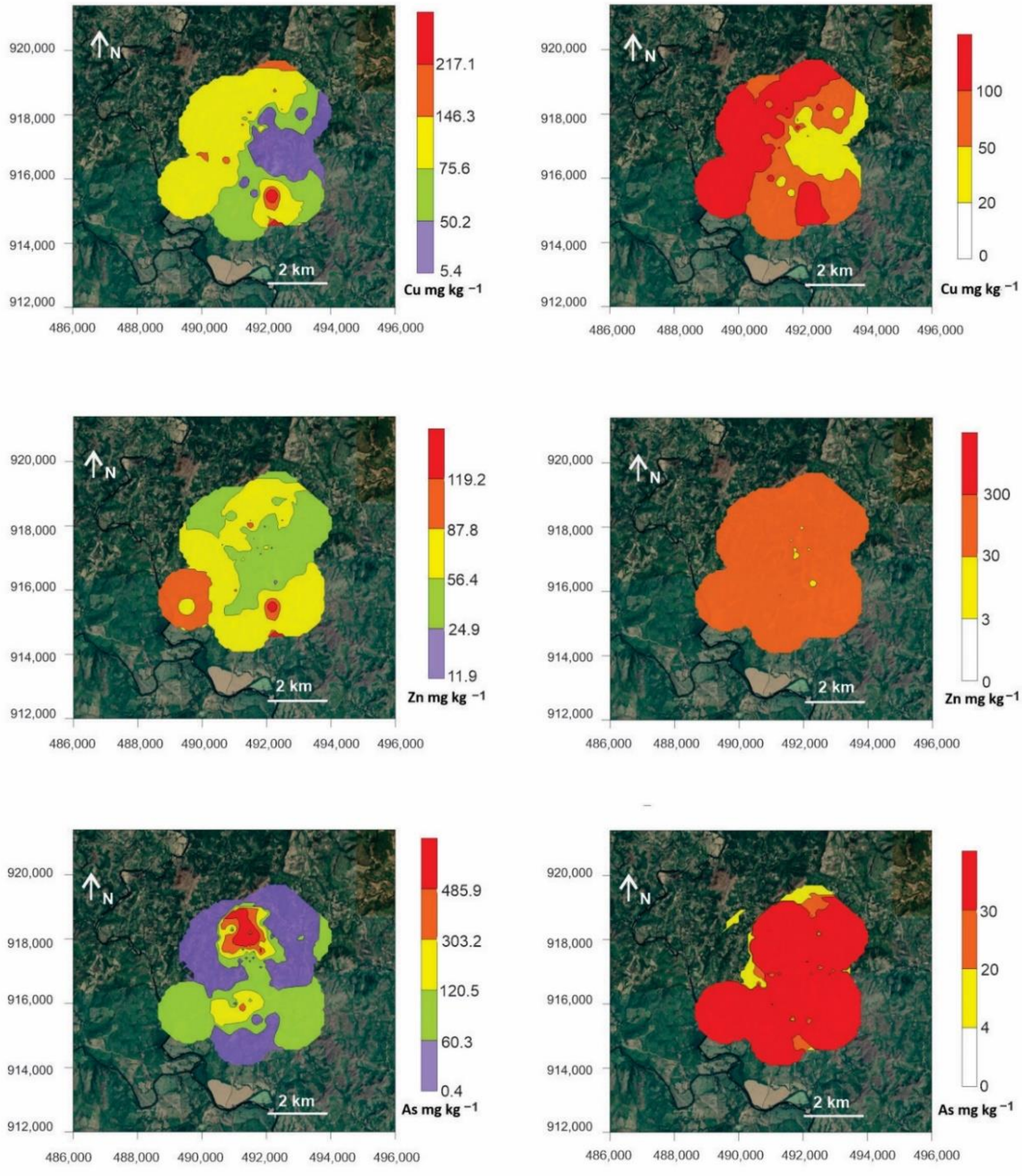
The average PTE concentrations for rocks from outcrops, as determined by ED-XRF (ST2), were: Cu (40.3 mg kg$^{-1}$), Zn (22.8 mg kg$^{-1}$), As (122.7 mg kg$^{-1}$), Sb (25.7 mg kg$^{-1}$), Ba (239.7 mg kg$^{-1}$) and T(Hg) (0.17 mg kg$^{-1}$).

### 3.3.2. Spatial Variability

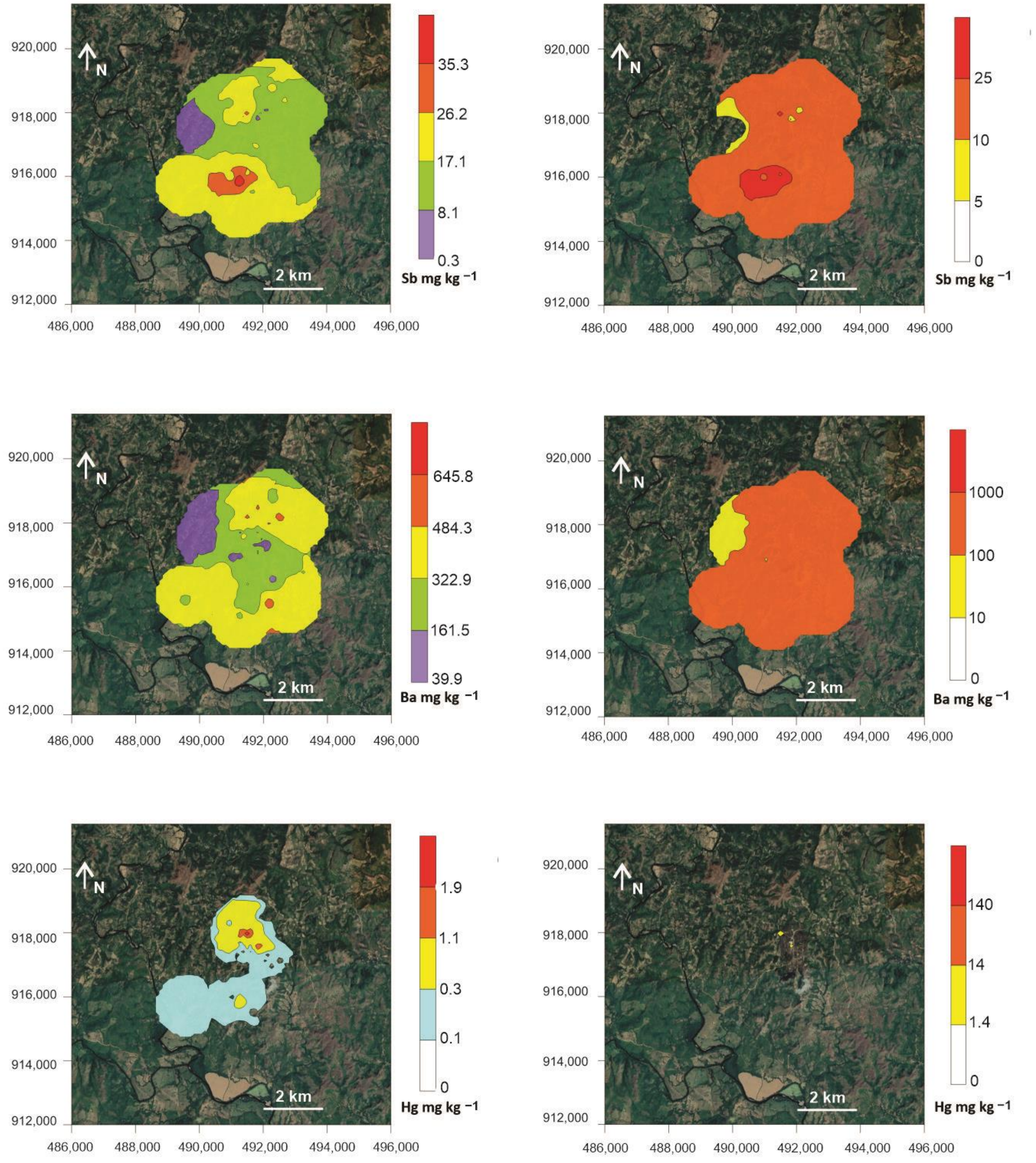
Isoconcentration maps were generated to analyze the geographical distribution of the analytical results. One set of maps indicates the concentration thresholds (minimum value, average–1σ, average, average + 1σ, average + 2σ), while another set displays the results according to the guideline values indicated in Table 3.5 for agricultural, residential and industrial uses (Zn, As, Ba and Hg according to the Panama Standard; Cu and Sb according to the Costa Rica Standard). The PTE concentrations were high over almost the entire perimeter of the study area, and surpassed the Cu and As guideline values, even for industrial-use levels, while Zn, Sb and Ba exceeded the values set out in the standard for residential use. The exception was Hg, which exceeded the value for agricultural use only in tailings (Figure 3.2A,B).

**Table 3.5.** Soil guidelines for the PTEs for Panama and Costa Rica (all values are expressed as mg kg$^{-1}$).

| Soil Guidelines | Uses | Cu | Zn | As | Sb | Ba | Hg | Reference |
|---|---|---|---|---|---|---|---|---|
| Panama | Others | | 3 | 4 | | 10 | 1.4 | |
| Maximum permissible limits of soil | Residential | | 30 | 20 | | 100 | 14 | [51] |
| contaminants for human health | Industrial | | 300 | 30 | | 1000 | 140 | |
| Costa Rica | Prevention Value | 20 | 300 | 5 | 2 | 150 | 0.5 | |
| Intervention value | Agricultural | 20 | 450 | 35 | 5 | 300 | 12 | |
| (Concentration above which there are | Residential | 50 | 1000 | 55 | 10 | 500 | 36 | [52] |
| potential direct or indirect risks to human health) | Industrial | 100 | 2000 | 150 | 25 | 750 | 70 | |


920,000
918,000
916,000
914,000
912,000
486,000
488,000
490,000
492,000
494,000
496,000
N
2 km
217.1
146.3
75.6
50.2
5.4
Cu mg kg −1
100
50
20
0
Cu mg kg −1
119.2
87.8
56.4
24.9
11.9
Zn mg kg −1
300
30
3
0
Zn mg kg −1
485.9
303.2
120.5
60.3
0.4
As mg kg −1
30
20
4
0
As mg kg −1

(**A**)



(**B**)

**Figure 3.2.** (**A**) Distribution maps for Cu, Zn, and As. Left: according to the statistical figures; right: according to the soil guideline values listed in Table 5 (yellow: agricultural limit; orange: residential limit; red: industrial limit). Distribution maps of PTEs generated using the concentration values for soils (surrounding areas), soils (mining areas), stream sediments, terrace sediments, tailings, cyanidation ponds and pithead sediments. (**B**) Distribution maps for Sb, Ba and Hg. Left: according to the statistical figures; right: according to the soil guideline values listed in Table 5 (yellow: agricultural limit; orange: residential limit; red: industrial limit). Distribution maps of PTEs generated using the

concentration values for soils (surrounding areas), soils (mining areas), stream sediments, terrace sediments, tailings, cyanidation ponds and pithead sediments.

### 3.3.3. Mineralogical Analysis

Table 3.6 presents the estimated percent abundance of the identified minerals for the selected samples from soils, terrace sediments and stream sediments. The diffractograms of studied samples are compiled in Figure S1. The main mineral phases identified in soils were quartz (89%), kaolinite (10%) and illite (1%), while terrace sediments were composed of quartz (84%), kaolinite (11%), feldspar (3%), illite (1%) and chlorite (1%). Stream sediments comprised quartz (84%), kaolinite (11%), and chlorite (5%). The found mineral phases were similar in soils and sediments (terrace sediments and stream sediments) and the main phases were quartz and kaolinite. The presence of PTEs could be associated with clay fractions, such as kaolinite and illite [53], due to no characteristic minerals of these PTEs being detected in the XRD analysis. Consequently, the most plausible explanation is the absorption/adsorption of the PTEs by clays, as they were the minerals with the highest representation.

**Table 3.6.** The estimated percent abundance of the mineral phases identified for the selected samples.

| Sample | Sample Type | Kaolinite (%) | Illite (%) | Chlorite (%) | Quartz (%) | Feldspar (%) |
|---|---|---|---|---|---|---|
| TR EU 3 | Terrace sediments | traces | n.d. | n.d. | 100 | n.d. |
| TR J1 | Terrace sediments | 10 | n.d. | traces | 85 | 5 |
| TR J2 | Terrace sediments | 5 | n.d. | n.d. | 90 | 5 |
| TR J3 | Terrace sediments | 15 | 5 | n.d. | 75 | 5 |
| TR R2 | Terrace sediments | 15 | n.d. | n.d. | 85 | n.d. |
| TR R9 | Terrace sediments | 15 | n.d. | n.d. | 85 | n.d. |
| TRB | Terrace sediments | 15 | n.d. | 5 | 80 | n.d. |
| TERR 17 | Terrace sediments | 10 | n.d. | 5 | 75 | 10 |
| SDEU2 | Stream sediments | 10 | n.d. | 25 | 65 | n.d. |
| SDJ2 | Stream sediments | 10 | n.d. | n.d. | 90 | n.d. |
| SDJ3 | Stream sediments | 10 | n.d. | 5 | 85 | n.d. |
| SDR2 | Stream sediments | 15 | n.d. | n.d. | 85 | n.d. |
| SDR9 | Stream sediments | 15 | n.d. | n.d. | 85 | n.d. |
| SED17 | Stream sediments | 5 | n.d. | traces | 95 | n.d. |
| SA6S | Soils (surrounding areas) | 10 | n.d. | n.d. | 90 | n.d. |
| SR5S | Soils (surrounding areas) | 10 | n.d. | n.d. | 90 | n.d. |
| SR6S | Soils (surrounding areas) | 10 | n.d. | n.d. | 90 | n.d. |
| S2LS | Soils (surrounding areas) | 10 | 5 | n.d. | 85 | n.d. |

n.d.: not detected; traces: signal appears but is below the detection limit (<100 ppm).

### 3.3.4. DHA and Correlations with Edaphic Parameters and PTEs

The DHA values were higher in soils than in terrace sediments and were lower in stream sediments (63.27 > 37.47 > 24.79 µg TPF $g^{-1}$ $d^{-1}$), contrary to what was reported in soils and sediments in Morro do Ouro, the largest industrial gold mine in Brazil [54]. The DHA values of the present work were lower than those measured in other contaminated soils in the Ventanas Cu smelter, situated in the Puchuncaví Valley of Central Chile (110 mg TPF $g^{-1}$ $d^{-1}$) [55], in Almadenejos located in the mining district of Almadén, Spain (484 mg TPF $g^{-1}$ $d^{-1}$) [36], and in restored soils from mine sites (140–580 mg TPF $g^{-1}$ $d^{-1}$) reported by Mukhopadhyay and Maiti (2010) [56]. To seek correlations between pollution of the area and its biological activity, a statistical analysis was performed. Table 3.7 presents the average values of the DHA results, the physicochemical parameters, and the concentrations of PTEs, total cyanide (T-CN), complex cyanide (C-CN) and easily releasable cyanide (E-CN) for soils, terrace sediments and stream sediments. The same trend was found in the OM (5.3 > 4.2 > 3.4%) and CEC (10.61 > 9.74 > 9.08 cmol $kg^{-1}$) data, while As showed higher concentrations in stream sediments and terrace sediments and lower concentrations in soils (188.9 > 146.5 > 55.7 mg $kg^{-1}$). Some elements (Cu and Zn) presented higher concentrations in soils than in sediments, while total cyanide presented a more complex fractionation.

**Table 3.7.** Summary of the average values and standard deviation of edaphic parameters, DHA (in µg TPF $g^{-1}$ $d^{-1}$) and concentrations of PTEs and cyanide expressed in mg $kg^{-1}$. Abbreviations: EC, electrical conductivity; ORP, oxidation reduction potential; OM, organic matter; CEC, cationic exchange capacity; T-CN, total cyanide; C-CN, complex cyanide; and E-CN, easily released cyanide.

| Sample Type | pH | EC dS $m^{-1}$ | ORP mV | OM % | CEC cmol $kg^{-1}$ | Cu | Zn | As | Sb | Ba | Hg | DHA | T-CN | C-CN | E-CN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Terrace sediments | 5.3 ± 1.0 | 0.14 ± 0.22 | 489.2 ± 132.6 | 4.2 ± 2.2 | 9.7 ± 2.4 | 66.0 ± 32.0 | 56.5 ± 19.1 | 146.5 ± 206.6 | 18.8 ± 9.7 | 365.2 ± 119.8 | 0.59 ± 1.44 | 37.47 ± 43.31 | <1.0 | <1.0 | <1.0 |
| Stream sediments | 5.7 ± 0.6 | 0.07 ± 0.05 | 441.3 ± 117.3 | 3.4 ± 2.4 | 9.1 ± 2.0 | 74.0 ± 59.0 | 77.7 ± 44.3 | 188.9 ± 145.3 | 25.5 ± 13.0 | 429.5 ± 137.8 | 0.30 ± 0.31 | 24.79 ± 34.13 | 1.3 ± 1.5 | 1.2 ± 1.1 | <1.0 |
| Soils (surrounding areas) | 5.3 ± 0.4 | 0.07 ± 0.05 | 507.0 ± 86.0 | 5.3 ± 2.2 | 10.6 ± 4.5 | 111.7 ± 127.4 | 80.4 ± 45.6 | 55.7 ± 50.7 | 19.0 ± 6.0 | 430.8 ± 127.1 | 0.08 ± 0.08 | 63.27 ± 43.39 | 1.0 ± 0.8 | <1.0 | <1.0 |

### 3.3.5. Multi-Elemental Analysis

According to the mineralogical analysis, the samples were very similar (soils, terraces sediments and stream sediments), which is why we grouped them all together to perform the dendrogram and PCA. In the dendrogram obtained from the cluster analysis (Figure 3.3), Cu appears to be associated with Zn in one group, while As, Hg, Sb and Ba appear in another group. To determine the strength of the relationships between DHA and edaphic parameters, multivariate principal component analysis (PCA) was used (Figure 3.4, Table 3.8). Although the relationships were not so strong, the most significant in the first main component (PC1) and positively related to DHA (0.384) were T-CN (0.464), OM (0.379), C-CN (0.369), E-CN (0.333) and CEC (0.202), and negatively related to ORP (−0.334) and Ba (−0.160); while in the second principal component (PC2), As (−0.489), Sb (−0.424) and Hg (−0.423) were negatively related.

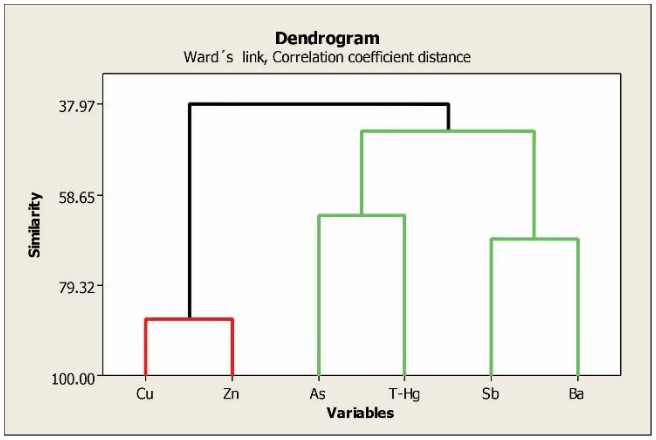


**Figure 3.3.** Dendrogram of the relations between the concentrations of PTEs in the study. Dendrogram generated with the data from soils, terrace sediments and stream sediments.

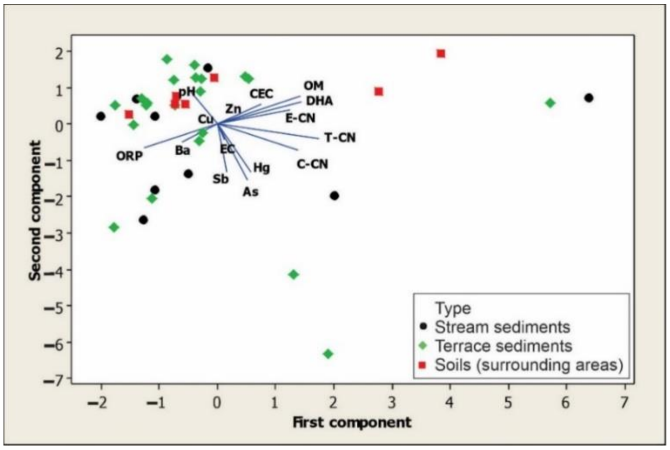


**Figure 3.4.** DHA and relationship with edaphic parameters, PTEs and cyanide. Generated with the data from soils, terrace sediments and stream sediments.

**Table 3.8.** Principal component analysis matrix for the relationship between DHA and edaphic parameters. Numbers in bold correspond to PC1 or PC2 more significative.

| Variable | PC1 | PC2 |
|---|---|---|
| pH | −0.131 | 0.319 |
| EC | 0.034 | −0.141 |
| ORP | **−0.334** | −0.204 |
| OM | **0.379** | 0.247 |
| CEC | **0.202** | 0.177 |
| Cu | −0.018 | −0.019 |
| Zn | 0.074 | 0.048 |
| As | 0.141 | **−0.489** |
| Sb | 0.044 | **−0.424** |
| Ba | **−0.160** | −0.161 |
| Hg | 0.154 | **−0.423** |
| DHA | **0.384** | 0.190 |
| T-CN | **0.464** | −0.125 |
| C-CN | **0.369** | −0.227 |
| E-CN | **0.333** | 0.122 |

### 3.3.6. Pollution Index (PI) and Pollution Load Index (PLI)

Table 3.9 presents the PI and PLI values, and Figure 3.5 provides the PLI map. According to the evaluation criteria for PI and PLI presented in Table 3.1, the PI indicated serious pollution (PI > 3) in the different studied areas. Within these, the tailings and the pithead that showed the highest PI values due to the materials of both areas were the main sources of PTEs in the nearby environment.

**Table 3.9.** The PI and PLI average values and standard deviation calculated for the different sample types in the Remance mine area.

| Type | PI Cu | PI Zn | PI As | PI Sb | PI Ba | PI Hg | PLI |
|---|---|---|---|---|---|---|---|
| Soils (mining area) [a] | 1.3 ± 1.1 | 0.6 ± 0.3 | 1.4 ± 1.4 | 0.9 ± 0.2 | 0.4 ± 0.2 | 1.6 ± 2.4 | 0.7 ± 0.3 |
| Soils (surrounding areas) [a] | 1.9 ± 1.8 | 0.8 ± 0.5 | 0.9 ± 1.1 | 1.1 ± 0.4 | 0.7 ± 0.4 | 1.0 ± 0.9 | 0.7 ± 0.4 |
| Terrace sediments [a] | 0.8 ± 0.4 | 0.7 ± 0.2 | 5.4 ± 7.4 | 6.6 ± 3.0 | 0.7 ± 0.2 | 15.9 ± 37.9 | 1.9 ± 1.2 |
| Stream sediments [a] | 1.1 ± 0.6 | 0.9 ± 0.5 | 5.8 ± 5.3 | 1.3 ± 0.7 | 0.8 ± 0.2 | 6.1 ± 7.5 | 1.6 ± 0.8 |
| Tailings [b] | 11.1 ± 15.3 | 1.0 ± 0.5 | 33.0 ± 12.0 | 59.3 ± 18.7 | 1.6 ± 0.7 | 9.1 ± 7.5 | 7.3± 3.0 |
| Cyanidation ponds [b] | 1.6 ± 1.0 | 1.3 ± 0.8 | 2.2 ± 1.1 | 4.7 ± 2.4 | 1.1 ± 0.3 | 1.1 ± 0.5 | 1.6 ± 0.3 |
| Pithead sediments [b] | 57.6 | 5.5 | 270.4 | 7.3 | 0.2 | 4.1 | 9.2 |

[a] This work. [b] Values calculated with the data obtained from González-Valoys et al. 2021 [26].

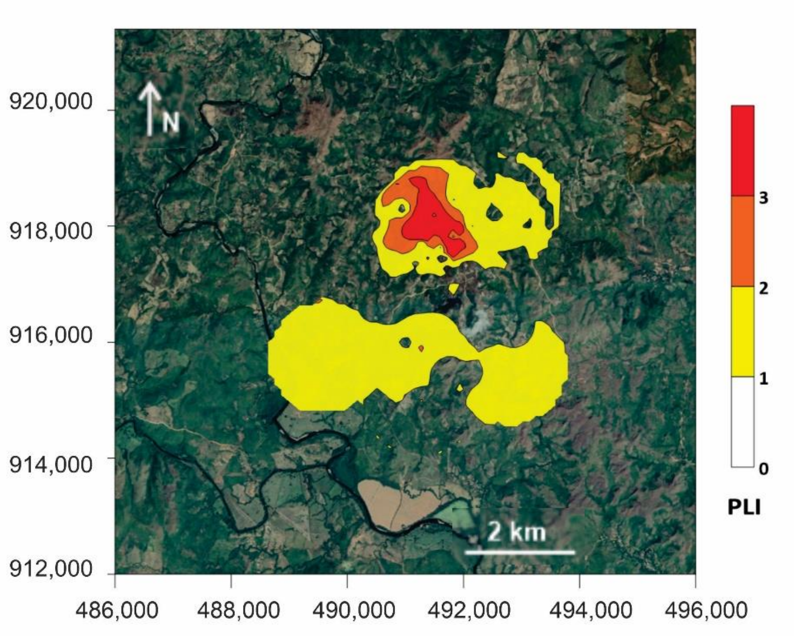


**Figure 3.5.** Distribution map of PLI for Cu, Zn, As, Sb, Ba and Hg. Distribution maps of PLI generated using the concentration values for soils (surrounding areas), soils (mining areas), stream sediments, terrace sediments, tailings, cyanidation ponds and pithead sediments.

The PLI followed this order: pithead sediments> tailings> terrace sediments> stream sediments = cyanidation ponds > soils from the mining area and soils (from the mining and surrounding areas). The PLI map shows an area with moderate to considerable damage corresponding to and around the tailings and pithead area, followed by slight damage to the surrounding area and south of the mining concession.

### 3.3.7. Toxicity Response Coefficient (Er) and Potential Ecological Risk Index (RI)

The values calculated for Er and RI of Cu, Zn, As, Sb and Hg are shown in Table 3.10, while Figure 3.6 presents the geographical distribution for RI. According to the evaluation criteria presented in Table 3.1 for Er and the toxicity according to each element, the Er values suggests that tailings have a damaging role in the area, as well as the pithead; thus the terrace sediments and stream sediments have been significantly impacted and represent important sources of risk due to their content of As, Hg and Sb; in the case of soils from the mining area, Hg is the only major concern.

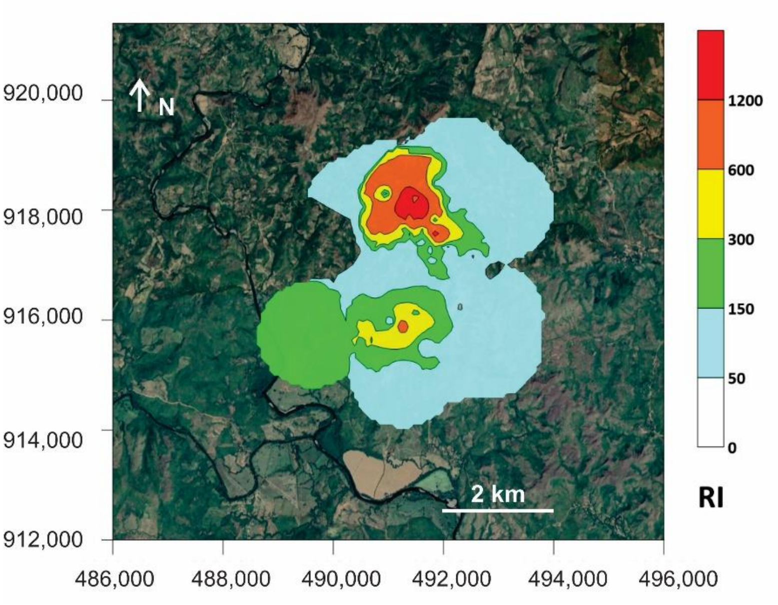


**Figure 3.6.** Geographical distribution of RI for Cu, Zn, As, Sb and Hg. Distribution maps of RI generated using the concentration values for soils (surrounding areas), soils (mining areas), stream sediments, terrace sediments, tailings, cyanidation ponds and pithead sediments.

**Table 3.10.** Average values and standard deviation of Er and RI for the different sample types.

| Type | Er Cu | Er Zn | Er As | Er Sb | Er Hg | RI |
|---|---|---|---|---|---|---|
| Soils (surrounding area) | 9.5 ± 8.8 | 0.8 ± 0.5 | 8.9 ± 10.8 | 7.8 ± 2.5 | 38.1 ± 35.4 | 65 ± 44 |
| Soils (mining area) | 6.4 ± 5.4 | 0.6 ± 0.3 | 14.1 ± 13.6 | 6.5 ± 1.2 | 65.5 ± 97.4 | 93 ± 108 |
| Terrace sediments | 4.1 ± 2.0 | 0.7 ± 0.2 | 51.6 ± 72.7 | 44.2 ± 22.1 | 605.6 ± 1481.2 | 706 ± 1554 |
| Stream sediments | 5.5 ± 2.9 | 0.9 ± 0.5 | 55.3 ± 52.8 | 9.0 ± 4.8 | 233.1 ± 295.0 | 304 ± 337 |
| Tailings [a] | 55.5 ± 76.7 | 1.0 ± 0.5 | 330.2 ± 119.7 | 415.1 ± 131.1 | 365.9 ± 299.0 | 1168 ± 509 |
| Cyanidation ponds [a] | 7.8 ± 5.0 | 1.3 ± 0.8 | 22.0 ± 10.6 | 32.7 ± 16.9 | 44.7 ± 19.6 | 109 ± 32 |
| Pithead sediments [a] | 287.9 | 5.5 | 2704.3 | 51.3 | 165.3 | 3214 |

[a] Values calculated with the data obtained from González-Valoys et al. 2021 [26].

The average RI values and their distribution indicate a gradation in risk as follows: pithead sediments (extreme risk); tailings and terrace sediments (serious risk); stream sediments (high risk); cyanidation ponds, soils from the mining area and soils from the surrounding areas (mild risk). One remarkable finding indicated that the areas at higher risk coincided with those with higher PLI values for As, Sb, Ba and Hg (Figure 3.5), with an extensive area representing a serious to extreme RI that also corresponded to the area near tailings and pithead sediments.

### 3.3.8. Human Health Risk Assessment

#### 3.3.8.1. Non-carcinogenic Risk (HI)

The limit for HI and HQ risks is 1; those that exceed this value are considered high risk [48]. The average estimated total HI (soil ingestion, dermal contact and inhalation) risks assumed for children and adults in the different scenarios (residential, recreational, agricultural) are presented in Supplementary Table S3. Figure 3.7B represents the distribution of the HI risks for children in the residential and recreational scenarios. In the residential scenario for children, the value was exceeded in all areas and in this order: pithead sediments > tailings > terrace sediments > stream sediments > soils from the mining area > soils from the surrounding areas> cyanidation ponds (150.31 > 19.03 > 5.29 > 5.12 > 2.18 > 1.67 > 1.30, respectively). In the recreational scenario, the HI limit was exceeded in the following areas: pithead sediments> tailings> terrace sediments> stream sediments (39.53 > 5.00 > 1.39 > 1.35, respectively) (Table S3).

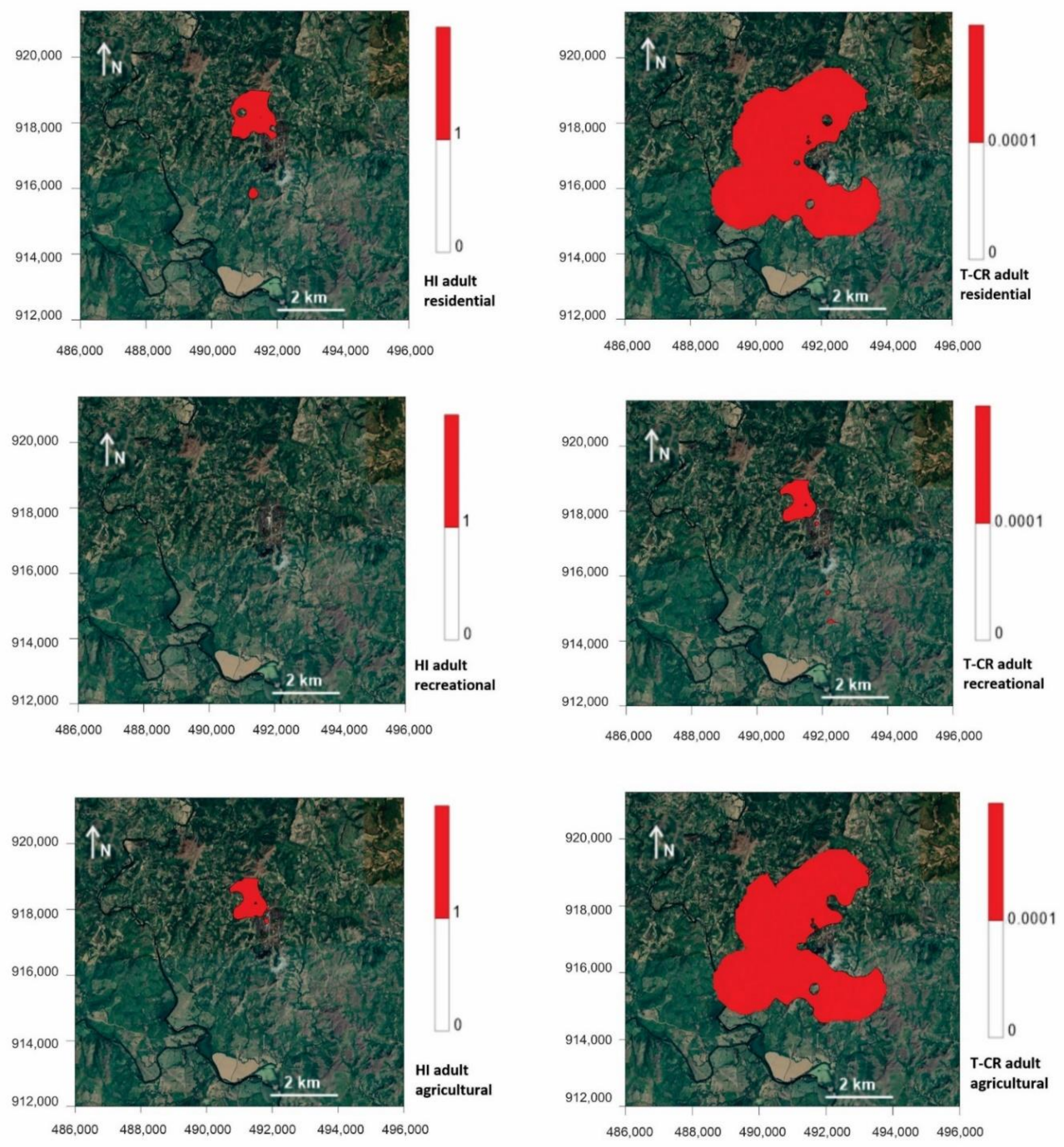
The HI map for adults in the residential, agricultural and recreational scenarios is shown in Figure 3.7A, and the average values are summarized in supplementary Table S3. The HI risks for adults were surpassed in pithead sediments in both the residential and agricultural scenarios (17.44 and 11.94, respectively), and also in tailings in the same two scenarios (2.20 and 1.51, respectively). This threshold in the recreational scenario was surpassed only in pithead sediments (4.59).

The HI risks were much higher for children than for adults, and the ingestion route contributed the most. In it, As showed the highest values (exceeding HQ). The HQ value through which HI risks were represented by PTEs was evaluated and exceeded by As through the ingestion route for children (residential) and adults (residential and agricultural), and through dermal contact for children in the residential scenario.

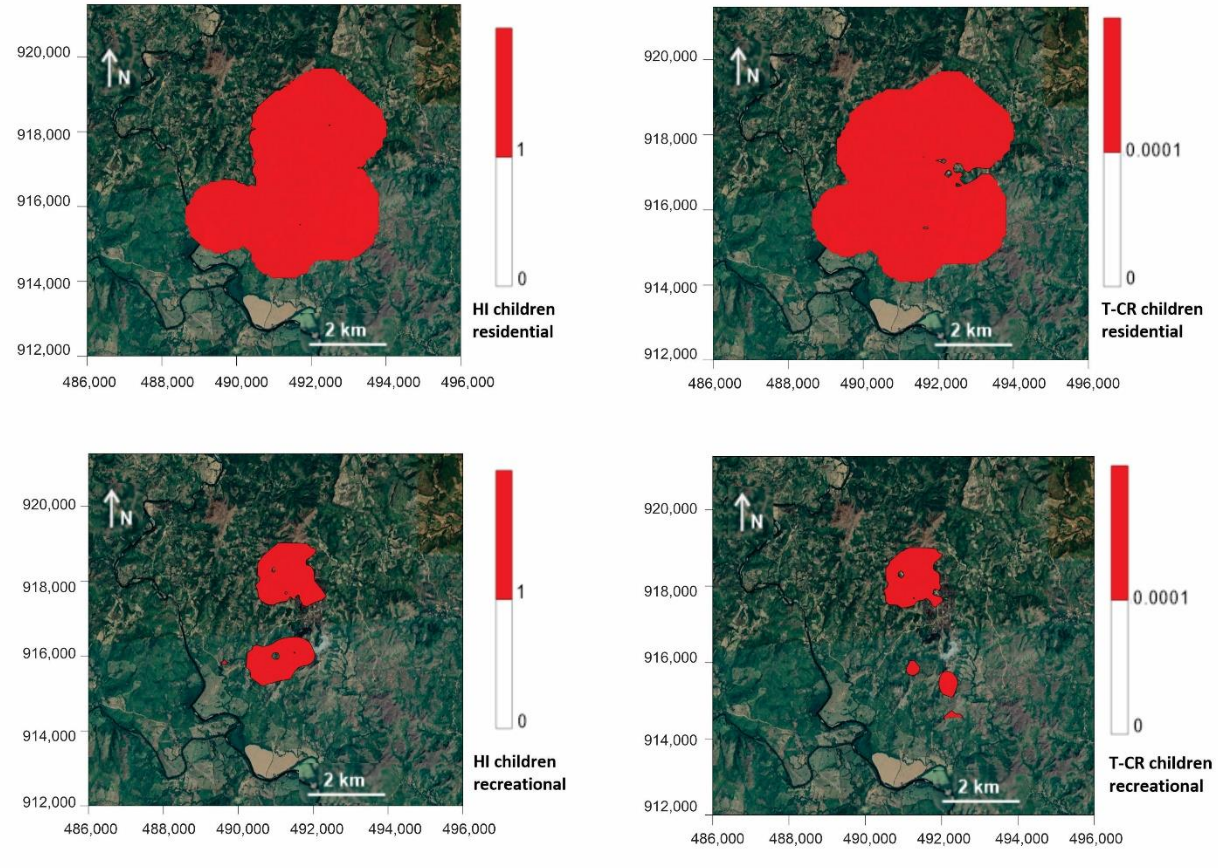
#### 3.3.8.2. Carcinogenic Risk (CR)

The acceptable CR risk level was set to equal $1 \times 10^{-6}$ for an individual PTE and to equal $1 \times 10^{-4}$ for the sum of carcinogenic PTEs [19,48]. Values exceeding these are considered CR. The average values of total CR (soil ingestion, dermal contact and inhalation) represented by the materials studied for children and adults in the different scenarios (residential, recreational, agricultural) are presented in supplementary Table S4. Figure 3.7B also presents the CR maps for children in the residential and recreational scenarios. For the children in the residential scenario, the following areas were above the acceptable limit: pithead sediments > tailings >

stream sediments = terrace sediments > soils from the surrounding areas> soils from the mining area ($6.6 \times 10^{-3} > 8.6 \times 10^{-4} > 3.1 \times 10^{-4} = 3.1 \times 10^{-4} > 2.3 \times 10^{-4} > 1.9 \times 10^{-4}$, respectively). In the recreational scenario, pithead sediments ($1.7 \times 10^{-3}$) and tailings ($2.3 \times 10^{-4}$) were above the acceptable value.



(**A**)



(**B**)

**Figure 3.7.** (**A**) Non-carcinogenic risk and carcinogenic risk maps for adults in the residential, recreational and agricultural scenarios. Risk calculated by the concentration values for soils from surrounding areas, soils from mining areas, stream sediments, terrace sediments, tailings, cyanidation ponds and pithead sediments. (**B**) Non-carcinogenic risk and carcinogenic risk maps for children in the residential and recreational scenarios. Risk calculated by the concentration values for soils from surrounding areas, soils from mining areas, stream sediments, terrace sediments, tailings, cyanidation ponds and pithead sediments.

Figure 3.7A depicts the CR maps for adults in the residential, agricultural and recreational scenarios; values are presented in supplementary Table S4. The acceptable value for the residential scenario was exceeded in the following areas: pithead sediments> tailings>

stream sediments> terrace sediments> soils from the surrounding areas> soils from the mining area ($3.8 \times 10^{-3} > 4.9 \times 10^{-4} > 1.8 \times 10^{-4} > 1.7 \times 10^{-4} > 1.3 \times 10^{-4} > 1.0 \times 10^{-4}$, respectively). That for the agricultural scenario was exceeded in this order: pithead sediments> tailings> stream sediments = terrace sediments> soils from the surrounding areas ($3.5 \times 10^{-3} > 4.5 \times 10^{-4} > 1.6 \times 10^{-4} = 1.6 \times 10^{-4} > 1.1 \times 10^{-4}$, respectively). In the recreational scenario, this value was exceeded in pithead sediments ($1.0 \times 10^{-3}$) and tailings ($1.3 \times 10^{-4}$). CR risks were much higher for children than adults, and the highest risk route was soil ingestion, followed by dermal contact. The acceptable value for a single PTE ($1 \times 10^{-6}$) was exceeded for Cu and As in the residential and agricultural scenarios.

## 3.4. Discussion

Observing the dispersion maps of Remance PTEs (Figure 2) with respect to local legislation, the total concentrations of As and Cu are those that represent a potential impact on the area, taking into consideration that a study of mobile concentrations (bioavailability) is required to ensure that these elements are indeed present in concerning concentrations. The PCA showed that DHA was favored by the presence of OM and cyanide species in soils, terraces and stream sediments. Furthermore, As and Hg were positive factors (PC1) if DHA was present, as Campos et al. (2018) [36] described in a mining and metallurgical complex of Hg. In the Remance mine scenario, only the higher Cu concentrations seemed to affect soil health in terms of DHA levels. This is surprising evidence for a gold mine with cyanidation during the metallurgical process, but it evidences the need to merge some risk indices for an appropriate initial risk assessment. It is worth mentioning that a complete risk assessment involves acquiring a big dataset that includes data on the pollutants in all environmental compartments and local food supplies, as well as a complete study of the local population's life habits, such as the origin of the food they eat, the time they spend in local polluted areas, among many more [57–59].

A first risk assessment stage should involve the precise delimitation of affected areas. For this purpose, it is necessary to apply indices capable of comparing the levels of PTEs in polluted areas with background areas. Although some indices properly describe the release of certain elements to the environment, a complex scenario such as the Remance mine requires combining a group of elements with similar dispersion patterns. As shown in Figure 5, the PLI shows the impact mainly of the tailing area, pithead sediments, and its surroundings, showing how the contamination has spread from the tailings and pithead sediments; the other zone with a lower degree of impact is to the south of the mine, where excavation work took place. The information provided by the PLI data seems more meaningful than the application of single enrichment factors or applying similar indices to single elements [60].

A second stage should provide information about the degree of effects to biota. It is necessary to state that establishing the bioavailability and transfer rates of PTEs can be challenging, but some indices can provide an initial view of these effects to biota based on a generic dataset. Tailings and pithead are the source of contamination by PTEs affecting the surrounding soils and downstream sediments, as evidenced by the Er and RI. Distribution maps delimit two small areas with considerable damage, including mining materials and some sediments downstream. With this simple approach, it is possible to better delimit the areas indicated by PLI that probably affect biota. The final stage must evaluate the effects of these restricted areas on the local population's health. As some elements of the Remance mine are carcinogenic, a combination of HI and CR indices is needed to better delimit risk areas. As expected, risk areas are small dimensions for children's recreational use (both HI and CR), but delimit an area with larger CR dimensions for agricultural use. Obviously, HI and CR for children in residential areas appear with larger values, except HI for adults. The main factors related to the distribution of risk areas were the presence of As, Sb and Hg, which is consistent with many other case studies of mining and industrial pollution in China [61]. Another remarkable finding was that the CR risks for adults and for agricultural uses were wider than expected, as the RI only revealed mild damage for soil samples. Looking at the pollutants that exceeded the accepted levels of risk to human health, the main one was As because it can cause skin, liver and lung cancer, while excess Cu can cause abnormalities of the nervous system [17].

The ecological and health risk assessments of the Remance area revealed that these mining areas are complex scenarios in which many (synergistic and antagonistic) factors must be considered. Although soil health did not seem to be affected by the presence of PTEs, or was even positively affected by them, these PTEs can pose a high risk in some areas, especially areas with recreational uses for children and agricultural uses.

## 3.5. Conclusions

The abandoned Remance mine poses a risk for the health of the environment and its inhabitants, as different indicators revealed. In particular, the RI best expressed the environmental risk, which coincided with the results of CR and HI to human health.

The areas with the highest risk were pithead sediments, tailings, terrace sediments and stream sediments, which were the areas that still had a strong impact due to mining activity and, to a lesser degree, impacted the mining work area, cyanidation ponds and soils. These results were corroborated by soil health as assessed through DHA, which showed that soil health was better than that of terrace sediments and stream sediments.

According to Er and PI, the elements that posed a risk for the environment were As>Hg>Sb>Cu. The main HI was constituted by As through ingestion and dermal contact, and As and Cu for the CR through ingestion and dermal contact. In all cases, the worst scenario was for children, and for adults in residential, recreational and agricultural scenarios. This is a major concern because peasants live in the study area with their families, and they perform agricultural work and live there on a generally permanent basis.

From a human health point of view, the most relevant pollutant was As because it can cause skin, liver and lung cancer and represented HI and CR through ingestion and dermal contact pathways. More details on the bioavailability of elements are needed in order to realistically assess the risks related to the presence of this element in the area.

Given all of the above considerations for both environmental and human health, it is necessary to set up environmental management programs in these areas to establish the best remediation strategies [62–64] and help preserve the right to health and to live in a clean environment.

**Supplementary Materials:** The following are available online at www.mdpi.com/xxx/s1. Table S1: Sample codes and typology, along with geographic coordinates, Table S2: Result of samples, Table S3: Non-carcinogenic risk, Table S4: Carcinogenic risk, and Figure S1: Diffractograms.

## 3.6. Declarations

**Author Contributions:** Conceptualization, A.C.G.-V., J.M.E., J.A., T.M.-D., E.M., R.J.-B., E.G., M.V.-L., E.G.-O., F.J.G.-N. and P.H.; Data curation, A.C.G.-V., J.M.E., J.A., E.M.G.-N., R.J.-B., R.G.-G. and P.H.; Formal analysis, A.C.G.-V., J.A., E.M.G.-N., E.G., R.G.-G. and P.H.; Funding acquisition, A.C.G.-V., J.A., T.M.-D., M.V.-L., R.G.-G., F.J.G.-N. and P.H.; Investigation, A.C.G.-V., J.M.E., J.A., E.M.G.-N., T.M.-D., E.M., R.J.-B., E.G., M.V.-L., E.G.-O., R.G.-G., F.J.G.-N. and P.H.; Methodology, A.C.G.-V., J.M.E., J.A., E.M.G.-N., R.J.-B., E.G., F.J.G.-N. and P.H.; Project administration, A.C.G.-V., J.A., T.M.-D., R.J.-B., F.J.G.-N. and P.H.; Resources, A.C.G.-V., J.A., E.M.G.-N., T.M.-D., E.M., E.G., M.V.-L., R.G.-G., F.J.G.-N. and P.H.; Software, A.C.G.-V., J.M.E., J.A., E.M.G.-N., E.M., E.G., R.G.-G. and P.H.; Supervision, J.M.E., J.A.C., T.M.-D., R.J.-B. and P.H.; Validation, A.C.G.-V., J.M.E. and P.H.; Visualization, A.C.G.-V., J.M.E. and P.H.; Writing—original draft, A.C.G.-V., J.M.E., J.A.C., E.G., R.G.-G. and P.H.; Writing—review and editing,

A.C.G.-V., J.M.E., J.A.C., J.A., E.M.G.-N., T.M.-D., E.M., R.J.-B., E.G., M.V.-L., E.G.-O., R.G.-G., F.J.G.-N. and P.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** This study was funded by the Secretaria Nacional de Ciencia,Tecnología e Innovación (SENACYT); the Institute for the Training and Use of Human Resources (IFARHU) of Panama (270-2019-109); and Fondos para Grupos de Investigación UCLM (2020-GRIN-27011).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors thank the Secretaria Nacional de Ciencia,Tecnología e Innovación (SENACYT), the Sistema Nacional de Investigación de Panamá (SNI), the Institute for the Training and Use of Human Resources (IFARHU) of Panama, the Technological University of Panama (UTP), the University of Castilla-La Mancha (UCLM), the University of Oviedo and the Autonoma University of Madrid (UAM) for their research support, the National Directorate of Mineral Resources of the Ministry of Commerce and Industry (MICI) of Panama for granting access to the Remance mine.

**Conflicts of Interest:** The authors declare no conflict of interest.

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## 3.8. Supplementary Materials

**Table supplementary S1**. Samples codes, typology and geographical coordinates

| Typology | Sample codes | Geographical coordinates (WGS 84, 17 P) | |
|---|---|---|---|
| | | N | W |
| Soils (surrounding area) | SA5 | 917617 | 491615 |
| | SA6 | 916982 | 491801 |
| | SA7 | 916805 | 491225 |
| | SA8 | 916582 | 490786 |
| | SA9 | 916963 | 492249 |
| | SA10 | 917145 | 492519 |
| | SA11 | 918018 | 492167 |
| | SA12 | 918180 | 492508 |
| | SEU1 | 915530 | 492786 |
| | SEU2 | 915494 | 492181 |
| | SEU3 | 916237 | 492298 |
| | SJ1 | 918483 | 491876 |
| | SJ2 | 918750 | 492277 |
| | SR1 | 915039 | 491251 |
| | SR2 | 915540 | 491662 |
| | SR3 | 915981 | 491042 |
| | SR4 | 916072 | 491461 |
| | SR5 | 915741 | 489599 |
| | SR6 | 916087 | 492841 |
| | SR7 | 918296 | 490953 |
| | SM1 | 917551 | 490221 |
| | SM2 | 918056 | 490481 |
| | S1 | 918067 | 493044 |
| Soils (mining area) | SA1 | 918019 | 492109 |
| | VP1 | 917450 | 491718 |
| | VM2 | 917570 | 491365 |
| | 1 | 917440 | 491373 |
| | 2 | 917304 | 491470 |
| | 3 | 917437 | 491606 |
| | 4 | 917296 | 491759 |
| | 5 | 917092 | 491795 |

| | | | |
|---|---|---|---|
| | 6 | 917008 | 491502 |
| | 7 | 917346 | 492079 |
| | 8 | 917133 | 492076 |
| | 9 | 917325 | 491968 |
| | 10 | 917301 | 492152 |
| | 11 | 916900 | 491055 |
| | 12 | 917791 | 491523 |
| | 13 | 916948 | 491277 |
| | 14 | 917029 | 491678 |
| | 15 | 917686 | 491283 |
| | 16 | 917352 | 491194 |
| Terrace sediments | TR EU1 | 915546 | 492834 |
| | TR EU2 | 915540 | 492810 |
| | TR EU 3 | 915530 | 492801 |
| | TR J1 | 918024 | 491479 |
| | TR J2 | 918022 | 491458 |
| | TR J3 | 918170 | 491488 |
| | TR J4 | 918500 | 491992 |
| | TR J5 | 918379 | 492672 |
| | TR R1 | 915005 | 491255 |
| | TR R2 | 915901 | 491261 |
| | TR R3 | 916047 | 491441 |
| | TR R4 | 915728 | 489595 |
| | TR R5 | 916075 | 492852 |
| | TR R9 | 917992 | 491484 |
| | TR#16 | 918071 | 493038 |
| | TR 18L | 917938 | 492432 |
| | TR 19L | 917945 | 492419 |
| | TR 20L | 917920 | 492444 |
| | TR B | 917510 | 491947 |
| Stream sediments | SDEU 1 | 915546 | 492834 |
| | SDEU 2 | 915540 | 492810 |
| | SDEU 3 | 915530 | 492801 |
| | SDJ 2 | 918022 | 491458 |

| | | | |
|---|---|---|---|
| | SDJ 3 | 918170 | 491488 |
| | SDJ 4 | 918500 | 491992 |
| | SDJ 5 | 918379 | 492672 |
| | SDR 1 | 915005 | 491255 |
| | SDR 2 | 915901 | 491261 |
| | SDR 3 | 916047 | 491441 |
| | SDR 4 | 915728 | 489595 |
| | SDR 5 | 916075 | 492852 |
| | SDR 9 | 917992 | 491484 |
| | SD# 16 | 918071 | 493038 |
| | SD 18L | 917938 | 492432 |
| | SD 19L | 917945 | 492419 |
| | SD 20L | 917920 | 492444 |
| | SD B | 917510 | 491947 |
| Tailings* | R JI (Tailing 1) | 917912 | 491364 |
| | R J2 (Tailing 1) | 917890 | 491323 |
| | R LD (Tailing 2) | 917954 | 491925 |
| | SA4 (Tailing 3) | 917668 | 491818 |
| | SED A1 (Tailing 3) | 917573 | 491859 |
| Cyanidation ponds* | R1 LD | 917835 | 491845 |
| | TR Rel 1L | 917835 | 491845 |
| | SA3 | 918050 | 492113 |
| | SD R3 L | 918052 | 492112 |
| Pithead sediments* | SDJ1 | 918024 | 491479 |
| Outcrops | VEU1 | 915617 | 492294 |
| | VEU2 | 916237 | 492298 |
| | AR1 | 915005 | 491255 |
| | AJ1 | 918170 | 491488 |
| | AJ2 | 918024 | 491479 |
| | VM1 | 917920 | 491556 |
| | V HUATI | 917570 | 491365 |

* Values taken from González-Valoys et al. 2021 [26].

**Table supplementary S2.** Edaphic parameters

| Typology | Sample codes | pH | EC (dS $m^{-1}$) | OM (%) | Cu mg $kg^{-1}$ | Zn mg $kg^{-1}$ | As mg $kg^{-1}$ | Sb mg $kg^{-1}$ | Ba mg $kg^{-1}$ | T-Hg mg $kg^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Soils (surrounding area) | SA5 | 4.9 | 0.01 | 2.2 | 19.4 | 20.8 | 33.8 | 16.6 | 307.6 | 0.14 |
| | SA6 | 5.0 | 0.07 | 3.3 | 25.9 | 40.1 | 101.9 | 20.4 | 334.7 | 0.20 |
| | SA7 | 4.9 | 0.04 | 4.4 | 35.0 | 35.1 | 54.3 | 17.2 | 211.1 | 0.05 |
| | SA8 | 5.1 | 0.04 | 8.0 | 167.9 | 89.9 | 0.8 | 20.0 | 487.4 | 0.08 |
| | SA9 | 4.8 | 0.03 | 2.2 | 20.5 | 33.3 | 19.2 | 12.6 | 170.6 | 0.05 |
| | SA10 | 4.7 | 0.02 | 2.8 | 19.0 | 45.4 | 13.0 | 12.9 | 318.4 | 0.03 |
| | SA11 | 5.8 | 0.10 | 5.5 | 24.4 | 43.8 | 24.8 | 15.5 | 743.2 | 0.04 |
| | SA12 | 6.1 | 0.09 | 4.4 | 168.2 | 98.1 | 0.4 | 16.3 | 665.7 | 0.00 |
| | SEU1 | 5.6 | 0.05 | 5.4 | 129.8 | 91.7 | 58.5 | 17.1 | 505.8 | 0.05 |
| | SEU2 | 5.4 | 0.01 | 4.5 | 396.9 | 166.1 | 15.4 | 19.5 | 599.9 | 0.00 |
| | SEU3 | 4.8 | 0.03 | 4.7 | 19.2 | 18.5 | 69.0 | 13.7 | 95.6 | 0.03 |
| | SJ1 | 5.1 | 0.03 | 5.0 | 109.8 | 59.3 | 5.4 | 16.0 | 568.8 | 0.01 |
| | SJ2 | 5.7 | 0.12 | 10.2 | 161.6 | 53.5 | 18.1 | 19.1 | 209.5 | 0.04 |
| | SR1 | 5.1 | 0.04 | 3.7 | 45.5 | 53.3 | 33.7 | 22.1 | 133.2 | 0.10 |
| | SR2 | 5.4 | 0.03 | 6.2 | 29.4 | 50.7 | 0.4 | 15.2 | 158.6 | 0.06 |
| | SR3 | 5.6 | 0.04 | 6.4 | 131.6 | 97.2 | 8.6 | 18.9 | 475.7 | 0.01 |
| | SR4 | 5.7 | 0.04 | 4.4 | 101.6 | 59.1 | 2.9 | 15.6 | 393.9 | 0.05 |
| | SR5 | 5.8 | 0.15 | 6.4 | 137.3 | 133.9 | 168.1 | 31.9 | 473.1 | 0.23 |
| | SR6 | 5.4 | 0.09 | 7.0 | 38.7 | 70.3 | 116.4 | 16.2 | 403.6 | 0.05 |
| | SR7 | 4.9 | 0.02 | 5.2 | 89.1 | 44.7 | 0.4 | 13.3 | 217.7 | 0.06 |
| | SM1 | 4.7 | 0.03 | 6.1 | 129.9 | 64.8 | 0.4 | 0.3 | 40.0 | 0.01 |
| | SM2 | 5.0 | 0.03 | 7.3 | 108.8 | 42.8 | 4.8 | 12.6 | 79.9 | 0.10 |
| | S1 | 4.8 | 0.02 | 2.5 | 40.5 | 32.2 | 67.6 | 13.8 | 449.0 | 0.06 |
| | Average | 5.2 | 0.05 | 5.1 | 93.5 | 62.8 | 35.5 | 16.4 | 349.7 | 0.06 |
| | Standard deviation | 0.4 | 0.04 | 2.0 | 85.6 | 35.9 | 44.2 | 5.4 | 198.0 | 0.06 |
| | Max | 6.1 | 0.15 | 10.2 | 396.9 | 166.1 | 168.1 | 31.9 | 743.2 | 0.23 |
| | Min | 4.7 | 0.01 | 2.2 | 19.0 | 18.5 | 0.4 | 0.3 | 40.0 | 0.00 |
| Soils (mining area) | SA1 | 5.1 | 0.03 | 2.0 | 19.6 | 31.3 | 128.1 | 14.0 | 349.2 | 0.18 |
| | VP1 | 4.4 | 0.13 | 2.0 | 19.2 | 35.0 | 111.9 | 15.4 | 257.3 | 0.10 |
| | VM2 | 5.2 | 0.04 | 1.7 | 116.9 | 47.0 | 56.4 | 14.4 | 543.3 | 0.10 |
| | 1 | 6.1 | 0.02 | 6.7 | 119.9 | 88.4 | 39.1 | 13.8 | 216.6 | 0.02 |
| | 2 | 6.1 | 0.01 | 8.1 | 101.6 | 73.5 | 48.8 | 12.3 | 182.3 | 0.14 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 3 | 5.8 | 0.02 | 5.8 | 16.6 | 28.4 | 23.5 | 10.9 | 157.7 | 0.05 |
| | 4 | 5.9 | 0.02 | 8.1 | 24.8 | 12.8 | 102.0 | 9.2 | 68.3 | 0.03 |
| | 5 | 6.3 | 0.02 | 8.3 | 15.0 | 15.7 | 28.5 | 13.8 | 399.3 | 0.14 |
| | 6 | 6.4 | 0.03 | 6.9 | 19.8 | 31.3 | 116.6 | 14.6 | 211.6 | 0.03 |
| | 7 | 6.3 | 0.03 | 13.5 | 23.1 | 73.3 | 0.4 | 10.9 | 86.9 | 0.03 |
| | 8 | 6.1 | 0.03 | 9.0 | 36.4 | 41.8 | 28.1 | 14.1 | 147.9 | 0.04 |
| | 9 | 5.9 | 0.04 | 13.3 | 22.8 | 74.9 | 11.5 | 11.0 | 133.1 | 0.05 |
| | 10 | 6.3 | 0.01 | 8.4 | 16.8 | 14.7 | 25.4 | 11.2 | 123.6 | 0.03 |
| | 11 | 6.2 | 0.01 | 8.5 | 131.2 | 57.2 | 20.4 | 12.9 | 60.3 | 0.06 |
| | 12 | 6.0 | 0.01 | 6.0 | 52.7 | 33.5 | 208.4 | 19.1 | 229.8 | 0.72 |
| | 13 | 6.2 | 0.05 | 13.0 | 107.9 | 62.7 | 16.2 | 15.6 | 103.4 | 0.05 |
| | 14 | 6.0 | 0.04 | 10.1 | 26.0 | 26.4 | 75.6 | 18.4 | 259.4 | 0.20 |
| | 15 | 5.7 | 0.01 | 15.2 | 166.0 | 74.5 | 0.4 | 16.2 | 88.9 | 0.02 |
| | 16 | 6.1 | 0.01 | 9.3 | 129.2 | 68.4 | 30.3 | 12.5 | 192.9 | 0.03 |
| | Average | 5.9 | 0.03 | 8.2 | 61.3 | 46.9 | 56.4 | 13.7 | 200.6 | 0.11 |
| | Standard deviation | 0.5 | 0.03 | 3.8 | 51.8 | 23.9 | 54.4 | 2.6 | 123.5 | 0.16 |
| | Max | 6.4 | 0.13 | 15.2 | 166.0 | 88.4 | 208.4 | 19.1 | 543.3 | 0.72 |
| | Min | 4.4 | 0.01 | 1.7 | 15.0 | 12.8 | 0.4 | 9.2 | 60.3 | 0.02 |
| Terrace sediments | TR EU1 | 6.5 | 0.03 | 1.7 | 39.8 | 49.1 | 84.4 | 16.2 | 391.3 | 0.04 |
| | TR EU2 | 6.1 | 0.15 | 6.5 | 60.4 | 60.5 | 68.9 | 17.1 | 327.3 | 0.05 |
| | TR EU 3 | 6.5 | 0.04 | 2.5 | 58.0 | 67.5 | 119.0 | 19.8 | 391.5 | 0.05 |
| | TR J1 | 4.9 | 0.07 | 4.3 | 109.3 | 82.5 | 121.9 | 19.9 | 427.0 | 0.34 |
| | TR J2 | 3.8 | 0.19 | 5.7 | 126.6 | 65.0 | 714.5 | 41.8 | 511.0 | 1.54 |
| | TR J3 | 3.0 | 1.02 | 2.2 | 55.4 | 27.0 | 95.7 | 17.7 | 528.1 | 0.85 |
| | TR J4 | 6.0 | 0.11 | 6.1 | 109.9 | 72.1 | 24.7 | 13.1 | 368.5 | 0.04 |
| | TR J5 | 5.0 | 0.07 | 5.1 | 60.4 | 45.4 | 43.2 | 14.1 | 300.2 | 0.03 |
| | TR R1 | 6.2 | 0.04 | 3.1 | 119.9 | 94.8 | 29.7 | 19.2 | 386.0 | 0.02 |
| | TR R2 | 5.0 | 0.03 | 1.7 | 26.8 | 18.5 | 391.0 | 36.2 | 227.9 | 0.71 |
| | TR R3 | 4.6 | 0.06 | 3.4 | 22.7 | 48.8 | 45.8 | 13.4 | 134.1 | 0.16 |
| | TR R4 | 5.5 | 0.07 | 5.7 | 100.9 | 72.1 | 69.3 | 16.7 | 263.9 | 0.20 |
| | TR R5 | 5.4 | 0.10 | 7.7 | 23.3 | 64.8 | 4.4 | 11.5 | 204.8 | 0.04 |
| | TR R9 | 4.4 | 0.08 | 2.0 | 56.0 | 46.3 | 676.2 | 39.3 | 511.5 | 6.47 |
| | TR#16 | 5.0 | 0.04 | 2.2 | 47.6 | 34.8 | 49.1 | 16.4 | 430.1 | 0.05 |
| | TR 18L | 5.8 | 0.08 | 2.5 | 68.8 | 51.3 | 37.1 | 16.8 | 446.6 | 0.03 |
| | TR 19L | 5.4 | 0.19 | 5.4 | 61.8 | 60.4 | 71.6 | 14.7 | 341.1 | 0.16 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | TR 20L | 6.7 | 0.13 | 3.8 | 56.7 | 43.5 | 36.6 | 15.1 | 398.1 | 0.03 |
| | TR B | 4.6 | 0.20 | 9.5 | 35.3 | 46.3 | 219.5 | 17.0 | 169.4 | 0.96 |
| | Average | 5.3 | 0.14 | 4.3 | 65.2 | 55.3 | 152.7 | 19.8 | 355.7 | 0.62 |
| | Standard deviation | 1.0 | 0.22 | 2.2 | 32.7 | 18.8 | 210.3 | 8.9 | 115.0 | 1.48 |
| | Max | 6.7 | 1.02 | 9.5 | 126.6 | 94.8 | 714.5 | 41.8 | 528.1 | 6.47 |
| | Min | 3.0 | 0.03 | 1.7 | 22.7 | 18.5 | 4.4 | 11.5 | 134.1 | 0.02 |
| Stream sediments | SDEU 1 | 5.8 | 0.34 | 11.6 | 47.5 | 59.1 | 59.0 | 14.1 | 319.2 | 0.06 |
| | SDEU 2 | 6.0 | 0.04 | 3.6 | 113.3 | 66.8 | 139.6 | 23.3 | 315.0 | 0.07 |
| | SDEU 3 | 6.3 | 0.07 | 4.2 | 65.9 | 45.4 | 55.0 | 13.6 | 242.2 | 0.09 |
| | SDJ 2 | 5.5 | 0.08 | 2.3 | 145.6 | 128.6 | 272.0 | 27.6 | 512.0 | 0.32 |
| | SDJ 3 | 5.0 | 0.12 | 2.9 | 133.2 | 81.4 | 348.5 | 29.6 | 549.0 | 0.70 |
| | SDJ 4 | 6.3 | 0.09 | 5.6 | 101.6 | 72.5 | 27.6 | 16.5 | 384.0 | 0.03 |
| | SDJ 5 | 6.4 | 0.03 | 2.8 | 101.1 | 77.8 | 43.0 | 21.3 | 359.2 | 0.03 |
| | SDR 1 | 5.8 | 0.01 | 1.3 | 22.4 | 27.5 | 44.5 | 13.6 | 551.1 | 0.03 |
| | SDR 2 | 5.9 | 0.02 | 0.9 | 36.8 | 38.5 | 430.0 | 55.9 | 376.2 | 0.33 |
| | SDR 3 | 6.1 | 0.05 | 2.4 | 37.9 | 57.2 | 379.2 | 53.2 | 349.4 | 0.49 |
| | SDR 4 | 5.5 | 0.02 | 2.5 | 100.8 | 59.8 | 46.8 | 19.8 | 244.2 | 0.06 |
| | SDR 5 | 6.1 | 0.03 | 2.1 | 42.4 | 46.4 | 76.4 | 16.2 | 399.5 | 0.03 |
| | SDR 9 | 5.6 | 0.07 | 2.6 | 136.2 | 166.6 | 233.5 | 29.6 | 513.1 | 0.32 |
| | SD# 16 | 5.5 | 0.02 | 1.6 | 37.1 | 29.0 | 69.7 | 15.5 | 396.8 | 0.06 |
| | SD 18L | 6.4 | 0.04 | 1.9 | 73.1 | 57.2 | 54.5 | 18.7 | 644.7 | 0.03 |
| | SD 19L | 6.3 | 0.05 | 2.2 | 48.5 | 80.2 | 71.6 | 16.6 | 425.6 | 0.20 |
| | SD 20L | 5.9 | 0.06 | 1.9 | 65.0 | 53.0 | 51.0 | 17.3 | 452.7 | 0.02 |
| | SD B | 4.6 | 0.16 | 8.7 | 32.6 | 47.4 | 179.5 | 15.5 | 142.7 | 0.88 |
| | Average | 5.8 | 0.07 | 3.4 | 74.5 | 66.3 | 143.4 | 23.2 | 398.7 | 0.21 |
| | Standard deviation | 0.5 | 0.08 | 2.7 | 40.0 | 34.1 | 131.7 | 12.5 | 125.5 | 0.25 |
| | Max | 6.4 | 0.34 | 11.6 | 145.6 | 166.6 | 430.0 | 55.9 | 644.7 | 0.88 |
| | Min | 4.6 | 0.01 | 0.9 | 22.4 | 27.5 | 27.6 | 13.6 | 142.7 | 0.02 |
| Tailings* | Average | 4.1 | 0.29 | 0.8 | 77.7 | 27.0 | 614.1 | 17.8 | 376.2 | 1.37 |
| | Standard deviation | 0.8 | 0.57 | 0.2 | 107.4 | 15.2 | 222.7 | 5.6 | 164.6 | 1.12 |
| | Max | 4.8 | 1.31 | 1.1 | 269.0 | 48.0 | 948.0 | 25.5 | 568.0 | 3.23 |
| | Min | 2.8 | 0.02 | 0.6 | 21.5 | 12.0 | 368.0 | 11.2 | 188.0 | 0.50 |
| Cyanidation ponds* | Average | 4.9 | 0.09 | 5.3 | 10.9 | 37.1 | 41.0 | 1.4 | 253.9 | 0.17 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Standard deviation | 0.2 | 0.02 | 1.7 | 7.0 | 22.9 | 19.7 | 0.7 | 64.8 | 0.07 |
| | Max | 5.2 | 0.12 | 7.5 | 20.1 | 71.0 | 60.0 | 2.3 | 327.0 | 0.26 |
| | Min | 4.7 | 0.06 | 3.3 | 5.4 | 22.0 | 17.3 | 0.6 | 170.5 | 0.08 |
| Pithead sediments* | SDJ1 | 3.9 | 0.52 | 12.9 | 403.0 | 153.0 | 5030.0 | 2.2 | 55.4 | 0.62 |
| Outcrops | VEU1 | 7.6 | 0.05 | 0.4 | 12.7 | 4.4 | 36.8 | 40.6 | 152.5 | 0.06 |
| | VEU2 | 8.3 | 0.09 | 0.7 | 0.0 | 6.5 | 603.5 | 28.1 | 66.1 | 0.02 |
| | AR1 | 7.9 | 0.05 | 0.5 | 64.7 | 10.5 | 16.1 | 12.3 | 77.2 | 0.68 |
| | AJ1 | 5.5 | 0.50 | 0.7 | 39.7 | 60.0 | 146.0 | 25.0 | 52.8 | 0.23 |
| | AJ2 | 4.6 | 0.22 | 0.2 | 118.0 | 58.5 | 13.0 | 17.0 | 1020.0 | 0.10 |
| | VM1 | 5.7 | 0.01 | 0.6 | 18.4 | 10.2 | 4.8 | 14.2 | 124.7 | 0.01 |
| | V HUATI | 7.0 | 0.03 | 0.2 | 28.4 | 9.6 | 39.1 | 42.9 | 184.9 | 0.11 |
| | Average | 6.7 | 0.13 | 0.5 | 40.3 | 22.8 | 122.7 | 25.7 | 239.7 | 0.17 |
| | Standard deviation | 1.4 | 0.17 | 0.2 | 40.1 | 25.0 | 217.3 | 12.3 | 347.4 | 0.23 |
| | Max | 8.3 | 0.50 | 0.7 | 118.0 | 60.0 | 603.5 | 42.9 | 1020.0 | 0.68 |
| | Min | 4.6 | 0.01 | 0.2 | 0.0 | 4.4 | 4.8 | 12.3 | 52.8 | 0.01 |

* Values taken from González-Valoys et al. 2021 [26].

**Table supplementary S3.** HI in children and adults in different scenarios

| Type | HI children residential | HI children residential Range | HI children recreational | HI children recreational Range | HI adult residential | HI adult residential Range | HI adult agricultural | HI adult agricultural Range | HI adult recreational | HI adult recreational Range |
|---|---|---|---|---|---|---|---|---|---|---|
| Soils (surrounding area) | 1.67 ± 1.42 | 0.07 - 6.18 | 0.44 ± 0.37 | 0.02 - 1.62 | 0.19 ± 0.16 | 0.01 - 0.71 | 0.13 ± 0.11 | 0.01 - 0.48 | 0.05 ± 0.04 | 0.00 - 0.19 |
| Terrace sediments | 5.29 ± 6.61 | 0.54 - 22.86 | 1.39 ± 1.74 | 0.14 - 6.01 | 0.61 ± 0.76 | 0.06 - 2.64 | 0.42 ± 0.52 | 0.04 - 1.81 | 0.16 ± 0.20 | 0.02 - 0.69 |
| Stream sediments | 5.12 ± 4.32 | 1.44 - 14.75 | 1.35 ± 1.14 | 0.38 - 3.88 | 0.59 ± 0.50 | 0.16 - 1.69 | 0.40 ± 0.34 | 0.11 - 1.16 | 0.15 ± 0.13 | 0.04 - 0.45 |
| Soils (mining area) | 2.18 ± 1.67 | 0.39 - 6.92 | 0.57 ± 0.44 | 0.10 - 1.82 | 0.25 ± 0.19 | 0.04 - 0.80 | 0.17 ± 0.13 | 0.03 - 0.55 | 0.07 ± 0.05 | 0.01 - 0.21 |
| Tailings* | 19.03 ± 6.82 | 11.40 - 29.26 | 5.00 ± 1.79 | 3.00 - 7.70 | 2.20 ± 0.79 | 1.32 - 3.39 | 1.51 ± 0.54 | 0.90 - 2.32 | 0.58 ± 0.21 | 0.35 - 0.89 |
| Cyanidation ponds* | 1.30 ± 0.57 | 0.63 - 1.87 | 0.34 ± 0.15 | 0.17 - 0.49 | 0.15 ± 0.07 | 0.07 - 0.22 | 0.10 ± 0.05 | 0.05 - 0.15 | 0.04 ± 0.02 | 0.02 - 0.06 |
| Pithead sediments* | 150.31 | _ | 39.53 | _ | 17.44 | _ | 11.94 | _ | 4.59 | _ |

* Values calculated from values taken from González-Valoys et al. 2021 [26].

**Table supplementary S4.** T-CR in children and adults in different scenarios

| Type | T-CR children residential | T-CR children residential Range | T-CR children recreational | T-CR children recreational Range | T-CR adult residential | T-CR adult residential Range | T-CR adult agricultural | T-CR adult agricultural Range | T-CR adult recreational | T-CR adult recreational Range |
|---|---|---|---|---|---|---|---|---|---|---|
| Soils (surrounding area) | 2.3E-04 ± 1.7E-04 | 5.3E-0.5 - 8.1E-04 | 6.0E-05 ± 4.4E-05 | 1.4E-05 - 2.1E-04 | 1.3E-04 ± 9.1E05 | 2.9E-05 - 4.4E-04 | 1.1E-04 ± 8.3E-05 | 2.7E-05 - 4.0E-04 | 3.3E-05 ± 2.4E-05 | 7.7E-06 - 1.2E-04 |
| Terrace sediments | 3.1E-04 + 2.6E-04 | 5.1E-05 - 1.1E-03 | 8.0E-05 ± 6.8E-05 | 1.4E-05 - 2.8E-04 | 1.7E-04 ± 1.5E-04 | 2.8E-05 - 6.2E-04 | 1.6E-04 ± 1.4E-04 | 2.6E-05 - 5.6E-04 | 4.5E-05 ± 3.9E-05 | 7.4E-06 - 1.6E-04 |
| Stream sediments | 3.1E-04 ± 1.8E-04 | 9.6E-05 - 6.7E-04 | 8.2E-05 ± 4.8E-05 | 2.5E-05 - 1.8E-04 | 1.8E-04 ± 1.0E-04 | 5.4E-05 - 3.8E-04 | 1.6E-04 ± 9.5E-05 | 4.9E-05 - 3.4E-04 | 4.6E-05 ± 2.7E-05 | 1.4E-05 - 9.9E-05 |
| Soils (mining area) | 1.9E-04 ± 1.0E-04 | 4.6E-05 - 3.4E-04 | 4.9E-05 ± 2.7E-05 | 1.2E-05 - 9.1E-05 | 1.0E-04 ± 5.6E-05 | 2.5E-05 - 2.0E-04 | 9.5E-05 ± 5.2E-05 | 2.3E-05 - 1.8E-04 | 2.7E-05 ± 1.5E-05 | 6.7E-06 - 5.2E-05 |
| Tailings* | 8.6E-04 ± 3.7E-04 | 4.7E-05 - 1.3E-03 | 2.3E-04 ± 9.8E-05 | 1.2E-04 - 3.5E-04 | 4.9E-04 ± 2.1E-04 | 2.7E-04 - 7.5E-04 | 4.5E-04 ± 1.9E-04 | 2.5E-04 - 6.8E-04 | 1.3E-04 ± 5.6E-05 | 7.1E-05 - 2.0E-04 |
| Cyanidation ponds* | 6.9E-05 ± 1.8E-05 | 4.8E-05 - 8.8E-05 | 1.8E-05 ± 4.8E-06 | 1.3E-05 - 2.3E-05 | 3.9E-05 ± 1.1E-05 | 2.8E-05 - 5.0E-05 | 3.6E-05 ± 9.6E-06 | 2.5E-05 - 4.6E-05 | 1.0E-05 ± 2.8E-06 | 7.3E-06 - 1.3E-05 |
| Pithead sediments* | 6.6E-03 | _ | 1.7E-03 | _ | 3.8E-03 | _ | 3.5E-03 | _ | 1.0E-03 | _ |

* Values calculated from values taken from González-Valoys et al. 2021 [26].

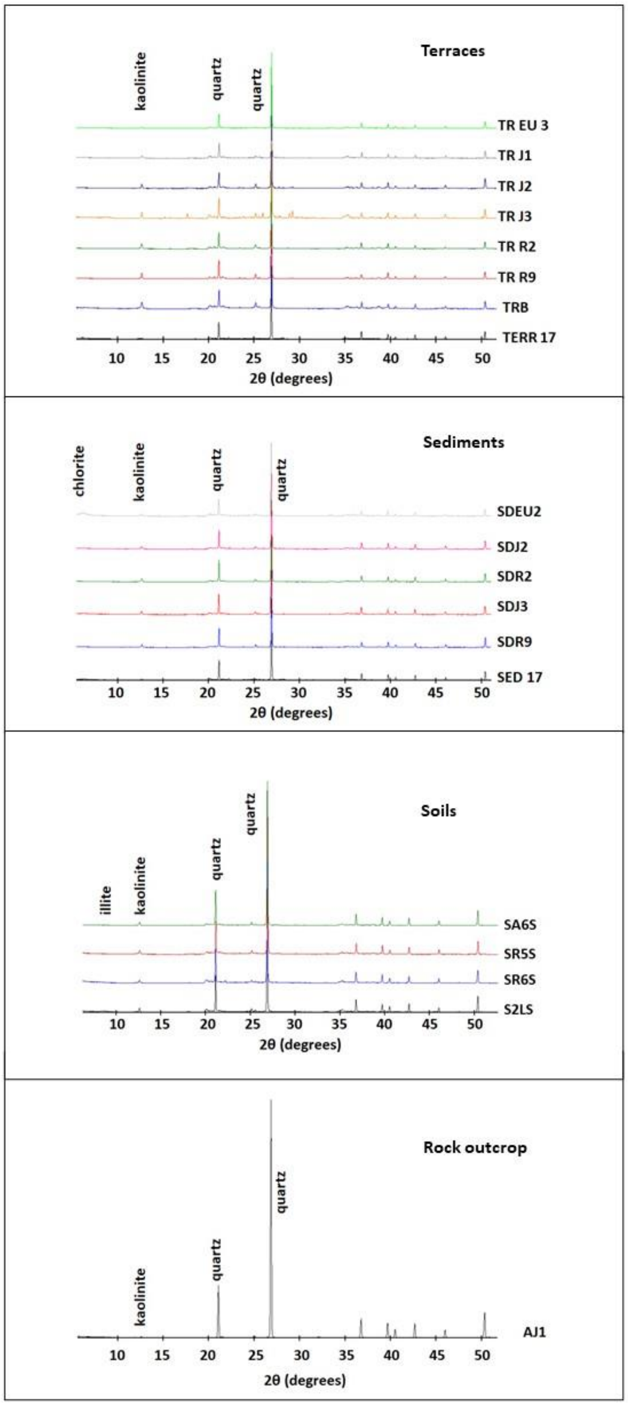

**Figure S1: Diffractograms.**

# AN APPROACH FOR EVALUATING THE BIOAVAILABILITY AND RISK ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS USING EDIBLE AND INEDIBLE PLANTS – THE REMANCE (PANAMA) MINING AREA AS A MODEL

Environ Geochem Health
https://doi.org/10.1007/s10653-021-01086-8

ORIGINAL PAPER

# An approach for evaluating the bioavailability and risk assessment of potentially toxic elements using edible and inedible plants—the Remance (Panama) mining area as a model

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Received: 1 June 2021 / Accepted: 31 August 2021

**Abstract** Mining affects the environment, particularly through the persistence of accumulation of tailings materials; this is aggravated under tropical climatic conditions, which favours the release of potentially toxic elements (PTEs) bioavailable to the local flora and fauna and supposing a risk to human health. The Remance gold mine (Panamá), exploited intermittently for more than 100 years, and has remained derelict for over 20 years. Within the area live farmers who carry out subsistence agriculture and livestock activities. The objective of this study has been to study the transference of PTEs in the local agricultural soil-plants system, with the goal of identifying their bioavailability to perform a human risk assessment. The results obtained of the Bioaccumulation coefficient in local plants show very weak to strong absorption of As (< 0.001–1.50), Hg (< 0.001–2.38), Sb (0.01–7.83), Cu (0.02–2.89), and Zn (0.06–5.32). In the case of Cu in grass (18.3 mg $kg^{-1}$) and plants (16.9 mg $kg^{-1}$) the concentrations exceed the maximum authorised value in animal nutrition for ruminants (10 mg $kg^{-1}$). The risk to human health for edible plants exceeds the non-carcinogenic risk for rice, corn, cassava, and tea leaves for Sb (HQ 19.450, 18.304, 6.075, 1.830, respectively), the carcinogenic risk for Cu

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**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s10653-021-01086-8.

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# 4 AN APPROACH FOR EVALUATING THE BIOAVAILABILITY AND RISK ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS USING EDIBLE AND INEDIBLE PLANTS – THE REMANCE (PANAMA) MINING AREA AS A MODEL

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## Abstract

Mining affects the environment, particularly through the persistence of accumulation of tailings materials; this is aggravated under tropical climatic conditions, which favors the release of potentially toxic elements (PTEs) bioavailable to the local flora and fauna and supposing a risk to human health. The Remance gold mine (Panamá), exploited intermittently for more than 100 years, has remain derelict for over 20 years. Within the area live farmers, who carry out subsistence agriculture and livestock activities. The objective of this study has been to study the transference of PTEs in the local agricultural soil-plants system, with the goal of identifying their bioavailability to perform a human risk assessment. The results obtained of the Bioaccumulation coefficient (BAC) in local plants show very weak to strong absorption of As (<0.001-1.50), Hg (<0.001- 2.38), Sb (0.01- 7.83), Cu (0.02- 2.89) and Zn (0.06- 5.32). In the case of Cu in grass (18.3 mg $kg^{-1}$) and plants (16.9 mg $kg^{-1}$) the concentrations exceed the maximum authorized value in animal nutrition for ruminants (10 mg $kg^{-1}$). The risk to human health for edible plants exceeds the non-carcinogenic risk for rice, corn, cassava and tea leaves for Sb (HQ 19.450, 18.304, 6.075, 1.830, respectively), the carcinogenic risk for Cu (CR = $2.3 \times 10^{-3}$, $7.7 \times 10^{-4}$, $1.1 \times 10^{-3}$, $1.0 \times 10^{-3}$, respectively), and the carcinogenic risk for As in rice, corn and tea leaves (CR= $8 \times 10^{-5}$, $3 \times 10^{-5}$, $3 \times 10^{-5}$, respectively). Urgent measures are needed to alleviate these effects.

**Keywords**: Potentially toxic elements (PTEs), plants, bioavailability, risk assessment, food

## 4.1. Introduction

Soil quality is affected by the presence of PTEs, which is largely due to anthropogenic activity (Rogival et al., 2007; Zhuang et al., 2009; Hooda, 2010; Bravo et al., 2017). Mining activity strongly impacts the environment because it implies exposing the minerals that contain PTEs to atmospheric conditions (Kamunda et al., 2016; Palansooriya et al., 2020). In particular, abandoned mining tailings become sources of environmental contamination (Santos et al., 2016; Chaabani et al., 2017; Kaninga et al., 2020) when they are exposed to environmental conditions like rain and wind, which influences the entire food chain from soils to plants and animals and, directly or indirectly, to human beings (Getaneh & Alemayehu, 2006).

For example, Cu is an essential micronutrient, which participates in the transfer of electrons, but it can be toxic to plants and humans in large quantities (Gómez-Armesto et al., 2015; Bravo et al., 2015). Zn is linked with enzymes and participates in three plant functions: catalytic, coercive, structural (Bravo et al., 2015). Ba is the trace element found at the highest concentrations in soil (Bravo et al., 2015), while Sb, As and Hg are non-essential trace elements. All these elements are named by Hooda (2010) as PTEs, whose presence in soil poses a serious soil quality problem and a human health risk (Rascio and Navari-Izo, 2011; Sun et al., 2018).

The concentration of PTEs in plants depends on several factors, such as abundance and speciation ((bio)availability) in soil, type of plant and its age, depth of roots, among others (Cunha et al., 2014). The ability of plants to take up nutrients can be measured by the bioaccumulation coefficient (BAC), which is calculated as the ratio between the concentration of the element in a plant (any plant tissue, e.g. root, leaf or fruit) and its content in soil (Kabata-Pendias, 2011; Cunha et al., 2014; Bravo et al., 2017), to observe the element's bioavailability in soil (Bravo et al., 2017). The bioaccumulation coefficient (BAC) applied to PTEs describes the transfer from soil to plants, while the bioconcentration coefficient (BC) describes a plant's ability to adsorb PTEs from soil when they appear in an available form (Gruszecka-Kosowska, 2020).

Many plants are used for direct human consumption as they form part of the population's diet, such as fruit and cereals. The human health risk posed by eating them as part of their daily diet can be assessed and determined by calculating the non-carcinogenic and carcinogenic risks of the PTEs they contain (Gruszecka-Kosowska, 2019; Gruszecka-Kosowska, 2020). Eating plants can also affect human beings indirectly via ruminant animals because they form part of the food chain and can also affect ruminant animals' health (Aquilina et al., 2016; Pareja-Carrera et al., 2021).

According to the World Population Prospects, each state should promote its own research in relation to their agricultural regions and agroecosystems (UN, 2015). The National Secretary of Science and Technology (SENACYT) and the Institute for the Training and Use of Human Resources (IFARHU) of Panama promote a project in the abandoned Remance gold mine, where tailings are exposed to the climate conditions of wind and rain, which can affect surrounding soils and plants. The peasants who live within the old mine perimeter grow products for their own consumption and graze livestock, even in those areas very close to tailings. The objective of this study was to analyse the degree that mining activity affected flora in relation to the concentration of PTEs and their bioavailability by bearing in mind the human risk assessment and evaluating the health risk.

## 4.2. Materials and Methods

### 4.2.1. Study area

The Remance gold mine is located in the village of Remance, a district of San Francisco, in the Veraguas province in the Republic of Panama, Central America. From a geological point of view, a hydrothermal alteration covers an area of some 10 km$^2$, and the epithermal gold deposit is hosted on a bed of pyroclastic rocks (Nelson & Ganoza, 1999). The gold deposit comprises a system of veins in which the principal vein contains the largest ore quantities, along with minor, but still revelant, veins like Santa Rosa and Consuelo, which are subterranean and have sporadic outcrops (Nelson & Ganoza, 1999).

The mine has been exploited intermittently by different companies for over 200 years, between 1800 and 1998. The last exploitation company was "Minera Remance S.A", which operated the mine between 1989 and 1999 (Nelson & Ganoza, 1999) by applying the cyanidation process to extract precious metal (Gómez, 2008). Nowadays the mine is abandoned, and there are still three tailing ponds with mining waste exposed to environmental conditions, which could be sources of pollution for soils, water bodies and flora (González-Valoys et al., 2021a).

According to the Köppen climate classification map, the climate in the study area corresponds to the Ami type. It is a humid tropical climate, with the influence of monsoons, and an annual rainfall of >2,250 mm that concentrates (60%) in the four wettest months (August-November). The rain rates of dry months (January-March) drop below 60 mm, and the average temperature of the coolest month is >18°C (Dirección de Meteorología de ETESA, 2007).

Pasture predominates in the old mine area, with stubble and shrubby vegetation no higher than 5 m and a few small mixed broadleaf forest patches. Some small settlements are found in the area, and the commonest annual crops are rice, sugarcane and corn (Ministerio de Ambiente Panamá, 2012), as well as other crops like cassava, banana, beans, among others. Cattle raising and horse grazing are also observed.

### 4.2.2. Sampling

Plant sampling was performed between May and June 2019, and in January 2020. Table 4.1 offers the collected samples, together with their common name, family, taxa and frequency for 75 samples, Table ST1 presents the coordinates. The location map of samples appears in Figure 4.1. The studied tissue was leaves or edible plant parts. Together with each plant, a soil sample was collected to determine the BAC to evaluate the transfer of PTEs from soil to plants, and the available fraction was noted to evaluate the BC.

The edible part was taken from edible plants, while 30-40 leaves were collected from the rest of the plant as composite samples using gloves and scissors. Samples were placed in a paper envelope and stored at room temperature before being analysed. Soil samples were collected at 0-30 cm deep inside a PVC tube, which was placed inside soil to obtain samples (González-Valoys et al., 2021b). Soil samples (approx. 3 kg each) were placed in a plastic bag using a plastic shovel to be stored at ambient temperature.

**Table 4.1.** plant samples taken for the study. Edible plants in bold. The common names in italics are in Spanish.

| Family | Taxon | Common name | Frequency |
|---|---|---|---|
| *Anacardiaceae* | *Anacardium excelsum (Bertero & Balb. ex Kunth) Skeels* | *Espavé* | *3* |
| *Annonaceae* | *Xylopia frutescens* Aubl. | *Malagueto macho* | *4* |
| *Araceae* | morphospecies | - | 1 |

| | | | |
|---|---|---|---|
| *Araliaceae* | *Schefflera morototoni (Aubl.) Maguire, Steyerm. & Frodin* | *Mangabe* | *1* |
| *Asteraceae* | *Baccharis trinervis* Pers. | - | *1* |
| *Asteraceae* | ***Ayapana stenolepis (*****Steetz) R.M. King & H. Rob.** | ***Tea leaves*** | *1* |
| *Bombacaceae* | *Pseudobombax septenatum* (Jacq.) Dugand | *Barrigón* | *2* |
| *Boraginaceae* | *Heliotropium indicum L.* | Turnsole, indian heliotrope | *2* |
| *Burseraceae* | *Bursera simaruba* (L.) Sarg. | *Indio desnudo* | *2* |
| *Clusiaceae* | *Garcinia madruno (Kunth) Hammel* | *Satro* | *1* |
| *Connaraceae* | *Cnestidium rufescens* Planch. | - | *1* |
| *Convolvulaceae* | *Ipomoea batatas* (L.) Lam. | Yam or sweet potato | *1* |
| *Cyperaceae* | *Rhynchospora cephalotes* (L.) Vahl | Grass | *2* |
| *Dennstaedtiaceae* | *Pteridium caudatum (L.) Maxon* | Fern | *2* |
| *Dilleniaceae* | *Curatella americana* L. | *Chumico* | *4* |
| *Euphorbiaceae* | *Mabea occidentalis* Benth. | *Caciquillo* | *2* |
| *Euphorbiaceae* | ***Manihot esculenta*** **Crantz** | **Cassava,** ***yuca*** | *1* |
| *Fabaceae-Mimosoideae* | *Acacia mangium* Willd. | *Acacia* | *1* |
| *Fabaceae-Mimosoideae* | *Acacia sp.* | *Acacia* | *1* |
| *Fabaceae-Mimosoideae* | *Calliandra magdalenae (Bertero ex DC.) Benth.* | - | *1* |
| *Fabaceae-Mimosoideae* | *Cojoba rufescens* (Benth.) Britton & Rose | *Coralillo* | *1* |
| *Fabaceae-Mimosoideae* | *Zygia longifolia (Humb. & Bonpl. ex Willd.) Britton & Rose* | *Pichindé* | *1* |
| *Fabaceae-Papilionoideae* | *Andira inermis* (W. Wright) Kunth ex DC. | *Harino* | *4* |
| *Gleicheniaceae* | *Dicranopteris pectinata* (Willd.) Underw. | Fern | *1* |
| *Lauraceae* | *Nectandra* sp. | *Sigua* | *1* |
| *Lygodiaceae* | *Lygodium venustum* Sw. | *Crespillo* | *2* |
| *Malpighiaceae* | *Byrsonima crassifolia* (L.) Kunth | *Nance* | *2* |
| *Malvaceae* | *Guazuma ulmifolia* Lam. | *Guácimo* | *3* |
| *Malvaceae* | mophospecies | - | 3 |
| *Melastomataceae* | *Miconia argentea* (Sw.) DC. | *Papelillo* | *1* |
| *Melastomataceae* | *Mouriri myrtilloides* (Sw.) Poir. | . | *1* |
| *Moraceae* | *Brosimum alicastrum Sw.* | *Berba, cacique,* breadnut | *1* |
| *Myrtaceae* | *Eugenia* sp. | *Guayabillo* | *1* |
| *Piperaceae* | *Piper leptocladum* C. DC. | *Cordoncillo* | *1* |
| *Poaceae* | morphospecies | Grass*, pasto* | 12 |
| *Poaceae* | ***Oryza sativa*** **L.** | **Rice,** ***arroz*** | *1* |
| *Poaceae* | ***Zea mays*** **L.** | **Corn,** ***maíz*** | *1* |
| *Rubiaceae* | *Alibertia edulis* (Rich.) A. Rich. | Trumpet | *1* |
| *Rubiaceae* | ***Declieuxia fruticosa*** **(Willd.) Kuntze** | ***Tea leaves*** | *1* |
| *Rubiaceae* | *Genipa americana* L. | *Jagua* | *1* |
| *Sapindaceae* | *Cupania americana L.* | *Gorgojo,* weevil | *1* |

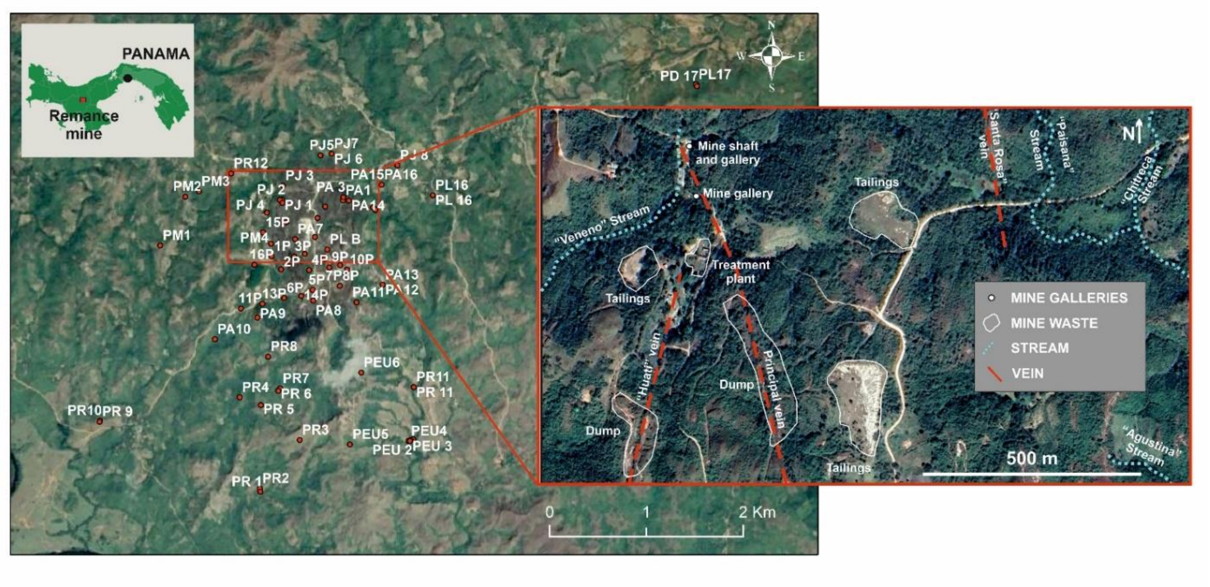

**Fig.4.1.** Location map of the plant samples taken within the Remance gold mine perimeter.

### 4.2.3. Processing and analysing samples

Leaf samples were washed with deionised water to eliminate dust impurities, were left at ambient temperature for 4 days and then left to dry for 3 more days at 36°C in a stove. Finally, samples were crushed by a domestic grinder to increase homogeneity. In the same way, soil samples were dried at ambient temperature, disaggregated with the help of a manual roller and sieved to less than 2 mm. The aliquots taken for the analysis (50 g) were further ground in an agate mortar until the diameter of the material was below 100 µm.

The elements Cu, Zn, As, Ba, Sb and T-Hg were studied because in a previous study of the tailings from the abandoned gold mine, they are the PTEs that were above the value of the Panama soil standard ( González-Valoys et al., 2021a). The Cu, Zn, As, Sb and Ba determinations were made in both sample kinds, namely plants pressed into tablets and soil in a powder form**,** by energy dispersion X-ray fluorescence spectroscopy (ED-XRF) in Epsilon One equipment (PAnalytical brand). Total Hg (THg) was determined by Zeeman atomic absorption spectroscopy with high-frequency modulation of light polarisation (ZAAS-HFM) using commercial equipment Lumex RA-915M with a pyrolytic attachment (PYRO-915+). Certified reference materials were used to check both precision and accuracy: NIST 2710A (Montana soil) and LGC7162 (strawberry leaves). Recovery percentages between 80-100 % (ED-XRF) and 95-100 % (ZAAS-HF) were obtained.

Based on high As and Cu concentrations determined by the ED-FRX analysis, a set of 12 soil samples was selected to evaluate the BC. In this way, the sequential extraction in three stages proposed by the European Community Bureau of Reference (BCR) was carried out in accordance with the procedure described by Sahuquillo et al. (1999): in step 1 (S1) the exchangeable and bound to carbonates fraction is extracted with acetic acid; in step 2 (S2) the reducible fraction (bound to Fe and Mn oxides), is extracted with hydroxylamine hydrochloride; and in step 3 (S3) the oxidizable fraction (bound to organic matter and sulphides) is extracted using a digestion with hydrogen peroxide first and then ammonium acetate. This method is widely used for evaluating the fractionation of metals and has been applied to study a wide variety of solid samples, including different mining waste types (Marguí et al., 2007; García-Ordiales et al., 2019). Hence the first three fractions were considered potentially labile or reactive fraction plant uptake or bioaccessible to humans (Madrid et al., 2007; Kelepertzis & Stathopoulou, 2013).

Measurements of Cu and As in the BCR extracts were taken by high-resolution atomic absorption spectroscopy (HR-AAS) in ContrAA-800 equipment (Analytik Jena brand) using the flame and the graphite furnace techniques, respectively. Samples were also subjected to microwave-assisted acid digestion with aqua regia according to EPA method 3051A (USEPA, 2007) to analyse pseudo-total concentrations (Melaku et al., 2005; Higueras et al., 2017). In all cases, solutions were filtered with Whatman filters (8µm). As a quality control of total contents, analyses of blanks and random duplicates were performed. Certified reference material NIST 2710A was also digested and analysed in triplicate, with 95% and 98% recovery for Cu and As, respectively. Blanks and certified reference material BCR 701 were also used in the BCR extractions with recoveries between 95-102% for Cu (As is not certificated in this reference material).

### 4.2.4. Soil-To-Plant Transfer Indices

Two indices were used to determine the transfer of PTEs from soil to plant: BAC and BC. The BAC is a key component for quantifying differences in metal bioavailability by describing the transfer of PTEs from soil to plant (Inacio et al., 2014; Gruszecka-Kosowska, 2019). The ratio between the concentration of the element in the plant and the element concentration in soil was calculated (Kabata-Pendias, 2011; Bravo et al., 2015).

$$BAC = C_{\text{leaves or edible part plant}} / C_{\text{soil}}$$

where $C_{\text{leaves or edible part plant}}$ is the concentration of a particular PTE (mg $kg^{-1}$) in the leaves or edible part of the plant, and $C_{\text{soil}}$ is the total concentration of a particular PTE in soil samples (mg $kg^{-1}$).

Bioconcentration coefficient (BC): describes the plant's capacity to adsorb PTEs from soil when PTEs appear in an available form (Inacio et al., 2014; Gruszecka-Kosowska, 2019). BC is calculated as the ratio between the PTE concentration in leaves or edible parts and the available concentrations of PTE in soil (Wang et al. 2006):

$BC = C_{\text{leaves or edible part plant}}/C_{\text{soil available}}$

where $C_{\text{leaves or edible part plant}}$ is the concentration of a particular PTE (mg $kg^{-1}$) in the leaves or the edible part plant and $C_{\text{soil available}}$ is the concentration of a particular PTE in soil samples (mg $kg^{-1}$) obtained from the BCR three-stage sequential extraction procedure because it is considered potentially labile or the reactive fraction plant uptake (Madrid et al., 2007; Kelepertzis & Stathopoulou, 2013).

### 4.2.5. Human Health Risk Assessment

This assessment was performed by the following parameters: daily intake rate (DIR), average daily dose (ADD), hazard quotient (HQ) and carcinogenic risk (CR).

Daily intake rate (DIR) was calculated as the sum of consumed food (WHO, 2005; Gruszecka-Kosowska, 2019) which, in this case, included rice (grain), corn (grain), cassava (tuber) and tea leaves.

$DIR = \Sigma (C_{food} \times IR_{food}/BW)$

where $C_{food}$ is the concentration of a particular PTE in food (rice, corn, cassava, tea leaves) (mg $kg^{-1}$), IR is the ingestion rate (g $person^{-1}$ $day^{-1}$) in food and BW is body weight (70 kg for adults) (USEPA, 2011). Table 4.2 presents the IR values used to calculate the DIR for an adult and corresponds to: the IR value of Panama as reported in a consultancy by the FAO (Kennedy et al., 2021) for rice; the minimum value for America (García-Casal et al., 2018) for corn considering that Panama consumes corn-based products to a lesser extent than the rest of Central America; the values reported in Nigeria (Afolami et al., 2020) for cassava; an average value reported for Pakistan (commercial black tea brands) (Idrees et al., 2020) and China (tea leaves)(Zhang et al., 2018). Here "teas" are taken to correspond to the herbs used locally for infusions (*Ayapana stenolepis* and *Declieuxia fruticosa*).

The ADD was calculated as the sum of the consumed food (USEPA 1989, Gruszecka-Kosowska, 2019):

$ADD = \Sigma (C_{food} \times IR_{food} \times EF \times ED \times 10^{-3}) / AT \times BW$

where $C_{food}$ is the PTE concentration in the investigated food (mg $kg^{-1}$), $IR_{food}$ is the intake rate of cereals (g $person^{-1}$ $day^{-1}$), EF is exposure frequency: 365 d $y^{-1}$, ED is exposure duration with

30 y for adults (USEPA, 2011), AT is the average time in days with ED × 365 for non-carcinogens, and 70 y × 365 for carcinogens (USEPA, 2001; Gruszecka-Kosowska, 2019), BW is body weight (70 kg) and $10^{-3}$ is a unit conversion factor.

**Table 4.2.** The IR values for different types of edible plants.

| **Type of plant** | **IR (g person$^{-1}$ day$^{-1}$)** | **Reference** |
|---|---|---|
| Rice, grain | 125.2 | Kennedy et al., 2021 |
| Corn, grain | 50.0 | García-Casal et al., 2018 |
| Cassava, tuber | 42.0 | Afolami et al., 2020 |
| Tea leaves | 10.9 | Idrees et al., 2020/ Zhang et al., 2018 |

The non-carcinogenic risk represents the risk of daily exposure to PTEs (Gruszecka-Kosowska, 2019). The HQ is the non CR, where a value of 1 refers to the threshold reference value as suggested by the US Environmental Protection Agency (Pan et al., 2019), and is calculated as follows (USEPA, 1989):

$$HQ = ADD/RfD$$

where HQ is the hazard quotient and RfD is the reference dose for a particular PTE. The RfD values for the PTEs (USEPA, 2019) in this study are presented in Table 3. The total non CR (HQt) value for the investigated PTEs was calculated as so (USEPA, 1989)

$$HQt = HQ_1 + HQ_2 + . . . + HQ_n$$

where HQ are the hazard quotient values for the 1-n PTEs here in investigated.

The CR values of the PTEs from dietary exposure were calculated by the formula (USEPA, 1989, Gruszecka-Kosowska, 2019):

$$CR = ADD \times SF$$

where CR is carcinogenic risk and SF is the oral slope factor over a lifetime for a particular PTE. The SF plays a key role being that the daily toxin intake results in an incremental risk of an individual developing cancer (Pan et al., 2019). Table 4.3 presents the SF values for the carcinogenic elements (Pan et al., 2019) in this study. The total CR value appears as the sum of the partial CR values (USEPA, 1989).

$$CRt = CR_1 + CR_2 + . . . + CR_n$$

where CR are the carcinogenic risk values for the 1-n PTEs here in investigated.

**Table 4.3.** The RfD value of the non-carcinogenic elements and the SF for carcinogenic elements.

| Element | RfD (mg $kg^{-1}d^{-1}$) | SF (mg $kg^{-1}d^{-1}$) |
|---|---|---|
| Cu | $4.0 \times 10^{-2}$ | 1.7 |
| Zn | $3.0 \times 10^{-1}$ | |
| As | $3.0 \times 10^{-4}$ | 1.5 |
| Sb | $4.0 \times 10^{-4}$ | |
| Ba | $2.0 \times 10^{-1}$ | |
| Hg | $3.0 \times 10^{-4}$ | |

### 4.2.6. Statistical analysis

Microsoft Excel spreadsheets were used to manage the result. Minitab 15 was employed to analyse the statistical parameters of the analytical results.

## 4.3. Results

### 4.3.1. PTEs and BAC

The synthetic statistical parameters for the group of samples are provided in Table 4.4 and SF1, all the obtained results for plants are expressed in ST2. The Cu concentrations in plant leaves varied between 4.3 and 57.3 mg $kg^{-1}$, while the BAC values indicated that Cu absorption was a weak to strong absorption accumulation in plants. It was remarkable that *Xylopia frutescens Aubl* was the species with the highest accumulation. The Zn concentrations in plant leaves were between 5.7 and 273.1 mg $kg^{-1}$, while the BAC values indicated that Zn absorption went from weak to strong absorption accumulation in plants. In this case, Araceae *morphospecies* was the plant taxon with the most accumulation. The As concentrations in plant leaves were between < 0.1 and 54.5 mg $kg^{-1}$, while the BAC values indicated very weak to strong absorption accumulation. The taxon with the most accumulation was *Poaceae morphospecies*. The Sb concentrations in plant leaves were between < 1.0 and 9.7 mg $kg^{-1}$, while the BAC values denoted a weak absorption to strong accumulation, with *Declieuxia fruticosa* (Willd) Kuntze

**Table 4.4.** Value of the PTEs in leaves and soils for Cu, Zn, As, Sb and Ba expressed as mg $kg^{-1}$, Hg in ng $g^{-1}$ and BAC per element.

| Element | Range plant | Mean plant | Stand. dev. Plant | Range soil* | Mean soil* | Stand. dev. soil* | Range BAC | Mean BAC | Stand. dev. BAC | Description | Plant with most accumulation or absorption |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 4.3-57.3 | 16.9 | 9.6 | 5.4-396.9 | 70.3 | 61.1 | 0.02-2.89 | 0.46 | 0.47 | Weak absorption to strong accumulation | *Xylopia frutescens* Aubl. |
| Zn | 5.7-273.1 | 31.1 | 34.9 | 12.0-166.1 | 54.4 | 27.5 | 0.06-5.32 | 0.7 | 0.75 | Weak absorption to strong accumulation | *Araceae morphospecies* |
| As | <0.1-54.5 | 2.4 | 9.4 | <0.8-714.5 | 110.6 | 171 | <0.001-1.50 | 0.06 | 0.21 | Very weak absorption to strong accumulation | *Poaceae morphospecies* |
| Sb | <1.0-9.7 | 3.5 | 1.8 | <0.6-41.8 | 16.1 | 6.3 | 0.01-7.83 | 0.48 | 1.15 | Weak absorption to strong accumulation | *Declieuxia fruticosa* (Willd.) Kuntze |
| Ba | <5.0-319.9 | 31.1 | 45 | 40.0-743.2 | 310.9 | 166.8 | <0.001-0.93 | 0.14 | 0.2 | Very weak to moderate absorption | *Anacardium excelsum (Bertero & Balb. ex Kunth) Skeels* |
| Hg | <0.1-191.2 | 18.5 | 29.5 | <5.0-6470.0 | 276.1 | 797.7 | <0.001-2.38 | 0.27 | 0.42 | very weak absorption to strong accumulation | *Anacardium excelsum (Bertero & Balb. ex Kunth) Skeels* |

*Values of the PTEs in soil taken from González-Valoys et al., (2021b) being the species with most accumulation. The Ba concentrations in plant leaves went from <5.0 to 319.9 mg kg$^{-1}$, and BACs indicated very weak to moderate absorption. The Hg concentrations in leaves were between < 0.1 and 191.2 ng g$^{-1}$, while the BAC values indicated a very weak absorption to strong accumulation, with *Anacardium excelsum (Bertero & Balb. ex Kunth) Skeels* being the taxon with the highest accumulation rate for these elements. All the plants here in indicated with maximum concentrations corresponded to non-edible plants.

Table 4.5 is a compendium of the Cu, Zn, As, Sb, Ba and Cu concentrations in plants from different countries around the world in both uncontaminated and contaminated areas to compare these values to those obtained at the Remance gold mine for edible products like rice (grain), corn (grain), cassava (tuber), tea leaves (medicinal plants), grass (leaves) and plants in general (leaves).

For rice, the average Cu concentration value at Remance (5.2 mg kg$^{-1}$) was slightly higher than that reported by Kabata-Pendias (2011) for contaminated sites (4.0 mg kg$^{-1}$), while the As contents (0.2 mg kg$^{-1}$) were higher than the value for uncontaminated sites (0.005 mg kg$^{-1}$), but lower than the reference level for contaminated sites (1.2 mg kg$^{-1}$) (Kabata-Pendias, 2011). The concentrations of Sb (4.4 mg kg$^{-1}$) and Ba (12.1 mg kg$^{-1}$) were higher than those reported in agricultural soils in Italy (1.1 mg kg$^{-1}$, 9.3 mg kg$^{-1}$, respectively) (Nadimi-Goki et al., 2014). The average value of the Zn concentrations (17.9 mg kg$^{-1}$) was similar to the values reported for uncontaminated sites (18.0 mg kg$^{-1}$) (Kabata-Pendias, 2011) and in agricultural areas (15.5-24.6 mg kg$^{-1}$) (Rothenberg et al., 2011; Nadimi-Goki et al., 2014; Rajatheja et al., 2021). Finally, the Hg concentrations were lower than the detection limit (< 0.001 mg kg$^{-1}$).

For corn Cu, Zn, As, Sb and Ba were higher than in agricultural soils (Gruszecka-Kosowska, 2020; Adaev et al., 2021), while Zn was higher than cassava in agricultural soils (Danso et al., 2001). In tea leaves, the average Cu concentration fell within the same range as in uncontaminated areas (Kabata-Pendias, 2011), and Zn concentrations were much higher than those reported for commercial tea by Idrees et al (2020). In grass and plants, Cu, As, Sb and Ba were higher than in the uncontaminated sites reported by Shtangeeva et al. (2020 b).

**Table 4.5.** Comparative table of the uncontaminated and contaminated sites in several countries for rice, corn, cassava, tea leaves, grass and plants in general; in relation to the concentration of potentially toxic elements (Cu, Zn, As, Sb, Ba and Hg in mg kg$^{-1}$).

| Plant | Site | Cu | Zn | As | Sb | Ba | Hg | Reference |
|---|---|---|---|---|---|---|---|---|
| Rice, grains | Uncontaminated sites-different countries | | 18.0 | <0.1 | | | | Kabata-Pendias, 2011 |
| | Agricultural soils-China | 2.7 | 18.0 | | | | 0.004 | Rothenberg et al., 2011 |
| | Agricultural soils-Italy | 4.8 | 24.6 | < 0.1 | 1.1 | 9.3 | | Nadimi-Goki et al., 2014 |
| | Agricultural soils-Sri Lanka | 2.2 | 15.5 | 0.1 | | | | Rajatheja et al., 2021 |
| | Contaminated site-different countries | 4.0 | | 1.2 | | | 4.900 | Kabata-Pendias, 2011 |
| | Remance mining area-Panama | 5.2 | 17.9 | 0.2 | 4.4 | 12.1 | <0.001 | This work |
| Corn, grains | Uncontaminated sites-different countries | | 30.5 | 1.8 | < 2.0 | | 0.037 | Kabata-Pendias, 2011 |
| | Agricultural soils-Brazil | 1.7 | 17.5 | < 0.1 | | 2.7 | < 0.030 | Yada et al., 2020 |
| | Agricultural soils-Poland | 0.5 | 7.4 | <0.1 | <0.1 | | 0.002 | Gruszecka-Kosowska, 2020 |
| | Agricultural soils-Czech Republic | 1.4 | 6.5 | | | | | Adaev et al, 2021 |
| | Industrial area-Greece | 2.3 | 16.0 | 0.2 | 0.4 | | | Antoniadis et al., 2019 |
| | Coal mining-contaminated soil-China | 1.7 | 22.7 | | | 6.1 | | Hussain et al., 2019 |
| | Contaminated site-different countries | | | | | | 0.105 | Kabata-Pendias, 2011 |
| | Remance mining area-Panama | 4.3 | 22.0 | 0.2 | 4.7 | 11.7 | <0.001 | This work |
| Cassava, tuber | Agricultural soils-Ghana | | 7.4 | | | | | Danso et al., 2001 |
| | Agricultural soils-Nigeria | 11.2 | < 0.1 | | | | | Adejumo et al., 2019 |
| | Remance mining area-Panama | 7.5 | 9.0 | <0.1 | 4.1 | 18.5 | <0.001 | This work |
| Tea, leaves | Uncontaminated sites-different countries | 20.0 | | | | | 0.040 | Kabata-Pendias, 2011 |
| | Black tea-Pakistan | 8.9 | 1.4 | | | | | Idrees et al., 2020 |
| | Remance mining area-Panama | 19.2 | 88.8 | 0.6 | 4.7 | 35.5 | 0.002 | This work |
| Grass, leaves | Uncontaminated sites-different countries | 6.0 | 31.5 | 2.8 | | | | Kabata-Pendias, 2011 |
| | Uncontaminated sites-Russia | 14.6 | 47.4 | <0.1 | | | | Shtangeeva et al., 2020 a |
| | Uncontaminated sites-Russia | 12.6 | 37.0 | 0.2 | 0.1 | 7.3 | | Shtangeeva et al., 2020 b |
| | Contaminated sites-different countries | 42.0 | | 31.2 | | | | Kabata-Pendias, 2011 |
| | Coal mining-contaminated soil-China | 18.5 | 86.4 | | | 41.4 | | Hussain et al., 2019 |
| | Remance mining area-Panama | 18.3 | 27.3 | 5.5 | 3.0 | 13.7 | 0.019 | This work |
| Different types of plant leaves | Uncontaminated sites-different countries | | | | | 7.5 | | Kabata-Pendias, 2011 |
| | Uncontaminated sites-Russia | 15.0 | 34.2 | 0.1 | | | | Shtangeeva et al., 2020 a |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Uncontaminated sites-Russia | 9.2 | 50.0 | 0.2 | 0.1 | 19.0 | | Shtangeeva et al., 2020 b |
| Coal mining-contaminated soil-China | 7.1 | 43.1 | | | 25.4 | | Hussain et al., 2019 |
| Gold mining-Ethiopia | 36.9 | 96.0 | 8.8 | 0.3 | | | Getaneh & Alemayehu, 2006 |
| Remance mining area-Panama | 16.9 | 31.1 | 3.4 | 3.9 | 36.5 | 0.021 | This work |

### 4.3.2. Statistical analysis

Figure 4.2 presents the dendrogram for the PTEs studied in Remance plant leaves and ST3 presents Pearson's correlation. Pearson's correlation showed that Cu was significantly related to Zn, meanwhile As was related both to Ba and Hg, and Ba appears as related to Hg. After a multivariate analysis, the relation among these six PTEs is displayed in the dendrogram of Figure 4.2. This statistical approach clearly separated PTEs into two subgroups: one with Cu and Zn, and another including As, Hg, Ba and Sb.

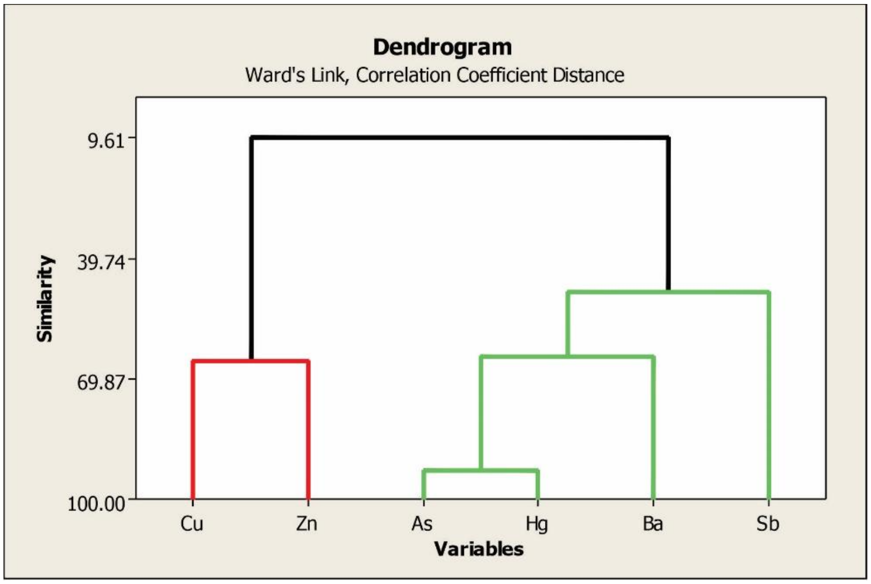

**Fig. 4.2.** Dendrogram shows results of cluster analysis (Ward's method) and linkage distance between parameters of the PTEs found in the leaves samples.

### 4.3.3. Transfer of PTEs from soils to plants

Figures 4.3 show a combined graph of the percentages taken in each step of the BCR sequential extraction for Cu and As, respectively. The total extracted PTEs are displayed in ST3. It is possible to consider the first three BCR steps (S1+S2+S3) to be the fractions, including the potentially labile or reactive species, while the residual fraction can be taken as unavailable for transport, plant uptake or as bioaccessible to humans (Madrid et al., 2007; Kelepertzis et al., 2013). The first fraction corresponds to the water-soluble fraction, which is easily exchangeable and interpreted as the most mobile and bioavailable for the environment (Pérez-López et al., 2008). Fraction 2 (metals bound to oxides Fe and Mn) and fraction 3 (complexed with sulphides and organic matter) can be mobilised under increasing reducing or oxidising conditions, respectively (Kelepertzis et al., 2013). For Cu, fractions 1, 2 and 3 averaged 4.45, 9.15 and 4.34%, respectively, with an average total labile fraction of 17.94% and fraction 2 with the highest contribution (Figure 3). For As, fractions 1, 2 and 3 averaged 0.04, 0.40 and 1.39%, respectively, with an average total labile fraction of 1.82% and fraction 3 with the highest contribution (Figure 4.3).

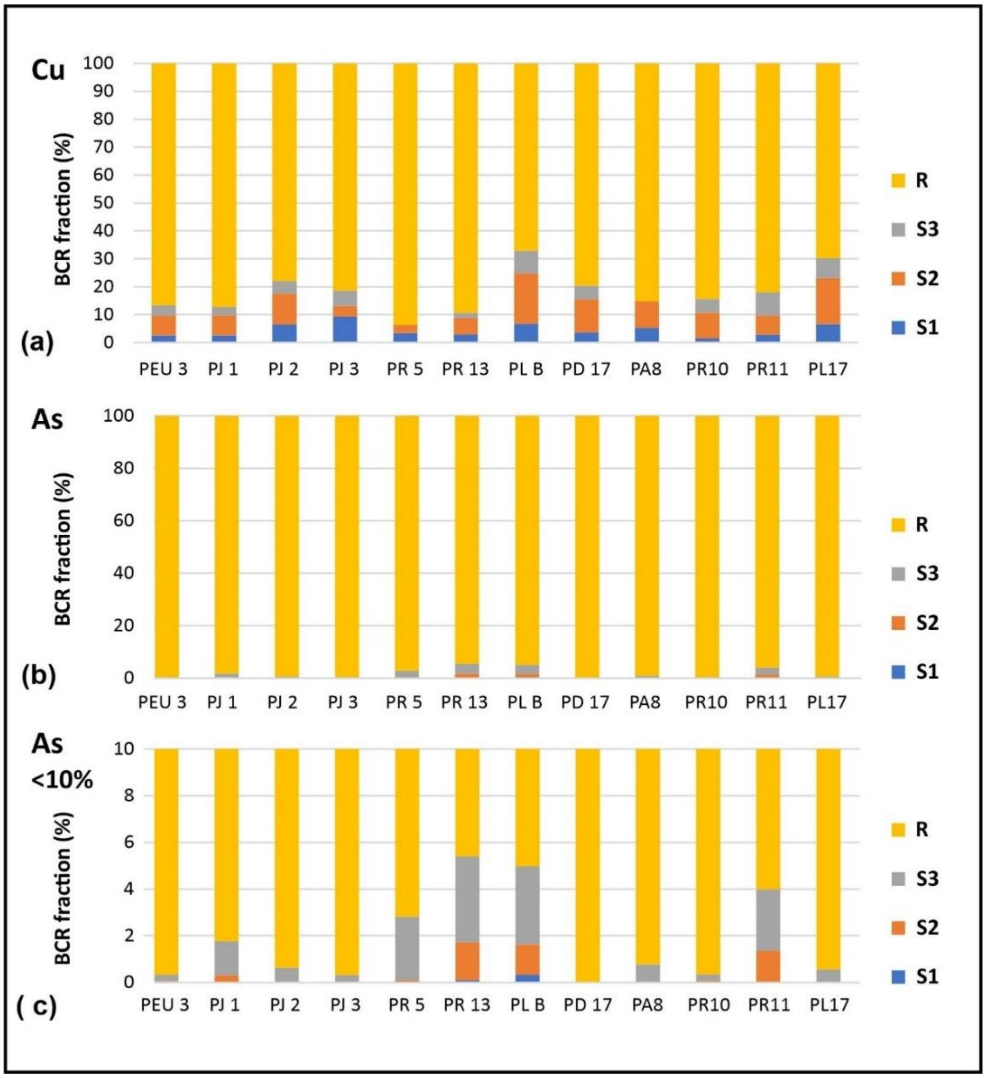

**Fig. 4.3.** Combined bar graph for the BCR fractions and the residual in the plant-associated soil samples. (a) Cu fraction. (b) As fraction. (c) Detail of the fraction of As less than 10%.

Table ST4 presents the BAC and BC for a group of samples with high As and Cu contents in soil. These coefficients were used to evaluate the bioavailability of PTEs, and the plant's capacity to bioaccumulate Cu and As and to bioconcentrate their available fraction. Figure 4.4 shows a bar graph to compare the fraction available in soil (obtained by BCR) and the concentration in the leaves of plants for Cu and As. Cu is seen as an essential element for plants, and appears as being more available in soil (BCR), while plants show good uptake capacity and often high accumulation rates (average BC 3.97). As, which is scarcely available in most soils (mean BC: 0.88), also has lower uptake rates.

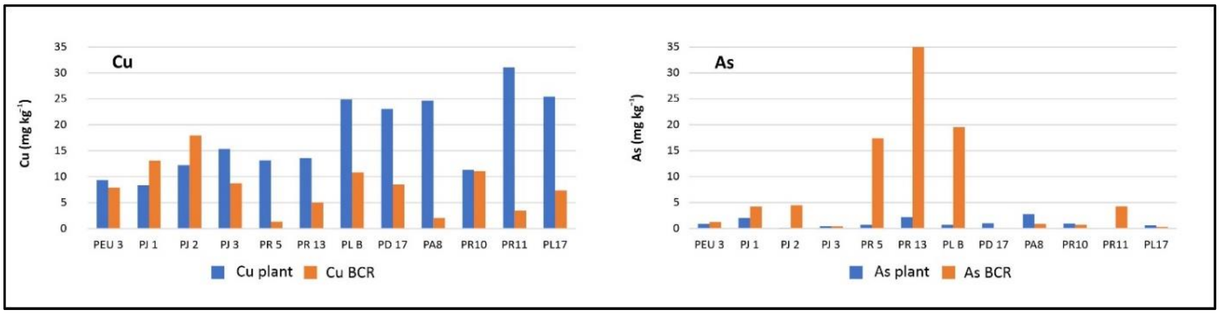

**Fig. 4.4.** Bar graph comparing Cu and As concentration in leaves and available fraction (BCR S1+S2+S3).

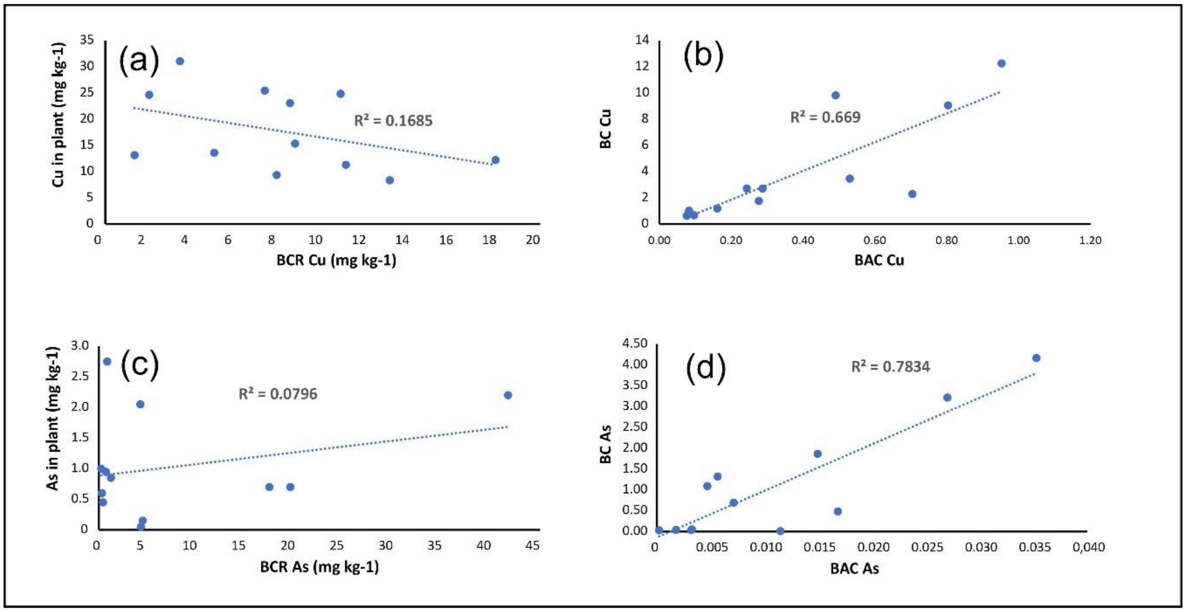

**Fig. 4.5.** (a) Cu concentration in the plant vs available Cu concentration in the soil (BCR). (b) Bioconcentration and bioaccumulation of Cu in the plant. (c) As concentration in the plant vs available As concentration in the soil (BCR). (d) Bioconcentration and bioaccumulation of As in the plant.

Figure 4.5A shows the correlation detected by Pearson's test between the Cu concentration in plants and the Cu fraction available in soil, which is weakly negative. Figure 4.5C shows the relation between the As concentration in plants and the As fraction available in soil. No clear correlation is noted, albeit a very weakly positive one, which seems to be dominated by having low As absorption concentrations available in soil. Figures 4.5B and 4.5D show the positive and closer relation between the BAC and BC indices for Cu and As, respectively.

### 4.3.4. Human Health Risk Assessment

#### 4.3.4.1. Daily Intake Rates

Table 4.6 shows the DIR values of PTEs for the edible products obtained from the Remance gold mine. The inhabitants' diet is based on products like rice, corn or cassava, which are produced locally and consumed daily, with tea leaves consumed sporadically as medicinal tea. The DIR values of each edible product are compared to the provisional maximum tolerable daily intakes (PMTDI) (mg kg$^{-1}$ bw day$^{-1}$) (Gruszecka-Kosowska, 2020) as so: Cu 0.5 (FAO/WHO, 2001), Zn 1 (FAO/WHO, 2001), As 0.0021 (FAO/WHO, 1989), Sb 0.006 (WHO, 2008), Ba 0.02 (EU, 2012), Hg 0.0006 (FAO/WHO, 2011). The values of Cu DIR (2.024 to 9.301), Zn DIR (5.370 to 32.015), Sb DIR (0.716 to 7.780) and Ba DIR (4.562 to 21.642) exceeds the PMTDI in all foods, while As DIR (0.078 to 0.268) exceeds in food, except for cassava, and the Hg DIR is only marked in tea leaves (0.0008 to 0.0028) and exceeds the PTMDI.

**Table 4.6.** The DIR (mg kg$^{-1}$day$^{-1}$) values of PTEs for the food products obtained from the Remance gold mine.

| Edible plants | ID | DIR Cu | DIR Zn | DIR As | DIR Sb | DIR Ba | DIR Hg |
|---|---|---|---|---|---|---|---|
| Rice, grain | PR15 | 9.301 | 32.015 | 0.268 | 7.780 | 21.64 | 0.00009* |
| Corn, grain | PR16 | 3.036 | 15.679 | 0.107 | 3.321 | 8.36 | 0.00004* |
| Cassava, tuber | PR8 | 4.470 | 5.370 | 0.030* | 2.430 | 11.10 | 0.00003* |
| Tea leaves | PM1 | 2.024 | 8.074 | 0.101 | 0.732 | 4.56 | 0.00078 |
| Tea leaves | PM4 | 3.963 | 19.550 | 0.078 | 0.716 | 6.49 | 0.00280 |
| **PMTDI** | | **0.500** | **1.000** | **0.002** | **0.006** | **0.02** | **0.00060** |

PMTDI: provisional maximum tolerable daily intakes (mg kg$^{-1}$day$^{-1}$).
* Calculations use the half of the detection limit.

#### 4.3.4.2. The Non-Carcinogenic Risk of PTEs

The non CR of PTEs was evaluated with the HQ, which was set at 1 (USEPA, 1989). Values exceeding 1 were considered a non CR. Figure 4.6A shows the HQ for the PTEs of the studied edible plant and ST5 values. As we can see, the HQ value was exceeded by Sb in them all and in this order: rice> corn> cassava > tea leaves (19.451> 18.304> 6.075> 1.830). Cu, Zn, As, Ba and Hg did not exceed the value of 1 for HQ. The total HQ value (sum of the HQ for PTEs) of all the edible plants exceeded 1, which means that it represents a non CR.

### 4.3.4.3. The Carcinogenic Risk of PTEs

The acceptable CR risk level was set to equal 1 x $10^{-6}$ for an individual PTE and to equal 1 x $10^{-4}$ for the sum of carcinogenic PTEs (USEPA, 1989). Values exceeding this are considered a CR. Figure 4.6B shows the CR for Cu and Figure 4.6C for As and the ST5 includes the complete values. The acceptable CR value is exceeded by As in rice (7.67 x $10^{-5}$), corn (3.06 x $10^{-5}$) and tea leaves (2.22 x $10^{-5}$ to 2.89 x $10^{-5}$). Excess Cu was obtained in all the edible plants (5.10 x $10^{-4}$ to 2.34 x $10^{-3}$) in this order: rice > cassava > tea leaves > corn. This is the same order for the total CR.

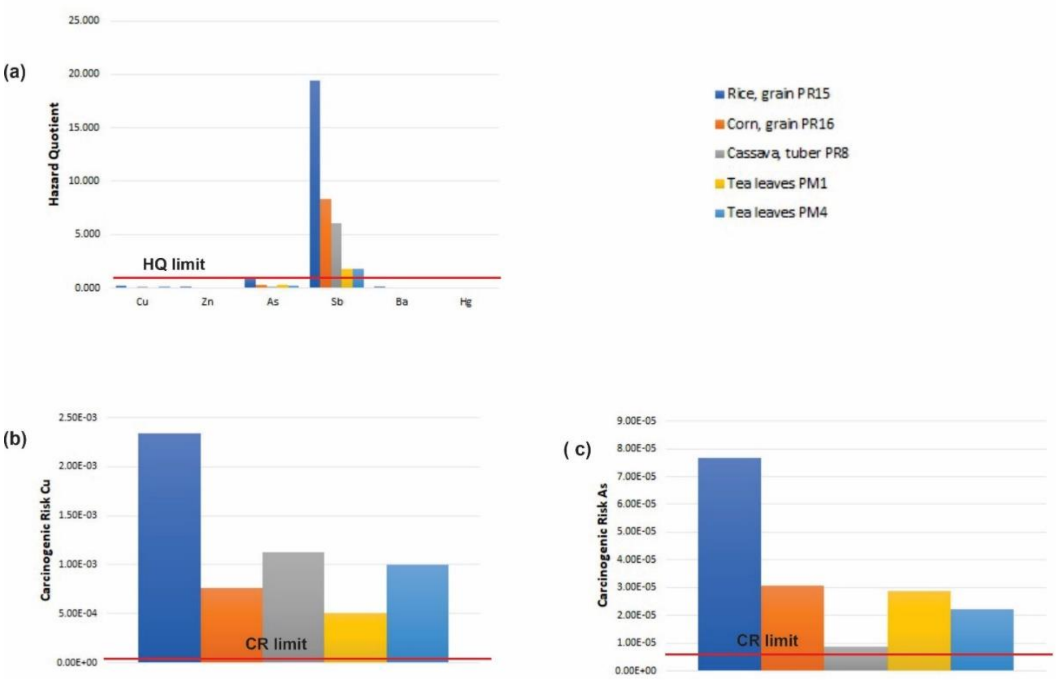

**Fig. 4.6.** (a) Bar chart for non-carcinogenic (HQ) risk for PTEs in edible plants from the Remance gold mine. (b) Carcinogenic risk for Cu in edible plants studied for the Remance gold mine. (c) Carcinogenic risk for As in edible plants studied for the Remance gold mine.

### 4.3.5. Animal Nutrition for Ruminants

In the Remance mining area and its surroundings, peasants perform subsistence livestock work and graze horses. The mean Cu value in grass (*Poaceae morphospecies*) was 18.3 mg kg$^{-1}$ and was 16.9 mg kg$^{-1}$ in plants in general. These values exceed the maximum authorized for Cu (10 mg kg$^{-1}$) for complete feed requirements in animal nutrition for ruminants (e.g. cattle, cows, horses) of the National Research Council, USA (NRC, 2001; Aquilina et al., 2016; López-Alonso & Miranda, 2020). The mean Zn value in grass was 27.3 mg kg$^{-1}$, and 31.1 mg kg$^{-1}$ in plants in general. Both these values exceed the estimated value of the daily diet requirement for cattle for Zn (22.8 mg kg$^{-1}$) (NRC, 2001). For As, Ba, Sb and Hg, the National Research Council of the USA does not establish an estimated value for the daily diet requirements of cattle.

## 4.4. Discussion

Given that the soils and plants in the surroundings of the abandoned Remance gold mine present high concentrations of PTEs, such as Cu, Zn, As, Sb, Ba and Hg, associated with mineralisation (Nelson & Ganoza, 1999), it is essential to identify the degree to which plants, and especially the crops grown by farmers like rice, corn, cassava, among others, are affected (Ministerio de Ambiente Panamá, 2012). It is also necessary to identify the risks for livestock and as collateral risks for human health. The mean concentration of the PTEs in the leaves of a diversity of studied plants come in this order, Zn=Ba>Cu>Sb>As>Hg, while BAC is related to the total amount of PTEs present in soil. and the degree to which a plant absorbs them comes in this order, Zn> Sb> Cu> Hg> Ba>As. All this indicates that essential trace elements like Zn and Cu (Arif et al., 2016) are absorbed by plants and accumulate more than non-essential elements (Bravo et al., 2015) like Hg, Ba and As.

The exception can be Sb, which being non-essential, has been strongly absorbed and accumulated by plants (Mykolenko et al., 2018), even as As, which is in larger total concentrations in the soil, evidencing the availability of these PTEs, which was corroborated with the BCR extraction (where the labile or available fractures are extracted for transport and plants) (Madrid et al., 2007; Kelepertzis et al., 2013) for As and Cu, where Cu was much more available than As.

For the soil-plant transfer of PTEs, a weakly negative linear regression between the Cu concentration in plants *vs*. the available Cu fraction in soil (BCR) was found. Although Cu is an essential element for plants, it is toxic for them if it appears in soil in large quantities (Adrees et al., 2015; Shabbir et al., 2020; Rather et al., 2020; Kumar et al., 2021). The relation between bioavailability indices BAC and BC (Kelepertzis et al., 2013) was positive, which reveals that plants' ability to bioaccumulate Cu is enhanced, as does its ability to bioconcentrate it when Cu is available in soil.

The scenario is different for As because the relation between the element in plants and in soil is not as clear. Although this relation was very weakly positive, it seemed to be dominated by having low absorbed As concentrations available in soil. This is a general rule, except for *Schefflera morototoni,* which absorbs As more efficiently by having mechanisms to tolerate and accumulate this toxic element. One remarkable fact is that, although As is more available in the soil, plants do not always absorb it more, mainly because it is not an essential element (Ackova, 2018) and can be more related to each plant species' capacity to exclude or tolerate this PTE (Dixit et al., 2015; Chamba et al., 2017). The relation between bioavailability indices BAC and BC was positive, which indicates that a plant's ability to bioaccumulate As increases, as does its ability to bioconcentrate As when it is available in soil.

The mean concentration of both Cu and Zn in the leaves of the plants around the Remance gold mine, compared to plants from other parts of the world, fell within the ranges known for between uncontaminated (Shtangeeva et al., 2020 a) and contaminated zones (Hussain et al., 2019), while the As, Sb and Ba values were similar to those reported from contaminated areas (Getaneh & Alemayehu, 2006; Hussain et al., 2019). More specifically, the Cu concentrations in grass were similar to those from contaminated areas (Hussain et al., 2019), while As, Sb and Ba obtained higher values than those reported in uncontaminated areas (Shtangeeva et al., 2020 b), and the Zn concentrations were similar to those from uncontaminated areas (Kabata-Pendias, 2011). All these values imply harmful effects on the health of the cattle grazing in the study area for these PTEs because they are higher than those recommended for the animal nutrition of ruminants (Johnsen & Aaneby, 2019), as is the case of Cu and Zn (NRC, 2001). However, there are no estimated requirements set for cattle according to the National Research Council, USA, for the other PTEs (As, Sb, Ba, Hg).

The human health risk posed by eating edible plants grown in areas with PTEs can be evaluated with the PMTDI (Gruszecka-Kosowska, 2020). This value was exceeded for Cu, Zn, Sb and Ba in all the studied edible plants (rice, corn, cassava, tea leaves), and for As in rice, corn and tea leaves, and for Hg only in tea leaves. Although some of these elements can be considered essential for plants or humans, they can be toxic to human health if consumed in excess, such as Cu, which brings about abnormalities in the nervous system, liver and kidneys, and even death, or Zn, which reduces the immune function and HDL cholesterol, and also causes fever. Non-essential PTEs can cause cirrhosis, cancer of the skin, liver and lungs, or embryo theratogenesis (As), respiratory system damage (Sb), gastroentheritis, muscle paralysis, ventricular fibrillation and extrasystoles (Ba) neurological damage (mercurialism), asthenic-vegetative syndrome or Minamata disease, kidney damage, toxicity to foetus and teratogenic embryo (Hg) (Bini & Wahsha, 2014).

The HQ values, with which the non-carcinogenic risk of edible plants is evaluated (Gruszecka-Kosowska, 2020), were exceeded for Sb, which places rice, corn, cassava and tea leaves at risk levels. The long-term intake of small amounts of Sb may induce chronic antimony poisoning, while Sb exposure has been shown to induce DNA damage and oxidative stress, and to generate reactive oxygen species (ROS) causing apoptosis. As Sb geochemical behaviour is similar to that of As, it is likely that DNA damage induced by Sb follows similar pathways to those for As (Franco et al., 2009; Bini & Wahsha, 2014).

The acceptable CR was surpassed by all the edible plants for Cu, and also for As in rice, corn and tea leaves, which meant that the total acceptable CR was exceeded by all the studied edible plants, and pose a risk for the health of the people who eat them in the studied mining area. One of the most important risks could come through As as long-term exposure can lead to skin lesions, internal cancers, neurological problems, pulmonary disease, peripheral vascular disease, hypertension and cardiovascular disease, and diabetes mellitus (Smith et al., 2000; Jaishankar et al., 2014).

The Remance gold mine is an abandoned mine. When abandoned mines are not properly shut down, they pose an environmental problem that also affects the inhabitants of their surroundings (Kaninga et al., 2020; Khlelifi et al., 2020). Therefore, environmental surveillance programmes need to be set up and to avoid harming populations.

## 4.5. Conclusion

The flora and crops of the Remance gold mine bioaccumulated the herein studied PTEs in this order: Zn> Sb> Cu> Hg> Ba> As. This finding indicates that this area has absorbed mostly essential elements like Zn and Cu, along with Sb which is non-essential, but has a very high affinity to be absorbed by plants. Of the major elements in soil, such as As and Cu, Cu was more available than As. This revealed that plants bioconcentrated Cu more than As despite As found in a larger total quantity in soil.

The BAC *vs.* BC relation was positive for both the tested Cu and As elements, which denotes that plants' ability to bioaccumulate and bioconcentrate is linked with the availability of elements in soil.

The relation between the Cu concentration in plants and the amount of Cu available in soil was weak and not very significant, as is the case for As. What this implies is that the amount of As available in soil was not directly linked with its concentration in plants and this could, in turn, be linked with the mechanisms that each plant species possesses to absorb and bioaccumulate, or exclude, As.

The average Cu and Zn concentrations present in the grass and plants around the Remance gold mine exceeded the recommended requirements for the animal nutrition of ruminants according to the National Research Council, USA. So this could pose some health risks for the livestock grazing in this area.

Sb was the PTE that posed the main non CR. As and Cu were the PTEs that represented a CR because they exceeded the acceptable CR limit in the studied edible plants (rice, corn, cassava, tea leaves) that are planted and consumed by peasants as part of their daily diet.

We recommend the study area being bioremediated to reduce the posed risk for the environment and the people inhabiting the area.

## 4.6. Declarations

**Funding information**: Open Access funding provided thanks to the CRUE- 747 CSIC agreement with Springer Nature. This study was funded by the National Secretary of Science and Technology (SENACYT) and the Institute for the Training and Use of Human Resources (IFARHU) of Panama (270-2019-109), and by Fondos para Grupos de Investigación UCLM (2019-GRIN-27011).

**Conflicts of Interest/Competing interest:** The authors declare no conflict of interest.

**Availability of data and material**: Not applicable.

**Code availability**: Not applicable.

**Author Contributions:** The paper was written by Ana C. González-Valoys, Ulises Jiménez, Rita Rodríguez, Tisla Monteza-Destro, Miguel Vargas-Lombardo, Eva M. García-Noguero, José María Esbrí, Raimundo Jiménez-Ballesta, Francisco J. García-Navarro and Pablo Higueras. The conceptualization of the study was done by Pablo Higueras, Raimundo Jiménez-Ballesta, Francisco J. García-Navarro and José María Esbrí. Plants were collected by Ana González-Valoys and Rita Rodríguez and were identified by botanical biologist Ulises Jimenez. The laboratory analyses were carried out by Ana González-Valoys and Eva M. García-Noguero.

**Animal research**: Not applicable.

**Ethics approval**: Not applicable.

**Consent to participate**: Not applicable.

**Consent for publication**: Not applicable.

**Acknowledgments:** The authors thank the National Secretary of Science and Technology (SENACYT), the Institute for the Training and Use of Human Resources (IFARHU) of Panama, the Technological University of Panama (UTP), the University of Castilla-La Mancha (UCLM) and the Autonoma University of Madrid (UAM) for their research support, and to the National Directorate of Mineral Resources of the Ministry of Commerce and Industry (MICI) of Panama for granting access to the Remance mine. They also thank Mr. Doroteo

Concepción and Francisco Hernández for their guidance in the Remance area and their knowledge of local plants. Thanks also go to Marcial González for his collaboration with this work. Thanks to Helen Warburton (Scientific English) for the revision of the English style of the manuscript

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## 4.8. Supplementary Materials

### **ST1. Suplementary table**: common name, family, taxon and geographical coordinates

| Area | ID | Family | Taxon | Common name | Geographical coordinates (WGS 84, 17 P) | |
|---|---|---|---|---|---|---|
| | | | | | **N** | **W** |
| Soils | PA7 | *Annonaceae* | *Xylopia frutescens* Aubl. | *Malagueto macho* | 917617 | 491615 |
| | PA8 | *Malvaceae* | mophospecies | | 916982 | 491801 |
| | PA9 | *Malvaceae* | mophospecies | | 916805 | 491225 |
| | PA10 | *Malvaceae* | mophospecies | | 916582 | 490786 |
| | PA11 | *Annonaceae* | *Xylopia frutescens* Aubl. | *Malagueto macho* | 916963 | 492249 |
| | PA12 | *Malpighiaceae* | *Byrsonima crassifolia* (L.) Kunth | *Nance* | 917145 | 492519 |
| | PA13 | *Gleicheniaceae* | *Dicranopteris pectinata* (Willd.) Underw. | Fern | 917145 | 492519 |
| | PA14 | *Dilleniaceae* | *Curatella americana* L. | *Chumico* | 918015 | 492170 |
| | PA15 | *Fabaceae-Papilionoideae* | *Andira inermis* (W. Wright) Kunth ex DC. | *Harino* | 918180 | 492508 |
| | PA16 | *Anacardiaceae* | *Anacardium excelsum (Bertero & Balb. ex Kunth) Skeels* | *Espavé* | 918180 | 492508 |
| | PEU 4 | *Malvaceae* | *Guazuma ulmifolia* Lam. | *Guácimo* | 915530 | 492786 |
| | PEU 5 | *Poaceae* | morphospecies | Grass*, pasto* | 915494 | 492181 |
| | PEU 6 | *Dilleniaceae* | *Curatella americana* L. | *Chumico* | 916237 | 492298 |
| | PJ5 | *Poaceae* | morphospecies | Grass*, pasto* | 918483 | 491876 |
| | PJ7 | *Lygodiaceae* | *Lygodium venustum* Sw. | *Crespillo* | 918500 | 491992 |
| | PR2 | *Rubiaceae* | *Alibertia edulis* (Rich.) A. Rich. | Trumpet | 915039 | 491251 |
| | PR3 | *Asteraceae* | *Baccharis trinervis* Pers. | | 915540 | 491662 |
| | PR4 | *Connaraceae* | *Cnestidium rufescens* Planch. | | 915981 | 491042 |
| | PR7 | *Piperaceae* | *Piper leptocladum* C. DC. | *Cordoncillo* | 916072 | 491461 |
| | PR8 | *Euphorbiaceae* | ***Manihot esculenta* Crantz** | **Cassava, *yuca*** | 916402 | 491336 |
| | PR10 | *Sapindaceae* | *Cupania americana L.* | *Gorgojo,* weevil | 915741 | 489599 |
| | PR11 | *Boraginaceae* | *Heliotropium indicum L.* | Turnsole, indian heliotrope | 916087 | 492841 |
| | PR12 | *Poaceae* | morphospecies | Grass, *pasto* | 918296 | 490953 |
| | PM1 | *Rubiaceae* | ***Declieuxia fruticosa* (Willd.) Kuntze** | ***Tea leaves*** | 917551 | 490221 |
| | PM2 | *Poaceae* | morphospecies | Grass, pasto | 918056 | 490481 |
| | PM3 | *Convolvulaceae* | *Ipomoea batatas* (L.) Lam. | Yam, sweet potato | 918110 | 490621 |
| | PL16 | *Bombacaceae* | *Pseudobombax septenatum* (Jacq.) Dugand | *Barrigón* | 918071 | 493038 |
| | PL17 | *Burseraceae* | *Bursera simaruba* (L.) Sarg. | *Indio desnudo* | 919217 | 495758 |
| Mining work | PA1 | *Fabaceae-Papilionoideae* | *Andira inermis (W. Wright) Kunth ex DC.* | *Harino* | 918019 | 492109 |
| | PA6 | *Annonaceae* | *Xylopia frutescens Aubl.* | *Malagueto macho* | 917464 | 491715 |
| | PM4 | *Asteraceae* | ***Ayapana stenolepis (*Steetz) R.M. King &** | ***Tea leaves*** | 917570 | 491365 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | **H. Rob.** | | | |
| | 1P | *Poaceae* | *morphospecies* | Grass, *pasto* | 917440 | 491373 |
| | 2P | *Malpighiaceae* | *Byrsonima crassifolia (L.) Kunth* | *Nance* | 917304 | 491470 |
| | 3P | *Poaceae* | *morphospecies* | Grass, *pasto* | 917437 | 491606 |
| | 4P | *Fabaceae* | *Acacia mangium* Willd. | *Acacia* | 917296 | 491759 |
| | 5P | *Euphorbiaceae* | *Mabea occidentalis* Benth. | *Caciquillo* | 917092 | 491795 |
| | 6P | *Poaceae* | morphospecies | Grass, *pasto* | 917008 | 491502 |
| | 7P | *Dennstaedtiaceae* | *Pteridium caudatum (L.) Maxon* | Fern | 917346 | 492079 |
| | 8P | *Cyperaceae* | *Rhynchospora cephalotes* (L.) Vahl | Grass | 917133 | 492076 |
| | 9P | *Euphorbiaceae* | *Mabea occidentalis* Benth. | | 917325 | 491968 |
| | 10P | *Melastomataceae* | *Miconia argentea* (Sw.) DC. | *Papelillo* | 917301 | 492152 |
| | 11P | *Poaceae* | morphospecies | Grass, *pasto* | 916900 | 491055 |
| | 12P | *Poaceae* | morphospecies | Grass, *pasto* | 917791 | 491523 |
| | 13P | *Cyperaceae* | *Rhynchospora cephalotes* (L.) Vahl | Grass | 916948 | 491277 |
| | 14P | *Poaceae* | morphospecies | Grass, *pasto* | 917029 | 491678 |
| | 15P | *Dilleniaceae* | *Curatella americana L.* | *Chumico* | 917686 | 491283 |
| | 16P | *Poaceae* | morphospecies | Grass, *pasto* | 917352 | 491194 |
| Tailings | PA 3 | *Rubiaceae* | *Genipa americana* L. | *Jagua* | 918050 | 492113 |
| | PA 4 | *Fabaceae-Mimosoideae* | *Acacia sp.* | *Acacia* | 917639 | 491819 |
| | PA 5 | *Dennstaedtiaceae* | *Pteridium caudatum* (L.) Maxon | Fern | 917639 | 491819 |
| | PJ 4 | *Poaceae* | morphospecies | Grass, *pasto* | 917890 | 491323 |
| | PL REL 1 L | *Annonaceae* | *Xylopia frutescens Aubl.* | *Malagueto macho* | 917835 | 491845 |
| | PL REL 2 L | *Dilleniaceae* | *Curatella americana* L. | *Chumico* | 917954 | 491925 |
| Riverside of water bodies | PEU 1 | *Fabaceae-Papilionoideae* | *Andira inermis* (W. Wright) Kunth ex DC. | *Harino* | 915546 | 492834 |
| | PEU 2 | *Lauraceae* | *Nectandra* sp. | *Sigua* | 915540 | 492810 |
| | PEU 3 | *Burseraceae* | *Bursera simaruba* (L.) Sarg. | *Indio desnudo* | 915530 | 492801 |
| | PJ 1 | *Moraceae* | *Brosimum alicastrum Sw.* | *Berba, cacique,* breadnut | 918024 | 491479 |
| | PJ 2 | *Fabaceae-Mimosoideae* | *Cojoba rufescens* (Benth.) Britton & Rose | *Coralillo* | 918022 | 491458 |
| | PJ 3 | *Anacardiaceae* | *Anacardium excelsum (Bertero & Balb. ex Kunth) Skeels* | *Espavé* | 918170 | 491488 |
| | PJ 6 | *Lygodiaceae* | *Lygodium venustum* Sw. | Fern | 918500 | 491992 |
| | PJ 8 | *Fabaceae-Papilionoideae* | *Andira inermis (W. Wright) Kunth ex DC.* | *Harino* | 918379 | 492672 |
| | PR 1 | *Clusiaceae* | *Garcinia madruno (Kunth) Hammel* | *Satro* | 915005 | 491255 |
| | PR 5 | *Fabaceae-Mimosoideae* | *Zygia longifolia (Humb. & Bonpl. ex Willd.) Britton & Rose* | *Pichindé* | 915901 | 491261 |
| | PR 6 | *Anacardiaceae* | *Anacardium excelsum (Bertero & Balb. ex Kunth) Skeels* | *Espavé* | 916047 | 491441 |

| | | | | | |
|---|---|---|---|---|---|
| PR 9 | *Fabaceae-Mimosoideae* | *Calliandra magdalenae (Bertero ex DC.) Benth.* | | 915728 | 489595 |
| PR 11 | *Boraginaceae* | *Heliotropium indicum* | Turnsole, indian heliotrope | 916087 | 492841 |
| PR 13 | *Araliaceae* | *Schefflera morototoni (Aubl.) Maguire, Steyerm. & Frodin* | *Mangabe* | 917992 | 491484 |
| PL 16 | *Bombacaceae* | *Pseudobombax septenatum (Jacq.) Dugand* | *Barrigón* | 918071 | 493038 |
| PD 17 | *Malvaceae* | *Guazuma ulmifolia* Lam. | *Guácimo* | 919198 | 495767 |
| PL 18 L | *Araceae* | morphospecies | | 917938 | 492432 |
| PL 19 L | *Melastomataceae* | *Mouriri myrtilloides* (Sw.) Poir. | | 917945 | 492419 |
| PL 20 L | *Myrtaceae* | *Eugenia* sp. | *Guayabillo* | 917920 | 492444 |
| PL B | *Malvaceae* | *Guazuma ulmifolia* Lam. | *Guácimo* | 917510 | 491947 |
| PR 15 | *Poaceae* | ***Oryza sativa* L.** | **Rice, *arroz*** | 917411 | 491917 |
| PR 16 | *Poaceae* | ***Zea mays* L.** | **Corn, *maíz*** | 917411 | 491917 |

**ST2**. Results for plants and BAC in the present study. Value of the PTEs in plant and soil samples for Cu, Zn, As, Sb and Ba expressed as mg kg$^{-1}$, Hg in ng g$^{-1}$.

| ID plant | Cu plant | BAC Cu | Zn plant | BAC Zn | As plant | BAC As | Sb plant | BAC Sb | Ba plant | BAC Ba | Hg plant | BAC Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PA7 | 26.1 | 1.35 | 37.9 | 1.82 | < 0.1 | 0.00 | 4.3 | 0.26 | < 5.0 | 0.01 | 7.8 | 0.05 |
| PA8 | 24.7 | 0.95 | 43.8 | 1.09 | 2.8 | 0.03 | < 1.0 | 0.02 | 18.3 | 0.05 | 15.8 | 0.08 |
| PA9 | 45.1 | 1.29 | 84.2 | 2.40 | 0.9 | 0.02 | < 1.0 | 0.03 | < 5.0 | 0.01 | 6.8 | 0.14 |
| PA10 | 18.9 | 0.11 | 32.0 | 0.36 | < 0.1 | 0.00 | 2.5 | 0.13 | 24.3 | 0.05 | 4.0 | 0.05 |
| PA11 | 21.7 | 1.06 | 16.1 | 0.48 | < 0.1 | 0.00 | < 1.0 | 0.04 | < 5.0 | 0.01 | 2.6 | 0.06 |
| PA12 | 14.5 | 0.76 | 8.6 | 0.19 | 0.4 | 0.03 | 1.8 | 0.14 | 27.8 | 0.09 | 0.6 | 0.02 |
| PA13 | 4.9 | 0.26 | 9.4 | 0.21 | < 0.1 | 0.00 | 4.2 | 0.32 | 19.7 | 0.06 | 5.2 | 0.16 |
| PA14 | 10.9 | 0.44 | 20.8 | 0.48 | < 0.1 | 0.00 | 4.0 | 0.25 | 36.4 | 0.05 | 3.0 | 0.08 |
| PA15 | 7.3 | 0.04 | 5.7 | 0.06 | < 0.1 | 0.00 | 4.8 | 0.29 | < 5.0 | 0.00 | 0.1 | 0.00 |
| PA16 | 9.2 | 0.05 | 11.3 | 0.11 | < 0.1 | 0.00 | 3.9 | 0.24 | 13.8 | 0.02 | 11.9 | 2.38 |
| PEU4 | 13.4 | 0.10 | 22.7 | 0.25 | < 0.1 | 0.00 | 4.6 | 0.27 | 22.6 | 0.04 | 5.6 | 0.12 |
| PEU5 | 8.3 | 0.02 | 12.6 | 0.08 | < 0.1 | 0.00 | 4.7 | 0.24 | 15.2 | 0.03 | 7.8 | 1.56 |
| PEU6 | 21.7 | 1.13 | 17.1 | 0.92 | 0.6 | 0.01 | 3.0 | 0.22 | 13.7 | 0.14 | 1.6 | 0.06 |
| PJ5 | 31.4 | 0.29 | 53.9 | 0.91 | < 0.1 | 0.00 | < 1.0 | 0.03 | < 5.0 | 0.00 | 0.1 | 0.01 |
| PJ7 | 57.3 | 0.35 | 37.0 | 0.69 | 0.1 | 0.01 | 1.7 | 0.09 | 9.7 | 0.05 | 5.0 | 0.11 |
| PR2 | 5.4 | 0.12 | 6.0 | 0.11 | < 0.1 | 0.00 | 4.9 | 0.22 | < 5.0 | 0.02 | 0.1 | 0.00 |
| PR3 | 14.8 | 0.50 | 29.3 | 0.58 | < 0.1 | 0.00 | 5.1 | 0.34 | 45.0 | 0.28 | 0.1 | 0.00 |
| PR4 | 10.4 | 0.08 | 44.8 | 0.46 | < 0.1 | 0.00 | < 1.0 | 0.03 | 160.6 | 0.34 | 9.4 | 1.61 |
| PR7 | 15.2 | 0.15 | 40.2 | 0.68 | < 0.1 | 0.00 | 7.3 | 0.47 | 23.5 | 0.06 | 7.5 | 0.14 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PR8 | 7.5 | 0.07 | 9.0 | 0.15 | < 0.1 | 0.00 | 4.1 | 0.26 | 18.5 | 0.05 | 0.1 | 0.00 |
| PR10 | 11.3 | 0.08 | 103.4 | 0.77 | 1.0 | 0.01 | 4.1 | 0.13 | 49.8 | 0.11 | 16.4 | 0.07 |
| PR11 | 31.1 | 0.80 | 41.0 | 0.58 | < 0.1 | 0.00 | 7.2 | 0.44 | 105.0 | 0.26 | 8.3 | 0.18 |
| PR12 | 20.2 | 0.23 | 33.8 | 0.76 | 1.2 | 1.50 | 3.5 | 0.26 | < 5.0 | 0.01 | 6.9 | 0.12 |
| PM1 | 13.0 | 0.10 | 51.9 | 0.80 | 0.7 | 0.81 | 4.7 | 7.83 | 29.3 | 0.73 | 5.4 | 0.86 |
| PM2 | 16.2 | 0.15 | 26.7 | 0.62 | 0.6 | 0.13 | 2.9 | 0.23 | < 5.0 | 0.03 | 0.8 | 0.01 |
| PM3 | 39.0 | 0.36 | 46.0 | 1.07 | 2.1 | 0.44 | 7.4 | 0.59 | 32.9 | 0.41 | 14.1 | 0.14 |
| PL16 | 31.6 | 0.78 | 24.5 | 0.76 | 0.7 | 0.01 | 3.4 | 0.24 | 24.8 | 0.06 | 4.0 | 0.07 |
| PL17 | 25.5 | 0.53 | 34.1 | 0.45 | 0.6 | 0.01 | 2.9 | 0.20 | 21.2 | 0.04 | 13.7 | 0.21 |
| 1P | 25.2 | 0.21 | 21.2 | 0.24 | < 0.1 | 0.00 | 1.8 | 0.13 | 8.6 | 0.04 | 4.8 | 0.20 |
| 2P | 10.1 | 0.10 | 8.5 | 0.12 | < 0.1 | 0.00 | 3.2 | 0.26 | 103.3 | 0.57 | 29.6 | 0.22 |
| 3P | 20.5 | 1.23 | 51.5 | 1.81 | 0.4 | 0.01 | 2.0 | 0.18 | 9.8 | 0.06 | 9.0 | 0.19 |
| 4P | 7.6 | 0.30 | 9.5 | 0.74 | 0.7 | 0.01 | 3.2 | 0.34 | 36.4 | 0.53 | 6.5 | 0.25 |
| 5P | 11.2 | 0.75 | 13.8 | 0.88 | 0.6 | 0.02 | 3.4 | 0.25 | 10.5 | 0.03 | 19.4 | 0.14 |
| 6P | 13.5 | 0.68 | 11.7 | 0.37 | 0.3 | 0.00 | 2.6 | 0.18 | < 5.0 | 0.01 | 10.5 | 0.36 |
| 7P | 11.0 | 0.48 | 17.9 | 0.24 | 0.6 | 0.69 | 4.5 | 0.41 | 52.3 | 0.60 | 16.6 | 0.57 |
| 8P | 14.0 | 0.38 | 14.2 | 0.34 | < 0.1 | 0.00 | 2.4 | 0.17 | 6.7 | 0.04 | 16.1 | 0.41 |
| 9P | 12.5 | 0.55 | 26.0 | 0.35 | 0.6 | 0.05 | 3.1 | 0.28 | 8.7 | 0.06 | 37.9 | 0.71 |
| 10P | 13.6 | 0.81 | 13.5 | 0.92 | 0.3 | 0.01 | 1.2 | 0.11 | 7.6 | 0.06 | 13.7 | 0.43 |
| 11P | 19.8 | 0.15 | 20.2 | 0.35 | < 0.1 | 0.00 | 2.1 | 0.16 | 10.6 | 0.18 | 7.2 | 0.12 |
| 12P | 24.2 | 0.46 | 24.4 | 0.73 | 0.2 | 0.00 | 2.4 | 0.13 | 6.6 | 0.03 | 27.9 | 0.04 |
| 13P | 11.2 | 0.10 | 13.6 | 0.22 | < 0.1 | 0.00 | 2.7 | 0.17 | 6.5 | 0.06 | 8.7 | 0.16 |
| 14P | 9.8 | 0.38 | 21.5 | 0.81 | 0.2 | 0.00 | 3.6 | 0.20 | 9.6 | 0.04 | 17.2 | 0.08 |
| 15P | 7.7 | 0.05 | 21.9 | 0.29 | 0.2 | 0.25 | 5.0 | 0.31 | 51.8 | 0.58 | 16.6 | 0.71 |
| 16P | 20.0 | 0.15 | 22.7 | 0.33 | 0.6 | 0.02 | 2.0 | 0.16 | 12.8 | 0.07 | 14.9 | 0.56 |
| PA1 | 17.8 | 0.90 | 19.5 | 0.62 | 0.5 | 0.00 | 3.3 | 0.24 | < 5.0 | 0.01 | 0.1 | 0.00 |
| PA6 | 18.6 | 0.97 | 20.2 | 0.58 | 0.6 | 0.01 | 9.7 | 0.63 | 10.5 | 0.04 | 6.6 | 0.07 |
| PM4 | 25.5 | 0.22 | 125.6 | 2.67 | 0.5 | 0.01 | 4.6 | 0.32 | 41.7 | 0.08 | 17.7 | 0.17 |
| PA 3 | 21.0 | 1.71 | 15.9 | 0.55 | 1.0 | 0.02 | 2.2 | 3.67 | 28.5 | 0.17 | 21.7 | 0.27 |
| PA 4 | 19.6 | 0.63 | 32.9 | 0.87 | 2.2 | 0.00 | 3.6 | 0.26 | 35.5 | 0.09 | 28.7 | 0.07 |
| PA 5 | 9.5 | 0.31 | 22.4 | 0.59 | 54.5 | 0.08 | 5.8 | 0.43 | 76.3 | 0.20 | 191.2 | 0.47 |
| PJ 4 | 10.9 | 0.49 | 27.5 | 2.29 | 51.8 | 0.14 | 5.5 | 0.49 | 36.2 | 0.15 | 99.7 | 0.17 |
| PL REL 1 L | 15.6 | 2.89 | 23.1 | 0.33 | < 0.1 | 0.00 | 5.6 | 3.47 | 12.9 | 0.05 | 3.8 | 0.02 |
| PL REL 2 L | 10.6 | 0.48 | 18.0 | 1.38 | 35.7 | 0.08 | 5.5 | 0.29 | 319.9 | 0.76 | 126.1 | 0.15 |
| PEU 1 | 8.8 | 0.22 | 9.4 | 0.19 | < 0.1 | 0.00 | 3.6 | 0.22 | 10.9 | 0.03 | 5.4 | 0.15 |
| PEU 2 | 7.2 | 0.12 | 15.9 | 0.26 | < 0.1 | 0.00 | 4.5 | 0.26 | 16.3 | 0.05 | 41.2 | 0.86 |
| PEU 3 | 9.4 | 0.16 | 12.7 | 0.19 | 0.9 | 0.01 | 3.7 | 0.18 | 31.6 | 0.08 | 35.6 | 0.73 |
| PJ 1 | 8.4 | 0.08 | 27.3 | 0.33 | 2.1 | 0.02 | < 1.0 | 0.03 | 47.4 | 0.11 | 43.2 | 0.13 |
| PJ 2 | 12.2 | 0.10 | 25.3 | 0.39 | 0.2 | 0.00 | 3.7 | 0.09 | 14.0 | 0.03 | 39.4 | 0.03 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PJ 3 | 15.4 | 0.28 | 19.0 | 0.70 | 0.5 | 0.00 | 3.2 | 0.18 | 18.5 | 0.04 | 15.1 | 0.02 |
| PJ 6 | 11.6 | 0.11 | 43.9 | 0.61 | < 0.1 | 0.00 | < 1.0 | 0.04 | < 5.0 | 0.01 | 3.3 | 0.08 |
| PJ 8 | 17.9 | 0.30 | 11.3 | 0.25 | 0.9 | 0.02 | 2.4 | 0.17 | 12.2 | 0.04 | 25.8 | 0.77 |
| PR 1 | 6.3 | 0.05 | 42.2 | 0.45 | 0.6 | 0.02 | 3.2 | 0.17 | 38.5 | 0.10 | 32.4 | 1.34 |
| PR 5 | 13.2 | 0.49 | 25.8 | 1.40 | 0.7 | 0.00 | 3.6 | 0.10 | 36.0 | 0.16 | 36.0 | 0.05 |
| PR 6 | 9.5 | 0.42 | 11.9 | 0.24 | 1.0 | 0.02 | 4.1 | 0.31 | 124.7 | 0.93 | 14.5 | 0.09 |
| PR 9 | 15.2 | 0.15 | 21.4 | 0.30 | 0.4 | 0.01 | 2.6 | 0.15 | 27.6 | 0.10 | 10.5 | 0.05 |
| PR 11 | 31.1 | 1.33 | 41.0 | 0.63 | < 0.1 | 0.01 | 7.2 | 0.63 | 105.0 | 0.51 | 8.3 | 0.22 |
| PR 13 | 13.6 | 0.24 | 57.4 | 1.24 | 2.2 | 0.00 | < 1.0 | 0.01 | 16.2 | 0.03 | 86.3 | 0.01 |
| PL 16 | 31.6 | 0.66 | 24.5 | 0.71 | 0.7 | 0.01 | 3.4 | 0.20 | 24.8 | 0.06 | 4.0 | 0.08 |
| PD 17 | 23.1 | 0.29 | 23.6 | 0.30 | 1.0 | 0.04 | 3.0 | 4.92 | 39.0 | 0.07 | 16.2 | 0.41 |
| PL 18 L | 24.1 | 0.35 | 273.1 | 5.32 | 2.0 | 0.05 | 5.2 | 0.31 | 22.5 | 0.05 | 4.0 | 0.13 |
| PL 19 L | 11.7 | 0.19 | 12.3 | 0.20 | 0.5 | 0.01 | 3.7 | 0.25 | 33.0 | 0.10 | 30.9 | 0.19 |
| PL 20 L | 23.8 | 0.42 | 35.8 | 0.82 | < 0.1 | 0.00 | 3.5 | 0.23 | 43.8 | 0.11 | 8.8 | 0.30 |
| PL B | 24.9 | 0.70 | 38.1 | 0.82 | 0.7 | 0.00 | 2.5 | 0.14 | < 5.0 | 0.01 | 8.2 | 0.01 |
| PR 15 | 5.2 | 0.15 | 17.9 | 0.39 | 0.2 | 0.00 | 4.4 | 0.26 | 12.1 | 0.07 | 0.1 | 0.00 |
| PR 16 | 4.3 | 0.12 | 22.0 | 0.47 | 0.2 | 0.00 | 4.7 | 0.27 | 11.7 | 0.07 | 0.1 | 0.00 |
| Mean | 16.9 | 0.46 | 31.1 | 0.70 | 2.4 | 0.06 | 3.5 | 0.48 | 31.1 | 0.14 | 18.5 | 0.27 |
| Stand. dev. | 9.6 | 0.47 | 34.9 | 0.75 | 9.4 | 0.21 | 1.8 | 1.15 | 45.0 | 0.20 | 29.5 | 0.42 |
| Max | 57.3 | 2.89 | 273.1 | 5.32 | 54.5 | 1.50 | 9.7 | 7.83 | 319.9 | 0.93 | 191.2 | 2.38 |
| Min | 4.3 | 0.02 | 5.7 | 0.06 | < 0.1 | < 0.001 | < 1.0 | 0.01 | < 5.0 | < 0.001 | 0.1 | < 0.001 |

**ST3.** Pearson's correlation for PTEs in leaves

| | **Cu** | **Zn** | **As** | **Sb** | **Ba** |
|---|---|---|---|---|---|
| **Zn** | 0.313 | | | | |
| | *0.006* | | | | |
| **As** | -0.127 | -0.022 | | | |
| | *0.277* | *0.850* | | | |
| **Sb** | -0.203 | 0.024 | 0.232 | | |
| | *0.081* | *0.838* | *0.045* | | |
| **Ba** | -0.113 | 0.003 | 0.411 | 0.140 | |
| | *0.334* | *0.982* | *0.000* | *0.230* | |
| **Hg** | -0.205 | -0.046 | 0.855 | 0.125 | 0.453 |
| | *0.078* | *0.692* | *0.000* | 0.287 | *0.000* |

**ST4**. BAC and BC for a group of samples with high As and Cu contents in soil

| ID | Cu plant (mg kg-1) | BCR Cu S1 S2 S3 (mg kg-1) | BC Cu | BAC Cu | As plant (mg kg-1) | BCR As S1 S2 S3 (mg kg-1) | BC As | BAC As |
|---|---|---|---|---|---|---|---|---|
| **PEU 3** | 9.4 | 7.88 | 1.19 | 0.16 | 0.9 | 1.23 | 0.69 | 0.007 |
| **PJ 1** | 8.4 | 13.08 | 0.64 | 0.08 | 2.1 | 4.23 | 0.48 | 0.017 |
| **PJ 2** | 12.2 | 17.94 | 0.68 | 0.10 | 0.2 | 4.47 | 0.03 | 0.000 |
| **PJ 3** | 15.4 | 8.73 | 1.76 | 0.28 | 0.5 | 0.41 | 1.09 | 0.005 |
| **PR 5** | 13.2 | 1.34 | 9.82 | 0.49 | 0.7 | 17.38 | 0.04 | 0.002 |
| **PR 13** | 13.6 | 5.00 | 2.72 | 0.24 | 2.2 | 41.73 | 0.05 | 0.003 |
| **PL B** | 24.9 | 10.82 | 2.30 | 0.70 | 0.7 | 19.53 | 0.04 | 0.003 |
| **PD 17** | 23.1 | 8.49 | 2.72 | 0.29 | 1.0 | <0.42 | NP | 0.035 |
| **PA8** | 24.7 | 2.01 | 12.26 | 0.95 | 2.8 | 0.86 | 3.22 | 0.027 |
| **PR10** | 11.3 | 11.07 | 1.02 | 0.08 | 1.0 | 0.72 | 1.32 | 0.006 |
| **PR11** | 31.1 | 3.43 | 9.06 | 0.80 | < 0.1 | 4.29 | NP | NP |
| **PL17** | 25.5 | 7.33 | 3.47 | 0.53 | 0.6 | 0.32 | 1.87 | 0.015 |

NP: Calculation not possible

**ST5.** HQ and CR for the PTEs of the studied edible plant

| Food | ID | HQ Cu | HQ Zn | HQ As | HQ Sb | HQ Ba | HQ Hg | HQt |
|---|---|---|---|---|---|---|---|---|
| Rice, grain | PR15 | 0.233 | 0.107 | 0.894 | 19.451 | 0.108 | 0.0003 | 20.792 |
| Corn, grain | PR16 | 0.076 | 0.052 | 0.357 | 8.304 | 0.042 | 0.0001 | 8.831 |
| Cassava, tuber | PR8 | 0.112 | 0.018 | 0.100 | 6.075 | 0.056 | 0.0001 | 6.260 |
| Tea leaves | PM1 | 0.051 | 0.027 | 0.337 | 1.830 | 0.023 | 0.0026 | 2.270 |
| Tea leaves | PM4 | 0.099 | 0.065 | 0.260 | 1.791 | 0.032 | 0.0093 | 2.256 |
| **Food** | **ID** | **CR Cu** | | **CR As** | | | | **CR t** |
| Rice, grain | PR15 | 2.34E-03 | | 7.67E-05 | | | | 2.42E-03 |
| Corn, grain | PR16 | 7.65E-04 | | 3.06E-05 | | | | 7.96E-04 |
| Cassava, tuber | PR8 | 1.13E-03 | | 8.57E-06 | | | | 1.14E-03 |
| Tea leaves | PM1 | 5.10E-04 | | 2.89E-05 | | | | 5.39E-04 |
| Tea leaves | PM4 | 9.99E-04 | | 2.22E-05 | | | | 1.02E-03 |

In color red calculations use the half of the detection limit.

# DISCUSIÓN GENERAL

# 5 DISCUSIÓN GENERAL

Los resultados de la caracterización de la zona principal de actividad minera que comprende tres relaves expuestos a las condiciones climáticas, los sedimentos de la bocamina y las lagunas secundarias, muestra que los contaminantes de interés por sus concentraciones elevadas lo constituyen el As, Cu, Zn, Sb, Ba, Hg y cianuro (González-Valoys et al., 2021a). Son los mismos contaminantes que han sido encontrados en los sedimentos de los arroyos y sedimentos de terrazas de estos arroyos (González-Valoys et al., 2021b), como la quebrada Veneno, quebrada Chitreca, y quebrada La Máquina, que son los más impactados por la contaminación, debido a que los relaves descargan sobre estas, y la abrupta orografía del lugar favorece su diseminación amplia, lo cual produce que la principal fuente de dispersión de la contaminación sea por escorrentía.

En cuanto a los suelos de las áreas de labores mineras y los suelos del entorno muestran menor grado de impacto de la contaminación que los sedimentos de los arroyos y de las terrazas (González-Valoys et al., 2021b), indicando que, si bien la contaminación se difunde por la acción del viento, la mayor contribución la tiene la escorrentía de los materiales contenidos en los relaves y los sedimentos de la bocamina, que se incorporan al sistema fluvial general a partir de los arroyos. Dicha contaminación esparcida por la zona también afecta a la flora del lugar, habiéndose encontrado estos mismos EPTs (As, Cu, Zn, Sb, Ba, Hg) en las plantas comestibles y no comestibles de la zona, con una absorción de débil a fuerte, y en concentraciones similares a las de áreas contaminadas en otras partes del mundo (González-Valoys et al., 2021c). Por los resultados anteriores, y por la distribución de los contaminantes mostrada en los mapas de contaminación levantados de la zona, es posible apreciar que los relaves y los sedimentos de la bocamina son el foco más importante de la contaminación, y se observa cómo ésta se disemina a partir de éstos en el entorno; habiendo otro foco de contaminación a la parte sur de la concesión minera (González-Valoys et al., 2021b), donde se realizaron excavaciones a cielo abierto en el Cerro Tullido, detectándose una diseminación de la contaminación de este cerro a los arroyos que nacen de él.

En cuanto a la salud del suelo, entendida como aquella capacidad del suelo de funcionar como un ecosistema vivo para sustentar plantas, animales y el ser humano (Sadras et al., 2020), y el indicador biológico utilizado, la actividad enzimática por la actividad deshidrogenasa (DHA), indica que la calidad de los sedimentos de arroyos y de las terrazas es menor que la correspondiente al suelo de las zonas próximas de la mina, y esta actividad enzimática es menor que la encontrada en otras zonas mineras del mundo (Mukhopadhyay & Maiti, 2010; Meier et al., 2017; Campos et al., 2018).

La DHA estaría favorecida por la materia orgánica (OM), y por las especies de cianuro (fácilmente liberable, cianuro complejado, cianuro total), mientras que es afectada negativamente por el potencial de oxidorreducción (ORP) y el Ba (González-Valoys et al., 2021b). Esto se ve traducido en la salud de las plantas, ya que la vegetación observada en la zona es del tipo arbustiva, principalmente (Ministerio de Ambiente, 2012), y se muestra como la presencia de EPTs, ya sea por la mineralización de la zona, o por la contaminación del suelo que implica, influye sobre la flora del lugar, produciendo que las plantas puedan bioacumular y bioconcentrar EPTs, según el mecanismo de cada planta para absorber o excluir dichos elementos (González-Valoys et al., 2021c).

El potencial riesgo ecológico (RI) en la zona relacionado con la presencia de los EPTs (As, Cu, Zn, Sb y Hg) coincide con los mapas de contaminación, donde se evidencia que el foco que afecta la zona son los relaves y los sedimentos de la bocamina, teniendo éstos un riesgo ecológico extremo a serio para la biota del lugar. Además, se observa cómo han afectado los sedimentos de las terrazas, que conservan aún un riesgo ecológico serio; los sedimentos de los arroyos un riesgo ecológico alto; y, con un riesgo ecológico medio, las lagunas secundarias, los suelos de labores mineras y los suelos de la zona del entorno (González-Valoys et al., 2021b). Lo cual ha afectado al ecosistema del lugar, como se ha observado en las plantas comestibles y no comestibles, con riesgos potenciales para los animales del lugar, y para la salud humana (González-Valoys et al., 2021c).

La evaluación del riesgo sanitario humano es muy importante, ya que en la zona habitan campesinos que desarrollan labores ganaderas y agrícolas de subsistencia como la siembra de arroz, maíz, yuca, frijoles, hojas de té, los cuales forman parte casi exclusiva de su dieta (González-Valoys et al., 2021c). Como se observó del estudio previo, el suelo se halla impactado con un grado de contaminación de ligero a considerable, por lo cual constituye un riesgo para la vida humana, en los diversos escenarios residencial, agrícola y recreativo, tanto para adultos como niños, siendo los principales contaminantes As y Cu, tanto para el riesgo no carcinogénico como para el carcinogénico, por las vías de ingestión accidental y contacto dérmico (González-Valoys et al., 2021b). Estos mismos contaminantes presentes en el suelo, son absorbidos por las plantas comestibles y no comestibles del lugar, siendo así un riesgo para la salud de los rumiantes locales y para los seres humanos que viven y obtienen su sustento in situ (González-Valoys et al., 2021c); siendo los EPTs de mayor consideración en las plantas comestibles: el Sb para el riesgo no carcinogénico; y As y Cu para el riesgo carcinogénico (González-Valoys et al., 2021c).

Sobre los efectos a la salud humana de los principales contaminantes identificados se puede decir que: la ingesta de Sb en pequeñas cantidades de manera prolongada puede inducir daños al sistema respiratorio, daños al ADN y estrés oxidativo de las células provocando su apoptosis (Bini y Wahsha, 2014). El Cu, si bien es un nutriente esencial en pequeñas cantidades, consumido en exceso provoca anomalías en el sistema nervioso, hígado, riñones, e incluso efectos letales (Bini y Wahsha, 2014). La exposición a largo plazo de As puede generar cánceres internos, enfermedad pulmonar, problemas neurológicos, enfermedad vascular periférica, hipertensión y enfermedad cardiovascular, diabetes mellitus (Smith et al., 2000; Jaishankar et al., 2014), cirrosis, cáncer de piel, hígado y pulmones, o teratogénesis embrionaria (Bini y Wahsha, 2014). Por lo cual se amerita darle seguimiento a esta zona, y los posibles efectos a la salud de sus moradores.

# CONCLUSIONES GENERALES

# 6 CONCLUSIONES GENERALES

A pesar de que el cese de la última operación minera fue hace más de 20 años, la zona de la mina de oro de Remance todavía se mantiene impactada; siendo los sedimentos de la bocamina, y los tres relaves expuestos a las condiciones climáticas, el foco de contaminación para la mayor parte de la zona del entorno, incluidos y siendo los más afectados los sedimentos de los arroyos y sus terrazas, los cuales contienen elementos potencialmente tóxicos, incluyendo As, Cu, Zn, Sb, Ba, Hg, y cianuro.

El potencial riesgo ecológico que mantiene la zona para la biota del lugar es de extremo a serio en los lugares mencionados como foco de contaminación (sedimentos bocamina y relaves); de serio a alto en los sedimentos de los arroyos y sus terrazas; y medio en los suelos de labores mineras y suelos en derredor. Lo cual ha afectado a la salud del suelo y sedimentos, teniendo una baja actividad deshidrogenasa (DHA), y a las plantas comestibles y no comestibles que han absorbido estos contaminantes, y cuyos contenidos en EPTs representan un riesgo para la salud de animales y a los moradores de la zona.

Tanto el suelo como las plantas comestibles cultivadas (arroz, maíz, yuca, hojas de té) en la zona para el sustento de sus habitantes contienen cantidades significativas de EPTs, que representan un riesgo a la salud humana, tanto no carcinogénico como carcinogénico. Siendo en el suelo el As y el Cu los contaminantes que sobrepasan los límites establecidos para el riesgo no carcinogénico y carcinogénico, para niños y adultos, por las vías de ingestión accidental y por contacto dérmico, en el escenario residencial y el escenario agrícola. En las plantas comestibles, el riesgo no carcinogénico es sobrepasado por el Sb, y el riesgo carcinogénico por el As y el Cu. La exposición prolongada a estos contaminantes puede inducir graves efectos sobre la salud humana, como daño al ADN (Sb), afectación del sistema nervioso, hígado y riñones (Cu), y diversos tipos de cáncer (As).

Debido a los riesgos que representa la zona para la biota y sus pobladores, se hace necesario establecer un plan de remediación, empezando por aquellas zonas identificadas como foco de contaminación, siendo de esta manera esta Tesis Doctoral el estudio básico para plantear futuros planes de remediación de la zona.

Se requieren también estudios de bioaccesibilidad para aquellos EPTs identificados con riesgo a la salud humana. Este modelo de estudio debería ser replicado a otras zonas mineras de Panamá que han quedado en abandono, y sin medidas de remediación suficientes; también para estudios de línea base antes del inicio de la actividad minera, y así, establecer niveles de restauración de la zona.

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# 7 REFERENCIAS ADICIONALES

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# ANEXO I. GALERÍA DE IMÁGENES

1. Vista aérea de la Mina de Oro de Remance, Veraguas, Panamá.

2. Ruinas de la planta de proceso.

3. Vista aérea del relave 1, empleado como cancha de futbol y con viviendas cercanas.

4. Toma de muestra sobre el relave 1.

5. Relave 2.

6. Toma de muestra sobre el relave 3.

7. Galería de mina Tun 488 donde brota agua subterránea procedente de la mina.

8. Muestreo de sedimentos y terrazas en la quebrada Veneno.

9. Muestreo de sedimentos y terrazas en la quebrada Chitreca.

10. Muestreo de sedimentos y terrazas en la quebrada El Torno.

11. Muestreo de sedimentos y terrazas en la quebrada La Máquina.

12. Galerías de la mina.

13. Muestreo de sedimentos en la laguna secundaria 1.

14. Laguna secundaria 2.

15. Laguna “Bebedero de vacas”.

16. Muestreo de suelo.

17. Vivienda rural en la zona.

18. Viviendas.

19. Ganadería de subsistencia.

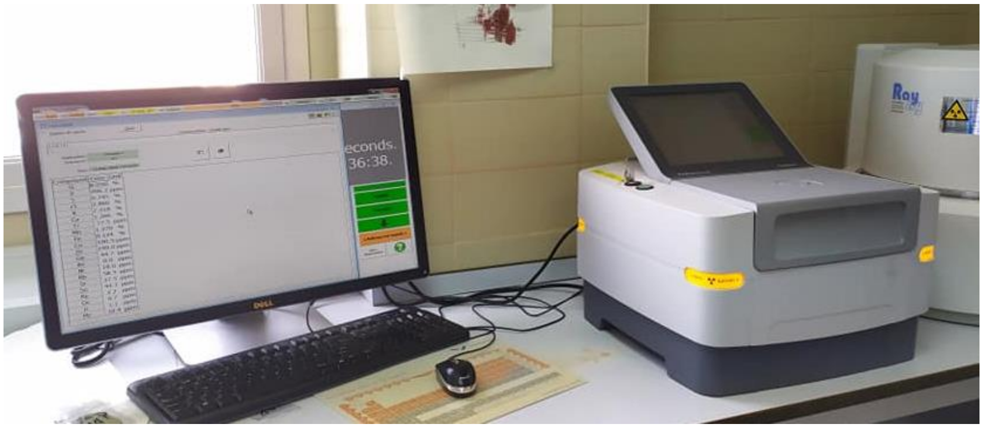
20. Agricultura de subsistencia.

21. Plantas recolectadas.

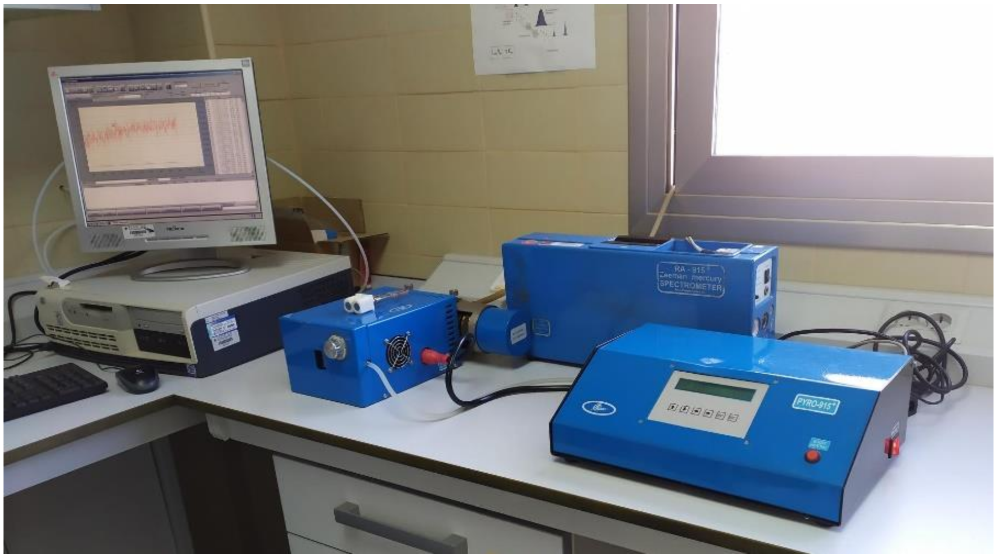
22. Prensado de plantas para su identificación (herbarización).

23. Cuarteo de muestras de suelo recolectadas.

24. Rocas de Remance para estudio petrográfico.

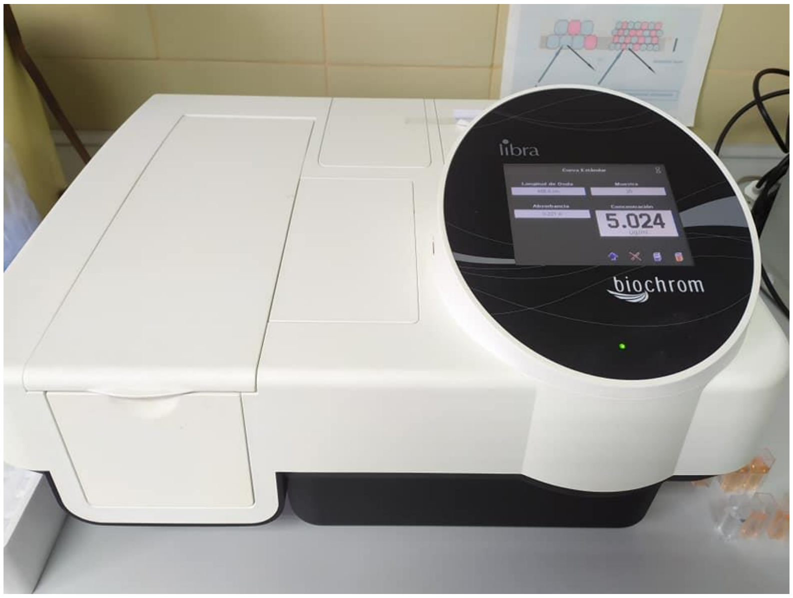


25. Equipo de espectroscopia de fluorescencia de rayos X por dispersión de energía (ED-XRF), en el Instituto de Geología Aplicada (IGeA), Almadén, España.



26. Equipo de espectroscopía de absorción atómica Zeeman con modulación de polarización de luz de alta frecuencia (ZAAS HFM) para la determinación de mercurio total, en el IGeA.

27. Equipo de espectroscopía de absorción atómica de alta resolución (HR-AAS), en la Escuela Técnica Superior de Ingenieros Agrónomos de Ciudad Real, España.



28. Espectrofotómetro UV visible en el IGeA.

# ANEXO II. PUBLICACIONES EN CONGRESOS

**Comunicación presentada en el “European Geosciences Union General Assembly 2021, Viena (Austria), abril de 2021**

EGU21-8236
https://doi.org/10.5194/egusphere-egu21-8236
EGU General Assembly 2021

# Risks associated with the presence of cyanide in waste materials in an abandoned gold mine, Panama

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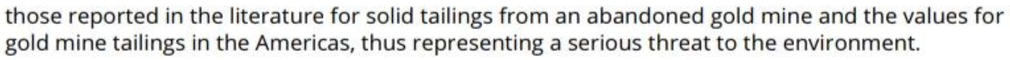
The inadequate treatment of waste materials in mine tailings, the closure stage not carried out correctly, carries risks due to the residues of potentially toxic elements (PTEs) that it may contain. In Panama, environmental regulations are recent, and even so the regulations are not strictly enforced, leaving a problem for the adjacent communities. Such is the case of the Remance Gold Mine, in Veraguas, Panama; this area has been exploited intermittently for over a hundred years, by different companies; the last period of exploitation was between 1989 and 1999, through a cyanidation process to extract the precious metal. Currently three tailing dams with mining waste are exposed to climatic conditions such as rain and wind, in addition to this, within the mine area and its surroundings live peasants who carry out subsistence activities such as agriculture and livestock. The purpose of this study was to evaluate the remaining potentially toxic elements and the persistence of cyanide in the tailings, and whether the remaining quantity represents a risk to human health and the environment, according to current environmental regulations in Panama and America. For this purpose, samples have been taken from the tailings and adjacent areas that could be directly related to the cyanidation process, geochemical analysis such as pH, CEC, conductivity, organic matter, potentially toxic elements and total cyanide have been carried out. The most concerning aspects of the results obtained here have been the contents of Ba (between 55 and 610 mg $kg^{-1}$), Zn (between 12 and 153 mg $kg^{-1}$), Sb (between 0.6 and 25.5 mg $kg^{-1}$) and Hg (between 0.1 and 3.2 mg $kg^{-1}$), which, according to the criteria of land use quality standards in Panama and American countries, correspond to values above the permissible limits for agricultural and residential land use. Meanwhile the levels of As (between 17.3 and 5030 mg $kg^{-1}$) and Cu (between 5.4 and 403 mg $kg^{-1}$) are higher than the legally established values for industrial land use. Far more significant are the values for total cyanide (between 1.4 and 518 mg $kg^{-1}$), revealing the persistence of this chemical over time. These cyanide values are far higher than



those reported in the literature for solid tailings from an abandoned gold mine and the values for gold mine tailings in the Americas, thus representing a serious threat to the environment.

## Comunicación presentada en la II Jornada de Jóvenes Investigadores de la Sociedad Española de Mineralogía SEM/SEM-CAT, Universidad Autónoma de Barcelona (España), marzo de 2021

Macla nº 25. 2021 • Revista de la Sociedad Española de Mineralogía 36

# Riesgos ambientales asociados a la gestión inadecuada de residuos mineros en una explotación minera de oro, Remance, Panamá

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**Palabras Clave:** Relaves, Elementos potencialmente tóxicos (EPT), cianuro total, mina de oro. **Key Words:** Tailings, Potentially toxic elements (PTEs), Total cyanide, Gold mine.

## INTRODUCCIÓN

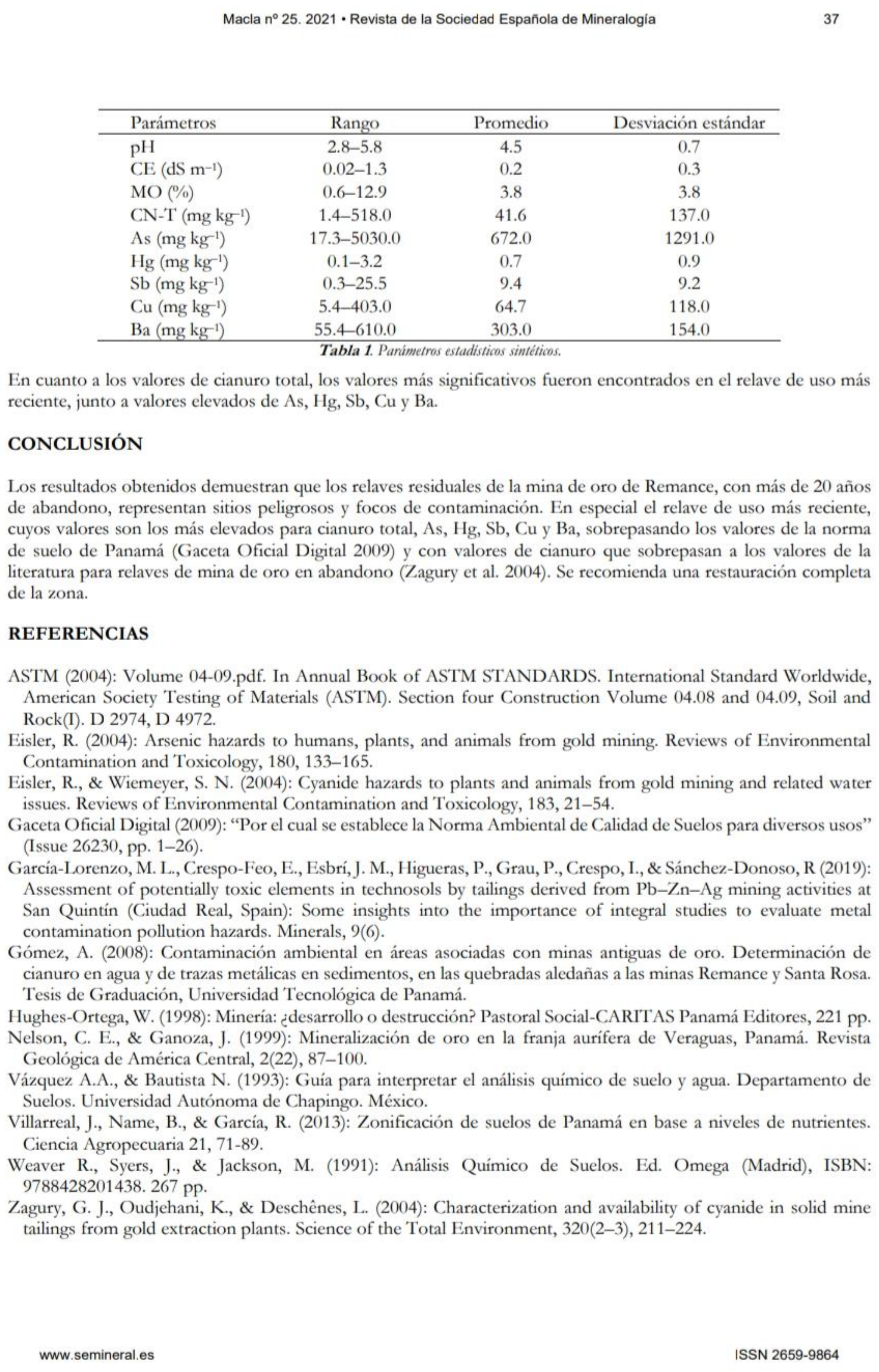
La minería es una actividad muy importante y necesaria para la sociedad, que debe ser desarrollada de manera responsable, ya que de no tener los cuidados necesarios sus residuos pueden ser focos latentes de contaminación al medio ambiente (García-Lorenzo et al. 2019). En Panamá la legislación ambiental es relativamente reciente (Gaceta Oficial Digital 2009), incumpliéndose en la mayoría de los casos la etapa de cierre. La mina de oro de Remance ha sido explotada por más de cien años de manera intermitente, siendo el periodo más reciente desde 1989 a 1999, por la empresa Minera Remance S.A (Nelson y Ganoza 1999), la cual dejó tres acumulaciones de relaves expuestas a condiciones ambientales de meteorización. La compañía recibió múltiples acusaciones por los moradores locales de contaminar los cuerpos de aguas aledaños (Hughes-Ortega 1998). La empresa empleaba el proceso de cianuración para la extracción del preciado metal (Gómez 2008). El cianuro es un compuesto tóxico que, de no ser tratado adecuadamente, puede representar graves problemas para el medio ambiente, debido a su persistencia y efectos nocivos a la salud (Eisler y Wiemeyer 2004), sumado a la presencia de otros elementos potencialmente tóxicos (EPTs) presentes en los residuos mineros (Eisler 2004). El objetivo de este estudio es conocer los riesgos ambientales asociados a la gestión inadecuada de los residuos mineros en la mina de Remance, Panamá.

## MÉTODOS

Se tomaron un total de 13 muestras, incluyendo los relaves mineros y las zonas adyacentes relacionadas a la actividad minera, para realizar análisis de laboratorio y conocer su composición geoquímica. Se realizaron análisis de pH y conductividad con el medidor multiparamétrico de mesa Orion Versa Star Pro (en una suspensión 1:5 p/v) (ASTM D 4972), de la materia orgánica por pérdida de peso a 455°C (ASTM D 2974) (ASTM 2004), y de la capacidad de intercambio catiónico por el método potenciométrico (Weaver et al. 1991). Las muestras también se enviaron a Activations Laboratories Ltd. en Canadá para realizar los ensayos de cianuro total (analizado a través del Analizador de flujo segmentado SAN Plus), y los elementos potencialmente tóxicos a través de espectrometría de masas de plasma de acoplamiento inductivo (ICP-MS).

## RESULTADOS Y DISCUSIÓN

Los resultados estadísticos sintéticos son presentados en la tabla 1. Los valores de pH se encuentran entre fuerte a débilmente ácido; según Villarreal et al (2013) los suelos de la República de Panamá son predominantemente ácidos debido al clima lluvioso. Los valores de conductividad eléctrica corresponden a suelos no salinos a moderadamente salinos (Vázquez y Bautista 1993). El contenido de materia orgánica más bajo fue encontrado en los relaves.



| Parámetros | Rango | Promedio | Desviación estándar |
|---|---|---|---|
| pH | 2.8–5.8 | 4.5 | 0.7 |
| CE (dS m⁻¹) | 0.02–1.3 | 0.2 | 0.3 |
| MO (%) | 0.6–12.9 | 3.8 | 3.8 |
| CN-T (mg kg⁻¹) | 1.4–518.0 | 41.6 | 137.0 |
| As (mg kg⁻¹) | 17.3–5030.0 | 672.0 | 1291.0 |
| Hg (mg kg⁻¹) | 0.1–3.2 | 0.7 | 0.9 |
| Sb (mg kg⁻¹) | 0.3–25.5 | 9.4 | 9.2 |
| Cu (mg kg⁻¹) | 5.4–403.0 | 64.7 | 118.0 |
| Ba (mg kg⁻¹) | 55.4–610.0 | 303.0 | 154.0 |

***Tabla 1****. Parámetros estadísticos sintéticos.*

En cuanto a los valores de cianuro total, los valores más significativos fueron encontrados en el relave de uso más reciente, junto a valores elevados de As, Hg, Sb, Cu y Ba.

## CONCLUSIÓN

Los resultados obtenidos demuestran que los relaves residuales de la mina de oro de Remance, con más de 20 años de abandono, representan sitios peligrosos y focos de contaminación. En especial el relave de uso más reciente, cuyos valores son los más elevados para cianuro total, As, Hg, Sb, Cu y Ba, sobrepasando los valores de la norma de suelo de Panamá (Gaceta Oficial Digital 2009) y con valores de cianuro que sobrepasan a los valores de la literatura para relaves de mina de oro en abandono (Zagury et al. 2004). Se recomienda una restauración completa de la zona.

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# ANEXO III. OTRAS PUBLICACIONES

Environmental Earth Sciences (2021) 80:176
https://doi.org/10.1007/s12665-021-09497-7

ORIGINAL ARTICLE

# Hydrochemistry of groundwater from Tocumen sector, Panamá city: an assessment of its possible usage during emergency events

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Received: 23 March 2020 / Accepted: 10 February 2021

**Abstract**
In Panama City, the water supply sources for the population come mainly from surface waters, but in times of drought and extreme natural phenomena, the need to resort to underground sources is explored. This paper concerns an exploratory investigation with the aim of assessing the quality of groundwater in the southeastern part of the Province of Panama and to determine its possible use as drinking water during extreme natural phenomena. Monthly monitoring over a period of 15 months was carried out. The study included the sampling and analysis of groundwater by different physic-chemical, hydrochemical and biological parameters. The results showed that most of the parameters in the analysed groundwater conformed to the Panamanian drinking water norm and the water potability diagram, this is a convenient source of raw water for purification. As for other uses for this water source, it should be used with caution since it represents a medium risk of soil salinization for irrigation water; and it is a moderately hard water for industrial uses.

**Keywords** Groundwater · Rainwater · Hydrochemical study · Water security · Panama

## Introduction

The achievement of universal water security and availability is one of the main agenda items of the UN Sustainable Development Goals (Savenije and Van der Zaag 2008). To achieve the goal of water security, particularly in rapidly expanding cities, the identification of safe and sustainable water resources is an absolute necessity (Saraswat et al. 2019).

Groundwater is the major source of water in most parts of the world. The presence certain ions at concentrations that are too high or too low is a major concern, as these ions make the groundwater unsuitable for various purposes (Brindha and Elango 2011). The volume of surface and groundwater in Panama is large due to its Tropical climate, but the quality must be studied to verify its potential use as resource.

In Panama, rivers and reservoirs are the main sources for drinking water. Although the water resource is abundant, there are problems with the distribution and the means of capture since the degree of deterioration of the surface waters is increasing due to the demographic pressure and the deficient wastewater sanitation systems. A viable way to alleviate this problem is water harvesting in those communities that have abundant rainfall – as in other tropical countries such as Australia and Africa (Nduka & Orisakwe 2010; Chubaka et al. 2018).

In Panama it is necessary to identify other sources of water, such as groundwater and rainwater harvesting, to ensure the supply of drinking water to the population, particularly in the face of extreme weather events. Also, as occurred in other parts of the world, the effect of climate change and the pressure on groundwater for irrigation produces significant reductions in this resource (Buvaneshwari et al. 2017; Niu et al. 2017). As a consequence, it is necessary to have a knowledge of water dynamics (El-Sayed et al.

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2018), to study water quality (Chidya et al. 2015; Tubau et al. 2017), to evaluate the possibilities for use and required treatment, and to identify possible risks related to its uncontrolled usage (Rojas Fabro et al. 2015).

The quality of groundwater is significantly influenced by the local and regional geological context (Ochoa-González et al. 2015; Taheri et al. 2017), by anthropogenic activities (Abiye et al. 2018; Niu et al. 2017; Vadiati et al. 2016; Zheng et al. 2017), due to the infiltration of domestic and industrial waste, and by atmospheric conditions and precipitation (AlSuhaimi et al. 2016; Appelo and Postma 2004). Therefore, water quality is subject to constant daily, seasonal and climatic changes, which makes it necessary to regularly monitor the physicochemical and microbiological parameters of groundwater (Vadiati et al. 2016; Zheng et al. 2017).

In this context, the main objective of this study was to characterize the physicochemical and microbiological quality of groundwater in the Panama area and its potential uses for irrigation and for domestic or human consumption, particularly for use in emergencies. Thus, this study was focused on providing valuable information on the quality of groundwater and rainwater in the southeastern area of Panama City because this resource may be important in future climate scenarios in the region. Currently this aspect is poorly studied and exploited. The results of this work can be applied to other regions that are affected by similar problems in a global change scenario.

## Material and methods

### Study area

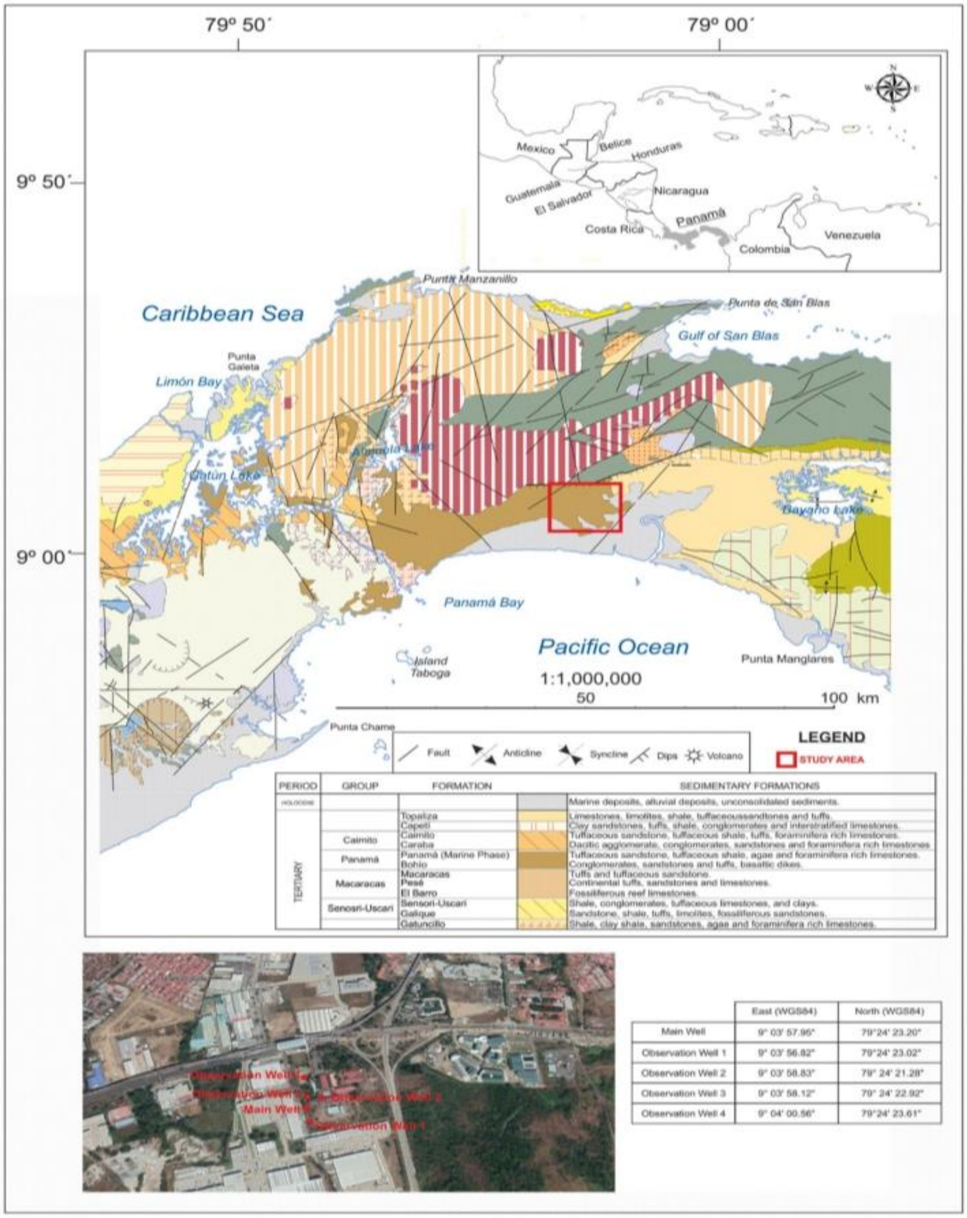
Panama is a narrow territorial belt in which the Central American Isthmus ends. It has a mountain range that divides the country into two very defined zones: to the north it extends the Caribbean slope and to the south the Pacific slope (Guardia 1988). The study area is located on the Pacific slope, in the southeastern part of Panama City, within the Tocumen Research Campus of the Technological University of Panama, and within an area of 14 067, 56 m$^2$, with geographic limits: 9° 04′ 01.20″ N, 79° 24′ 24.69″ W; 9° 03′ 56.34″ N, 79° 24′ 23.29″ W; 9° 03′ 57.09″ N, 79° 24′ 20.45″ W and 9° 04′ 01.92″ N, 79° 24′ 21.82″ W. The area belongs to the low regions and coastal plains, which correspond to depressed zones constituted by marine sedimentary rocks. The geological map of the study area is shown in Fig. 1. The area is located within the Group and Formation Panama (Marine Phase), of Tertiary age, and consists mainly of tuffaceous sandstone, tuffaceous shale, and algae- and foraminifera-rich limestones (Guardia 2018). According to a geotechnical study of an observation well in the study area, the soil corresponds to clayey gravel with sand and the substrate, to healthy sediments with discontinuities spaced at different angles that show the circulation of flows (Arrocha 2015). The aquifer is semi-confined (Vega 2004); in a pumping test at constant flow for 72 h carried out in October 2015, it was determined that with a flow of 20 gallons per minute, 100% efficiency is obtained and the well stabilizes at 6.15 m (Alpirez et. al 2015). The hydraulic gradient is relatively low, with a value of $6.10\times10^{-4}$; taking into consideration that the area is flat and with little slope, the flow direction goes from south to north (Alpirez 2015). The climate directly influences the recharge of the aquifer, since it recharges during the rainy season, and the static level decreases with the dry season, in the absence of rain (González 2016).

The weather is tropical rainy with an annual rainfall greater than 1000 mm and during the year there are several dry months with rains of less than 60 mm. The average monthly temperature during the year is greater than 18 °C, which corresponds to the aforementioned climate. The average annual relative humidity is 79.2% (ETESA 2019), which is high and is consistent with the type of climate and its proximity to the sea. The location is an area of high evapotranspiration, i.e., between 1326 and 1343 mm, as a consequence of the annual temperate temperatures. On this Pacific slope, there is an extended and unique rainy season that begins between April and May and persists until November. There is also a dry season that is established between December and the end of April, with an almost total absence of rain (IGNTG 1988). The area is coastal and is highly influenced by human and industrial residential activity.

### Field sampling

The groundwater samples were taken from a single well, located at the geographical coordinates: 9°03′57.95″ N and 79°24′23.20″ W, which has an extraction pump; said sample was taken monthly from January 2014 to March 2015, it is the depth of the well is 24.00 m, with a water table of 2.40 m and an elevation of 18 m above sea level; on these basis, a total of 15 samples were taken. Two rainwater samples was taken near to the production well, in the months of October and December 2014, with a device to capture rainwater that was cleaned for this work. The sampling design, analytical procedures and quality controls for methods, such as blank, traceable reference materials to NIST and at least 10% analysis of duplicate samples, for duplicates the criteria is a difference of less than 5%, all based on the instructions of the Standard Methods for Examination of Water and Wastewater 22nd Edition 2012 (American Chemical Society 2012) and those established by the laboratory.

The samples were taken in polyethylene containers and preserved at 4 °C for physicochemical tests; the portion of the sample for metals was also preserved with 50% $HNO_3$



| PERIOD | GROUP | FORMATION | | SEDIMENTARY FORMATIONS |
|---|---|---|---|---|
| HOLOCENE | | | ■ | Marine deposits, alluvial deposits, unconsolidated sediments. |
| TERTIARY | | Topaliza | ■ | Limestones, limolites, shale, tuffaceoussandtones and tuffs. |
| | | Capeti | ▥ | Clay sandstones, tuffs, shale, conglomerates and interstratified limestones. |
| | Caimito | Caimito | ▨ | Tuffaceous sandstone, tuffaceous shale, tuffs, foraminifera rich limestones. |
| | | Caraba | | Dacitic agglomerate, conglomerates, sandstones and foraminifera rich limestones |
| | Panamá | Panamá (Marine Phase) | ■ | Tuffaceous sandstone, tuffaceous shale, agae and foraminifera rich limestones. |
| | | Bohio | | Conglomerates, sandstones and tuffs, basaltic dikes. |
| | Macaracas | Macaracas | ■ | Tuffs and tuffaceous sandstone. |
| | | Pesé | | Continental tuffs, sandstones and limestones. |
| | | El Barro | | Fossiliferous reef limestones. |
| | Senosri-Uscari | Sensori-Uscari | ▨ | Shale, conglomerates, tuffaceous limestones, and clays. |
| | | Galique | | Sandstone, shale, tuffs, limolites, fossiliferous sandstones. |
| | | Gatuncillo | ▩ | Shale, clay shale, sandstones, agae and foraminifera rich limestones. |

| | East (WGS84) | North (WGS84) |
|---|---|---|
| Main Well | 9° 03' 57.95" | 79°24' 23.20" |
| Observation Well 1 | 9° 03' 56.82" | 79°24' 23.02" |
| Observation Well 2 | 9° 03' 58.83" | 79° 24' 21.28" |
| Observation Well 3 | 9° 03' 58.12" | 79° 24' 22.92" |
| Observation Well 4 | 9° 04' 00.56" | 79°24' 23.61" |

**Fig. 1** Geological map of the study area ( adapted from IGNTG 2018)

and filtered; the sample for microbiology tests was taken in sterile containers and preserved at 4 °C. Determinations of nitrates (SM 4500 $NO_3^-$ B), phosphates (SM 4500-P D), chlorides (4500-$Cl^-$ B), sulfates (SM 4500-$SO_4^{2-}$E), bicarbonates (SM 2320 B), total suspended solids (SM 2540-D), total solids (SM 2540 B), total dissolved solids (SM 2540-C), turbidity (SM 2130 B), majority cations (iron, calcium, magnesium, manganese, sodium and potassium)

(SM 3111B); as well as the microbiological assays of total coliforms and E. coli (Colilert defined enzyme–substrate method, SM 9223 B), were carried out in the Laboratory of Industrial Analysis and Environmental Sciences (LABAICA) at the Experimental Center of Engineering (CEI), Technological University of Panama (UTP); the laboratory is accredited to the National Accreditation Council of Panama (CNA). As quality control for samples, the percentage (%) error in the ion balance of samples was calculated, and was lower than 5%, which confirms that the results obtained in the laboratory are very reliable (Dieng et al. 2017).

The field parameters, including reactivity (pH), contents in salts (estimated by electrical conductivity, EC) and temperature were determined with multiparameter probes (YSI 556 MPS and HANNA HI991301); the major cations iron, calcium, magnesium, manganese, sodium and potassium were determined by Atomic Absorption (Shimadzu AA-7000) in triplicate; the major anions nitrate, phosphate and sulfate were determined by visible ultraviolet spectrophotometry (Shimadzu UV-1800); chloride and bicarbonate were determined by titration; turbidity was evaluated with a turbidimeter in duplicate (HACH 2100AN) and suspended solids, total solids, and total dissolved solids were measured by gravimetry (JP Selecta 2,000,201 furnace). The microbiological assays of total coliforms and E. coli were carried out by the Colilert defined enzyme–substrate method, 9223 B Standard Methods for Examination of Water and Wastewater 22nd Edition 2012 (American Chemical Society 2012).

The results were interpreted by assessing diagrams (Ghesquière et al. 2015) such as Piper, Stiff, Schoeller–Berkaloff logarithmic diagram (Chihi et al. 2015), water classification diagram for irrigation, potability diagram and water chemistry. The results were compared with the Panama standard for water and drinking water and thus the water was classified to determine its possible uses.

## Results

### Hydrochemical characteristics

The results of the physicochemical parameters for groundwater and rainwater are presented in Table 1 and the major anions and cations are shown in Table 2.

The temperature of the groundwater remained constant throughout the year and it was in the range 28.1–30.1 °C. The pH varied between 6.64 and 7.70 in the dry season and from 6.50 to 7.36 during the rainy season. The slight decrease in the groundwater pH values during the rainy season is associated with the recharge of the aquifer with more acidic rainwater (pH range between 4.8 and 5.2) when compared with the stored groundwater. The electric conductivity (EC) values ranged from 686 to 760 µS/cm for the dry season and from 720 to 836 µS/cm in the rainy season; these values reflect the estimated contents of salts, which is also related with the total dissolved solids (TDS), ranging between 384 and 515 mg/L (Table 1). The slight increase in the conductivity during the rainy season is consistent with the pH behaviour, thus supporting the idea that the slight acidity of the rain solubilizes anions such as $Cl^-$ and

**Table 1** Results of the physicochemical analysis for samples of groundwater and rainwater in a single point

| Month | T (°C) | EC (µS/cm) | pH | TDS (mg/L) | TSS (mg/L) | TS (mg/L) | Turb (NTU) |
|---|---|---|---|---|---|---|---|
| January 2014 | 29.1 | 686 | 6.64 | 391 | < 1 | 428 | 0.14 |
| February 2014 | 29.1 | 710 | 7.30 | 389 | < 1 | 433 | 0.26 |
| March 2014 | 30.1 | 730 | 7.40 | 446 | < 1 | 464 | 0.18 |
| April 2014 | 29.1 | 700 | 6.90 | 384 | < 1 | 484 | 0.20 |
| May 2014 | 29.1 | 750 | 6.90 | 465 | < 1 | 552 | < 0.10 |
| June 2014 | 30.1 | 740 | 6.90 | 480 | 1 | 488 | 0.40 |
| July 2014 | 29.1 | 836 | 7.00 | 444 | < 1 | 434 | 0.20 |
| August 2014 | 28.9 | 766 | 7.36 | 515 | < 1 | 518 | 0.44 |
| September 2014 | 30.0 | 720 | 6.50 | 410 | 2 | 435 | < 0.10 |
| October 2014 | 29.1 | 750 | 6.60 | 475 | 1 | 486 | < 0.10 |
| November 2014 | 28.1 | 760 | 6.70 | 473 | 1 | 480 | 0.16 |
| December 2014 | 29.1 | 760 | 6.80 | 494 | < 1 | 499 | 0.24 |
| January 2015 | 28.1 | 729 | 7.50 | 445 | < 1 | 477 | 0.25 |
| February 2015 | 28.5 | 708 | 7.70 | 431 | < 1 | 530 | 0.38 |
| March 2015 | 30.0 | 720 | 6.70 | 474 | < 1 | 472 | 0.28 |
| October 2014 Rain | 24.1 | 16.2 | 5.20 | 14 | 1 | 26 | < 0.10 |
| December 2014 Rain | 25.1 | 16.5 | 4.80 | 16 | 3 | 27 | < 0.10 |

*EC* Electric conductivity, *TDS* total dissolved solids/estimated content in salts, *TSS* total suspended solids, *TS* total solids, *Turb* turbidity

**Table 2** Results for major anions and cations in groundwater and rainwater

| Month | $PO_4^{3-}$-P (mg/L) | $NO_3^-$ (mg/L) N-NO3 | $SO_4^{2-}$ (mg/L) | $Cl^-$ (mg/L) | $HCO_3^-$ (mg/L $CaCO_3$) | $Ca^{2+}$ (mg/L) | $Mg^{2+}$ (mg/L) | $Na^+$ (mg/L) | $K^+$ (mg/L) | $Fe^{2+}$ (mg/L) | $Mn^{2+}$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| January 2014 | <0.03 | 0.12 | 68.31 | 15.60 | NR | 22.40 | 9.80 | 48.63 | 0.66 | <0.02 | <0.01 |
| February 2014 | <0.03 | <0.01 | 64.85 | 13.90 | NR | 18.60 | 8.50 | 80.70 | 0.47 | <0.02 | <0.01 |
| March 2014 | <0.03 | 0.02 | 77.15 | 11.20 | NR | 16.00 | 9.70 | 74.00 | 0.64 | <0.02 | <0.01 |
| April 2014 | <0.03 | 0.06 | 77.87 | 14.45 | 232.57 | 16.40 | 11.70 | 74.00 | 0.57 | <0.02 | <0.01 |
| May 2014 | <0.03 | NR | 127.30 | 18.42 | 225.00 | NR | | | | | |
| June 2014 | <0.03 | 0.04 | 106.60 | 19.62 | 215.40 | | | | | | |
| July 2014 | <0.03 | 0.06 | 89.60 | 20.54 | 234.44 | | | | | | |
| August 2014 | <0.03 | 0.05 | 91.70 | 22.37 | 240.40 | | | | | | |
| September 2014 | <0.03 | 0.10 | 78.54 | 16.30 | 266.49 | 57.21 | 7.65 | 103.10 | 0.8 | <0.02 | <0.01 |
| October 2014 | <0.03 | 0.17 | 89.30 | 21.03 | 268.50 | 55.94 | 7.04 | 85.08 | 0.79 | <0.02 | <0.01 |
| November 2014 | <0.03 | 0.02 | 101.25 | 21.08 | 253.50 | 58.97 | 6.78 | 77.22 | 0.79 | <0.02 | <0.01 |
| December 2014 | <0.03 | 0.04 | 94.58 | 21.67 | 256.04 | 47.83 | 5.03 | 97.74 | 0.73 | <0.02 | <0.01 |
| January 2015 | <0.03 | 0.08 | 73.64 | 16.34 | 278.85 | 47.02 | 5.71 | 85.37 | 0.76 | <0.02 | <0.01 |
| February 2015 | <0.03 | 0.02 | 72.73 | 15.65 | 270.61 | 43.04 | 5.40 | 88.88 | 0.82 | <0.02 | <0.01 |
| March 2015 | <0.03 | 0.07 | 90.91 | 15.65 | 256.03 | 58.30 | 7.73 | 81.86 | 0.83 | <0.02 | <0.01 |
| October 2014 Rain | <0.03 | 0.06 | <1.00 | 6.40 | 0.20 | <0.03 | <0.0005 | 0.14 | 1.33 | <0.02 | <0.01 |
| December 2014 Rain | <0.03 | 0.25 | 1.38 | 3.47 | 1.70 | <0.03 | <0.0005 | 1.64 | 0.27 | <0.02 | <0.01 |

*NR* not recorded

$SO_4^{2-}$ and leads to an increase in the conductivity of the waters. According to the World Health Organization (Who 2011), specific conductivity values of less than 900 µS/cm for groundwater correspond to fresh water.

### Microbiological characteristics

The results of the microbiological analyses for groundwater are presented in Table 3.

The values for the groundwater are variable in total coliforms. In the dry season, the values range from 3 to 2,909 NMP/100 mL and in the rainy season from < 1 to 411 NMP/100 mL. The values for E. coli in the dry season range from < 1 to 12.4 MPN/100 mL and in the rainy season from < 1 to 19 MPN/100 mL. Comparison of the two sets of microbiological data shows that E. coli was much lower than total coliforms in the groundwater analysed.

## Discussion

Evaluation of the physicochemical characteristics of groundwater using the relative order of abundance in meq/L (Dieng et al. 2017; Sako et al. 2016) shows that the major cations analysed are $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and for the anions $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$. This order was consistent throughout the sampling campaign in both the dry and rainy seasons.

In the case of rainwater, the values for the cations are below the limit of detection for $Ca^{2+}$, $Mg^{2+}$, $Fe^{2+}$ and $Mn^{2+}$, with $Na^+ > K^+$ detected in meq/L. For anions, the order of abundance in meq/L is $Cl^- > SO_4^{2-} > HCO_3^- > NO_3^-$. As a general rule, turbidity in rainwater is caused by collected atmospheric solid substances that can be either inorganic or organic (Ratnoji and Singh 2014; Sillanpää et al. 2018). The turbidity values were less than 1 NTU and this shows that the rainwater and groundwater had not been physically polluted according to the technical regulation for drinking water of Panamá (Direccion General de Normas y Tecnología Industrial 1999). This finding also supports the low influence of anthropic sources on the atmosphere in the case of rainwater.

**Table 3** Results of the microbiological analyses for groundwater

| No | Month | Total C. (NMP/100 mL) | E. coli (NMP/100 mL) |
|---|---|---|---|
| 1 | January 2014 | > 2005 | 12 |
| 2 | February 2014 | 5 | < 1 |
| 3 | March 2014 | 22 | < 1 |
| 4 | April 2014 | 10 | < 1 |
| 5 | May 2014 | 36 | 2 |
| 6 | June 2014 | 411 | 12 |
| 7 | July 2014 | < 1 | < 1 |
| 8 | August 2014 | 10 | < 10 |
| 9 | September 2014 | 517 | 10 |
| 10 | October 2014 | 15 | 1 |
| 11 | November 2014 | 200 | 19 |
| 12 | December 2014 | 48 | 5 |
| 13 | January 2015 | 3 | < 1 |
| 14 | February 2015 | 64 | < 1 |
| 15 | March 2015 | 2909 | 5 |

The diagrams proved to be very useful to interpret data, to classify the type of water and to identify possible uses (Custodio and Llamas 1976). The Piper diagram (Fig. 2) for groundwater during the sampling period corresponds to sodium bicarbonate-type, except in the month of November, when it corresponds to magnesium bicarbonate-type (Hernández-Antonio et al. 2017; Niu et al. 2017) but with close similarities to the sodium bicarbonate-type. Over the months, the major cations and anions varied in a parallel manner, thus indicating that simple exchange reactions occur in the water (Guo et al. 2017; Singh et al. 2017). The composition of the groundwater, in which the major anion is $HCO_3^-$ and the major cations are $Na^+$ and $Ca^{2+}$, is explained by the composition of the local soils and rocks with calcium carbonate content (González, 2016), which has been reported in other carbonate rock areas (AlSuhaimi et al. 2016; Guo et al. 2017; Zhang et al. 2018; Zheng et al. 2017). In coastal areas with these characteristics, there have been reports that describe cation exchange phenomena (Sako et al. 2016; Taheri et al. 2017; Zheng et al. 2017), where the substrate has high concentrations of $Na^+$ and, being in a medium

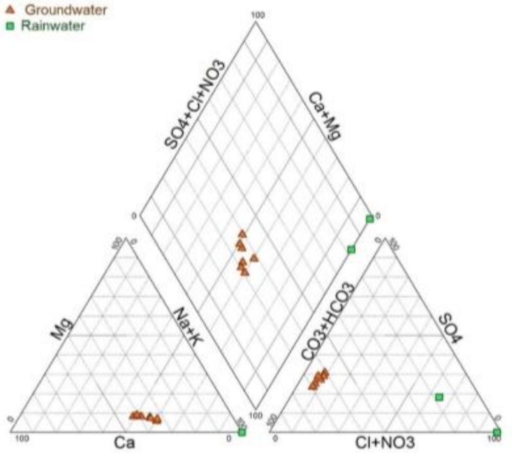


**Fig. 2** Comparative Piper diagrams showing the relative compositions of groundwater and rainwater

saturated with $Ca^{2+}$, $Na^+$ is released into the solution and $Ca^{2+}$ is trapped by the ground. Therefore, the high content of $HCO_3^-$ is associated with a high $Na^+$ content (Custodio and Llamas 1976; Niu et al. 2017; Ormachea Muñoz et al. 2016).

In the case of rainwater, the Piper diagram (Fig. 2) corresponds to a water with sodium and potassium chloride, which is consistent with the effect of marine aerosol, characteristic of coastal environment, as the main source of rainwater (Custodio and Llamas 1976).

On comparing the Piper diagrams for groundwater and rainwater (Fig. 1), it is evident that rainwater could be enriched in the cations $Ca^{2+}$, $Mg^{2+}$ and $Na^+$, and anions $Cl^-$, $SO_4^{2-}$ and $HCO_3^-$, due to its passage through the rocks for the infiltration effect. The order of filtration in clay-like membranes (Custodio and Llamas 1976) for anions from low to high delay is: $HCO_3^- > SO_4^{2-} > Cl^-$. This is the same order found in the groundwater under investigation and it is due to the nature of the local sedimentary rocks. The order of concentration for the cations is $Na^+ > Ca^{2+} > Mg^{2+}$ and this is also explained by the nature of the rocks being infiltrated and by their proximity to the coast.

The modified Stiff diagrams for both types of water (Fig. 3) allow one to appreciate month by month how the composition of the ions varies and that rainwater, which has very low concentration of ions, is enriched with $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, $SO_4^{2-}$ and $Cl^-$ when entering the aquifer.

The use of the diagram for the classification of water for irrigation, according to the U.S. Salinity Laboratory Staff for groundwater (Fig. 4) (Dhanasekarapandian et al. 2016; Selvakumar et al. 2017), is of great interest for assessing the possibility of agricultural use. All of the results are concentrated along the line for classifications C2 and C3, and they also fall within field S1. This implies that these waters are associated with a potential salinization risk for soils that is medium to high, with a risk of alkalization. These waters can be used for irrigation, but only on salt-tolerant crops with good drainage, and there is a need for soil washing processes to avoid changes in reactivity (Custodio and Llamas 1976). The low conductivity and ion concentrations of rainwater make it suitable for use for both agricultural and irrigation purposes according to the U.S. Salinity Laboratory Staff.

According to the water potability diagram (Zabala et al. 2016) (Fig. 5), groundwater appears to be suitable to obtain drinking water, i.e., it is acceptable as raw water for a purification process to bring it up to drinkable standards. For rainwater, the diagram (Fig. 5) indicates that it is appropriate for purification by pH adjustment alone, with an average value of 5 – a parameter that must be adjusted to neutrality (AlSuhaimi et al. 2016).

The average values for groundwater and rainwater (is referred for groundwater since September 2014 to March 2015, and for rainwater is referred the average value for

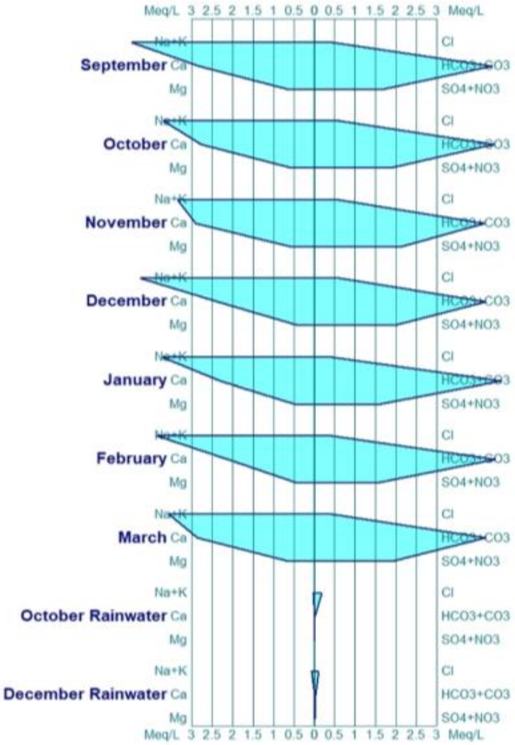


**Fig. 3** Comparative Stiff diagrams showing the relative compositions of groundwater and rainwater

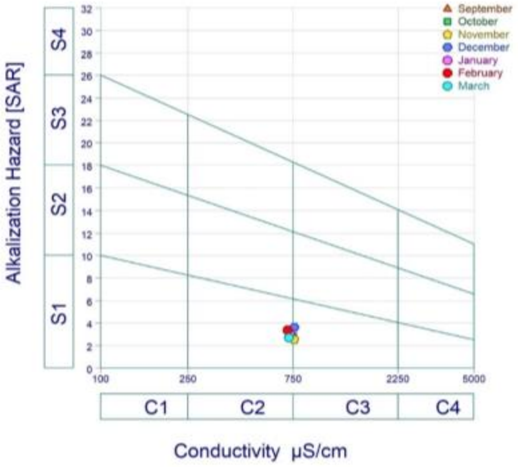


**Fig. 4** Classification diagram for irrigation waters and for groundwater in dry and rainy seasons

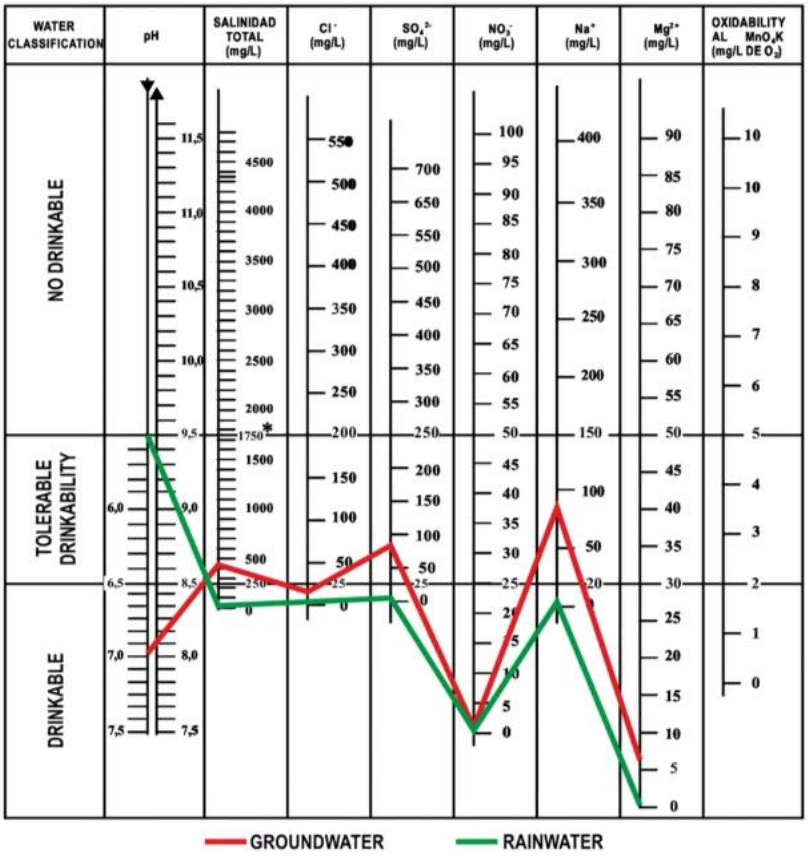


**Fig. 5** Water potability diagram for groundwater and rainwater

the October and December 2014) were compared with the guide values of the national Norm DGNTI-COPANIT 23–395-99 for drinking waters not distributed by pipelines (Ministerio de Comercio e Industrias 1999), which is similar to the World Health Organization standards (WHO 2011) (Table 4), as well as with values for reused water for irrigation, Norm DGNTI-COPANIT 24–99 (Ministerio de Comercio e Industrias 2000) for reused water (Table 5). The results for total coliforms and E. coli, which were used for comparison with faecal coliforms, do not fulfil the requirements for water not distributed by pipelines either in groundwater. Groundwater meets most of the physicochemical parameters except for alkalinity and hardness. Rainwater complies with physicochemical parameters except for pH. In terms of hardness, the groundwater was very hard, with 158.19 mg/L total hardness as $CaCO_3$; while rainwater corresponds to soft water, in the month of October (month of greatest rainfall) and December (transition from rainy to dry season).

With respect to the regulations for reused water, for both waters the parameters tested meet the required standards for the purposes of crop irrigation, aquaculture in the culture of fish and aquatic plants, urban uses in the irrigation of green areas, and industrial use for boiler cooling. It would be necessary to adjust the pH of rainwater.

## Conclusions

The results of this study concern the sustainability of groundwater and rainwater as a raw water supply for different purposes in relation to international standards. The quality of both groundwater and rainwater in Panama City seem to be suitable for use in different applications during periods of drought. The hydrogeochemical values and the microbiological quality of the water allow its direct use for large consumers such as for irrigation and aquaculture uses. However, for human supply both of these waters

**Table 4** Comparison of values for groundwater and rainwater with standards for drinking water

| Parameters | Norm DGNTI-COPANIT 23–395-99 Not distributed by pipes | Groundwater | Fulfilment | Rainwater | Fulfilment |
|---|---|---|---|---|---|
| Faecal coliform bacteria No. colonies/100 mL | 0 | <1 to 19 (NMP/100 mL) | Not fulfil | – | – |
| Total coliform bacteria No. colonies/100 mL | 10 | 3 to 2,909 | Not fulfil | – | – |
| Turbidity NTU | 1.0 | 0.23 | Fulfil | 0.8 | Fulfil |
| pH | 6.5–8.5 | 6.5–7.7 | Fulfil | 4.8–5.2 | Not fulfil |
| Alkalinity as $CaCO_3$ mg/L | 120.00 | 264.29 | Not fulfil | 0.95 | Fulfil |
| Chloride mg/L | 250.00 | 18.25 | Fulfil | 4.94 | Fulfil |
| Iron mg/L | 0.30 | <0.02 | Fulfil | <0.02 | Fulfil |
| Manganese mg/L | 0.1 | <0.01 | Fulfil | <0.01 | Fulfil |
| Nitrate mg/L | 10.00 | 0.07 | Fulfil | 0.16 | Fulfil |
| Sodium mg/L | 200.00 | 88.46 | Fulfil | 0.89 | Fulfil |
| Total dissolved solids mg/L | 500.00 | 457.43 | Fulfil | 15.00 | Fulfil |
| Sulfates mg/L | 250.00 | 85.85 | Fulfil | 1.38 | Fulfil |
| Total hardness as $CaCO_3$ mg/L | 100.00 | 158.19 | Not fulfil | 0 | Fulfil |

**Table 5** Comparison of values for groundwater and rainwater with the norms for reuse of water treated for irrigation

| Parameters | Norm DGNTI-COPANIT 24–99 Reused water | Groundwater | Fulfilment | Rainwater | Fulfilment |
|---|---|---|---|---|---|
| Chloride mg/L | 200.00 | 18.25 | Fulfil | 4.94 | Fulfil |
| Iron mg/L | 5.000 | <0.02 | Fulfil | <0.02 | Fulfil |
| Manganese mg/L | 0.200 | <0.01 | Fulfil | <0.01 | Fulfil |
| Sulfate mg/L | 350.00 | 85.85 | Fulfil | 1.38 | Fulfil |
| Electric conductivity EC dS/m | 3.000 | 0.735 | Fulfil | 0.015 | Fulfil |

require simple treatments to achieve the necessary quality, which makes them a very interesting alternative resource during periods of drought.

This study provides a first approach to the potential uses of these waters in terms of their quality. Future studies should be aimed at gaining an in-depth knowledge of their characteristics if there are potential contaminants not evaluated in this work, such as heavy metals, and the volume of resources available to evaluate the potential of application of both types of water in this area.

**Acknowledgments** The authors thank the Technological University of Panama (UTP) and its Research Centers that provided collaboration for this research work. Thanks are due to the Center for Hydraulic and Hydrotechnical Research (CIHH) and the Experimental Center for Engineering (CEI), and within the latter the Laboratory of Industrial Analysis and Environmental Sciences (LABAICA), Ing. David Vega and Dr. Cecilio Hernández. Thanks are also due to Dr. Freddy Ortiz of USFDA/EPA for all his collaboration, and Neil Thompson (PhD in Chemistry, Scientific English) for the revision of the English style of the manuscript. To the National Secretary of Science and Technology (SENACYT) and the Institute for the Training and Use of Human Resources (IFARHU) of Panama, for their help for research.

**Authors contributions** The paper was written by Ana González, Miguel Vargas Lombardo, Pablo Higueras, Francisco Jesús García Navarro, Efrén García Ordiales and Raimundo Jimenez Ballesta. Ana González performed the field and laboratory work.

**Funding** This study was funded by the National Secretary of Science and Technology (SENACYT) and the Institute for the Training and Use of Human Resources (IFARHU) of Panama (270–2019-109); and Fondos para Grupos de Investigación UCLM (2019-GRIN-27011).

## Compliance with ethical standards

**Conflict of interest** The authors declare no conflict of interest.

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**Artículo original, sometido a la revista Environmental Earth Sciences, bajo revisión menor, noviembre 2021.**

## CHARACTERIZATION OF THE SOIL AND ROCK HOSTING OF AN AQUIFER WITH POSSIBLE USES FOR DRINKING WATER AND IRRIGATION IN SE PANAMA CITY, USING GEOTECHNICAL, GEOPHYSICAL AND GEOCHEMICAL PARAMETERS

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### Abstract

The supply of water to populations is a basic need that has been threatened more frequently in recent years due to climate change, which renders seeking other sources of water essential. The hydrochemistry of the groundwater of the aquifer located in the UTP Tocumen was characterized in a previous research work to determine its possible use as a source of drinking water and irrigation water. The objective of this study is to characterize the soil and rock hosting the aquifer to acquire more information about them with a view to possibly exploit an alternative source of drinking water. To this end, a 10 meter-depth survey was conducted to obtain soil and rock samples from the area, and to characterize geotechnical and geochemical parameters. A 2D electrical resistivity tomography was used to create a lithological model of the aquifer and to correlate the data. Soil is residual of the technosol type, considered permeable with a transmissivity level that favors rainwater infiltration, followed by the soil-rock interface where rock is weathered. It´s followed by a sedimentary rock corresponding to marly siltstones with a certain degree of tectonic fractures that allow water infiltration and its accumulation in the rocks, constituting the aquifer. In the 2D electrical resistivity, two water accumulations were identified: a superficial and a deep one. There was a good correlation between the aquifer water's chemistry and the rock geochemistry.

**Keywords:** aquifer, marlstone, electrical resistivity, groundwater, Tocumen.

## 1. Introduction

Water is a prime resource needed for human consumption, agriculture, livestock and industry that comes in increasingly short supply. Tropical countries with high to very high pluviosity traditionally have an adequate amount of rainfall. However, two aspects typically affect this situation: first, irregular rain distribution, with heavy storm episodes that are difficult to control in water storage terms; second, lack of adequate infrastructure to collect and store the enormous amounts of water deposited during such events. This is the case of Panama City, the capital of the Republic of Panama.

Panama City, with a population of 880691 (Contraloría General de la República de Panamá 2010), is located on the Pacific Ocean coast. According to the Köppen climate classification, Panama City has a tropical savanna climate (Köppen Aw), which is slightly drier than a tropical monsoon climate. The average annual precipitation is 1900 mm (74.8 in). The wet season is from May to December, and the dry season from January to April (Dirección de Hidrometeorología de ETESA 2007). Throughout the year, temperatures average around 27°C (81°F) (https://web.archive.org/web/20080630020659/http:/wwis.inm.es/076/c01221.htm).

Furthermore, flooding events like those which occurred in December 2010 (the so-called “Storm of the Purisima”), lead to torrential rains that increase the turbidity of reservoir lakes and disable the drinking water production in water treatment plants, and sometimes occur in this region. It took almost 3 months to solve this problem and, thus, left Panama City without this vital liquid (La Estrella de Panama 2012). Moreover, climate change has caused drought periods for some years that have threatened the water supply and the transit of ships through the Panama Canal (El País 2020; Diario Las Américas 2020). In light of this, groundwater could be an appropriate alternative to water supply during such catastrophic events, or during possible drought periods.

The present study intends to obtain a better understanding of the nature of the groundwater stored in the Tocumen sector, located to the ENE of the town center (González-Valoys et al. 2021). We extended our previous research work to study the host soil and rocks to understand the relation between water and its hosts based on the site’s geophysical properties (electric resistivity), and the geotechnical parameters of soil and rock, the physicochemical and geochemical parameters of soil and rock, and the chemical composition of the water contained therein (De Caro et al. 2017; Shomar 2015). This synergic combination of techniques was expected to provide reliable information to assess the possibilities of this aquifer being used as a reliable water supply (Abdel-Satar et al. 2017; Armengol et al. 2017; Chidya et al. 2015; Zhang et al. 2018).

The study area is located close to both the urban area and the Pacific coast, where human and industrial activities are conducted that may negatively impact the aquifer (Appelo & Postma 2004; Bakhshipour et al. 2016; Jordanova et al. 2013).

## 2. Materials and Methods

### 2.1 Study area

The study site is located at latitude 9°3’57.93” N and longitude 79° 24’23.22” W in the southeast coastal area of the Isthmus of Panama (Figure 1). The Tocumen sector of Panama City corresponds to an industrial and residential sector where part of the Technological University of Panama is located and constitutes the ENE outskirts of the city. Its topography is almost plain, with marshes and mangroves extending from the site to the coast (~ 5000 m).

The area has a characteristic tropical climate (Awi type, savanna tropical climate) according to the Köppen climate classification map, with annual rainfall >1000 mm (Dirección de Hidrometeorología de ETESA 2007). Figure 2 shows the climograph with ETESA meteorological station data from 2012 to 2020 (Dirección de Hidrometeorología de ETESA 2021). We can see that the dry season includes the months of January to March (lowest rainfall) and the rainy season goes from April to December, when the rainiest months are October and November. Regarding the environmental temperature, the highest temperatures occur in dry months.

The geology of the area includes marine sedimentary rocks that correspond to the Panama Formation from the Tertiary age. It consists mainly of tuffaceous sandstones, tuffaceous shales and limestones (Guardia 2018). The petrographic analysis of the rock in this area shows that it comprises marly siltstone (marl), with a clastic structure and a uniform texture, formed from silt-sized fragments of micrite, shells and microfossil fragments (microforaminifers) with abundant chloritic-clayey material, sporadic fragments of silicates (including quartz, and especially feldspars, rare Fe-Mg minerals), some traces of carbonous material and very rare magnetite (Gutiérrez 2021).

**Fig. 1** Study area location map

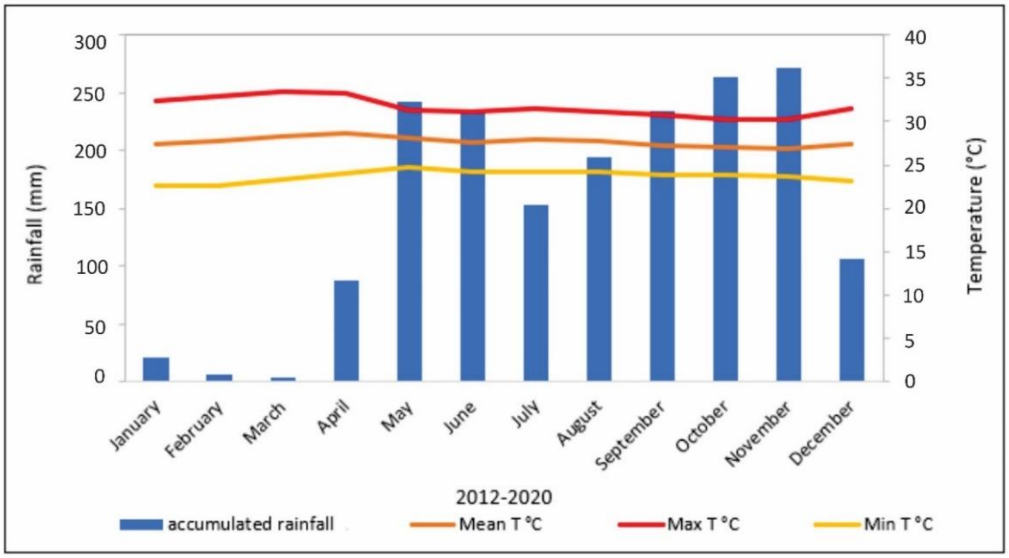


**Fig. 2** Climograph: Tocumen weather station 2012–2020

A shallow water well (24 m deep) is sporadically used for water production by means of a small pump (1.5 Hp), which was installed at the site in 1993 (Vega 2004). A preliminary test determined that at a pumping flow of 2.52 L/s, the well's efficiency (UTP-ET) was 87.9%. The Cooper & Jacob Method (Kruseman et al. 1970) gave a preliminary transmissivity (T) value of 21.1 $m^2$/day, and a storage coefficient (S) of 2.08 x $10^{-3}$ was obtained by the Theis Method (Kruseman et al. 1970). Given this S value, the aquifer is semiconfined and presents vertical percolation according to the Abatement *vs*. Time curve (Vega 2004). A pumping test run at constant flow for 72 h in October 2015 determined that 100% efficiency is obtained at a flow of 1.26 L/s, and the well stabilizes at 6.15 m (Alpirez et al. 2015). The hydraulic gradient is relatively low with a value of 6.10 x $10^{-4}$. Given that the area is flat with only a slight slope, the flow direction is south to north (Alpirez et al. 2015).

The aquifer's recharge is very important (Abiye et al. 2018; Barbera et al. 2018; Healy & Cook 2002; Martínez et al. 2017). Figure 3 is the graph of the temporal evolution of the watertable in the studied well (Centro de Investigaciones Hidráulicas e Hidrotécnicas 2016) *vs.* rainfall (Dirección de Hidrometeorología de ETESA 2021) for 2014, which shows that the rainfall in the area directly influences the watertable in the well because in dry months, the water level lowers when rain is absent. The much higher rainfall that falls during the rainy season rapidly produces a net recharge of the water level in the well.

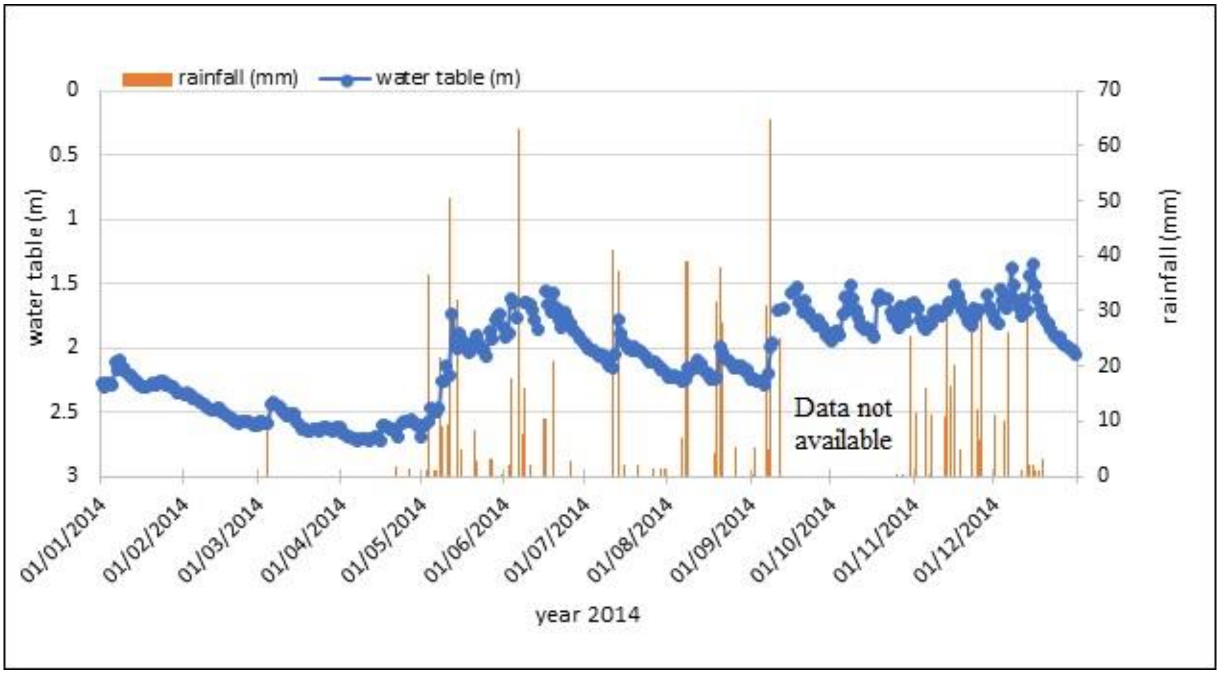


**Fig. 3** Temporal evolution of the water table vs. rainfall 2014.

## 2.2 Analytical work

Fieldwork was carried out between June and August 2015 during the rainy season. Laboratory studies were conducted at the Experimental Engineering Center (CEI) of the Technological University of Panama.

The methodology herein applied is based on several complementary techniques: a 10 meter-deep well was drilled in the area to allow the soil and rock to be sampled and characterized using physicochemical and geotechnical parameters, as well as a chemical analysis. In addition, geophysics employed with 2D electrical resistivity tomography (ERT) (Mojica et al. 2013; Ho et al. 2017; Benabdelouahab et al. 2018) provided a basic scenario of the lithologies in the area and allowed a lateral interpretative extension of the data provided by the section obtained in the well.

The Geotechnical Laboratory (LABGEO) of the Technological University of Panama drilled a 10 meter-deep well with a diameter of 75.7 mm in the area adjacent to the water extraction well (24 m deep) where the hydrogeochemical study was carried out (Fig. 4a). Drilling was performed using a rotary diamond drilling machine (Acker, model AD-II) with a double-tube recovery system. The water table was detected at a depth of 2.50 m 24 h after drilling ended (Arrocha 2015). During drilling, the Rock Quality Designation (RQD) parameter was estimated. This parameter indicates the degree of jointing or fracture in a rock mass measured as a percentage, where an RQD of 75% or more shows good quality hard rock and one less than 50% denotes low quality weathered rock (The Constructor 2018).

In parallel, the Engineering and Applied Sciences Research Laboratory (LIICA) of the Technological University of Panama performed a 2D electrical resistivity tomography over a 40-meter length using a Syscal R1 resistivity meter (http://www.iris-instruments.com/syscal-r1plus.html) with a multicable system powered by a 12V battery. Forty-one electrodes were employed with a 1-meter separation, whose Wenner-Schlumberger configuration allowed good resolution tomography to be obtained at a depth of 8 m. Data was processed using the Earthlmanger 2D software (https://www.agiusa.com/agi-earthimager-2d) and exported to Surfer 12 (https://www.goldensoftware.com/products/surfer) for representation purposes (Mojica 2015).

Four samples were taken from the drill's profile, corresponding to the different lithologies observed on it (Table 1; Fig. 4). The samples corresponding to complete soil and to fragments of underlying rock were taken using gloves, stored in plastic bags and kept at room temperature until analysis.

Sample preparation included sieving the soil sample to separate the > 2 mm fraction. Rock fragments were crushed and then also sieved to < 2 mm. The samples for the geochemical analyses were prepared by CEMEX, including grinding to < 100 µm.

**Table 1** Identification of samples

| Identification | Depth | Visual description | Stratigraphy |
|---|---|---|---|
| Sample 1 | 0.00–0.10 m | Topsoil, brown. | Organic layer, including vegetation waste. |
| Sample 2 | 0.10–1.00 m | Brown soil. | Soil, constituted by clayey gravel with sand. |
| Sample 3 | 1.00–2.90 m | Light brown rock, weathered. | Sedimentary, weathered rock, very poor quality, light brown in color. |
| Sample 4 | 2.90–10.00 m | Light gray rock, healthy. | Sedimentary rock with moderately soft hardness (RH-2), weak resistance, of regular to excellent quality, and light gray in color. |

The physicochemical parameters were determined by the Industrial Analysis and Environmental Sciences Laboratory (LABAICA). The applied methodologies included: ASTM D 4972 (for pH and EC) in a 1:5 suspension (w/V) using a multiparameter benchtop Orion Versa Star Pro device; ASTM D 2974 for organic matter content by weight loss at 455°C; cationic exchange capacity (CEC) by the potentiometer method (Weaver et al. 1991); calcium carbonate determination according to Skinner & Halstead (1958); sulfate determination based on ASTM D1580 (ASTM 2004); chloride determination as per AASTHO T-291 (2013). The geochemical analyses included $SiO_2$, $Al_2O_3$, $Fe_2O_3$, CaO, MgO, $SO_3$, $Na_2O$ and $K_2O$, and were carried by CEMEX Panama following the X-ray fluorescence technique.

Non organic soil (Sample-2) was also characterized by determining the Atterberg limit (ASTM D4318), and granulometry (ASTM C6913) by a texture classification according to the Unified Soil Classification System (USCS) (ASTM D 2487) (ASTM 2004).

Mechanical unweathered rock behavior (three subsamples from sample 4) was established by axial compression testing (ASTM D 7012) (ASTM 2004) using an ELE International device (model ACCU-TEK 350 digital series).

**Fig. 4** Study area: a) Drilling of well; b) Drill hole profile.

## 3. Results

### 3.1 Geotechnical Tests

The geotechnical parameters (Table 2) indicated that soil (Sample-2) corresponded to the GC group (clay gravel with sand), according to the results obtained from the grain size and the Atterberg limits for the USCS (Unified Soil Classification System).

**Table 2** Classification (granulometric analysis and consistency limits**)**

| **Hole** | **Sample -2** |
|---|---|
| Sampling depth (m) | 0.10 – 1.00 |
| USCS classification | GC |
| Description | Clay gravel with sand |
| Color | Light brown |
| Liquid Limit, LL | 61 |
| Plastic limit, PL | 26 |
| Plasticity index, PI | 35 |

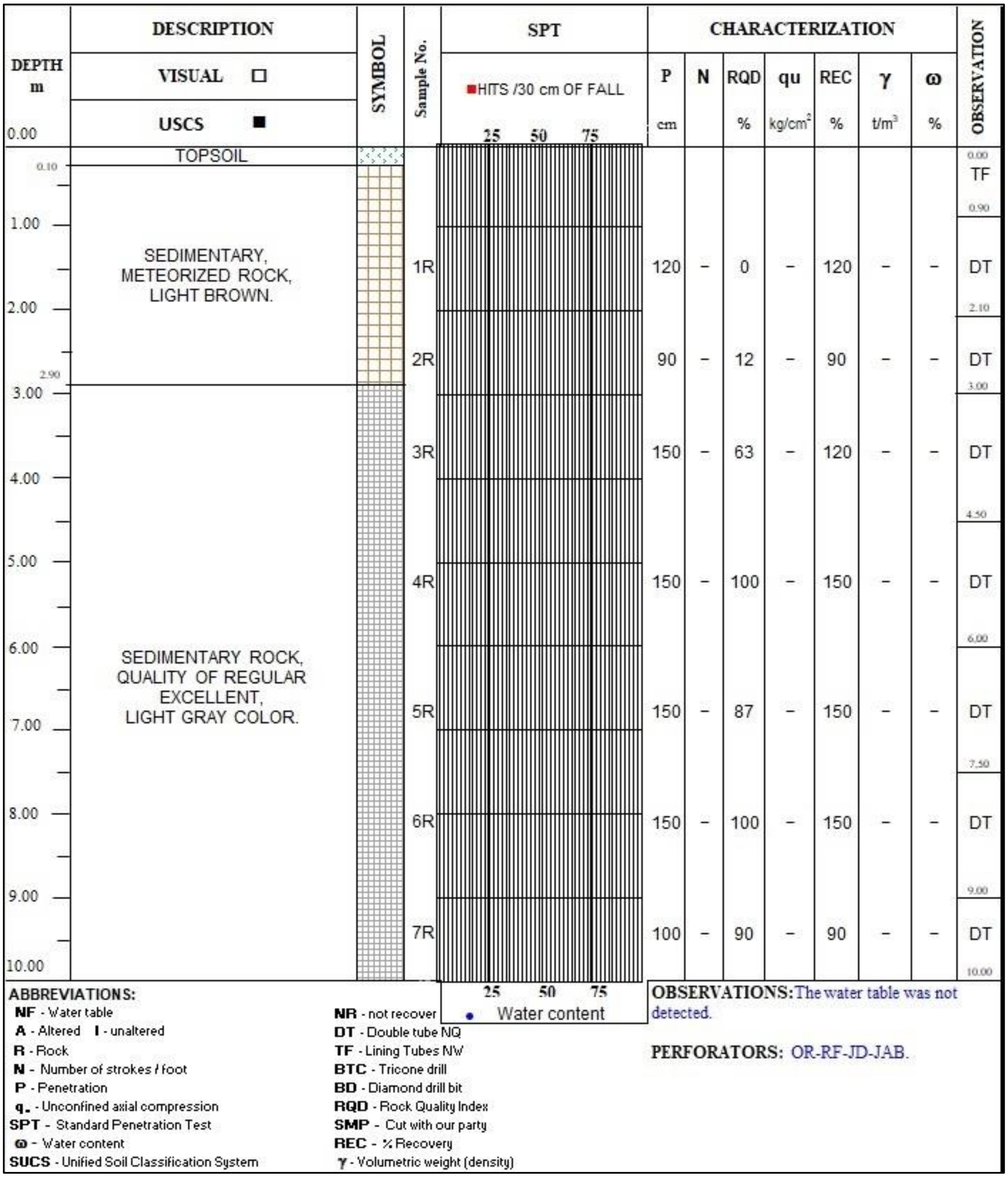
The results of the axial compression test carried out on three subsamples of sample 4 (4-1, 4-2, 4-3) are presented in Table 3. These values can be considered normal for lutitic rocks (Kiamco et al. 2004). As well, the results of the visual inspection of discontinuities observed in the rock within the interval 2.9 to 10 m (samples 3 and 4) are presented in Table 4. Figure 5 shows the drilling profile at a 10-meter depth and indicates the parameters estimated by visual inspection.

**Table 3** Axial compression to rock cores

| Hole | Sample | Depth **(m)** | $q_u$ (kg/cm$^2$) | $\gamma_m$ **(kg/m$^3$)** | $v_s$ (m/s) | $E_{av}$ (kg/cm$^2$) |
|---|---|---|---|---|---|---|
| **H-1** | **sample 4-1** | **6.40** | **151** | **2064** | **618** | **19 266** |
| | **sample 4-2** | **7.60** | **161** | **2175** | **869** | **40 179** |
| | sample 4-3 | **9.80** | **185** | **2149** | **899** | **42 478** |

**Table 4** Description of discontinuities.

| | | | |
|---|---|---|---|
| **1. Discontinuity spacing** | **Description** | **Spacing** | **Designation of rock mass** |
| | Spaced to widely spaced | 0.60 to 2.00 m | Massive to solid |
| **2. Condition of discontinuities** | **Roughness** | **Opening** | **Filling thickness** |
| | Wavy smooth | Moderately open to closed | Very thin film |
| **3. Designation of rock quality** | From regular to excellent | | |
| **4. Persistence of discontinuities** | Cannot be defined | | |
| **5. Orientation** | Joints dive at different angles | | |
| **6. Presence of water in discontinuities** | The fracture is dry, but evidences flow circulation, such as stains and leaching. | | |



| Sample No. | P cm | N | RQD % | qu kg/cm² | REC % | γ t/m³ | ω % | OBSERVATION |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | 0.00 TF 0.90 |
| 1R | 120 | – | 0 | – | 120 | – | – | DT 2.10 |
| 2R | 90 | – | 12 | – | 90 | – | – | DT 3.00 |
| 3R | 150 | – | 63 | – | 120 | – | – | DT 4.50 |
| 4R | 150 | – | 100 | – | 150 | – | – | DT 6.00 |
| 5R | 150 | – | 87 | – | 150 | – | – | DT 7.50 |
| 6R | 150 | – | 100 | – | 150 | – | – | DT 9.00 |
| 7R | 100 | – | 90 | – | 90 | – | – | DT 10.00 |

**ABBREVIATIONS:**

- **NF** - Water table
- **A** - Altered **I** - unaltered
- **R** - Rock
- **N** - Number of strokes / foot
- **P** - Penetration
- **q.** - Unconfined axial compression
- **SPT** - Standard Penetration Test
- **ω** - Water content
- **SUCS** - Unified Soil Classification System
- **NR** - not recover
- **DT** - Double tube NQ
- **TF** - Lining Tubes NW
- **BTC** - Tricone drill
- **BD** - Diamond drill bit
- **RQD** - Rock Quality Index
- **SMP** - Cut with our party
- **REC** - % Recovery
- **γ** - Volumetric weight (density)

**OBSERVATIONS:** The water table was not detected.

**PERFORATORS:** OR-RF-JD-JAB.

**Fig. 5** Drilling profile of the drill hole.

### 3.2 Electrical Resistivity Tomography

This technique is widely used in hydrogeological studies because it allows the possible presence of groundwater to be detected from the interpretation of resistivity images, as well as an interpretation of the site’s stratigraphy, without having to drill; that is, non invasively (Kumar et al. 2016, Wahab et al. 2021). The employed electronic configuration corresponds to an arrangement of the Wenner-Schlumberger type, which allows the structure to be visualized laterally and in depth, with good resolution and depth for research in the study area. The 2D electrical resistivity tomography had 19 depth levels and 380 apparent resistivity values and thus provided a distribution section of the measured data. This representation is the result of the inversion that provides a distribution of the electrical resistivity of subsoil at a real depth (8 m) (Mojica 2015).

The 2D tomography study confirmed the presence of groundwater, which coincided with the limit between the weathered and unweathered rocks (Mojica et al. 2012; Mojica 2018), as shown in Figures 6 and 7. The smooth inversion method (see Figure 6) included three interactions and an RMS calculation error of 2.58%. The robust inversion method (Figure 7) involved three interactions and an RMS calculation error of 2.83% (Mojica, 2015). Although the error in the robust inversion was slightly larger than that for the soft one, both figures basically showed the same calculated electrical resistivity profile for the terrain. Both figures show the inversion profile in comparison to the drilling profile. The calculated electrical resistivity tomography corresponded very well with the mechanical drilling profile of the terrain. The surface layer, corresponding to topsoil and soil, is shown in green and presents intermediate resistivity values (≈ 15 Ω m). The resistivity areas (depicted in blue in the profile, ≈ 10 Ω m) seen in this layer indicate the presence of moisture on the ground surface as tomography was performed during the rainy season. The high resistivity layer (in yellow and red, ≈ 24 Ω m), identified at greater depths, should represent a healthy sedimentary rock. Finally, at the bottom, there is an additional low resistivity area (blue, ≈ 10 Ω m) that indicates a high moisture content, meaning the presence of groundwater in the aquifer.

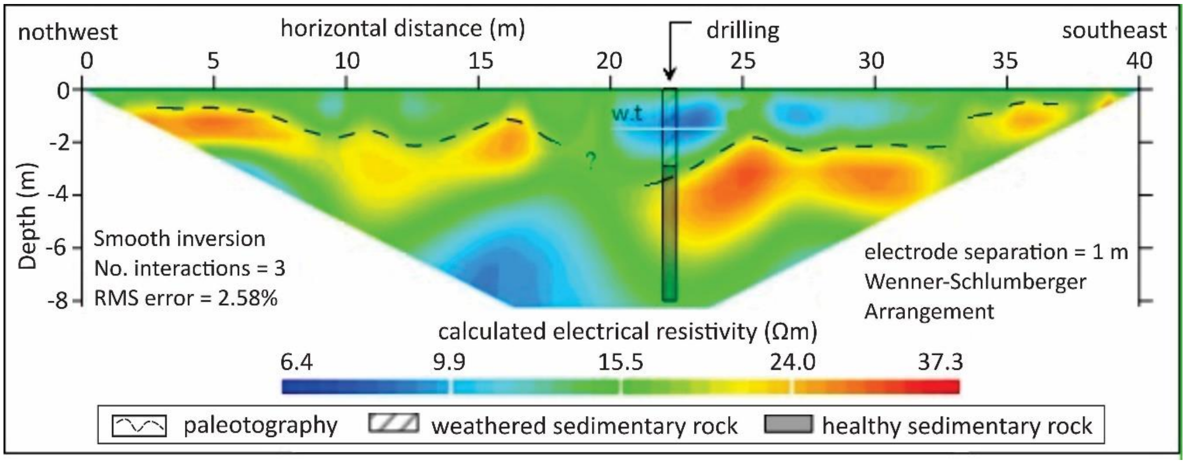


**Fig. 6** Electrical resistivity tomography obtained using soft inversion as a restriction of the least square optimization method. w.t: water table.

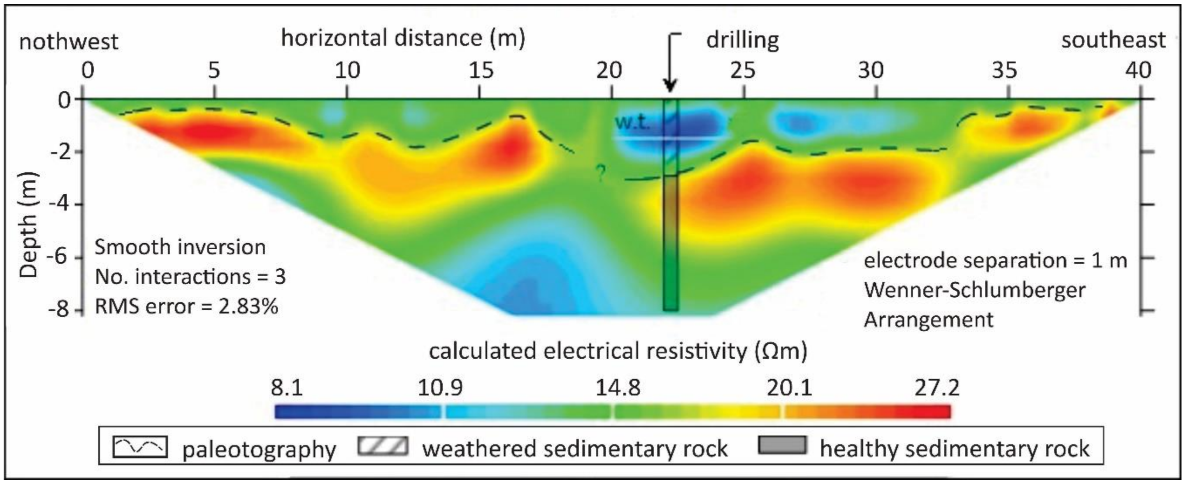


**Fig. 7** Electrical resistivity tomography obtained by using robust inversion as a restriction of the least squares' optimization method. w.t: water table.

### 3.3 Soil and rock physicochemical tests

Table 5 presents the results of the different physicochemical tests performed on the soil and rock at the site. Reactivity (pH) ranged from 8.2 in the topsoil to 7.6 in marlstone. Following the same trend with depth, the percentage of organic matter content lowered from 6.0 to 1.6, $SiO_2$ from 59.2 to 54.7, $Al_2O_3$ from 13.2 to 10.0, and $Fe_2O_3$ from 6.6 to 4.6. EC increased considerably with depth (from 0.2 to 2.2 dS/cm) and, thus suggests increased salinity. The following increased: $CaCO_3$ from 5.1% to 19.1%, CEC from 24.3 to 46.2 meq/100 g, CaO content from 1.8 to 4.0, MgO from 2.0 to 2.5 and $Na_2O$ from 1.4 to 2.4.

**Table 5** The physicochemical parameters and geochemical analysis for soil and rock.

| Parameters | Sample 1 | Sample 2 | Sample 3 | Sample 4 |
|---|---|---|---|---|
| pH | 8.2 | 8.4 | 8.8 | 7.6 |
| Electric conductivity (dS/cm) | 0.3 | 0.3 | 0.2 | 2.2 |
| Organic matter content (%) | 6.0 | 5.7 | 4.1 | 1.6 |
| Calcium carbonate (%) | 5.1 | 6.1 | 11.8 | 19.1 |
| Sulfates (mg/kg) | < 0.02 | <0.02 | <0.02 | 0.28 |
| Chlorides (mg/kg) | < 1.0 | 22.1 | 11.0 | < 1.0 |
| Cation Exchange Capacity (meq/100 g) | 24.3 | 27.9 | 40.6 | 46.2 |
| $SiO_2$ (%) | 59.2 | 58.9 | 57.4 | 54.7 |
| $Al_2O_3$ (%) | 13.2 | 12.5 | 11.2 | 10.0 |
| $Fe_2O_3$ (%) | 6.6 | 5.8 | 4.2 | 4.6 |
| CaO (%) | 1.8 | 2.5 | 3.5 | 4.0 |
| MgO (%) | 2.0 | 2.0 | 1.8 | 2.5 |
| $SO_3$ (%) | 0.1 | 0.1 | 0.1 | 4.9 |
| $Na_2O$ (%) | 1.4 | 1.4 | 1.4 | 2.4 |
| $K_2O$ (%) | 0.9 | 0.8 | 0.9 | 0.8 |

## 4. Discussion

Based on the results obtained for the physicochemical and geotechnical parameters, the profile studied corresponds to relatively soft and fractured sedimentary rock, overlaid by residual soil with a lower than expected thickness for this region. In particular, soil extends to a 1-meter depth and consists of a very thin "A"-type horizon that is very rich in organic matter, whereas the rest of the soil corresponds to a "C"-type horizon, with the marked presence of a gravel fraction. This AC soil is not at all characteristic of soils in areas characterized by a savanna tropical climate, where rainy weather favors much more complete soil profiles. Accordingly, soil can be interpreted as a technosol or anthrosol, and possibly corresponds to a more complete soil partly dismantled by human activities in a residential/industrial area (Ruiz et al. 2020). The study area corresponds to a type-C soil profile, which is dense soil and soft rock, as its cutoff velocity value (vs) is 694 m/s.

The rest of the profile (1-10 m depth) is solid rock, constituted by marlstones with sedimentary stratification. It is possible to distinguish between the depth from 1 to 2.9 m, which corresponds to partly weathered rock, as evidenced by its light brown color (evidencing the preliminary formation of Fe oxyhydroxides), and the rest of the profile (2.9 to

10 m depth), where rock appears unweathered with the original grayish color. The discontinuities in both the weathered and healthy sedimentary rocks (marlstone; see Table 4) suggest that water circulates through them, which indicates rainwater infiltration through rocks and, thus, replenishes the aquifer (Arrocha 2015; Medici et al. 2016). The values for the axial compression not confined to the rock cores in subsamples 4 are similar to those reported in marl rocks from Saudi Arabia and Jordan (Shaqor et al. 2008; Mustafa et al. 2017).

In particular, the RQD values, together with the observational data for fracturation-related discontinuities (Table 4), indicate healthy rock with a very low degree of tectonic fracturation. In addition, the discontinuities in rock evidence water flow which, together with the lack of evident intergranular porosity and permeability, suggests that the aquifer is hosted in fractured rock (Healy & Cook 2002). The pumping test also evidences a semiconfined aquifer, as shown in the previous report by Vega (2004).

The electrical tomography profile interpretation allows us to deduce an irregular topography in contact between soil and rock substrate (Figure 8). This topography, formed by grooves and peaks, is probably related to the fracturing observed in the test core. This character also allows us to differentiate two aquifer types, both fractured. The upper aquifer, hosted in soil, corresponds to a free aquifer concentrated in areas with strongly fractured rocks and which, in turn, is delimited by some type of impermeable fracture. The lower aquifer corresponds to a semiconfined aquifer, presents less fracturing and is delimited by fractures, such as those observed in the drilling profile. It is assumed to be in contact with the upper aquifer through some of these fractures.

Figure 9 illustrates an attempt made to correlate the results obtained from the geotechnical profile, the 2D electrical resistivity tomography and geochemistry. This figure presents the drilling profile at 10 m, together with variations in the calculated electrical resistivity and some geochemical parameters such as CEC, % $CaCO_3$, pH and % organic content. We can see that the calculated electrical resistivity of subsoil decreases in the layer of clayey gravel and sedimentary rock to the watertable (1.5 m), and then increases at a depth of 4 m before lowering again at a depth of 8 m.

Soil and rock physicochemical tests indicate that reactivity (pH) varies between 7.4 and 8.5 in different layers, corresponding to moderately alkaline soils (Weaver et al. 1991). Thus, the organic layer, the clay gravel and healthy sedimentary rock had a moderate alkaline pH, while the weathered sedimentary rock had a marked alkaline pH greater than 8.5.

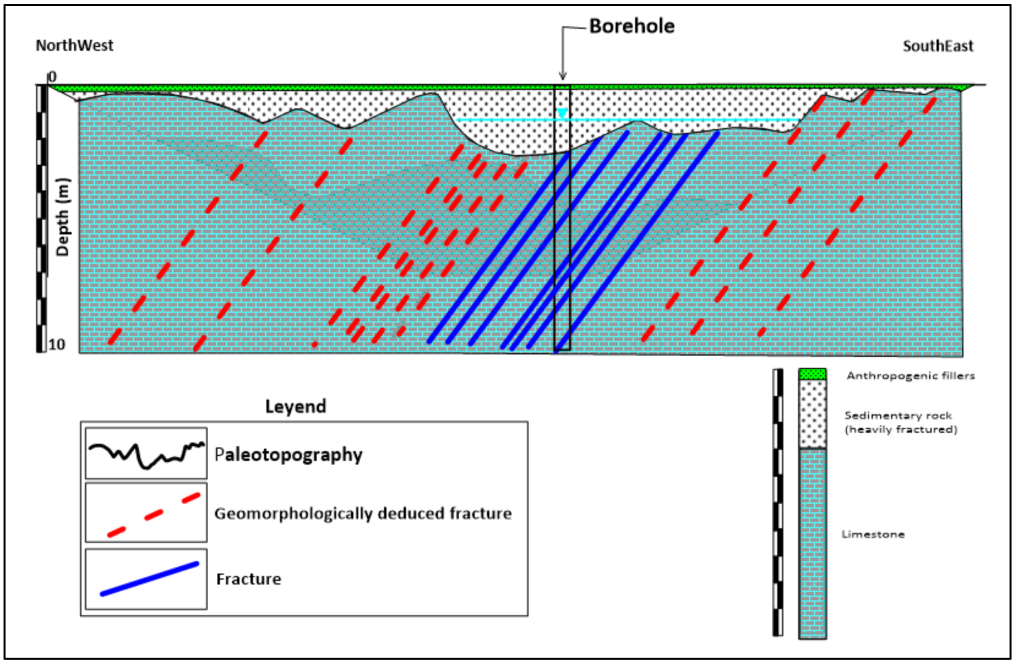


**Fig. 8** Electrical tomography profile (top image). Geological profile interpreted based on the lithology and fracturing of the borehole (bottom image).

Based on the EC soil classification table proposed by Vázquez and Bautista (1993), an EC from 0 to 2.0 dS/m corresponds to non-saline soils, and one of 2.1–4.0 dS/cm, to low salinity soils. As such, the organic layer, soil and weathered rock (0.2 to 0.3 dS/m) correspond to a non-saline terrain, whereas the healthy sedimentary rock, with an EC of 2.2 dS/m, should have an even lower salt content.

Organic matter content is, as expected, higher in the thin topsoil layer (6.0%) and lowers with depth. It takes a value of 5.7% in the "C" horizon and is much lower in rock (4.1% in the weathered sedimentary rock, possibly indicating some infiltration of colloidal organic matter from the overlying soil, and 1.6% in the healthy sedimentary rock).

The $CaCO_3$ content values increase with depth, with values of 5.1% for the organic layer, 11.8% for weathered rock and 19.1% for the healthy sedimentary rock. These values imply that this host rock is calcareous marlstone. However, it is not easy to determine whether the lower $CaCO_3$ content for the weathered rock corresponds to an original difference in composition, possibly in marlstone sequences (Derriche & Cheikh-Lounis 2004), or if this difference results from the higher degree of weathering at this level, which would imply the partial hydrolysis and washing of this component. In any case, the chemistry of the local groundwater, which is of the sodium bicarbonate type with $HCO_3^-$ values in groundwater

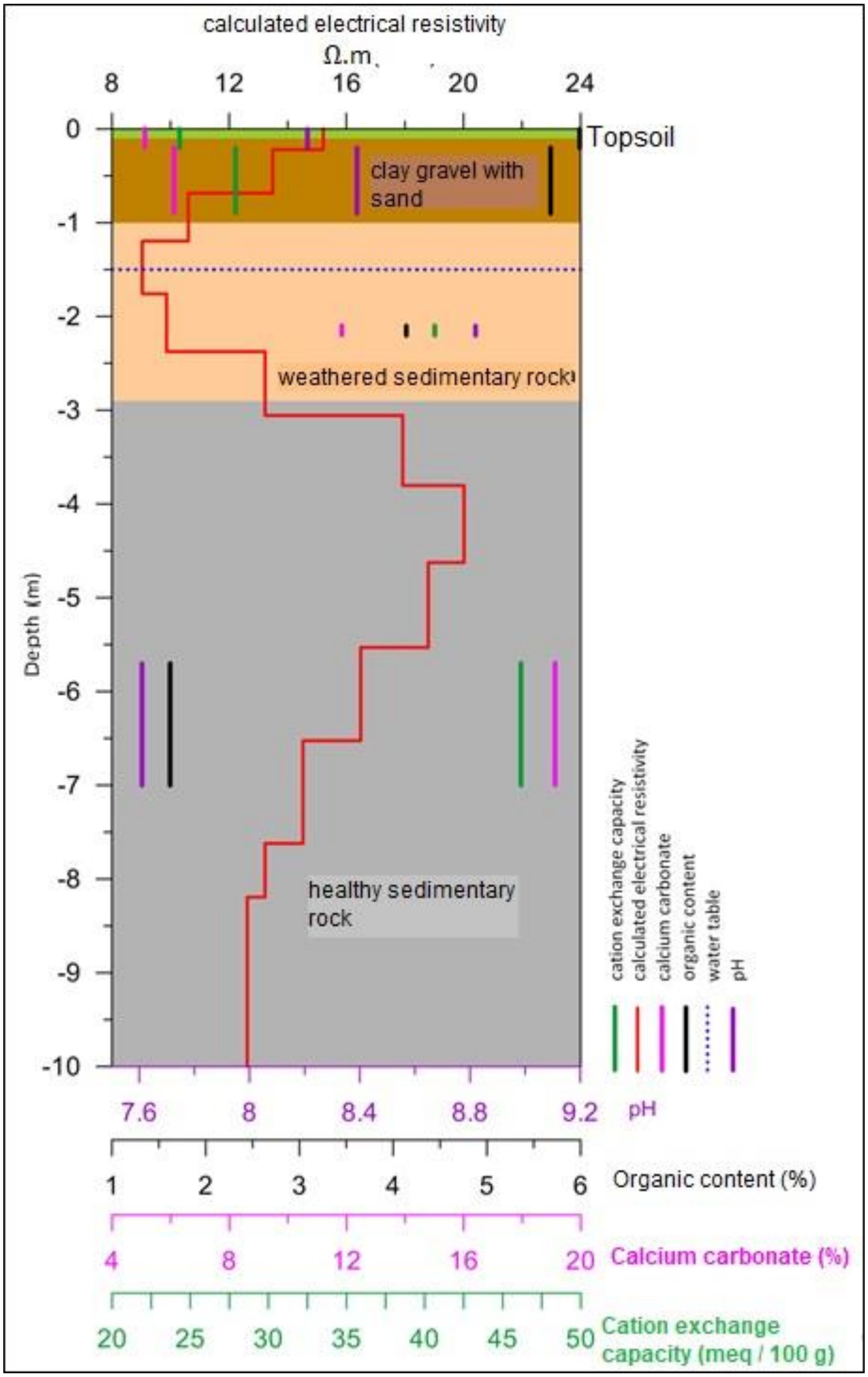


**Figure 9.** Graphical representation of the stratigraphy of the profile, including values for the geochemistry and the determined electrical resistivity parameters.

ranging from 215.40 and 278.85 mg/L (González-Valoys et al. 2021), clearly indicates the contribution of this lithology to its composition, as indicated by other studies in waters obtained from marlstone (Wersin et al. 2016).

The first three layers have sulfate values below the detection limit (0.02 mg/kg) of the employed method, the value of the last layer being 0.28 mg/kg $SO_4^{2-}$. These are low values for this anion, which is usually low in marlstone lithology (Derriche & Cheikh-Lounis 2004). As expected, and in parallel to the sulfate values, % $SO_3$ is very low in the three most superficial samples and is higher in the deepest one. Groundwater has sulfate values of between 64.85 and 127.30 mg/L (González-Valoys et al. 2021) and, thus, suggests the dissolution of the sulfates contained in marls, as evidenced by another study about the waters obtained for this lithology (Wersin et al. 2016).

Chloride ions have the particularity of moving and dissolving in the soil profile according to runoff and precipitation (Custodio & Llamas 1976; Tan et al. 2017). The samples for this study were taken during the transition from the dry to the rainy season, and after the first rains had mobilized soluble salts to the second layer. The presence of this anion may be related to the influence of marine aerosols, which are deposited on topsoil and then filter down to, and are concentrated in, the "C" horizon, to act in this location as a proto-"B" horizon. Concentrations in the marlstone rock are lower than the unit, indicating that chloride salts are absent in the rock (Derriche & Cheikh-Lounis 2004). The chloride values in groundwater were between 11.20 and 22.37 mg/L (González-Valoys et al. 2021). In this case, marl rock does not provide chlorides, but allows chloride-containing water to infiltrate from the surface (Appelo & Postma 2004; Shomar 2015).

CEC is soil's ability to retain and exchange different mineral elements. This parameter depends on the texture of soil and organic matter content (Weaver et al. 1991). The CEC values are 24.3 meq/100g for sample 1, 27.9 meq/100g for sample 2, 40.6 meq/100g for sample 3 and 46.2 meq/100g for sample 4, and are higher in rock. The interchangeable cations of the analyzed samples are likely to be $K^+$, $Ca^{2+}$, $Fe^{2+}$, $Na^+$ and $Al^{3+}$ (Custodio & Llamas 1976). The increase in CEC with depth explains the corresponding rise in % CaO, % $Na_2O$ and % MgO, which are the main cations in the analyzed groundwater (González-Valoys et al. 2021; Armengol et al. 2017; Martinez et al. 2017). The soil fertility parameter corresponds to medium fertility soil (Vázquez & Bautista 1993), which is useful to know if it is to be used for cultivation and planting purposes.

The concentration of other metal oxides, such as $SiO_2$, $Al_2O_3$ and $Fe_2O_3$, lowers as depth increases. Indeed, their values lower with each layer. $K_2O$ content remains low in all the layers as potassium is a minority cation in this type of sedimentary rock (Oke et al. 2017).

## 5. Conclusions

The studied profile corresponds to sections including a portion of soil, that are around 1 m in depth, and a marl-type rock which is much thicker than the drilled depth (10 m). Soil is probably a partial section of the original soil, and is likely to have been partially excavated and dismantled by human activities.

According to the edaphological characterization, the studied residual soil corresponds to technosol or anthrosol, and can be considered a permeable and transmissive level that favors rainwater infiltration, as confirmed by the good correspondence between rainfall and the water table rise. These characteristics also promote the infiltration of the chlorides present in soils as a result of transportation in marine aerosols from the nearby ocean. However, soil seems to act as a chemical barrier to this process by favoring the immobilization of this cation at this level.

The underlying sedimentary rock corresponds to a marl, particularly to marly siltstone, with a $CaCO_3$ content of 19.1%. It has a low, but measurable, content in sulfates, and a very low to null content in chlorides. Upon visual inspection, it is evident that the rock close to the soil-rock interface is weathered, as denoted by a brownish color indicative of the incipient oxidation of the Fe minerals present in rock. As also evidenced by the visual inspection, and confirmed by the RQD determinations, rock presents a certain degree of tectonic fracturation, which is likely to allow water to infiltrate and accumulate in rock, thus, constitute an aquifer.

The 2D electrical resistivity tomography confirmed the relevance of this technique for the study of the presence of water in soil and subsoil. In this case, the technique proved its ability to accurately identify the soil-rock interphase topography and was also able to identify two water accumulations: one superficial, associated with the presence of water in soil, and a deeper one, related to the fractured aquifer. This technique correctly identifies areas with higher fracturation ratios, which may be interesting for the detailed research of favorable sites for deeper drilling to obtain bigger water reserve volumes.

A good agreement appears between the chemistry of water, as characterized in a previous study, and that of the rock studied in the drill section, especially as regards the presence of carbonates and sulfates an, alkaline pH, and medium to high CEC. These characteristics make local water suitable for use for irrigation and as a source of drinking water.

Based on our results, we recommend a more complete study of the possibilities of water production in this area, which would include the more extensive use of electrical tomography to find the most favorable areas, characterized by higher tectonic fracturation. Other elements to bear in mind during this study would be to avoid proximity to the coast so that the infiltration of chlorides from marine aerosols would be minimized. The water chemistry should also be the subject of further studies, including the characterization of potential pollutants related to human activities, given the area's proximity to industrial and residential areas.

**Declarations**

**Funding information**: This study was funded by the Secretaría Nacional de Ciencia, Tecnología e Innovación (SENACYT), the Instituto para la Formación y Aprovechamiento del Recurso Humano (IFARHU) of Panama (270-2019-109), and Fondos para Grupos de Investigación UCLM (2020-GRIN-27011).

**Conflicts of Interest/Competing interest:** The authors declare no conflict of interest.

**Availability of data and material**: Not applicable.

**Code availability**: Not applicable.

**Author Contributions**: The paper was written by Ana González Valoys, Miguel Vargas Lombardo, Eric Gutiérrez, Jonatha Arrocha, Efrén García Ordiales, Pablo Cienfuegos, Francisco Jesús García Navarro, Raimundo Jimenez Ballesta and Pablo Higueras. The physico-chemical soils and rock samples were processed and analyzed by Ana González Valoys. Geotechnical tests were performed by Jonatha Arrocha and petrography by Eric Gutiérrez.

**Animal research**: Not applicable.

**Ethics approval**: Not applicable.

**Consent to participate**: Not applicable.

**Consent for publication**: Not applicable.

**Acknowledgments:** The authors thank the Technological University of Panama for its collaboration during this research work, the Centro de Investigaciones Hidráulicas e Hidrotécnicas (CIHH), the Centro Experimental de Ingeniería (CEI) and its laboratories, the Laboratorio de Geotecnia (LABGEO), the Laboratorio de Investigación en Ingeniería y Ciencias Aplicadas (LIICA) and the Laboratorio de Análisis Industriales y Ciencias Ambientales (LABAICA). We also thank CEMEX Panama for collaborating with the X-ray fluorescence determinations, and the human team in each laboratory, especially David Vega, Dr. Alexis Mojica, Dr. Cecilio Hernández, Fidedigna de Ortiz, José Pérez and Ana Franco. The Secretaría Nacional de Ciencia, Tecnología e Innovación (SENACYT) and the Instituto para la Formación y Aprovechamiento de Recursos Humanos (IFARHU) of Panama, the Sistema Nacional de Investigación de Panamá (SNI), and the University of Castilla-La Mancha (UCLM), the

University of Oviedo and the Autonomous University of Madrid (UAM) are also thanked for supporting this research. Thanks also go to Andrew Frankland (Scientific English) and Helen Warburton (Scientific English) for revising the English style of the manuscript.

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