Cumulative heavy metal contamination in mining areas of the Rimac, Peru basin

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HIGHLIGHTS

• Persistent metal contamination exists: each metal exceeded water quality standards every year.
• Mines and mining history have significant effects on Lima’s water supply, not addressed by the current permitting, remediation, monitoring and source control systems.
• No time trends observed in median contamination over the seven-years of data. This is a very short period relative to the mining history. Extreme contamination events, however, did increase slightly over time.
• Spatial trends are present, with more contamination upstream near mines and downstream before reaching Lima. These trends are not explained by recent production and flow data, but suggested inclusions for future analysis include historical mining production, effluent treatment, remediation, natural leaching, informal mining, and legacy sites.

KEY WORDS: Water quality, heavy metals, mining, cumulative effects, Peru, water contamination

ABSTRACT

The Rimac river provides drinking water to Lima, the capital of Peru. Mines upstream release heavy metals into the river, but these can also be introduced by natural leaching, informal mining, and waste from previous mines. The effect of mining on water resources in Peru has instigated social conflict; identifying likely sources of contamination can suggest whether conflicts were related to real impacts or perceptions. This study models heavy metal concentrations using the mass of minerals produced by upstream mines to assess the contribution of mines to downstream pollution. We also analyze temporal and spatial trends in water quality data, using quantile analysis to evaluate median and extreme pollution. Historical water quality data from the Peruvian government was used, including concentrations of iron, cadmium, lead, chromium, copper, zinc, and manganese. These were measured twice monthly over seven years at 29 points in the Rimac basin. Concentrations that exceeded Peruvian water quality standards were modeled with monthly flow and mine production data, using multiple linear regression, at three metallurgical and mining sites. The data was compared with key events such as conflict, mine closures, and regulation changes. Analysis showed that 100% of the metals studied exceeded the water quality standards every year. Time trends were not present in median pollution, but in the 90th, 95th, and 99th percentiles we observe increasing severity of the maximum pollution observations. Spatial analysis showed higher contamination in the upstream and downstream portions of the basin which may indicate cumulative effects. The approach taken in this study is worth repeating, given the possibility of distinguishing current water quality impacts from long-term cumulative effects.
1. INTRODUCTION

This paper assesses cumulative effects of water contamination through a basin-level quantitative analysis of water and mining related data. The Rimac Basin in Peru, which drains to the largest Peruvian City, Lima, is considered for the analysis given the history of mining in the upper catchments of the river, and the importance of the water supply to Lima. Cumulative effects of mining on water quality can occur even if the pollutant loads from individual mines are well regulated, and may be manifest as trends in space (e.g., downstream) and/or in time. While the potential for cumulative effects of mining on riverine systems is recognized, there is not much literature that quantifies such long-term effects. Since water quality degradation is noted as a source of mining-water conflict in Peru (Bebbington and Williams, 2008), an examination of the available data in the Rimac basin was of interest. The typical regulatory process for mine effluents is usually composed of an initial environmental impact assessment, an assessment of the waste load capacity of the water body, followed by a prescription for the permissible load and discharge of pollutants from the mine. While environmental monitoring of the river system is often done, the analysis of spatial and temporal trends to inform the regulatory process to attribute the outcomes to specific permitted discharges is rarely done. This provides one context for the work presented here – an initial assay of typical environmental data that has been historically collected to see if such cumulative effects can be identified with the quantity and quality of environmental data that may be typically available in a setting such as Peru. The remainder of this section provides the context for the specific pollutants of interest, a definition of cumulative effects and an overview of the Peruvian setting. The data and methods used are reviewed in the next section, followed by a discussion of the main findings and of the future directions.

1.1 EFFECTS OF HEAVY METALS IN WATER

Many heavy metals and transition metals are essential for human health (Hanikenne, Merchant and Hamel 2009), but high doses are toxic, in part because metals bond to sulfur groups, interrupting cellular activity and contributing to oxidative damage. Negative health impacts of heavy metals have been observed in Peru (Ramos 2008). High levels of dissolved or colloidal metals are usually detrimental to the natural environment. They pose a risk to flora and fauna, especially to aquatic biota (Besser, Finger and Church 2007), and the effects are compounded due to bioaccumulation. Heavy metals and low pH are known to be inversely correlated to plant growth, and the presence of heavy metals damages plant cell structures and inhibits enzymatic activity (Chibuike and Obiora 2014).

The definition of heavy metals is not uniform in the current literature. Following the pragmatic definition suggested by (Hübner, Astina and Herberta 2010), the heavy metals we consider in this study include iron, manganese, cadmium, copper, lead, zinc, and chromium.
1.2 CUMULATIVE EFFECTS

Cumulative effects are defined as “the impact on the environment which results from the incremental impact of the action when added to other past, present, and reasonably foreseeable future actions” (Council on Environmental Quality 1997). Cumulative effects are especially important when considering heavy metals. Metals are a conservative contaminant not readily transformed in a way that removes them from an ecosystem. In the mining industry, cumulative effects can be caused by space crowding, time crowding, interactions, or indirect effects (Kaveney, Kerswell and Buick 2015). Considering cumulative effects requires a catchment-based approach to water management (International Council on Mining and Metals 2015). Cumulative effects of any certain or reasonably foreseeable actions should be considered within Environmental Impact Assessments both in the U.S. and in Peru. A standard method for their evaluation does not exist (Environmental Law Alliance Worldwide 2010), but best practices have been suggested (Solomon, et al. 2016), (Kaveney, Kerswell and Buick 2015).

Cumulative effects are not seen as a regulatory issue by the permitting agency of the Peruvian government (personal communication with Peruvian government official, Oct 2016). However, consideration of cumulative effects can only be effective if sustained throughout the process, including the creation of laws and standards, impact assessment, permitting, fines, and regional environmental studies. Understanding water risk and accumulation of heavy metals not only protects the environment and human health, it also helps companies and governments know what is a sustainable investment. Water treatment and other infrastructure used to be 10% of mining companies’ infrastructure cost; now it’s 30% (Gillespy 2016). To make better use of all infrastructure, mines are increasingly located in clusters. The cumulative impacts of such arrangements are not well understood, but are important.

1.4 WATER AND MINING IN PERU

Mineral commodities account for 60% of Peru's exports, primarily gold, copper, and zinc (Ernst&Young 2015). Peru is South America’s most water-stressed country and every year mining and metallurgy release over 13 billion m³ of effluents into Peru’s bodies of water (Bebbington and Williams 2008). Connections between mining and water risks are many. Based on discussions with the Peruvian National Water Authority, the present study is the first of mineral transport in surface water in Peru (personal communication, 2016).

Water availability is one point of contention related to mining in Peru. In southern Peru, water tables are reported to be declining and entire lakes have been depleted due to mining operations (personal communication with mining industry personnel, 2016). Mine openings are limited to locations where a reliable water source can be secured. At times, mining projects previously approved by the government have been cancelled due to the expectation of water competition between agriculture and mining, for example in Tambogrande (Markham 2003) where Manhattan Minerals abandoned plans to mine a copper and gold deposit. It is also
notable that water resources in Peru can become a point of collaboration (Valdez Humbser 2012), not only competition. However, places where water availability has improved as a result of synergistic development and responsible mining operation pass largely unnoticed and undocumented.

In addition to water quantity impacts, changes to water quality are a major effect of mining in Peru. Contamination from mining affects population centers, which are concentrated to the west of the Andes, as well as fragile ecosystems to the west. Active mines, closed or abandoned mines, informal mining, natural leaching, agriculture and other industries often affect water quality in the same basin. Regulation and monitoring was non-existent when mining first was established in Peru, resulting in environmental risks from over 4,000 high risk legacy sites today nation-wide (Defensoria Del Pueblo 2015).

1.5 REGULATORY AND SOCIAL CONTEXT

Levels of heavy metals in surface water in Peru are governed by the Environmental code of 1990 with regulatory updates by the Ministry of Environment for mining effluents in 1996 and for water bodies in 2008 (Llontop 2010). Effluents from mines are regulated by Maximum Permissible Limits (MPL). The effluents mix with surface water which is regulated via Standards of Environmental Quality (ECAs for the name in Spanish). Exceedance of MPLs can be fined, as can discharge without a permit and established MPLs, but there are no sanctions regarding ECAs unless causality can be proven. Ideally, the MPLs for each mine in an area would be determined such that if all are being met, the ECAs are also maintained. For this, an understanding of cumulative effects would be necessary, but MPLs might not be adequate even in isolation. MPLs are determined within Environmental Impact Assessments (EIA), which the mining company submits to the government. The agency that approved these documents, previously within the Department of Energy and Mines, had limited capacity to challenge the claims and reports prepared by mining companies. Upon review of six approved EIAs for Peruvian mining projects, we found that rather than predicting amounts of heavy metals released, the EIAs commonly cite the regulations that pertain to specific bodies of water and make a written assurance that the mine will pollute only within those limits. When a mine’s discharge surpasses their MPL, fees may be symbolic or forgiven. The agency responsible for fines, OEFA (the Organism of Environmental Evaluation and Oversight), saw its power decreased with Article 19 of Law 30230. This is popularly known as the paquetazo ambiental, meaning “environmental package” that has burdensome consequences.

The perceived unfairness or ineffectiveness of these processes create a lack of trust by local communities. This exacerbates social conflict over mining’s effect on water resources (Slack 2013) and often slows or halts extraction. This has occurred at the mines Tia Maria, Las Bambas, La Zanja, Conga, Antamina, Yanacocha and others in Cajamarca and Piura. Both the impacts of a mine on critical water resources and the perception of impacts are factors in social unrest (International Council on Mining and Metals 2012). For example, communities upstream of mines have reported pollution, indicating that “mining is associated with contamination through perception as well as reality” (Budds 2015). Environmental Impact Assessments which
consider cumulative effects would improve neighboring communities’ trust that all impacts are being considered (Slack 2013).

Over the last decade, progress has been made toward improving regulation, reporting, and monitoring on a project basis. This includes updated Environmental Quality Standards in 2008 (Llontop 2010) and 2015, and a requirement for citizen involvement and monitoring. It is usually nominal, but at least 30 communities are actively monitoring water quality (UNDP 2016). These recent developments may improve understanding and reduction of negative project impacts. However, the impacts of multiple mining projects and contamination sources are still not well understood.

1.6 RIMAC BASIN

The Rimac River starts at an elevation of over 5,000 meters above Mean Sea Level in the Andes mountain range and has three main tributaries: Blanco, Aruri, and Huaycoloro. It then goes to the La Atarjea treatment plant before entering Lima, the capital of Peru, as potable drinking water. Water-intensive industries in the Rimac basin include agriculture, hydropower generation, and mining. The mines are mostly located in the Andes mountain range, where most springs and headwaters are located. The distribution of key water resources and mines in Rimac is representative of many other basins and shown in Figure 1 and Figure 2.

![Figure 1: The Rimac basin shown with glaciers (white), lakes (dark blue), springs (light blue diamonds), and areas at high risk for debris flow (dark blue diamonds).](image1)

![Figure 2: Rimac River with the main tributaries. Mines are shown in red including those in exploration, and the water quality monitoring stations are shown in blue.](image2)

Water-related risks in the Rimac basin include debris flow and diminishing glaciers. Earthquakes are common, and there are tailing dams near seismic faults (personal communication with National Water Authority, 2016). The Rimac basin has environmental degradation and a long history of mining. Of 1,185 sources of contamination within the basin, 60 are mine effluents which are all in the upstream section of the basin (K-Water; Yooshin Engineering; Pyunghwa
There are 274 high-risk legacy sites in the Rimac basin (K-Water; Yooshin Engineering; Pyunghwa Engineering 2015). Analysis of the Rimac basin is facilitated by more data availability than for most areas of Peru, and the results are important to decision makers in Lima. Understanding contamination in the Rimac basin was identified as especially vital because it becomes drinking water for the eight million people in Lima.

In one study of water quality, cadmium and chromium were below the permissible limits, but elevated levels of arsenic and lead were found (Juárez 2012). Contamination of heavy metals decreased in the early 2000s, but still exceed permissible limits and need to be further treated (Llontop 2010). In 2004, concentrations of cadmium were found along the entirety of the Rimac basin that exceeded Swiss and World Health Organization limits, as well as high concentrations of copper, lead, zinc and arsenic at many locations. The high levels of cadmium may be caused by mining both directly and indirectly. Processing of sphalerite and pyrite found in the region forms sulfuric acid, which facilitates leaching of minerals such as cadmium present in the natural geology. All but arsenic were attributed to mining based on the geochemistry of the region and the mining activity. At the time of that study only arsenic exceeded the legal limits (Méndez 2005), but the Peruvian water quality standards have since been updated. In the San Mateo district of Rimac, exceedances of cadmium, lead, manganese, arsenic and iron motivated a suggestion for improved treatment of the effluent of nearby mining company San Juan S.A. (Llontop 2010), though no direct link was shown. Heavy metals in streambed sediments also exceeded limits in Rimac and the two adjacent basins (Rivera, et al. 2007).

2. DATA AND METHODS

2.1 DATA COLLECTION

All government agencies are required to report water-related data to the National Water Authority. Any Peruvian citizen has access to any information held by the government, though obtaining it is a long and complicated process (Valdez Humbser 2012). The information is provided as a physical copy, which does not facilitate analysis, understanding, or subsequent action.

The data and background information for this study were obtained online and through personal meetings with government agencies, consulting companies, mining companies, non-profits, and communication with researchers who have done similar studies. The data used for the analysis and respective sources are listed in Table 1.

<table>
<thead>
<tr>
<th>Data</th>
<th>Details</th>
<th>Source</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water quality</td>
<td>Metal concentrations, monthly from 2004-2011</td>
<td>General Direction of Environmental Health</td>
<td>(DIGESA, 2010)</td>
</tr>
<tr>
<td>Mine production</td>
<td>Monthly per metal, per mine</td>
<td>Ministry of Energy and Mining</td>
<td>(MINEM, 2016)</td>
</tr>
</tbody>
</table>
There are potential issues with water quality data. A community organizer and resident of Chosica, a town located on the Rimac river, shared the perception that National Water Authority chooses to take samples far from the mining operations where they know it is least likely to be contaminated (personal communication, 2016). Officially, all sampling is done according to a planned experimental design, with consistent locations. For the data we used, two of the years provided geographic coordinates for the collection of the samples, of which only one varied significantly (by about 0.5km), indicating that the locations for this data were relatively consistent. However, another government agency mentioned changing the location of monitoring due to excavation that was being done just upstream of the monitoring station (personal communication, 2016), to avoid undue influence of sediment from the contaminating event on the sample. It is possible that true contamination is higher than the available data, due to attempts to avoid sampling in the most contaminated areas. In addition, based on discussions with people who have worked in mines, NGOs, community members and governments, mining companies are reported to know when the government agencies plan to take water samples, so they could preemptively shut down some of the operations on that day.

Data that were not obtained for this study, and represent potentially important gaps in the analysis, include: (1) flow data for each point of the basin studied, and (2) locations of informal mining hubs and estimates of their production.

Data was collected during trips to Lima in May 2016 and October 2016. Interviews were held with over 60 stakeholders to understand the local context and complexities that affect water quality in mining regions. Meetings were held with government agencies, non-profits, community members, environmental monitoring committees, universities, and mining companies.

2.2 GEOGRAPHIC SITING

A trip along the entirety of the Rimac River and part of the Blanco River enabled verification of the geographical data obtained and status of mines. The geographically referenced data was

<table>
<thead>
<tr>
<th>Volumetric flow</th>
<th>Monthly since early 1900s for one station, middle of the basin</th>
<th>National Water Authority</th>
<th>(ANA, 2014)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monitoring station locations</td>
<td>29 stations along the Rimac river and tributaries</td>
<td>DIGESA reports, validated by researcher accompanying ANA</td>
<td>(Juarez, 2012)</td>
</tr>
<tr>
<td>Mine locations</td>
<td>20 mines and mining operations, 6 active within the study period</td>
<td>SNL Metals and Mining Database, validated with various online sources</td>
<td>(SNL, 2016)</td>
</tr>
<tr>
<td>Locations of water bodies</td>
<td>Lakes, rivers, glaciers and basin boundaries</td>
<td>Autoridad Nacional del Agua</td>
<td>(ANA, 2014)</td>
</tr>
</tbody>
</table>

**Table 1: Data used and sources**
mapped using ArcMAP, RStudio, and Google Earth. The basin’s distribution of water resources, mining areas, legacy sites, monitoring locations, and main towns were analyzed. Key areas were chosen where multiple water quality stations and mines or mineral processing were active during the time period of the study. For each of the areas chosen, events such as mine closures, openings, sales, and social conflict were identified by reviewing historical Peruvian news sources and mining investment news.

A town in the middle of the basin, Chosica, had the most complete streamflow data and was used to represent flow basin-wide. There is more precipitation at higher elevations in the Rimac basin, but all rivers within the basin have similar annual cycles (Méndez 2005). Flow patterns at other places along the river are expected to be similar to Chosica, with a scaling behavior that relates to the drainage area at the location and water extraction.

2.3 NETWORK DEVELOPMENT

To understand cumulative effects, complete development of a cause-effect network “which defines the interconnections for the web of effects” is critical (Solomon, et al. 2016). We created a network for Rimac, excluding mines that were not active during the study period and monitoring stations that had little or no data. We identified points in the network that could be modeled on a regional level, i.e. a monitoring station that had a major mine or mineral processing plant immediately upstream and another monitoring station upstream of the mine.

Many mines were identified in the Rimac basin, as well as areas under exploration and legacy sites. Only a few mines and mineral processing sites had production data during the period of this study, and are shown in red in Figure 3.

**Figure 3: The network connections used for modeling in the Rimac basin.**
The three mines considered part of the Casapalca mining complex (Los Quenales, Americana, and Rosaura) are consolidated as a cluster. The coordinates of sampling sites and network dependencies are available in the supplementary materials. The network shown in Figure 3 includes flow from outside of the basin due to a re-routing tunnel (Graton tunnel) that brings water from the Atlantic side of the Andes to the Pacific side. It also includes a separate possible source of mining contamination, indicated by the red line extending from the top right of the graph. These are the Ticlio and Morococha mines; though outside the sampling network, they are close enough that they could be a source of contamination.

The black dots in Figure 3 are water quality monitoring sites that were active during the study period. The water quality detection limits and water quality standards for each metal are shown in Figure 4.

![Figure 4: Detection Limit and Water Quality Standard for Each Metal.](image)

In all cases, the detection limit was less than the water quality standard. This allowed all exceedances of the standards to be quantified. Because we were interested in exceedance of the water quality standards, and all the censored data was below the standards, some of the analyses and modeling could be done using generalized linear models appropriate for threshold exceedance data (Schwarz, et al. 2006).

For each time \( t \) where there is a reading of water quality, concentration \( C \) of contaminant \( c \) is provided at a given location (longitude \( x \), latitude \( y \), and elevation \( z \)). This is assigned to the nearest station \( s \), even in cases when the exact \( x, y, z \) values vary between years. Likewise, production \( P \) is summed where the mine location \( x, y, z \) is within a small diameter \( \delta \) of a central location \( x^*, y^*, z^* \), and owned by the same parent company, thereby designated as being within ball \( \beta \): this is called mine location \( l \).
Thus, two- or three-dimensional spatial relationships are reduced to a subset of linear structures where causal effects can be modelled. Where the spatial arrangement from upstream to downstream is $s_i \rightarrow l \rightarrow s_{i+1}$, the model dependencies are as follows, such that downstream concentration is influenced by the concentration upstream of the mine and the production of the mine or mining cluster.

$$f(C_{s_{i+1},t,c} | C_{s_{i},t,c}, P_{m,t,l})$$  \text{EQUATION 2}$$

Three regions were identified with water quality readings both upstream and downstream of a mine or mine operations, where the mine was also classified as medium or large by the data provider MINEM and there were at least 12 months of production during the study period.

### 2.4 PRODUCTION

For the production data, a rank and sum method was used to derive an index. The rank of each observation for a specific metal $m$ and mining location $l$ was identified within its time series, and used to replace the observation magnitude.

$$R_{m,t,l} = rank\{P_{m,t,l}\}_{t=1}^{T}$$  \text{EQUATION 3}$$

For mines that were active during the entire study period, total months $T = 84 = 12 \text{ months} \times 7 \text{ years}$, though some locations had fewer than 84 values. These ranks were then summed to form the index time series as shown in $S_{t,l} = \sum_{m} R_{m,t,l} | m \in \{Cd, Cu, Pb, Ag, Zn, Au\}$  \text{Equation 4}, summed over the six minerals produced.

$$S_{t,l} = \sum_{m} R_{m,t,l} | m \in \{Cd, Cu, Pb, Ag, Zn, Au\}$$  \text{EQUATION 4}$$

This method allows a comparison of metals that have very different ranges and units, and reduces the undue influence of outliers. This index was then used as a predictor for trends in water quality. Using a similar process, we also normalized the production and tested that as a predictor. Thus, the model equation $(f(C_{s_{i+1},t,c} | C_{s_{i},t,c}, P_{m,t,l})$  \text{Equation 2}) is more specifically represented with $S_{t,l}$ or the normalized production in place of $P_{m,t,l}$. 

### 2.5 WATER QUALITY

Water quality data from 2004 to 2016 was compiled from four Peruvian government agencies - the General Direction of Health (DIGESA), the National Water Authority (ANA), Lima’s Drinking
Water and Sewer Service (SEDAPAL), the Organism of Environmental Evaluation and Oversight (OEFA), as well as other short-term monitoring by community groups, non-profits, and academics (Méndez 2005), (Llontop 2010). Comparisons showed that the DIGESA data was more frequently and regularly recorded than any of the other sources, so it alone was used in the data analysis. The data available in this consistent and complete format ended in 2010.

The reports provided many water quality parameters, but we used only heavy metals. While sulfates and pH may be informative in mining areas, they can also be affected by other industries. Heavy metals in the Rimac basin are most likely introduced by natural geochemistry or mining. We chose a subset of seven metals based on the completeness of the data available.

For most measurements, month and year were provided but not the date or time. All measurements were assigned a decimal time at the midpoint of each month.

Concentrations below the detection limit (DL) of the measurement technique had been reported as DL, <DL, or 0. There were also NA values which were assumed to be distinct, representing non-completion of a test. The detection limit varied by metal and changed during the study period presumably due to improving measurement techniques, creating multiply censored data. We compiled a database across all stations and determined the detection limit for each metal as the lowest reading excluding 0 values, which were likely inconsistent reporting and were considered the same as <DL. We converted all 0, DL, and <DL values to DL.

\[ c_{s,t,c} = \begin{cases} c_{s,t,c} & c_{s,t,c} > DL \\ DL & c_{s,t,c} \leq DL \end{cases} \]  

Equation 5

Normally, this would then require censored regression. But because we later convert to binary values based on exceedance, for which all thresholds are above the DL as seen in Figure 4, we treat the resulting data as an indicator of contamination rather than censored data.

There were many missing values in the original data; over sixty percent of the expected results were reported as NA or left blank. To complete the data we used multiple imputation by chained equations (van Buuren and Oudshoorn, 2007), with five imputations using predictive mean matching.

To compare between metals, the value of interest is not concentration but rather how much a concentration exceeds the water quality standard (ECA) for a given metal contaminant \( c \). The exceedance ratio \( E \) for each time and station was calculated according to \( E_{s,t,c} = \frac{c_{s,t,c}}{ECA_c} \)  

Equation 6.

\[ E_{s,t,c} = \frac{c_{s,t,c}}{ECA_c} \]  

Equation 6
The legal limits \( ECA \) were obtained from a DIGESA water quality report and varied for each metal. The ECAs are determined by the classification of each water body. The Rimac River, upstream of Lima’s water treatment plant, is categorized as "Category 1": superficial waters destined to produce drinking water. The sub-category "A2" indicates that it can be made potable with conventional treatment as opposed to simply disinfection or more advanced treatment (Dirección General de Salud Ambiental 2010).

The filled matrix with concentration values was also subjected to a quantile analysis. For each percentile \( i \), a new matrix was created with binary values depending on whether the concentration at a given station, month, and contaminant exceeded the \( i^{th} \) percentile of all data for that contaminant. An aggregate exposure index \( I \) was then computed by summing this binary exceedance index over the seven metals, for each sampling date at each station.

\[
q_{s,t,c,i} = \begin{cases} 
0, & C_{s,t,c} \leq Q_i \\
1, & C_{s,t,c} > Q_i 
\end{cases} \quad \text{EQUATION 7}
\]

\[
I_{s,t,i} = q_{s,t,Cd,i} + q_{s,t,Cu,i} + q_{s,t,Cr,i} + q_{s,t,Pb,i} + q_{s,t,Zn,i} + q_{s,t,Mn,i} + q_{s,t,Fe,i} \quad \text{EQUATION 8}
\]

Where \( i = \{50, 90, 99, 95\} \). This resulted in a single number per time period, per station, that was used for trend identification.

Given the history of mining, heavy metals likely accumulated in the period preceding our study. Thus, natural processes including attenuation, advection, adsorption by sediments, erosion and sediment transport may lead to random fluctuations in the concentration measurements over space and time. By focusing on the extreme values of contamination we reduce the effects of such processes and are better able to identify significant events and trends within the study period, and explore corresponding sources. This leads to the focus on the upper quantiles of the data.

2.6 EXPLORATORY ANALYSIS

The distribution and trends of data were analyzed using Mann Kendall tests, seasonal Mann Kendall, and local regressions. Similar tests were done for each station, and for each metal. Trends were analyzed for the whole basin, each mining location, and for the downstream stations right before Lima.

The normalized production of each metal for a given mine was plotted over time. Abrupt changes were compared to events such as social conflict, fines, changes in regulation, or changes in mine ownership or operation. The metal exceedances over time were graphed with the time trends of mine production, to visually identify correlations between water quality and mine production. This was also done quantitatively using correlation matrices for each area. For more details on the mine-specific analyses, see (Butler 2017).
2.7. NETWORK MODEL

To study basin-wide effects, a variety of models were tested with water quality as the outcome variable. We modelled the first principal component of water quality for the whole basin with flow as the predictor variable, and did the same for the farthest downstream stations. Then, the principle component of the farthest upstream station was added as a predictor, as was flow. Finally, the time series produced by each quantile analysis was modeled with the summed production rank time series.

To model a given metal at the selected stations downstream of mining locations, the outcome variables tested were concentration and log(concentration). The predictor variables included flow, log(flow), lagged flow, decimal time, and time squared. Selection of variables, transformations, and lags were guided by the USGS SPARROW water quality model, adapted for heavy metals (Schwarz, 2006). Further details on the model design and outcomes are not elaborated here but are available at (Butler 2017). When doing linear models of just one metal we primarily used zinc because it had the most complete data. As predictors, we also included concentrations of other metals at the same station, concentrations of the same metal at upstream stations, and logarithms thereof. Visual comparison of the production and quality plots suggested times when an exogenous variable might have had an effect that cannot be captured by flow, time, and the concentrations of other metals.

3. RESULTS AND DISCUSSION

The key findings of the temporal and spatial analyses are presented in this section with figures.

- **Figure 5: Maximum exceedance for each month, across all stations and metals.** The incidence of extreme pollution, surpassing the legal water quality standards, increases over time.
- **Figure 6: trend over time for the 50th, 90th, 95th, and 99th percentiles.** The 50th percentile shows variation but no net trend over time. As we increase to higher percentiles, an upward time trend appears.
- **Figure 7: Production, summed ranks for all mines and mineral processing in the basin over time.** Production varies according to mine closures, opening and other events. The trend is similar to a local regression of the 50th percentile of water quality.
- **Figure 8: spatial trends for the 50th, 90th, 95th, and 99th percentiles.** The overall trend is upwards, but the more descriptive pattern is a U-shape with higher contamination far upstream and downstream, and lower in the middle of the basin.

Other findings are summarized briefly and include:

- The variables that helped predict water quality were distinct for each of the three mining locations.
- At none of the locations was the model satisfactorily successful in explaining water quality variation, using production, upstream pollution, and flow as predictors.
The spatial network needed to be modified to include connections not indicated by surface water flow direction alone.

TEMPORAL TRENDS

For each month, the maximum exceedance was determined, and the time series are shown in Figure 5.

![Figure 5: Maximum exceedance for each month, across all stations and metals.](image)

This exceedance ratio represents the number of times by which the water quality standard was surpassed. The blue line is a linear regression and the green is a local regression. The linear regression shows that the extreme pollution events started at about 10 times the water quality standard, and increased to 40 times the standard. A Mann Kendall test revealed a tau value of 0.224 and a 2-sided p-value of 0.0031, indicating an increasing trend as seen in the plot. A Mann Kendall test was done for each station separately, and all but four stations also had increasing trends.

Exceedances were also considered separately per metal. For each of the seven metals, the ECA was exceeded every year. For plots of each metal and Mann-Kendall test results for the upstream stations, see (Butler 2017). Lead and iron consistently had many readings exceeding the limits, more than the other metals.

Next we present the results of the percentile analysis of temporal trends. For each date, the number of metals exceeding the $i^{th}$ percentile at any station was summed and plotted in Figure 6. This shows a time trend representing the high and extreme values of heavy metal contamination, basin-wide.
The local regression is shown in green and linear regression in blue. There was no time trend for the 50\textsuperscript{th} percentile, confirmed by a Mann-Kendall test. For the higher percentiles, there was a slight upward trend but not statistically significant. Seasonal Mann-Kendall also did not show a strong trend. The plot of the 99\textsuperscript{th} percentile data is very similar to the maximum exceedance trend in Figure 5. Though the method to arrive at the plots was different, both methods addressed the goal of understanding events of extreme contamination and the trend over time. The results of the Mann-Kendall tests for each percentile are given in Table 2.

<table>
<thead>
<tr>
<th>Percentile</th>
<th>Tau</th>
<th>2-sided p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>50\textsuperscript{th}</td>
<td>-0.048</td>
<td>0.52367</td>
</tr>
<tr>
<td>90\textsuperscript{th}</td>
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<td>0.17076</td>
</tr>
<tr>
<td>95\textsuperscript{th}</td>
<td>0.103</td>
<td>0.17652</td>
</tr>
<tr>
<td>99\textsuperscript{th}</td>
<td>0.179</td>
<td>0.026744</td>
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</table>
While the median contamination shows no discernible time trends, there is an upward trend for extreme incidents. The magnitude of this trend is based on the increasing number of contamination incidents per month. In the 99th percentile graph in Figure 6, we see the 0.179 tau value represents an average increase from 1 exceedance per month to 3. This finding suggests that most of the extreme violations are recent. These severe pollution events, as defined by a large number of metals exceeding the higher percentiles, are a grave concern for the environment and human health for reasons explained in the introduction.

The time trends of water quality were not explained by mining production over this 7-year period. The representation of the summed mining activity in the basin over time is given in Figure 7. As discussed previously, the ranks are calculated for each mineral at each mine, which is summed monthly to obtain a basin-wide representation of mining activity.

Unlike contamination over time, production has distinct time trends: a steady increase, a decrease, and a sharp increase. This is a similar trend to the local regression of the median (50th percentile) in Figure 6, though the final increase starts in different years. The major changes in Figure 7 correspond to mine opening and closures, and a dramatic increase in the refinery’s production. By modeling the water quality time trend using the production summed over the basin, we confirmed that neither production nor flow are significant predictors.

SPATIAL TRENDS

Water quality was found to be most compromised at the upstream and downstream parts of the basin. This trend was seen in each of the four percentile analyses. These are presented in Figure 8, and the corresponding Mann-Kendall test results in Table 3.
Figure 8: Spatial trends for the 50th, 90th, 95th, and 99th percentiles.
An upward trend is present in all percentiles, but it is most pronounced in the 99th percentile. The graphs show an upward trend, but the more specific pattern is a U-shape; the highest presence of heavy metals is in the upstream and downstream sections with a lower presence in the middle of the basin. We expected higher heavy metal concentrations at the upstream monitoring locations, due to the presence of more mines. Mining in Peru happens mostly along the Andes mountain range which includes the upper portion of the Rimac basin. The mineral-rich area has historic and active mines, and it’s also possible there is more natural leaching in the highlands than in the downstream locations.

The increase in contamination at the downstream locations is a possible indicator of cumulative effects. As the Rimac river reaches the flatter section from Chosica to Lima, heavy metals carried with sediments have more time to settle to the riverbed. Desorption processes could then lead to the high readings in the aqueous phase seen in this analysis.

Though spatial flow data was not used in this analysis, the middle of the basin is where flow rate is the highest in the Rimac River (Zoi Environment Network, 2014). Since the water quality data used is concentration of heavy metals, the addition or extraction of water quantity may also affect the reading of heavy metals. It is possible that the overall metal mass is consistent throughout the basin, but the addition of water from tributaries causes the concentration to drop in the middle of the basin. Farther downstream after station 18, most of the river water is extracted at the La Atarjea drinking water plant, treated, and distributed to the city. Stations 19-23, downstream of the treatment plant, are the ones with the high concentrations. This could reflect desorption from sediments and lower flows, or it could also reflect the contribution of effluent from the treatment plant.

It is unlikely that drinking water extraction provides a full explanation for the downstream increase in heavy metals. First, the observations of increased contamination begin at station E16, which is upstream of the plant. Second, the plant extracts the water, but does not treat for metals. The heavy metals observed in this study upstream of La Atarjea remain in Lima’s water supply. They do not return to the river’s diminished quantity of flow, and therefore the plant is not expected to effect concentration.

It is likely that flow volume and cumulative effects both influence the spatial trends in heavy metal concentration. Spatially distributed flow data would be necessary to differentiate the relative contribution of the two factors.

<table>
<thead>
<tr>
<th>Percentile</th>
<th>Tau</th>
<th>2-sided p-value</th>
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</thead>
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</table>

**Table 3: Mann-Kendall results for spatial trend going downstream**
MINE LEVEL ANALYSES AND MODELS

Downstream of the Casapalca mining complex, one spike in water contamination coincided with a peak in production, and another coincided with a fine for soil contamination and deadly conflicts instigated by job loss and poor working conditions at the mine. However, the third major spike did not coincide with major events and was at a time when production was only half its average value. The production at Casapalca mine does not explain variance or trends in the downstream concentration of any metals.

Near the Coricancha mine, the largest spike in exceedance of water quality standards came shortly after the mine began production. However, the second highest peak of exceedance occurs when the mine is not operating, indicating that other factors may be responsible for the heavy metal loading in Rimac in those instances. Comparison with key events explains the extreme changes in production and possibly heavy metal loadings not captured in the model parameters. It is possible that infrastructure work during rehabilitation released metals into the environment. Land shifting near tailings, which has the potential to cause a significant release of heavy metals, did not coincide with a peak in water quality exceedances. This indicates that the potential problem was addressed in time such that it did not noticeably affect heavy metal concentrations.

At the Cajamarquilla refinery, the two largest spikes in nearby water contamination were around the same time as production increases. However, the monitoring station where the highest concentration was observed was not downstream of the refinery. It was on the main branch of the river, upstream of where the refinery’s impact theoretically joins the river. Closer investigation revealed that the refinery is close enough to the main river to have a direct effect, not only through the tributary as expected. At that station, exceedance of the zinc concentration was successfully modeled using the concentration of manganese at the same station, and production of copper and zinc at the refinery. The adjusted $R^2$ was 0.9623, with a p-value of less than $2.2 \times 10^{-16}$ and residual standard error of 0.04313. Modeling other water quality measurements and trends were less successful.

For all areas of the basin considered, modeling zinc downstream of a mine was most successful. This compares well with previous studies: “zinc found in the water samples is likely to come from the polymetallic mines situated in the region” (Méndez 2005), whereas lead, for example, may be due in part to active mines but is also likely influenced by a large abandoned mine (Ministerio de Energía y Minas 1997).

The mineral production was not significantly correlated with metal concentration in downstream water bodies at any of the three mining locations. All such correlations were below 0.5. Correlation between the concentration of one metal with the concentration of other metals, however, went up to 0.96, and the correlations were generally higher in the downstream sections of the basin.
The predictor variables for a given metal were different for each area. In some instances, the best covariates were different metals at the same station. In others, it was exceedances of the same metal, one or two stations upstream. Exceedance data more than two stations upstream was not significant in any of the places studied. Flow was not a key variable in the main three regression models, but could become important if seasonality is more directly incorporated into a model.

SUMMARY

Our approach to detect cumulative effects includes separating pollution into tiers of extremity. By analyzing quantiles rather than only mean values, we identified that current production may influence the median whereas cumulative effects may be more aptly captured in the highest percentiles of extreme pollution events. Peru was an appropriate case study given the widespread prevalence of mines of varying sizes and a long history of mining.

There was little temporal trend in overall metal contamination in the Rimac basin, over the seven years considered. This is likely due to the long history of mining in the region, which makes a seven-year period insufficient to detect long-term trends. It is a possible indicator that temporal cumulative effects are already well underway. If the ecosystems are already impacted by past mining, then it is difficult to distinguish a measurable impact of current mining production on contamination. It’s also possible that there are other mine-related parameters that are more predictive than monthly production, such as amount of waste deposited or remediation expenditures.

While there was no trend in the average mineral contamination, a small temporal trend became apparent when considering extreme pollution. This is critical because while low levels of heavy metals are acceptable or even beneficial, high levels of heavy metals are the primary concern. Many analyses of water quality only consider averages, and this study indicates that trends in extreme events may be important in quantifying cumulative effects in mining regions. In fact, it was the median trend of mineral contamination that was similar to the summed production in the basin over time, whereas high percentiles of contamination steadily increased. This is initially counter-intuitive and is perhaps why previous studies have not taken such an approach.

The spatial trend was distinct, with increased metal concentration in the upper and lower parts of the basin. It was not explained by production, trends over time nor completely by the localization of the mining activity. Using river flow at one location over time did not explain the contamination, but it is possible that the spatial dimension of flow can help predict contamination levels. Perhaps concentrations, which are used for water quality standards, are not the best metric for understanding accumulation of heavy metals from mining. Total mass may be more influenced by mine production. Even so, the locations of water quantity addition and extraction did not completely correspond to the spatial changes in contamination. It is likely that cumulative effects are a factor in the spatial dimension as well.
Overall, the model parameters of this study did not predict water quality. This is an important result, indicating that additional variables such as natural leaching, informal mining, and legacy sites may contribute significantly to the heavy metal loading. Exogenous variables such as conflict and changes in mine operation seem to be important yet complicated factors. While conflict may affect mine production and therefore can indirectly affect water quality, poor water quality may also affect or instigate conflict. The 2008 regulation change did not have an obvious effect on the time trends and would be more important in a study that uses data beyond 2010.

Model improvements would be possible with more consistency in sampling. Unfortunately, the most distinct observation has been that an institutional restructuring led to a decrease in data post-2011.

The most successful model occurred through a connection that was not part of the original network. We recommend a methodology that can reconstruct the network or re-assign importance of each connection stochastically based on the data. Though having surface flow models could be helpful, that alone would not have sufficiently predicted the direction of contamination in the Rimac basin. This could be well supported by a machine learning algorithm. Using such a model to iterate the possible inputs and determine which are significant would allow a more exhaustive approach and robust model evaluation than was done in this study.

A result of immediate importance is that all metals studied exceeded the water quality standards at least once each year. If mines usually meet the Maximum Permissible Limit in their effluent, then clearly these MPLs are not accurately considering cumulative effects. Analysis such as is done here can help identify which mines are most contributing to exceedance of a given metal at a given location. This would allow permitting to be done such that it considers the local conditions and cumulative effects. Alternatively, if a mine's production is not directly linked to exceedance of ECAs, then other causal relationships need to be explored before taking action. In the case of the Rimac basin, it seems that mining has a significant impact on the water quality. This may eventually lead to external liability for the mines due to long-term impacts on the largest metropolitan area. The likelihood of cumulative effects, both in space and time, indicate that remediation is needed to stop the flow of heavy metal contamination entering Lima.

The approach taken in this study is worth repeating in other areas, given the possibility of distinguishing current average water quality trends from cumulative effects caused by long-term environmental legacies and by the presence of multiple mines in one basin. It may also have applicability to other considerations of cumulative effects, such as toxicity in biota from bioaccumulation, conflict over resources, or human health affected by a compounding of ailments. Complex cumulative effects, being poorly understood and scarcely studied, call for an approach that distinguishes average impacts from extreme events.
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Ernst&Young. 2015. Peru’s mining & metals investment guide. Lima: Ernst & Young.


UNDP. 2016. Diálogo y gobernanza de los recursos naturales en el Perú: 24 avances representativos. Lima: Programa de las Naciones Unidas Para el Desarrollo - PNUD.


SUPPLEMENTARY MATERIALS:

NETWORK COORDINATES AND DEPENDENCIES:

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<th>Description</th>
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N.B. that Station 02c is thought to be located downstream of the Casapalca mining complex, which agrees with its description and patterns of the monitoring network design, but does not agree with the coordinates given here.

Spatial trends showing station labels instead of distance as in the paper: