Science of the Total Environment 1011 (2026) 181192

Contents lists available at ScienceDirect

Science of the Total Environment

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

National-scale river water quality in the Philippines: establishing baselines in a mineralised megadiverse nation

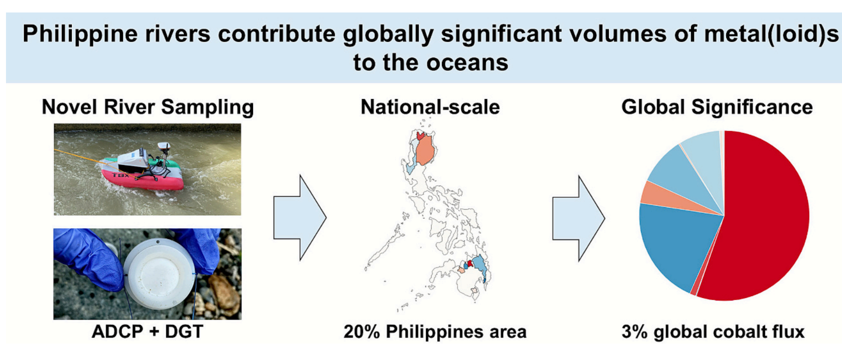
Emma Biles [a,b,*], Richard David Williams [b,h], Decibel Faustino-Eslava [c], Loucel Cui [c], Francis Ian Gonzalvo [c], Kim Bryan Cabrera [c], Manilyn Casa [c], Craig MacDonell [b], Maria Regina V. Regalado [c], Laura Quick [b], Justine Perry Domingo [b], Trevor Hoey [d], Niklas J. Lehto [e], Karen Ann Hudson-Edwards [f], Thomas J. Coulthard [g], Patrick Byrne [a]

[a] *School of Biological and Environmental Sciences, Liverpool John Moores University, UK*
[b] *School of Geographical and Earth Sciences, University of Glasgow, UK*
[c] *School of Environmental Science and Management, University of the Philippines Los Baños, Philippines*
[d] *Department of Civil and Environmental Engineering, Brunel University London, UK*
[e] *Faculty of Agricultural and Life Sciences, Lincoln University, New Zealand*
[f] *Camborne School of Mines, University of Exeter, UK*
[g] *Energy and Environment Institute, University of Hull, UK*
[h] *Earth Sciences New Zealand, Hamilton, New Zealand*

HIGHLIGHTS

- First national-scale baseline survey of metal(loid) contaminants in Philippine rivers
- Philippines yields 3 % (Co), 0.6 % (Cr), 1.2 % (Cu), and 1.7 % (Ni) flux to the global ocean.
- Background mineralisation can mask mining impacts when monitored at catchment outlets.
- DGT is recommended as a measure of ecologically relevant metal(loid) concentrations.
- Riverine metal(loid) flux is critical to understanding catchment metal(loid) transport.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Flux
Metal(loid)
Nutrient
Bioavailable
Passive sampling
Catchment

ABSTRACT

Mining underpins the global economy, is crucial to achieving net-zero targets yet can cause significant degradation of river health. Critical to managing this risk are national river monitoring programmes ideally incorporating pre-mining baseline water quality data to evaluate the impacts of mining and the success of mine site rehabilitation. We obtained metal(loid) flux, concentration, and bioavailability baseline data across the Philippines, a country with limited environmental datasets, globally significant biodiversity, and considerable mineral wealth, to establish nationwide benchmarks of water quality prior to an industrialisation of mining operations. Through sampling 10 major catchments, we show the Philippines contributes proportionally large volumes of metal(loid)s to the oceans (3 % Co, 1.7 % Ni, 1.2 % Cu, 0.6 % Cr). These large fluxes are not solely

* Corresponding author at: School of Biological and Environmental Sciences, Liverpool John Moores University, UK.
E-mail addresses: e.c.biles@ljmu.ac.uk, emma.biles@glasgow.ac.uk (E. Biles).

https://doi.org/10.1016/j.scitotenv.2025.181192
Received 13 May 2025; Received in revised form 30 November 2025; Accepted 9 December 2025
Available online 15 December 2025

from mining-impacted catchments but also from mineralised catchments with no large-scale mining. This suggests that an apportionment approach, where contaminant contributions are allocated to baseline and anthropogenic sources, would be beneficial to catchment managers and help identify and prioritise remedial interventions. Additionally, C_{DGT} (bioavailable) metal(loid) concentrations varied substantially across the Philippines, demonstrating the need for water quality guidelines based on ecologically-relevant metal(loid) concentrations. This study establishes the first nationwide ground-truthed baselines of hydrology and water quality in the Philippines, providing a reference point for future management and a statement of current condition. Beyond the Philippines, our monitoring approach can be adopted in other mineralised nations so that the future impacts of mining and the efficacy of sustainable mining approaches can be effectively monitored and reported on.

1. Introduction

Mining is a vital industry with a global market value of nearly USD 2.1 trillion in 2023 (Research and Markets, 2024). The global transition to net-zero is predicted to drive continued growth in the mining sector, especially for technology-critical elements (such as Cr, Cu and Ni) that are widely used in clean energy systems and technologies (International Energy Agency, 2023). Mining can bring enormous societal benefits by contributing to the gross domestic product of resource-rich nations and by supplying the raw materials to drive economic growth worldwide (Worlanyo and Jiangfeng, 2021). However, the economic benefits of mining come at the expense of global environmental degradation estimated to cost from USD 0.4 to 5 trillion every year (Arendt et al., 2022). Examples of environmental impacts of mining can include increased water scarcity (Meißner, 2021), water and air pollution (Dehkordi et al., 2024), biodiversity loss (Sonter et al., 2018), increased greenhouse gas emissions (Cox et al., 2022), and contamination of floodplains (Macklin et al., 2023).

Critical to mitigating these impacts are pre-mining environmental datasets which can help to identify any departure from background conditions due to mining and also to evaluate the success of mine site rehabilitation (Nordstrom, 2015). However, in many nations, the start of large-scale mining pre-dates national environmental monitoring programmes and baseline environmental data simply do not exist. Therefore, methods have been developed to measure the impacts of mining. In the United Kingdom (UK), the peak in metal mining occurred in the 1850s and in 2025 there were an estimated 5000 abandoned metal mines (Environment Agency, 2025; Sinnett and Sardo, 2020). In 2011, the Water and Abandoned Metal Mine programme (WAMM) established a national (England and Wales) monitoring strategy and estimated approximately 1500 km of river length to be impacted by legacy metal mine pollution (Environment Agency, 2025). This led to a legally binding target to half the length of rivers impacted by metal mine pollution by 2038 (UK Parliament, 2023). While this is an important legislative achievement, it is likely that many mined river catchments had elevated metal concentrations before mining. Therefore, there may be some uncertainty in estimates of mining impacts. In the USA, where there are an estimated 500,000 abandoned mines (Gutierrez, 2020), research has focussed on establishing pre-mining water quality, notably using the proximal analogue approach (Naus et al., 2005; Runkel et al., 2018). However, reconstructing pre-mining water quality is extremely challenging, requiring significant technical expertise and the existence of mineralised, but not mined, analogue catchments.

In mineralised nations with limited environmental datasets and where large-scale mining has not yet started on an industrial scale, there is a timely opportunity to establish environmental baselines as part of a sustainable mining approach (Domingo et al., 2024). The Philippines is one of the most mineralised countries in the world (Domingo et al., 2024; O'Callaghan, 2009). Mining occurs as both small-scale artisanal operations (Robles et al., 2022) and 58 large-scale mines that had a metallic minerals total production value of USD 4.5 billion in 2024, with Au (50 %), Ni (37 %) and Cu (11 %) being dominant (Department of Environment and Natural Resources - Mines and Geosciences Bureau, 2025). However, the potential for mining in the Philippines is far greater, with over USD 1 trillion worth of untapped metal reserves (Australian Trade and Investment Commission, 2023; Philippine Statistics Authority, 2017). Following the lifting of a 9-year moratorium on new mineral agreements in 2021 (Executive Order No. 130 (GOV.PH, 2021)), there is expected to be substantial growth in the mining sector in the country. These new mining activities will take place in a country that is only one of eighteen that are classified as mega-biodiverse (Scarano et al., 2024), with exceptionally high levels of endemism (~50 %) in both vascular plants and invertebrates (Aureo et al., 2020; Posa et al., 2008), and with thriving coral reef systems thought to be the some of the largest and most diverse in the world (Carpenter and Springer, 2005; Licuanan et al., 2019). Furthermore, the Philippines is ranked in the top 10 countries most affected by extreme weather events, with climate change predicted to increase flooding and landslides (Adil et al., 2025). Given the possible impacts on river water quality, a national-scale baseline water quality dataset would provide a foundation for effective and adaptive environmental management that can detect and attribute water quality changes due to mining.

Critical parameters in a river monitoring programme should be contaminant flux (product of river discharge and contaminant concentration) from river catchments to the sea and the concentrations of bioavailable trace metal(loid)s. Monitoring trace metal(loid) flux in river catchments is vital to quantify mine contaminant transport to coastal and marine environments and to identify the future vector in the context of landscape change (e.g. new mines and mine site rehabilitation) and climate change (Mayes et al., 2010; Runkel et al., 2016). Characterisation of mine contaminant flux in the UK and USA has developed clear evidence of the impact of legacy and contemporary mining activities in river catchments, facilitated the rehabilitation of mines, and has shaped government policies on river catchment management (Byrne et al., 2020; Mayes et al., 2010; Runkel et al., 2023). Contaminant fluxes have not been measured in the Philippines, making it difficult to establish the impacts of mining in river catchments. Information about aqueous contaminant concentrations complements flux data and provides an indication of risks to humans and ecosystems. In general, water quality guidelines for mine contaminants (trace metal(loid)s) are established for filtered (<0.45, or < 0.22 μm) concentrations of grab water samples. However, metal(loid)s are present in water in different dissolved chemical forms, not all of which are considered bioavailable (Väänänen et al., 2018). Hence, water quality standards based on total or filtered concentrations potentially overestimate ecotoxic concentrations, especially in mined and mineralised regions with elevated background metal concentrations (Rodríguez et al., 2021).

Considering the trajectory towards increased mineral resource exploitation in the Philippines, here we present the first nationwide assessment of river water quality and contaminant flux for major Philippines rivers. Our aims are to: i) quantify the flux of mining and non-mining contaminants from major river catchments to near-coastal waters, and ii) examine river water quality and trace metal(loid) and nutrient bioavailability in major catchments. To achieve these aims we explored the use of novel technologies such as acoustic Doppler current profilers (aDcp), to accurately measure river discharge for contaminant flux calculations, and diffusive gradients in thin-films (DGT) passive samplers, for measurements of trace metal(loid) bioavailability. Our analysis established an environmental baseline for Philippine rivers and provides the foundation for national-scale river water quality monitoring programmes in mineralised nations.

2. Methodology

2.1. Study catchments and sampling rationale

Ten river catchments across the islands of Luzon and Mindanao were selected for sampling based on their importance nationally for water supply and biodiversity (Fig. 1). Nine of these catchments are considered major river basins (catchment area greater than 1000 km^2) (Tabios III, 2020) and include the Abra, Agno, Apayao-Abulug, and Cagayan in Luzon; and the Ranao (also known as the Agus), Agusan, Cagayan-de-Oro, Buayan-Malungon (also known as the Malungon), and Tagaloan in Mindanao. A tenth medium-sized catchment (land area greater than 250 km^2) in Mindanao, the Sumlog, was also selected. The primary ore deposits in the Philippines are porphyry Cu deposits (Cu, V), nickel laterite (Co, Ni), nickel sulfide (Ni, Cu), and podiform Cr deposits within ophiolites (Cr) (Cooke et al., 2011). Although As is present in Philippines rivers, it is mainly of geothermal origin (Webster, 1999). The catchments were categorised based on the degree of mining activity occurring (Fig. 1B). Five catchments were classified as having '*large and small-scale mining*' present, all with notable and exploited deposits of Ni, Au, and Cu (Fig. 1E). The remaining five catchments were classified as '*mineralised, no large-scale mining*'. While no large-scale mining activities are present in the latter catchments, small-scale, including artisanal, mining operations may be occurring. The predominant catchment land cover across all catchments is annual cropping (24.4 %; Fig. 1D). The proportion of urban areas within the study catchments are generally low, ranging from 0.8 % (Abra) to 3.9 % (Agno). Annual average rainfall is highest in the southeastern catchments in Mindanao (3590 mm yr^{-1} in Agusan) and lowest in Luzon (1870 mm yr^{-1}in Cagayan) (Fig. 1C).

2.2. Field data acquisition

Samples were acquired at the outlet of each river catchment to the ocean upstream of the tidal limit. These locations represent the integrated effects of catchment pressures, enabling the total flux of metal [loid]s and nutrients from Philippine catchments to near-coastal waters to be estimated.

2.2.1. River water sampling

River water quality was monitored at each study site over four-day periods in March 2023 (Luzon catchments) and August 2023 (Mindanao catchments). Grab water samples were collected from below the water surface, at the closest position to the river's thalweg that could be accessed safely at the same time each day. To quantify the filtered concentrations of metal(loid)s and nutrients in the water, samples were passed through mixed cellulose ester type syringe filters (0.22 μm pore diameter) then stored in polypropylene sample tubes. A second set of unfiltered samples were collected as above to allow measurement of the

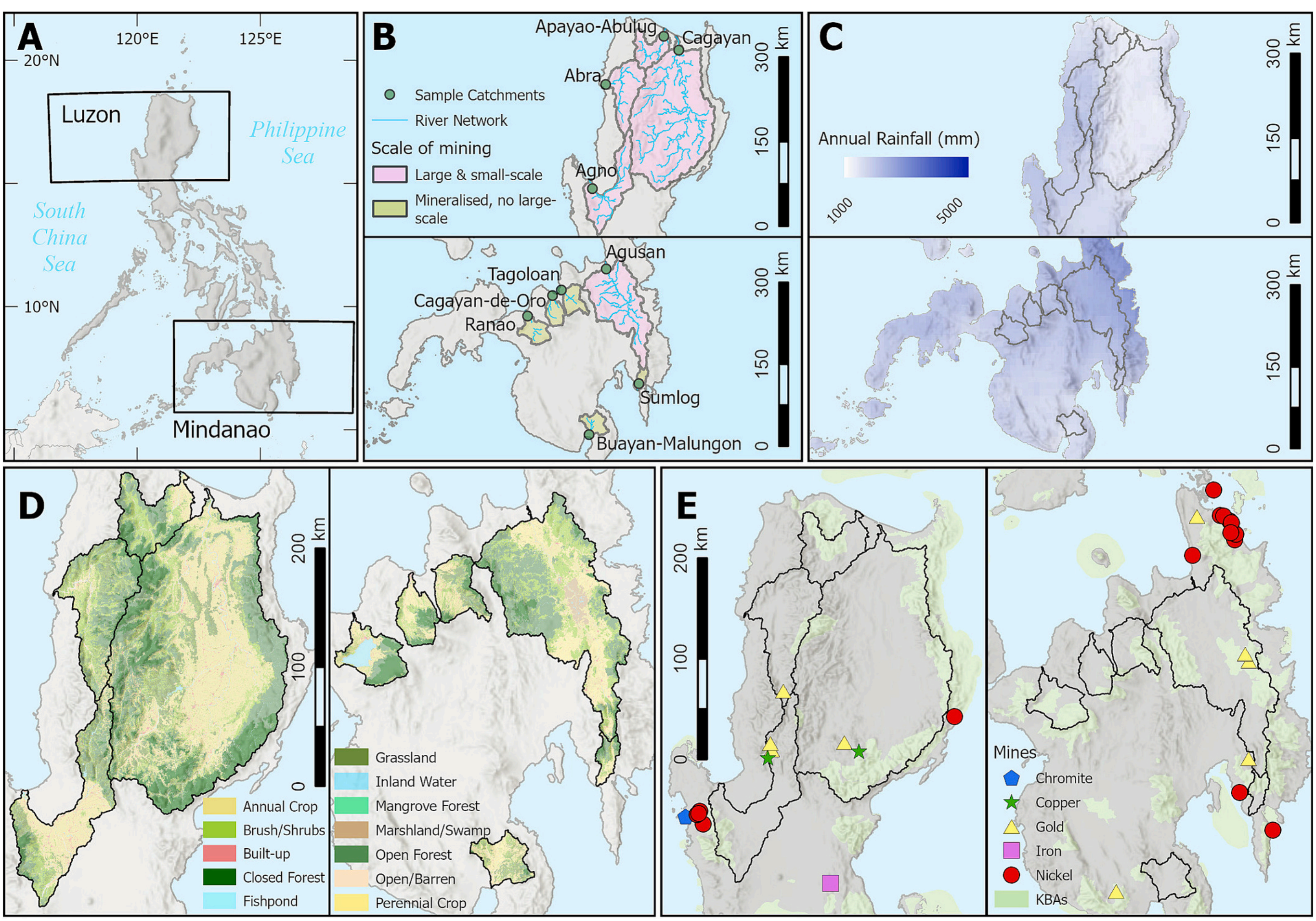


Fig. 1. Study catchments across the Philippines. (A) Location of Philippine islands (Global Administrative Areas, 2022) showing the areas of Luzon and Mindanao where sampling was undertaken. (B) Location of Luzon and Mindanao study catchments, with river network and catchment classification based on small- and large-scale mining presence (Boothroyd et al., 2023; Esri, 2025). (C) Annual rainfall in 2021 across Luzon and Mindanao study areas (Huffman et al., 2021). (D) Land cover within each study catchment (NAMRIA, 2020). (E) Key biodiversity areas (KBAs) and mineral resource hotspots across the Philippines (Domingo et al., 2024).

unfiltered metal(loid) concentration in the water. All samples were cooled (ca. 5 °C) for local transport, before being frozen (−20 °C). Samples were subsequently transported on ice to the United Kingdom (UK) (due to analytical constraints in the Philippines) by air and then stored at −20 °C until analysis (see below).

Diffusive gradients in thin-films (DGT) samplers with dual cation and anion-binding resins (Chelex-Titanium Oxide LSNX-NP probes (Panther et al., 2013), supplied by DGT Research Ltd., Lancaster, UK), were used to estimate trace metal(loid) bioavailability. The DGT resin layer mostly binds free ions and ions that can be released by labile or partially labile complexes. Therefore, DGT can provide unique information about the bioavailability of metal(loid)s (Davison and Zhang, 2012; Zhang et al., 1995). A DGT sampler accumulates solute over the length of its deployment via diffusion through a well-defined material diffusive layer and into a strongly-binding resin gel layer. The rate of this accumulation is determined mostly by a number of established factors (probe dimensions, length of the diffusive pathway and the solute diffusion coefficient) and the unknown dynamic factors in the sampling medium: the media temperature, the concentration of the free solute ion and the fraction of the total solute that can be released into its free ion species in the diffusion layer within the deployment time. At the end of the deployment, the total amount of resin-bound solute can be determined and used to calculate the time-averaged concentration of labile solute in the water over the length of the deployment (Davison and Zhang, 2012). In this work, triplicate DGT samplers were deployed into water at each grab sample location for a coincident four-day period inside polyvinyl chloride cages (see Supplementary information (SI) 1). The DGT deployment time and the average river water temperature (mean of daily measurement), were used to calculate the DGT time-averaged metal(loid) concentrations. For background calibration, 'field blank' DGT samples, stored in their pre-packaged weak NaCl solution, were exposed to local site conditions when sampler DGTs were being deployed and collected.

2.2.2. Hydrology

River discharge at each study site was measured each day during the four-day monitoring period using acoustic Doppler current profilers (aDcps; Muste et al., 2004) mounted on rQPOD remote control boats. As water depth varied considerably across the 10 study sites, a Sontek RS5 aDcp was deployed in water depths <6 m (Sumlog, Tagoloan, and Buayan-Malungon catchments) and a Sontek M9 aDcp was deployed in water depths >6 m (Agno, Cagayan, Apayao-Abulug, Abra, Agusan, Ranao, and Cagayan-de-Oro catchments). At least six transects of aDcp measurements were taken across the width of each river on each day to achieve a mean discharge with a coefficient of variation (COV) of <0.03. These daily mean discharge calculations were then combined with concurrent daily unfiltered grab sample measurements to calculate daily catchment solute fluxes. A mean of the four days of fluxes was then used to estimate the annual flux and yield.

Some long-term river flow data were available from permanent gauging stations close to all sampling sites, except the Sumlog (Hoey et al., 2024). However, records were typically not temporally continuous and observations to develop level-discharge rating relationships were too sparse for the discharge estimates to be reliable. Historical information (Hoey et al., 2025) was therefore used to estimate the flow percentile represented by the discharge observations (see SI1).

2.3. Laboratory analyses

2.3.1. Grab water samples

Water samples for trace metal(loid) and major cation analysis (unfiltered and filtered) were acidified to 2 % with trace metal grade nitric acid (HNO_3) in the laboratory. We focused our analyses on As, Co, Cr, Cu, Ni, V due to their frequent detection in this study, known toxicities at low concentrations, and importance to the Philippine mining sector. Trace metal(loid) analysis was performed on an Agilent 7900 ICP-MS. The results were validated using a certified reference material for river water, SLRS-6 (National Research Council Canada, 2015). Nutrient (SO_4^{2-}, HPO_4^{2-}, NO_3^-) analysis was performed on a Metrohm 930 Compact IC Flex with an A Supp 5 column. Detection limits for the analytes are reported in SI1. A number of other analytes were also measured but were not considered further in the rest of this paper (see SI1).

2.3.2. DGT processing and analysis

DGT binding layers were extracted from the samplers and initially acidified in 1 mL of 1 M trace metal free hydrochloric acid (HCl) for elution over a period of 16 h. The binding layers were then removed from the acid and placed into 1 mL of 1 M trace metal free sodium hydroxide (NaOH) for 16 h. The HCl and NaOH eluents were then combined and acidified by adding trace metal-free HCl to achieve a final acid concentration of at least 2 % for ICP-MS analysis. Hydrochloric acid was used in place of HNO_3 for sample acidification and as matrix on the ICP-MS as HNO_3 may experience competition effects with phosphorus when using the LSNX-NP type DGT binding layer (DGT Research, 2025). DGT were eluted for a total of 32 h to achieve the best elution recovery results following Devillers et al. (2017), who determined that an 8–48 h elution was suitable for most analytes but a 24–48 h elution was needed for maximal Cr recovery.

DGT time-averaged concentrations (C_{DGT}) were calculated using Fick's law: $C_{DGT} = M \times \delta^{mdl}/(D^{mdl} \times A_p \times t)$, where M is the mass of solute bound by the resin layer, δ^{MDL} is the thickness of the material diffusion layer (0.094 cm), D^{mdl} is the solute diffusion coefficient in the diffusion layer (obtained from DGT Research Ltd.), A_p is the geometric area of the exposed DGT device window, and t deployment time (Davison and Zhang, 2012). To calculate M from the ICP-MS measured eluent concentration (C_e) the formula $M = C_e(V_{bl} + V_e)/f_e$ was used, where V_{bl} is the volume of the DGT binding layer (0.2 mL), V_e is the volume of eluent (2 mL), and f_e is the elution factor (0.9 for a 90 % complete elution).

2.4. Statistical analysis

Catchment flux and yield data were found to be non-normally distributed (Kolmogorov–Smirnov tests ($p < 0.05$)) and were Log_{10}-transformed to achieve normality ($p > 0.05$). One-way ANOVA were used to compare fluxes and yields across catchment groupings ('*large and small-scale mining*' and '*mineralised, no large-scale mining*') with no significant differences observed ($p > 0.05$). Levene's tests confirmed homogeneity of variance ($p > 0.05$). Unfiltered, filtered, and C_{DGT} concentration data were also log_{10}-transformed after non-normality was confirmed, as above. One-way repeated measures ANOVA was used to assess differences among concentration fractions (unfiltered, filtered, and C_{DGT}). Two-way ANOVA tests examined differences in concentrations with catchment and analyte as fixed factors, as well as interactions between the factors. Concentrations between catchment groupings were compared using one-way ANOVA. All analyses were conducted using OriginPro 2025 (OriginLab Corporation, 2025) and significance was assumed when $p < 0.05$, if significance was found then a Tukey's post-hoc test was ran for pairwise comparison.

3. Results

3.1. Catchment metal(loid) and nutrient flux

Our catchment monitoring represented approximately 19 % of the total land area of the Philippines. Analysis of historical hydrological data (see SI1) demonstrates our sampling captured moderate to very low flows across each of our catchments; we therefore assumed that fluxes calculated from these data were representative of baseline (low flow) conditions. The highest estimated annual fluxes across our catchments (Fig. 2) were for nutrients SO_4 (432,195 t yr^{-1}), followed by NO_3

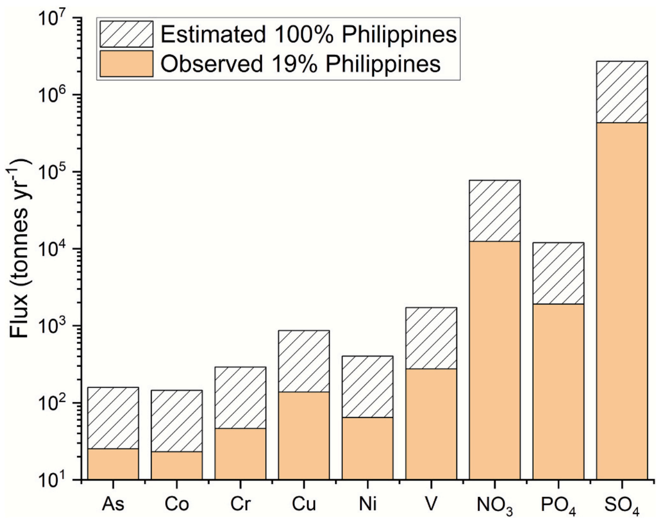


Fig. 2. Estimated annual flux of trace metal(loid)s and nutrients from observed measurements from 10 Philippine catchments, and scales to the whole country's land area.

(12,389 t yr^{-1}), and PO_4 (1908 t yr^{-1}). Trace metal(loid) fluxes were considerably lower, with V having the highest flux (274 t yr^{-1}) and Co having the lowest (23 t yr^{-1}).

Scaling these data to the whole of the Philippines (298,170 km^2), we estimated national baseline fluxes for each of our metal(loid)s and nutrients, with metal(loid) fluxes generally in the range of 10^2 to 10^3 t yr^{-1} and nutrient fluxes ranging between 10^4 and 10^6 t yr^{-1}. The Philippines accounts for 0.23 % of global land area (World Bank Group, 2022); therefore, we could expect Philippine baseline fluxes to account for a similar percentage of global estimates. The most recent global flux estimates for Co, Cr, Cu and Ni (Poulton and Raiswell, 2000) were 4×10^3, 4×10^4, 6×10^4 and 2×10^4 t yr^{-1}, respectively. Our Philippines estimates for Co, Cr, Cu and Ni (1.22×10^2, 2.43×10^2, 7.25×10^2, 3.38×10^2 t yr^{-1} respectively) accounted for 3 % Co, 0.6 % Cr, 1.2 % Cu and 1.7 % of Ni fluxes globally.

A closer look at the contaminant loads from our 10 study catchments (Fig. 3) shows that the Cagayan had the highest combined total flux (1.44×10^5 t yr^{-1}), and the Agno had the highest combined total yield (2.28×10^4 kg km^{-2} yr^{-1}; catchment yield representing flux normalised to catchment area). Meanwhile, the Sumlog catchment had the lowest combined total flux (2.13×10^3 t yr^{-1}), and the Ranao had the lowest combined total yield (1.54×10^3 kg km^{-2} yr^{-1}). Out of the analytes measured, SO_4 accounted for above 94 % of catchment flux and yield in all catchments except for the Cagayan-de-Oro (46 %) and Tagoloan (60 %).

The Cagayan and Tagoloan catchments were of particular interest as they frequently (66 % of the time) exhibited the highest metal(loid) and nutrient fluxes among all catchments and, as a mean, accounted for 47.5 % of each metal(loid) and nutrients' total catchment flux. The Tagoloan catchment was notable for its high Ni flux (57.5 t yr^{-1}), accounting for 89.5 % of the total Ni measured across all catchments (64.3 t yr^{-1}), whilst the Cagayan catchment had a particularly high PO_4 flux (584 t yr^{-1}), accounting for 30.6 % of the total (1908 t yr^{-1}).

Despite often having some of the largest metal(loid) and nutrient fluxes, the Cagayan catchment had some of the lowest yields (Fig. 4), while Cagayan-de-Oro and Tagoloan tended to have the highest and second highest yields and made disproportionate contributions to metal (loid) and nutrient loads out to sea.

There were no statistically significant differences between catchments with '*large and small-scale mining*' activities and '*mineralised, no large-scale mining*', in terms of total metal(loid) or nutrient fluxes or yields ($p > 0.05$). There were, however, statistically significant differences when comparing individual metal(loid)s and nutrients. Sulfate fluxes and yields, as well as As fluxes, were found to be significantly greater in '*large and small-scale mining*' catchments ($p < 0.05$).

3.2. Water quality and metal(loid) bioavailability

We focused our analyses on As, Co, Cr, Cu, Ni, V across the 10 studied Philippine catchments due to their frequent detection in this study, known toxicities at low concentrations, and importance to the Philippine mining sector. The cumulative trace metal(loid) concentrations varied across each of the catchments and in each of the different fractions (unfiltered, filtered and C_{DGT}). This was most clear in the Tagoloan catchment where the mean unfiltered Ni concentration was 38.6 μg L^{-1}, the filtered fraction was 0.8 μg L^{-1}, and the C_{DGT} fraction was 1.4 μg L^{-1} (Fig. 5). When compared to other catchments, only the Abra, Agno, Apayao-Abulug and Cagayan also contained detectable levels of Ni in their unfiltered fraction, and those that did contained less than 10 % of the Tagoloan's concentration. Similar, although less extreme, differences between catchments and fractions were recorded for all of the trace metal(loid)s (Fig. 5).

In the Philippines, river water quality is classified under five broad surface water guidelines laid out by the Department of Environment and Natural Resources (2016) (see SI1). The strictest limits for each (unfiltered) metal(loid) within these guidelines are As (0.01 mg L^{-1}), Cu (0.02 mg L^{-1}) and Ni (0.02 mg L^{-1}), whilst no guidelines exist for Co, Cr, and V. In our study, these metal(loid) concentration guidelines were only exceeded within the Tagoloan catchment, and only for Cu and Ni. Guidelines also exist for the nutrients, NO_3 (7 mg L^{-1}), PO_4 (0.025 mg L^{-1}), and SO_4 (250 mg L^{-1}). Mean NO_3 and SO_4 concentrations in our study were below these guidelines. However, mean PO_4 concentrations were consistently above the guidelines in all catchments.

Unfiltered trace metal(loid) concentrations were found to be significantly different ($p < 0.05$) from each other within each of our study catchments and cumulatively different across our 10 study catchments (Fig. 5). Additionally, the unfiltered, filtered, and C_{DGT} fractions were found to be significantly different from each other ($p < 0.05$). In the filtered fraction 84 % of sample concentrations were lower than their equivalent in the unfiltered fraction, and in the C_{DGT} fraction 94 % of sample concentrations were lower than their equivalent in the unfiltered fraction, along with 87 % being lower than their equivalent filtered fraction. No significant differences were found in any of the concentration data when '*large and small-small scale mining*' catchments were compared to '*mineralised, no large-scale mining*' catchments ($p > 0.05$).

Ratios (C_{DGT} / unfiltered or filtered concentration) were used to compare C_{DGT} measurements to mean unfiltered and filtered measurements to assess bioavailability. High ratios (near 1) indicated a large fraction of the unfiltered and/or filtered fraction was measured by C_{DGT}, and therefore was considered bioavailable, whilst low ratios indicated the opposite. Concentrations, as a mean, measured by DGT were more similar to filtered concentrations (ratio nearer 1) (Fig. 6B) than unfiltered concentrations (Fig. 6A), with C_{DGT} concentrations representing 42 % of the unfiltered concentration (as a mean), and 78 % of the filtered concentration (as a mean upon removing one large outlier; 99 % with it included). Filtered and unfiltered Co, Cr, Cu, and Ni concentrations were often close to zero or below detection limits, which impacted their ratio calculations leading to high ratios (above 1) or low ratios (near zero). This was less of a problem with C_{DGT}, that accumulates solute over the length of the deployment and hence can measure relatively lower concentrations than in water samples themselves. High ratios (above 1) could also have been caused due to the C_{DGT} fraction being calculated from a time-averaged sample that has measured conditions over the length of the deployment, rather than measuring 'snapshot' values like the unfiltered and filtered fractions.

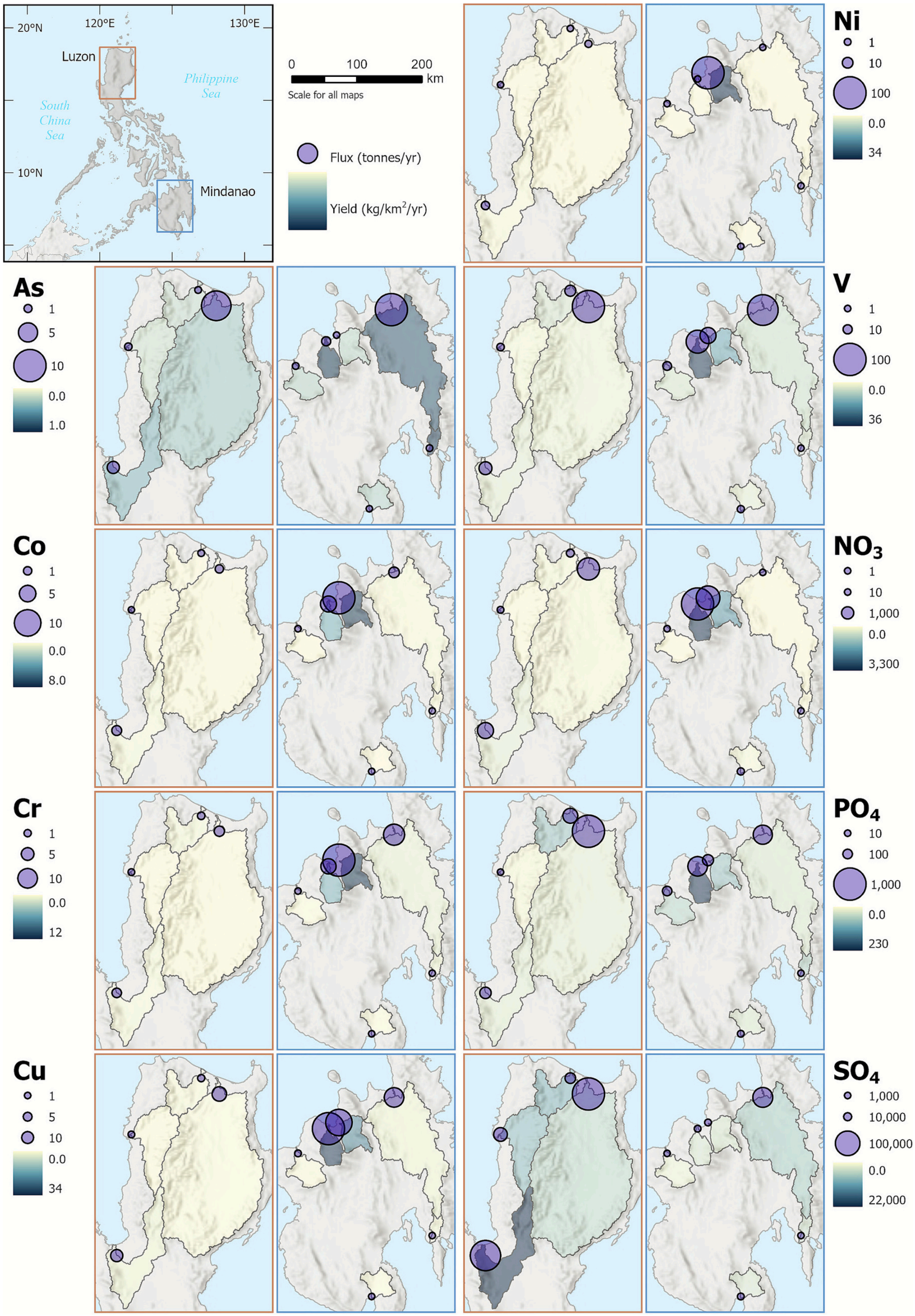


Fig. 3. Mean ($n = 4$ days) estimated yearly unfiltered trace metal(loid) and nutrient flux and subsequent catchment yield nationally across 10 Philippine catchments. Flux in tonnes yr^{-1} at the outlet of each catchment is represented by a purple circle. Yield in kg km^{-2} yr^{-1} is represented by the catchment background colour. Note that the scales are different for each trace metal(loid) and nutrient due to the different magnitudes of fluxes and yields (see SI2).

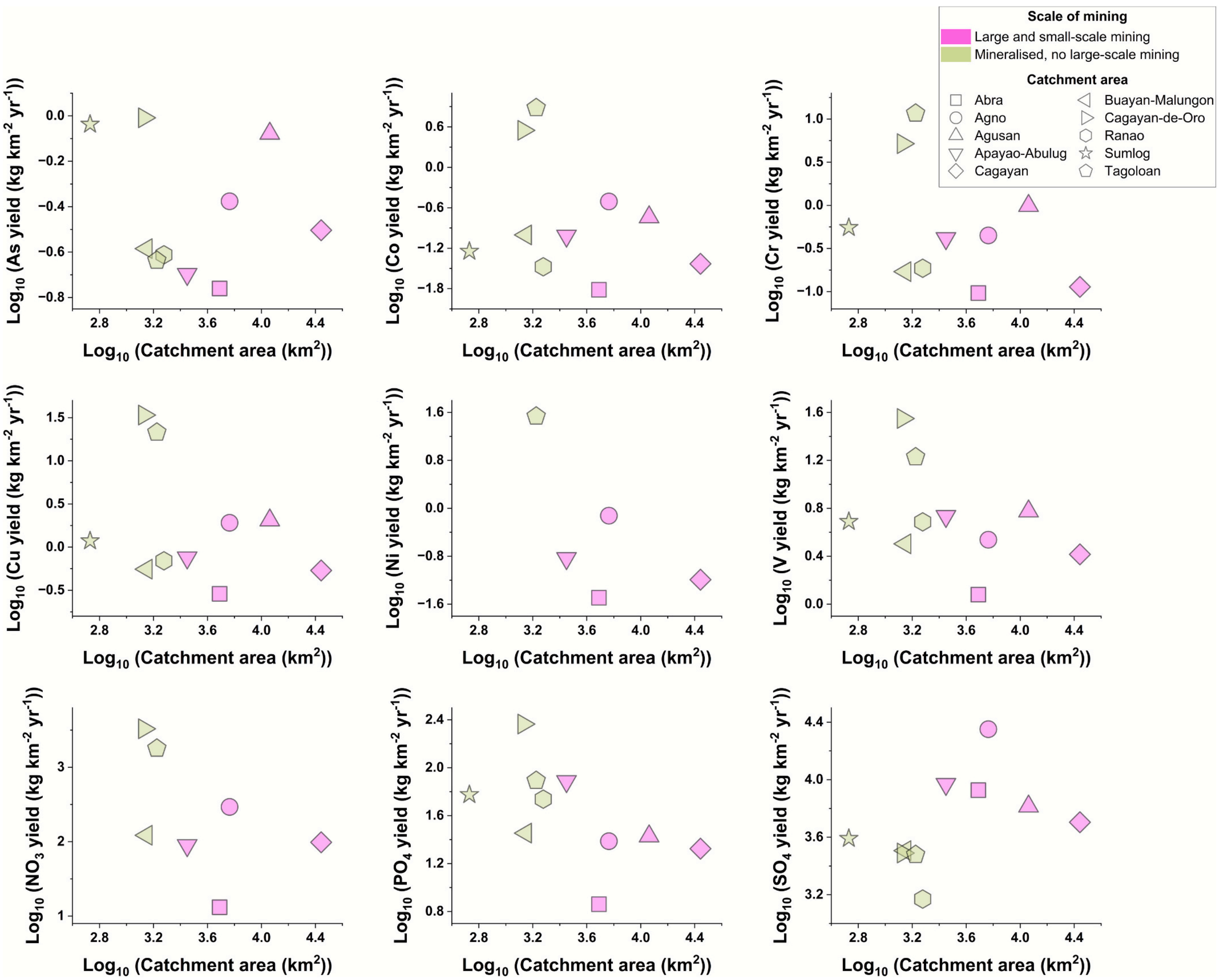


Fig. 4. $\log_{10}$ comparison of mean annual trace metal(loid) and nutrient yield and area across 10 Philippine catchments. Catchments are omitted if concentrations were below detection limits (see SI2).

4. Discussion

4.1. The Philippines contributes proportionally large amounts of metal (loids) to global oceans

Martin and Meybeck (1979) compiled the first global estimates of particulate and trace metal(loid) flux from the land to the oceans. They gathered concentration data from 20 of the world's major rivers (often one sample per river), covering approximately 25 % of the global land drainage area to oceans, and used a discharge estimate based on a global theoretical calculation of the water cycle (Baumgartner and Reichel, 1975) to calculate their metal(loid) flux (Martin and Meybeck, 1979). Their estimates have been used as a global reference for metal(loid) fluxes (Carey et al., 2002; Hollister et al., 2022), with refinement of their dissolved flux calculations by Martin and Whitfield (1983) and Poulton and Raiswell (2000). Poulton and Raiswell (2000), estimated global Co, Cr, Cu and Ni dissolved fluxes as 4×10^3, 4×10^4, 6×10^4 and 2×10^4 t yr^{-1}, respectively, and based on land area alone, the Philippines should account for 0.23 % of these fluxes (1×10^1, 1×10^2, 1.5×10^2 and 5×10^1 t yr^{-1}, respectively). Our results provide the first direct assessment of this contribution and indicate that the Philippines contributes unfiltered fluxes of 1.22×10^2, 2.43×10^2, 7.25×10^2, 3.38×10^2 t yr^{-1} of Co, Cr, Cu and Ni, respectively, which represents 3 %, 0.6 %, 1.2 % and 1.7 % of Co, Cr, Cu and Ni global flux. This suggests that there is likely an under representation of the contribution of smaller watersheds and Pacific Island nations in global metal(loid) flux calculations.

Estimates of global flux and our estimates of Philippines flux should be treated with caution due to the theoretical scaling applied and the scarcity of datapoints. The global flux estimates lack any observed discharge measurements, whilst both the global and Philippines datasets apply scaling from 20 to 25 % of land area to 100 %. Our estimates also potentially underestimate flux due to our sampling being biased towards low to moderate flows (see SI1), potentially missing large flushing events such as those that occur during a typhoon, of which the Philippines experiences five per year on average (Williams et al., 2020). Estimates of chemical flux typically use long-term averages of river discharge and chemical concentration rather than observed data (Zhang and Hirsch, 2019). Given that large flushing events are known to increase sediment and dissolved loads (Blaen et al., 2017; Lloyd et al., 2016) these would have been accounted for within the theoretical global discharge value but not our own. Our results are unusual in that they combine measured values of concurrent discharge and concentration to generate nation-wide estimates of fluxes across the Philippines. This is the first Philippine national-scale ground-truth quantification of the

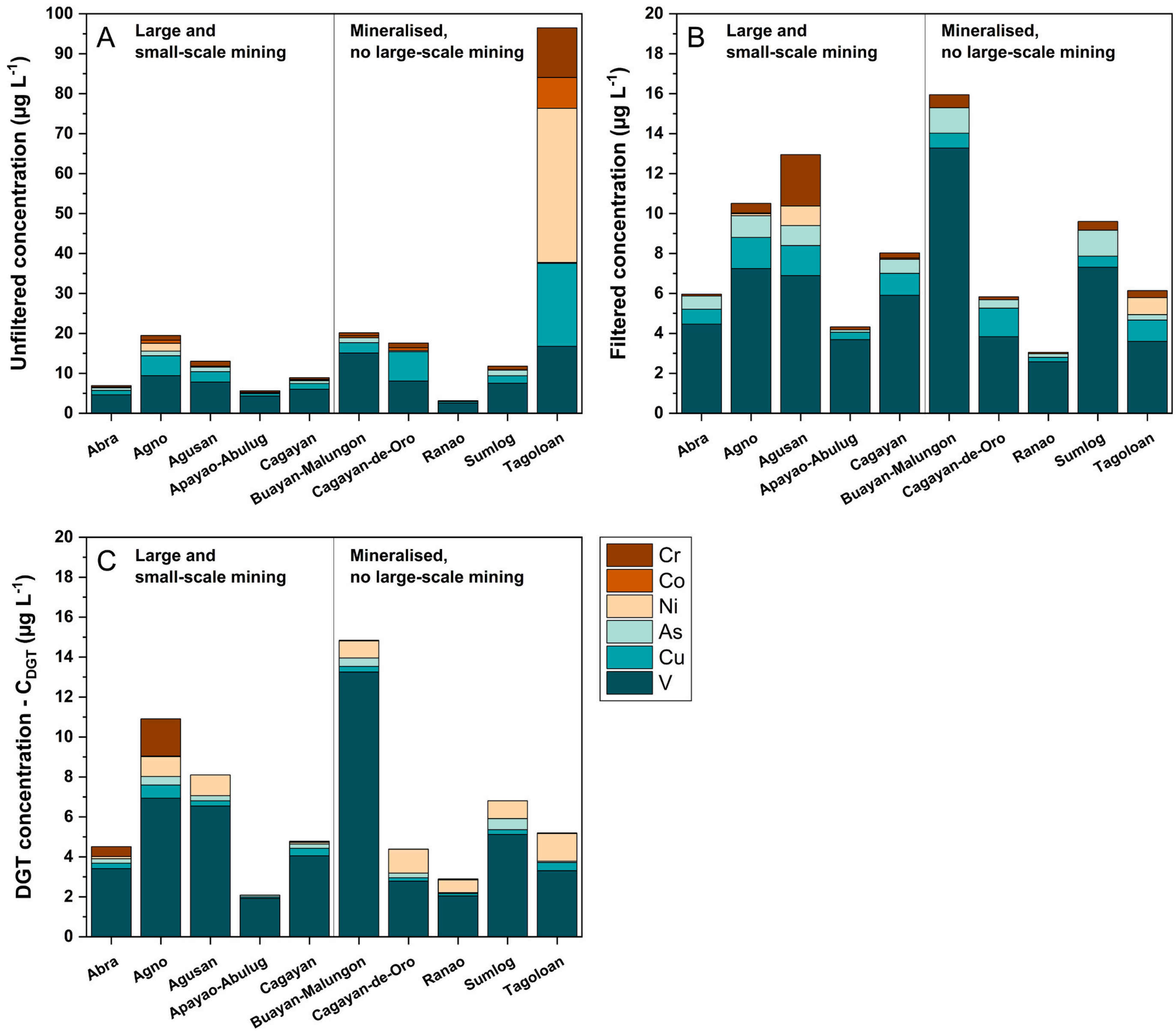


Fig. 5. Cumulative plots showing mean ($n = 4$) unfiltered (A), filtered (B), and C_{DGT} (C) trace metal(loid) concentrations from each of the 10 national catchments. Catchments have been sorted into groups based on whether they have '*large and small-scale mining*' or are '*mineralised, no large-scale mining*' (see SI2).

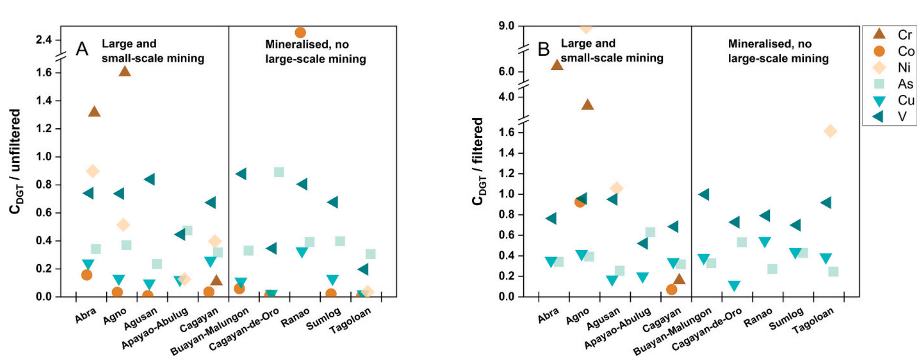


Fig. 6. Ratios of C_{DGT} to unfiltered (A) and filtered (B) concentrations. High ratios (near 1) indicate a large fraction of the unfiltered and/or filtered fraction was measured by C_{DGT}, and therefore represent high bioavailability, whilst low ratios (near 0) indicate the metal(loid) was less bioavailable. Catchments are sorted into groups based on whether they contain '*large and small-scale mining*' or are '*mineralised, no large-scale mining*' (see SI2).

trace metal(loid) and nutrient flux from land to the sea; and sets a reference point from which the impacts of future mining activities and mine site rehabilitation can be evaluated.

4.2. An absence of flux measurements limits the identification of contaminant sources within catchments

Interestingly, when comparing fluxes and yields between '*large and small-scale mining*' catchments and '*mineralised, no large-scale mining*' catchments our data show no significant differences between the two groups. This suggests that background concentrations of metal(loid)s and nutrients are elevated within some Philippine catchments. We can see this in Fig. 4 in which the Cagayan-de-Oro and Tagoloan catchments have the highest yields for every metal(loid) (except for As (Tagoloan) and Ni (Cagayan-de-Oro)) despite both being small '*mineralised, no large-scale mining*' catchments. These catchments are therefore contributing proportionally more metal(loid)s to the ocean than the '*large and small-scale mining*' catchments, despite elevated metal(loid) fluxes often being associated with, and attributed to, the presence of mining (Mayes et al., 2013). This highlights a crucial consideration for future management within the Philippines: background mineralisation can yield metal(iod) levels equivalent to and greater than those from mining activities within catchments. Therefore, without monitoring catchment fluxes, it becomes hard to disentangle background and anthropogenic contaminant sources and thus assess the impacts of mining operations.

Beyond mining, Philippine catchments face pressures from agriculture, industry, and urbanisation, with individual catchments within our study being shown to face NO_3 and PO_4 pressures that are commonly associated with agricultural pollution (Ockenden et al., 2017). This is seen particularly in the Cagayan-de-Oro and Tagoloan catchments where both NO_3 and PO_4 fluxes and yields are high, and no large-scale mining operations take place. Monitoring of nutrient and metal(loid)s is also important for the Philippines, as excessive nutrient inputs into catchments can lead to eutrophication which can have detrimental effects on biodiversity by creating hypoxic or anoxic zones in receiving waters (Chislock et al., 2013). Given that several marine protected areas exist directly outside of the mouths of the Cagayan-de-Oro and Tagoloan catchments (Horigue et al., 2012), prioritising future monitoring of nutrient fluxes from these catchments can help with conservation efforts in these areas to protect the local environment and industry (Domingo et al., 2024).

Our baseline data have shown the variability in metal(loid) and nutrient fluxes and yields across the Philippines. However, continued routine monitoring of catchment flux is necessary to identify sources of contaminants, document the impacts of future anthropogenic activities, and evaluate the efficacy of any remediation strategies. One well established method of monitoring catchment flux that has been integral to assessing legacy and contemporary mining impacts in the USA, helping to shape catchment management approaches and remediate mine sites, is the total maximum daily load (TMDL) model (H. Wang et al., 2025). This model can be used to establish the total volume of contaminants that can be discharged to a waterbody whilst maintaining environmental quality standards. The approach allocates contaminant loads to identified point and non-point sources of contamination (e.g. mining) within a catchment (United States Environmental Protection Agency, 2024). If these loads are exceeded, this will be observed downstream as a breach of environmental quality standards. The TMDL approach therefore uses river contaminant flux data to set limits on the volume of contaminants that can be discharged to rivers in order to protect and improve river water quality. Unlike the USA, the Philippines has the opportunity to incorporate a similar TMDL modelling and monitoring approach to their catchment management before the predicted growth of their mining sector.

4.3. Universal river water quality standards for trace metal(loid)s in Philippine rivers may misrepresent ecosystem risk

In addition to gaining an understanding of contaminant mass transport, accurate measurement of bioavailable concentrations are critical to determining environmental risk and potential ecotoxicity. In the Philippines, surface water quality guidelines are broad; covering drinking water protected areas to navigational waters within five classifications and setting limits that are predominantly based solely on unfiltered concentrations (Department of Environment and Natural Resources, 2016). In Europe and the USA, environmental guidelines for river water quality are based on filtered and bioavailable fractions as these are widely established to closely represent toxicity in natural waters (European Commission, 2009; United States Environmental Protection Agency, 1991). That said, the unfiltered fraction is still monitored as particulates can re-release previously bound metal(loid)s into the unfiltered (potentially dissolved) fraction (Adams et al., 2020), biota can still ingest and uptake metal(loid) particulates (United States Environmental Protection Agency, 2021), and measuring the unfiltered fraction ensures that total metal(loid) fluxes are not underestimated (Ccanccapa-Cartagena et al., 2023). Additionally, although the unfiltered and filtered fractions can be measured directly, there is no agreed upon method for the direct measurement of the bioavailable fraction. Instead, this fraction is typically predicted by numerical models. The Metals Bioavailability Assessment Tool (M-BAT) is used in the UK to make assessments based on filtered concentrations alongside physicochemical parameters to predict bioavailability (UKTAG, 2014). The Philippines would need to create a similar model to recognise differences in the bioavailability of different contaminants, or use a direct measurement of bioavailability if they are to consider creating new guidelines.

Diffusive gradients in thin-films are thought to sample solutes in water in a way that emulates uptake by biota, therefore reflecting bioavailability and potential toxicity (R. Wang et al., 2025). This includes considering time-weighted average concentrations that integrate contaminate fluxes over timescales that are more relevant to local biota than the single measurements from grab samples (Altier et al., 2019; Huang et al., 2016).

Utilising DGT in this study of Philippines rivers, we demonstrate how metal(loid) bioavailability can vary between catchments (Figs. 5 and 6). In Fig. 6, for example, Cr was shown to be highly bioavailable (ratio > 1) in the Abra and Agno catchments but had limited bioavailability in the Cagayan (ratio < 1). We can see similarities in the Tagoloan catchment (Fig. 5), where the Cr concentration in the unfiltered fraction is close to $12\ \mu g\ L^{-1}$, whilst in all other catchments it is close to $1\ \mu g\ L^{-1}$. This could indicate a cause for concern, but the filtered Cr concentration is similar to all other catchments (near $0.5\ \mu g\ L^{-1}$) and the C_{DGT} concentration is below the ICP-MS detection limit (see SI1). This suggests that the Cr present in the Tagoloan's unfiltered fraction is not bioavailable and therefore potentially less harmful to biota than in other catchments (unless in toxic Cr(VI) form which LSNX-NP DGT do not bind (Gao et al., 2019)). Cumulative metal(loid) concentrations in the unfiltered, filtered, and C_{DGT} fractions were all found to be significantly different from each other, individual metal(loid) concentrations were found to be significantly different from each other, and individual catchment cumulative metal(loid) concentrations were also significantly different from each other. This variability between fractions, metal(loid)s, and catchments suggests there may be a need for the Philippines to develop catchment specific concentration guidelines for each metal(loid) and potentially consider creating filtered and bioavailable guidelines alongside unfiltered ones to help evaluate ecological risk. DGT ratios (C_{DGT} / unfiltered or filtered concentration) could be the first step towards this challenge and creating bioavailable environmental quality standards as has been recently accomplished with the EU Monitool project (Rodríguez et al., 2021).

5. Conclusions

We have established the first nationwide ground-truthed baselines of hydrology and water quality in the Philippines, providing a reference point for future management and a statement of current condition. Although based on limited coverage of the hydrological regime, our national-scale sampling has shown that globally the Philippines contributes proportionally large quantities of metal(loid) flux to the oceans, accounting for 3 %, 0.6 %, 1.2 % and 1.7 % of Co, Cr, Cu and Ni, respectively, compared to an expected estimate of 0.23 % based on land area. Additionally, our results have shown that background mineralisation, not just mining activities, can act as a large contributor to metal(loid) yields and fluxes within catchments. This has demonstrated the importance of establishing metal(loid) flux for the understanding of mass transport within catchments and has highlighted the need for management tools such as TMDLs (total maximum daily load) to identify and apportion metal(loid) and nutrient loads.

Our approach has presented several scientific methods that could be adopted in future national monitoring programmes and has shown that metal(loid) and nutrient concentrations, speciation, fluxes, and yields all vary across national catchments. This has emphasised the benefits of using multiple methods of assessment to make catchment management decisions and has demonstrated that environmental quality standards should be uniquely determined for each catchment. Our study also took the first steps towards creating C_{DGT} environmental quality standards for metal(loid) bioavailability in the Philippines, establishing a bioavailability monitoring framework that can be expand upon. Beyond the Philippines, our methodology can be adapted in other mineralised nations, allowing for the effective monitoring and reporting of future mining impacts within catchments as well as the assessment of remedial interventions. Critical future research needs in the Philippines are to expand coverage of metal(loid), nitrate and phosphate fluxes and C_{DGT} spatially and temporally, to capture changes in metal(loid) bioavailability and flux driven by seasonal and event-scale hydrological and biogeochemical processes.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2025.181192.

CRediT authorship contribution statement

Emma Biles: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Richard David Williams:** Writing – review & editing, Project administration, Investigation, Funding acquisition, Conceptualization. **Decibel Faustino-Eslava:** Project administration, Funding acquisition, Conceptualization. **Loucel Cui:** Writing – review & editing, Project administration, Investigation, Funding acquisition, Conceptualization. **Francis Ian Gonzalvo:** Investigation. **Kim Bryan Cabrera:** Investigation. **Manilyn Casa:** Investigation. **Craig MacDonell:** Visualization, Formal analysis. **Maria Regina V. Regalado:** Investigation. **Laura Quick:** Investigation. **Justine Perry Domingo:** Writing – review & editing. **Trevor Hoey:** Funding acquisition, Formal analysis. **Niklas J. Lehto:** Writing – review & editing. **Karen Ann Hudson-Edwards:** Writing – review & editing, Funding acquisition. **Thomas J. Coulthard:** Writing – review & editing, Funding acquisition. **Patrick Byrne:** Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Funding acquisition, Conceptualization.

Funding

This investigation was funded by the Department of Science and Technology - Philippine Council for Industry, Energy, and Emerging Technology Research and Development (DOST-PCIEERD) and the UK Research and Innovation - Natural Environment Research Council (UKRI-NERC), grant NE/W006871/1.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Local Government Units are thanked for assistance in enabling monitoring and sampling activities.

Data availability

Data used to produce Figs. 3 to 6 can be found in Supplementary Information 2 at https://doi.org/10.1016/j.scitotenv.2025.181192.

References

Adams, W., Blust, R., Dwyer, R., Mount, D., Nordheim, E., Rodriguez, P.H., Spry, D., 2020. Bioavailability assessment of metals in freshwater environments: a historical review. Environ. Toxicol. Chem. 39 (1), 48–59. https://doi.org/10.1002/etc.4558.

Adil, L., Eckstein, D., Kunzel, V., Schafer, L., 2025. Climate Risk Index 2026 – who suffers most from extreme weather events? https://www.germanwatch.org/en/93310.

Altier, A., Jiménez-Piedrahita, M., Uribe, R., Rey-Castro, C., Galceran, J., Puy, J., 2019. Time weighted average concentrations measured with Diffusive Gradients in Thin films (DGT). Anal. Chim. Acta 1060, 114–124. https://doi.org/10.1016/J.ACA.2019.01.056.

Arendt, R., Bach, V., Finkbeiner, M., 2022. The global environmental costs of mining and processing abiotic raw materials and their geographic distribution. J. Clean. Prod. 361, 132232. https://doi.org/10.1016/J.JCLEPRO.2022.132232.

Aureo, W., Reyes, T., Mutia, F.C., Jose, R., Sarnowski, M.B., 2020. Diversity and composition of plant species in the forest over limestone of Rajah Sikatuna protected landscape, Bohol, Philippines. Biodivers. Data J. 8, 1–23.

Australian Trade and Investment Commission, 2023. Mining in the Philippines: a new chapter. URL, Austrade. https://www.austrade.gov.au/en/news-and-analysis/analysis/mining-in-the-philippines-a-new-chapter. (Accessed 8 May 2025) (WWW Document).

Baumgartner, A., Reichel, E., 1975. World Water Balance: Mean Annual Global, Continental and Maritime Precipitation, Evaporation and Runoff. Elsevier Science Ltd.

Blaen, P.J., Khamis, K., Lloyd, C., Comer-Warner, S., Ciocca, F., Thomas, R.M., MacKenzie, A.R., Krause, S., 2017. High-frequency monitoring of catchment nutrient exports reveals highly variable storm event responses and dynamic source zone activation. J. Geophys. Res. Biogeosci. 122, 2265–2281. https://doi.org/10.1002/2017JG003904.

Boothroyd, R.J., Williams, R.D., Hoey, T.B., MacDonell, C., Tolentino, P.L.M., Quick, L., Guardian, E.L., Reyes, J.C.M.O., Sabillo, C.J., Perez, J.E.G., David, C.P.C., 2023. National-scale geodatabase of catchment characteristics in the Philippines for river management applications. PLoS One 18, e0281933. https://doi.org/10.1371/JOURNAL.PONE.0281933.

Byrne, P., Onnis, P., Runkel, R.L., Frau, I., Lynch, S.F.L., Edwards, P., 2020. Critical shifts in trace metal transport and remediation performance under future low river flows. Environ. Sci. Technol. 54, 15742–15750. https://doi.org/10.1021/acs.est.0c04016.

Carey, A.E., Nezat, C.A., Lyons, W.B., Kao, S., Hicks, D.M., Owen, J.S., 2002. Trace metal fluxes to the ocean: the importance of high-standing oceanic islands. Geophys. Res. Lett. 29, 2–5. https://doi.org/10.1029/2002gl015690.

Carpenter, K.E., Springer, V.G., 2005. The center of the center of marine shore fish biodiversity: the Philippine Islands. Environ. Biol. Fish 72, 467–480. https://doi.org/10.1007/S10641-004-3154-4/METRICS.

Ccanccapa-Cartagena, A., Chavez-Gonzales, F.D., Paredes, B., Vera, C., Gutierrez, G., Valencia, R., Lucia Paz Alcázar, A., Zyaykina, N.N., Filley, T.R., Jafvert, C.T., 2023. Seasonal differences in trace metal concentrations in the major rivers of the hyper-arid southwestern Andes basins of Peru. J. Environ. Manag. 344, 118493. https://doi.org/10.1016/J.JENVMAN.2023.118493.

Chislock, M.F., Doster, E., Zitomer, R.A., Wilson, A.E., 2013. Eutrophication: causes, consequences, and controls in aquatic ecosystems. Nat. Educ. Knowl. 4, 10.

Cooke, D.R., Deyell, C.L., Waters, P.J., Gonzales, R.I., Zaw, K., 2011. Evidence for magmatic-hydrothermal fluids and ore-forming processes in epithermal and porphyry deposits of the Baguio district, Philippines. Econ. Geol. 106, 1399–1424.

Cox, B., Innis, S., Kunz, N.C., Steen, J., 2022. The mining industry as a net beneficiary of a global tax on carbon emissions. Commun. Earth Environ. 31 (3), 1–8. https://doi.org/10.1038/s43247-022-00346-4.

Davison, W., Zhang, H., 2012. Progress in understanding the use of diffusive gradients in thin films (DGT) – back to basics. Environ. Chem. 9, 1–13. https://doi.org/10.1071/EN11084.

Dehkordi, M.M., Nodeh, Z.P., Dehkordi, K.S., Salmanvandi, H., Khorjestan, R.R., Ghaffarzadeh, M., 2024. Soil, air, and water pollution from mining and industrial activities: sources of pollution, environmental impacts, and prevention and control methods. Results Eng. 23, 102729. https://doi.org/10.1016/J.RINENG.2024.102729.

Department of Environment and Natural Resources, 2016. DENR Administrative Order No. 2016-08.
Department of Environment and Natural Resources - Mines and Geosciences Bureau, 2025. Minerals Industry at a Glance.
Devillers, D., Buzier, R., Charriau, A., Guibaud, G., 2017. Improving elution strategies for Chelex®-DGT passive samplers. Anal. Bioanal. Chem. 409, 7183–7189. https://doi.org/10.1007/S00216-017-0680-4/TABLES/2.
DGT Research, 2025. Metals (Cationic and Oxyanionic) and P Using a Chelex/Tioxide BL.
Domingo, J.P.T., Jenkin, G.R.T., Quick, L., Williams, R.D., Hudson-Edwards, K.A., Tortajada, C., Byrne, P., Coulthard, T.J., Padrones, J.T., Crane, R., Gibaga, C.R.L., Vasilopoulos, G., Tungpalan, K., Samaniego, J.O., Biles, E., Tanciongco, A.M., Chambers, J.E., Quimado, M.O., Bautista, A.T., Gonzalvo, F.I.P., Aquino, K.A., Swift, R.T., Cui, L.E., Chalkley, R., Tibbett, M., Faustino-Eslava, D.V., Arcilla, C.A., 2024. Sustainable mining in tropical, biodiverse landscapes: environmental challenges and opportunities in the archipelagic Philippines. J. Clean. Prod. 468, 143114. https://doi.org/10.1016/J.JCLEPRO.2024.143114.
Environment Agency, 2025. Abandoned Metal Mines in England: Baseline Length of Rivers and Estuaries Polluted by Harmful Metals. GOV.UK.
Esri, 2025. World elevation coverage map. URL. https://www.arcgis.com/home/item.html?id=3af669838f594b378f90c10f98e46a7f. (Accessed 12 May 2025) (WWW Document).
European Commission, 2009. Common Implementation Strategy for the WFD, Guidance Document No. 19, Guidance on Surface Water Chemical Monitoring.
Gao, L., Gao, B., Xu, D., Sun, K., 2019. In-situ measurement of labile Cr(III) and Cr(VI) in water using diffusive gradients in thin-films (DGT). Sci. Total Environ. 653, 1161–1167. https://doi.org/10.1016/J.SCITOTENV.2018.10.392.
Global Administrative Areas, 2022. Download GADM data (version 4.1). URL. https://gadm.org/download_country.html. (Accessed 12 May 2025) (WWW Document).
GOV.PH, 2021. Amending Section 4 of Executive Order No. 79, S. 2012. Institutionalizing and Implementing Reforms in the Philippine Mining Sector, Providing Policies and Guidelines to Ensure Environmental Protection and Responsible Mining in the Utilization of Mineral. Bureau of Customs.
Gutierrez, M., 2020. Editorial for Special Issue "Sustainable Use of Abandoned Mines.". Minerals 10, 1015. https://doi.org/10.3390/MIN10111015.
Hoey, T.B., Tolentino, P., Guardian, E., Perez, J.E.G., Williams, R., Boothroyd, R., David, C.P.C., Paringit, E., 2024. Flood estimation for ungauged catchments in the Philippines: Annual Maximum Flow (AMAX) and catchment properties data - Enlighten Research Data. URL, Univ. Glas. https://researchdata.gla.ac.uk/1666/. (Accessed 13 May 2025) (WWW Document).
Hoey, T.B., Tolentino, P.L.M., Guardian, E.L., Perez, J.E.G., Williams, R.D., Boothroyd, R. J., David, C.P.C., Paringit, E.C., 2025. Flood estimation for ungauged catchments in the Philippines. Hydrol. Earth Syst. Sci. 29, 6181–6200. https://doi.org/10.5194/HESS-2024-188.
Hollister, A.P., Leon, M., Scholten, J., Beek, P., Gledhill, M., Koschinsky, A., 2022. Distribution and flux of trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U) in the Amazon and Pará River estuary and mixing plume. ESS Open Arch. 1–28.
Horigue, V., Aliño, P.M., White, A.T., Pressey, R.L., 2012. Marine protected area networks in the Philippines: trends and challenges for establishment and governance. Ocean Coast. Manag. 64, 15–26. https://doi.org/10.1016/j.ocecoaman.2012.04.012.
Huang, J., Bennett, W.W., Welsh, D.T., Li, T., Teasdale, P.R., 2016. "Diffusive gradients in thin films" techniques provide representative time-weighted average measurements of inorganic nutrients in dynamic freshwater systems. Environ. Sci. Technol. 50, 13446–13454. https://doi.org/10.1021/ACS.EST.6B02949/SUPPL_FILE/ES6B02949_SI_001.PDF.
Huffman, G., Bolvin, D., Braithwaite, D., Hsu, K., Joyce, R., Xie, P., 2021. Index of. URL. https://arthurhouhttps.pps.eosdis.nasa.gov/. (Accessed 12 May 2025) (WWW Document).
International Energy Agency, 2023. Energy Technology Perspectives 2023.
Licuanan, W.Y., Robles, R., Reyes, M., 2019. Status and recent trends in coral reefs of the Philippines. Mar. Pollut. Bull. 142, 544–550. https://doi.org/10.1016/J.MARPOLBUL.2019.04.013.
Lloyd, C.E.M., Freer, J.E., Johnes, P.J., Collins, A.L., 2016. Using hysteresis analysis of high-resolution water quality monitoring data, including uncertainty, to infer controls on nutrient and sediment transfer in catchments. Sci. Total Environ. 543, 388–404. https://doi.org/10.1016/J.SCITOTENV.2015.11.028.
Macklin, M.G., Thomas, C.J., Mudbhatkal, A., Brewer, P.A., Hudson-Edwards, K.A., Lewin, J., Scussolini, P., Eilander, D., Lechner, A., Owen, J., Bird, G., Kemp, D., Mangalaa, K.R., 2023. Impacts of metal mining on river systems: a global assessment. Science (80-.). 381, 1345–1350. https://doi.org/10.1126/SCIENCE.ADG6704/SUPPL_FILE/SCIENCE.ADG6704_MDAR_REPRODUCIBILITY_CHECKLIST.PDF.
Martin, J.M., Meybeck, M., 1979. Elemental mass-balance of material carried by major world rivers. Mar. Chem. 7, 173–206. https://doi.org/10.1016/0304-4203(79)90039-2.
Martin, J.M., Whitfield, M., 1983. The significance of the river input of chemical elements to the ocean. In: Trace Metals in Sea Water. Springer, Boston, MA, pp. 265–296. https://doi.org/10.1007/978-1-4757-6864-0_16.
Mayes, W.M., Potter, H.A.B., Jarvis, A.P., 2010. Inventory of aquatic contaminant flux arising from historical metal mining in England and Wales. Sci. Total Environ. 408, 3576–3583. https://doi.org/10.1016/j.scitotenv.2010.04.021.
Mayes, W.M., Potter, H.A.B., Jarvis, A.P., 2013. Riverine flux of metals from historically mined orefields in England and Wales. Water Air Soil Pollut. 224, 1425. https://doi.org/10.1007/s11270-012-1425-9.
Meißner, S., 2021. The impact of metal mining on global water stress and regional carrying capacities—a GIS-based water impact assessment. Resources 10, 120. https://doi.org/10.3390/RESOURCES10120120/S1.
Muste, M., Yu, K., Spasojevic, M., 2004. Practical aspects of ADCP data use for quantification of mean river flow characteristics; part I: moving-vessel measurements. Flow Meas. Instrum. 15, 1–16. https://doi.org/10.1016/J.FLOWMEASINST.2003.09.001.
NAMRIA, 2020. geoportal PH - land cover. URL. https://www.geoportal.gov.ph/. (Accessed 12 May 2025) (WWW Document).
National Research Council Canada, 2015. Certificate of Analysis Certified Reference Material SLRS-6 River Water Certified Reference Material for Trace Metals and Other Constituents.
Naus, C.A., McCleskey, R.B., Nordstrom, D.K., Donohoe, L.C., Hunt, A.G., Paillet, F.L., Morin, R.H., Verplanck, P.L., 2005. Questa baseline and pre-mining ground-water quality investigation. 5. Well installation, water-level data, and surface- and ground-water geochemistry in the Straight Creek drainage basin, Red River Valley, New Mexico, 2001–03. In: Sci. Investig. Rep., Scientific Investigations Report 2005–5088, p. 228. https://doi.org/10.3133/SIR20055088.
Nordstrom, D.K., 2015. Baseline and premining geochemical characterization of mined sites. Appl. Geochem. 57, 17–34. https://doi.org/10.1016/J.APGEOCHEM.2014.12.010.
O'Callaghan, T., 2009. Regulation and governance in the Philippines mining sector. Asia Pac. J. Public Adm. 31, 91–114. https://doi.org/10.1080/23276665.2009.10779358.
Ockenden, M.C., Tych, W., Beven, K.J., Collins, A.L., Evans, R., Falloon, P.D., Forber, K. J., Hiscock, K.M., Hollaway, M.J., Kahana, R., Macleod, C.J.A., Villamizar, M.L., Wearing, C., Withers, P.J.A., Zhou, J.G., Benskin, C.M.H., Burke, S., Cooper, R.J., Freer, J.E., Haygarth, P.M., 2017. Prediction of storm transfers and annual loads with data-based mechanistic models using high-frequency data. Hydrol. Earth Syst. Sci. 21, 6425–6444. https://doi.org/10.5194/hess-21-6425-2017.
OriginLab Corporation, 2025. OriginPro 2025.
Panther, J.G., Stewart, R.R., Teasdale, P.R., Bennett, W.W., Welsh, D.T., Zhao, H., 2013. Titanium dioxide-based DGT for measuring dissolved As(V), V(V), Sb(V), Mo(VI) and W(VI) in water. Talanta 105, 80–86. https://doi.org/10.1016/J.TALANTA.2012.11.070.
Philippine Statistics Authority, 2017. Mineral Accounts of the Philippines WAVES Wealth Accounting and the Valuation of Ecosystem Services.
Posa, M.R.C., Diesmos, A.C., Sodhi, N.S., Brooks, T.M., 2008. Hope for threatened tropical biodiversity: lessons from the Philippines. Bioscience 58, 231–240. https://doi.org/10.1641/B580309.
Poulton, S.W., Raiswell, R., 2000. Solid phase associations, oceanic fluxes and the anthropogenic perturbation of transition metals in world river particulates. Mar. Chem. 72, 17–31. https://doi.org/10.1016/S0304-4203(00)00060-8.
Research and Markets, 2024. Mining Market Opportunities and Strategies to 2033, The Business Research Company.
Robles, M.E., Verbrugge, B., Geenen, S., 2022. Does formalization make a difference in artisanal and small-scale gold mining (ASGM)? Insights from the Philippines. Extr. Ind. Soc. 10, 101078. https://doi.org/10.1016/J.EXIS.2022.101078.
Rodríguez, J.G., Amouroux, I., Belzunce-Segarra, M.J., Bersuder, P., Bolam, T., Caetano, M., Carvalho, I., Correia dos Santos, M.M., Fones, G.R., Gonzalez, J.L., Guesdon, S., Larreta, J., Marras, B., McHugh, B., Menet-Nédélec, F., Menchaca, I., Millán Gabet, V., Montero, N., Nolan, M., Regan, F., Robinson, C.D., Rosa, N., Rodrigo Sanz, M., Schintu, M., White, B., Zhang, H., 2021. Assessing variability in the ratio of metal concentrations measured by DGT-type passive samplers and spot sampling in European seawaters. Sci. Total Environ. 783, 147001. https://doi.org/10.1016/J.SCITOTENV.2021.147001.
Runkel, R.L., Kimball, B.A., Nimick, D.A., Walton-Day, K., 2016. Effects of flow regime on metal concentrations and the attainment of water quality standards in a remediated stream reach, Butte, Montana. Environ. Sci. Technol. 50, 12641–12649. https://doi.org/10.1021/acs.est.6b03190.
Runkel, R.L., Verplanck, P.L., Kimball, B.A., Walton-Day, K., 2018. Cinnamon Gulch revisited: another look at separating natural and mining-impacted contributions to instream metal load. Appl. Geochem. 95, 206–217. https://doi.org/10.1016/J.APGEOCHEM.2018.04.010.
Runkel, R.L., Verplanck, P.L., Walton-Day, K., McCleskey, R.B., Byrne, P., 2023. The truth is in the stream: use of tracer techniques and synoptic sampling to evaluate metal loading and remedial options in a hydrologically complex setting. Sci. Total Environ. 876, 162458. https://doi.org/10.1016/J.SCITOTENV.2023.162458.
Scarano, F.R., Fornero Aguiar, A.C., Mittermeier, R.A., Rylands, A.B., 2024. Megadiversity. Enc. Biodivers. 1, 868–884. https://doi.org/10.1016/B978-0-12-822562-2.00013-X.
Sinnett, D.E., Sardo, A.M., 2020. Former metal mining landscapes in England and Wales: five perspectives from local residents. Landsc. Urban Plan. 193, 103685. https://doi.org/10.1016/J.LANDURBPLAN.2019.103685.
Sonter, L.J., Ali, S.H., Watson, J.E.M., 2018. Mining and biodiversity: key issues and research needs in conservation science. Proc. R. Soc. B Biol. Sci. 285, 20181926. https://doi.org/10.1098/RSPB.2018.1926.
Tabios III, G.Q., 2020. Water Resources Systems of the Philippines: Modeling Studies, World Water Resources. Springer International Publishing, Cham. https://doi.org/10.1007/978-3-030-25401-8.
UK Parliament, 2023. The Environmental Targets (Water) (England) Regulations 2023.
UKTAG, 2014. UKTAG River & Lake Assessment Method Specific Pollutants (Metals) Metal Bioavailability Assessment Tool (M-BAT) by Water Framework Directive-United Kingdom Technical Advisory Group (WFD-UKTAG).
United States Environmental Protection Agency, 1991. Methods for the Determination of Metals in Environmental Samples (Washington DC).

United States Environmental Protection Agency, 2021. Factsheet on Water Quality Parameters Factsheet on Water Quality Parameters Metals.

United States Environmental Protection Agency, 2024. Overview of total maximum daily loads (TMDLs). URL, US EPA. https://www.epa.gov/tmdl/overview-total-maximum-daily-loads-tmdls. (Accessed 8 May 2025) (WWW Document).

Väänänen, K., Leppänen, M.T., Chen, X.P., Akkanen, J., 2018. Metal bioavailability in ecological risk assessment of freshwater ecosystems: from science to environmental management. Ecotoxicol. Environ. Saf. 147, 430–446. https://doi.org/10.1016/J.ECOENV.2017.08.064.

Wang, H., Guan, Y., Hu, M., Hou, Z., Ping, Y., Zhang, Z., Zhang, Q., Shang, F., Lin, K., Feng, C., 2025a. Enhancing pollution management in watersheds: a critical review of total maximum daily load (TMDL) implementation. Environ. Res. 264, 120394. https://doi.org/10.1016/J.ENVRES.2024.120394.

Wang, R., Lu, J., Wu, J., Lin, Y., Li, F., Zhang, C., Wang, J., Zhou, Y., Yue, X., 2025b. Use of the diffusive gradients in thin-films (DGT) technique for smart rapid biomonitoring of trace metals in aquaculture systems. Mar. Environ. Res. 204, 106913. https://doi.org/10.1016/J.MARENVRES.2024.106913.

Webster, J.G., 1999. The source of arsenic (and other elements) in the Marbel-Matingao river catchment, Mindanao, Philippines. Geothermics 28, 95–111.

Williams, L., Arguillas, M.J.B., Arguillas, F., 2020. Major storms, rising tides, and wet feet: adapting to flood risk in the Philippines. Int. J. Disaster Risk Reduct. 50, 101810. https://doi.org/10.1016/J.IJDRR.2020.101810.

Worlanyo, A.S., Jiangfeng, L., 2021. Evaluating the environmental and economic impact of mining for post-mined land restoration and land-use: a review. J. Environ. Manag. 279, 111623. https://doi.org/10.1016/J.JENVMAN.2020.111623.

World Bank Group, 2022. Land area (sq. km). URL, Data. https://data.worldbank.org/indicator/AG.LND.TOTL.K2. (Accessed 8 May 2025) (WWW Document).

Zhang, Q., Hirsch, R.M., 2019. River water-quality concentration and flux estimation can be improved by accounting for serial correlation through an autoregressive model. Water Resour. Res. 55, 9705–9723. https://doi.org/10.1029/2019WR025338.

Zhang, H., Davison, W., Miller, S., Tych, W., 1995. In-situ high-resolution measurements of fluxes of Ni, Cu, Fe, and Mn and concentrations of Zn and Cd in porewaters by DGT. Geochim. Cosmochim. Acta 59, 4181–4192.