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Increasing Nickel Concentrations in a Large River Network of South Tyrol, Eastern European Alps

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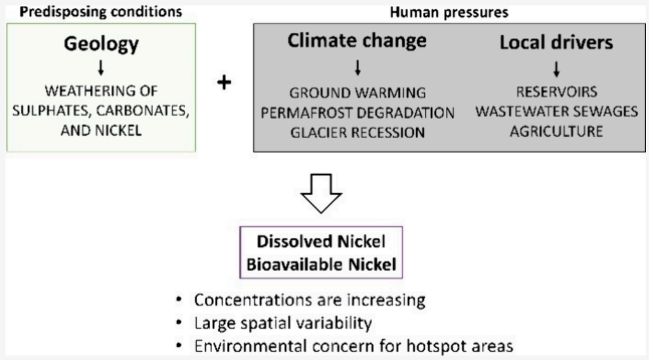
ABSTRACT: Climate change and cryosphere degradation may enhance the concentrations of heavy metals in high-mountain rivers. However, the downstream export of these contaminants to lower elevations is still overlooked. In this study, we investigated the spatial and temporal patterns of dissolved and bioavailable nickel concentrations in the upper Etsch/Adige river basin (1590 km^2; 54 sites) during the period of 2005−2023. Furthermore, we investigated the same concentrations seasonally (2022−2023) along a tributary (Schnals/Senales River), from the glacier origin down to the confluence with the Etsch River (13 sites). Concentrations of both nickel forms increased during the past decade by up to 4 times, yet only in river reaches draining the acidic metamorphic Ötztal Unit. Sulfide oxidation, more intense at sites featuring larger glaciers, rock glaciers, and permafrost extent in their catchment, enhanced nickel concentrations. Along the Schnals River, values were elevated in the proglacial waters (dissolved fraction up to 112 $\mu g\ L^{-1}$), gradually decreased moving to lower elevations, and dropped (from 20 to 30 to 2−5 $\mu g\ L^{-1}$) downstream of a large reservoir. Currently, bioavailable nickel concentrations exceed the EU environmental quality standards at 40% of the investigated sites, demonstrating sharp environmental implications that may be extended to other similar geological and cryospheric settings.



KEYWORDS: *biotic ligand model, R-INLA, GLMM, water quality, priority substances, water management*

INTRODUCTION

The ongoing reduction of glaciers and permafrost may affect the quality of water resources due to enhanced concentrations of solutes, including heavy metals.[1−5] In watersheds with metamorphic rocks, increasing trends of electrical conductivity and sulfate concentrations were detected in high-elevation lakes influenced by intact rock glaciers (i.e., ice-rich, permafrost-related rocky landforms)[6] starting from the late 90s and were related to permafrost degradation.[7,8] In general, high concentrations of solutes are commonly found at springs, lakes, and ponds influenced by intact rock glaciers and permafrost, with different combinations of trace elements (e.g., U and As, Ni, Mn, Al, and Fe) enriched depending on the study area.[2,9−17] Permafrost degradation is considered as the main driver of enhanced solute export from rock glaciers under predisposing lithological settings.[2] Furthermore, also freshwater ecosystems influenced by receding glaciers can have elevated concentrations of the same solutes found in intact rock glacier waters, due to enhanced subglacial weathering.[7,13,18] The combined solute export from receding glaciers and thawing permafrost can affect the water quality along entire river networks, where metal concentrations are generally negligible in water bodies not influenced by the cryosphere.[9,13,18,19] However, while the environmental drivers of water chemistry in cryosphere-influenced areas are relatively well studied at high elevations, little is known about the chemical conditions of their downstream river networks.[13,18]

Among the heavy metals of environmental concern in waters, nickel has received attention due to its negative effects on humans and aquatic organisms.[20,21] The metal toxicity in waters decreases with increasing concentrations of cations (e.g., Ca^{2+}), as these latter compete with metals for binding in tissues, and of organic (e.g., dissolved organic carbon (DOC)) or inorganic ligands that chelate and/or complexate metal ions.[22] This is accounted for in biotic ligand models[23] that can be utilized to calculate the bioavailable fraction of nickel. Such

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a parameter is used, for example, to define the water quality of river ecosystems.[24]

In this study, we investigated the dissolved and bioavailable nickel concentrations at 61 river reaches of the glacierized upper Etsch/Adige river basin (1590 km^2 in area; Eastern Italian Alps) during the period 2005−2023. Our aims were (i) to estimate the spatial and temporal trends of nickel concentrations during these two decades and (ii) to investigate how human (i.e., land use) and environmental (i.e., geology, hydrology, and cryosphere) drivers influenced the observed spatial-temporal patterns of such concentrations.

■ MATERIAL AND METHODS

Study Area. The upper Etsch/Adige river basin (South Tyrol/Alto Adige, Eastern Italian Alps) corresponds to the Vinschgau/Venosta valley, which develops on an eastern-western orientation. The river basin features a wide elevation range (355−3905 m a.s.l.) and a drainage area of about 1590 km^2 (outlet close to the village of Töll/Tel). The climate is continental without dry seasons at the valley bottom and progressively becomes polar tundra at higher elevations.[25] The runoff of the Etsch River mainly depends on the contribution from large tributaries influenced by glaciers and seasonal snow (Figure 1; Table S1.1). Geologically, the catchment belongs to the Austroalpine domaine. In the northern part, paragneisses and michaschists (Ötztal and Tessa/Monteneve/Marlengo Units) predominate. In the southern part, the lithology is more heterogeneous, with dominant quartzphyllites, orthogneisses, michaschists, amphibolites (Campo fault, Zebrù scale, Sesvenna Unit), carbonatic rocks (dolomites, marbles), and localized granites (Permian Pluton). Several faults occur in the basin, mostly located at the lithological discontinuities and partially associated with secondary overthrusting.[26,27]

The land use is dominated by forests and pastures in the tributary catchments and agriculture (mostly apple orchards) in the main valley bottom. Crops represent the major distributed source of anthropogenic pollution, whereas point sources are represented by sewages from wastewater treatment plants.[27] Hydropower schemes are a major environmental stressor for different rivers in the valley, which were dammed during the XX century (reservoirs of Reschen/Resia, Zufritt/Gioveretto, and Vernagt/Vernago). The area hosts ca. 38,000 inhabitants.[28]

Field Activities and Laboratory Analyses. We investigated 61 river locations ("sites") belonging to the Upper Etsch river network. In the period 2005−2023, 54 sites belonging to the hereafter called "ordinary monitoring network" (S1; Figure 1a) were sampled. These include eight sites along the main river (Etsch) and others along its main (Karlin/Carlino, n = 3; Saldur/Saldura, n = 6; Sulden/Solda-Trafoi, n = 3; Plima, n = 2; Schnals/Senales, n = 3), and minor (Allitz/Alliz, Puni, Ram, Ziel/Tel, Schlandraun/Silandro, and others; n = 29) tributaries (S1). The Etsch River was sampled monthly during the entire period only at Töll (517 m a.s.l.; Figure 1a), 2.5 km upstream from the river basin outlet. The other sites were irregularly monitored monthly to seasonally with different and heterogeneous timings over the years (Table S2.2). During 2022−2023, we conducted seven field campaigns (August and September 2022, and March, June, August, September, and October 2023) in a catchment (Schnals) where elevated dissolved nickel concentrations were previously found in the proglacial area.[18] There, sites belonging to the "Hotspot monitoring network" (n = 13)

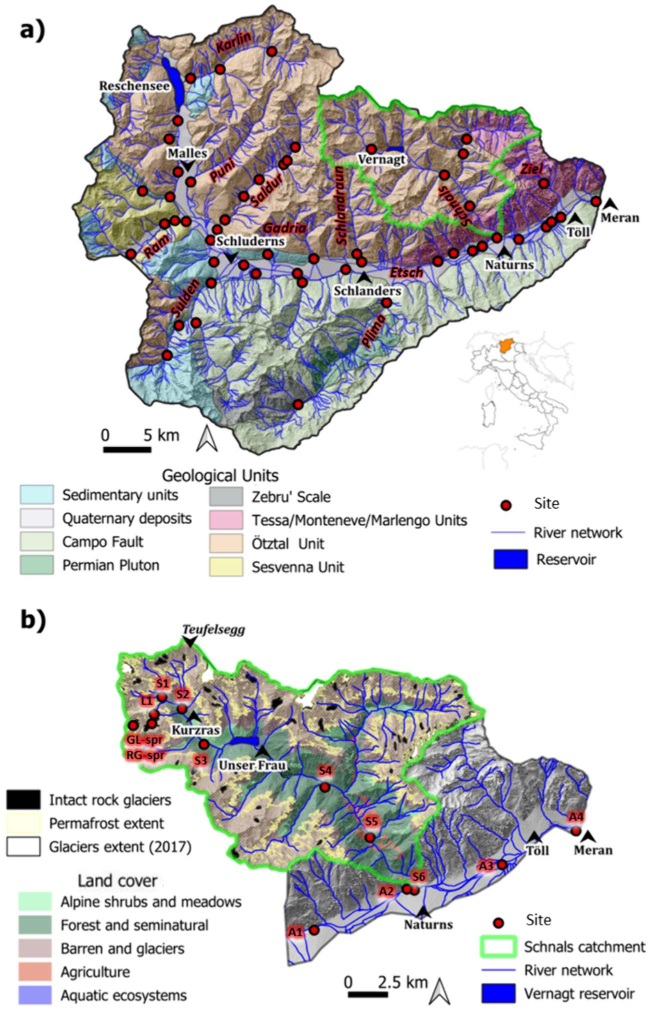

Figure 1. Maps of the study area. (a) Ordinary monitoring network (red points) within the Upper Etsch catchment; (b) the hotspot monitoring network. The outlet is represented in this work by the reach immediately upstream from the city of Meran/Merano.

included one glacier (GL-spr) and one intact rock glacier (RG-spr) spring, three sites along the main streams (L1, S1−S2) in the proglacial area, and seven sites also belonging to the ordinary monitoring network of the Schnals River (S3−S6) and the Etsch River, upstream (A1, A2) and downstream (A3, A4) from their confluence (Figure 1b).

We used prewashed PPE containers with double cap to collect water samples, with three replicates collected at each site. Samples were transported in thermal bags to the laboratory of chromatography and water analyses of the Environmental Protection Agency Bozen/Bolzano (APPA) within a few hours after collection. In the laboratory, following the standard methods,[29] we determined pH and electrical conductivity (EC) at 20 °C ($\mu S\ cm^{-1}$) and estimated the concentrations of major ions (Ca^{2+}, Na^+, K^+, Cl^-, HCO_3^-, and SO_4^{2-}) after filtration (0.2 μm) and acidification with HNO_3^- (pH = 3; cations). For ions, a charge balance error of lower than 10% was ensured. DOC was analyzed with catalytic combustion (Analytic Jena Multi N/C 3100) after filtration (glass microfiber filters; 0.7 μm[30]) and acidification with HCl (pH < 2), following standard procedures.[30] pH, EC, ions, and DOC were estimated during the same day of sampling. Within one month, concentrations of dissolved nickel ($\mu g\ L^{-1}$) were

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determined with inductively coupled plasma-mass spectrometry (ICP-MS) on samples that had been filtered (0.45 μm) and acidified (HNO_3^-; pH < 2) in the laboratory during the same day of sampling.[31]

Data Processing and Homogenization. We rescaled all values of dissolved nickel below the LOD (ranging between 0.5 and 2 μg L^{-1}) to 1 μg L^{-1}, except when only data belonging to 2018−2023 were analyzed (0.5 μg L^{-1}). We used the Bio-Met availability tool[32] to calculate the concentrations of bioavailable nickel (Bio_Ni; μg L^{-1}) based on the values of dissolved nickel (Ni; μg L^{-1}), Ca^{2+} (mg L^{-1}), DOC (mg L^{-1}), and pH (S2). We calculated the S-ratio[33] as $SO_4^{2-}/(SO_4^{-2} + HCO_3^-)$, based on μeq L^{-1} units. This index is commonly used in alpine hydrochemical studies to estimate the predominance of sulfuric acid vs carbonic acid-dominated weathering processes.[12,16,34,35] Generally, a low S-ratio (<0.4) testifies the prevalence of carbonate dissolution, intermediate values (S-ratio = 0.4−0.6) suggest the occurrence of carbonate dissolution coupled with sulfide oxidation, and a large S-ratio (>0.6) attests the prevalence of sulfide oxidation and/or, if present, the dissolution of gypsum/anhydrite.[12]

Based on the available geospatial information,[27] we calculated the main morphological, cryospheric, geological, and land use characteristics in the catchment drained by each site (Table 1).

Table 1. Main Variables Calculated Based on the Available Geospatial Information, Obtained with ArcGIS Pro[36]

category	variable
morphological	elevation (m a.s.l.), catchment area (km^2)
geological	geological unit cover (%), main geological unit (s)
cryospheric	glacier cover in the catchment (GCC; %) in 2005 and 2017, glacier loss in the catchment 2005−2017 (Gloss; %); intact rock glacier cover in the catchment (RGC; %); permafrost cover in the catchment (PCC; %)
land use	corine land cover (%); main land use (s)

Temporal Trends. Given the uneven distribution of our data in space and time (Figure S2.1; Tables S2.1 and S2.2), we selected different methods to estimate the spatial and temporal trends of Ni forms (i.e., Ni and Bio_Ni) concentrations in the ordinary monitoring network (Table S2.1). For the site "Etsch at Töll", we used the R software[37] to conduct the Seasonal Kendall Test,[38] followed by the Mann-Kendal test on single months (package *rkt* v 1.6)[39] to identify temporal trends. Since these tests require monotonic trends, we first plotted the monthly series to identify potential changes in trend directions and then analyzed separately periods with consistent trends. Two missing values (Table S2.2) were calculated based on the average between the previous and antecedent month in the series. To identify long-term tendencies while accounting for data seasonality, we used the R package *TSA* v 1.3.1[40,41] to decompose the trends of selected chemical, hydrological, and climatic variables. In trend decomposition, time series are commonly partitioned into long-term (trend), cyclic (seasonal), and residual (noise) parts. To identify changes in seasonal amplitudes of the variables, we decomposed the trends based on multiplicative models.[42] We performed this analysis for the concentrations of Ni forms and other chemical variables (SO_4^{2-}, HCO_3^-, S-ratio, pH, and DOC) and on monthly discharge (m^3 s^{-1}) at Töll. The same trend analyses were made for the bulk exports of Ni and Bio_Ni (g s^{-1}) that were calculated based on monthly discharge and concentrations in the samples collected each month, as well as for climatic variables (mean air temperature - T_{air}, °C; total precipitation, mm; duration of winter snow cover, days; number of days without snow in a year) at the reference automatic weather stations of higher (Teufelsegg, 3050 m a.s.l.; for snow height), intermediate (Vernagt, 1700 m a.s.l.), and lower (Schlanders, 561 m a.s.l.) elevations (Figure 1).

For the other locations of the ordinary monitoring network, we adopted a stepwise trend analysis, as suggested by Helsel and Hirsch.[43] Accordingly, we categorized different years into first (2005−2010), second (2011−2017), and third (2018−2023) year "intervals". Then, we used the software SPSS[44] to perform nonparametric comparisons among different intervals using the Kruskal−Wallis test with pairwise posthoc (all intervals available) or the Mann−Whitney *U* test (at locations where only two intervals were available). We performed these analyses at each site (i) merging all data belonging to each interval and (ii) considering single seasons separately, if applicable (i.e., with at least three samples for each interval and season). In this case, we distinguished the following seasons: winter (December/March), spring (April/June; generally associated with the freshet in the basin),[18] summer (July/August), and autumn (September/November). Finally, we calculated the enrichment of Ni forms between the first (or second for sites not monitored before 2010) and the third intervals as the relative (in %) difference of the median values between these two intervals.

Drivers of Nickel Concentrations. We used generalized linear mixed-effect models (GLMM) with barrier models to account for the spatial and temporal correlation of the data in a Bayesian framework. We used the integrated nested Laplace approximation (INLA)[45] tool with the R-INLA package,[46,47] and followed the procedure outlined by Zuur et al.[48,49] Covariates and interaction terms were selected based on Zuur et al.[50] (S2 for further information). We first estimated the relation between nickel concentrations (i.e., Ni and Bio_Ni response variables) and the selected chemical and environmental variables (Table 2). A first analysis was made only for those sites monitored seasonally/monthly during all intervals (n = 13) to account for spatial-temporal trends in concentrations ("spatial-temporal framework"). Then, we focused only on the third interval (2018−2023) to estimate the most recent drivers of concentrations ("present-days

Table 2. Set of Covariates and Interaction Terms (|) Selected for the Different Modelling Frameworks[a]

framework	fixed effects - chemistry	fixed effects - environment
spatial-temporal	Interval | pH | DOC + S-ratio | Ca^{2+}	Ötztal unit cover | season | interval
present-days	Ca^{2+}| pH + DOC | S-ratio	RGC | GCClog | Ötztal unit cover + PCC + season + catchment area
hotspot	EC | Ca^{2+} + pH + DOC + S-ratio	DOY | RGC | GCC

[a]The variable "Site" was considered as random effect. GLMM were run using a gamma distribution with log link function. GCClog: log-transformed GCC; DOY: Day of the year.

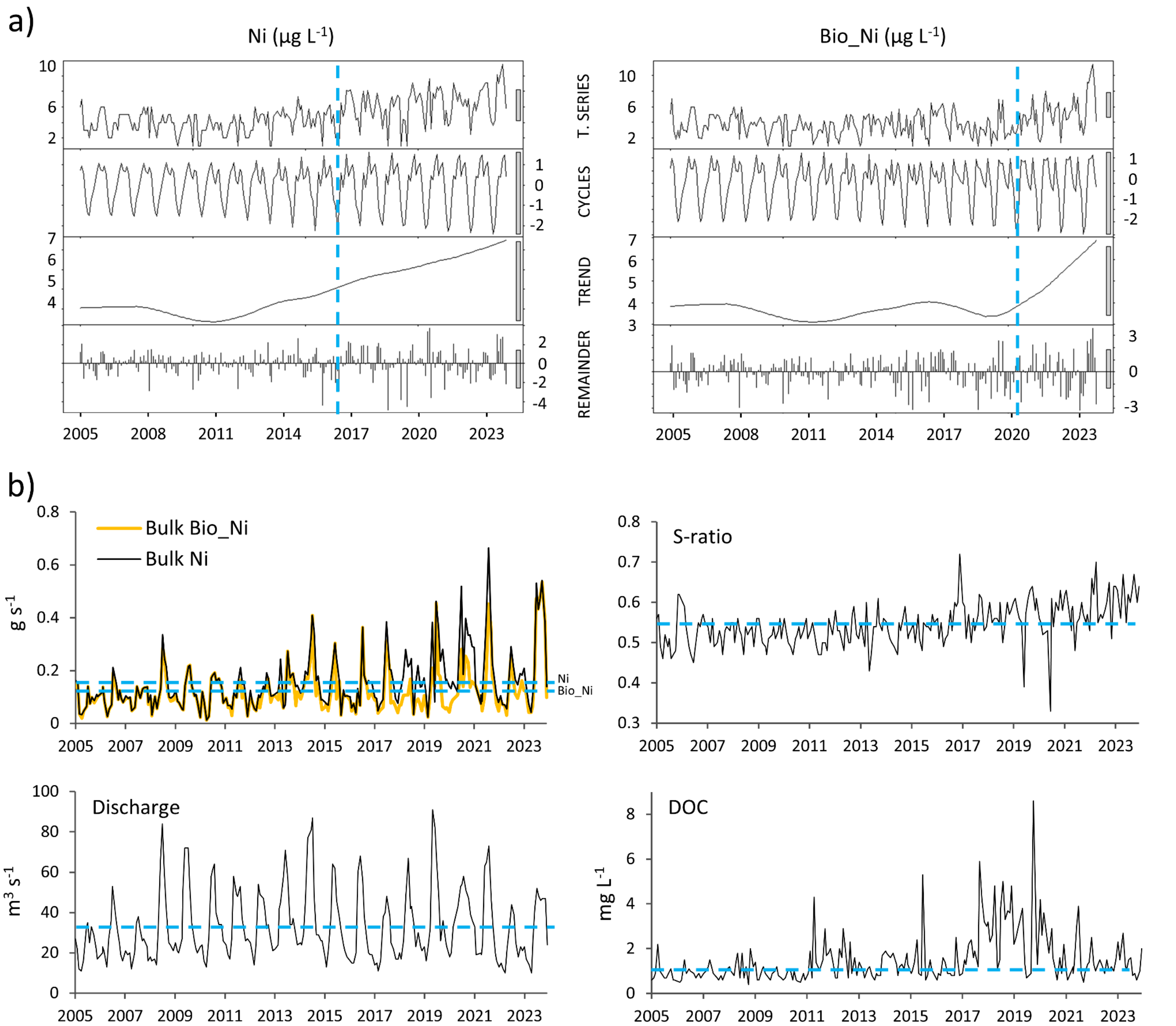

Figure 2. Trend analyses for the Etsch river at Töll. (a) Trend decomposition of Ni and Bio_Ni showing their time series, seasonal cycles, trend, and remainder residuals. Vertical dashed lines represent the change points detected by the Pettit test. (b) Time series of: bulk export of Ni (black line) and Bio_Ni (orange line), S-ratio, monthly discharge, and DOC concentrations. Dashed lines represent the mean values of each time series.

framework”), while including a higher number of sites (n = 34). Finally, we conducted the same analyses for the hotspot monitoring network (“hotspot framework”, n = 13).

RESULTS

Increasing Nickel Concentrations during the Last Ten Years. In the Etsch River at Töll, Ni slightly decreased during most months in the period 2005−2010 and strongly increased in the period 2011−2023. Bio_Ni had a significant (increasing) trend starting from 2020 (Figure 2a; Table 3). In the same period (2011−2023), S-ratio, Ca^{2+}, SO_4^{2}, pH, and EC also had significant trends (Table 3; Table S2.3), and the series of S-ratio was strongly aligned with that of Ni (Figure 2b). Monthly average discharge increased during 2005−2010, whereas it did not experience significant trends in the period 2011−2023 (Table 3, Figure 2b). The bulk Ni and Bio_Ni export significantly increased throughout the entire monitoring period, during which the air temperature at Schlanders and Vernagt also increased (more evidently at the latter, at higher elevation). The number of days without snow cover significantly increased with an overall reduction of 5 days year^{-1} at Teufelsegg (Figure S2.5).

Stepwise trend analyses revealed significant differences between the first/second and the third intervals at 10 sites (over 24) for Ni and at eight sites for Bio_Ni. At all sites where these differences were detected, the Ötztal Unit was the main geological group in the catchment (Figure S2.6). Only at 17 sites did the number of observations allow performing comparisons for single seasons, yet not all seasons could be compared for all sites. Autumn was the season more frequently associated with significant differences (n = 6 over 17 sites), followed by summer (n = 2 over 10), winter (n = 2 over 15), and spring (n = 0 over 15). The enrichment of Ni forms from the first/second to the third interval was slightly larger (yet not significantly) for Ni (159 ± 83%) than for Bio_Ni (133 ± 64%). Percentages of enrichment were large for sites mostly/only draining the Ötztal Unit (for Ni = 172 ± 89%, for Bio_Ni = 141 ± 70%), and negligible for the others (Ni = 110 ± 21%, Bio_Ni = 105 ± 12%; Figure S2.6).

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Table 3. Significant Trends, with Indicated Tau and Seasonal Kendall Slope Values, and the Mann-Kendall Test on Significant Months (Complete Results in Table S2.3)[a]

variable	period	Tau	slope	Sig. months
Ni	2005–2010	−0.19*	−0.00	Dec*
Ni	2011–2023	0.53***	0.33	Jan*, Feb*, May**, Jul***, Sep**, Oct***, Nov***, Dec***
Bio_Ni	2020–2023	0.41**	0.98	
Bulk Ni	2005–2023	0.35***	0.005	Jul***, Aug*, Sep**, Oct***, Nov**, Dec*
Bulk Bio_Ni	2005–2023	0.11*	0.001	
S-ratio	2011–2023	0.47***	0.08	Feb**, Mar*, May***, Jul***, Aug**, Oct*, Dec**
Ca^{2+}	2011–2023	0.15*	0.39	
SO_4^{2}	2011–2023	0.49***	2.4	Jan***, Feb***, Mar**, Apr***, Jul**, Aug *, Oct*, Dec*
pH	2011–2023	−0.16**	−0.01	Oct *
EC	2011–2023	0.32***	4.1	Jul*
discharge	2005–2010	0.36***	1.6	
T_{air}^{SCH}	2005–2023	0.10*	0.04	
T_{air}^{VER}	2005–2023	0.12**	0.08	
$NoSnow^{T}$	2005–2023	0.63***	5	na

[a]For slopes (i.e., units of trend per year), *p*-values are displayed (*$p < 0.05$, **$p < 0.01$, ***$p < 0.001$). Bulk Ni/Bio_Ni: bulk export of Ni/Bio_Ni; NoSnow: number of days without snow. [SCH]Schlanders, [VER]Vernagt, and [T]Teufelsegg weather stations.

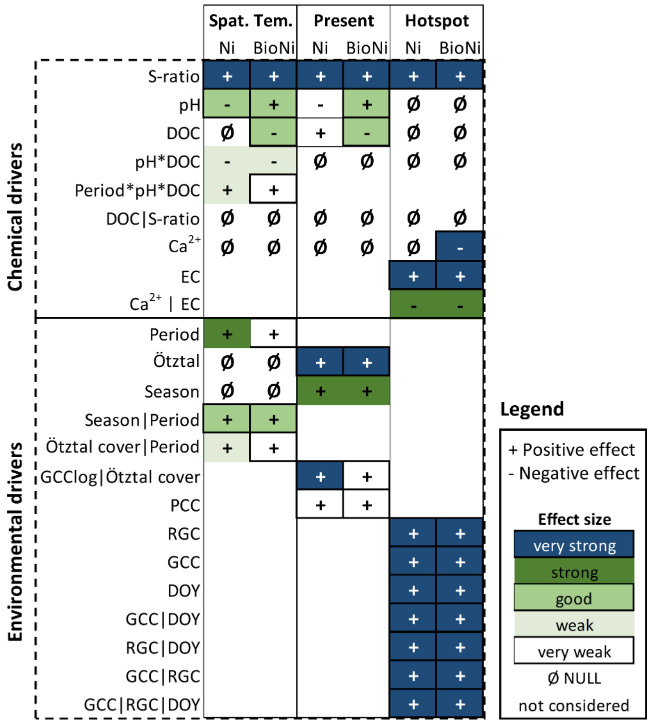

Figure 3. Graphical summary of the GLMM outcomes. For each modeling framework (spatial-temporal, present-day, and hotspot) and response variable (Ni and Bio_Ni), we show the important covariates and their interaction terms of the separate analyses on the chemical and environmental explanatory variables. For the effect size: very strong: absolute values of the lower quartile larger than 0.4; strong: 0.3–0.4; good: 0.2–0.3; weak: 0.1–0.2; very weak: variable important at 90% confidence intervals. See Supplementary S3 for further information on the GLMM outcomes.

Chemical and Environmental Drivers at Multiple Spatial-Temporal Scales. Among the chemical variables of the spatial-temporal framework of GLMM, the S-ratio had the strongest (and positive) effect on both Ni forms (Figure 3; Figure S3.8). pH was an important covariate too, with a decreasing and increasing effect on Ni and Bio_Ni, respectively. DOC had an important (and decreasing) effect only on Bio_Ni. The interaction between pH, DOC, and interval was also important (i.e., pH and DOC increasingly drove Ni forms from the first to the third interval). Among the environmental variables, the interval had the largest effect size on Ni and the little effect size (important only at 93% confidence) for Bio_Ni. Season, the interaction between season and interval (i.e., increasing from the first to the third interval, during summer and autumn), and the interaction between interval and Ötztal Unit cover had a positive effect on both Ni forms (Figure 3; Figure S3.8).

For the present-day framework, GLMM confirmed the importance of the S-ratio and highlighted that of EC and Ca^{2+}, increasing and decreasing the concentrations of both Ni forms, respectively, and more evidently for Bio_Ni. Among all environmental variables, Ötztal Unit cover and season had a positive effect on concentrations, more evidently for Ni than for Bio_Ni. PCC (yet only at 90% confidence), and the interaction between GCClog (at 90% for Bio_Ni) and Ötztal Unit cover had an important increasing effect as well (Figure 3; Figure S3.8).

Hotspot framework GLMMs confirmed the importance of the S-ratio and outlined those of EC, Ca^{2+}, and their interaction term. The variables DOY, GCC, and RGC and all their interaction terms were positively related to both Ni forms and more evidently for Bio_Ni (Figure 3; Figure S3.8). Indeed, concentrations were very high at the sampling locations above the Vernagt reservoir, particularly at the proglacial sites and at the springs from the glacier and intact rock glacier (Figure 4), with more evidence during the summer and autumn seasons (Figure S4.1). Downstream of the Vernagt reservoir, concentrations dropped, remained stable along the entire Schnals River, and slightly increased downstream from the confluence with the Etsch River (Figure 4).

When considering all the samples collected during the interval 2018–2023, the average concentrations of both Ni forms were much higher at the locations draining the Ötztal Unit (Figure 5). Ni and Bio_Ni were strongly related to the S-ratio with a partial influence from pH and DOC (Figure 6a; Supplementary S5). Sites with a larger cover from the cryosphere generally had higher values of Ni and Bio-Ni, particularly during autumn (Figure 6b). The only exception is the Allitz Creek (draining the Gadria catchment, Ötztal Unit) which features relatively high Ni form concentrations despite having no glaciers nor intact rock glaciers in the catchment.

DISCUSSION

In this study, we demonstrated a widespread increase of nickel concentrations (i.e., Ni and Bio_Ni) in the Upper Etsch river

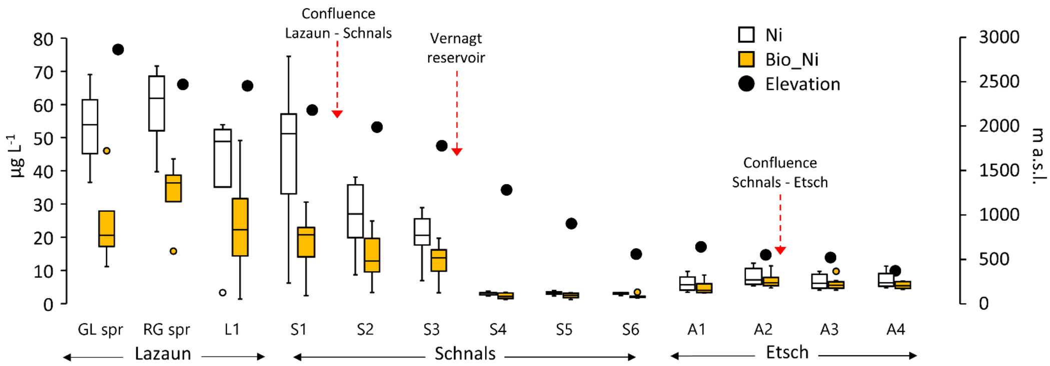

Figure 4. Outcomes of hotspot monitoring. For each site, the elevation (black circles) and box-whisker plots (boxes = interquartile ranges; whiskers = 1.5 times the interquartile ranges; dots = outliers) of Ni and Bio_Ni are shown. As reference, the location of major confluences and of the reservoir along the river network are highlighted (red arrows).

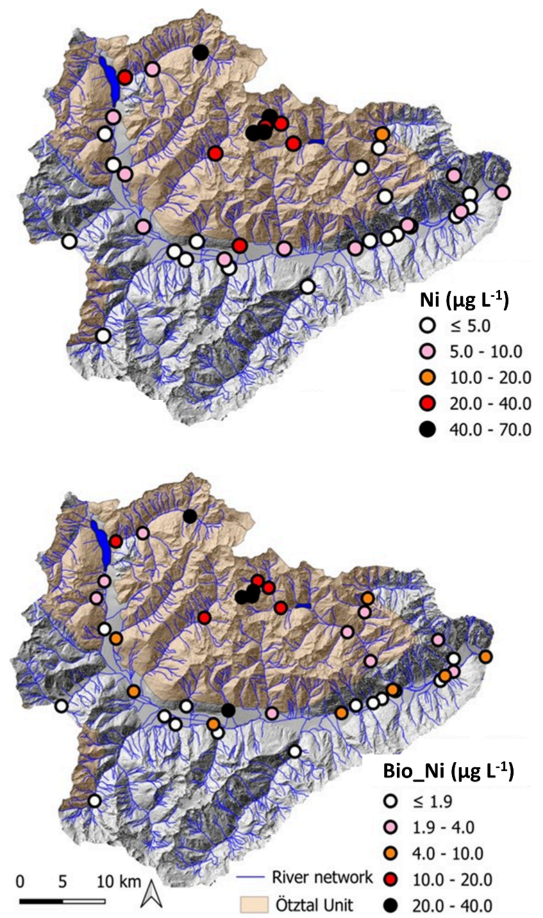

Figure 5. Summary maps showing the median values of Ni and Bio_Ni at different sites during the interval 2018–2023.

network throughout the past decade. Average Bio_Ni currently exceeds the standards of environmental quality at 46% of the investigated river stretches, and the share becomes 65% if only locations draining the Ötztal Unit are considered.

Sulfide Oxidation Enhances Nickel Concentrations. The strong relationship between nickel concentrations and the S-ratio, revealed by time series and univariate analyses, strongly suggests that sulfide oxidation is the main driver of these concentrations in the upper Etsch river network. Indeed, localized and very scarce gypsum formations are present only in the easternmost part of the basin,[52] and gypsum/anhydrite dissolution can be considered as a minor/absent driver of the prevalence of sulfates over carbonates in the river water. The process of sulfide oxidation involves the exposure of sulfur-bearing minerals to oxygen and water, with consequent production of SO_4^{2-}, H^+, and leaching of heavy metals (e.g., Ni, Zn, Mn, Cd, and Al) from the bedrock. In the analyzed river basin, the Ötztal Unit is mainly composed of biotite-plagioclase paragneisses and micaschists, with a minor presence of orthogneisses and rare/absent carbonatic rocks.[7,10] The bedrock contains abundant sulfide-bearing minerals like pyrite, chalcopyrite, and pyrrhotine.[53] Thus, we hypothesize that the oxidation of these sulfide-bearing minerals drives the weathering of nickel, even though this element is not particularly abundant in the host rock.[7,54]

Climatic and Cryospheric Forcing. In line with global trends, South Tyrol has been experiencing intense climatic changes during the last decades, with increasing air temperatures, shifting precipitation patterns, and widespread reduction of winter snow cover.[55,56] During the period 1997–2017 (latest inventory), the glaciers within the basin lost 29–49% of their extent, depending on the mountain range.[57] Positive climatic feedbacks also include a widespread permafrost warming and degradation.[58,59] Due to the kinetics of chemical reactions, sulfide oxidation is positively correlated to ambient temperature. Being this relationship potentially nonlinear at temperatures close to 0 °C,[60] even slight temperature increases may disproportionally enhance the oxidation rates at high elevation, where periglacial conditions occur.[1] At high elevations, ground warming also favors the degradation of permafrost, with consequent export of solutes, including heavy metals.[1,2,5] The loss of perennial ice allows oxygen and water to reach depths that were previously inaccessible, as the ice acts as an impermeable ground layer.[61−63] The opening of these new water pathways enhances weathering processes, enhanced by the large availability of scarcely weathered mineral surfaces[1,5] and accelerated by microbial activity.[64] Moreover, where permafrost ice is particularly enriched in ions and heavy metals, these solutes can be released in waters with melt. For example, at Schnals, high concentrations of sulfates and various heavy metals (e.g., Ni, Zn, Mn, Al, and Co) were found at various ice depths of the rock glacier feeding RG-spr.[52] Thawing rock glaciers are also recognized as efficient "weathering reactors"[15] because their creeping activity has a strong grinding effect on the rock inside and beneath the landform. The production of freshly ground rock fragments may enhance chemical weath-

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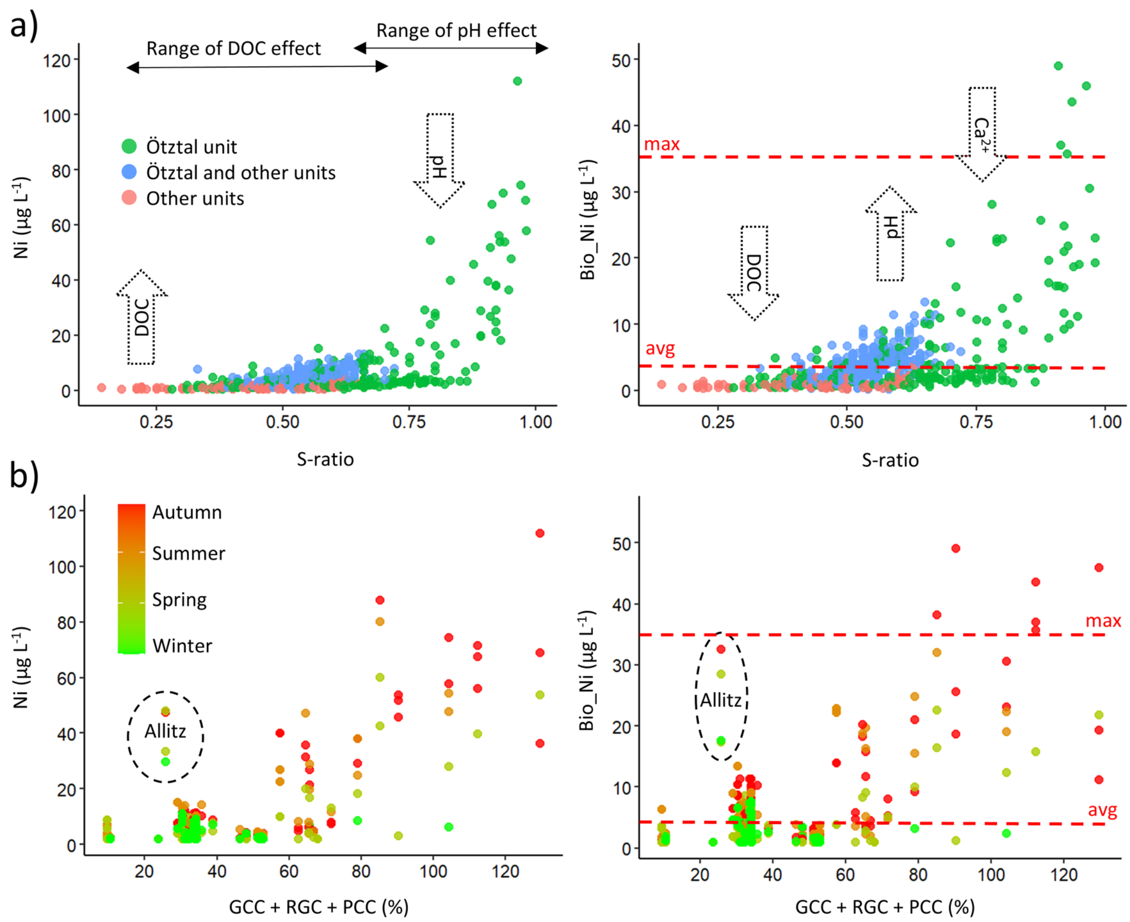

Figure 6. Scatterplots of Ni (left) and Bio_Ni (right) and the most important chemical (a) and environmental (b) variables. (a) S-ratio vs Ni forms scatterplots. Samples are colored based on the prevalence of the Ötztal unit in the catchment at the corresponding site. In our data set, the range of influence from DOC and pH on Ni was larger at lower and higher S-ratio values, respectively (see Figures S5.1 and S5.2). The spread of Bio_Ni at larger S-ratio may be related to the strong correlation between Ca^{2+} (hindering nickel bioavailability) and SO_4^{2-} (see Supplementary S2). (b) Scatterplots of the total cover of glaciers (GCC), intact rock glaciers (RGC), and permafrost (PCC) in the catchment and Ni forms. Samples from the Allitz Creek (Gadria catchment) are circled in both panels. Dashed lines indicate the EU standards of environmental quality based on average annual concentrations (avg) and maximum values (max) of Bio_Ni.[51]

ering, given the related supply of freshly exposed mineral surfaces.[10]

Even glaciers can contribute to the downstream export of solutes.[65] The fine sediments beneath temperate glaciers act as an aquitard where chemical weathering is intense.[66] Indeed, the glacier movement and the associated production of freshly ground mineral debris enhances solute concentrations in the glacier runoff, particularly during late summer and under prolonged glacier recession.[3,12,18,67]

To summarize, the combined effect from ground warming, permafrost degradation, and glacier recession occurring in the Ötztal Unit (i.e., paragneisses/michaschists lithologies) is suggested as a key driver for increased sulfide oxidation rates in the upper catchments of the Etsch River basin and the related downstream export of nickel. As revealed by GLMM analyses, the maximum increase in concentrations occurred in the warmest season, which is additional proof of the effect of the shrinking cryosphere. The strong correlation among the extent of permafrost, glaciers, and rock glaciers hindered the determination of how much each of them enhanced nickel concentrations along the river network. For the same reason, the nonlinear and complex relationship between nickel concentrations and air temperature challenges predictions on potential trajectories under climate change scenarios.

Influence of Hydrology and DOC. Some studies[1,68] suggested that enhanced sulfide oxidation may also result from a reduction of discharge (i.e., concentration-effect) and/or to the lowering of the water table (which would cause oxygenation of previously anoxic sediments). In this study, an overall dilution effect was detected during high flow events, at least at the sites where seasonal and monthly data were available (S1). Increasing discharge was also paralleled by declining nickel concentrations during the period of 2005–2010 at the river basin outlet. However, an overall decoupling between discharge and Ni was observed after 2010, as increasing concentrations were not paralleled by a decline of discharge. The dominant influence of chemical denudation over a possible concentration-effect is evident in the Etsch River at the site of Töll, where water discharge and bulk export of Ni forms are strongly positively related. Regarding the possible role of the declining groundwater table, its depth (recorded at Prad am Stilfserjoch/Prato allo Stelvio, in the upper part of the Etsch valley bottom) did not change during the period 2010–2023 (graph not shown). Therefore,

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hydrological variables cannot be considered as the main drivers of increased Ni concentrations.

Due to its chelation effect on metal ions, DOC can increase Ni concentrations,[69] with allochthonous forms (e.g., leaching from soil, vegetation, and human inputs) having a larger metal binding capacity than autochthonous ones.[70] The low DOC concentrations in the tributaries (<1−2 mg L^{-1}) and the larger values generally observed in the main river (Etsch) suggest that human activities (sewages, agriculture) are major DOC sources and that the leaching from soil and vegetation act as minor inputs. Accordingly, a weak positive relationship between Ni and DOC was found only for these downstream sites. Since Bio_Ni is inversely related to DOC concentrations,[24] the delayed onset of rising long-term concentrations at the outlet of the catchment might be related to a transient increase of DOC (the causes of which are currently unknown) during 2018−2020. In this period, Bio_Ni remained stable, while Ni was increasing. More in general, GLMM analyses revealed that the important negative effect from DOC on Bio_Ni was not paralleled by an important positive effect on Ni. Therefore, in the upper Etsch river basin, the concentrations and average lability of DOC had a buffering effect on Bio_Ni, overcoming the boosting effect on Ni.

Areas of Coupled Physical and Chemical Weathering. High concentrations of both Ni forms were also found in a tributary−the Allitz Creek - without any glacier or intact rock glacier, and with little permafrost cover in its watershed (Gadria catchment, Ötztal Unit). This catchment, which features a sackung (deep-seated gravitational slope deformation), is known for its frequent debris flows events leading to extremely high erosion rates at the Alpine scale.[71,72] There, the same processes involved in the intense physical weathering, with a widespread erosion of the parent bedrock and abundant supply of freshly ground sediments,[72] may also enhance the chemical weathering. These findings suggest that the Ni export in rivers is more widespread than previously hypothesized and might be not just related to the cryosphere degradation. Even though Allitz Creek exhibited a significant increase of Ni concentrations between the second and the third year-intervals, the limited number of samples (collected only in 2015 and 2018) hinders drawing any conclusion on the influence of climate change.

Do Reservoirs Decrease Heavy Metal Concentrations in Rivers? The presence of reservoirs in the basin sharply decreased the nickel concentrations along the river network at the locations draining the Ötztal Unit. This was evident not only along the Schnals River (hotspot monitoring) but also along the upper Etsch River where concentrations dropped below the Reschen/Haider reservoirs and did not experience any long-term increase in the period 2005−2023. The decreasing effect of reservoirs on heavy metal concentrations was also found in a study on the Yellow River in China,[73] and it was also suggested for proglacial lakes in South Tyrol.[13,18] However, it is unclear if the process is exclusive for dammed reservoirs, e.g., due to the complex systems of water abstractions artificially conveying water from other catchments, or if it can be extended also to natural lakes.

In the case of the Vernagt reservoir, the sudden increase of groundwater contribution below the dam (possibly related to the specific hydropower scheme) was the main reason for the disruption of natural gradients when moving away from glaciers and permafrost areas (S5). Indeed, the environmental flows in the Schnals River result from the seepage beneath the reservoir (personal communication from the hydropower plant company) and are not released from the lake waters. Downstream from the dam, concentrations did not increase because of increasing hydrological contribution from tributaries not/slightly influenced by the cryosphere and from groundwater inputs typical of the mountain block recharge.[74] Understanding if and how nickel (and other heavy metals like Mn, Zn, and Al)[18] accumulated in the bottom sediments within the Vernagt reservoir might be remobilized (e.g., during potential flushing operations)[75] and estimating the possible fate, transport, and environmental downstream effects and bioavailability would be of great environmental importance. Unfortunately, our data do not allow us any inference on this issue.

CONCLUSIONS

An increasing number of studies worldwide highlighted an augmented weathering and export of solutes, including heavy metals, in river networks, mostly at high elevation areas subjected to strong climate change and cryosphere loss. We demonstrated that such phenomena and their environmental significance can encompass geologically predisposed river basins as large as 1500 km^2. Given the increasing pace at which climate is changing and the cryosphere is degrading, we anticipate that nickel concentrations will increase further at locations draining paragneisses/michaschists lithologies. Disentangling the importance of structural deformations such as faults or sackungs on natural background levels and understanding the buffering effect of lakes and reservoirs is crucial to widen the geographical perspective of our work. This would help identify those hotspots where predisposing geology coupled with ongoing climatic changes enhances the concentrations of metals to levels of environmental and human health concern.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.4c00587.

Additional information on the study area and about data homogenization, additional information on the time series analyses, on GLMM analyses, on Hotspot monitoring, and additional figures on DOC and pH as well as additional statistical analyses (PDF)

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Notes

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