Communication

Fatima Haque*, Yi Wai Chiang, Rafael M. Santos*

Risk assessment of Ni, Cr, and Si release from alkaline minerals during enhanced weathering

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Abstract: Calcium- and magnesium-rich alkaline silicate minerals, when applied to soil, can aid in carbon dioxide sequestration via enhanced weathering. The weathering of these silicate minerals is also associated with the release of heavy metals such as Ni and Cr, depending on the composition of the parent rock, and also labile Si. This paper critically analyses the risk associated with the release of Ni. Cr. and Si from alkaline silicate minerals as a result of enhanced weathering to evaluate its potential to be applied as a soil amendment. Based on the available data in the literature, this study evaluates the soil contamination level and quantifies the risk these elements pose to human health as well as the environment. To assess these potential threat levels, the geoaccumulation index was applied, along with the method recommended by the US Environmental Protection Agency for health risk assessment. The main findings of this study indicate the potential release of Ni, Cr, and Si to exceed the soil quality guideline value. The geochemical index suggests that the analyzed samples are in the class 0-3 and represents sites that lie between uncontaminated zones to highly contaminated zones. The hazard index value for Ni and Cr is greater than unity, which suggests that Ni and Cr release poses a non-carcinogenic risk. The probability of labile Si concentration in the soil to exceed the critical value is found to be 75%.

Keywords: alkaline minerals, risk assessment, geoaccumulation index, weathering release, soil chemistry

1 Introduction

Atmospheric carbon dioxide concentrations and other greenhouse gasses (GHGs) have increased as a consequence of anthropogenic activities resulting in a rise in overall global temperatures and extreme weather events (Shurpali et al. 2019). There is a global commitment to reduce GHG emissions, and carbon dioxide capture and storage (CCS) is seen as an essential strategy for reducing CO₂ emissions. Long-term atmospheric CO₂ sequestration can be made possible through weathering of Ca silicates and Mg silicates because the released Ca²⁺ and Mg²⁺ are precipitated as soil inorganic carbonates. Formation of pedogenic carbonates offers a sink for plant-derived carbon that is effectively permanent and an amount of pedogenic inorganic carbonate held within the soil is between 720°C and 950°C (Schlesinger 1985; Baties 1996). Ideal alkaline minerals for enhanced weathering are calcium and magnesium silicates, including olivine group ((Mg,Fe)₂SiO₄) minerals, such as forsterite (Mg₂SiO₄) and favalite (Fe₂SiO₄), pyroxenoid group ((Ca,Na,Fe^{II},Mg)(Cr,Al,Fe^{III},Mg,Mn,Ti,V)Si₂O₆) minerals, such as wollastonite (CaSiO₃) and enstatite (MgSiO₃), and serpentine group minerals ((Mg,Fe^{II})₃Si₂O₅(OH)₄) (Kwon et al. 2011). For example, in the case of wollastonite (mainly CaSiO₃), two moles of CO₂ react with one mole of CaSiO₃ resulting in one mole of carbon sequestered as pedogenic carbonate (CaCO₃) and one mole of carbon is released as CO2. Haque et al. (2019a) provide a detailed literature review on the use of alkaline mineral soil amendments as a climate change "stabilization wedge." Renforth et al. (2015), Renforth et al. (2009), and Washbourne et al. (2015) studied carbon sequestration in urban soils used for construction projects and reported pedogenic inorganic carbonate accumulation due to enhanced weathering of alkaline minerals. Haque et al. (2019b) studied the co-benefits of wollastonite weathering in agricultural soil to grow green beans and corn.

Along with the release of the divalent cation $(Ca^{2+}$ and $Mg^{2+})$, enhanced weathering of silicate minerals is also associated with the release of heavy metals such as

^{*} Corresponding author: Fatima Haque, School of Engineering, University of Guelph, 50 Stone Road East, Guelph, Ontario, N1G 2W1, Canada, e-mail: fhaque@uoguelph.ca

^{*} Corresponding author: Rafael M. Santos, School of Engineering, University of Guelph, 50 Stone Road East, Guelph, Ontario, N1G 2W1, Canada, e-mail: santosr@uoguelph.ca
Yi Wai Chiang: School of Engineering, University of Guelph, 50 Stone Road East, Guelph, Ontario, N1G 2W1, Canada

Ni and Cr, depending on the composition of the parent rock. Hence, excessive use of alkaline minerals can be associated with these possible negative effects. The release of metals contained in the mineral composition during the weathering (e.g., Ni, Mn, Cr) may pose an environmental risk (Mehta et al. 2019). For example, the dissolution of olivine is associated with Ni releases and plant uptake (ten Berge et al. 2012). On the other hand, some of these same metals act as micronutrients required by plants. Therefore, their presence can be beneficial, as long as their soil concentration does not exceed toxic levels (Silva et al. 2005). Several studies report about the release of Ni during the dissolution of olivine. The release of bioavailable Ni from olivine into the food chain and the wider environment could set limits to permissible olivine doses (Vasiluk et al. 2019). ten Berge et al. (2012) reported a range of 0.09-1.383 mg/kg of bioavailable Ni while growing ryegrass (Lolium perenne L.) in olivine treated soil, which is very low when compared with the toxicity threshold of 10 mg/kg of bioavailable Ni (Kabata-Pendias 2011) and 45 mg/kg of Ni (based on soil quality guideline of environmental health). Pastures grew over basaltic fines accumulated 2.17 mg/kg as bioavailable Ni (Néel et al. 2007), whereas the one grown on serpentine-derived soils accumulated higher levels of bioavailable Ni (11.1-39.3 mg/kg) (Miranda et al. 2009). Fernandez et al. (1999) reported Ni content of 12–34 mg/kg in the foliage of various crops grown over serpentine-treated soils, with highest values for sugar beet (Beta vulgaris L.). These can result in high Ni accumulation in kidney tissue of grazing cattle (Miranda et al. 2009).

Alkaline silicate minerals are also associated with the release of Si, which is a beneficial element in plant nutrition, and crops such as sugarcane and rice require it for their growth. A certain level of "labile Si" must be present for the optimum growth of these crops. Amending the soil with alkaline silicate minerals will lead to the release of free silica in the soil which takes some time before it can form crystalline silica (quartz). A portion of this free silica forms monomeric silicic acid (H₄SiO₄) in the soil, which is the plant-available form of Si primarily taken up by the plants (Dietzel 2000). There have been only limited studies that attempt to identify critical values for labile Si. Gillman et al. (2002) propose critical values of 20–150 mg/kg Si.

The release of Ni, Cr, and Si, especially in agricultural soils, creates a global environmental issue, particularly, incorporation of Ni and Cr into the food chain that may affect animal and human health. This review paper critically analyzes the available information collected from the literature on the release of Si, Ni, and Cr due to enhanced weathering reactions. Risk assessment tools are

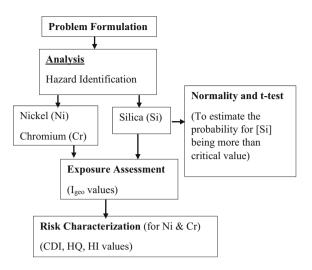


Figure 1: A general framework of the risk assessment protocol used in this study.

used to understand the environmental and health risk associated with the release of these elements. The main objective of this study includes risk characterization for Ni and Cr release on human health based on hazard index (HI), calculated using hazard quotient (HQ), and chronic daily intake (CDI) values hazard index (HI) values. If the HI value is less than unity, then the exposed human is not at risk. The risk-on environment was characterized using geochemical index (I_{geo}) analysis, which categorizes the data into different classes (0-6), where class 0 indicated "non-contaminated" condition and class 6 implies "extreme contamination" (Kowalska et al. 2018). For Si, there have been only limited studies that attempt to identify critical values for labile Si, and reference dose (RfD) value is not identified; hence, HI values could not be estimated. Instead, the normality test is carried out on the Si data to estimate the probability at which the concentration of labile Si ([Si]) is more than that of the critical value (100 mg/kg). The geochemical index (I_{geo}) was also measured. Figure 1 outlines the general framework of the risk assessment protocol used in this study. This paper provides a meta-analysis tool to statistically interpret the results from different studies into a single estimate of the effect of the release of Ni, Cr, and Si from alkaline silicate minerals as a result of enhanced weathering.

2 Material and method

2.1 Data collection and processing

This study systematically reviews related literature articles to collect the data on the amount of Ni, Cr, and

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labile (i.e. extractable) Si expected to be released from alkaline minerals as a result of enhanced weathering (Table 1). Data were collected from articles following standard methods for chemical analysis, including sample extraction/digestion with acids or salts (for example, nitric acid, hydrochloric acid, and potassium dihydrogen phosphate), and analyzed using atomic absorption spectroscopy (AAS), X-ray fluorescence (XRF), and inductively coupled plasma mass spectroscopy (ICP-MS) (Silva et al. 2005; Soubrand-Colin et al. 2005; ten Berge et al. 2012). The alkaline minerals are globally distributed worldwide. For example, olivine, a major constituent of dunite rock, is mined in several countries including Spain, Italy, Norway, Sweden, Austria, Greece, Cyprus, and Turkey (Schuiling and Krijgsman 2006).

The world reserves of wollastonite are estimated to exceed 100 million tonnes with large reserves in China, Finland, India, Mexico, Spain, Canada, and the United States (Ober 2018) For this meta-analysis paper, data were collected from journals reporting work on alkaline silicates in Queensland (basalt), Netherlands (olivine), Spain (basalt), British Columbia (basanite), and France (basanite). Usually, magnesium-rich silicates contain Ni and Cr as their innate composition, because the cation radius of Mg²⁺ (0.72 Å) is similar to that of Ni²⁺ (0.69) and Cr²⁺ (0.62); hence, Mg²⁺ has more affinity to be replaced by Ni²⁺ and Cr²⁺ (Railsback 2006). Hence, in this paper, Ni and Cr are analyzed in particular, and Si which is the primary compositional element of silicate minerals.

Table 1: Information on the different weathered minerals and mineral-amended soils analyzed, based on the available literature

Sample	Type of soil/parent rock/location of the soil derived from the mineral rock		Si (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	Ref.
S1	Haplorthox (basalt) (Queensland)	Mean	519.54	_	_	Gillman et al. (2002)
		Range	155.5-1233.2			
		SD	420.12			
S2	Haplorthox (basalt fan) (Queensland)	Mean	488.28	_	_	Gillman et al. (2002)
		Range	164.6-1220.4			
		SD	399.79			
S 3	Tropudult (Queensland)	Mean	364.50	_	_	Gillman et al. (2002)
		Range	36.5-1029.5			
		SD	379.19			
S4	Haplorthox (metamorphic rock) (Queensland)	Mean	348.70	_	_	Gillman et al. (2002)
		Range	30.9-988.7			
		SD	367.82			
S5	Dystropept (basalt alluvium) (Queensland)	Mean	558.92	_	_	Gillman et al. (2002)
		Range	232.2-1195.1			
		SD	364.14			
S6	Dystropept (granite alluvium) (Queensland)	Mean	445.00	_	_	Gillman et al. (2002)
		Range	133.8-1108.9			
		SD	371.79			
S 7	Haplorthod (Beach ridge) (Queensland)	Mean	260.32	_	_	Gillman et al. (2002)
		Range	20.4-829			
		SD	311.93			
S 8	Olivine-amended soil (Netherlands)	Mean	20.99	0.59	_	ten Berge et al. (2012)
		Range	15.9-32.08	0.13-1.38		
		SD	6.53	0.49		
S9	GNT (granite powder generated by cutting with a	Mean	151.43	51.4	156	Silva et al. (2005)
	band saw) (Spain)	Range	60.2-483.9	_	_	
		SD	73.33	8.1	44	
S10	GPM (granite powder generated by cutting with a	Mean	181.58	28.50	33.00	Silva et al. (2005)
	band saw, and diamond-edged disc saw) (Spain)	Range	14.9-436.8	_	_	
		SD	100.59	12.50	6.40	
S11	Coquihalla serpentine belt (British Columbia)	Mean	46.67	94.20	110.80	Bulmer and
		Range	_	55-138	28-209	Lavkulich (1994)
		SD	_	94.20	65.76	
S12	Olivine mountains (British Columbia)	Mean	58.33	82.25	4.50	Bulmer and
		Range	46.67-93.33	58-128	3.0-7.0	Lavkulich (1994)
		SD	20.21	27.17	1.66	

Table 1: continued

Sample	Type of soil/parent rock/location of the soil derived from the mineral rock		Si (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	Ref.
S13	Ultramafic soil from Shulaps (high elevation)	Mean	29.17	62.38	43.50	Bulmer and
	(British Columbia)	Range	0-46.67	5-122	3-127	Lavkulich (1994)
		SD	22.59	48.44	45.72	
S14	Ultramafic soil from Shulaps (low elevation) (British	Mean	70.00	141.83	51.67	Bulmer and
	Columbia)	Range	0-93.33	6-277	6-138	Lavkulich (1994)
		SD	35.64	102.27	45.70	
S15	Basanite (Mauriac) (France)	Mean	17.90	198.33	346.67	Soubrand-Colin
		Range	15.02-17.9	168-214	293-376	et al. (2005)
		SD	2.62	21.45	38.00	
S16	Basalt (Labarriere) (France)	Mean	14.39	94.33	184.00	Soubrand-Colin
		Range	11.9-18.57	31–219	50-427	et al. (2005)
		SD	2.98	88.16	172.13	
S17	Basalt (Poinsac) (France)	Mean	19.52	142.67	271.67	Soubrand-Colin
		Range	18.39-20.81	126-155	236-330	et al. (2005)
		SD	1.00	12.23	41.59	
S18	Basanite (Saint Christorphe) (France)	Mean	18.37	262.33	517.00	Soubrand-Colin
		Range	16.47-20.86	237-291	455-629	et al. (2005)
		SD	1.84	22.17	79.35	
S19	Basanite (Les Chirouzes) (France)	Mean	17.56	161.33	318.00	Soubrand-Colin
		Range	15.45-19.46	125-218	273-381	et al. (2005)
		SD	1.65	40.60	45.89	
S20	Basanite (Pierrefort) (France)	Mean	16.04	237.00	443.67	Soubrand-Colin
		Range	13.44-18.53	142-287	270-552	et al. (2005)
		SD	2.08	67.21	124.29	

[&]quot;-" denotes information not available; extractable Si values from Soubrand-Colin et al. (2015) were assumed to be 0.01% of total Si in reported mineral compositions; extractable Si values from Bulmer and Lavkulich (1994) were assumed to be 5% of reported values to account for the three-step sequential extraction method that used dithionite-citratebicarbonate, acid ammonium oxalate, and potassium pyrophosphate, to break down the silicates.

The mean, range, and standard deviation values of these elements from Table 1 were collated. In addition, to substantiate the comparisons with standards, percentile values (10th, 25th, 50th, 75th, and 90th) of their concentrations were analyzed in comparison with soil quality guideline values (Table 2). All the statistical analyses for the data were performed by Excel for Windows (Microsoft Office Professional Plus 2013).

Table 2: The percentile concentrations (mg/kg) for labile Si, Ni, and Cr for the different sampling sites in Table 1

Percentile	Si (mg/kg)	Ni (mg/kg)	Cr (mg/kg)
10th	17.4	33.2	34.2
25th	19.2	62.4	49.7
50th	64.3	94.3	170.2
75th	352.9	161.3	325.3
90th	491.8	229.6	434.1
Mean	182.4	119.8	206.7
SQG_E	100	45	64

2.2 Hazard Analysis

2.2.1 Index of geoaccumulation

The geoaccumulation index ($I_{\rm geo}$) was introduced by Müller (Müller 1969) and has been widely employed in metal studies (Li et al. 2014). It validates the evaluation of environmental contamination by comparing the differences between experimental and preindustrial concentrations. In this study, the $I_{\rm geo}$ for the soils of examined mines was computed using the following modified equation (1):

$$I_{\text{geo}} = \log_2 \left(\frac{C_n}{1.5 \text{SQG}_{\text{E}}} \right) \tag{1}$$

where C_n is the measured concentration of every trace metal found in the agricultural soil (mg/kg) and SQG_E is the soil quality guideline value (for the environmental health) of the heavy metals found in the soil (mg/kg), which is given in Table 2 (CCME 2007, 2015). The constant 1.5 is used due to potential differences in the data (Li et al. 2014).

Table 3: Seven classes comprising the geoaccumulation i	index and class	distribution for	labile Si. Ni.	and Cr
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Class	Value	Consequence/impact	Class distribution (% of sites analyzed, per element)			
			Si	Ni	Cr	
0	$I_{\rm geo} \leq 0$	Not contaminated	55	30.8	33.3	
1	$0 < I_{\text{geo}} < 1$	Uncontaminated to moderately contaminated	15	23.1	25	
2	$1 < I_{geo} < 2$	Moderately contaminated	30	46.2	25	
3	$2 < I_{geo} < 3$	Moderately to heavily contaminated			16.7	
4	$3 < I_{geo} < 4$	Heavily contaminated				
5	$4 < I_{geo} < 5$	Heavily to extremely contaminated				
6	$5 < I_{\text{geo}}$	Extremely contaminated				

The geoaccumulation index consists of seven classes or grades (Table 3), and the highest class 6 corresponds to a 100-fold increase above the soil quality guideline values.

pathway for Ni and Cr is due to ingestion and dermal absorption only, which was estimated using equations (3) and (4).

Ingestion:

2.3 Health risk assessment for Ni and Cr

Human health risk assessment can be used to estimate the hazard nature of the elements of concern and the probability of adverse health effects in humans who may be exposed to these chemicals (Health Canada, 2010). Owing to behavioral and physiological differences, the analyses were performed for adults and children, assuming they lived in close proximity to the examined areas. The health risks due to Ni and Cr exposure were estimated and analyzed.

2.3.1 Exposure assessment

The general exposure equations are based on equations provided by McBean (2018). To calculate levels of human exposure to heavy metals, the chronic daily intake (CDI) (mg/kg day) is estimated by using equation (2):

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT}$$
 (2)

where C is the chemical concentration in a particular exposure medium (mg/L, mg/kg, mg/m³), IR is the ingestion rate (L/day, kg/day, m³/day), EF is the exposure frequency (day/year), ED is the exposure duration (year), BW is the bodyweight of the exposed individual (kg), and AT is the time period over which the dose is averaged (day).

In contaminated soils, ingestion and dermal absorption are the main routes among the potential exposure pathways for Ni and Cr (Li et al. 2014). Therefore, one of the assumptions used in this study that the exposure

$$CDI_{I} = \frac{C \times SIR \times EF \times ED}{BW \times AT}$$
 (3)

where CDI_I is the average daily intake of Ni and Cr from soil ingestion (mg/kg day), C_S is the heavy metal concentration found in the soil (mg/kg), and SIR is the ingestion rate of soil (mg/day).

Dermal absorption:

$$CDI_{D} = \frac{C \times SA \times AF \times ABS \times EF \times ED}{BW \times AT}$$
 (4)

where CDI_D is the average daily intake of Ni and Cr from dermal absorption (mg/kg day), SA is the exposed skin surface area (cm²), AF is the adherence factor (mg/cm² day), and ABS is the dermal absorption factor (unitless).

2.4 Non-carcinogenic risk assessment

Non-carcinogenic hazards are generally characterized by the hazard quotient (HQ). The hazard quotient is the ratio of the chronic daily intake and the reference dose (RfD) of a particular element. The hazard quotient was determined by equation (5):

$$HQ = \frac{CDI}{RfD}$$
 (5)

where RfD is the chronic reference dose for the chemical (mg/kg day). To evaluate the overall potential for noncarcinogenic effects posed by more than one chemical or element, a Hazard index (HI) is calculated, as given by equation (6).

$$HI = \sum HQ_i = \sum \frac{CDI_i}{RfD_i}$$
 (6)

For the HI value less than unity, the health of the exposed adults or children is not at risk. For the HI value exceeding one, there is a risk of occurrence of adverse health effects. The values used for the parameters mentioned in equation (2)–(6) is given in Table S1.

2.5 Data analysis for Si

For the data available from the work of ten Berge et al. (2012), a *t*-test was conducted to check if there is a difference in the concentration of labile Si in the soil, before and after the application of olivine. A hypothetical *t*-test on a single data gives information on how the alkaline mineral amendment changes the soil composition in terms of labile Si. To estimate the probability at which the concentration of labile Si is more than that of the critical value (100 mg/kg), normality test (based on COV and Shapiro Wilks test) was conducted on the available data.

3 Results and discussion

3.1 Categorization of collected data

Based on the data available in the literature, the samples collected from different sites have been categorized from S1 to S20, the description of which has been summarized in Table 1 along with the mean, range, and SD. Gillman et al. (2002) amended highly weathered soils with basalt rock derived from seven different parent rock (S1–S7). Data for olivine and granite as a soil amendment are also presented (S8–S10). Bulmer and Lavkulich (1994) studied the weathering and geochemical evolution of ultramafic soils at four areas in British Columbia (S11–S14). Soubrand-Colin et al. (2005) examined six weathering profiles of alkali basalts and basanites (S15–S20).

As shown in Table 2 and Figure 2, the mean and median concentrations of Si, Ni, and Cr, both exceed the corresponding SQG_E value for soils. The mean concentration of Si, Ni, and Cr is 1.8 times, 2.7 times, and 3.2 times higher than the environmental quality for Ontario soil (SQG_E values). The 90% percentile concentration for labile Si (491.8 mg/kg), Ni (229.6 mg/kg), and Cr (434.1 mg/kg) lies higher than the SQG_E value (100, 45, and 64 mg/kg, respectively). From this analysis, it can be seen that the soils treated with alkaline mineral or

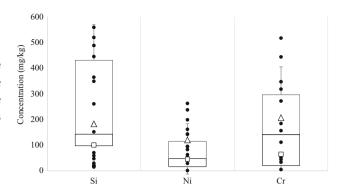


Figure 2: Box whisker plot for labile Si, Ni, and Cr (mg/kg) for the different sampling sites. ($\Delta = mean$, $\Box = SQG_E$ values).

derived from one contain elevated concentrations of Si, Ni, and Cr.

3.2 Contamination assessment based on geoaccumulation index

Figure 3 shows the distribution of the $I_{\rm geo}$ values for Si, Ni, and Cr, which lies in a range from lower than 0 up to 3. Table 3 shows the class distribution of the geoaccumulation indices for these elements, which was conducted based on the classification system using $I_{\rm geo}$ values. For the given set of the data analyzed in this study, 55%, 30.8%, and 33.3% of the sites analyzed are not contaminated with Si, Ni, and Cr, respectively, and they fall into class 0, which corresponds to $I_{\rm geo}$ value less than 0. 30%, 46.2%, and 25% of the analyzed sites are moderately contaminated with Si, Ni, and Cr, respectively, and 16.7% lies in class 3 (moderately to heavily contaminated) for Cr. Amann et al. (2020) also acknowledged the release of potentially

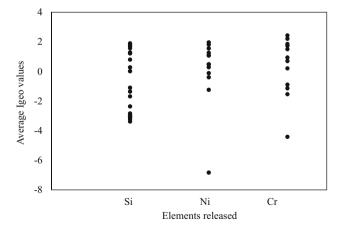


Figure 3: Average $I_{\rm geo}$ values of labile Si, Ni, and Cr for different sites analyzed.

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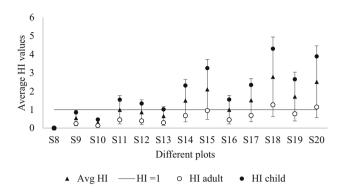


Figure 4: Average HI values (±standard deviation) for different plots. Ni and Cr data for S1–S7 is not available, hence the graph shows the HI values from S8–S20.

harmful trace elements is a potential side effect of olivine weathering and reported that the Ni concentration exceeded the limit of drinking water quality in the Netherlands. Thus, they do not recommend the use of Ni and Cr rich olivine for enhanced weathering in agricultural soils, which can be seen from the $I_{\rm geo}$ values that a minimum of 46.2%, and 41.7% of the analyzed sites are contaminated with Ni and Cr, respectively.

3.3 Noncarcinogenic risk from Ni and Cr

The values used for the estimation of CDI and HQ have been summarized in Table S1 (in the Supplementary Material). Based on the CDI values for ingestion and dermal absorption, it was seen that dermal absorption can be the main exposure pathway for Ni. The chronic daily intake of Ni through the ingestion pathway for an adult is 1.1 \times 10⁻⁴ mg/kg, whereas the chronic daily intake through the dermal absorption pathway for an adult is 2.9×10^{-4} mg/kg day. By contrast, for adult, the average daily intake of Cr through ingestion and dermal absorption pathways are 1.7×10^{-4} and 5.3×10^{-5} mg/kg day, respectively, hence indicating that ingestion can be the main exposure pathway for Cr. Additionally, the risk on human health due to Ni and Cr was characterized by HI value. Figure 4 shows the variation in the average HI values deduced from the different sites, and for samples S14-S20, average HI value exceeds unity, hence suggesting that alkaline mineral application pose non-carcinogenic risks to the surrounding populations. Hseu and Lai (2017) report about the Ni in the rice grown on serpentine derived soil in Taiwan exceeds the threshold which is consensus with the HI results of the meta-analyzed statistical data presented in this study.

Following the results of the noncarcinogenic risk assessment, the cumulative probabilities of the hazard

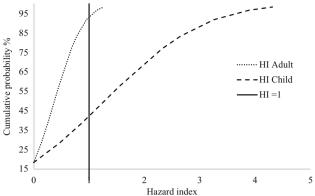


Figure 5: Cumulative probabilities for non-carcinogenic risks for two population groups.

quotients of exposed populations are shown in Figure 5, which is consistent with the results of hazard index analysis. The HI for a child is more than that for an adult. Compared with adults, children have a higher susceptibility to exposure to environmental contaminants per unit body weight due to their behavioral and physiological characteristics, such as hand-to-mouth activities for soils, higher dermal surface area, higher respiration rates per unit body weight, and increased gastrointestinal absorption of some contaminants (McBean 2018).

3.4 Data analysis for Si

3.4.1 *t*-Test

For the data available from the work of ten Berge et al. (2012), the t-test was conducted to check if there is a difference in the concentration of labile Si in the soil, before and after the application of olivine. Labile Si in control unamended soil is 14 mg/kg, and in the amended soil collected from different plots are 16.65, 15.9, 19.32, 32.08 mg/kg, with a mean of 20.9 mg/kg and SD of 7.5 mg/kg. A t-test on this data shows that the t statistic (t*) to be 1.85, which is less than the critical statistic (t_c), (2.353, for $\alpha = 5$ %). This implies that there is no significant evidence to indicate a difference in the concentration of Si in the soil after the application of olivine to the soil.

3.4.2 Estimation of probability of [Si] being greater than the critical value

To estimate the probability of labile Si concentration being greater than the critical value using equation (7),

Table 4: Shapiro Wilks test to check the normality of the data

Plots	Si (mg/kg)	i ^a	X_i^b	X_{n-i+1}^{c}	$X_{n-i+1} - X_i^d$	$\mathbf{a}_{n-i+1}^{\mathbf{e}}$	b_i^f
S6	19.5	1	19.5	558.9	539.4	0.515	277.8
S7	21.0	2	21.0	519.5	498.6	0.329	164.0
S8	29.2	3	29.2	488.3	459.1	0.2521	115.7
S9	46.7	4	46.7	445.0	398.3	0.1939	77.2
S10	58.3	5	58.3	364.5	306.2	0.1447	44.3
S11	70.0	6	70.0	348.7	278.7	0.1005	28.0
S12	151.4	7	151.4	260.3	108.9	0.0593	6.5
S13	181.6	8	181.6	181.6	0.0	0.0196	277.8
S14	260.3	9	260.3	151.4	-108.9		164.0
S15	348.7	10	348.7	70.0	-278.7		115.7
S16	364.5	11	364.5	58.3	-306.2		$b(\Sigma b_i) = 713.6$
S17	445.0	12	445.0	46.7	-398.3		W = 0.9
S18	488.3	13	488.3	29.2			$W_{\rm c} = 0.835$
S19	519.5	14	519.5	21.0		$W > W_c$	Normally distributed
S20	558.9	15	558.9	19.5			
Mean	237.5						
SD	200.5						
COV	0.8						

^a Number of samples. ^b Data arranged in ascending order. ^c Data arranged in descending order. ^d Difference between X_i and X_{n+i} . ^eCoefficient for Shapiro Wilk test for normality. ^fProduct of data in column "d" and "e".

the first step is to check if the collected data are normally distributed, which is done based on the coefficient of variance (COV) and Shapiro Wilks test (as the number of samples is less than 50). Table 4 shows the result, taking the samples S6-S20 for calculation which represents a normally distributed data set. The coefficient of skewness (C_s) is 0.37 which indicates that the data set is essentially skewed. Additionally, the value of COV is less than unity (0.8), hence indicating that the data is normally distributed, which is also supported by the results of Shapiro Wilks test, as the Shapiro Wilks statistic (*W*) is greater than the critical value (for $\alpha = 5\%$); hence, the data do not show significant evidence of nonnormality.

Since the data are normally distributed, the probabilities for a normal distribution are usually evaluated based on "standard normal distribution", where the z value is calculated by equation (7):

$$z = \frac{x - \text{mean}}{\text{SD}} \tag{7}$$

Using the z (-0.69) value, it was estimated that the probability of concentration of labile Si being greater than the critical value ($x = 100 \,\mathrm{mg/kg}$) is 75%. This implies, application of alkaline minerals to the soil can be limited due to labile Si release, and this must be managed by controlling the rate of application of the minerals.

4 Risk management

Alkaline silicate mineral-derived or -amended soil rich in Ni and Cr (heavy metals) and deficient of essential nutrients is undesirable for traditional agricultural practices. To mitigate soil contamination with any element, efficient control of the release sources and strict enforcement of environmental regulations is required. If the purpose of the soil amended with or derived from an alkaline mineral source is to grow agricultural crops, then certain plants can be grown which require these elements as microcurrents for their growth. For example, Si is a beneficial element for plant nutrition, especially for crops such as sugarcane and rice which require a certain level of "labile Si" for their optimum growth. Another way to mitigate the concentration of Si in the soil is by phytoremediation, where phytoaccumulator plants can be grown, Mustard green (Brassica juncea) and rapeseed (Brassica napus) have been reported to be used for the phytoaccumulation of Si (Rahman et al. 2016). Kidd et al. (2018) suggest the use of Ni-hyperaccumulator *Odontarrhena* sp. to bioaccumulate Ni in the plant biomass, that can be incinerated to produce Ni-enriched ash or "bio-ore" from which Ni metal can be recovered. This agromining method offers sustainable metal recovery along with mitigating the environmental impacts associated with Ni-rich alkaline minerals enhanced weathering.

In the long-term, one way of managing the labile Si, Ni, and Cr concentration is by controlling the rate of application of mineral rock into the agricultural soil, which can be estimated using the following equation (8):

Rate of application

critical value for element × soil density × accumulation depth (8)

Total extractable concentration of element in the mineral rock Conflict of interest: The authors declare no conflict of

The rate would depend on the parent rock, soil density, as well as the accumulation depth. For example, in the case of olivine for Ni, the maximum rate of application for olivine (containing 3 g Ni/kg of olivine) is 112.5 tonne ha⁻¹, and for Cr, it is 3,200 tonne ha⁻¹ (for olivine containing 150 mg Cr/kg of olivine). The appropriateness of these values depends on the soil density and accumulation depth.

5 Conclusion

Enhanced weathering of alkaline silicate minerals to sequester CO₂ as soil carbonates are also associated with the release of metals contained in the mineral composition during the weathering (Ni, Cr) as well as labile Si which may pose an environmental risk. The release of Ni, Cr, and Si, especially in agricultural soils, creates a global environmental issue, particularly, incorporation of Ni and Cr into the food chain that may affect animal and human health. This would subsequently lower the potential use of alkaline minerals for the purpose of terrestrial enhanced weathering. This study provides a meta-analysis tool to statistically interpret the results from different studies into a single estimate of the effect of the release of Ni, Cr, and Si from alkaline silicate minerals as a result of enhanced weathering. The main findings of this study indicate the potential release of Ni, Cr, and Si to exceed the SQG_E value. The I_{geo} value suggests the analyzed samples are in the class 0-3 and represents sites that lie between uncontaminated zones to highly contaminated zones. The HI value for Ni and Cr is greater than unity, which suggests that Ni and Cr release pose a non-carcinogenic risk. The probability of labile Si concentration in the soil to exceed the critical value is 75%. Hence, the main significance of this study is to provide a statistical methodology to characterize the risk associated with the release of heavy metals, depending on the composition of the parent rock, thus helping other researchers to estimate the risk associated with the use of alkaline minerals as a soil amendment on the environment as well as on human health. This would also aid in designing the risk management strategy to mitigate the risk in the long term. In this study, the risk management strategy proposed includes controlling the rate of application of the mineral and growing hyperaccumulator plants.

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