# Application of Geochemistry and VNIR Spectroscopy in Mapping Heavy Metal Pollution of Stream Sediments in the Takab Mining Area, NW of Iran

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Abstract: This study considered the possibility of using visible and near infrared (VNIR) spectral absorption feature parameters (SAFPs) in predicting the concentration and mapping the distribution of heavy metals in sediments of the Takab area. In total, 60 sediment samples were collected along main streams draining from the mining districts and tailing sites, in order to measure the concentration of As, Co, V, Cu, Cr, Ni, Hg, Ti, Pb and Zn and the reflectance spectra (350–2500 nm). The quantitative relationship between SAFPs (Depth<sub>500nm</sub>, R<sub>610/500nm</sub>, R<sub>1344/778nm</sub>, Area<sub>500nm</sub>, Depth<sub>2200nm</sub>, Area<sub>2200nm</sub>, Asym<sub>2200nm</sub>) and geochemical data were assessed using stepwise multiple linear regression (SMLR) and enter multiple linear regression (EMLR) methods. The results showed a strong negative correlation between Ni and Cr with Area<sub>2200nm</sub>, a significant positive correlation between As and Asym<sub>2200nm</sub>, Ni and Co with Depth<sub>2200nm</sub>, as well as Co, V and total values with Depth<sub>500nm</sub>. The EMLR method eventuated in a significant prediction result for Ni, Cr, Co and As concentrations based on spectral parameters, whereas the prediction for Zn, V and total value was relatively weak. The spatial distribution pattern of geochemical data showed that mining activities, along with the natural weathering of base metal occurrences and rock units, has caused high concentrations of heavy metals in sediments of the Sarough River tributaries.

Key words: heavy metals, SAFPs, VNIR spectroscopy, multiple linear regression, Takab, Iran

# **1** Introduction

Mining and ore-processing activities are the main processes by which heavy metals are released into the environment, affecting the geochemical characterization of the surrounding soil and sediment (Kodirov and Shukuov, 2009; Xiaochun et al., 2010; Darwish, 2011; Luo et al., 2012; Chaudhary et al., 2013; Lark et al., 2017;). Contamination of soil and sediments with heavy metals in downstream areas of mining sites is an ever-growing worldwide concern. As such, an environmentally-friendly method is needed to rapidly detect the contaminated areas and control the rehabilitation process (Schwartz et al., 2012). Sampling of stream sediments has been used as a useful technique for assessing the spatial distribution of heavy metals in the surface environment. Despite its widespread use, a complete procedure of geochemical mapping which involves sampling, sample preparation and laboratory analysis, is time-consuming and imposes huge costs on any project. Therefore, scientists have been seeking to find new technologies to facilitate and accelerate the procedure of geochemical projects.

Reflectance spectroscopy covering the visible and near infrared ranges (400–2400 nm) is a rapid, straightforward and nondestructive analytical method which can be used to predict and quantify heavy metal content in soil and sediment (Omran, 2016; Wetterlind et al., 2013). Heavy metals, as a rule do not show characteristic absorption features in the visible and near-infrared region of the spectrum (Pandit et al., 2010; Zhang et al., 2010; Liu et al., 2011; Schwartz et al., 2012). They might be detected indirectly through the spectral variation of minerals such as clay, iron-manganese oxides and organic matter (OM), as heavy metals are adsorbed onto their faces (Schwartz et al., 2012). The binding reaction of heavy metals on the surfaces of clay and oxide minerals may result in variations in the shapes of their absorption peaks (e.g., depth, area or

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asymmetry of reflectance spectra) at around 2200 nm and 500–1000 nm, respectively (Choe et al., 2008).

The effective conjugation between VNIR-SWIR spectroscopy and geostatistical tools has facilitated the preparation of heavy metal distribution maps and determining the spatial extent of a polluted area (Chen et al., 2015; Chakraborty et. al., 2017). Meanwhile, the possibility of extending the results obtained from ground derived spectral data to hyperspectral data, has developed the applicability of this technique for mapping the heavy metal polluted areas on HyMAP images during the last decades (Choe et al., 2008; Zhang et al., 2010; Mulder et al., 2011; Liu et al., 2011; Chen et al., 2012; Croft et al., 2012; Omran, 2016). Considering these advantages, VNIR -SWIR spectroscopy is commonly used as a preliminary step in deciding upon sampling and analysis strategies in most geochemical mapping projects (Shi et al., 2007).

Several quantitative spectroscopic researches for assessing heavy metal contamination have been carried out during the past decade (Ji et al., 2010; Pandit et al., 2010; Gannouni et al., 2012; Todorova et al., 2014; Ong and Cudahy, 2014; Gholizadeh et al., 2015b; Sakizadeh et al., 2015; Omran, 2016; Chakraborty et al., 2017). Choe et al. (2008) derived spectral absorption feature parameters (SAFPs) in the range of 400-2400 nm from spectral variation associated with heavy metals in sediments in the Rodalquilar mining area in Spain. According to the results, the ratio of 610 to 500 nm (R<sub>610,500 nm</sub>), absorption area at 2200 nm (Area<sub>2200 nm</sub>) and asymmetry of the absorption feature at 2200 nm (Asym<sub>2200 nm</sub>) indicated good correlations for concentrations of Pb, Zn, and As, respectively. Also, the result of their study showed similar spatial patterns between spectral gradient maps derived from HyMAP images and ground-derived spectral parameters as well as geochemical gradient maps along major streamlines. Later, Choe et al. (2009) applied the spectral absorption feature parameters to quantify the heavy metal content of soil around an abandoned Au-Ag mine using stepwise (SMLR) and enter (EMLR) multiple linear regression methods. Omran (2016) demonstrated the possibility of using the VNIR-SWIR spectroscopy chemometrics technique in the prediction of heavy metals in Bahr El Baqar soils, Egypt. Chakraborty et al. (2017) examined the feasibility of using the visible near infrared spectra for detecting soil As pollution in the eastern peripheries of Kolkata city, India. The results showed that there is a close association between As content, organic matter and Fe-/Al-oxides in the soil.

The Takab area in the North West of Iran is a significant mineralized zone with large gold deposits and many mineral indices of heavy metals. The area has faced a serious environmental challenge during past decades.

Mining and mineral processing activities have caused a vast pollution, especially in downstream areas. Development of irrigated farmlands and gardens along with polluted streams has increased the risk of exposure to toxic metals among the residents of the region. Considering the above, it can be concluded that after years of mining which has caused extensive distribution of toxic elements, stream sediments should be used in geochemical mapping for the identification of spatial distribution patterns of heavy metals.

This study aims to investigate the applicability of using spectral absorption feature parameters (SAFPs) to predict and map the distribution of heavy metals in sediments along the main streams of the Takab mining area.

# 2 Geological Background

The Takab mining area, North West of Iran, is located between longitudes  $47^{\circ} 00' - 47^{\circ} 17'E$  and latitudes  $36^{\circ} 30'$  $-36^{\circ} 45'N$ , which covers an area approximately 753 km<sup>2</sup> (Fig. 1). The area is generally covered by mountains, especially in the northern parts. The topography varies from 3320m (Belghais Mountain) above mean sea level in the head reaches in the north-eastern part, to 1420m above mean sea level at the outlet in the south-western part of the area. The Sarough River is the main surface water resource for drinking and agricultural usage. The Zarshuran, Aq-Darreh and Ahmad Abad Streams are the main branches of the Sarough River which cross the mining districts.

Based on a 1:100,000 scale geology map of the study area (Fig. 1a), the oldest rock units are mainly composed of epidote schist, chlorite schist, serpentinite schist and quartzite of lower Precambrian age, which are overlain by metamorphosed ultramafic rocks, including serpentinite, serpentine schist and metamorphosed gabbro and basalt. These rocks underlie thick bedded crystalline limestone and dolomite of the upper Precambrian sequence. The black shale and carbonate intercalations that host the main part of the gold mineralization composes the upper unit, which is covered by rhyolitic tuff, sandstones and green shale. The Precambrian unit is followed upward by dolomite, limestone, shale, and sandstone deposits of Cambrian age. An extensive part of the area is covered by Oligo-Miocene sedimentary deposits composed of gypsiferous marl, limestone and sandstone, associated with basaltic and andesitic volcanic rocks. Travertine deposits and alluvium fans are the youngest lithologies in this area (Babakhani and Ghalamghash, 1995). There is an abundance of hot springs notably nearby travertine deposits which are generated from fluids of an active hydrothermal system related to the volcanic setting of the



study area (Alavi et al., 1982).

Mineralization in the Takab area resulted from hydrothermal fluids released from deep and semi-deep intrusions of Cenozoic rock, which has caused a vast variety of mineralizations, such as gold, arsenic, antimony, copper, mercury, lead and zinc (Ghorbani, 1999). Zarshuran and Aghdarreh are the main deposits of the area that are classified as gold deposits of the Carlin type (Maghsoudi et al., 2005). According to historical documents, gold exploitation in Takab goes back to 1400 years ago (Zavosh, 1977). The signs of ancient mine workings as washing gold-bearing sands, has been discovered along Zarshuran stream. The location of mines, base metal occurrences and tailing sites in the study area is shown in Fig. 1a.

The Zarshuran and Aq-Darreh mines are located upstream of the Zarshuran and Aq-Darreh streams, respectively. According to previous studies, a high concentration of heavy metals in water and bed sediments of these streams has placed them amongst the heaviest polluted rivers of the world (Modabberi & Moore 2004; Rahimsouri et al., 2013).

# **3** Materials and Methods

### 3.1 Sediment sampling and preparation

Dry sediment samples were collected from 60 sampling sites along the main streams that drain from the mining districts and tailing sites from August to October 2015. Sediments were prepared in the field by drysieving through a 2mm polyethylene mesh on wooden frames to remove stones and debris. All the samples were stored in plastic bags and sent back to the camp. Samples were air-dried at room temperature, ground using an agate mortar and then passed through a 230 mesh nylon sieve to achieve a sediment fraction smaller than 63 µm. A portion of the prepared sediment samples was sent to the laboratory of the Geological Survey of Iran (GSI) for chemical analysis and another portion was used for spectral measurement in the laboratory of the Tarbiat Modarres University (TMU). It should be noted that 15 sediment samples (accounting for 25% of total samples) were selected randomly as test samples for evaluating the accuracy of the prediction models, and thus only 45 samples (training samples) entered the procedure of geochemical and spectral data processing and modeling.

### **3.2 Chemical Analysis**

For chemical analysis, sediment samples were prepared via a total extraction method by using aqua regia solution (1:3 ratio of HNO<sub>3</sub> to HCl). The concentration of Co, V,

Cu, Cr, Ni, Hg, Ti, Pb and Zn was determined by inductively coupled plasma mass spectrometry (ICP–MS), whereas As concentration was determined by atomic fluorescence spectrophotometry (AFS).

### **3.3 Spectroscopy analysis**

Reflectance spectra of the sediments were measured using a Fieldspec®3 spectrometer (ASD, Fr, USA) in a dark room to prevent stray light interference. The instrument covers the visible and near infrared (350–2500 nm) range. The samples were placed in a  $60\times15\times8$  mm holder. The spectral measurement was performed using a contact probe, which involves contact measurements with a spot size of 42 mm. A 150W halogen lamp with a fieldof-view of 45° at nadir was set as the light source. The recalibration of the spectrometer was conducted after every 3 samples using a white BaSO<sub>4</sub> panel. Sediment samples were scanned 20 times. The average spectral curve of the samples was prepared using ViewSpec Pro ver.6 (ASD, Inc) software, which offers a spectral resolution of 1 nm.

# **4 Results and Discussions**

### 4.1 Geochemical analysis

The statistical processing was carried out using SPSS ver.21 (SPSS Inc., USA) and Microsoft Excel 2010 software. The descriptive statistics for the heavy metal content in the sediments of the study area are presented in Table 1. The highest concentration of the ten heavy metals belonged to Ti ranging from 994 ppm to 8408 ppm, with the mean value of 3444 ppm. The mean concentration of heavy metals in the study area followed the descending order of Ti>As> Zn> Pb, Cr> V> Ni> Cu> Co> Hg.

To evaluate the possibility of observing adverse biological effects in the sediments of the study area, the heavy metal content of the samples was compared with Canadian Sediment Quality Guidelines (CCME, 2002) using two assessment values. The lower value, referred to as the Threshold Effect Level (TEL), represents the concentration below which adverse biological effects are expected to rarely occur. The upper value, referred to as the Probable Effect Level (PEL), defines the level above which adverse effects are expected to frequently occur. The results showed that the concentration of As in all sediment samples was higher than the TEL threshold value. In terms of contamination level, Ni (95%), Cr (88%) and Pb (73%) ranked in first to third, respectively. This means that adverse effects caused by the presence of these elements are expected to occur. To evaluate the risk of adverse effects caused by the elements that have a higher concentration of TEL values, calculating the PEL is

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Table 1 Descriptive statistics of heav	v metal concentration (	(nnm) in sediments of st	udv area and CSOGs values
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Sample	Hg	Pb	Со	Cr	Cu	Ni	Ti	V	Zn	As	Total
<u>S1</u>	0.38	42.78	9.07	61.61	13.56	34.56	2503.70	52.25	72.03	188.00	2977.94
S2	0.76	54.98	5.28	35.98	6 64	15 74	1666 19	32.28	66.06	238.00	2121.92
\$3	2.73	69.84	8.02	34 32	19.05	19 19	2193.82	49.61	84 20	139.00	2619 79
S4	0.15	39.86	22.94	64.21	18.62	40.63	5726.94	92.05	99.05	280.00	6384.44
85	0.15	22.77	57.12	1347 38	19.43	1699 55	994 87	49.06	153 75	84 30	4428 37
S6	0.49	374 14	20.06	106.18	33.45	114 19	3591 25	113 32	916.32	370.00	5639 40
S7	0.15	219.46	28.79	352.10	29.25	325 39	3958 75	130.19	1295.87	435.00	6774 94
S8	0.15	550.42	20.45	75 32	51.20	40.73	4470 35	141 31	396.06	379.00	6125.00
59	0.15	259.81	16 71	57.34	31.20	45.97	3445.61	111.16	703 11	418.00	5089 47
S10	0.15	38.66	12.84	52.10	18.61	33.77	2659.62	75.05	75 25	65 30	3031 35
S11	0.15	43 31	23.47	53.97	32.33	53.47	5415.35	156.66	145 74	56 50	5980.96
\$12	0.15	36.89	15.07	139 54	20.75	90.61	3106.81	81.35	315 74	186.00	3992.91
S12 S13	0.15	72 38	18.51	229.29	23.80	200.35	2999 70	75.63	546 44	372.00	4538.24
\$14	0.15	46.11	16.00	62.60	22.00	47.04	3948 31	101.14	91.57	28.00	4362.92
\$15	0.15	20.04	8 25	20.24	0.30	20.48	2106.69	35 44	32.65	20.00	2334.83
S16	0.25	61.09	8.05	61.36	16.05	20.48	1752 57	52.68	85.52	411.00	2475.01
\$17	0.15	60.27	17.61	88.21	77.24	40.03	2576.28	122.08	140.22	120.00	4270.40
S17 S18	1 11	212.48	15.07	53 77	115.22	49.03	2020 71	01.84	227.10	120.00	2702.63
S10	0.15	212.48	17.10	44.70	26.12	25.51	2929.71	120.95	227.19	21.70	4401.00
519	0.15	272.39	26.40	501.24	20.15	25.51	4106 59	150.85	235.49	21.70	5459 09
S20 S21	0.15	22.84	10.40	64.21	19.90	257.77	4190.38	170.74	76.00	8 50	1078 11
521	0.15	32.84	18.21	120.20	28.33	55.51 70.16	3842.03	170.77	76.90	8.30	42/8.14
522	0.15	0/.0/	21.//	130.20	30.03	/9.10	3834.47	128.02	90.17	41.20	4448.85
523 524	2.37	121.99	/.58	37.37	12.07	14.58	1924.55	48.81	//.6/	118.00	2365.59
S24	18.22	1139.67	19.55	93.00	32.38	67.74	3164.47	115.50	539.40	6509.00	11698.93
825	0.39	89.76	13.61	57.81	23.26	35.31	2/15.32	75.24	14/.//	280.00	3438.48
S26	0.22	68.14	12.03	40.51	35.09	29.42	2556.61	/4.15	85.42	62.00	2963.58
S27	0.56	25.93	13.41	45.87	26.86	34.42	2461.46	64.11	/8.95	32.20	2/83./8
S28	0.15	24.64	13.91	48.53	63.75	39.54	2699.72	76.12	/1.46	50.50	3088.32
S29	0.15	20.61	15.76	49.58	25.49	42.63	2811.43	76.48	104.62	52.60	3199.35
\$30	0.15	35.60	15.92	69.63	31.47	62.46	2778.36	78.04	148.31	165.00	3384.93
\$31	1.16	18.08	17.30	29.30	22.15	37.60	2290.23	50.52	56.00	12.30	2534.64
S32	0.20	64.63	18.10	104.11	35.13	74.07	3422.63	120.20	78.07	62.20	3979.33
\$33	3.90	199.69	25.77	80.00	36.36	96.13	3964.88	114.17	244.53	374.00	5139.42
S34	1.35	333.96	20.06	42.33	16.98	38.29	4082.17	140.57	100.95	81.50	4858.16
S35	1.39	30.85	17.13	36.26	14.52	32.27	3293.35	126.11	81.54	48.00	3681.43
S36	0.15	32.26	26.09	124.70	32.63	45.50	4902.98	181.96	80.70	34.80	5461.77
S37	0.15	37.09	33.13	127.56	56.77	56.91	8408.21	178.33	83.61	18.00	8999.77
S38	0.15	72.05	24.73	82.66	32.22	48.74	5177.64	166.51	84.33	33.20	5722.22
S39	0.15	81.06	21.95	57.24	30.62	32.91	5704.14	139.03	81.00	31.60	6179.71
S40	0.15	39.82	21.81	98.52	20.50	56.20	3893.50	133.86	117.66	56.20	4438.22
S41	0.15	39.82	22.27	119.83	21.77	56.09	3475.23	136.08	96.42	141.00	4108.66
S42	0.15	29.86	18.56	78.11	16.70	37.64	3045.88	104.98	94.81	60.00	3486.70
S43	0.22	75.59	12.81	92.37	20.21	32.98	2956.23	96.10	83.59	75.60	3445.70
S44	0.27	12.14	10.81	73.99	16.97	30.69	3249.13	75.64	53.34	11.50	3534.48
S45	0.35	13.85	11.87	64.25	18.50	32.61	3514.83	85.46	64.75	42.30	3848.77
Min	0.15	12.14	5.28	29.24	6.64	14.58	994.87	32.28	32.65	8.50	2121.92
Max	18.22	1139.67	57.12	1347.38	115.32	1699.55	8408.21	181.96	1295.87	6509.00	11698.93
Mean	0.90	117.75	18.26	117.75	29.61	96.04	3444.95	102.84	191.99	277.05	4397.14
Median	0.15	54.98	17.30	64.25	23.80	40.63	3293.35	101.14	91.57	75.60	4108.66
St.deviation	2.75	191.30	8.47	205.36	19.35	251.67	1285.32	40.63	247.55	959.02	1791.50
Skewness	5.97	3.97	2.20	5.28	2.55	6.17	1.40	0.17	3.00	6.52	1.91
Kurtosis	37.82	18.86	9.15	30.64	8.44	39.74	4.05	-0.89	9.73	43.24	5.63
PEL Values	0.5	91.3		90	197	36			315	17	
%Anomaly	24.4	22.2		311	0	60			15.5	93 3	
TEL Values	0.2	35		37.3	357	18			123	59	
%Anomaly	44.4	73 3		88.8	15.5	95 5			33.3	100	
/or monuny	т.т.	د.د ،		00.0	10.0	0.01				100	

also necessary. According to the results, no sediment samples exceeded the PEL level for Cu, whereas 93.3% of As, 60% of Ni, 31% of Cr, 24% of Hg, 22% of Pb and 15% of Zn contents were higher than thresholds.

### 4.2 Spectral analysis

The spectral analysis was performed with IDL DISPEC v.3.6 (ITC-UT). The continuum-removed signal (CRS) analysis was used to enhance the spectral absorption features of measured reflectance spectra, decide the best data (Gholizadeh et al. 2015a), minimize any brightness differences and emphasize the spectra's absorption bands (Ren et al., 2009). Spectral absorption feature parameters (SAFPs) such as peak depth, area, band ratio and asymmetry were derived from spectral curves. Parameters related to the shape of the absorption peak (depth, area and asymmetry) were calculated from transformed spectra, whereas the band ratio was measured from the raw reflectance spectra. Table 2 shows the descriptive statistics for spectral feature parameters derived from laboratory

analysis.

# 4.3 Correlation analysis between geochemical data and spectral parameters

According to the Kolmogorov-Simonov normality test, the data of heavy metal concentration and values of Area<sub>500nm</sub> and Area<sub>2200nm</sub> did not approach a normal distribution. Therefore, the data were transformed into a log scale for further statistical analysis. Pearson's correlation coefficient was used to assess the relationship between spectral parameters and heavy metals concentration in the sediment samples (Table 3).

As showed the highest correlation coefficient with Asym<sub>2200nm</sub> (0.76) at a significant level of 0.01. Ni and Cr each had a strong negative correlation coefficient with Area<sub>2200nm</sub> which was -0.77 and -0.76, respectively. The Depth<sub>2200nm</sub> had a positive correlation with Ni (0.62). There was a positive relationship between Depth<sub>500nm</sub> with Co (0.64), V (0.61) and Zn (0.54). Depth<sub>2200nm</sub> showed a positive correlation with Co (0.6). Total concentration of heavy metals had a positive correlation coefficient with Depth<sub>500nm</sub> (0.64) and Depth<sub>2200nm</sub> (0.53).

# 4.4 Predictive model for assessing heavy metal concentration

Stepwise Multiple Linear Regression (SMLR) and Enter Multiple Linear Regression (EMLR) were used to assess the quantitative relationship between spectral absorption feature parameters and heavy metals concentration in sediments by establishing the regression equations (Table 4). To validate data, the parameters in the range of  $R^2$ (>0.5), RPD (>1.3) and SEE (<0.4) were applied (Chang et al., 2001).

For the SMLR model Depth<sub>500nm</sub>, Depth<sub>2200nm</sub>, log

Area<sub>2200nm</sub>, log Area<sub>500nm</sub> and Asym<sub>2200nm</sub> were mainly used as predictors. Prediction of Ni ended in most reliable results ( $R^2=0.75$ , SEE=0.17) using Depth<sub>2200nm</sub>, log Area<sub>2200nm</sub> and Asym<sub>2200nm</sub>, as well as for Cr ( $R^2$ =0.66, SEE=0.149) using Depth<sub>2200nm</sub> and log Area<sub>2200nm</sub>. The prediction of Co using three predictors (log Area<sub>500nm</sub>, Depth<sub>500nm</sub> and log Area<sub>2200nm</sub>) revealed a statistically significant result ( $R^2$ =0.62, SEE=0.09). The results showed a moderate prediction for As using Asym<sub>2200nm</sub> as a predictor ( $R^2$ =0.58, SEE=0.273). In contrast, the prediction results of V and total value using Depth<sub>500nm</sub> showed a weak relationship  $(R^2=0.36 \text{ and } 0.41)$ . respectively). Also, the result showed that there is a relatively weak relationship between Zn concentration and spectral parameters such as Depth<sub>500nm</sub> and Asym<sub>2200nm</sub>  $(R^2=0.48, SEE=0.187)$ . In the EMLR model, heavy metals were quantified using all spectral parameters in the regression as predictors. The results indicated a significant prediction performance for Ni, Cr, Co and As with R<sup>2</sup> values of 0.79, 0.68, 0.67 and 0.64, respectively. The calculated  $R^2$  values of 0.55 and 0.51 indicated that the prediction for Zn and V was relatively weak. In terms of total value, calculating the coefficient of determination  $(R^2 = 0.48)$  showed that there was a relatively weak prediction result based on SAFPs.

### 4.5 Evaluation of predictive models

The validation of the prediction equations was implemented using 15 test samples which were excluded from the data processing and modeling procedure. The best predictive regression equations were selected based on the highest coefficient of determination ( $R^2$ ) and the lowest standard error of estimation (SEE) as the fitness indicators of the models. Accordingly, enter multiple

Table 2 Descriptive statistics	of SAFPs of sediment	samples of study are	ea derived from l	aboratory analysis
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-			-	-			
	R <sub>610/500nm</sub>	R <sub>1344/778nm</sub>	Depth <sub>500nm</sub>	Depth <sub>2200nm</sub>	Area <sub>500nm</sub>	Area <sub>2200nm</sub>	Asym <sub>2200nm</sub>
Min	1.256	1.003	0.508	0.267	10.95	3.19	-0.490
Max	2.057	1.259	0.743	0.555	279.17	77.51	0.210
Mean	1.506	1.121	0.659	0.398	69.9	50.48	0.078
Median	1.479	1.116	0.661	0.393	60	49.33	0.110
St.deviation	0.166	0.063	0.053	0.072	50.28	12.19	0.115
Skewness	1.104	0.209	-0.757	0.427	0.21	-0.08	-3.176
Kurtosis	1.639	-0.436	0.665	-0.489	0.63	0.42	13.579

#### Table 3 Pearson's correlation coefficient between spectral parameters and heavy metals concentration in sediments

	R <sub>1344/778nm</sub>	R <sub>610/500nm</sub>	Depth <sub>500nm</sub>	Depth <sub>2200nm</sub>	log(Area500nm)	log(Area2200nm)	Asym <sub>2200nm</sub>
Log(Hg)	-0.05	-0.06	-0.33*	-0.24	-0.04	0.24	0.21
log(Pb)	-0.05	-0.13	0.26	0.32*	-0.09	0.11	.402**
log(Co)	0.08	0.10	0.64**	0.60**	-0.01	-0.58**	-0.05
log(Cr)	-0.02	-0.21	0.44**	0.56**	-0.33*	-0.76**	0.13
log(Cu)	0.26	0.24	0.50**	0.22	0.14	-0.09	-0.04
log(Ni)	-0.02	-0.10	0.54**	0.62**	-0.28	-0.77**	0.18
log(Ti)	0.09	0.28	0.46**	0.32*	0.34*	0.30*	-0.20
log(V)	0.15	0.14	0.61**	0.42**	0.15	-0.01	-0.23
log(Zn)	0.01	0.01	0.54**	0.52**	-0.11	-0.16	.397**
log(As)	-0.05	-0.01	0.09	0.14	-0.05	0.06	.763**
log(Total)	0.13	0.18	0.64**	0.53**	0.11	-0.19	0.04

\*\* Correlation is significant at the 0.01 level (2-tailed). \* Correlation is significant at the 0.05 level (2-tailed).

	Table	4 Linear regressions	(SMLR, EMLF	A) between heav	v metal concentration a	nd SAFPs of s	ediment samp	les
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	Predictor	F	p-value	$R^2$	<sup>a</sup> SEE	<sup>b</sup> RPD	°SDV	Equation
Stepwise m	ultiple linear regression (SMLI	R)	•					·
<u>^</u>	Depth <sub>500nm</sub>	30.35	0.000	0.414	0.146			$Log(Co) = -0.28 + 2.28 Depth_{500nm}$
$\mathbf{L} = \mathbf{r}(\mathbf{C} \cdot \mathbf{r})$	Depth <sub>500nm</sub> , log(Area <sub>2200nm</sub> )	28.7	0.000	0.578	0.125			Log(Co)=0.69+1.83 Depth <sub>500nm</sub> -0.41 log (Area <sub>2200nm</sub> )
Log(Co)	Depth <sub>500nm</sub> ,log(Area <sub>2200nm</sub> ),	22.20	0.026	0 (21	0.000	156	0.14	Log(Co)=0.71+1.69 Depth <sub>500nm</sub> -0.52 log(Area <sub>2200nm</sub> )+0.15
	Log(Area <sub>500nm</sub> )	22.38	0.030	0.021	0.090	1.50	0.14	log(Area <sub>500nm</sub> )
$L_{og}(Cr)$	Log(Area <sub>2200nm</sub> )	59.15	0.000	0.579	0.189			Log(Cr)=3.95-1.23 log(Area <sub>2200nm</sub> )
Log(CI)	Log(Area <sub>2200nm</sub> ), Depth <sub>2200nm</sub>	40.92	0.003	0.661	0.149	1.67	0.25	Log(Cr)=3.09-1.04 log(Area <sub>2200nm</sub> )+1.36Depth <sub>2200nm</sub>
	Log(Area <sub>2200nm</sub> )	63.53	0.000	0.596	0.232			Log(Ni)=4.08-1.42 log(Area2200nm)
Log(Ni)	Log(Area <sub>2200nm</sub> ), Depth <sub>2200nm</sub>	54.73	0.000	0.723	0.194			Log(Ni)=2.85-1.15 log(Area <sub>2200nm</sub> )+1.93Depth <sub>2200nm</sub>
Lug(INI)	Log(Area <sub>2200nm</sub> ),	41 50	0.033	0.752	0 170	1.82	0.31	$L_{00}(Ni) = 2.9 - 1.17 \log(Areasson) + 1.81 Dentheseo + 0.54 Asymptotecter$
	Depth2200nm, Asym2200nm	41.50	0.055	0.752	0.170	1.02	0.51	Log(101)=2.9 1.17 log(Alca2200nm)+1.01Deput2200nm+0.54ASyItt2200nm
Log(V)	Depth <sub>500nm</sub>	24.89	0.000	0.367	0.1	1.1	0.11	Log(V)=0.53+2.18 Depth <sub>500nm</sub>
Log(Zn)	Depth <sub>500nm</sub>	17.43	0.000	0.288	0.206			$Log(Zn) = -0.21 + 3.51 Depth_{500nm}$
Log(Zii)	Depth500nm, Asym2200nm	19.35	0.000	0.480	0.187	1.28	0.24	Log(Zn)=-0.45+3.71 Depth <sub>500nm</sub> +1.32Asym <sub>2200nm</sub>
Log(As)	Asym <sub>2200nm</sub>	59.93	0.000	0.582	0.273	1.46	0.4	Log(As)=1.68+3.54 Asym <sub>2200nm</sub>
Log(Total)	Depth <sub>500nm</sub>	29.83	0.000	0.410	0.072	1.25	0.09	Log(Total)=2.37+1.88 Depth <sub>500nm</sub>
Enter multip	ble linear regression (EMLR)							
Log(Co)		10.72	0.000	0.670	0.088	1 58	0.14	$\log(\text{Co}) = -0.3 + 1.54 \text{ R}_{1344/778nm} - 0.33, \text{ R}_{610/500nm} - 0.35 \text{ Depth}_{500nm} + 1.6$
Log(CO)		10.72	0.000	0.070	0.000	1.50	0.14	Depth <sub>2200nm</sub> +0.53 log(Area <sub>500nm</sub> )-0.61 log(Area <sub>2200nm</sub> )+0.2 Asym <sub>2200nm</sub>
Log(Cr)		11.41	0.000	0.683	0 148	1.68	0.25	$\log(Cr) = 2.4 + 0.73 R_{1344/778nm} - 0.15 R_{610/500nm} - 0.34 Depth_{500nm} + 1.64$
Log(CI)		11.41	0.000	0.005	0.140	1.00	0.25	Depth <sub>2200nm</sub> +0.15 log Area <sub>500nm</sub> -1.09 log Area <sub>2200nm</sub> +0.41 Asym <sub>2200nm</sub>
Log(Ni)		1977	0.000	0 789	0 173	1 84	0.32	$\log(Ni) = 1.74 + 0.31 R_{1344/778nm} + 0.82 R_{610/500nm} + 0.16 Depth_{500nm} + 1.84$
Log(III)	Depth <sub>500nm</sub> , Depth <sub>2200nm</sub> ,	17.77	0.000	0.707	0.175	1.04	0.52	Depth <sub>2200nm</sub> -0.38 log(Area <sub>500nm</sub> )-1.1 log(Area <sub>2200nm</sub> )+0.61Asym <sub>2200nm</sub>
I og(V)	R <sub>610/500nm</sub> , R <sub>1344/778nm</sub> ,	5 4 5	0.000	0 508	0.098	1 32	0.13	*log(V)=0.45+0.31 R <sub>1344/778nm</sub> =0.92R <sub>610/500nm</sub> +2.97Depth <sub>500nm</sub> =0.32
LUG(V)	Log(Area <sub>500nm</sub> ),	5.45	0.000	0.500	0.070	1.52	0.15	Depth <sub>2200nm</sub> +0.57 log(Area <sub>500nm</sub> )+0.03 log(Area <sub>2200nm</sub> )-0.3 Asym <sub>2200nm</sub>
Log(Zn)	log(rea2200nm), Asym 2200nm	6 50	0.000	0.552	0 1 7 8	14	0.25	*log(Zn)=1.02-2.27 R <sub>1344/778nm</sub> +0.96R <sub>610/500nm</sub> +5.19Depth <sub>500nm</sub> -0.73
Log(ZII)		0.50	0.000	0.552	0.170	1.4	0.25	Depth <sub>2200nm</sub> -1.01 log(Area <sub>500nm</sub> )+0.42log(Area <sub>2200nm</sub> )+1.15Asym <sub>2200nm</sub>
I og(As)		9 30	0.000	0.638	0 274	1 53	0.42	*logAs=-0.42+0.29 R <sub>1344/778nm</sub> +1.15R <sub>610/500nm</sub> +0.64Depth <sub>500nm</sub> +0.66
105(113)		7.50	0.000	0.050	0.274	1.55	0.72	Depth <sub>2200nm</sub> -0.87 log(Area <sub>500nm</sub> )+0.52log(Area <sub>2200nm</sub> )+3.59 Asym <sub>2200nm</sub>
Log(Total)		5.00	0.000	0 486	0.079	1 26	0.1	*log(Total)=1.35+1.45R <sub>1344/778nm</sub> -0.22R <sub>610/500nm</sub> -0.14Depth <sub>500nm</sub> +1.51
Log(Total)		5.00	0.000	5.100	0.077	1.20	0.1	Depth <sub>2200nm</sub> +0.37 log(Area <sub>500nm</sub> )-0.12 log(Area <sub>2200nm</sub> )+0.13 Asym <sub>2200nm</sub>

a, Standard error of estimate. b, Ratio of prediction deviation. c, Standard deviation of validation set. \* The optimal predicting equations.

linear regression analysis showed higher predictive performances for all heavy metals and total value rather than the stepwise method. Heavy metal contents of test samples were calculated from the optimal models and then were transformed from a log-scale to original values to enable comparison with the analytical results. The relationship between measured and predicted heavy metal concentrations by the EMLR model was illustrated in scatter plots as representative of the validation process (Fig. 2). Graphs for Ni, Cr, Co and As contents displayed more scatter around the 1:1 line than for the Zn and V. It was assumed that the prediction was relatively poor at higher concentrations rather than lower contents of heavy metals.

# 4.6 Mapping the spatial distribution of geochemical and spectral data

The aim of preparing gradient maps is to compare the spatial distribution pattern of elements in the geochemical distribution maps with that in the maps associated with the spectral parameter values. A geographic information system (GIS) facilitates the integration and processing of different data sets to create thematic maps which show the spatial distribution of a variable through an area. A variety of interpolation methods are employed to prepare surface color maps. Ordinary Kriging (OK) is a valid estimation method which has been used widely in environmental

sciences to identify spatial distribution patterns of variables. It auto- correlates the primary variables among the sampled locations to predict values at un-sampled locations to produce visually appealing gradient maps and expresses the spatial trends in each dataset (Nas, 2009).

In the present study, Ordinary Kriging was employed to estimate the concentrations of As, Sb, Pb, Zn, Cd, Ni, Cr, Hg, V, Co and Cu as well as spectral absorption feature parameters in stream sediments, with the aid of the geostatistical analyst extension in ArcGIS 10.1 (ESRI, Redlands, USA). The interpolation process was performed between neighboring points within a 100-m-wide buffer zone of river network in the study area. The created gradient maps visualized the variations of both geochemical and spectral parameters along the streamlines beyond the specific sampling sites and identified the hot spot areas where heavy metals were being released into the environment. Generally, heavy metals from the same source might have similar distribution patterns in soils and sediments (Chang et al., 2009).

As shown in Fig. 3, the distribution patterns of Ni and Cr concentrations were similar. The color legend of the Area<sub>2200nm</sub> map was inverted because of the negative correlation with Ni and Cr concentrations. The Area<sub>2200 nm</sub> gradient map showed relatively comparable patterns with both geochemical maps. Extremely high concentrations of Ni and Cr were recorded in the upstream parts of the



Fig. 2. Scatter plots of predicted vs. measured values for (a) Ni, (b) Cr, (c) Co, (d) As, (e) Zn and (f) V concentrations (ppm).

Zarshuran and Ahmad Abad streams, representing a marked decrease in downstream sections. Since the concentration of Ni and Cr in Carlin-type gold deposits is relatively low, it seemed that their distribution was controlled by a factor other than mining activities. Based on the 1:100,000 scale geological map (Fig. 1b), the location of Ni and Cr anomalies was compatible with outcrops of metamorphosed ultramafic-mafic rocks at the Zarshuran mine. This complex (Sr unit) which is mainly composed of serpentinite, serpentine schist, meta-gabbro and meta-basalt (Babakhani & Ghalamghash, 1995), is considered to be a metamorphosed ophiolite, which could be a possible source for gold and associated elements (Asadi et al., 2000).

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In Fig. 4, the gradient map of As concentrations illustrates a similar spatial pattern to the  $Asym_{2200}$  map. As concentration showed a marked increase in sediment samples at the headwater, near the Zarshuran and Agh

Darreh mining sites, which decreased gradually towards downstream areas. It was assumed that the great abundances of As- bearing minerals such as orpiment (As<sub>2</sub>S<sub>3</sub>), realgar (AsS) and arsenical pyrite (FeAsS<sub>2</sub>), which accompany Au-As mineralization, was the potential source of arsenic. Also, the black shales and limestones which host gold mineralization in Zarshuran and Agh Darreh deposits have a high concentration of arsenic (Asadi et al., 2000; Modabberi and Moore, 2004; Rahimsouri et al., 2012).

In Fig. 5, the gradient maps of Co, V and total concentrations was compared with the maps illustrating the Depth500nm and Depth2200nm values. The spectral gradient maps showed a similar trend with geochemical maps in most sections of stream channels, especially along the Agh Darreh and Zarshuran streams, but values on the Depth500nm and Depth220nm maps were lower than those on the geochemical maps along the downstream





Fig. 4. Gradient maps showing the spatial distribution patterns of (a) As and (b) Asym<sub>2200 nm</sub> in sediment samples.

parts of the Ahmad Abad stream. The high concentrations of Co and V in the sediments were measured in streams draining from Oligo-Miocene volcaniclastic outcrops to the north of the study area.

The concentration of Hg, Zn, Pb and Cu in sediments was mainly high in the vicinity of mines and mineral occurrences in the study area. Hg content was significantly elevated in downstream areas from abandoned Hg mines along the Agh Darreh stream and the Zarshuran tailing site. Cinnabar (HgS) is a subordinate ore mineral in the waste piles which plays a major role in releasing Hg into the rivers. Extremely high values of Zn were found in the headwater of the Zarshuran stream, draining from the Zarshuran mine area. According to previous studies (Asadi et al., 2000), sphalerite is one of the most abundant sulfide minerals in the Zarshuran deposit. The results showed that the sediments of the Zarshuran, Agh Darreh and Ahmad Abad streams are extremely polluted by Pb. Weathering of galena (PbS) and Pb bearing sulfosalts in the ore tailings of Zarshuran and Agh Darreh releases Pb into the river system which causes a vast pollution of the bed sediments. Also, occurrences of Pb abandoned mines in the headwater of the Ahmad Abad stream were described as a source of Pb in sediments. There are occurrences of vein type sulphide mineralization to the east of the study area, which commonly involves pyrite, chalcopyrite and tetrahedrite (Asadi et al., 2000). Concentration of Cu in the sediments of the rivers which drain this area is extremely high. Also, weathering of Cu minerals in the waste of the Zarshuran mine was considered to be the other source of this element in this area.

### **5** Conclusion

This study considered the possibility of using visible and near-infrared spectral parameters in estimating the concentration of heavy metals in sediment samples from the Takab mining area, and mapping their spatial distribution pattern. The results showed that the spectral parameter values such as Depth<sub>500nm</sub>, Depth<sub>2200nm</sub>, Area<sub>2200nm</sub> and Asym<sub>2200nm</sub> were comparable with heavy metal concentration data, but the R<sub>1344/778nm</sub>, R<sub>610/500nm</sub> and Area<sub>500nm</sub> parameters showed a weak relationship between the two datasets (R < 0.5). The result of Pearson's correlation coefficient showed a strong positive correlation between As and Asym<sub>2200nm</sub>, a negative correlation coefficient between Ni and Cr with Area2200nm and a positive correlation between Ni and total values with Depth<sub>2200nm</sub>, as well as Co, V, Zn and total values with Depth<sub>500nm</sub>. The correlation coefficient between Ti, Hg, Pb and Cu and spectral parameters was lower than 0.5, which indicates a weak correlation. Multiple linear regression

0.5 2 4km

690000

695000

700000

685000

680000



bution patterns of (a) Co, (b) V, (c) total concentration, (d) Depth<sub>500nm</sub> and (e) Depth<sub>2200nm</sub> in sediment samples.

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employing the enter method showed superior performance when compared with the stepwise method. The results obtained from validation of the data showed a good predictive capacity for Ni, Cr, Co and As, whereas Zn, V and total values gave a weak predictive result. It is assumed that the weak predictive performance of some heavy metals may be caused by the occurrences of overlapping bands and the limited number of molecules that spectrally responded in the visible and near-infrared range (Ben-Dor et al., 1999).

The geochemical gradient maps were prepared in the GIS system to identify the distribution patterns and possible sources of heavy metals in the study area. Carlintype deposits showed enrichment in the heavy metals and metalloids such as As, Sb, Hg, Zn and Tl. Also, polymetallic veins and disseminations of sulfide minerals are the other source of base metals (Cu, Pb, Zn) in the addition. the high Takab area. In background concentration of heavy metals in rock units are considered as geogenic sources of heavy metals in the study area, such as gold- bearing black shale and limestones (As), mafic metamorphosed rocks (Ni, Cr) and volcaniclastics (Co, V). It seems that mining activities, along with the natural weathering of mineral occurrences and rock units, has caused high concentrations of heavy metals in the sediments of the Sarough River tributaries.

The descriptive statistics of the geochemical data indicated that in most of the sediment sampling sites, concentrations of heavy metals, especially As, exceeds the TEL and PEL standard limits which demonstrate the possibility of adverse biological effects occurring. Finally, the results of this study showed that some of the groundderived spectral parameters of sediment samples can be used in the prediction of heavy metal concentrations in the Takab area. Therefore, use of the VNIR spectroscopic analysis in predictions of concentrations and geochemical mapping of heavy metals is proposed as a time and costeffective method, prior to designing sampling strategies in investigating geochemical anomalies.

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