Criticality of Iron and Its Principal Alloying Elements

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ABSTRACT Because modern technology depends on reliable supplies of a wide variety of materials and because of increasing concern about those supplies, a comprehensive methodology was created to quantify the degree of criticality of the metals of the periodic table. In this paper, we apply this methodology to iron and several of its main alloying elements (i.e., vanadium, chromium, manganese, and niobium). These elements represent the basic metals of any industrial society and are vital for national security and economic well-being. Assessments relating to the dimensions of criticality – supply risk, vulnerability to supply restriction, and environmental implications – for 2008 are made on the global level and for the United States. Evaluations of each of the multiple indicators are presented, with aggregate results plotted in "criticality space", together with Monte Carlo simulation-derived "uncertainty cloud" estimates. Iron has the lowest supply risk, primarily because of its widespread geological occurrence. Vanadium displays the highest cradle-to-gate environmental implications, followed by niobium, chromium, manganese, and iron. Chromium and manganese, both essential in steel making, display the highest vulnerability to supply restriction, largely because substitution or substitution at equal performance is not possible for all end-uses. From a comprehensive perspective, we regard the overall criticality as low for iron and modest for the alloying elements we evaluated.

KEYWORDS Chromium, Manganese, Niobium, Vanadium, Industrial ecology, Metal sustainability, Criticality assessment, Depletion time, By-product recovery, Life cycle assessment

INTRODUCTION

Iron and steel are the basic metals of any industrial society. Globally, iron is the most widely used metal and steel making is one of the world's largest industries[1]. Raw steel production (steel is an iron-based alloy containing up to 2% carbon) accounts for nearly 25% of industrial and 9% of anthropogenic process carbon emissions [2]. Steel is used with alloying elements (elements other than carbon, such as chromium, niobium, manganese, vanadium, molybdenum, and tungsten) to obtain specific physical and chemical properties, such as heat and corrosion resistance, high strength, and high abrasion resistance [3]. As an example, stainless steel contains 11 to 26% chromium to provide a high level of corrosion resistance. It is these properties that make alloyed steels versatile in a multitude of today's products and applications, with more than 3,500 different steel products currently utilized [3] in a diverse array of products that includes construction equipment and appliances, machine tools, military weapons, pipelines, and vehicles [3,4].

Global raw steel production is not limited by resource availability, because iron ore is globally abundant [4] and end-of-life recovery rates are high [5]. From an individual element perspective, iron's predominant use is as steel in construction, transportation, machinery, and other steel products [6,7]. Chromium is widely used in stainless and alloy steels, chemicals, and refractory products [8]. Vanadium and manganese are principally used in iron-based steels, with smaller amounts going into superalloys, chemicals, and batteries [9–13]. Niobium finds use mostly in microalloyed high-strength-low-alloy (HSLA) steels, stainless steels, and superalloys [13,14]. Because many of the unique properties of alloyed steels are due to the additional alloying elements, the criticality of these elements is of significant interest.

In 2008, the United States Research Council (NRC) published a criticality assessment methodology for metals [15] that formed the basis for a series of other criticality assessments (some of which developed alternative methodologies and addressed one or more of the metals that are the subject of this paper; see the review by Erdmann and Graedel (2011)) [16]. Building upon the NRC report, a more comprehensive criticality methodology was published by Graedel et al. (2012) [17] and was subsequently applied to the elements of the geological copper family [18]. In the present work, we apply this methodology to assess the criticality of iron and several of its alloying elements – vanadium (V), chromium (Cr), manganese (Mn), and niobium (Nb) – on a global level and at the national scale for the United States. Results for other common alloying elements of iron, such as nickel, molybdenum, and tungsten, will be presented in a forthcoming publication that evaluates the superalloys metals group.

MATERIALS AND METHODS

The criticality methodology is described in Graedel et al. (2012) [17] with recent modifications presented in Harper et al. (2014) [19]. The methodology axes are supply risk (SR), environmental implications (EI), and vulnerability to supply restriction (VSR). The criticality assessment is carried out for a base year of 2008 for the globe and at the national level for the United States. Recent modifications relate to the introduction of a materials assets (MA) indicator in the VSR axis (see also Graedel and Nassar (2013) [20]) which replaces the “percentage of population utilizing” indicator used previously. Results are presented in three-dimensional criticality space, with uncertainty clouds derived by assigning each input parameter an uncertainty range and distribution and then using Monte-Carlo analysis. Further details and a summary of the components and indicators of the criticality methodology are available in the Supporting Information (see Table S1 to S4).

Supply Risk (SR). SR at the national level (medium term outlook) consists of the following components: geological, technological, and economic (GTE), social and regulatory (S&R), and geopolitical (GP). At the global level (long term outlook), SR is comprised only of the GTE component. Each component, in turn, is comprised of two indicators: depletion time (DT) and companion metal fraction (CF) for GTE, policy potential index (PPI) and human development index (HDI) for S&R, and worldwide governance indicators-political stability and absence of violence/terrorism (WGI-PV) and global supply concentration (GSC) for GP. The evaluation approach for each indicator is described in Graedel et al. (2012) [17], and the result for each is transformed to a 0 to 100 (low to high SR) common scale. The results for the components and for the overall SR are generated by equally weighting the indicators and the components, respectively. Other weightings are an option if it is felt that some indicators are more important than others.

Using information about the lifetimes of products in use, recycling rates, and process losses during production (see Supporting Information, Table S5 for a summary of all DT parameters), the DT model calculates the amount of time it would take to deplete the geological reserves (medium term outlook, used in the national assessments) or reserve base (long term outlook, used in the global assessments) of each metal at the current rate of demand given the expected future supply from recycling.

The companion metal fraction (CF) refers to the fraction of an element obtained as a byproduct with another metal (Table S18 in Supporting Information). Approximately 82% of vanadium production occurred as a byproduct in 2008, with 62% attributed to steelmaking slag, 12% attributed to alumina and oil residues, 7% to spent catalysts (the catalysts collect vanadium during the refining of some crude oils), and 1% to uranium residues [21]. Iron and chromium were not mined as companion metals in 2008. More recently, some mines have recovered chromite from platinum tailings from the UG2 seam in South Africa [12]. According to RMG (2006) [22] and in 2005, roughly 4% of global manganese produced was generated as a companion of iron ore in the Urucum Mine, Brazil. Niobium production occurs sometimes as a companion to tantalum mining and processing of tin slag. Approximately 13% of niobium is derived from mining of tantalum-containing ores and processing of tin slag, based upon an average derived from information from the Tantalum-Niobium International Study Center [23].

Global mine and refinery production data are taken from United States Geological Survey (USGS) Yearbooks and World Mining Data [12,24] , and reserve and reserve base estimates originate from USGS Mineral Commodity Summaries [25]. Sub-national mining data were available for Australia [26], Canada [27], and the United States [28]. Where production values were reported in gross weight rather than elemental concentration (e.g., iron content), conversion factors were obtained from industry experts or derived using atomic weight ratios (see Supporting Information for details). Several of the supply risk indicators – PPI, HDI, WGI – PV, and GSC – were weighted by each metal's production (see Supporting Information for details).

Environmental Implications (EI). The cradle-to-gate environmental impacts of metal production are captured using life-cycle assessment (LCA). The indicator consists of impacts to human health and ecosystem damage per kilogram of metal at the factory gate. These are calculated using SimaPro7.3 LCA software and the ReCiPe 1.06 Endpoint World H/H impact assessment method [29]. Results are normalized to a 0 to 100 scale [17]. Life cycle inventory data for iron, chromium, and manganese are available from the Ecoinvent database [30,31]. Data for vanadium are available from TU Delft (2001) [32] as given in the IDEMAT 2001 database in SimaPro7.3. For niobium (consisting of ferroniobium and metallic niobium), inventory data are obtained from various sources [33–35] as described in further detail in the Supporting Information (Table S23).

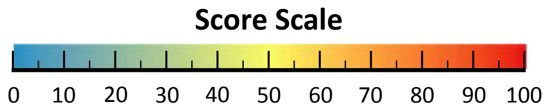
Vulnerability to Supply Restriction (VSR). VSR consists of a number of components that vary depending upon the organizational level (in this paper, global and national) being evaluated. Components at the global level include importance (I) and substitutability (S), whereas the national level is comprised of importance (I), substitutability (S), and susceptibility (SU). Each component, in turn, is comprised of indicators that are described in detail in Graedel et al (2012) [17]. At the global level, I is comprised solely of material assets (MA) and S of substitute performance (SP), substitute availability (SA), and environmental impact ratio (ER). At the national level, I is comprised of material assets (MA) and national economic importance (NE). Substitutability is comprised of the substitute performance (SP), substitute availability (SA), environmental impact ratio (ER), and net import reliance ratio (IRR). Susceptibility (SU) is comprised of net import reliance (IR) and the global innovation index (GII). Results for each indicator are transformed to a 0 to 100 (low to high) common scale.

Substitutability is evaluated by detailing the end uses of each metal of focus and the percentage of metal production employed in each end use category. In this paper, end uses are reported either at the sector level (e.g., construction, transportation, and chemicals), or by steel type (e.g., HSLA steel, stainless steel, and titanium alloys). The former end use categories are generally used in the DT model, because it is more tractable to assign a lifetime to a sector rather than a steel type. End use by steel type, however, is preferentially utilized to determine primary substitutes, because it is often more accurate to determine potential substitutes by steel type rather than by sector. The primary substitute is the material that may be used if the metal of focus is not available. SP is determined on a qualitative basis by evaluating each substitute's performance as poor, adequate, good, or exemplary, and these ratings translate directly into a numerical scale [17]. Applications, primary substitutes, and SP are detailed in Table S24 in Supporting Information. SA is determined by calculating SR for each primary substitute determined in Table S24 (see Table S19 in Supporting Information).

RESULTS

Figure 1 presents component and indicator assessments on a 0 to 100 scale for iron and its alloying metals for 2008, at national and global levels. The median values (also called the default values) for each score are listed in the columns labeled “D”. The columns labeled “U” show the uncertainty range by providing the 5th percentile, the median, and the 95th percentile. These scores are used to calculate the overall SR score for the medium term (SR_M) and long term (SR_L).

Figure 1. Resulting criticality assessment values for indicators, components, and parameters of iron and its alloying elements. DT_M = depletion time (medium-term time scale); CF = companion metal fraction; PPI = Policy Potential Index; HDI = Human Development Index; WGI-PV = World Governance Indicators – Political Stability & Absence of Violence/Terrorism; GSC = global supply concentration, SR_M = supply risk (medium-term time scale); DT_L = depletion time (long-term time scale); SR_L = supply risk (long-term time scale); EI = environmental implications; SP = substitute performance; SA = substitute availability; ER = environmental impact ratio; NE = national economic importance; MA_N = material assets (national); IRR = net import reliance ratio; IR = net import reliance; GII = Global Innovation Index; VSR_N = vulnerability to supply restriction (national); MA_G = material assets (global); VSR_G = vulnerability to supply restriction (global). For each indicator, component, and axis score, four values are provided per metal. Under the column labeled "D", the default value is provided; this value is obtained when all of the stated assumptions are utilized. Under the column labeled "U", three values from the uncertainty analysis are provided: the 5th percentile, the mean, and the 95th percentile in that order, from top to bottom. Note that values reported for all indicators are based on the appropriately weighted and scaled "transformed" scores (see [17] for details). More information regarding the assumptions and uncertainty analysis is provided in the Supporting Information. Note that the DT_M was used to calculate GTE_M. Values are reported to the nearest whole number and colored according to the following color ramp:



(A) Supply Risk Scores
(B) Environmental Implications Scores
(C) Vulnerability to Supply Restriction – National (United States)
(D) Vulnerability to Supply Restriction - Global

(A)

Element	Geological, Technological, and Economic								Social and Regulatory						Geopolitical						Supply Risk			
	DT_M		DT_L		CF		GTE_M		PPI		HDI		S&R		WGI-PV		GSC		GP		SR_M		SR_L	
	D	U	D	U	D	U	D	U	D	U	D	U	D	U	D	U	D	U	D	U	D	U	D	U
V	0	0	0	0	82	73	41	36	59	51	67	59	63	57	66	58	80	80	73	69	**59**	**56**	**41**	**36**
		0		0		82		41		59		67		63		65		80		73		**59**		**41**
		0		0		93		46		69		77		70		72		81		76		**62**		**46**
Cr	96	95	86	80	0	0	48	47	63	56	65	59	64	60	58	51	75	73	66	63	**60**	**58**	**43**	**40**
		96		86		0		48		64		66		65		58		75		67		**60**		**43**
		97		91		0		49		72		73		70		65		77		70		**62**		**45**
Mn	89	85	0	0	4	3	46	44	54	47	72	66	63	58	66	59	82	80	74	70	**61**	**59**	**2**	**2**
		89		0		4		46		54		72		63		66		82		74		**61**		**2**
		92		0		5		48		62		80		69		72		84		77		**63**		**2**
Fe	9	0	0	0	0	0	4	0	54	48	73	68	63	60	60	55	75	72	67	64	**45**	**42**	**0**	**0**
		9		0		0		4		54		74		64		60		75		67		**44**		**0**
		20		0		0		10		60		82		69		65		78		71		**47**		**0**
Nb	80	71	76	65	13	10	46	42	49	38	73	59	61	52	62	48	97	97	79	73	**62**	**58**	**44**	**39**
		81		76		12		47		49		73		63		60		97		79		**62**		**44**
		87		83		15		50		64		89		72		72		98		85		**66**		**48**

(B)

Element	Human Health (supply source-weighted average points)	Ecosystems (supply source-weighted average points)	EI	
			D	U
V*	1.24	0.12	**7**	**6**
				7
				9
Cr	0.28	0.01	**2**	**2**
				2
				3
Mn	0.13	0.01	**1**	**1**
				1
				1
Fe	0.09	0.01	**1**	**1**
				1
				1
Nb	0.59	0.05	**4**	**4**
				4
				5

* Represents primary vanadium production [32].

(C)

Element	Importance						Substitutability										Susceptibility						VSR	
	MA_N		NE		I		SP		SA_M		ER		IRR		S		IR		GII		SU		VSR_N	
	D	U	D	U	D	U	D	U	D	U	D	U	D	U	D	U	D	U	D	U	D	U	D	U
V	67	60	1	1	34	31	65	58	64	60	34	28	57	47	55	51	91	76	29	23	60	52	50	47
		67		1		34		64		64		35		55		55		91		29		60		49
		73		1		37		71		68		44		66		58		100		36		66		52
Cr	100	100	11	9	56	55	65	48	59	43	60	43	50	33	58	49	66	55	29	23	47	41	58	54
		100		11		56		65		59		60		49		58		66		29		47		58
		100		14		57		80		75		77		66		67		79		36		55		61
Mn	99	94	28	21	64	59	89	85	92	89	96	93	88	85	91	89	100	84	29	23	64	56	73	70
		99		28		63		89		92		96		88		91		100		29		63		72
		100		36		68		92		94		98		91		93		100		36		67		75
Fe	94	89	51	39	72	65	52	44	43	42	100	99	10	8	51	49	13	11	29	23	21	18	48	45
		94		51		72		50		43		100		10		51		13		29		21		48
		99		66		80		59		44		100		12		53		16		36		25		51
Nb	89	83	2	2	46	42	49	42	62	59	92	79	35	31	59	55	100	84	29	23	64	56	56	53
		89		2		46		47		62		90		36		58		100		29		63		55
		95		3		49		53		64		99		42		62		100		36		67		58

(D)

Element	Importance		Substitutability								Vulnerability to Supply Restriction	
	MA_G		SP		SA_L		ER		S		VSR_G	
	D	U	D	U	D	U	D	U	D	U	D	U
V	26	24	65	59	47	42	35	29	49	46	**38**	**36**
		26		64		47		36		49		**38**
		28		71		51		45		53		**40**
Cr	69	67	68	54	41	27	60	46	56	48	**63**	**58**
		69		68		40		60		56		**63**
		72		82		54		75		65		**67**
Mn	36	34	95	93	96	95	96	95	96	95	**66**	**65**
		36		95		96		96		96		**66**
		39		96		97		98		97		**67**
Fe	54	53	57	49	26	22	100	97	61	58	**58**	**55**
		54		56		26		100		61		**56**
		56		64		30		100		64		**58**
Nb	59	57	42	34	43	36	86	67	57	49	**58**	**54**
		59		41		43		84		55		**57**
		62		48		47		98		61		**60**

Vanadium. SR is 59 (medium term) and 41 (long term). DT is zero in the medium and long term, indicating depletion times of 100 years or longer, assuming current global rates of recycling and demand. CF is high because primary production from vanadium-rich ores accounted for only about 18% of total vanadium production in 2008 [21]. Production of vanadium from steel slags (62%) is driven by the economics of the steel [36] and vanadium is considered a companion. Vanadium from oil residues and spent catalysts (together 19%) is considered a companion, because the source of the vanadium is crude oils that deposit the element on refining catalysts. Production from uranium residues (1%) and alumina is considered companion production as well. GSC is 80, because only a few countries (South Africa (36%), China (35%), Russia (26%), Kazakhstan (2%), and Japan (1%)) produced vanadium in 2008 [12]. Vanadium's environmental impact score is 7 and is higher than any of the other metals considered in this study, but still at the low end of the 0 to 100 ordinal scale. VSR is moderate at 50 for the United States and 38 for the globe. IR is 91 for the United States which is at the higher end of the criticality scale, illustrating that vanadium was mostly imported in 2008.

Chromium. DT is 96 in the medium term (corresponds to 13 years before year 2008 geological reserves are depleted) and 86 (i.e., 31 years before the geological reserves indicated for 2008 are depleted) in the long-term. DT scores are high as a result of high demand when compared to USGS reserves/reserve base estimates, relatively long in-use lifetimes (see Table S5 in Supporting Information) that delay chromium-steel availability to offset primary production, and a moderately high recycling rate of 54% [8,37]. However, world chromium resources, at greater than 3.7 billion tons of chromium content (i.e., 12 billion metric tons shipping grade chromium converted into metal content) [25], are roughly 100 times more than the reserve base estimate used to derive DT_L. DT largely depends on the reserve and reserve base estimates used, with larger estimates reducing the DT score. This results in an SR score of 60 at the national level (medium term) and 43 at the global level (long term), while the VSR scores are 58 at the national level and 63 at the global level. This is, in part, because substitution is not possible in industrial machinery (e.g., turbines) operating at high temperatures, where chromium's primary function is to provide oxidation and corrosion resistance [38–41] (see Supporting Information for a detailed discussion). However, we find that partial substitution may be possible in buildings and infrastructure, transportation, and household appliances (Table S24). Chromium's use in building and infrastructure is dominated by alloy steels, because of its hardenability characteristics, which are used, for example, in elevators, metal furniture, and boilers, with manganese reported as a good substitute [41]. Transportation is dominated by trains, passenger cars, and motorcycles [8] with aluminum being an adequate substitute. Aluminum is also a possible substitute for household appliances (e.g., dishwashers and washing machines [8]), together with plastics [41]. MA is high at both national and global levels due to large per capita in-use stock estimates (about 87 kg chromium per capita for the United States and 20 kg per capita for the globe) in relation to the sum of total in-use stock and reserves (United States) or reserves base (globe). Global in-use stock values result from the DT model, whereas the United States per capita in-use stock is estimated by extrapolating the global in-use stock estimates via nominal gross domestic product [17,19].

Manganese. SR scores for manganese are 61 in the medium term and 2 in the long term. DT is 89 (i.e., 27 years before geological reserves are depleted) in the medium term and 0 (i.e., ≥100 years before the reserve base is depleted) in the long term. This is due to the large difference in 2008 reserves (500 Tg chromium content) and reserve base (5.2 Pg chromium content) estimates [25]. Process losses are 36% [42], which is slightly higher than for the other metals investigated and is a result of the strong deoxidation capacity of manganese used in steelmaking to remove sulfur and that results in high manganese losses to the slag [43]. Jones (1994) [44] indicates that the use of manganese in batteries and chemicals was used in a dissipative way, so we assign an end-of-life recycling rate of zero to these end-uses in our DT model. VSR is 73 at the national level and 66 at the global level. Manganese's largest end use is in steel metallurgy[25] where it acts as a desulfurizing and deoxidizing agent in steel making (see Supporting Information for a detailed discussion), and no satisfactory substitutes have been identified for this end use [25]. For manganese's other uses, we find that plastics (i.e., bottle-grade polyethylene terephthalate) may be a suitable substitute for aluminum alloys used, for example, in metal cans [45], and lithium could substitute for manganese in battery applications, assuming a technology switch from dry-cell to lithium batteries (Table S24). ER is high due to the fact that lithium is associated with higher cradle-to-gate environmental burdens than manganese (see Table S23). In addition, IR at the United States level is high, as manganese was mostly imported in 2008.

Iron. Mine deposits of iron are widespread and recycling rates are high (58-87%) [46]. As a result, DT is found to be 9 in the medium term (i.e., 95 years before geological reserves are depleted) and zero in the long term (indicating depletion times of around 100 years or longer). Iron is not a companion metal (CF is 0). Iron's medium term SR is 45, which is lower than for any of the other elements investigated. The long term SR consists of the average of DT and CF and is zero. For the United States, VSR is moderate at 48. NE is high for iron when compared to the other elements considered in this study, because of high consumption in relation to the United States gross domestic product. Substitutability of iron is possible using materials like wood, aluminum, and fiber-reinforced polymers [3] (see Supporting Information for a detailed discussion). These substitutes have low- to medium SR themselves, but higher environmental burdens [31], which results in an ER of 100 (see Table S23 in Supporting Information). The depletion time model results in an estimate of global per capita iron in-use stock of 4.1 metric tons in 2008. This is used to calculate an MA_G of 41. Our estimate is similar to per capita in-use stock estimates reported elsewhere [47,48]. In our study, for the United States, per capita in-use stock is estimated at 17.8 kg iron per capita in 2008 and MA_N is 94. This estimate is slightly higher than estimates of 9.3 to 14.3 kg iron per capita reported in the literature for prior years [47].

Niobium. SR is 62 in the medium term and 44 in the long term. The fact that most niobium is mined in Brazil (92%) and Canada (7%) [12] is reflected in the high GSC. DT is 80 (39 years before reserves are depleted) in the medium term and 76 (44 years before the reserve base is depleted) in the long term. However, according to USGS (2009) [25], world niobium resources are sufficient to supply projected demands, given that the extractable global resources are estimated at 480 Tg (this compares to a reserve base of 3 Tg [25] used in the DT model). VSR for the United States (56) and the globe (58) are roughly similar. The high IR indicator of 100 reflects the fact that no niobium was mined in the United States in 2008. The high ER score is governed by the fact that all potential substitutes (i.e., vanadium, molybdenum, and tantalum) display higher cradle-to-gate environmental burdens than niobium (see Table S23 in Supporting Information).

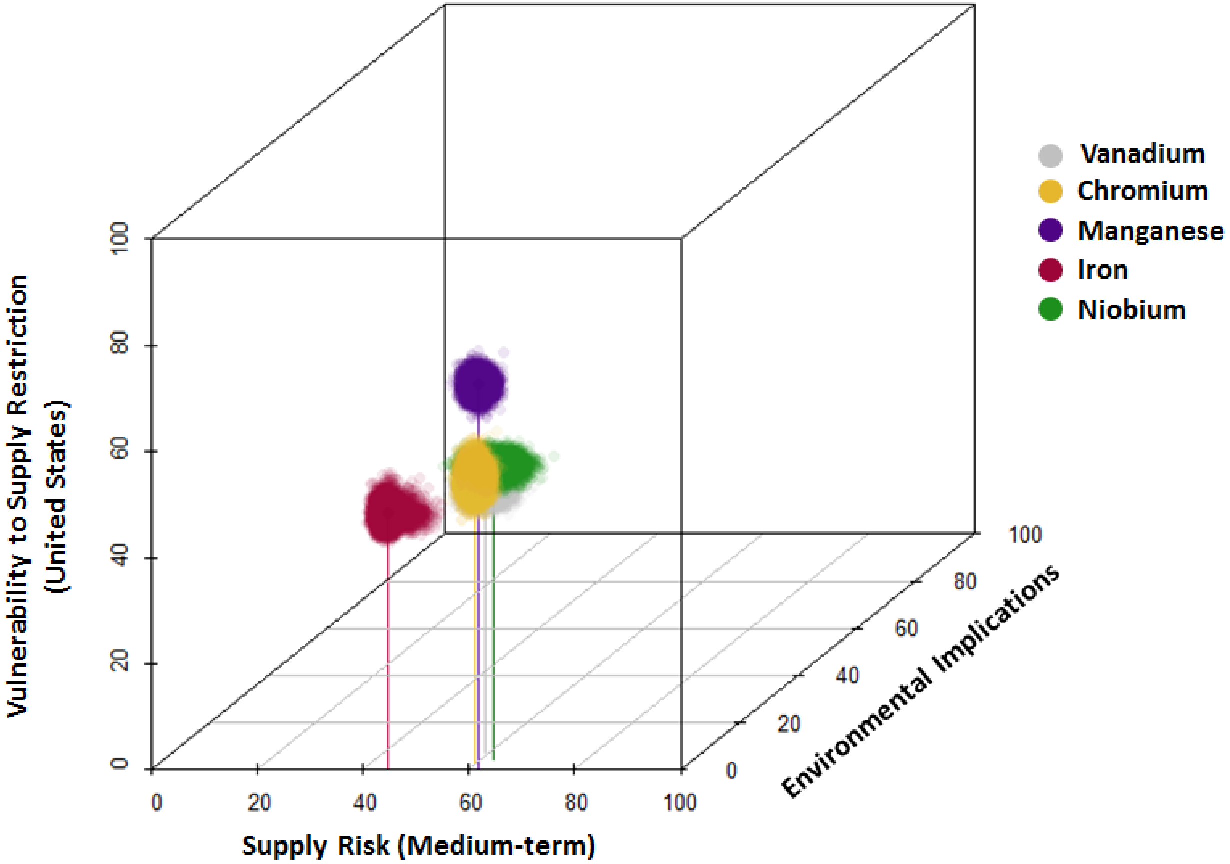
Results in three-dimensional criticality space. Figure 2 shows the results for iron and its principal alloying elements in "criticality space", at the national (a) and global (b) levels. Several characteristics are immediately apparent from the diagrams. Firstly, environmental burdens of iron and its principal alloying elements are on the lower end of the 0 to 100 EI axis, which has been designed to display the wide range of environmental burdens of all metals of the periodic table on a per kilogram basis (functional unit). As such, it shows iron and its alloying elements in relative comparison to all other elements. We note, however, that environmental issues occurring during the use or end-of-life phases are not captured in our assessment. While environmental implications for vanadium and niobium are highest on a per kilogram basis, if the functional unit is changed to global mine production in 2008, iron had, by far, the largest environmental burdens, due to its enormous production quantity (Figure S2 in Supporting Information).

The second feature of Figure 2 is that there are some obvious differences between the United States and global assessments, which emphasizes that there is no universal criticality evaluation for a metal. Rather, the evaluation is a function of organizational level and of the supply and demand characteristics of the organization (e.g., country or planet). Third, there is only modest diversity in SR at the United States level (where vanadium, chromium, manganese, and niobium are just above median values and iron just below), but somewhat more diversity at the global level (modest SR for vanadium, chromium, and niobium, and very low SR for iron and manganese). There is slightly greater assessment diversity on the VSR axis. Vanadium, iron, and niobium are generally moderate (their major uses have good substitutes), while chromium and especially manganese are moderate to high on the national and global level. Uncertainty clouds (Figure 2) and upper and lower percentiles of each parameter (Figure 1), derived using Monte-Carlo analysis, indicate that uncertainties of each parameter are small enough to analyze overall trends. However, where uncertainty clouds overlap, a direct comparison of elements may be difficult.

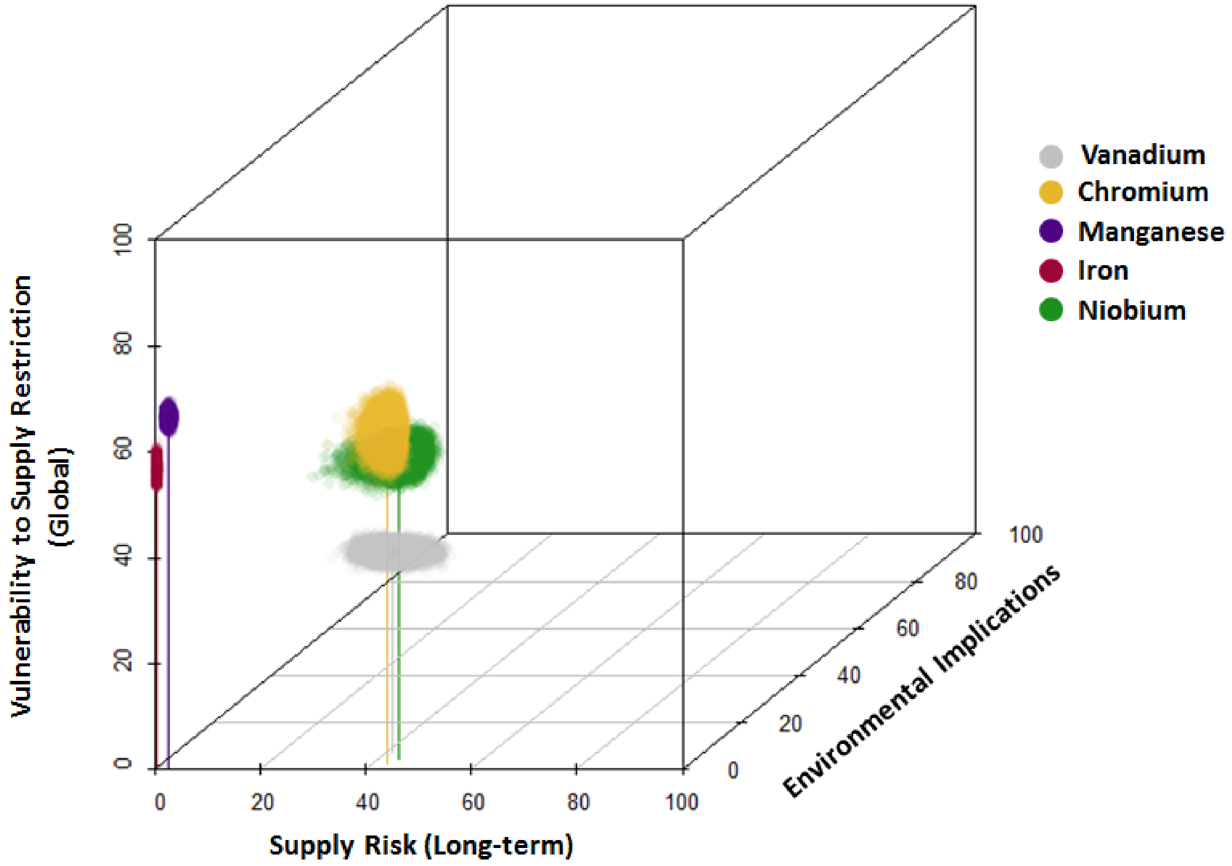
The criticality danger areas on these diagrams is the region of high SR and high VSR (upper right region in the X-Y portion of the 3D diagram) and, even more problematic, at the high SR, high-EI, high VSR region (back-right-top). In no case do any of the elements investigated approach either of these regions, either at the national or global levels. We conclude that the criticality of these metals from both global and United States perspectives is modest for vanadium, chromium, manganese, and niobium, and low for iron.

Figure 2: Locations of iron and its alloying elements in criticality space: (a) national level, for the United States (2008 epoch), and (b) global level (2008 epoch). The highest level of criticality is at 100, 100, 100 (back right top). The figure are created using R programming language [49] with the Scatterplot 3D plugin [50].

(A)



(B)



DISCUSSION

A legitimate comment on the results presented above is that they reflect the decision to apply equal weighting to all of the indicators, some of which might be regarded as more important than others. As a consequence, criticality becomes not a precisely defined statistic, but one reliant in part on value choices. To explore the consequences of that situation, we imagine a quite different choice from that of equal weighting: weighting PPI, HDI, and ER at zero while ignoring the EI axis completely, and retaining equal weighting for the remaining indicators. This choice essentially ignores social and regulatory considerations. With the exception of iron, the results for SR and VSR turn out to change at most by about 7%, and to lesser degrees in nearly all cases. Iron's change (-23% for SR_M and -12% for VSR_M) is found to be more pronounced because of larger relative differences between PPI, HDI, and ER compared to the other indicators. Nevertheless, it can be concluded that the methodology is reasonably robust even to quite dramatically different weightings of the indicators.

It is also of interest to compare our criticality results with those of other evaluations, which we do in Table 1.

Table 1. Comparison of criticality results to other studies (adapted from Erdmann and Graedel (2011) [16])

Metal	**EU Study** [10]	**DOD Study** [51]	**IW Consult Study** [52]	**NEDO study** [53]	**NRC Study** [15]	**Oakdene Hollins Study** [54]	**This study (Global and United States)**
V	Not critical	No shortfall	Not investigated	Not critical	Not critical	Not insecure	Modest criticality
Cr	Not critical	Cr metal: shortfall (718 short tons); all other forms of Cr: no shortfall	Medium risk	Not critical	Not investigated	Not insecure	Modest criticality
Mn	Not critical	Mn metal (electrolytic): shortfall (7,406 short tons); all other forms of Mn: no shortfall	Medium risk	Not critical	Critical	Not investigated	Modest criticality
Fe	Not critical	Not investigated	Low to medium risk	Not investigated	Not investigated	Not insecure	Low criticality
Nb	Critical	No shortfall	High risk	Critical	Critical	Not insecure	Modest criticality

There are seven different studies shown in the table, including the present study. All agree, for studies in which evaluations were carried out, that iron and vanadium are of low concern. Two of five studies other than ours find chromium to be of high risk or to have shortfalls (one study omitted the element). Similar concern but higher shortfalls are derived for manganese metal. In the case of niobium, however, five of the six studies other than ours express varying degrees of concern, generally due to the high geographical concentration of niobium production. The results are quite strongly dependent on the different assessment methodologies chosen in the various studies, some rather detailed, some less so. In any event, with the possible exception of niobium, there is relatively good agreement among the several studies.

We conclude by emphasizing a consideration that we mentioned in a previous publication by Nassar et al. (2012) [18]: there is no such thing as “critical” or “not critical”, and we have avoided making such a distinction. There are, however, metals that are more critical than others under some conditions, for some users, and for some time scales. This immediately suggests that policy options should be explored when the higher criticality situations are encountered. The real value of criticality analysis is not whether a particular metal is labeled “critical”, it is the assessment and presentation of the status of that metal by a variety of relevant criteria. Doing so enables issues of concern to be identified and addressed by actions such as substitution, alternative sourcing, revisions to corporate or national strategy, or other measures. By doing so, the mineral resources of the planet can be responsibly utilized over the long term in ways that improve human lives while paying attention to environmental issues and to resource sustainability over the long term.

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SUPPORTING INFORMATION

This information is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES

(1) World Steel Association. Key facts about the world steel industry http://worldsteel.org/media-centre/key-facts.html (accessed May 13, 2013).

(2) Allwood, J. M.; Cullen, J. M.; Milford, R. L. Options for Achieving a 50% Cut in Industrial Carbon Emissions by 2050. *Environ. Sci. Technol.* **2010**, *44*, 1888–1894.

(3) Fenton, M. D. *Mineral Commodity Profiles--Iron and Steel*; Open-File Report 2005–1254; U.S. Geological Survey: Reston, VA, 2005.

(4) USGS. *Mineral Commodity Summaries 2012*; U.S. Geological Survey: Reston, VA, 2012.

(5) Graedel, T. E.; Allwood, J.; Birat, J.-P.; Buchert, M.; Hagelüken, C.; Reck, B. K.; Sibley, S. F.; Sonnemann, G. What Do We Know About Metal Recycling Rates? *J. Ind. Ecol.* **2011**, *15*, 355–366.

(6) Wang, T.; Müller, D. B.; Graedel, T. E. Forging the Anthropogenic Iron Cycle. *Environ. Sci. Technol.* **2007**, *41*, 5120–5129.

(7) MCI. *World Steel Industry*; Metals Consulting International (MCI), 2009 http://cdn.steelonthenet.com/kb/files/World_steel_industry_review_2009.pdf (accessed December 13, 2012).

(8) Johnson, J.; Schewel, L.; Graedel, T. E. The Contemporary Anthropogenic Chromium Cycle. *Environ. Sci. Technol.* **2006**, *40*, 7060–7069.

(9) BHP Billiton. *Manganese Ore Industry: Global Overview*; BHP Billiton, 2010 http://www.manganese.org/__data/assets/pdf_file/0015/81411/08-0-_Ore_PT.pdf (accessed May 3, 2013).

(10) EC. *Critical raw materials for the EU*; Report of the Ad-hoc Working Group on defining critical raw materials; European Commission (EC): Brussels, Belgium, 2010.

(11) Roskill. *The economics of vanadium, 9th edition*; Roskill Information Services: London, 2000.

(12) USGS. *2010 Minerals Yearbook*; Vol 1: Metals and Minerals; U.S. Department of the Interior, U.S. Geological Survey: Reston, Virginia, 2010.

(13) USGS. *Historical Statistics for Mineral and Material Commodities in the United States*; U.S. Geological Survey, 2011.

(14) IAMGOLD. *Niobec Tour Presentation*; IAMGOLD Corporation, 2009 http://www.iamgold.com/Theme/IAmGold/files/presentations/Niobec%20Tour%20200909%20-%20%20Niobec%20Presentation%20FINAL.pdf (accessed September 17, 2012).

(15) NRC. *Minerals, Critical Minerals, and the U.S. Economy*; U.S. National Research Council, National Academies Press: Washington D.C., 2008.

(16) Erdmann, L.; Graedel, T. E. Criticality of Non-Fuel Minerals: A Review of Major Approaches and Analyses. *Environ. Sci. Technol.* **2011**, *45*, 7620–7630.

(17) Graedel, T. E.; Barr, R.; Chandler, C.; Chase, T.; Choi, J.; Christoffersen, L.; Friedlander, E.; Henly, C.; Jun, C.; Nassar, N. T.; et al. Methodology of Metal Criticality Determination. *Environ. Sci. Technol.* **2012**, *46*, 1063–1070.

(18) Nassar, N. T.; Barr, R.; Browning, M.; Diao, Z.; Friedlander, E.; Harper, E. M.; Henly, C.; Kavlak, G.; Kwatra, S.; Jun, C.; et al. Criticality of the Geological Copper Family. *Environ. Sci. Technol.* **2012**, *46*, 1071–1078.

(19) Harper, E.; Kavlak, G.; Burmeister, L.; Eckelman, M.; Erbis, S.; Espinoza, V.; Nuss, P.; Graedel, T. Criticality of the geological zinc, tin, and lead family. *Rev.* **2014**.

(20) Graedel, T. E.; Nassar, N. T. The criticality of metals: a perspective for geologists. *Geol. Soc. Lond. Spec. Publ.* **2013**, *393*, SP393.4.

(21) Roskill. *Vanadium: Global Industry Markets and Outlook, 12th edition*; Roskill Information Services: London, 2010.

(22) RMG. *Raw Materials Data Software - The Mining Database*; Raw Materials Group: Stockholm, Sweden, 2006.

(23) TIC. Tantalum - Raw Materials and Processing http://tanb.org/tantalum (accessed Apr 18, 2013).

(24) Weber, L.; Zsak, G.; Reichl, C. *World Mining Data*; Vol. 26; International Organizing Committee for the World Mining Congresses: Vienna, 2011.

(25) USGS. *Mineral Commodity Summaries 2009*; U.S. Geological Survey: Reston, VA, 2009.

(26) Australian Bureau of Statistics. *Mineral Commodities, 2001-02 to 2010-11*; Australian Bureau of Statistics: Canberra, 2011.

(27) Natural Resources Canada. *Mineral Production - Annual Statistics: Mineral Production of Canada, by Province and Territory, 2008*; Natural Resouces Canada, 2009.

(28) USGS. *2008 Minerals Yearbook*; Vol I. Metals and Minerals; U.S. Geological Survey: Reston, VA, 2008.

(29) Goedkoop, M.; Heijungs, R.; Huijbregts, M.; De Schryver, A.; Struijs, J.; Van Zelm, R. *ReCiPe 2008, A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level; First edition Report I: Characterisation*; 2009.

(30) Classen, M.; Althaus, H.-J.; Blaser, S.; Scharnhorst, W.; Tuchschmidt, M.; Jungbluth, N.; Faist-Emmenegger, M. *Life Cycle Inventories of Metals, Data v2.0*; ecoinvent report No. 10; Ecoinvent Centre, ETh Zurich: Dübendorf, CH, 2009.

(31) Ecoinvent. *Ecoinvent Life Cycle Inventory database v2.2*; Swiss Centre for Life Cycle Inventories, 2010.

(32) TU Delft. IdEMAT Life Cycle Inventory Database http://www.idemat.nl/ (accessed Aug 27, 2012).

(33) Albrecht, S.; Cymorek, C.; Eckert, J. Niobium and Niobium Compounds. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA, 2000.

(34) BIO Intelligence Service. *Environmental Impacts of some Raw Materials through LCA Methods*; A project under the EU Framework contract ENV.G.4/FRA/2008/0112; Paris, 2010.

(35) UBA. *ProBas - Lebenszyklusdatenbank [Life Cycle Inventory Database]*; Umweltbundesamt (German Federal Environmental Agency) and Öko-Institut: Dessau (Germany); Freiburg (Germany), 2010.

(36) Largo Resources. Largo Resources: An Emerging Market Leader for Vanadium and Tungsten Production, 2011 http://www.largoresources.com/files/LGO%20Corporate%20Presentation,%20June,%202011.pdf (accessed December 29, 2012).

(37) Reck, B. K.; Gordon, R. B. Nickel and chromium cycles: Stocks and flows project part IV. *JOM* **2008**, *60*, 55–59.

(38) Floreen, S. An examination of chromium substitution in stainless steels. *Metall. Trans. A* **1982**, *13*, 2003–2013.

(39) Glenn, M. L.; Bullard, S. J.; Larson, D. E.; Rhoads, S. C. Partial replacement of chromium in stainless steel. *J. Mater. Energy Syst.* **1985**, *7*, 75–81.

(40) Loria, E. A. Discussion of "an examination of chromium substitution in stainless steels."*Metall. Trans. A* **1983**, *14*, 2185–2187.

(41) OTA. *Strategic Materials: Technologies to Reduce U.S. Import Vulnerability*; OTA-ITE-248; U.S. Congress, Office of Technology Assessment (OTA): Washington D.C., 1985.

(42) Jones, T. S. Manganese Recycling in the United States in 1998. In *Flow Studies for Recycling Metal Commodities in the United States*; Sibley, S. F., Ed.; U.S. Department of the Interior, U.S. Geological Survey (USGS): Reston, VA, 2004.

(43) Jeong, Y.-S.; Matsubae-Yokoyama, K.; Kubo, H.; Pak, J.-J.; Nagasaka, T. Substance flow analysis of phosphorus and manganese correlated with South Korean steel industry. *Resour. Conserv. Recycl.* **2009**, *53*, 479–489.

(44) Jones, T. S. *Manganese Materials Flow Patterns*; U.S. Bureau of Mines Information Circular 9399; United States Department of the Interior, Bureu of Mines, 1994.

(45) CPM. *Manganese Market Outlook - Executive Summary*; CPM Group: New York, USA, 2012 http://www.buchansminerals.com/Portals/0/PDFs/Manganese_Market_Outlook_2012_ExecutiveSummary.pdf (accessed December 28, 2012).

(46) World Steel Association. *The three Rs of sustainable steel*; World Steel Association: Brussels/Beijing, 2010.

(47) Pauliuk, S.; Wang, T.; Müller, D. B. Steel all over the world: Estimating in-use stocks of iron for 200 countries. *Resour. Conserv. Recycl.* **2013**, *71*, 22–30.

(48) Pauliuk, S.; Milford, R. L.; Müller, D. B.; Allwood, J. M. The Steel Scrap Age. *Environ. Sci. Technol.* **2013**, *47*, 3448–3454.

(49) R Core Team. *R: A language and environment for statistical computing*; R Foundation for Statistical Computing: Vienna, Austria, 2003.

(50) Ligges, U.; Mächler, M. Scatterplot3d - an R Package for Visualizing Multivariate Data. *J. Stat. Softw.* **2003**, *8*, 1–20.

(51) DOD. *Strategic and Critical Materials: 2013 Report on Stockpile Requirements*; U.S. Department of Defense (DOD), 2013 https://www.dnsc.dla.mil/Uploads/Materials/dladnsc2_9-13-2011_15-9-40_FY10%20Ops%20Report%20-%2005-06-2011.pdf (accessed August 6, 2013).

(52) IW Consult. *Rohstoffsituation Bayern - keine Zukunft ohne Rohstoffe: Strategien und Handlungsoptionen (Raw materials situtation in Bavaria - no future without raw materials: strategies and opportunities of action)*; IW Consult GmbH Köln, 2011 http://www.rohstoffstrategie-bayern.de/fileadmin/user_upload/rohstoffstrategie/dokumente/vbw_Studie_Rohstoffe_Bayern_web.pdf (accessed September 17, 2013).

(53) NEDO. *Trend Report of Development in Materials for Substitution of Scarce Metals*; Report No: 08007835-0 08007838-0; New Energy and Industrial Technology Development Organization (NEDO): Tokyo, 2009.

(54) Morley, N.; Eatherley, D. *Material Security: Ensuring resource availability for the UK economy*; Oakdene Hollins: Chester, UK, 2008.