



Research Article

The role of pedogenesis and natural fertiliser as vectors for essential metal content in agricultural topsoils, Central India



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Abstract

Essential trace metals are well known for their environmental toxicity and for being part of complex bio-chemical cycles. Their role as critical micronutrients, delivering vital health benefits, is less widely discussed and understood, holding back strategies for combatting malnutrition. Crops grown on many Indian soils suffer from deficiencies in essential metals, notably iron (Fe), zinc (Zn), and molybdenum (Mo). The list of deficient metals will likely grow due to increasing future crop demand. Geostatistical analysis of soils and farmyard manure (FYM), the predominant fertiliser, implies that residual oxide minerals carry high concentrations of the essential trace metals Fe, Zn, copper (Cu), chromium (Cr), nickel (Ni), cobalt (Co), manganese (Mn) not only in soil but also in FYM (especially Fe, Cr, Cu, Co and Ni). A geochemical survey across a road traverse of 600 km, encompassing an area of c. 15,000 km², was conducted in Central India to evaluate reported essential metal deficiency in key agricultural topsoils. Importantly, our evaluation of the element cycling in this system reveals that despite high bulk concentrations, some key metals remain bio-unavailable. In effect, the existence of refractory (weathering-resistant) oxides is likely a significant factor for deficiency symptoms in the soil–plant–fertiliser cycle. Further, mass balance calculations of the bioavailable pool of metals imply that only Fe and Mn are present in sufficient quantities to combat deficiency problems. Notwithstanding this limitation of FYM, its high organic carbon content, as well as its importance for Zn, Cu and Fe, validates its traditional use to maintain the fertility and physical condition of Indian topsoils.

Keywords Soil · India · Manure · Metals · Agriculture · Fertiliser

1 Introduction

Essential metals are often referred to as ‘heavy metals’ in the literature and there is ample evidence that high concentrations in soils cause risks to human health, plants, animals and ecosystems. Heavy metals can present risks to food security in a variety of ways, including direct ingestion, contact with contaminated soil, introduction into the

food chain, contamination of groundwater, reduction in food quality via phytotoxicity (disruption of cell membrane functions, chlorosis, and necrosis) and harm to soil microorganisms [1]. However, in small quantities, essential metals are indispensable micronutrients for plants, animals and humans [2]. They are normally present in animal and plant cells as well as tissues, and are a necessary part of their nutrition and physiology and the evaluation of

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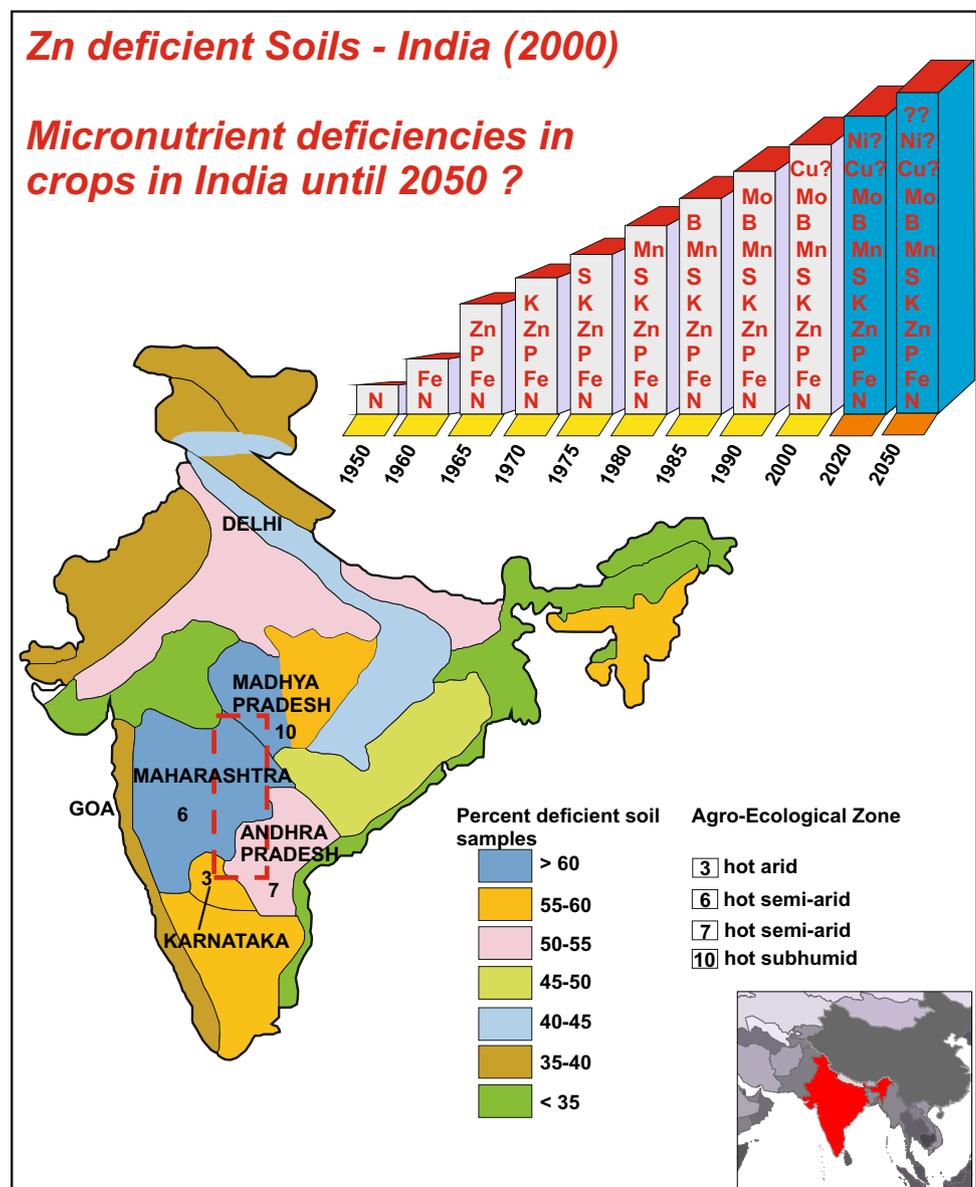
deficiency levels consequently not less important for food security plans. The natural availability of essential metals is not ubiquitous or uniform, so that different regions of the world can have deficiencies and/or surfeit of one or more of these elements. These variations are being mapped to understand current and future agricultural potential given predicted future rise of population. Presently, the World Health Organisation (WHO) recognises only Fe as a crucial micronutrient for global health. However, Zn deficiency in soils also has consequential effects upon crops and ultimately human populations that over-depend on local crops [3–5]. Likewise, Mn deficiency is emerging as a threat to sustaining high levels of food production [6].

Advances in analytical chemistry offer growing awareness that other metals are bio-essential nutrients, most

only at trace levels [7]. For instance, Cu, Mo and Co sustain growth and health of plants, animals and humans [8]; plant growth and bacteria require Ni [9]; and Cr(III) is discussed as being bio-essential [7] as a co-factor for insulin [10].

In India, the importance of the soil-crop-human micronutrient deficiency chain is documented for Zn, Fe, Mn and Mo [11, 12] with direct knock-on effect on the health of those people who rely on local crops as their main diet [13]. To date, burgeoning population growth has been sustained with the “Green Revolution”, referring to the increase in agricultural production since 1950 (Fig. 1) [6], yet it is anticipated that by the year 2050, 1.5 billion people will live in India, with many relying on local food sources. To increase yield, farmers are now cultivating high yielding varieties (HYV) of crops to meet

Fig. 1 Impact of “The Green Revolution” in the past, present and future (illustrated as blue beams) on the emergence of micronutrient deficiencies (including essential metals) in crops in India (modified after [6]). In addition, the percentage of Zn deficient soils in the different agro-ecological zones of India [89] are illustrated according to the classification of the [83]. The overview map in the lower, right corner of the figure shows the Indian state territory in red colour



the exploding food demand [14], resulting in additional removal of micronutrients from soils. It is likely that further essential metals (e.g., Ni, Cu) will become deficient in Indian soils. The latest developments in biofortification (e.g., the ability of rice to uptake high concentrations of Fe and Zn [15]; will cause further stress on the essential metal status of farmed soils as there is very little scope for expanding the area of cultivated land [6].

Despite the large number of humans at risk, little is known about the origin of deficiency of most essential metals. This includes the mineralogical composition of the soil and its geological substrate, parameters influencing plans for improved sustainable land use in large parts of India. Two basic geological factors appear underappreciated within the Indian context. First, earlier aggressive chemical weathering has affected large areas under intensive agricultural cultivation. Most essential metals are lost during the formation of new secondary soil minerals [16–18] and the residual regolith becomes strongly depleted (Supplemental Figure 1). Second, large tracts of the subcontinent are underlain by cratonic crust that has remained tectonically stable for a long time, limiting removal of the depleted residual soils via erosion. Within the tropics, soils become vertically separated from active rock breakdown by up to 25–50 m. On such soils, crops struggle to access freshly released nutrients at depth [19].

Notwithstanding these gaps in knowledge, there is growing appreciation for the need of strategies to combat essential metal deficiencies. Balanced fertilisation practices are now being developed, including customised fertiliser products, complex fertiliser formulations and organic matter enrichment [6]. Most small-scale Indian farmers use traditional farming practices, however, and cannot afford bespoke fertilisers, relying instead on FYM. Therefore, uptake and release of essential metals by grazing livestock is of interest [20] but few data exist for the bulk composition of FYM, resultant cycling of multi-essential trace metals, and the role of organic carbon (C_{org}).

This study aims to help closing this knowledge gap through mineralogical/geochemical investigation, complementing insight from pedology and agricultural studies. The aim was to explore how geochemistry could distinguish between bio-available and immobile pools of essential metals in soils, thereby assessing whether FYM contains sufficient bio-essential trace metals to offset deficiencies in Central Indian soils and informing if application of FYM could help to convert refractory soil metals into bioavailable fractions, as previously suggested for Zn and Cu [21].

2 Sampling strategy

2.1 Selection of the lithology and soil types of the study area

A reconnaissance-type sampling strategy achieved a representative and meaningful overview of the range of topsoils and cropping types over a large area in Central India. Twenty agricultural topsoils were sampled along a road traverse of c. 600 km, encompassing many lithological substrates (Fig. 1; Supplemental Figure 1), including: Deccan basalt ($n = 11$); clay-rich basaltic alluvium ($n = 1$); tonalite-trondhjemite-granodiorite (TTG) gneisses ($n = 5$); and grey shale ($n = 3$) (Table 1). Soils developed on Deccan basalt & alluvium, TTG, and grey shale classify as ‘vertisols’ ($n = 17$), whereas the lateritic materials developed over Deccan basalt are ‘ferralsols’ ($n = 3$). The investigated soils support a variety of crops (e.g., maize, rice, lentils, cotton, wheat, millet). At each GPS-recorded locality (Supplemental Table 1), 100–200 g of sample was taken from a depth of 5–15 cm and soil type, underlying geology and crop type (Table 1) were noted. It was anticipated that lithological control over metal depletion would be exposed by this sampling strategy. The studied samples cover four of the main Indian agro-ecological zones (Madhya-Pradesh, Maharashtra, Andhra Pradesh and Karnataka), all of which display some of the highest Zn deficiency (Fig. 1).

2.2 Chemical and mineralogical characteristics of vertisols and ferralsols

The study area is known for prolific (historic) cotton production, with vertisols locally called “black cotton soils”. The region of their main occurrence is the Deccan plateau between 15° and 25° north latitude and 73° and 80° east longitude [22]. Newbold [23] first described this soil type as chemically consisting of silica (SiO_2) together with calcium (CaO), aluminium (Al_2O_3), iron (Fe_2O_3) and minor portions of vegetable and animal debris. Smectite is the dominant clay mineral in these vertisols. Non-expanding clay minerals (kaolinite, micas, chlorites, palygorskite and vermiculites) and carbonate (both pedogenic and non-pedogenic) also occur [24–26]. The typically dark colour of vertisols results from clay-organic complexes, whilst Fe–titanium (Ti)–Mn oxides also contribute to the pigmentation [27].

Most vertisols are inherently fertile and studies in India [28, 29] and elsewhere [30] have demonstrated that the high clay content exerts dominant control over essential pools of Fe, Mn, Zn, Cu, Co and Ni and their

Table 1 Selected major elements, organic carbon content C_{org} (wt%), CIA and essential metal concentrations ($\mu\text{g/g}$) (Zn, Cu, Ni, Cr, Co, Mo) in agricultural topsoil samples from Central India (n = 20)

Sample	Na ₂ O (wt%)	K ₂ O (wt%)	CaO (wt%)	MgO (wt%)	Al ₂ O ₃ (wt%)	Fe ₂ O ₃ (wt%)	TiO ₂ (wt%)	MnO (wt%)	C _{org} (wt%)	CIA	Zn ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)	Co ($\mu\text{g/g}$)	Mo ($\mu\text{g/g}$)	Underlying geology	Age of rock—basement	Soil type	Crop type
S38	0.78	0.6	4.4	4.14	13.9	13.85	2.11	0.21	0.87	60	111	211	58	50	48	<1	Deccan basalt	Phanerozoic—cratonic	Vertisol	Cotton
S10	0.42	0.58	5.63	3.23	12.5	11.55	1.85	0.19	1.82	64	91	142	97	150	53	<1	Deccan basalt	Phanerozoic—cratonic	Vertisol	Wheat
S9	0.4	0.52	5.13	3.34	12.55	11.75	1.89	0.24	0.95	65	92	149	95	160	54	<1	Deccan basalt	Phanerozoic—cratonic	Vertisol	Maize
S16	0.25	0.58	3.56	2.42	14.35	13.05	2.39	0.25	1.31	67	93	166	99	140	56	<1	Deccan basalt	Phanerozoic—cratonic	Vertisol	Lentils
S29	0.11	0.91	3.1	2.29	13.45	10.4	1.8	0.22	1.02	78	84	130	89	110	44	<1	Deccan basalt	Phanerozoic—cratonic	Vertisol	Millet
S7(ChQ)	0.29	0.4	2.32	1.94	15.2	19.95	2.99	0.37	1.83	76	129	281	81	90	82	<1	Deccan basalt	Phanerozoic—cratonic	Vertisol	Wheat
S8	0.82	0.28	3.92	2.74	14.05	15.2	2.53	0.25	0.82	62	128	222	71	70	57	<1	Deccan basalt	Phanerozoic—cratonic	Vertisol	Wheat
S5	0.6	0.42	20.5	2.68	8.95	9.79	1.64	0.14	0.73	79	78	134	42	50	29	<1	Deccan basalt	Phanerozoic—cratonic	Vertisol	Cotton
S6	0.58	1.71	1.8	2.1	13.55	9.39	1.57	0.18	0.85	72	88	111	70	100	35	<1	Basaltic alluvium	?—cratonic	Vertisol	Wheat
S25	0.06	0.87	0.39	0.55	21	17.45	2.16	0.37	1.15	96	59	127	130	290	73	2	Deccan basalt	Phanerozoic	Ferralsol	Lentils
S28	0.04	0.32	0.58	0.55	20.2	29.6	3.4	0.19	1.3	97	129	342	133	340	61	<1	Deccan basalt	Phanerozoic	Ferralsol	Lentils
S26	0.04	0.29	0.62	0.53	20.4	29.5	2.87	0.16	1.69	98	124	302	131	340	62	1	Deccan basalt	Phanerozoic	Ferralsol	Rice
Chhindwara basalt	2.43	0.28	10.55	5.46	12.93	15.07	2.23	0.23	36	113	213	56	59	52	<1	Parent rock				
Bidar basalt	2.46	0.16	10.99	6.93	13.72	13.4	2.16	0.19	37	105	180	93	156	52	<1	Parent rock				
NV1 basalt	2.26	0.49	10.3	5.62	13.2	16.17	2.83	0.21	37	146	295	82	84	—	—	—	Parent rock			

Table 1 (continued)

Sample	Na ₂ O (wt%)	K ₂ O (wt%)	CaO (wt%)	MgO (wt%)	Al ₂ O ₃ (wt%)	Fe ₂ O ₃ (wt%)	TiO ₂ (wt%)	MnO (wt%)	C _{org} (wt%)	CIA	Zn (µg/g)	Cu (µg/g)	Ni (µg/g)	Cr (µg/g)	Co (µg/g)	Mo (µg/g)	Underlying geology	Age of rock—basement	Soil type	Crop type
S13	0.69	1.28	3.31	2.59	12.35	8.26	1.66	0.15	1.2	66	71	73	84	170	30	<1	Granite-gneiss	Precambrian—cratonic	Vertisol	Lentils
S14	1.04	0.96	8.28	2.8	12.35	9.65	1.79	0.16	1.27	60	79	107	63	100	35	<1	Granite-gneiss	Precambrian—cratonic	Vertisol	Maize
S15	1.13	0.62	6.88	3.3	13.85	12.1	2.08	0.17	1.35	59	95	151	65	90	40	<1	Granite-gneiss	Precambrian—cratonic	Vertisol	Wheat
S37	1.94	3.7	1.81	0.61	14.8	3.72	0.58	0.03	1.66	60	49	29	24	30	9	<1	Granite-gneiss	Precambrian—cratonic	Vertisol	Rice
S36	1.99	4.1	1.74	0.45	13.9	3.04	0.45	0.02	0.98	59	39	24	19	30	7	<1	Granite-gneiss	Precambrian—cratonic	Vertisol	Rice
TTG gneisses (n=11)**	4.95	1.55	3.07	0.68	15.1	3.72*	0.3	0.07		50	19	1	2	24	5	-	Parent rock			
SD	0.83	0.5	0.78	0.31	1.26	0.58	0.07	0.12		-	4	0	0	15	1	-				
Sample S21	0.45	1	0.83	0.77	9.96	5.24	0.91	0.16	0.67	80	33	41	51	80	29	<1	Grey shale	Neoproterozoic—cratonic	Vertisol	Lentils
S19	1.92	0.57	2.19	1.02	13.8	7.08	1.38	0.12	0.89	67	53	65	64	100	28	<1	Grey shale	Neoproterozoic—cratonic	Vertisol	Millet
S18	0.16	0.16	1.51	1.98	14.4	13.55	2.99	0.26	1.33	95	92	213	159	270	51	<1	Grey shale	Neoproterozoic—cratonic	Vertisol	Millet
Grey shale (n=3)**	0.39	2.11	0.69	1.12	10.7	5.13	0.61	-		75	57	15	25	60	61	-	Parent rock			
SD	0.26	0.66	0.52	0.83	2.01	4.76	0.24	-		-	59	8	21	11	27	-				

*The Fe₂O₃ (wt%) was converted from FeO (wt %) using the equation

Table 1 (continued)

Sample	Na ₂ O (wt%)	K ₂ O (wt%)	CaO (wt%)	MgO (wt%)	Al ₂ O ₃ (wt%)	Fe ₂ O ₃ (wt%)	TiO ₂ (wt%)	MnO (wt%)	C _{org} (wt%)	CIA	Zn (µg/g)	Cu (µg/g)	Ni (µg/g)	Cr (µg/g)	Co (µg/g)	Mo (µg/g)	Underlying geology	Age of rock—basement	Soil type	Crop type
Indian Standard [49]											300–600	135–270	75–150	–	–	–	FeO = Fe2O3 *0.8998; **n = number of samples that have been used			
European Union Standard [51]											300	140	75	150			To calculate the average concentrations in rocks			
Ecotoxicological limit											720	190	210	230						

To simulate the bedrock compositions of the topsoils, typical parent rock compositions from the literature are presented [18, 43–45]. Additionally, the underlying geology and soil type are presented. Bold text shows major- and trace elements, the CIA weathering index and parameters of the biogeochemical environment. Numbers in italics represent bedrock compositions as well as safe- and ecotoxicological limits of essential trace metals

plant availability. The C_{org} content also correlates with extractable forms of essential metals (Zn, Cu, Mn, Fe) [29, 31], whereas soil pH (c. 7–8) and higher CaCO₃ contents result in lower concentrations of Fe, Mn and Zn [30, 31]. In view of the high smectite content of the vertisols, it is surprising that the study area is among the most metal-deficient regions in Central India, indicating that only a small fraction of metals is bioavailable [31].

According to the UN Food and Agriculture Organization (FAO), ferralsols consist of highly weathered red- and yellow-coloured substrate arising from the accumulation of Fe- and Al oxides and oxy-hydroxides, with kaolinite a dominant mineral. These soils typically form on geologically old parent materials, which have lain exposed for long periods, and where the resulting intensive leaching has resulted in very low fertility [16, 18, 32, 33]. It is also likely that a fraction of essential metals redistributes into inert pedogenic or residual resistant original Fe oxides [33–35]. Therefore, while bulk composition may indicate otherwise, ferralsols often require addition of fertilisers to supply essential metals in bioavailable form.

Complementing the soil samples, we obtained FYM samples (dung; whole cowpats) at representative locations (Fig. 1; Supplemental Table 1). One single sample (P4) contained a high amount of hay bedding whereas the rest are considered to represent FYM from grazing stock (see Supplemental Table 1 for details).

3 Materials and methodology

3.1 Bulk soil elemental analyses

Soil samples were initially stored in plastic bags and allowed to air dry prior to being sealed. At Trinity College Dublin (TCD), samples were heated in an oven at 60 °C for 96 h to dryness. These were then sieved to collect the ≤ 2 mm soil fraction. From this subsample of ca. 40 g were pulverised in an agate mill in preparation for major and trace element analyses at ALS Minerals, Loughrea, Ireland. Measurements followed the standard procedures of ALS and method numbers (supplemental file). Major element [sodium (Na₂O), potassium (K₂O), (CaO), magnesium (MgO), Al₂O₃, Fe₂O₃, TiO₂, MnO], C_{org} (wt%) and essential trace metal concentrations (Zn, Cu, Ni, Cr, Co, Mo) (µg/g) are listed in Table 1. The full dataset with 51 additional analyses (mainly trace elements considered; non-essential is listed in the supporting information (Supplemental Table 2).

The degree of weathering is listed in Table 1, calculated as the chemical index of alteration (CIA): Al₂O₃/(Al₂O₃ + C

$aO + Na_2O + K_2O) \times 100$, where CaO represents the molar proportion of Ca in silicate-bearing minerals only [37].

To determine the total C_{org} (TOC, wt%) of the soil samples 30–50 mg of the powdered sub-sample was acidified with HCl to remove the inorganic [36]. Analyses of the TOC were then undertaken using an Elementar Vario EL cube instrument at TCD (see Sect. 3.2 for more detail).

3.1.1 DTPA extraction on soils for Zn, Cu, Co, Ni, Mo, Cr, Fe

The DTPA extraction method of Lindsay and Norvell [37] was used on a subsample of 10 g weighed into flasks. To this was added 20 mL of the DTPA extracting solution, and samples were mounted on a shaker table and run for 2 h at 160 rpm. Next, the solution was filtered through a Whatman No. 2 filter paper and the filtrate collected in

pre-cleaned flasks before decanting into test tubes for inductively coupled plasma optical emission spectrometry (ICP-OES) analysis using a Varian Liberty Series II. For the calibration of the instrument response a multi-element standard (Merck CertiPur ICP multi-element standard solution IV) and different dilution factors were used: 0.5, 1, 5 and 10 mg/L for Cu, Cr, Mo, Co, and Ni; and a single element standard for Fe at 50 and 100 mg/L (for instrument method parameters and analyte settings see Supplemental Table 3). A quality control (QC) multi-element standard at 1 mg/L (AccuStandard ICP multi-element standard solution IV) was used. Calibration, blank and QC solutions were prepared using the same DTPA extraction solution as the soil samples.

Calibration coefficients were greater than 0.999. The internal blank levels for all elements of interest were

Table 2 DTPA-extractable Zn, Cu, Ni, Co and Fe of the Central Indian topsoil samples

Sample	Zn ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Co ($\mu\text{g/g}$)	Fe ($\mu\text{g/g}$)	Crop type	Soil type	Subcropping geology
S38	0.6	7.3	0.7	0.3	32.0	Cotton	Vertisol	Basalt
S10	0.9	12.0	1.2	0.4	39.8	Wheat	Vertisol	Basalt
S9	0.8	8.6	0.6	0.2	33.1	Maize	Vertisol	Basalt
S16	0.9	5.9	1.1	0.5	27.1	Lentils	Vertisol	Basalt
S29	0.7	5.2	1.3	0.3	24.9	Millet	Vertisol	Basalt
S7 (ChQ)	1.3	13.3	0.8	1.3	53.6	Wheat	Vertisol	Basalt
S8	1.5	12.1	0.9	0.3	50.9	Wheat	Vertisol	Basalt
S5	0.8	6.7	0.5	0.2	21.2	Cotton	Vertisol	Basalt
S6	0.5	4.9	0.9	0.3	29.4	Wheat	Vertisol	Basaltic alluvium
Minimum	0.5	4.9	0.5	0.2	21.2			
Maximum	1.5	13.3	1.3	1.3	53.6			
S25	0.8	8.1	1.4	3.2	24.2	Lentils	Ferralsol	Basalt
S28	2.5	8.3	1.1	1.0	18.8	Lentils	Ferralsol	Basalt
S26	4.0	7.9	1.3	1.3	19.6	Rice	Ferralsol	Basalt
minimum	0.8	7.9	1.1	1	18.8			
maximum	4	8.3	1.4	3.2	24.2			
S13	1.0	5.6	0.9	0.2	27.8	Lentils	Vertisol	TTG
S14	0.6	11.7	0.9	0.2	42.8	Maize	Vertisol	TTG
S15	0.5	14.4	0.8	0.2	51.1	Wheat	Vertisol	TTG
S37	2.0	10.0	1.1	0.4	91.8	Rice	Vertisol	TTG
S36	1.4	7.2	0.6	0.2	67.5	Rice	Vertisol	TTG
Minimum	0.5	5.6	0.6	0.2	27.8			
Maximum	2	14.4	1.1	0.4	91.8			
S21	0.4	3.0	1.4	0.6	23.2	Lentils	Vertisol	Grey shale
S19	1.5	9.2	2.6	1.4	37.6	Millet	Vertisol	Grey shale
S18	0.9	15.5	6.0	1.1	36.5	Millet	Vertisol	Grey shale
Minimum	0.4	3	1.4	0.6	23.2			
Maximum	1.5	15.5	6	1.1	37.6			

Bold text represents elements and parameters of the biogeochemical environment. Numbers in italics show the minimum and maximum concentrations of soils that developed over different subcropping geology

beyond detection limit. The mean concentration of two external blanks was $\leq 0.02 \mu\text{g/g}$. We listed the concentration of all essential metals of the soil samples in Table 2, except for Cr and Mo, which were beyond detection limit ($\leq 0.01 \mu\text{g/g}$).

3.2 FYM—trace element and C analyses

All FYM samples were air-dried prior to sub-sampling and sterilisation. In the laboratory, samples were then divided, recombined and mixed with a spatula to minimise heterogeneity [38], then oven dried at 60°C for 72 h. Two grams (2 g) of this material were then combusted in air at 500°C for 8 h (heating steps = $5^\circ\text{C}/\text{min}$) to remove C, N, sulphur (S) and residual water, and then weighted to determine the LOI for the conversion of the element concentrations.

For each ash sample, a 100 mg ash aliquot was next digested in thoroughly cleaned Savillex Teflon[®] beakers using a hydrofluoride-nitric (HF-HNO₃) (4:1) acid mixture at $\sim 160^\circ\text{C}$ for 72 h. After digestion, samples were dried down at 110°C to drive off silicon tetrafluoride (SiF₄). The fluoride residue was attacked twice with concentrated hydrochloric acid (HCl) (2 mL) at 160°C to liberate any residual metals associated with organic material. After the evaporation, 2 mL of concentrated HNO₃ were introduced to the residue for 24 h at 135°C , and a double conversion with HNO₃ followed. The converted residue was then taken up in 10 g of 20% HNO₃ to yield a nominal 1:100 parts total dissolved solid stock solution and put on the hotplate for 96 h to ensure complete dissolution of the samples. Trace element composition was determined at TCD using the method of Eggins et al. [39], incorporating modifications described in Kamber [40] and Babechuk et al. [41].

Approximately 4% of this stock was gravimetrically diluted to produce a 2% HNO₃ solution with an internal standard mixture containing ⁶Li, rhodium (Rh), rhenium (Re), bismuth (Bi), and uranium-235 (²³⁵U) for solution quadrupole ICP-MS (Q-ICP-MS) analysis on a Thermo Scientific iCap-Qs. During analytical runs, sample unknowns were preceded by blanks, calibration (USGS rock standard W-2a) and a quality control standard (BCR-2), and bracketed with monitor samples (one every 4–6 unknowns) for external drift correction [39]. The method reproducibility and accuracy were assessed using the long-term average of USGS and GSJ standards run as unknowns. The concentrations of the essential trace metals of interest reproduced better than 1% relative standard deviation (RSD) (1 sigma) for Cr, Co, Ni, Cu, at 2% RSD for Mo and 3% RSD for Zn. Furthermore, Fe reproduced at 0.5% and Ti at 0.8% RSD. The apparent reproducibility for Mo is poorer due to contamination of the second-generation USGS standards [42]. The highest blank contribution was for Zn ($< 0.00004 \mu\text{g/g}$). All other elements of interest had very

low blank contributions, which we corrected, and did not affect the final sample concentrations.

For the analysis of the C content only very small amounts (10–20 mg) of unashed FYM were required, and prepared in a zirconium oxide ball mill at TCD. Aliquots were measured for TOC (%) with an Elementar Vario EL cube instrument at TCD. The method has excellent precision and accuracy (better than 2% for samples of the type analysed here) through high performance combustion, matrix-independent results, and long-term stability of calibration.

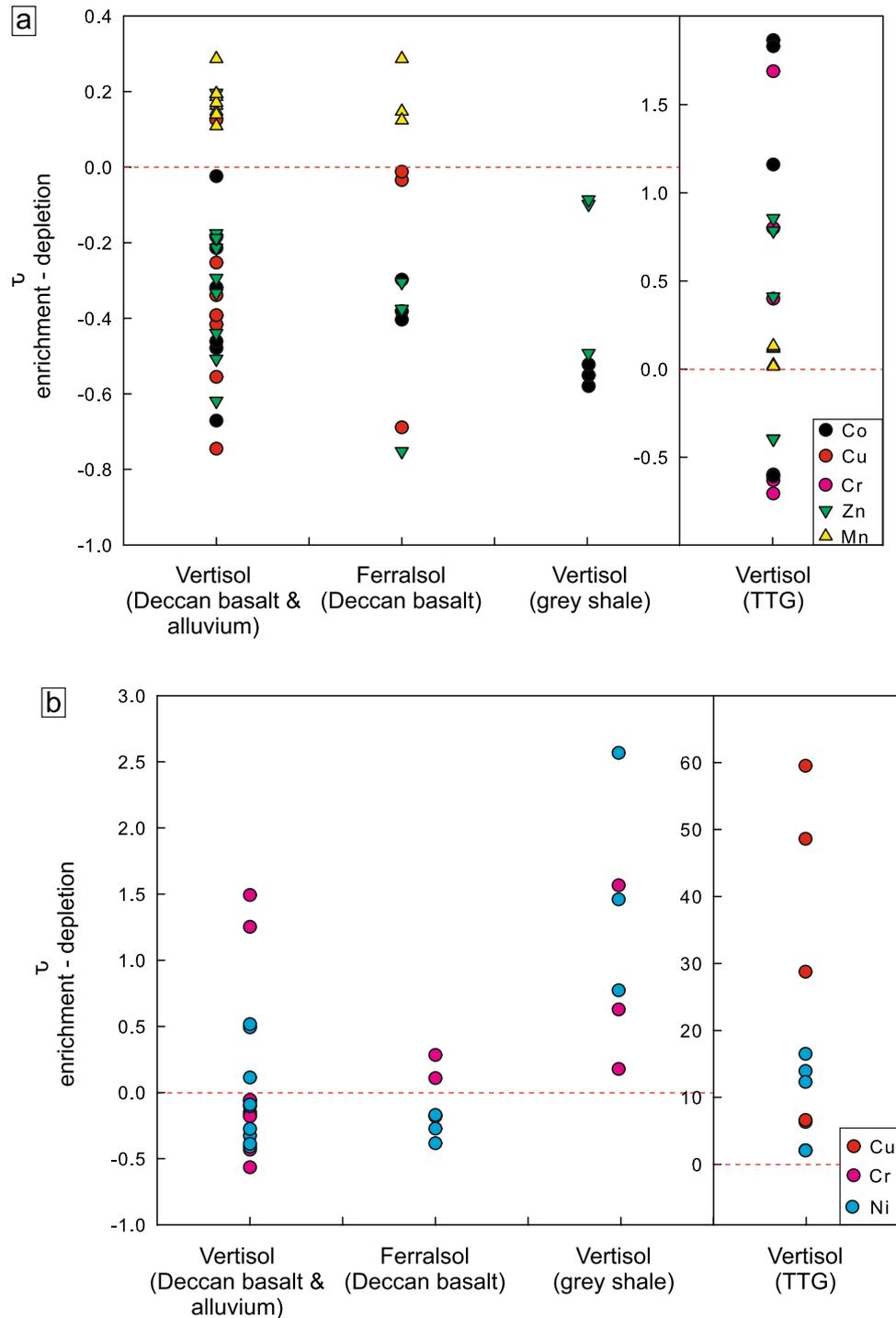
4 Results

4.1 The CIA and its relation to soil composition

For the analysed soils, the CIA ranged widely, increasing from 45 to 50 (unweathered) to 100 (complete breakdown of original silicates), reflecting the progressive removal of the labile cations (Ca²⁺, Na⁺, K⁺) from silicates and the concomitant relative enrichment in (Al³⁺). Other elements (Ti⁴⁺, Fe³⁺) are also enriched but these are not measured by the CIA calculation. Vertisols developed over Deccan basalt and alluvium show moderate CIA values (60–78), while those overlying TTG and grey shale vary between 59–66 and 67–95, respectively. Ferralsols overlying Deccan basalt have the expected very high CIA values (96–98). Compositions of relevant bedrocks close to the sample locations are reported in the literature [18, 43–45]. They include: Deccan basalt; TTG gneisses; and grey shale (Table 1). Most unaltered igneous rocks have CIA values between 40 and 50 [18], whereas average shale has higher CIA (65–70) [46]. In the study area, there is only one (grey) shale lithology with a documented CIA value of 75. One soil developed on grey shale (S19) has a lower CIA, suggesting that its bedrock was less weathered than the one literature analysis. The CIA values of all vertisol topsoils are consistent with saprolite containing substantial amounts of smectite [18] with the exception of one sample (S18) developed over grey shale (CIA = 95).

A robust way of quantifying absolute element loss and gain during local alteration/soil formation is calculation of tau values (τ), which determine enrichment-depletion of constituents relative to an immobile index element in the parent rock. Here, the concentration (C) of the immobile (i) element Nb was used to measure loss or gain of a more mobile element (j) relative to the concentration of the underlying parent rock (p) on which the soil (s) developed [47, 48]. Positive τ values indicate enrichment; negative values imply depletion:

Fig. 2 Tau enrichment-depletion diagrams of agricultural vertisols and ferralsols developed over different lithologies for Co, Cu, Cr, Zn and Mn (a) and Cu, Cr and Ni (b). The horizontal, red dashed lines illustrate the parent rock composition. Note that literature data of Co from NY1 basalt and Mn from grey shale were missing



$$\tau_{j,s} = \frac{(C_{j,s}/C_{i,s})}{(C_{j,p}/C_{i,p})} - 1$$

The first order finding from tau values (Fig. 2; supporting information; Supplemental Table 4) is that vertisols forming over basalt and alluvium have substantial depletion of essential trace metals, excepting Mn and

occasionally Cr and Ni. By contrast, vertisols developed over TTG are relatively enriched in essential trace metals. In only two TTG-hosted vertisols, from rice fields (S36, S37), do Cr, Co and Zn become depleted (Fig. 2a). Importantly, Cu and Ni in particular, exhibit extreme gains in all vertisols developed over TTG. Enrichment of Cu, Cr and Ni in vertisols that formed over shales is similarly evident (Fig. 2b), whereas Co and Zn show depletion. Ferralsols

and vertisols overlying basaltic parent rock show the same trends, excepting Ni (depleted). Only two ferralsol topsoils have Mo concentrations exceeding the 1 µg/g detection limit and for this reason, Mo was not further considered.

In summary, the tau calculations reveal that Co, Cu and Zn have the strongest tendency for depletion while Mn, Cr and Ni are often enriched. Importantly, there is no evidence for a characteristic weathering-controlled enrichment-depletion pattern that might relate to the underlying geology or soil type. From chemical data alone, it remains unclear why the most strongly weathered, major-oxide depleted vertisols and ferralsols contain high Zn, Cu, Ni and Cr concentrations, sometimes close to ecotoxicological limits that might even be a risk to crop and human health (Table 1) [49–51].

In view of this issue, mineralogy was next considered to test whether the presence of certain metals (Al, Ti, Fe, Mn) that tend to form minerals incorporating minor trace metals (Cr, Co, Cu, Ni, and Zn) result in observable strong metal concentrations in the associated derived soils. To evaluate this possibility, a Pearson’s correlation analysis was conducted with τ values of all samples (Table 3). This revealed that enrichments in Fe, Cr, Co, Cu, Ni and

Zn are moderately to strongly correlated with elevated Ti. Moreover, Mn correlates moderately with Cr, Co, Al and Fe. However, Al is anti-correlated with elevated Co, Cu and Ni without any observable relationship with Ti or Fe. This suggests that Al (and CIA) play a less dominant role for trace metal concentrations. Strong correlations between Cu, Ni and Zn and moderate correlations of Cr with Co, Ni and Zn suggest a similar partitioning of essential trace metal concentrations into specific minerals in the vertisols and ferralsols. The key minerals are Fe-, Ti- and Cr-bearing phases into which minor and trace metals substitute, with additional roles for the substitution relationships between minor to trace metals.

The essence of the major element geochemistry can be illustrated with binary diagrams for all soils, regardless of parent rock or soil type. For example, a strong correlation ($r^2=0.771$) exists between Fe₂O₃ (wt%) and TiO₂ (wt%) (Fig. 3a). Furthermore, a moderate correlation between Fe₂O₃ (wt%) and Al₂O₃ (wt%) is evident ($r^2=0.556$) (Fig. 3b). Behaviour of other major elements may be summarised as follows. There is a strong positive correlation between TiO₂ (wt%) and Zn ($r^2=0.748$), Cu ($r^2=0.882$) and Co ($r^2=0.736$) (Fig. 4a). Fe₂O₃ (wt%) correlates strongly

Table 3 Pearson product moment correlation between τ values

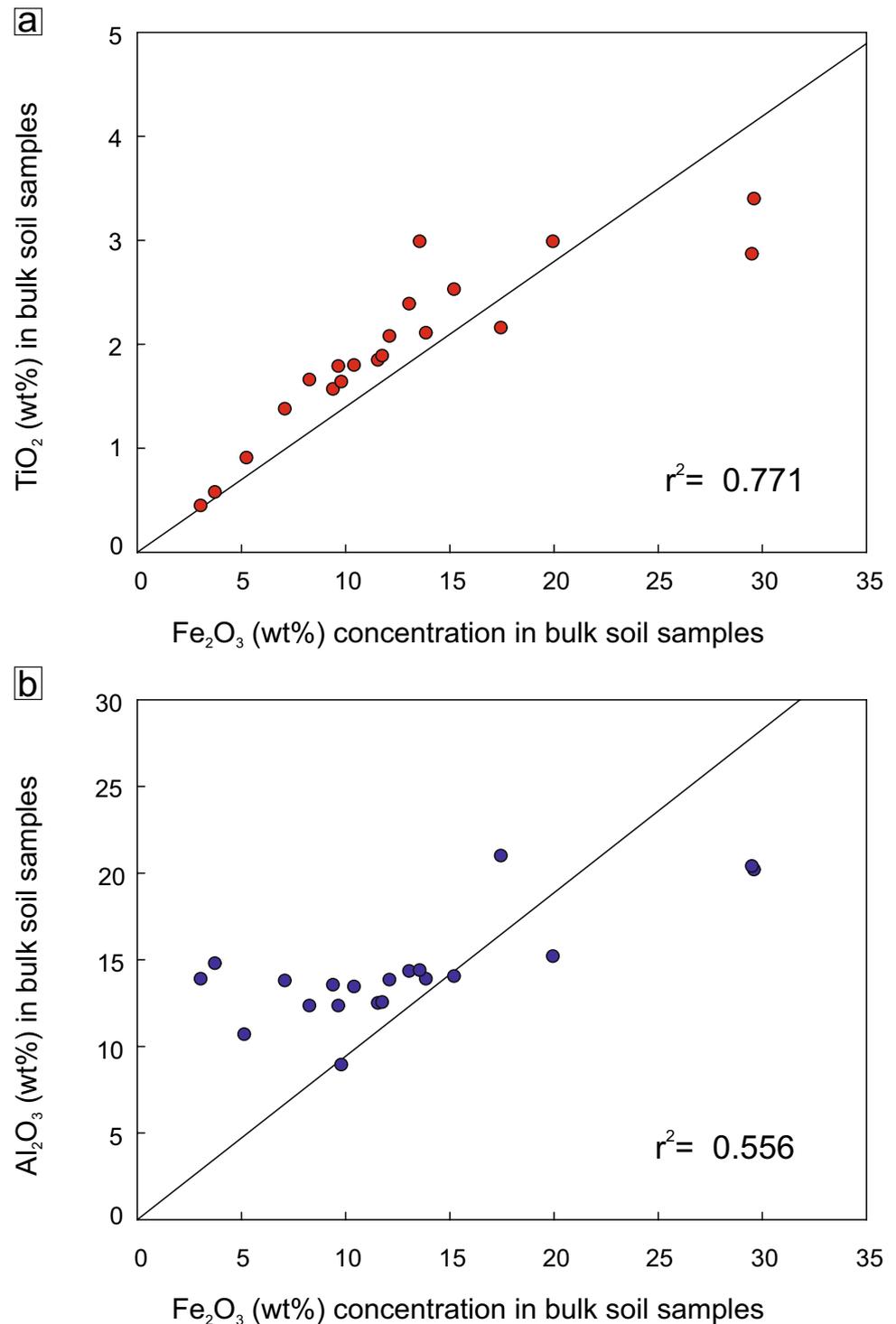
	Co	Cu	Ni	Zn	Mn	Al	Fe	Ti	
Cr	0.483		0.475	0.489	0.546		0.561	0.643	*
	4.96E-02		3.44E-02	2.88E-02	2.32E-02		1.01E-02	2.25E-03	**
	17		20	20	17		20	20	***
Co		0.952	0.905	0.927	0.586	-0.473		0.639	
		1.58E-07	5.88E-07	9.27E-08	2.78E-02	5.52E-02		5.73E-03	
		14	17	17	14	17		17	
Cu			0.907	0.885		-0.538		0.913	
			5.30E-07	2.32E-06		2.60E-02		3.07E-07	
			17	17		17		17	
Ni				0.841		-0.540		0.697	
				3.36E-06		1.39E-02		6.31E-04	
				20		20		20	
Zn							0.505	0.794	
							2.33E-02	2.97E-05	
							20	20	
Al					0.618		0.510		
					8.18E-03		2.2E-02		
					17		20		
Fe					0.583			0.676	
					1.40E-02			1.06E-03	
					17			20	

Note that all data are normalised to Nb

Bold numbers represent mean, median, minimum, maximum and standard deviation values of FYM in this study, while italic numbers show the same statistical values for New York Dairy Manures

*First cell content = correlation coefficient; **Second cell content = p value; ***Sample number variation due to missing elements in bedrocks from the literature

Fig. 3 Relationship of bulk soil TiO_2 (wt%) (a) and Al_2O_3 (wt%) (b) to Fe_2O_3 (wt%)



with Cu ($r^2=0.882$) and moderately with Zn ($r^2=0.628$) (Fig. 4b) and Co ($r^2=0.620$). Chromium and Ni concentrations moderately correlate with TiO_2 (wt%) (Ni: $r^2=0.635$; Cr: $r^2=0.449$) and Fe_2O_3 (wt%) (Ni: $r^2=0.508$; Cr: $r^2=0.584$) (Fig. 4a, b). Manganese correlates moderately with TiO_2 ($r^2=0.478$; not shown) and Fe_2O_3 (wt%) ($r^2=0.498$; Table 4). Moderate correlations (Fig. 4c) also exist between all

essential trace metals and Al_2O_3 (wt%), except for Zn. In the more moderately weathered soils, this likely reflects the insoluble nature of both Al_2O_3 and Fe_2O_3 (Fig. 3b) when in the highly evolved, kaolinite-rich ferralsols and two vertisol rice field samples (Table 1; S36, S37), r^2 values between Al_2O_3 (wt%) and metals remain moderate to low (Fig. 4d, e). These trends substantiate that the dominant

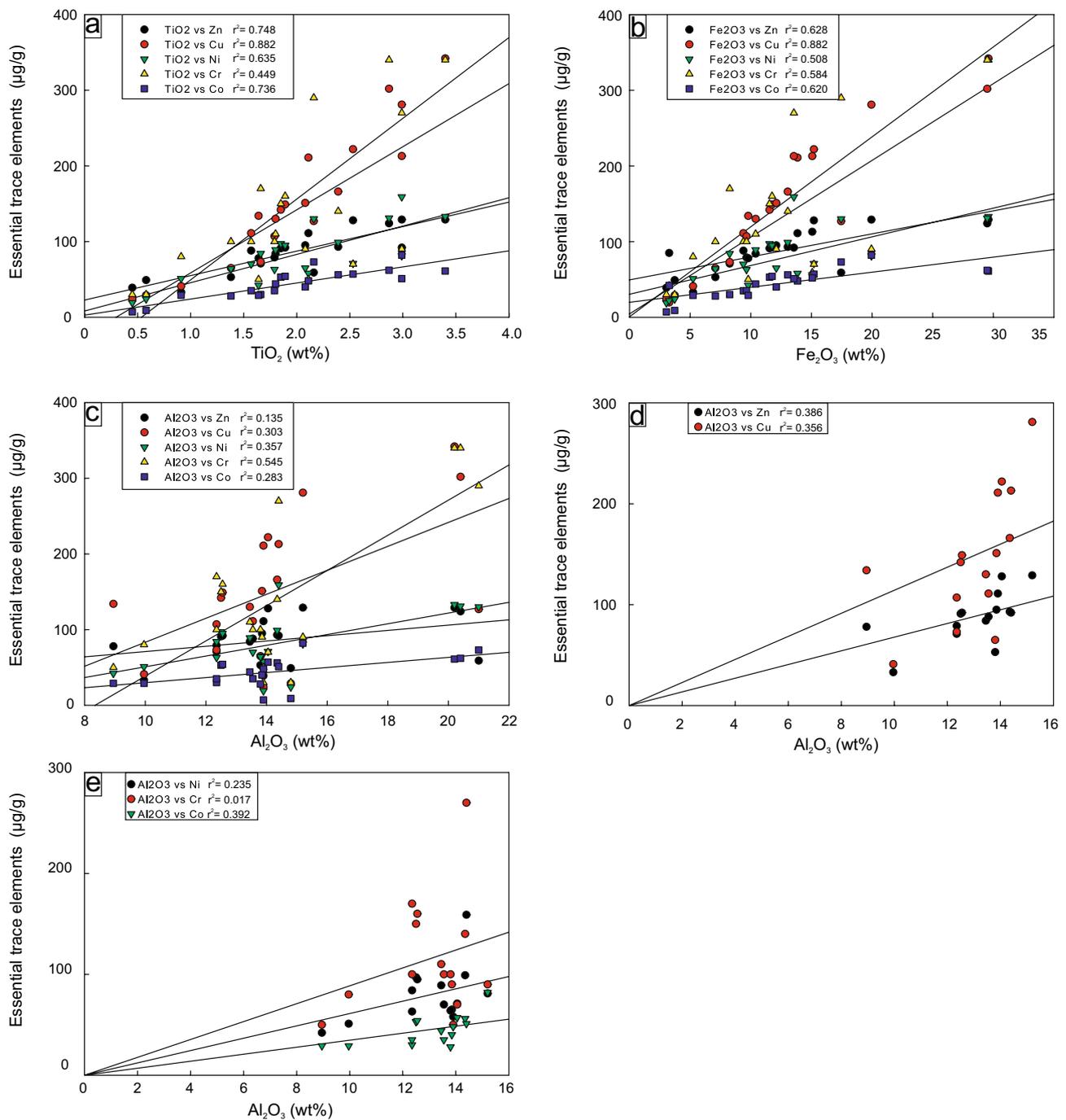


Fig. 4 Relationship of bulk soil essential trace metals (Zn, Cu, Ni, Cr, Co) to TiO₂ (wt%) (a), Fe₂O₃ (wt%) (b) and Al₂O₃ (wt%) (c). Additionally, 15 vertisols are illustrated to show the relationship of Zn, Cu (d) and Ni, Cr as well as Co (e) to Al₂O₃ (wt%)

association of essential metals is with Fe- and Ti-rich mineral phases in the vertisols and ferralsols. There is a minor relationship between Al phases and Zn, Cu, Ni and Co in most vertisols. Only Cr and Mn concentrations are clearly controlled by parent rock geology.

4.2 DTPA soil extractions of Zn, Cu, Ni, Cr, Co, Mo, Fe and their associations with bulk soil elements

The DTPA extraction data are listed in Table 2, including the minimum to maximum range. With few exceptions, the DTPA-essential metals display a similar range in all samples. Notable observations are the higher concentrations

Table 4 Pearson product moment correlation between bulk soil concentrations of C_{org} , Fe_2O_3 , MnO , Al_2O_3 (wt%), CIA and DTPA-extracted essential metals (Fe, Cu, Ni, Co, Zn) ($\mu\text{g/g}$)

	MnO	Al_2O_3	CIA	Fe	Cu	Ni	Co	Zn	
C_{org}					0.527			0.440	*
					0.02			0.05	**
Fe_2O_3	0.498			-0.441				0.609	
	0.03			0.05				0.004	
MnO							0.542		
							0.01		
Al_2O_3			0.583				0.701	0.651	
			0.01				0.001	0.002	
CIA				-0.575			0.659		
				0.01			0.002		
Fe					0.450				
					0.05				

*First cell content=correlation coefficient; **Second cell content= p value; **For pairs with p values greater than 0.050, there is no significant relationship between the two variables. In this case, values were omitted

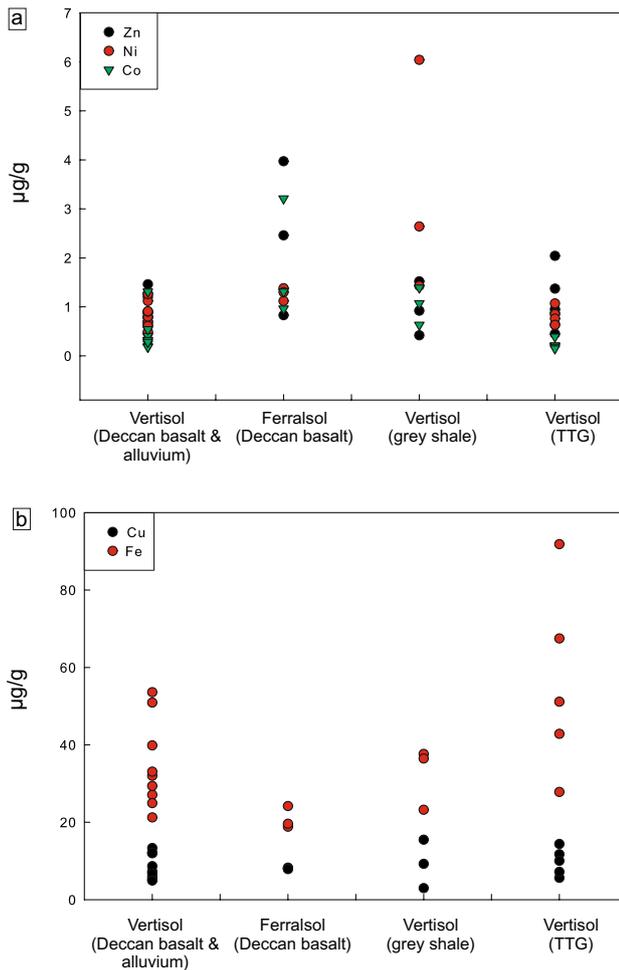


Fig. 5 DTPA concentration diagrams of agricultural vertisols and ferralsols developed over different lithologies for Zn, Ni, Co (a) as well as Cu and Fe (b)

of DTPA-extractable Fe from two vertisols from rice fields on TTG (S36 and S37) and elevated Ni from two vertisols (S18 and S19) on grey shale (Fig. 5). Furthermore, extractable Co (S25) and Zn concentrations (S26 and S28) are elevated in ferralsols developed over basalt. Regardless, the analysis of the DTPA-extractable essential metal data reveals that no first order control is exerted by the underlying geology and soil type. Consequently, we compared bulk soil elements (C_{org} , Fe_2O_3 , Al_2O_3 , MnO) and the CIA to extractable metals in all soil samples in an attempt to identify relationships.

The Pearson’s correlation analysis showed that there are modest-moderate correlations (Table 4), suggesting that the DTPA metal concentrations are held in the soils within different minerals or complexation states. The most notable correlations are between C_{org} (wt%) and extractable Zn and Cu ($p \leq 0.05$). Additionally, extractable Co and Zn correlate significantly with Al_2O_3 (wt%) ($p < 0.01$) (Table 4). Moreover, DTPA-extractable Cu correlates with Fe ($p < 0.05$), whereas inverse relationships between extractable Fe and Fe_2O_3 (wt%) ($p \leq 0.05$) as well as the CIA ($p \leq 0.01$) exist (Table 4). Extractable Co is the only metal associated with MnO (wt%) in the soil samples ($p \leq 0.01$), and extractable Zn is the only essential metal that shows a relationship with Fe_2O_3 (wt%) ($p < 0.01$). Extractable Ni is not associated with any specific bulk soil element and Co ($p < 0.01$) shows only a moderate relationship with the CIA.

4.3 FYM—element (C, Fe, Ti, Mn) and essential trace metal (Cr, Co, Ni, Cu, Zn, Mo) concentrations

Predictably, C content in the FYM samples is high (ca. 30–40 wt%), except for sample (P4) that contained hay

Table 5 Carbon, Fe and Trace Element Concentrations ($\mu\text{g/g}$, Dry Weight Basis) in Central Indian FYM ($n=18$) in comparison to New York Dairy Manures ($n=20$) [79]

Sample	Bedrock	C	Cr	Co	Ni	Cu	Zn	Mo	Fe	Ti	Mn
P10b	Basalt	36.7	31.2	10.3	20.6	52.8	251.5	1.9	16,776.0	2257.0	863.3
P1	Basalt	33.2	39.6	16.6	29.0	77.5	149.8	0.8	33,908.4	4859.8	1010.9
P4	Basalt	14.0	15.3	7.9	11.0	35.0	29.5	0.2	19,589.1	2850.2	339.7
P13	Basalt	40.8	49.3	17.5	34.8	100.0	201.1	1.8	31,406.7	4554.6	909.7
P10a	Basalt	38.9	9.8	7.2	10.6	62.0	226.0	0.7	13,621.5	1897.5	625.9
P3	Basalt	34.5	36.9	9.5	18.2	65.1	277.3	3.3	17,817.7	2659.1	896.6
P2	Basalt	31.0	27.9	17.3	23.3	88.3	186.2	0.9	35,164.1	4947.1	715.1
P16b	Basalt	40.1	50.0	12.3	28.7	109.6	306.0	4.4	29,629.9	4268.5	659.7
P7	Basalt	39.4	14.3	7.6	12.6	80.2	311.7	0.8	11,076.4	1813.7	697.8
P7(CHQ)	Basalt	33.0	42.4	24.8	30.2	111.8	123.7	1.1	48,952.2	6619.3	957.1
P16a	Basalt	37.8	39.3	13.8	30.0	79.0	300.7	1.7	21,819.9	3069.6	1346.5
P19	Granite-gneiss	38.1	15.3	7.9	11.6	47.9	199.7	1.1	14,236.9	2051.5	555.9
P18	Granite-Gneiss	33.6	2.6	1.3	1.9	12.1	147.3	4.1	2111.9	204.8	772.3
P12	Granite-gneiss	35.1	81.7	16.8	39.4	69.8	129.1	4.1	36,341.0	5358.8	780.8
P17a	Granite-gneiss	38.1	5.3	3.1	4.5	29.5	194.4	5.5	2595.4	260.8	1094.0
P14	Alluvium	37.7	46.3	8.3	26.6	62.7	216.2	3.2	15,932.8	2608.3	770.9
P11	Alluvium	35.8	28.3	10.0	19.7	63.1	228.0	1.7	19,494.0	3538.5	679.0
P15	Calcareous	36.7	21.3	5.8	13.2	31.1	160.6	2.4	9839.4	1365.6	606.3
	Mean	35.2	30.9	11.0	20.3	65.4	202.2	2.2	21,128.5	3065.8	793.4
	Median	36.7	29.8	9.8	20.2	64.1	200.4	1.8	18,655.9	2754.7	771.6
	Min	14.0	2.6	1.3	1.9	12.1	29.5	0.2	2111.9	204.8	339.7
	Max	40.8	81.7	24.8	39.4	111.8	311.7	5.5	48,952.2	6619.3	1346.5
	SD	6.0	19.7	5.9	10.6	27.8	73.2	1.5	12,470.4	1757.5	226.5
	Mean*	–	4.6	2.5	8.0	139.0	191.0	2.5	–	–	–
	Median*	–	4.0	1.9	5.0	64	162	2.3	–	–	–
	Min*	–	1	0.8	2	18	87	0.9	–	–	–
	Max*	–	13	7.2	35	1100	488	4.8	–	–	–
	SD*	–	2.6	1.7	9.5	242	115	0.95	–	–	–

bedding (< 15 wt%) (Table 5). Metals show a general pattern of concentration from high: Fe (10,000–35,000 $\mu\text{g/g}$), Ti (1500–5000 $\mu\text{g/g}$) and Mn (600–1100 $\mu\text{g/g}$); to moderate: Zn (30–300 $\mu\text{g/g}$), Cu (30–100 $\mu\text{g/g}$) and Cr (10–50 $\mu\text{g/g}$); to low: Co (5–20 $\mu\text{g/g}$) and Mo (c. 1–5 $\mu\text{g/g}$). Iron, Co, Ni, Cu, and Cr concentrations are strongly to moderately correlated with Ti ($r^2=0.983, 0.924, 0.724, 0.664$ and 0.559 , respectively) as shown in Fig. 6. This is an important observation because Ti has earlier been identified as a strong controlling phase for the association with essential metals in the bulk soils (Sect. 4.1; Figs. 3, 4). Manganese ($r^2=0.02$; not shown), Mo ($r^2=0.084$) (Fig. 6b) and Zn ($r^2=0.031$) (Fig. 6c) are not correlated to Ti, and their concentrations in FYM must therefore relate to a non-Ti-bearing phase. As with the bulk soil- and extractable chemistry, a first order relationship to the geology is absent. This can be illustrated, for example, with FYM samples from TTG regions that have the lowest but also the second highest Ti concentrations (Table 5).

5 Discussion

5.1 Bulk soil compositions—primary silicates and clays

Under most environmental conditions—Al typically remains immobile in soils with $5 < \text{pH} < 7.5$ because it is a significant constituent of clay minerals and hydroxides. Only in (sub)-tropical regions covered by forest (e.g., pod-sols) [52] Al solubilises due to high contents of organic ligands [53–56]. Secondary phases in typical soils initially form through breakdown of primary silicates [32, 57, 58]. At more advanced weathering intensity, the clays and any remaining primary silicates transform into kaolinite and finally into Al-hydroxide (gibbsite), which is extremely depleted in trace elements [16, 32]. Primary minerals (e.g., plagioclase and pyroxene) have CIA of 40–50, initial secondary minerals such as smectite or illite have CIA values of 70–85, and more advanced weathering produces kaolinite with CIA values of c. 100 [18]. The soil CIA may

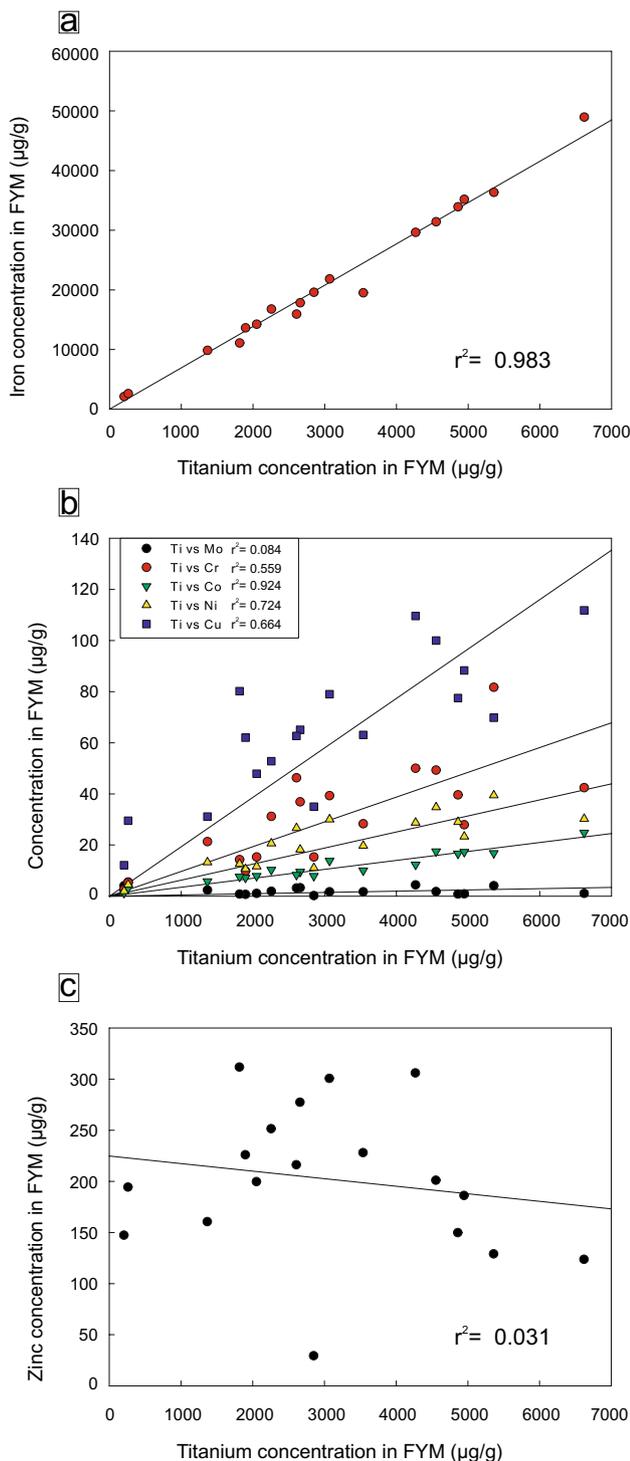


Fig. 6 Relationship concentrations of Fe (a), essential trace metals (Mo, Cr, Co, Ni, Cu) (b), and Zn (c) to Ti in FYM

therefore be a useful guide for the presence or absence of clays with appreciable metal content.

The CIA values in the vertisols (59–80) are similar to those in the uncultivated saprolitic subsoils described by

Babechuk et al. (2014), indicating that they still contain fertile rock debris and nutrient-rich clay minerals. The ferralsol topsoils (CIA 93–96) are kaolinite-rich (incidentally, the vertisol developed over grey shale, S18; CIA = 95 shows similar behaviour), indicating that the clay of these soils is typically poorer in essential metals, and thus likely problematic for agricultural fertility [16].

In terms of element behaviour, Al_2O_3 (wt%) displays modest correlations with Zn, Ni, Cu and Co concentrations in most vertisol topsoils of Central India (Fig. 6c). This implies that silicates and/or complex clay minerals are an important reservoir of Zn, Ni, Cu and Co, however, without being the main host of essential metals in Central Indian topsoils.

5.2 Bulk soil compositions—weathering resistant mineral phases

Refractory primary mineral phases may persist even in soils with elevated CIA, and thus significantly influence bulk elemental compositions. The presence of these type of refractory phases may be tracked using the behaviour of the least mobile elements.

5.2.1 Titanium and molybdenum

In parent rock, most Ti is not hosted in silicates but occurs in ilmenite (FeTiO_3) and rutile (TiO_2) and as impurity in the Fe-oxide magnetite (Fe_3O_4). This is especially the case in mafic igneous and metamorphic parent rocks. All these phases, along with other heavy inert minerals, often form the residual, undecomposed content in soils [59]. By contrast, only a small proportion of parent rock Ti occurs in primary silicates such as pyroxene, amphibole, biotite mica and garnet [60]. During oxidative chemical weathering of primary silicates, liberated Ti and Fe are rapidly redistributed into newly formed Fe–Ti hydrous oxides. This is also reflected in the low content of TiO_2 in dominant clay mineral groups ranging from 0–0.3 wt% (kaolinite), 0–0.5 wt% (smectite), 0–0.6 wt% (vermiculite), 0–0.8 wt% (illite) to 0–0.2 wt% (chlorite) [61]. The original primary mineral association of Fe and Ti and the secondary formation of Fe–Ti hydrous oxides thus explain the strong correlations between Fe and Ti in fine fractions of soils [62]. Molybdenum can also be associated with refractory minerals but in our dataset displays no relationship to the Fe–Ti mineral except in the two ferralsols (S25 and S26). In the other soils, Mo was likely originally hosted in sulphides but because concentrations are mainly below the detection limit of 1 $\mu\text{g/g}$, the inorganic soil constituents are clearly not a source of Mo.

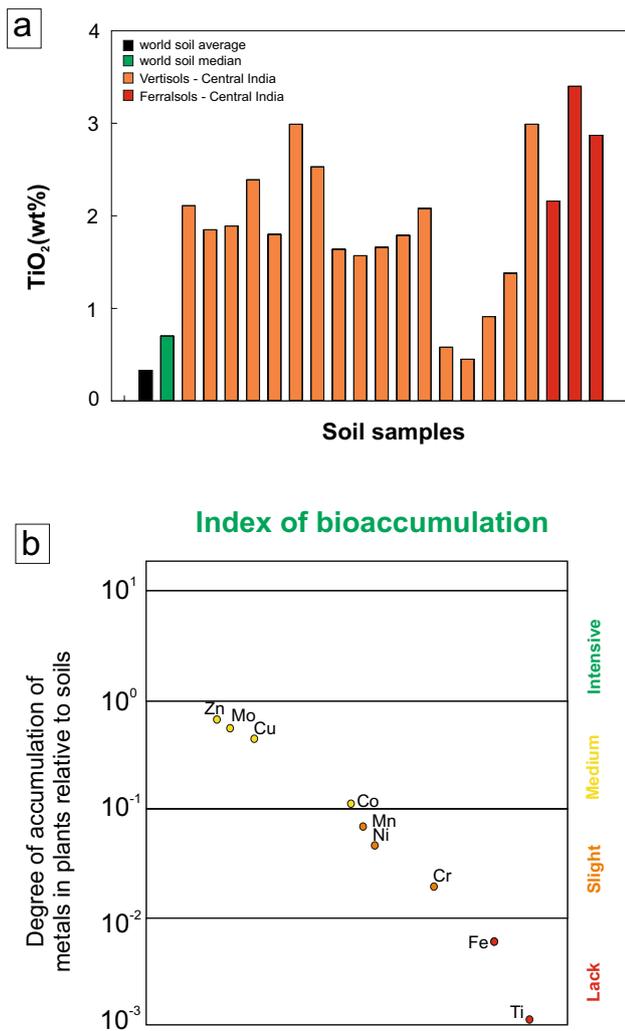


Fig. 7 Titanium (wt%) in soils—world average and median in comparison to vertisols and ferralsols from Central India (a); Index of bioaccumulation of (essential) metals. Note that Ti clearly lacks an accumulation in plants in comparison to soils (b)

5.2.2 Titanium as a potential vector towards deficiency status of soil Fe, Zn, Cu, Ni, Co and Cr

The global average and median of Ti in soils lie around 0.33% and 0.7%, respectively [60]. The vertisol and ferralsol samples from Central India display TiO₂ (wt%) much higher concentrations (Fig. 7a) (ca. 1–3.5%; n = 18 of 20; Table 1), which points to high quantities of inert residual oxides. Since Ti is not a bio-essential metal (Fig. 7b), its high abundance is not critical to agricultural practice on these soils. However, of relevance is the correlation of bio-essential metals Zn and Cu with TiO₂ (wt%), Fe₂O₃ (wt%) and $\tau_{Zn,Cu,Ni,s}$ with $\tau_{Fe,Ti,s}$ (Table 3; Fig. 4a, b). These relationships suggest that most Zn, Cu and Ni are bound in weathering resistant oxides. Similarly, the correlation of Co with

TiO₂ (wt%), Zn, Cu, Ni, Cr, Mn and $\tau_{Co,s}$ with $\tau_{Fe,Ti,Cu,Ni,Zn,Cr,Mn,s}$ further illustrates the dominance of oxide phases as hosts of metals in the cultivated vertisol- and ferralsol topsoils. Because Ti phases and other refractory minerals (e.g. zirconium-silicate) are dense, their occurrence in the topsoil horizons may not only reflect mass loss due to weathering but also loss of clays to erosion and transport by water [59] and winnowing wind [63].

5.3 Plant available essential metal contents in topsoils

5.3.1 Zinc, Cu and Fe and the importance of organic carbon

The Pearson’s correlation analysis reveals statistical relationships between DTPA metal extractions, elements (Al₂O₃, Fe₂O₃, MnO) and the CIA, the latter two reflecting bulk soil mineralogy (Table 4). However, the bio-availability of Zn and Cu is also controlled by TOC and both essential metals are commonly complexed by organic matter in weathered substrate in India [33, 64].

Since DTPA-extractable Fe and Cu moderately correlate, it is reasonable to infer that a substantial proportion of the bio-available Fe is associated with TOC. By contrast, Fe-oxides and clays are not the main source of bio-available Fe from the soil because of the moderate inverse correlation of DTPA extracted Fe and Fe₂O₃ (wt%) as well as the CIA. This finding agrees with studies on alluvial soils elsewhere in India, demonstrating that only a small fraction of the total Fe reserve is plant available [6], with the dominant Fe pool unavailable from crystalline, oxide/oxyhydroxide-bound and residual Fe fractions [6, 65].

Release of Zn to crops appears to be controlled by clay minerals, minor amounts of fertile rock debris with pyroxene [33], and possible exchange reactions on the surface sites of pedogenic oxides, as Zn concentration correlates with Al₂O₃ (wt%) and Fe₂O₃ (wt%). This agrees with the observation that complex clay minerals and residual primary phases contain modest amounts of essential metals like Zn that seem to be bio-available (Fig. 4d).

5.3.2 Chromium, Mo, Ni and Co

In soils, chromium occurs mainly (> 80%) in the chemically immobile residual fraction [59], such as in pedogenic Fe-oxides [34]. It is thus unsurprising that our measured Cr concentrations in the DTPA-extraction were below detection limit (< 0.01 µg/g), similar to simulated plant uptake of Cr with DTPA [66]. The very low DTPA-extraction concentrations ≤ 0.01 µg/g of Mo could reflect the low total content of Mo in the original bulk soil samples or its very early loss due to sulphide oxidation in the subsoil [67]. The concentration of extractable Ni is not relatable to a

specific phase on a statistically significant level, regardless of the fact that clays do contain Ni (Fig. 4c, e). The correlation of extractable Co with Al_2O_3 (wt%) suggests that primary silicates and clay minerals determine the release of Co to plants. Additionally, Mn-oxides also play a role for Co release, which is best explained by co-precipitation and consequent enrichment of Co under oxidising, near neutral conditions and potential mobility under acidic and reducing conditions [68, 69].

5.4 Essential metal deficiency status of topsoils

Accurate assessment of critical metal deficiency limits also depends on crop type and various growth factors controlled by the environmental conditions. Therefore, different DTPA values have been proposed as critical deficiency limits for micronutrients [70]. For example, Lindsay, Norvell [37] suggested soils with $> 4.5 \mu\text{g/g}$ of Fe in the DTPA-extract solution would not show Fe deficiency, yet such cut-off values are problematic because the DTPA-extraction cannot discern between different forms of Fe [71]. Regardless of the fact that the Fe concentration in the DTPA-extract solution likely overestimates the total value available to the plant, the generally high concentrations found in this study (Table 2) suggest that Fe deficiency is currently not a problem in the central Indian vertisol and ferralsol topsoils.

By contrast to Fe, the critical deficiency level for Zn is well established [70] and DTPA extractable Zn values of ca. $0.5 \mu\text{g/g}$ represent the critical lower limit for several crops but it is noted that suggested 'low' values of up to $2 \mu\text{g/g}$ can still lead to deficiency symptoms [72]. In previous Indian soil studies, average concentrations of DTPA-extractable Zn varied widely from 0.1 to $6.92 \mu\text{g/g}$, with a mean of $0.87 \mu\text{g/g}$. Soils in Central India apparently have even lower mean DTPA-Zn concentrations of $0.65 \mu\text{g/g}$ with the highest levels of deficiency in red loam (entisol) and black clayey soils (swell-shrink vertisol) of the central Deccan plateau [6]. Based on the defined critical level of Zn, two vertisol samples in this study (S6 derived from basaltic alluvium; S21 derived from grey shale) are clearly Zn deficient ($< 0.5 \mu\text{g/g}$), while most other topsoils reveal critically low levels ($< 2 \mu\text{g/g}$). Accordingly, based on the limited current data, vertisols and even ferralsols could be at risk of Zn deficiency in Central India, indicating that Zn supply from fertile rock debris and clays (see also Sect. 5.1) is insufficient for modern crops.

Extractable Cu concentrations are above the various proposed critical limits of $0.2 \mu\text{g/g}$ [37], $0.6 \mu\text{g/g}$ [71] and $2.5\text{--}3.0 \mu\text{g/g}$ [70]. The critical levels of Ni are not yet established. Globally, typical Ni values in food plants range between ca. $0.2\text{--}2.0 \mu\text{g/g}$ [59]. These values are comparable to the DTPA extractable Ni concentrations found in

this study, and we conclude Ni deficiency is unlikely to be a problem in the vertisol- and ferralsol topsoils. Similarly, a critical deficiency level for DTPA extractable Co has not yet been defined. Regardless, Co levels in plants rarely exceed concentrations above $1\text{--}2 \mu\text{g/g}$ [73], suggesting that the Co levels in the topsoil samples remain above critical level. Since the tentative critical level of Mo deficiency is $\sim 0.01\text{--}0.02 \mu\text{g/g}$ [70], it is not possible to determine bio-availability of Mo from our data.

5.5 Challenges and opportunities in the application of FYM as an essential metal fertiliser on farmland in Central India

The key finding of our agricultural vertisol and ferralsol study on Indian farmland is that Ti concentration could be an easy and inexpensive tracer to identify possible bio-unavailable essential metal pools in soil substrate. Previous studies demonstrated that Ti has an extremely low bioaccumulation index (i.e. the ratio between trace element concentrations in plants relative to soils) [59]. All other essential metals show higher indices, typically the order of $Ti < Fe < Cr < Ni < Mn < Co < Cu < Mo < Zn$ (Fig. 7b). Even though cattle may digest metals differently, the Indian FYM mainly revealed low concentrations of measured essential metals, except for Fe, Mn, Zn and Cu. Strikingly, except for Zn, Mo and Mn, most essential metals (Fe, Cr, Co, Ni, Cu) show a strong correlation with Ti (Fig. 6). The first order relationship between Ti with Fe, Cr, Co, Ni and Cu suggest that this represents material (including weathering-resistant minerals) from the topsoil itself, and that Ti concentration is thus a proxy for soil ingestion and thus "contamination" of the FYM. Thornton, Abrahams [74] and Green et al. [75] showed that the relatively high concentrations of Ti in soils together with very small amounts in herbage are conditions which permit usage of Ti concentration in livestock faeces as a stable marker of soil ingestion (see equation below). However, this assumes a herbage digestibility factor of 72% in monthly rotational pasture grass [75]. We performed a similar calculation with respect to the ten soils sampled at the same location as FYM.

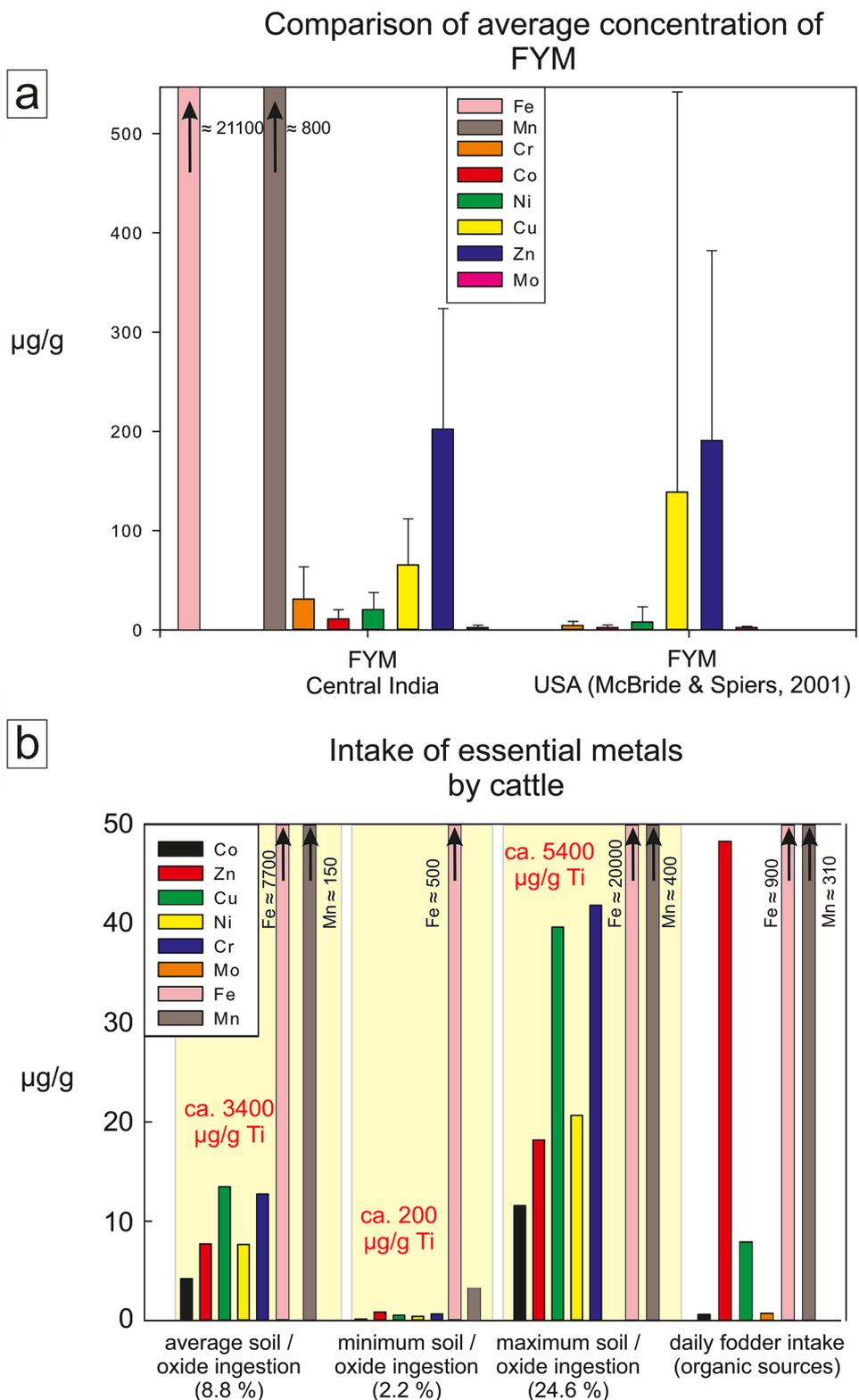
Equation:

$$\% \text{ Soil ingestion} = \frac{(1 - D_h)Ti_f}{Ti_s - D_hTi_f} \times 100$$

where D_h = digestibility of herbage, Ti_f = titanium in faeces, Ti_s = titanium in soil.

The results suggest that the amount of soil ingested by cattle ranges between 2 and 25% (Supplemental Table 6). Considering the daily mineral availability for essential metals (Zn, Cu, Co, Mo, Fe, Mn) from traditional foddering

Fig. 8 Comparison of average essential metal concentrations in FYM from this study to FYM from the USA [79] (a). Illustration of essential metal concentrations in FYM based on average-, minimum- and maximum- soil/oxide ingestion. Additionally, concentrations of Co, Zn, Cu, Mo, Fe and Mn from daily fodder intake (undigested organic sources) [72] are shown. Note the control of absolute Ti concentrations on essential metals (b)



in India, as well as a dietary intake of 11.5 kg per day for Indian cattle [76], the contribution of oxides to Mo intake is insignificant and low to moderate for Zn (5–40%). By contrast, the intake of Cu (45–500%) and Mn (30–130%)

varies between moderate to high values, but is extreme for Co (400–1800%) and Fe (350–2200%).

The C-content of the studied FYM is ca. 30–40% (dry weight), and comparable to previous studies [77]. The

Indian FYM samples have concentration levels of Zn, Cu and Mo comparable to the cow manure reported by McBride, Spiers [78] (Fig. 8a). Since the DTPA availability of these metals in the Indian soils is limited by factors previously described, and because there is no first order relationship between Ti, Zn, Mo and Mn in FYM, it thus appears likely that a mixture of digested fodder and food additives dominates the budget of Zn, Mo, Mn and possibly Cu in FYM (Supplemental Table 5; Supplemental Table 6). By contrast, the total Fe and Co intake of cattle is significantly related to soil, which can explain the strong r^2 correlation between Ti with Fe and Co (Fig. 6a, b). Importantly, Co, Cr, Ni and Fe show positive correlation to calculated soil ingestion (%) on a statistically significant level (Cr, Fe: $p < 0.01$; Ni, Co: $p < 0.05$) (Supplemental Table 7). However, Cu is also correlated with Co and Ni ($p < 0.01$) that are likely bound in weathering resistant Fe–Ti oxides in the Central Indian topsoils (Table 3; Fig. 4a, b). Refractory oxides could therefore also represent a metal contamination agent in FYM. In summary, our analysis demonstrates that essential metal concentrations in FYM are primarily associated with organic (fodder/plants) and inorganic (especially bio-unavailable refractory Fe–Ti minerals) pools that need careful distinction. Without assessment of these pools, FYM cannot be reliably evaluated as a natural metal fertiliser because otherwise it remains unclear which metals serve as bio-available crop micronutrients.

The absolute concentrations of essential metals in FYM and fodder sources can be illustrated with a multi-element histogram (Fig. 8b). This illustrates that absolute concentrations are much higher in FYM where the amount of oxide ingestion is elevated. By contrast, in examples of FYM with minor ingestion of oxides/soil, it is obvious that essential metals are not significantly biased by the inorganic, bio-unavailable pools. Furthermore, the digested fodder residue in such FYM is much lower in metal concentrations after the intake by cattle in comparison to the fodder sources. Considering its lack of bioactive role in the plant-soil cycle (Fig. 7b), the lowest Ti concentration in FYM can serve as a new vector towards the readily bio-available metal pool/residue in this natural fertiliser. Sample P18 (Table 5) is a most useful representative example for a mass balance calculation to estimate the potential of FYM as an essential metal fertiliser in India. This may be achieved by using the tons (t) that are annually available as FYM by cattle and the required fertiliser amount on Indian farmland.

Tandon [79] estimated that in 2010, 119 million t of livestock dung was potentially available as fertiliser in India, and approximately 37% of Indian livestock were cattle in 2014 [80]. Using these data as a first-order estimate for the year 2020, ca. 44 million t of FYM are available annually for manure production of which ca. 20% remain after

drying. By 2025 approximately 324,000 t Zn, 130,000 t Fe, 11,000 t Cu and 22,000 t Mn are required to ameliorate recognised essential metal deficiencies in Indian soils [81]. Fertiliser requirements for other essential metals are, to our knowledge, not published. Following this estimate approach using the least “soil/oxide contaminated” FYM sample (P18), the metal concentrations determined from this study indicate that the amount of Fe (ca. 72%) and Mn (155%) is sufficiently high to effectively counterbalance the net output of bio-available essential metals. By contrast, the levels of Cu (ca. 5%) and Zn (ca. 2%) are very clearly insufficient to correct the metal deficiency in agricultural soils in India, at least from an agro-industrial perspective (Fig. 9).

The above first-order calculation is likely to underestimate the potential of FYM as natural essential metal fertiliser due to the role of TOC. For instance, the application of FYM in a long-term experiment [21], involving 37 cycles and rotational cropping practices on Indian surface and sub-surface soils has proven to increase the concentrations of bio-available Zn and Cu in all soil fractions (exchangeable, carbonate-bound, oxide bound, organically bound and residual). Further, considering that TOC in the vertisols and ferralsols exerts control on the mobilisation of Zn, Cu and Fe to soil solutions (Table 4), it appears that the high C_{org} of ca. 35% in FYM (Table 5) is indispensable to maintain the fertility status of Indian soils of the type studied here, as well as also being an excellent source for Fe and Mn. This finding reinforces the important status of organic matter for the improvement of the soil structure, water retention, prevention of soil erosion as well as cycling and storage of plant nutrients. Since climatic conditions in India accelerate organic matter decomposition within soils, any significant net off-take of FYM would likely impoverish crop productivity [82] and further exacerbate the bio-availability of essential metals on farmland. This would be especially the case in vertisols whose physical conditions make them very difficult to cultivate and manage [83].

The importance of co-application of chemical fertilisers with manure for the essential metal availability from soils was highlighted in a review by Dhaliwal et al. [84]. The analysis of our data suggests that C-rich FYM could usefully be supplemented with sulphate salts of Zn, Fe and Cu. These are inexpensive and readily available [6]. To counterbalance the limited bio-available Zn in FYM, our calculations show that c. 318,000 t are additionally needed on Indian farmland per annum. Therefore, the cost of required sulphate salts for Zn would lie around 850 million US\$ for c. 1.5 million t. This is far more affordable than EDTA-chelated Zn, which would cost c. 24 billion US\$ for c. 2.7 million t [85] to complement the bio-available pool of Zn from FYM (Supplemental Table 8). By contrast, the

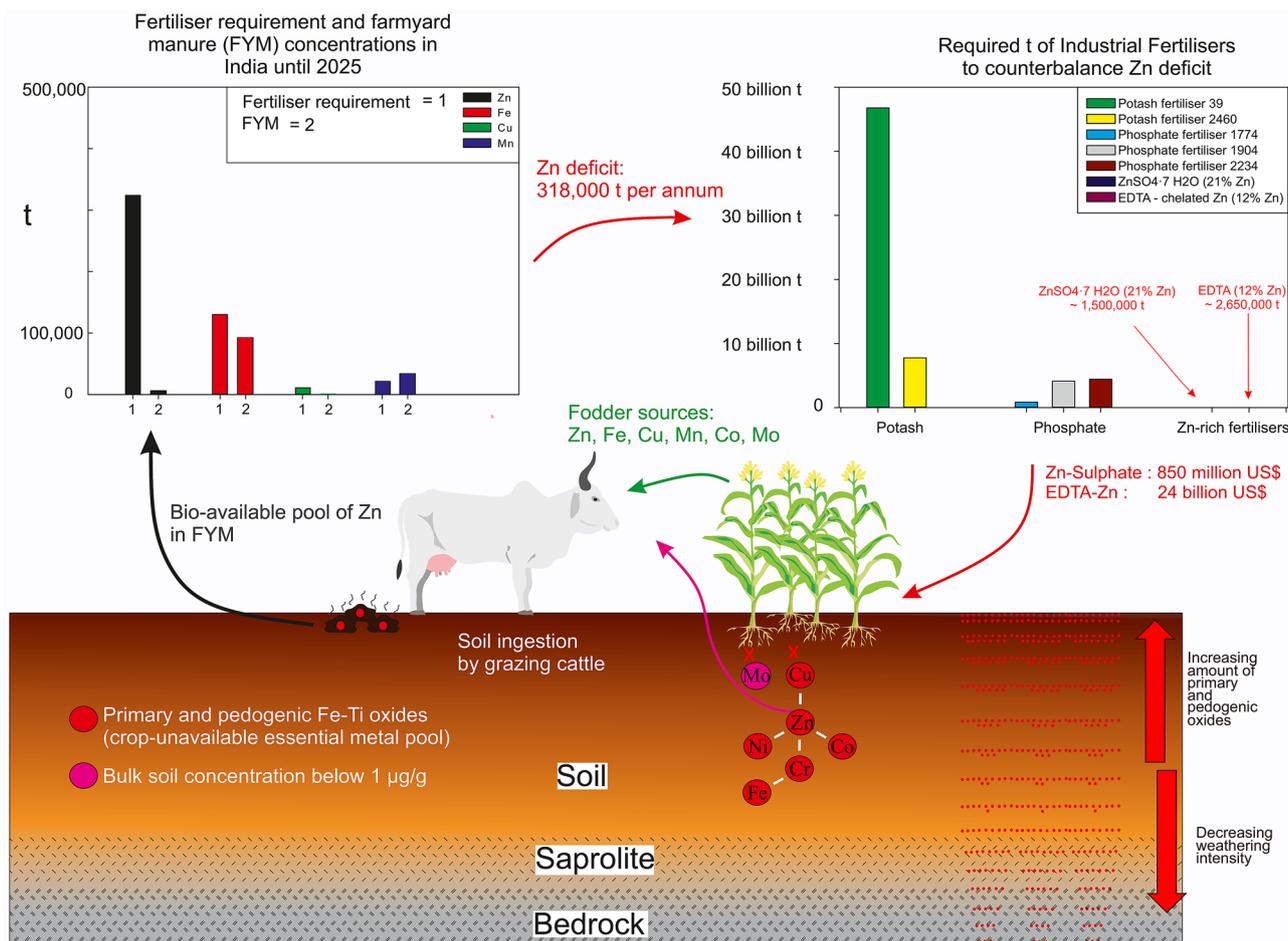


Fig. 9 A biogeochemical perspective on the fertiliser potential of FYM in India to ameliorate deficiencies of Zn, Fe, Cu and Mn until 2025, using a mass balance with the least oxide contaminated

FYM. Additionally, the annually required t of potash-, phosphate-, sulphate-, and EDTA-chelated fertilisers are illustrated that complement FYM

quantities of potash- or phosphate fertilisers required to address Zn and other essential trace metal deficits would be in the order of billions of t, costing trillions of US\$ [86], making them from the applied quantities on soil and cost an impossible essential trace metal fertiliser (Fig. 9; Supplemental Fig. 2). The disadvantage of the more affordable sulphate fertilisers is that in long-term experiments they have caused severe acidification of soil and harmed agricultural productivity and ecosystem functions. Therefore, Kidd et al. [87] proposed that long-term monitoring is required to establish if the co-application with FYM could counteract these adverse effects of sulphate salts. This is because FYM can buffer against soil acidification (> pH 5). Alternatively, the application of sulphate salts, FYM and lime could be a solution to achieve less acidic and more nutrient-rich soils in India and other developing countries to help meeting the future demands of multi-micronutrients in the soil, plant, animal and human continuum.

6 Summary and conclusion

Chemical and associated data analysis of Central Indian agricultural topsoils and FYM reveals the following:

- (1) Geochemistry can contribute to food security plans by helping to better quantify the inventory of bio-essential minerals (e.g., primary silicates, smectite, etc.) from those that “immobilise” key bio-available nutrients in the natural cycling of soil-crop-FYM-fertiliser application. Primary and secondary oxides in agricultural topsoils contain high concentrations of essential trace metals in bio-unavailable form. Only moderately weathered vertisols contain sufficient bio-essential minerals that can act as a reservoir of several essential metals (Zn, Cu, Co, possibly Ni). By contrast, Cr (held in oxide phases) and Mo (very low total content) are not bio-available from the inorganic soil constituents. With advanced weathering

and enrichment of oxides in the soil reservoirs, any original expected differences in concentrations of bio-available essential metals in different parent rocks or soil types will diminish significantly. Bulk analysis may indicate usable concentrations, but 'lock-up' of essential elements in highly residual Fe–Ti-rich (oxidative weathering-resistant) phases contributes significantly to metal-deficiency problems in this region. This observation implies that ecotoxicity levels of 'heavy metals' in oxidative environment require a careful evaluation of the mineralogical inventory to assess risks in the soil-crop-human health cycle, particularly in India where heavy metal enrichment in soils is accompanied by strong Fe-enrichment [88].

- 2) High quantities of Fe–Ti-rich phases are ingested by cattle and remain undigested. Hence, excepting Fe (c. 70%) and Mn (c. 150%), bio-available trace metal concentrations in FYM alone are likely insufficient to sustain the anticipated productivity of this land. This is exemplified by Zn and Cu that can only contribute 2% and 5% to the total fertiliser requirements annually. Regardless, the low levels of extractable Zn, Co, Mo and Cr are critical and the relationship between Zn and Cu with TOC and Cu with Fe provides evidence that organo-metallic complexes play an essential role in the availability of these micronutrients to plants. These findings underline the importance of traditional farming practices in India with C-rich FYM. We propose that the combination of C-rich FYM with affordable and widely available metal fertilisers could represent a successful way to combat multi-essential metal deficiencies in soils and crops and help to diminish the deficiency problems in the human diet in India to sustain food security, once potential risks have been evaluated in long-term studies.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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