

1 **Environmentally safe release of plant available potassium and micronutrients from**
2 **organically amended rock mineral powder**

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18 **Abstract**

19 The staggering production of rock dusts and quarry by-products of mining activities poses an
20 immense environmental burden that warrants research for value-added recycling of these rock
21 mineral powders (RMP). In this study, an incubation experiment was conducted to determine
22 potassium (K) and micronutrients (Zn, Cu, Fe and Mn) release from a quarry RMP to support plant
23 nutrition. Four different size fractions of the RMP were incubated with organic amendments (cow
24 dung and legume straw) under controlled conditions for 90 days. Samples were collected at
25 different intervals (7, 15, 30, 45, 60 and 90 days) for the analysis of available K and micronutrients
26 in the mineral-OM mixtures and leachates. There was a significant ($p < 0.05$) increase in pH of
27 leachates from the mineral-OM mixtures. The K release was significantly higher from the finer
28 size fraction of RMP. About 18.7% Zn added as RMP was released during the incubation period.
29 Zn release increased from 4.7 to 23.2 % as the particle size of RMP decreased. Similarly, Cu
30 release from RMP increased from 2.9 to 21.6%, with a decrease in the particle size. Fe and Mn
31 recovery from RMP recorded 11.2 and 6.6%, respectively. Combined application of OM and RMP
32 showed significantly higher nutrient release than other treatments. This study indicates that
33 effective blending of RMP with organic amendments could be a potential source of K and
34 micronutrients in agriculture without posing a risk of heavy metal contamination to the soil.

35

36 **Key words:** Nutrient recycling; Silicate powder; Organic matter; Potassium; Plant micronutrients;
37 Heavy metals.

38

39 **1. Introduction**

40 Limited supply of potassium (K) and micronutrients (e.g., Zn, Cu, Fe, Mn) is the most prevalent
41 constrain for plant growth worldwide, especially in organic agriculture where the nutrient supply
42 to crops is mainly derived from mineralization/decomposition of native and/or introduced organic
43 sources (e.g., manures and crop residues) and natural weathering of soil minerals (Torma et al.
44 2018). In conventional agriculture, micronutrients are supplied through commercial fertilizers,
45 which are not permitted in organic agriculture (Codex Alimentarius Commission 2007). The
46 nutrient requirements in organic agriculture may be externally met by the application of less
47 soluble sources such as manures, crop residues and rock mineral powders (RMP) (Basak and
48 Sarkar 2017). Presently, the main objective in the agricultural reforms worldwide is to promote a
49 system that supports environmental sustainability and quality production, and organic agriculture
50 is a promising practice to achieve this objective (COM 2004). Since synthetic sources are not
51 allowed in organic cultivation system, the demand of nutrients is to be met by alternative sources
52 such as organic materials and locally available geological materials (also termed as agro-minerals)
53 (Manning 2018). It is imperative to find alternative sources that meet the guidelines of organic
54 cultivation systems.

55 There are few but consistent reports on the use of multi-nutrient rock and mineral fertilizers in the
56 organic and conventional production systems (Fyfe et al. 2006). RMP have recently been reported
57 as a source of plant nutrients in Australia (Bolland and Baker 2000), Germany (von Wilpert and
58 Lukes 2003), Brazil (Theodoro and Leonardos 2006; Ramos et al. 2017; Dalmora et al. 2020a),
59 United Kingdom (Mohammed et al. 2014), and India (Basak 2019).

60 Organic farming encourages the application of natural and environmentally friendly alternative
61 nutrient sources alone or in combination to improve their individual effectiveness. The application

62 of RMP blended with composts was found as much as doubly effective in improving crop yields
63 compared to RMP alone (Theodoro and Leonardos 2006). The combined application of RMP with
64 organics (e.g., manure and compost) can be a promising approach because insoluble nutrients in
65 RMP can transform into bio-available forms by the action of organic acids produced during
66 organic matter decomposition (Basak et al. 2017). The organic acids promote mineral dissolution
67 directly through the supply of protons which attack the alumino-silicate structure of the rock. The
68 conjugate base is also responsible for forming a complex with metal ions (Al^{3+} , Fe^{2+} and Si^{4+}) in
69 the alumino-silicate framework, and subsequently releases nutrients in the solution (Song et al.
70 2015). The positive effect of organic acids on mineral dissolution thus can be defined as the sum
71 of the proton-promoted (H) and ligand-promoted (L) effects (Eq. 1) (Ullman and Welch 2002):

$$72 \quad R_t = RH + RL = k_1 aH^m + k_2 aL^n \text{ (Eq.1)}$$

73 where, R_t is the release of ions at time t ; m and n are empirical exponent constants; k_1 and k_2 are
74 kinetic rate constants for proton- and ligand-promoted dissolution; and aH and aL are activities of
75 proton- and ligand-promoted ion species.

76 The dissolution rate of mineral can further increase by the combined effects of organic acids and
77 CO_2 produced within the soil (e.g., soil respiration, organic matter decomposition) or drawn down
78 from the atmosphere because carbonic acid participates directly in the silicate weathering reaction
79 (Breeling et al. 2018). Following these reactions, plant micronutrients such as Cu, Zn, Fe and Mn
80 can become bioavailable in neutral to alkaline soil solutions in the form of organic complexes
81 (Rengel 2015).

82 Approximately 7-17 billion tons of rock dusts and quarry by-products are generated annually as a
83 result of mining activities globally including in Australia, Africa and Latin America (Renforth et
84 al. 2011). The mining by-products can be an environmental liability if left stagnating at the site for

85 long time. RMP obtained as mining byproducts are silicate minerals composed mainly of quartz,
86 plagioclase, mica and feldspar, but may vary considerably in their composition (Manning 2018).
87 RMP can serve as the source of multiple plant-nutrients when applied to soils (van Straaten 2002).
88 These practices would not only provide a low-cost source of plant nutrients to farmers (Codex
89 Alimentarius Commission 2007), but also would find a value-added option for sustainable quarry
90 by-product disposal. However, a number of factors are needed to be considered for selecting RMP
91 in agriculture such as (1) at what space RMP supplies nutrients to plants and does it meet the crop
92 demand, (2) how the particle size of RMP influences its nutrient release, and (3) how organic
93 amendments influence the nutrient release rates. Very little information is available in the literature
94 on the nutrient supplying potential, specially K and micronutrients of RMP from an agricultural
95 point of view.

96 To this end, here we evaluated a RMP collected from a quarry located in New South Wales (NSW),
97 Australia, as a source of K and micronutrients through various laboratory incubation experiments,
98 and also attempted to understand the implication of RMP utilization in the plant-soil nutrient
99 management system. We hypothesized that mineral dissolution will happen during the incubation
100 of RMP with organic matter due to the production of organic acids and CO₂ (Basak et al. 2017),
101 and the nutrient solubilization (bioavailability) will be facilitated by low molecular weight organic
102 acids produced during organic matter decomposition (Badr 2006).

103

104 **2. Materials and Methods**

105 *2.1. Rock mineral powder (RMP)*

106 The RMP was collected from the crushed by-product of a mining quarry located at Seaham, New
107 South Wales, Australia (32.799°S 151.635°E). The collected samples were ground in a steel

108 grinder. The RMP sample was distributed into four size fractions of particles using a mechanical
109 sieve shaker: (1) 16 mesh sieve (passed through 16-mesh sieve, but retained on 18-mesh sieve),
110 (2) 30 mesh sieve (passed through 30-mesh sieve, but retained on 36-mesh sieve), (3) 60 mesh
111 sieve (passed through 60-mesh sieve, but retained on 72-mesh sieve), and (4) 120 mesh sieve
112 (passed through 120-mesh sieve, but retained on 150-mesh sieve). The corresponding particle sizes
113 of the four different fractions were 1000, 500, 250 and 125 μm , respectively.

114

115 2.2. *Organic materials and quartz*

116 A well-decomposed cow dung and a legume (*Pisum sativum*) straw were purchased from a local
117 garden store (Bunnings Warehouse, Newcastle, Australia). The cow dung and legume straw were
118 oven dried at 35° C for 96 h, ground with a Wiley mill, and sieved through a 0.5-mm sieve for
119 further use. Guaranteed reagent (GR) grade quartz (SiO_2) particles (Merck, USA) were used as an
120 inert medium for the laboratory incubation study.

121

122 2.3. *Total elemental analysis*

123 The total elemental composition in percentage weight of oxides in the RMP sample (125 μm) was
124 determined by X-ray Fluorescence Spectroscopy (Axios MAX, PANalytical, Netherlands) using
125 standard-less software (Omnian software). Total K, micronutrients (Zn, Cu, Fe and Mn) and
126 potentially toxic element (PTE) contents in the RMP were analyzed by microwave assisted
127 digestion of the material in aqua regia (EPA 1996, Method 3050B). The RMP sample (0.1 g) was
128 weighted in a Teflon tube, treated with 10 mL of aqua regia. The sample was placed in the
129 microwave digestion system (CEM5000, CEM Corporation, USA) for digestion (750 W at 500 k
130 Pa for 30 min). Similarly, the cow dung and legume straw were digested in concentrated pure nitric

131 acid (HNO₃). Each digested sample was filtered through a 0.45- μ m nylon filter, and elements of
132 interest were analyzed using an inductively coupled plasma-mass spectrophotometer (ICP-MS)
133 (Agilent 7700 \times ICP-MS, Agilent Technologies Inc., USA). The ICP-MS was equipped with a
134 concentric nebulizer 7500 CX quadrupole mass analyzer and ORS collision chamber. Helium (5.5
135 purity) was used at an equal flow rate for all elements. Prior to measurements, the ICP-MS was
136 calibrated using a multi-elemental standard (ICP-AM-3 high priority standards, USA). Nitric acid
137 (2%) blanks and mid-level standards were run after every ten samples for quality control.

138

139 2.4. *Incubation Study*

140 An incubation experiment was conducted to determine K and micronutrients (Zn, Cu, Fe and Mn)
141 release from the RMP collected from the quarry. The different size fractions of the RMP were
142 incubated under controlled conditions with organic amendments. Finely ground legume straw (LS)
143 and cow dung (CD) were used as the organic amendments. The fine granular quartz sand was
144 washed and used as inert medium for the laboratory incubation studies. Six treatments consisting
145 of four size fractions of the RMP and organic materials were as follows:

146 T₁: Control (quartz sand)

147 T₂: Quartz + LS + CD

148 T₃: Quartz + LS + CD + RMP (2000 μ m)

149 T₄: Quartz + LS + CD + RMP (500 μ m)

150 T₅: Quartz + LS + CD + RMP (250 μ m)

151 T₆: Quartz + LS + CD + RMP (150 μ m)

152 The experiment was laid out in a completely randomized block design with three replications for
153 each treatment. Quartz was used as a base material in all the treatments. The quartz particles (size

154 0.2 -0.5 mm) were washed with dilute HCl (0.15%) twice to remove any unwanted materials, and
155 rinsed twice with distilled water. For the incubation study, air-dried 250 g quartz was mixed and
156 homogenized with 2.5 g of LS, 2.5 g of RMP and 25 g of CD. The study materials were moistened
157 to an optimum level (60% of water holding capacity), and incubated at 25°C for 90 days in dark.
158 Citric acid is the most common organic acid present in the rhizosphere of majority of plants
159 (Marschner 1995), and it was used for the incubation studies to simulate the chemical environment
160 as the rhizosphere. Each treatment was mixed with 150 mL of citric acid (0.01M) solution at the
161 start of the incubation.

162 The mixtures were then placed on a plastic funnel lined with Whatman No 1 filter paper, and fixed
163 on a 500 mL capacity conical flask. The moisture contents of the mixture were kept constant by
164 weighing the sample every alternative day and adding required volume of double distilled water.
165 Then the mixture was incubated for different periods (7, 15, 30, 45, 60 and 90 days) at $25 \pm 0.5^\circ$
166 C. Samples were collected at different intervals (7, 15, 30, 45, 60 and 90 days) for the analysis of
167 available K and micronutrients. Samples were leached frequently (once in 15 days) with distilled
168 water to analyze total soluble K and micronutrients following collection of the filtrate through a
169 suction pump. After filtration (Whatman No. 42 filter paper), K content in the leachate was
170 estimated on a flame photometer (FP 6420, MesuLab, China) following suitable dilution. A quality
171 control set consisting of a calibration blank and a mid-level calibration standard were run every
172 ten samples. The rate of K release from RMP was computed by fitting the data obtained from
173 leaching experiments in to the first order kinetic equation (Jardine and Sparks 1984) (Eq. 2):

174 $\ln(a - p) = \ln a - kt$ (Eq. 2)

175 where, a = amount of K release initially; p = amount of K release at a particular time ' t '; $(a - p)$ =
176 amount of K present finally, and k = rate constant. The kinetic data fitting was evaluated based on
177 the values of correlation coefficient (r) and standard error of estimate (SE).

178 The filtered leachates were also analyzed for Zn, Cu, Fe and Mn using ICP-MS (Agilent 7700 ×
179 ICP-MS, Agilent Technologies Inc., USA). The pH of the leachate was measured on a digital pH
180 meter (PHM 93, Mettler Toledo, USA). At the end of the incubation, the mixture from each
181 treatment was extracted with diethylenetriaminepentaacetic acid (DTPA) (Lindsay and Norvell
182 1978) and 0.05 M citric acid separately. The amounts of extracted Zn, Cu, Mn and Fe were
183 measured on ICP-MS. The different fractions of K in each treatment were analyzed following the
184 fractionation scheme depicted in Figure 1. Water soluble, exchangeable and non-exchangeable K
185 contents in the treatments were analyzed as per standard procedure (Page et al. 1982; Hanway and
186 Heidel 1952; Wood and DeTurk 1940).

187

188 2.5. *Statistical Analysis*

189 Data generated from the study were represented as means of three independent experiments. The
190 analysis of variance (one-way ANOVA) was conducted as per the experimental design
191 (Completely Randomized Design). The critical difference at $P = 0.05$ was estimated to compare
192 differences between means of individual treatments. Microsoft Excel (Microsoft Corporation,
193 USA) software packages were used for data calculation, tabulation and graphical representations.

194

195 3. **Results and Discussion**

196 3.1. *Characteristics of raw materials*

197 The RMP was a by-product originating from mining activities of various minerals. The host rock
198 mineralogy indicated that it was of volcanic origin with high N₂O and K₂O contents, and was
199 formed by fractional crystallization of mafic parent magma (Jenkins and Nethery 1992). An earlier
200 X-ray diffraction study of RMP indicated the presence of basic volcanic rock forming minerals
201 (Basak et al. 2018). The RMP was predominated with quartz, anorthite, albite, some K-feldspar,
202 mica and chlorite (Basak et al. 2018). The XRF data confirmed Si, Al, Fe, Mn and K contents in
203 decreasing order, and smaller proportions of Cu, Ca, Mg and P in the RMP (Table 1). Owing to
204 the nutritional contents, the RMP would have potential agricultural use, especially in nutrient-poor
205 soils (Ramos et al. 2015; 2019). The PTE contents of RMP obtained through ICP-MS analysis
206 indicated very low concentration of As (2.54 ppm), Cd (0.35 ppm), Hg (< 0.01 ppm) and Pb (0.59
207 ppm), which are not likely to pose an environmental risk (Dalmora et al. 2020a; 2020b). A
208 comparative chemical composition of the RMP and organic materials (CD and LS) are presented
209 in Table 2. The RMP contained an appreciable amount of total K (1.54%) and micronutrients
210 (14754, 3098, 14919 and 14839 mg kg⁻¹ Zn, Cu, Fe and Mn, respectively). Both the organic
211 materials contained >40% of total carbon. Apart from carbon, the LS contained notable amounts
212 of N (1.93%) and K (1.13%), while CD contained 0.69% N and 0.11% K on dry weight basis.

213

214 3.2. *pH of leachate*

215 In the case of quartz (control), the pH of the leachates was controlled by the pH of the eluent (i.e.,
216 0.01M citric acid), and the pH values varied from 2.7 to 3.3 irrespective of the incubation period
217 (Figure 2). However, treatments containing LS, CD and RMP resulted in notable changes of the
218 leachate pH values during the incubation period. Treatments containing RMP showed significantly
219 ($p < 0.05$) higher pH (5.7 - 6.8) in the leachate than the treatments without RMP (0.7 unit increase

220 in pH at the upper end). There was an increasing trend in pH values with advancement of the
221 incubation period, irrespective of the particle size of the RMP. Finer fraction of RMP had more
222 pronounced effect on increasing the pH value than the coarser fractions. This might be due to faster
223 dissolution of the finer fraction particles than coarser ones (Basak et al. 2018). The increase in pH
224 with the introduction of LS and CD might be due to the mineralization of N-rich organic materials.
225 Organic N contents in LS and CD were likely the main factor contributing to the pH rise of the
226 mixture because the ammonification process during organic matter decomposition consumes H^+
227 ions and raises the pH value (Wong and Swift 2003). The increase in pH with the addition of RMP
228 might be explained by the acid neutralization capacity (ANC) of the mineral powder (Weber et al.
229 2005). The dissolution reaction involving silicate minerals would have the potential to neutralize
230 acidity by consuming H^+ ions (Eary and Williamson 2006). Mineralization of organic carbon
231 leading to the production of OH^- ions by ligand exchange reaction as well as via the introduction
232 of basic cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) during the incubation might have raised the pH of the
233 medium (Anda et al. 2015). Increasing pH due to the positive liming effect from legume residue
234 (Tang and Yu 1999) and RMP (Eary and Williamson 2006) was reported to ameliorate soil acidity
235 to some extent. For example, olivine (Silva et al. 2013) and granite (van Noort et al. 2018) powders
236 were used as an effective alternative to conventional liming materials for correcting acidity of
237 agricultural and forest soils.

238

239 *3.3 Potassium release from RMP*

240 Water soluble K (WSK) released from various treatments during the leaching experiment is
241 presented in Figure 3. Results indicated that relatively higher amounts of K was released during
242 the initial period of leaching from all the treatments than the control (T_1). The K release rate sharply

243 decreased up to 45 days of leaching, then gradually decreased up to 90 days. Overall, blending
244 RMP with organic materials (LS and CD) showed significantly higher (2-3 folds) K release than
245 organic material only treatment, irrespective of the leaching period. However, variation of K
246 release among the treatments went down with the advancement of the leaching period. The
247 treatment containing 150 μm RMP (T_6) accounted for the highest K release followed by T_5 (250
248 μm), T_4 (500 μm) and T_3 (2000 μm). It might be due to the increase of reactive surface area with
249 the increase of fineness of the particles. The intercept and slope values obtained from the first order
250 kinetic equation also indicated an increasing K release trend with finer RMP particles (Table 3).
251 A higher dissolution rate can be expected as more exchange sites open up during the dissolution
252 reaction (de Fatima Tavares et al. 2018). The current results agree with the findings of Harley and
253 Gilkes (2000) and Basak et al. (2018) for K bearing silicate minerals.

254 The cumulative release of WSK from different treatments was computed by taking the sum of the
255 amounts of WSK (mg kg^{-1}) released at a particular time (Figure 3). The cumulative WSK release
256 was recorded notably higher in the case of treatment containing RMP as compared to the treatment
257 containing only organic materials (T_2). The smallest size fraction of the RMP (T_6) recorded the
258 highest cumulative WSK (46.2 mg kg^{-1}) which was significantly higher than the largest size
259 fraction (T_3) of RMP (25.8 mg kg^{-1}). Higher values of rate constant (slope) and intercept were
260 obtained with smaller particle size of the RMP (Table 2). The K solubilization from minerals can
261 be influenced by several geochemical factors, including pH, redox potential and chemical
262 environment present in the plant rhizosphere (Zhu et al. 2014). The exact geochemical conditions
263 of a natural environment might not be present under laboratory condition, but some factors such
264 as pH and redox potential are expected to play important roles both under laboratory and field
265 conditions (Wang et al. 2011). Current results indicated that organic materials improved the

266 bioavailability of K from RMP during the incubation. Mobilization of K from the RMP with
267 organic materials might have contributed considerably to WSK release (Basak et al. 2017). During
268 incubation, the K release from the RMP through solubilization by organic acids produced from
269 decomposition of organic matter might have attributed to WSK increase (Szmidt and Ferguson
270 2004). These results corroborated the outcome of other studies where a significant amount of K
271 release from waste mica (Basak 2018) and phonolite (de Fatima Tavares et al. 2018) powders were
272 studied when incubated with organic materials such as compost, cow manure and plant residues.

273

274 *3.4. Micronutrients release from RMP*

275 Total release of micronutrients (Zn, Cu, Fe and Mn) in the leachate throughout the incubation
276 period is presented in Table 4. A little amount of micronutrients was released from the treatment
277 T₂ containing only organic materials (LS and CD). The addition of RMP with organic materials
278 recorded a significant ($p < 0.05$) increase of micronutrients release. The extent of micronutrients
279 release increased with a decrease in particle size of the RMP, which followed the K release pattern
280 as discussed earlier. About 18.7% Zn added as RMP was released over the incubation period. The
281 Zn release increased from 4.7 to 23.2 % with a decrease in the particle size of RMP from 2000 to
282 150 μm . The release of Cu varied from 2.9 -21.6% of the total added amount via RMP, and a trend
283 similar to Zn showing increased release with increasing fineness of particles was observed. The
284 Fe and Mn release also followed the similar trend as in the case of Zn and Cu. Overall, Fe and Mn
285 recovery from RMP recorded about 11.2 and 6.6%, respectively. These results indicated that
286 micronutrients release during the incubation was significantly higher with the fine size fractions
287 of RMP than the coarse particles.

288 The solubility of micronutrients depends on the pH and redox potential of the medium (Violante
289 and Caporale 2015). The solubility of Zn is known to be more sensitive to pH, whereas Fe and Mn
290 solubility notably depends on the redox potential (Pan et al. 2014). Additionally, the humic acid
291 fraction of organic matter is responsible for immobilizing metal ions (Cu, and Zn) at pH < 6.5
292 (Chaudhary and Narwal 2005; Perelomov et al. 2018). On the other hand, Fe and Mn may convert
293 to their reduced forms under an anaerobic (low redox) condition leading to higher Fe and Mn
294 solubility. Under anaerobic condition, Fe³⁺ and Mn⁴⁺ act as electron acceptors, and are transformed
295 to their reduced counterparts, Fe²⁺ and Mn²⁺ (Sahrawat 2005). Micronutrients speciation may
296 approach in two opposite directions by organic matter application to soils. It can either reduce the
297 availability by making insoluble metal complexes, or increase the availability by solubilization
298 and release of organically complexed metals (Diacono and Montemurro 2010). In this study,
299 experiments conducted under controlled conditions were conducive for decomposition of the
300 organic materials, and an optimum microbial activity could be expected. It was reported that most
301 of the released micronutrients from organic matter might get re-fixed in the soil matrix (Stevenson
302 1991), which was not expected here as the experiment was conducted without a soil as such.
303 However, a decrease in micronutrient content was likely due to the formation of water insoluble
304 metal complexes (Chaudhary and Narwal 2005). In the current experiment, exact soil conditions
305 were not possible to create; but a weak citric acid was added to make the environment quite similar
306 to the rhizosphere. As a result, the micronutrient release in the leaching experiment did not follow
307 the trend that would exactly happen in the soil environment. Nevertheless, it was possible to give
308 an estimate of the micronutrient availability from RMP for plant nutrition by simulating the plant
309 rhizosphere chemistry using citric acid (Wang et al. 2015). Results of the present study thus

310 showed that RMP with organic materials could serve as a potential source of Zn, Cu, Fe and Mn
311 in soils.

312

313 *3.5. Potassium fractions after incubation*

314 Different fractions of K, i.e., water soluble K (WSK), exchangeable K (Ex-K) and non-
315 exchangeable K (NEx-K), in RMP were significantly influenced during the incubation and
316 leaching experiments (Table 5). The amount of WSK was recorded less as compared to Ex-K and
317 NEx-K. A substantial amount of WSK was released during the successive leaching events, which
318 might have caused the changes in K fractions. The treatment containing only organic materials
319 (T₂) recorded a significant amount of WSK (0.94 mg kg⁻¹), but contained a negligible amount of
320 Ex-K and NEx-K (Table 5). There was an increasing trend of K pools (WSK, Ex-K and NEx-K)
321 with decreasing particle size of the RMP. The treatment containing the smallest particle size (T₆)
322 recorded significantly ($p < 0.05$) higher Ex-K (28.2 mg kg⁻¹) and NEx-K (272.8 mg kg⁻¹) than
323 WSK (2.87 mg kg⁻¹). The readily dissolvable K present on the surface of RMP particles was first
324 removed by distilled water (WSK). Then, dilute salt solution (1N NH₄OAc) able to extract K by
325 exchanging with cations at the surface and wedge zones of the particles was considered as Ex-K.
326 The low-molecular weight organic acids such as citric acid having functional groups (–OH and –
327 COOH) tend to form organo-metal complexes with metal ions present in the mineral structure
328 (Lian et al. 2002), thus accelerating the K release from RMP. A large amount of K was extracted
329 by HNO₃ from the mineral structure (T₆) due to the release of K from partially opened and inter-
330 layer positions of minerals (Moritsuka et al. 2004). Overall, the high K release from the fine
331 particle size fraction of the RMP was likely to be due to the greater reactive surface area relative
332 to that of the coarser particles (Priyono and Gilkes 2008).

333

334 3.6. DTPA and citric acid extractable micronutrients after incubation

335 DTPA and citric acid are considered to be suitable extractants for studying plant available
336 micronutrients in soils (Bibiso et al. 2016). Both the extractants act as organic ligands; they reduce
337 the activity of micronutrient cations in the solution through formation of soluble organo-metal
338 complexes. Both the methods are well correlated for extracting plant available micronutrient
339 cations from the soil (Samourgiannidis and Matsi 2013). Micronutrients extracted by DTPA and
340 citric acid at the end of the incubation are presented in Table 6. Micronutrients release by both the
341 extractants were significantly ($p < 0.05$) higher in the treatments receiving RMP than the control.
342 Here again for both the extractants, micronutrients release increased with a decrease in particle
343 size of the RMP. The highest amount of Zn (7.34 mg kg^{-1}) was extracted with citric acid in the
344 treatment T₆ containing quartz + LS + CD + RMP ($150 \mu\text{m}$), which was significantly ($p < 0.05$)
345 higher than the rest of the treatments (Table 6). A similar trend was observed in the case of
346 micronutrients extraction by DTPA. There were significant differences ($p < 0.05$) in releasing Fe
347 and Mn due to a decrease in particle size of RMP, either extracted with DTPA or citric acid. Under
348 both DTPA and citric acid extractions, the highest Fe (8.84 mg kg^{-1}) and Mn (7.54 mg kg^{-1}) release
349 was recorded with treatment T₆ receiving the finest RMP particles. On average, increased
350 micronutrients (Zn, Fe and Mn) release was observed with citric acid than DTPA. This difference
351 was higher in case of fine sized RMP particles than large particles. Citric acid has high chelating
352 potential to trap metal cations due to its tridentate structure, and thus can effectively displace
353 adsorbed anions from mineral surfaces (Wang et al. 2015). Various mechanisms including ligand-
354 exchange reaction, dissolution of metal oxides from surfaces and formation of metal-organic
355 complexes attributed to higher micronutrient cations extraction by citric acid than DTPA (Shan et

356 al. 2002). The release of Cu from various treatments followed different trend than that of other
357 micronutrients. Notably lower Cu release was observed irrespective of treatments and extractants
358 than other micronutrients (Zn, Fe and Mn). Copper forms inner sphere complexes consisting of
359 one to two five-membered chelate rings in association with functional groups of organic matter
360 (Diaz-Barrientos et al. 2003). This suggested that Cu was strongly bound with organic matter
361 functional groups within the study pH range, and subsequently its availability could be reduced in
362 the environment (Maqueda et al. 2015). The Cu release was lower with citric acid compared to
363 DTPA but not showing a significant difference among the treatments, which warrants further
364 investigation.

365 Results of the present investigation indicated that Zn, Fe and Mn extracted from RMP at the end
366 of the incubation by 0.05 M citric acid and DTPA followed similar patterns except for Cu. DTPA
367 is considered to be an ideal extractant to study plant available micronutrients in the soil (Bibiso et
368 al. 2016), and can be used as a standard reference to test the efficiency of other extraction methods.
369 The DTPA method was originally developed for calcareous soil. However, results from the present
370 study indicated that the method was equally effective for the estimation of micronutrients in an
371 acidic condition. Micronutrients extraction by 0.05 M citric acid here followed a similar pattern as
372 DTPA, but quite higher values for Zn, Fe and Mn were obtained (Table 5). However, citric acid
373 did not show the increase of Cu extraction in the same way as DTPA method did. This may be
374 explained by the reduction of Cu availability due to the formation of strong complex with
375 functional groups of organic matter (Karlsson et al. 2006), as described earlier. Results indicated
376 that the RMP blended with organic materials could be used to meet Zn, Cu, Fe and Mn
377 requirements of crops in organic agriculture. These results agree with previous reports where the
378 application of silicate minerals improved growth and yield of maize (Basak et al. 2018), wheat

379 (Bolland and Baker 2000), sorghum (Kelland et al. 2020), and sugarcane (Theodoro and Leonardos
380 2006). The addition of RMP with organics showed a synergistic effect on micronutrients release
381 in adequate amounts to meet crop needs (Garcia-Mina et al. 2004).

382

383 *3.7 Environmental and agricultural implications*

384 This study was conducted under controlled laboratory conditions. An important question remains
385 open whether the release of K and micronutrients from RMP was sufficient to meet the demand of
386 agricultural crops in sustainable production. A pot culture study conducted earlier showed
387 significant improvement of yield, K and micronutrients uptakes in plants (*Zea maize* and *Ocimum*
388 *sanctum*) treated with the same RMP (7.5% application rate) collected from Seaham quarry, New
389 South Wales, Australia (Basak et al. 2018). Another important concern is environmental risks
390 associated with the potential release of harmful elements from RMP. The elemental compositions
391 of different RMP studied in majority of the studies did not show any environmental or human
392 health risk (van Straaten 2006; Kelland et al. 2020). However, waste minerals obtained from sludge
393 was found to contain critical amounts of Pb, As and Cr, and not allowed to use in agriculture
394 (Madaras et al. 2012). On the other hand, rock dusts collected from geological deposits and
395 mountain sides were evaluated under agricultural regulations, and were found to be free of toxic
396 elements (Manning 2018). The RMP used in the present investigation was evaluated earlier in a
397 pot study, and did not show any PTE risk (Basak et al. 2018). RMP release nutrient elements
398 slowly over the course of weathering and continuously supply them to plants throughout the plant
399 growth period (Harley and Gilkes 2000). There is negligible risk of over-dosage of a single nutrient
400 with RMP unlike often seen in the case of soluble fertilizers, and the slow weathering makes RMP
401 less prone to off-site contamination too (Gillman et al. 2002).

402 In the current study, organic materials (cow dung and legume straw) and citric acid were used to
403 simulate a soil chemical environment quite similar to a rhizosphere soil (Violante and Caporale
404 2015). A normal yield (4000 kg ha⁻¹) of maize (90-100 days) removes 372 g Zn, 3648 g Fe, 780 g
405 Mn and 308 g Cu ha⁻¹ from an agricultural soil (Takkar 1996). Considering the release of Fe during
406 the incubation period (90 days), 165.5 kg RMP ha⁻¹ is required to supplement the amount removed
407 by a maize crop. This amount of RMP can supply variable amounts of K and other micronutrients,
408 i.e., smaller or greater than the crop demands due to variable contents of K and micronutrients in
409 the RMP (Table 2) and their variable release patterns (Table 4). In this theoretical calculation, K
410 and micronutrients supply from the native soil is not included, which may underestimate the real-
411 time effect of RMP on crop yield. Nevertheless, this study demonstrated the potential of RMP as
412 K and micronutrient sources, and intrigued to conduct further field level evaluation of the RMP
413 combined with organic matters under ecological farming systems.

414

415 **4. Conclusions**

416 Results of this study suggested that the RMP contained significant amounts of K (1.54% total K)
417 and supplied essential micronutrients (Zn, Cu, Fe and Mn) when used in combination with organic
418 materials. During the incubation, 23.2, 21.6, 19.2 and 13.2% of total Zn, Cu, Fe and Mn present in
419 RMP were released. The RMP thus could be considered as a potential source of K as well as
420 micronutrients in crop production without any PTE accumulation risk. The combination of organic
421 materials and RMP in soil fertility replenishment strategies should further be investigated. Plant
422 roots can accelerate weathering of minerals through the prevalence of microbial activity hotspots,
423 production of organic acids, and a low pH environment. Plant intervention studies should be
424 undertaken to test the potential use of the RMP in organic farming. An effective blending of RMP

425 with organic amendments could be a potential source of K and micronutrients in the organic
426 farming system.

427

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432 Delhi, India.

433

434 **Data availability**

435 The data supporting the findings of this study are available within the article and/or its
436 supplementary materials.

437

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616

617 **Legend of figures**

618 **Fig. 1.** Flow chart depicting procedure of potassium fractionation scheme

619 **Fig. 2.** Effect of different treatments on the pH values of the collected leachate at different intervals
620 of incubation time

621 **Fig. 3.** Water soluble K (mg kg^{-1} mixture) release patterns (a), and cumulative water soluble K
622 release (b) from RMP during the incubation period

623

624 **Title of Tables**

625 **Table 1.** Chemical composition in percentage weight of oxide in the rock mineral powder

626 **Table 2.** Comparative chemical properties of the materials used in the study

627 **Table 3.** Rate constant (slope) and intercept of K release in leaching with water during incubation from
628 four size fractions of rock mineral powder fitted into the first order kinetic equation

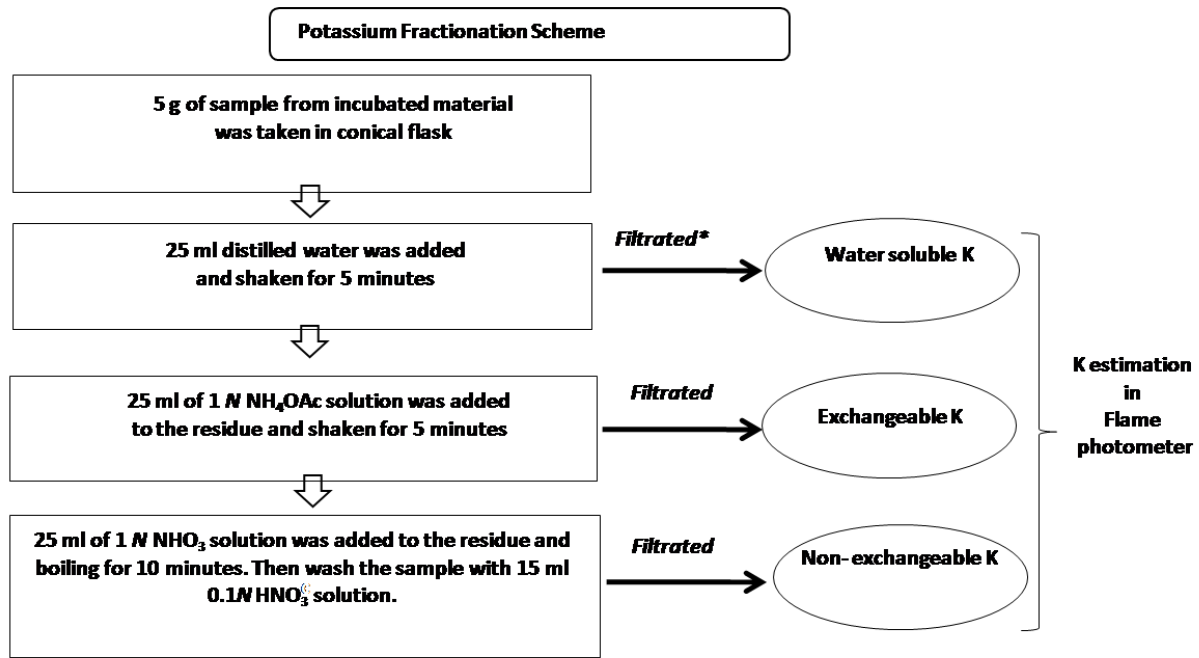
629 **Table 4.** Total amounts of micronutrients (Zn, Cu, Fe and Mn) released from different treatments during
630 the period (90 days) of incubation experiment

631 **Table 5.** Effect of various treatments on different fractions of K after completion of the incubation

632 **Table 6.** Effect of different treatments on extractable micronutrient (Zn, Cu, Fe and Mn) contents with
633 DTPA and citric acid after completion of the incubation

634

635 **Figures**

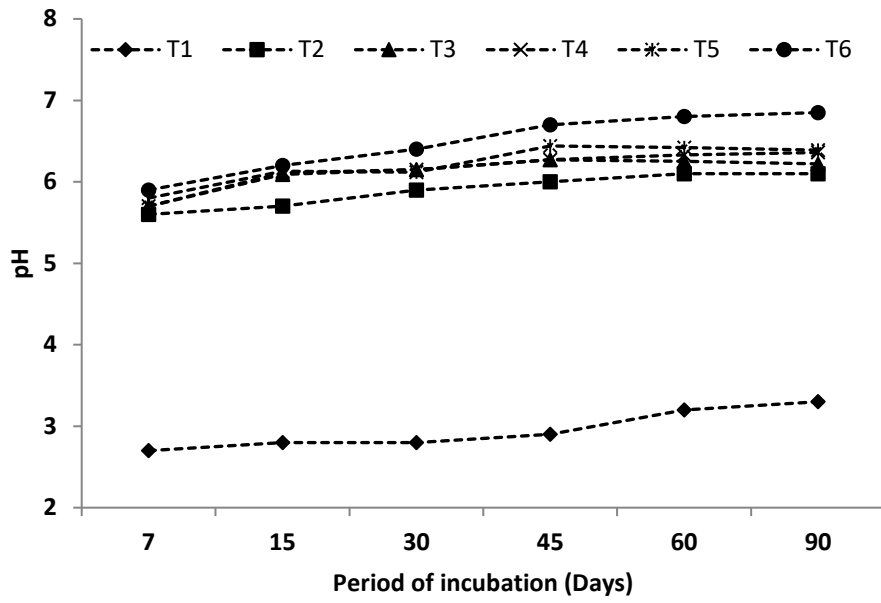


636 *Whatman No. 42 filter paper

637 **Fig. 1.**

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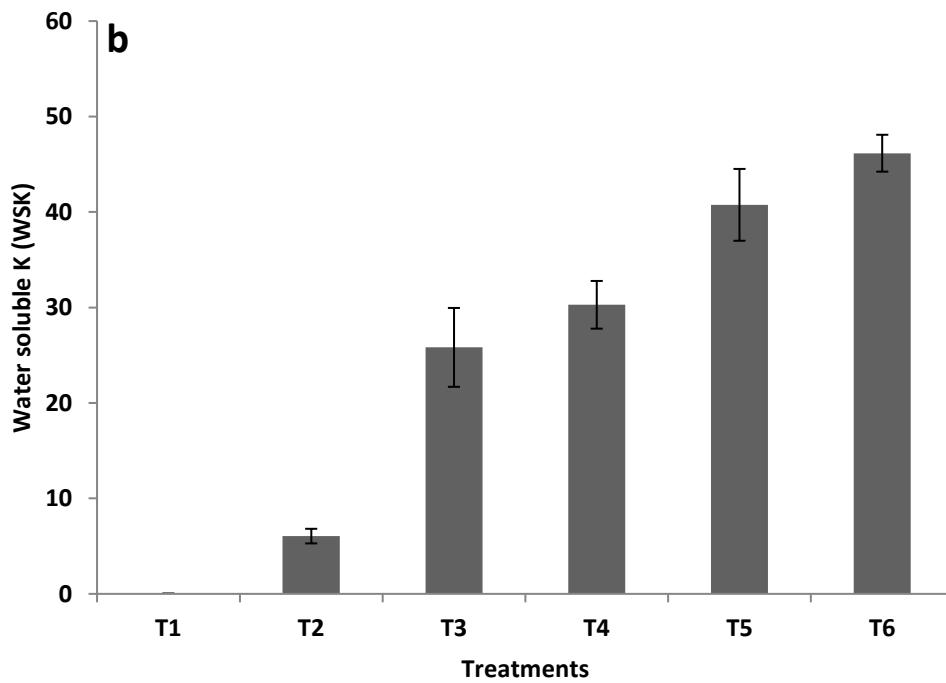
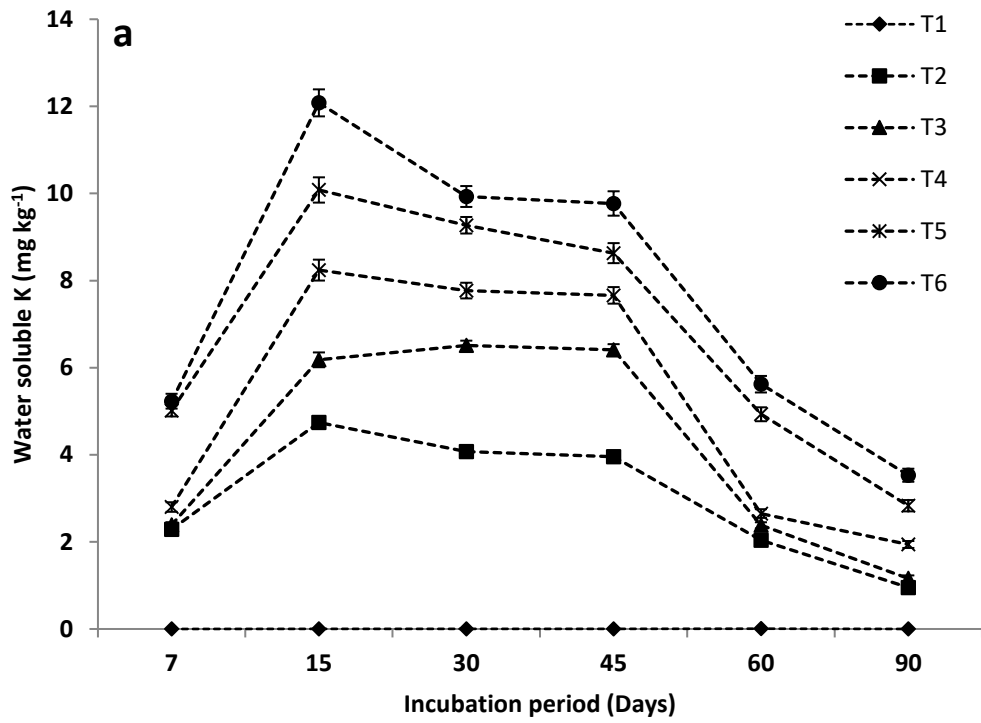
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640

641 **Fig. 2.**

642



643

644 **Fig. 3.**

645 **Tables**

646 **Table 1.** Chemical composition in percentage weight of oxide in the rock mineral powder

Oxides	Content (%)
SiO ₂	46.81
TiO ₂	1.24
Al ₂ O ₃	37.61
Fe ₂ O ₃	2.13
MnO	1.92
ZnO	1.82
CuO	0.33
MgO	0.59
CaO	1.25
Na ₂ O	1.17
K ₂ O	1.85
P ₂ O ₅	0.04
SO ₃	1.29
LOI*	1.42
Total	99.47

647

648 *Loss on ignition

649 **Table 2.** Comparative chemical properties of the materials used in the study

Material used	pH	TC (%)	TKN	C: N ratio	TK (%)	Zn (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Fe (mg kg ⁻¹)	Mn (mg kg ⁻¹)
Legume straw (LS)	5.4	42.3 (0.92)*	1.93 (0.17)	21.9	1.13 (0.09)	29.7 (1.44)	13.2 (0.79)	187.6 (2.92)	54.8 (3.24)
Cow dung (CD)	7.9	41.7 (1.12)	0.69 (0.10)	60.4	0.11 (0.007)	123 (9.2)	34 (2.8)	1121 (18.7)	266 (13.4)
Rock mineral powder (RMP)	8.7	-	-	-	1.54 (0.21)	14754 (124)	3098 (207)	14919 (14.7)	14839 (234)

650

651 *Value in the parenthesis standard deviation (SD), n = 3

652 [TC: Total carbon, TKN: Total Kjeldhal nitrogen, TK: Total potassium]

653

654 **Table 3.** Rate constant (slope) and intercept of K release in leaching with water during incubation from
655 four size fractions of rock mineral powder fitted into the first order kinetic equation

Size fractions (μm)	First-order equation parameters	
	Slop $\times 10^{-2}$ (h^{-1})	Intercept (mg kg^{-1})
1000	7.23	1.42
500	7.55	1.53
250	7.83	1.66
125	8.09	1.89

656

657

658 **Table 4.** Total amounts of micronutrients (Zn, Cu, Fe and Mn) released from different treatments during
 659 the period (90 days) of incubation experiment

Treatments	Zn (mg)	Cu (mg)	Fe (mg)	Mn (mg)
T ₁ : Control (quartz sand)	-	-	-	-
T ₂ : Quartz + RMP	1.710	0.134	2.372	0.378
T ₃ : Quartz + LS + CD + RMP (2000 µm)	1.883 (4.7)	0.251 (2.9)	2.510 (3.8)	0.526 (1.2)
T ₄ : Quartz + LS + CD + RMP (500µm)	2.962 (7.4)	0.906 (10.5)	5.330 (8.1)	1.623 (3.7)
T ₅ : Quartz + LS + CD + RMP (250µm)	6.765 (16.9)	1.535 (17.8)	9.015 (13.7)	3.642 (8.3)
T ₆ : Quartz + LS + CD + RMP (150 µm)	9.287 (23.2)	1.864 (21.6)	12.632 (19.2)	5.792 (13.2)

660

661

662 **Table 5.** Effect of various treatments on different fractions of K after completion of the incubation

Treatments	WSK	Ex K	Non Ex K
	(mg kg ⁻¹ mixture)		
T ₁ : Control (quartz sand)	0.00	0.00	0.00
T ₂ : Quartz + RMP	0.94	15.6	84.3
T ₃ : Quartz + LS + CD + RMP (2000 μm)	1.16	16.8	86.7
T ₄ : Quartz + LS + CD + RMP (500μm)	1.94	19.6	120.5
T ₅ : Quartz + LS + CD + RMP (250μm)	2.53	20.5	178.3
T ₆ : Quartz + LS + CD + RMP (150 μm)	2.87	28.2	272.8
<i>CD</i> *(<i>P</i> =0.05)	0.17	2.87	7.82

663

664 WSK: water soluble K; Ex K: exchangeable K; Non Ex K: non-exchangeable K

665 *Critical difference

666

667 **Table 6.** Effect of different treatments on extractable micronutrient (Zn, Cu, Fe and Mn) contents with
 668 DTPA and citric acid after completion of the incubation

Treatments	Zn	Cu	Fe	Mn
	(mg kg ⁻¹ mixture)			
DTPA				
T ₁ : Control (quartz sand)	0.00	0.00	0.00	0.00
T ₂ : Quartz + RMP	1.21	0.24	3.24	3.43
T ₃ : Quartz + LS + CD + RMP (2000 μm)	2.57	0.33	4.83	4.12
T ₄ : Quartz + LS + CD + RMP (500μm)	2.79	0.47	5.26	4.78
T ₅ : Quartz + LS + CD + RMP (250μm)	3.83	0.54	6.40	5.23
T ₆ : Quartz + LS + CD + RMP (150 μm)	5.32	0.67	7.37	6.87
<i>CD</i> * (<i>P</i> =0.05)	1.22	0.13	2.66	1.57
Citric acid				
T ₁ : Control (quartz sand)	0.00	0.00	0.00	0.00
T ₂ : Quartz + RMP	2.43	0.09	4.23	3.28
T ₃ : Quartz + LS + CD + RMP (2000 μm)	3.54	0.13	5.42	5.12
T ₄ : Quartz + LS + CD + RMP (500μm)	4.17	0.19	6.31	5.56
T ₅ : Quartz + LS + CD + RMP (250μm)	5.66	0.27	7.92	6.09
T ₆ : Quartz + LS + CD + RMP (150 μm)	7.34	0.34	8.84	7.54
<i>CD</i> * (<i>P</i> =0.05)	1.09	0.10	2.43	0.72

669

670 *Critical difference

671