



# Impact of potassium fertilisation on mobile proximal gamma-ray spectrometry: case study on a long-term field trial

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## Abstract

Mobile proximal gamma-ray spectrometry (GS) is an emerging approach to estimate soil texture directly in the field. It relies on gamma radiation emitted during the natural decay of potassium-40 (K-40) and other isotopes. The K-40 counts are correlated with total K content, mineralogical soil composition and therefore with soil texture. Yet, it is not clear if K fertilisation impacts the ratio of K-40 to total K which would necessitate to take the fertilisation history into account for soil sensing applications. To elucidate this question, a well-documented long-term experiment was selected. The soils of the Rengen grassland experiment (55 plots) were investigated for total K (XRF-K) and for K-40 via mobile proximal GS. No significant differences in XRF-K and K-40 were found between the treatments with and without K fertilisation, although formerly published results point to negative and positive K balances, respectively. Fertiliser analysis revealed a ratio of K-40 to total K that was almost identical to the natural abundance of 0.0117%. It was concluded that it is not necessary to take K fertilisation history into account when predicting soil texture from mobile proximal GS on agricultural land for, e.g., precision farming purposes.

**Keywords** Soil heterogeneity · Potash · K-40 · Isotope ratio · Proximal soil sensing

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## Introduction

Potassium (K) occurs in rocks, minerals, and soils and is a major nutrient for all plants. Three K isotopes occur naturally: the two stable forms K-39 (93.3%) and K-41 (6.7%), and the long-lived radioisotope K-40 (0.0117%) that emits gamma rays during its decay. Mobile GS is an emerging technique that utilizes correlations between K-40 and other features of the gamma spectra (i.e., Total Counts (TC), Uranium-238 (U-238), and Thorium-232 (Th-232)) and grain size classes to predict topsoil texture directly in the field, e.g., for precision farming applications (Priori et al., 2014; Heggemann et al., 2017; Pätzold et al., 2020). Using K-40 for such predictions presumes that the proportion of K-40 to total K in soil is more or less constant as it was stated in the field study by Wong and Harper (1999). An isotopic shift of the K isotopes due to K fertilisation would result in the need for correction of the K-40 counts prior to texture prediction on the basis on gamma recordings.

To replace K exported through crop yields, agricultural soils regularly receive K fertiliser. The application rate should be adapted to the specific harvest removal and therefore varies largely. At national scale, annual K fertiliser use in Europe is in the order of magnitude of 0.01 to 0.05 Mg ha<sup>-1</sup> (Öborn et al. 2005). Potassium fertilisers are produced from potash and rock salt deposits. To our knowledge, no striking hints exist that point to an aberration of the K-40 proportion in potassium fertiliser from the above mentioned natural abundance of 0.0117%. Accordingly, Chauhan et al. (2013) as well as Billa et al. (2015) reported that the specific K-40 activity in mineral fertiliser was in the expected range of natural K-40 abundance in rocks. The same information applies to German K fertilisers that were used in the Rengen Grassland Experiment (RGE), although no related studies have been published (personal communication by R. Elfrich, K+S Aktiengesellschaft, Kassel, Germany). In soil, the proportion of K-40 to total K might be affected by biological discrimination of the heavier isotope, i.e., a differentiated K-40 plant uptake and export via harvest. The IAEA (2010) reports transfer factors (TF) for the root uptake of K-40 by different crops in temperate environments from 0.73 to 1.3. In her detailed study on seven different pasture sites in Turkey, Cengiz (2019) measured a mean TF from soil to grassland species of 0.99±0.023. The recent modelling study by Nguyen et al. (2020) suggests that soils may become enriched in K-40 after long-term and excessive K fertilisation.

We could not find focused studies on the consequences of fertiliser application on mobile GS against the background of proximal soil sensing on agricultural land. In their review article, Reinhardt and Herrmann (2019) mention unpublished results indicating that long-term fertilisation leaves behind a shifted ratio between K-40 and total K isotope ratio. Hence, the authors claim further investigation. Wetterlind et al. (2012) conducted a GS campaign at the landscape scale and compared arable land with forested areas to detect fertilisation effects. In that study, differences in K-40 content as detected by proximal GS (1 m above ground) were attributed to effects caused by soil moisture, bulk density and soil depth but not to fertilisation.

To elucidate a possible fertilisation effect on gamma recordings under well-defined conditions, the RGE in the Eifel mountains (Germany) was selected. This plot experiment started in 1941 on formerly unfertilised heathland and comprises unfertilised as well as fertilised treatments with negative and positive K balances, respectively. Therefore, the RGE allows to study the K fertilisation effect on proximal GS in detail. We hypothesized that the differentiated long-term fertilisation history affects total K stocks in soil and, in conse-

quence, has also an impact on the K-40 counts recorded via mobile proximal GS. We further hypothesized that the ratio between total K and K-40 in soil was affected due to a potential isotopic shift in fertiliser and soil, probably resulting in a perturbation of the correlation between K-40 and clay content in soil.

## Material & methods

### Site properties, experimental design, and soil sampling

The RGE was set up in 1941 on the Rengen Grassland Research Station of the University of Bonn and is still continuing. It is located in the Eifel mountains (Germany, 50°13' N, 6°51' E) at 475 m a.s.l. with 811 mm annual precipitation and a mean temperature of 6.9 °C.

The experiment comprises 55 small plots of 3 by 5 m size. Besides the five Control plots which received neither lime nor fertiliser, five treatments are arranged in a randomized block design on ten plots each. The fertilised treatments are (i) Ca: only lime; (ii) CaN: lime and nitrogen; (iii) CaNP: lime, nitrogen, and phosphorus; (iv) CaNPK<sub>KCl</sub>: lime, nitrogen, phosphorus, and potassium chloride; (v) CaNPK<sub>K<sub>2</sub>SO<sub>4</sub></sub>: lime, nitrogen, phosphorus, and potassium sulphate. Only straight, i.e. single nutrient, mineral fertilisers are used. The fertilisation regime comprises only application or not of lime or a nutrient, i.e., dosage of applied nutrients is constant. No organic fertilisers were applied and no grazing was allowed since 1941. Annual K application in those treatments that receive K amounts to 133 kg K ha<sup>-1</sup>. For more details on the RGE, see Hejzman et al. (2010b). The sward is cut twice a year. Biomass yield was quantified, and on this basis, Hejzman et al. (2010) calculated a K input and output balance.

The area around the experiment plots was always managed like the Control plots (see below). Here, a soil pit adjacent to the control plots was sampled for detailed analyses (Table 1) and classified as Stagnic Cambisol.

The air-dried soil samples were pestled and sieved to 2 mm prior to subsequent analyses. The particle-size distribution in 0–0.4 m depth was analysed with the sieve-pipette-method in all 55 plots. Here, the mean clay, silt, and sand content was 19.9 ± 3.3%, 45.9 ± 2.9%, and 31.4 ± 1.6% (texture classes SiL and L). In a former study, no differences for SOC content and cation exchange capacity were found between the treatments (Pätzold et al. 2013).

**Table 1** Major soil properties of the reference soil profile at the edge of the RGE (horizon and texture class designation according to the FAO Guidelines for soil description)

Horizon	Depth	Bulk density	Texture Class	Clay content	SOC	pH	CEC <sub>eff</sub>	XRF-K
	[cm]	[g cm <sup>-3</sup> ]		[%]	[%]	[CaCl <sub>2</sub> ]	[cmol <sub>c</sub> kg <sup>-1</sup> ]	[g kg <sup>-1</sup> ]
Ah1	0–3	n.a.	SiL	23	4.78	4.1	6.1	14.6
Ah2	3–14	1.07	SiL	23	3.66	4.3	5.2	14.6
Bw	14–28	1.40	SiL	25	0.80	4.0	3.8	17.3
Bwg	28–43	1.53	L	26	0.42	4.0	4.1	20.0
Bg	43–62	1.59	L	25	0.23	4.0	5.3	23.2
C	62–80+	1.71	SiCL	28	0.21	3.9	7.2	22.0

## Total K content and stock in soil

Total element contents in soil are traditionally determined after digestion in hydrofluoric acid; yet, due to safety issues, this method is nowadays hardly accessible. X-ray fluorescence (XRF) yields comparable results (Weindorf & Chakraborty, 2020) and is considered a high-potential method for precision agriculture purposes, also for field application (Gebbers & Schirrmann, 2015; Büchele et al., 2019). Therefore, total K contents were determined by XRF in this study (XRF-K). Measurements were conducted using a wavelength dispersive spectrometer MagiX Pro from Panalytical, equipped with a water-cooled 4 kW Rh-tube. The soil samples were placed as loose powder in X-ray sample cups covered with a 6 µm X-ray Mylar® foil and measured under He atmosphere. The application was calibrated using 16 certified reference soil materials (CRM) from different institutions: GBW07402 und GBW07405 from National Research Centre for Certified Reference Materials (Beijing, China); NCS DC73023, NCS DC73030, NCS DC85109 and NCS DC87104 from National Analysis Centre for Iron and Steel (Beijing, China); TILL1, TILL2 and TILL3 from Canadian Centre for Mineral and Energy Technology – CANMET (Ottawa, Canada); BAM-U110 from Federal Institute for Materials Research and Testing – BAM; Soil-5 from International Atomic Energy Agency – IAEA (Vienna, Austria); VS2498-83 from ICRM-Centre (Moscow, Russia); NIST1646a, NIST2704, NIST2709 and NIST2710 from National Institute of Standards and Technology – NIST (Gaithersburg, USA).

To complement the gamma readings that mirror the radioactive decay to a soil depth of approximately 0.4 m, total potassium stocks in 0–0.4 m depth were calculated from XRF-K content in the respective samples and a bulk density (BD) of  $1.32 \text{ g cm}^{-3}$ . This BD was the weighted mean of measured BD's from 0 to 0.4 m depth of the reference profile at the edge of the experiment (Table 1). Variability of bulk density between plots is probably small because all soils fall into the texture classes SiL and L, and organic matter content varies only little between the treatments (Pätzold et al., 2013).

## Fertiliser analyses

Unfortunately, no fertiliser analyses have been conducted in the past for the RGE, and no archived fertiliser samples exist. To complement soil analyses, the currently used K fertilisers were analysed for total K and K-40. These products are single-nutrient fertilisers, commercialised by K+S Aktiengesellschaft (Kassel, Germany), and consist of KCl or  $\text{K}_2\text{SO}_4$ , respectively, with a water solubility of 100%.

To verify the K-40 as well as the total K content, 50 g of each fertiliser were dissolved in duplicate in 1 L of demineralized water. The K-40 activity of 1 L solution in a Marinelli cup (Type 133 N) was measured against water as a background in a HPGe Coaxial Photon Detector Gamma Ray Spectrometer (Ortec, Oak Ridge, Tennessee, USA) over a period of 86,400 s. The total K concentrations in the respective aqueous fertiliser solutions were measured using atomic absorption spectrometry at 766.5 nm after calibrating the instrument with commercial standard solutions.

## Proximal mobile GS in the field

Gamma spectra were recorded directly in the field in July 2022 after the second grass cut, i.e., at few centimeters biomass height. The utilized gamma spectrometer MS-2000 comprises a 2000 mL CsI-based scintillation detector with a photomultiplier unit and a multichannel analyser with 4096 channels (Medusa Radiometrics BV, Groningen, The Netherlands). The device was mounted on an open steel frame fixed to a car trailer hitch at 0.3 m above soil surface (Fig S1, supporting material). Gamma recordings were conducted in the center of each experimental plot. Measuring time was 1 min at a frequency of 1 Hz in order to rule out noise (Pätzold et al., 2020). Consequently, 60 spectra per plot were recorded, resulting in a total number of 3,300 evaluated spectra.

Spectra were processed with the spectrometer manufacturer's software "Gamman". The evaluation was performed in the "traditional fit mode". The results comprised the total counts (TC) and the regions of interest (ROI) for, K-40, and Th-232. The spectrometer was calibrated by the manufacturer (van der Graaf et al., 2011) for soil surface applications and provided the results in Bq kg<sup>-1</sup> for each ROI. With respect to the research question, results for Th-232 and U-238 were not evaluated in this study.

## Results & discussion

Total K content (XRF-K) in 0-0.4 m soil depth of the 55 plots ranged from 15.3 to 16.0 g kg<sup>-1</sup> and revealed no significant differences between the treatments (Table 2). Accordingly, the calculated K stocks varied only little. This small variation was surprising because the annual K balances as published by Hejman et al. (2010a) accounted for -26 (Control), -45 (Ca), -30 (CaN), -37 (CaNP), +8 (CaNPK<sub>KCl</sub>), and +35 (CaNPK<sub>K<sub>2</sub>SO<sub>4</sub></sub>) kg K ha<sup>-1</sup> a<sup>-1</sup> (Table 2), and the experiment is continuously running since 1941. The authors calculated these nutrient balances for the different RGE treatments with yield data from 20 years and biomass analyses from 2008. Estimating reliable K balances over time is challenging with respect to a number of uncertainties (Öborn et al., 2005). In the RGE, the striking changes in the floristic composition over time (Hejman et al., 2010b) led probably to a variation in K export over time. Therefore, a long-term K balance covering the entire experimental period of the RGE was not calculated.

**Table 2** Parameters of annual K balance and K-related soil properties (0-0.4 m depth) of the Rengen Grassland Experiment. Actual K stock was calculated from the XRF-K content in 0-0.4 m depth and bulk density from the reference profile (Table 1)

Treatment	K fertilisation [kg K ha <sup>-1</sup> a <sup>-1</sup> ]	K balance <sup>#</sup> [kg K ha <sup>-1</sup> a <sup>-1</sup> ]	XRF-K [g kg <sup>-1</sup> ]	K stock [kg ha <sup>-1</sup> ]
Control	0	-26	15.8±0.38	20,901
Ca	0	-45	15.7±2.29	20,755
CaN	0	-30	15.5±1.61	20,417
CaNP	0	-37	15.3±1.91	20,185
CaNPK <sub>KCl</sub>	133	+8	15.7±2.07	20,769
CaNPK <sub>K<sub>2</sub>SO<sub>4</sub></sub>	133	+35	16.0±1.80	21,061

<sup>#</sup> Hejman et al. (2010a); <sup>§</sup> Pätzold et al. (2013)

Yet, the K balance variation is not reflected by K content and stocks. Several reasons might have led to this result. First, the contribution of the subsoil, below 0.4 m depth, to K nutrition is unknown. When large amounts of K were taken up from greater depth, the net K export would have led to a smaller K decrease in the uppermost soil layers. However, no investigations were carried out on this question. Second, K losses through leaching by subsurface lateral flow are unknown but probable. Certain K losses under permanent grassland are in line with the literature, notably for non-grazed and minerally fertilised meadows (Kayser and Isselstein, 2005). In this study, the annual K surplus ranges in the same order of magnitude as the annual losses by subsurface flow on a poorly drained, silty clay grassland soil in Southwestern England that were found by Alfaro et al. (2004). It is therefore assumed that in the RGE, surplus K was leached over the experimental period, on this stagnic soil on a flat slope most probably by lateral subsurface flow. Subsurface flow is a documented phenomenon in the Rengen soils and led to considerable N losses (Thome et al., 1993); most likely, K was also leached in this soil that has a small CEC, particularly in the hydromorphic B horizons where lateral leaching processes probably occur (Table 1).

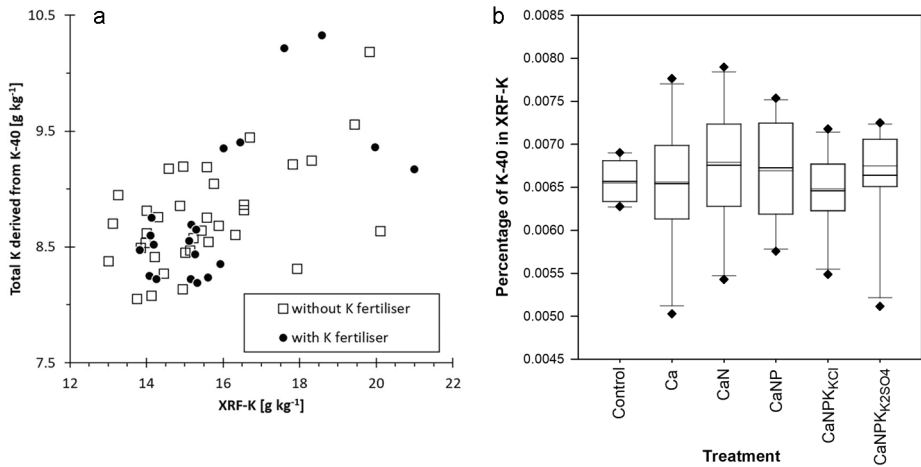
No significant differences between the Gamma information, neither for Total Counts nor for K-40 were observed for the treatments (Table 3). The measured counts are in the range of values which were observed earlier at a separate site, but in a similar geopedological environment of the Eifel mountains (Pätzold et al., 2020). For calculating the total K contents shown in Table 3, the natural abundance of K-40 was assumed (Wiechen et al., 2010). In consequence, they must not be confused with the XRF-K content, the latter classically regarded as total K.

The relationship between K-40 and XRF-K, expressed as % K-40 at the total K as determined by XRF, is shown in Fig. 1a. The correlation is weak, and no clear difference occurred in the ratio of XRF-K and K-40 counts between fertilised and unfertilised treatments (Fig. 1b). This might be primarily explained by the rather small data range, but also by the increased uncertainty of field GS as compared to laboratory methods. In contrast, Wong and Harper (1999) found a good log-linear correlation ( $r^2 = 0.94$ ) between XRF-K and uncalibrated K-40 counts; however, in their study, the XRF-K data span was large and ranged approximately from 0.5 to 13 g kg<sup>-1</sup>, thus only in parts covering the data range

**Table 3** Descriptive statistics for Total Counts (TC), K-40 content, and total K content (calculated on the basis of K-40) in soil for the different treatments of the Rengen Grassland Experiment. On each plot, 60 spectra were recorded within one minute directly in the field

Treatment Plots [N]	Control 5	Ca 10	CaN 10	CaNP 10	CaNPK <sub>KCl</sub> 10	CaNPK <sub>K<sub>2</sub>SO<sub>4</sub></sub> 10
TC [cps]						
Min	1031	992	1011	1013	1025	1026
Max	1045	1096	1081	1087	1092	1111
Mean ± SD	1037 ± 5.4	1039 ± 23.9	1045 ± 16.8	1042 ± 19.8	1047 ± 19.0	1052 ± 21.6
K-40 [Bq kg <sup>-1</sup> ]						
Min	319	298	307	299	303	305
Max	340	377	349	353	382	378
Mean ± SD	329 ± 7.7	321 ± 20.6	327 ± 12.9	322 ± 16.6	324 ± 24.6	327 ± 21.2
Total K [g kg <sup>-1</sup> ] <sup>#</sup>						
Min	10.1	9.4	9.7	9.4	9.6	9.6
Max	10.7	11.9	11.0	12.1	12.1	11.9
Mean ± SD	10.4 ± 0.24	10.1 ± 0.65	10.3 ± 0.41	10.2 ± 0.52	10.2 ± 0.78	10.3 ± 0.67

<sup>#</sup> calculated on the basis of K-40 according to Wiechen et al. (2010)



**Fig. 1** Relationship between the K contents yielded by the two methods in plots with and without mineral K fertilisation. **(a)** Total K in soil determined by (i) XRF and (ii) by proximal GS on 55 plots of the RGE. **(b)** boxplot for the K-40 abundance, i.e. the K-40 amount related to XRF-K contents (in %); the expected abundance was 0.0117% (see text). The boxplots shows mean, median, 10th, 25th, 75th, and 90th percentiles as well as min/max values

of this study. Naskar et al. (2019) compared gamma and XRF to determine K in silty to clayey soil samples from 21 sites in a natural ecosystem; under ideal lab conditions and after respective calibration, gamma spectrometry detected 66 to 214% (Median: 85%) of the K concentrations of XRF. In our study, XRF-K was considered a reference value for total K and the gamma recordings directly in the field. Although our gamma spectrometer was calibrated for soil surface measurements by the manufacturer, some external factors such as size of the footprint, density other than in the brick device used for calibration, attenuation by the sward, soil moisture attenuation greater than suggested by IAEA (2010), and signal origin greater than 0.4 m depth might have impacted the measurements (van der Veeke et al., 2021). It is concluded that mobile gamma should be considered with care when determining absolute total K content in the field, since XRF is a recognized reference method for total elemental content. However, it is stated that mobile GS and XRF led to the same conclusions on total K, although the K values between the methods differ more than expected.

The chemical and radiometric analyses revealed a total K content in the KCl-fertiliser of  $298 \text{ g kg}^{-1}$  and a K-40 activity of  $9,530 \text{ Bq kg}^{-1}$  fertiliser, respectively. For the  $\text{K}_2\text{SO}_4$ -fertiliser, the respective values were  $248 \text{ g kg}^{-1}$  and  $9,086 \text{ Bq kg}^{-1}$ . The K-40 counts equal a total K content of  $302 \text{ g kg}^{-1}$  for the KCl product and  $287 \text{ g kg}^{-1}$  for the  $\text{K}_2\text{SO}_4$  fertiliser when multiplied with the mass-related K-40 activity factor of  $0.0316 \text{ g Bq}^{-1}$  (Wiechen et al., 2010). This factor relies on the natural K-40 mass fraction of 0.0117%; the results of chemical and radiometric total K estimation suggest that the K-40 proportion in the fertiliser is very close to the natural mass fraction of K-40.

Although this field trial has been surveyed for a comparatively long time period, this case study has some data lacks and limitations and the results may perhaps not be simply generalised. Though, adequate study sites are scarce, and no similar investigation has been published so far. One of the major constraints of the study is perhaps the imperfect K balance. With respect to the dynamics of the floristic composition and related K export with

biomass over the long experimental period (Hejcman et al., 2007, 2010a, b), a comprehensive K balance for the entire experimental period is desirable but challenging and not subject of this study. Hejcman et al. (2010a) state a positive K balance in the fertilised treatments that was surprisingly, even in the long-term, not significantly reflected in the XRF-K contents (Table 2). This result suggests that K the surplus was leached. Clay and organic matter content as well as rather low CEC's were not significantly different between the treatments, making sorption of large amounts unlikely.

It is assumed but not investigated in this study that K deficiency or surplus affected K dynamics in soil, in particular cation exchange processes. The two isotopes K-39 and K-40, both from natural, i.e. weathering, as well as from fertiliser sources, were apparently subjected to similar sorption dynamics. Otherwise, a change in the K-40 abundance would have been observed. Note that in 1941 the experiment was set up on formerly uncultivated heathland. Therefore, anthropogenic changes of natural K-40 proportion in soil prior to the first fertiliser application are almost excluded.

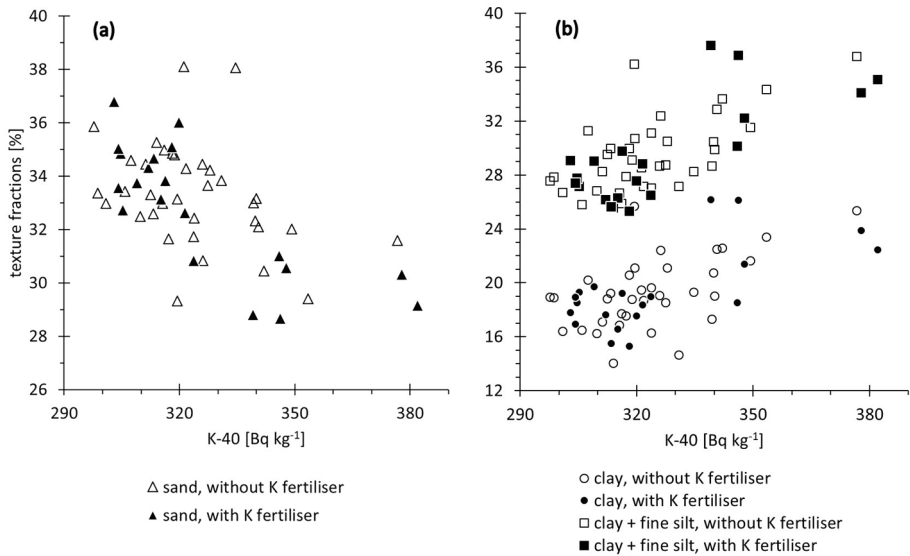
In general, shifts in plant uptake of different isotopes of a given element are well-known. However, for K the TF to different crops in temperate climate (IAEA, 2010) and, more specifically, for grassland (Cengiz, 2019) suggest that no important isotopic shift in soil K occurs due to plant uptake and export via harvest. Our study supports that assumption. Furthermore, during the K fertiliser production, no significant aberration of isotopic composition from the raw product and the geologic mean value is expected; this assumption was confirmed by the own fertiliser analyses and is in accordance with Billa et al. (2015). To summarize, it is assumed that neither K fertilisation nor K fractionation during plant uptake, if occurring at all, led to a significant shift of the proportion between K-40 and total K content in the fertilised as compared to the unfertilised plots. Consequently, the relationship between K-40 and soil texture was not affected by the fertilisation regime. The point clouds for fertilised and unfertilised plots overlap for sand, clay and clay+fine silt (Fig. 2).

In a similar geopedological environment, i.e. in stagnic soils from intensively weathered Lower Devonian sedimentary rock, we found a close correlation between soil texture and K-40. Though, in that earlier study the sand content ranged from 12 to 51% (Pätzold et al., 2020). In this study, we used only RGE data to avoid any uncertainty about the K fertilisation regime. Due to the small small texture variability, the correlation was small. The sand fraction on these sites is quartz-dominated (Heggemann et al., 2017). Consequently, a negative relation between sand content and K-40 was observed (Fig. 2a). On the contrary, the clay as well as the clay+fine silt fraction contain mica, illite and other potassium-rich minerals, leading to a positive relationship between these texture fractions and K-40 (Fig. 2b). Note that only local data were used in this study; under different geopedological conditions, aberrating relationships between gamma spectrum and soil texture may occur.

## Conclusions

For the first time, the possible influence of mineral K fertilisation on mobile GS has been systematically investigated in a precisely conducted long-term field trial against the background of proximal soil sensing. After 75 years of differentiated fertilisation, the proportion of K-40 at total K contents was not significantly affected despite positive and negative long-term K balances in the different treatments. It can be concluded that no major influence of





**Fig. 2** Relationship between the K-40 content measured directly in the field by proximal gamma spectrometry and the percentage of (a) sand, (b) clay and clay + fine silt, respectively, in fine earth in 55 plots without and with long-term (since 1941) K fertilisation of the Rengen Grassland Experiment

K fertilisation on the emerging technology of mobile proximal GS is to be considered. It is therefore not necessary to collect K fertilisation data prior to GS-based texture prediction.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s11119-023-10071-3>.

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## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

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