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Short Communication

Citric acid extraction—An underestimated method in forest nutrition?

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Abstract

Since recent studies reveal citric acid to be favorable for estimating plant-available P in soils, we investigated if it can also be used for assessing other nutrients. According to our results, it provides stronger correlations with the tree nutrition for Mg (beech, spruce), Ca+K (beech) and Fe (spruce) than the standard methods for determining exchangeable cations. Thus, when estimating plant-available P by citric acid-extraction, these cations should be additionally measured in ICP analysis.

Key words: European beech / exchangable cations / Norway spruce / plant-available nutrients

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1 Introduction

Citric acid extraction is considered as an applicable and cost-effective method for determining the plant-available P fraction in forest soils (*Manghabati* et al., 2018; *Fäth* et al., 2019). Since citric acid is, considering its solvent properties, quite similar to acidic humus solutions (*Schwarz* et al., 2015), it is obviously a suitable simulant for nutrient mobilization in the topsoil. So far, the estimation of plant-available nutrient cations (Ca, Mg, K, Fe, Mn) in Germany relies on one of two soil extraction methods for determining exchangeable cations by $BaCl_2$- or NH_4Cl-percolation, depending on the soil pH (*König* et al., 2005). Since the calibration of additional elements only implies a minor effort in chemical analysis, a determination of the above-mentioned nutrient elements in the citric acid extract would be a cost-effective supplement to the current standards.

2 Material and methods

In order to test the suitability of citric acid extraction for other nutrient elements, Bavarian spruce and beech sites of the second German National Forest Soil Inventory (NFSI II) were selected, representing a broad range of nutrient element availability by stratification according to six base saturation types (*Kölling* et al., 1996). We selected five NFSI II plots per type of base saturation with the highest ratio of spruce resp. beech. For the 60 plots, mineral soil samples from the depths 0–5 cm, 5–10 cm, 10–20 cm, 20–40 cm, and 40–80 cm were extracted with citric acid according to *König* et al. (2005). The element concentrations (Ca, Mg, K, Fe, Mn, P, S) were determined by atomic emission spectroscopy (ICP-AES; model Arcos, Spectro, Kleve). In analogy to *Fäth* et al. (2019), concentrations were converted into stocks (t ha^{-1}) and then aggregated per depth level down to 80 cm. Prior to regression analysis, aggregated stocks were examined for outliers per element and aggregation level using box plots. Referring to recent studies (*Manghabati* et al., 2018; *Fäth* et al., 2019), a logarithmic function was used to investigate the relationship between extracted nutrient stocks and foliar concentrations of spruce and beech. The same procedure was also done for the stocks of exchangeable cations (CEC) of the relevant nutrient elements already analyzed within the NFSI II. According to *Mellert* and *Göttlein* (2012), foliar nutrient concentrations serve as an important indicator for the nutritional status of trees.

3 Results and discussion

In many cases, citric acid-soluble nutrient stocks in the soil provided at least as good correlations with tree nutrition as exchangeable nutrient stocks determined with $NH_4Cl/BaCl_2$ (Tab. 1). This was particularly evident for beech, where citric acid soluble Ca-, Mg-, and K-stocks clearly delivered the best coefficients of determination. For spruce, neither $NH_4Cl/BaCl_2$- nor citric acid-extraction resulted in significant correlations with foliar K-concentrations, whereas for Ca and Mg all correlations were highly significant. In the case of Mn, the existing NH_4Cl-/$BaCl_2$-method was a clearly better predictor for tree nutrition, especially for spruce. For Fe, however, once the CEC-method (beech) and once citric acid (spruce) was the best predictor. Citric acid did not appear to be a suitable method for the determination of plant-available S in the soil (no significant correlations), whereas this method delivers, as we expected, suitable results for P (*Manghabati* et al., 2018; *Fäth* et al., 2019). When comparing the R^2 for spruce and beech, the large differences, particularly in case of K and Fe, might reveal tree species specific nutrient uptake strategies.

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Table 1: Coefficients of determination (R^2) and significance levels for the logarithmic relationship between the citric acid-soluble (Index "cit"), as well as the exchangeable (determined by NH_4Cl-/$BaCl_2$-percolation; Index "CEC") nutrient stocks in the soil and the respective foliar nutrient concentrations of spruce and beech.[a]

Spruce	Ca_{CEC}	Ca_{cit}	Mg_{CEC}	Mg_{cit}	K_{CEC}	K_{cit}	Fe_{CEC}	Fe_{cit}	Mn_{CEC}	Mn_{cit}	P_{cit}	S_{cit}
0–5 cm	__0.40***__	__0.42***__	__0.39***__	__0.47***__	0.11	0.05	0.11	0.16*	__0.39***__	0.02	__0.36***__	0.00
0–10 cm	__0.42***__	__0.42***__	__0.38***__	__0.45***__	0.08	0.08	0.12	_0.22**_	__0.39***__	0.05	_0.31**_	0.02
0–20 cm	0.46***	0.45***	0.39***	0.47***	0.04	0.07	0.01	_0.25**_	__0.50***__	0.08	_0.28**_	0.01
0–40 cm	__0.54***__	__0.51***__	__0.38***__	__0.48***__	0.01	0.05	0.01	_0.24**_	__0.50***__	0.08	0.18*	0.01
0–80 cm	__0.57***__	__0.50***__	_0.30**_	__0.41***__	0.00	0.03	0.02	0.23*	_0.48**_	0.06	0.07	0.04
Beech	Ca_{CEC}	Ca_{cit}	Mg_{CEC}	Mg_{cit}	K_{CEC}	K_{cit}	Fe_{CEC}	Fe_{cit}	Mn_{CEC}	Mn_{cit}	P_{cit}	S_{cit}
0–5 cm	__0.66***__	__0.75***__	__0.54***__	__0.65***__	_0.26**_	__0.38***__	0.19*	0.06	_0.29**_	0.03	__0.57***__	0.00
0–10 cm	__0.68***__	__0.73***__	__0.58***__	__0.64***__	0.21*	__0.40***__	_0.30**_	0.18*	0.20*	0.01	__0.52***__	0.04
0–20 cm	__0.68***__	__0.70***__	__0.53***__	__0.61***__	0.18*	__0.50***__	0.27*	0.22*	0.14	0.00	__0.38***__	0.04
0–40 cm	__0.65***__	__0.63***__	__0.50***__	__0.55***__	0.11	__0.44***__	0.31*	0.14*	0.18	0.00	_0.27**_	0.00
0–80 cm	__0.71***__	__0.59***__	__0.45***__	__0.59***__	0.16*	0.23*	0.30*	0.08	0.23*	0.01	0.21*	0.00

[a] *$p < 0.05$; _**$p < 0.01$_; __***$p < 0.001$__; best R^2 of each element and tree species is underlined, when significant.

A comparison of the citric acid-extractable P concentrations of this study (determined in the laboratories of TUM) with the results measured in a former P-study in the laboratories of LWF (*Fäth* et al., 2019) revealed a very good relationship between the two datasets ($R^2 = 0.95$) and a high accordance among the absolute values (regression line almost corresponded to the 1:1 line). These results reveal this simple and economic method to provide a high inter-laboratory reproducibility, which is of great importance for big forest soil inventories.

For soil samples with pH_{KCl} below 4.5, citric acid extracts had a relatively constant pH of about 2.5 (Fig. 1). In the case of samples with pH_{KCl} between 4.5 and 8.0, citric acid was partly buffered by the soil, but did not, except some outliers, entirely lose its acidic properties. Consequently, a previous pH stratification, as done for determining CEC, seems not to be necessary. This is underlined by the fact that nearly all outliers are samples from the depth levels 40–80 cm with a very high carbonate content (up to 10%). As best correlations with tree nutrition mostly appear in the topsoil, which is in line with *Fäth* et al. (2019), the inhibition of citric acid by samples of high carbonate content is of minor importance for the estimation of plant-available nutrients.

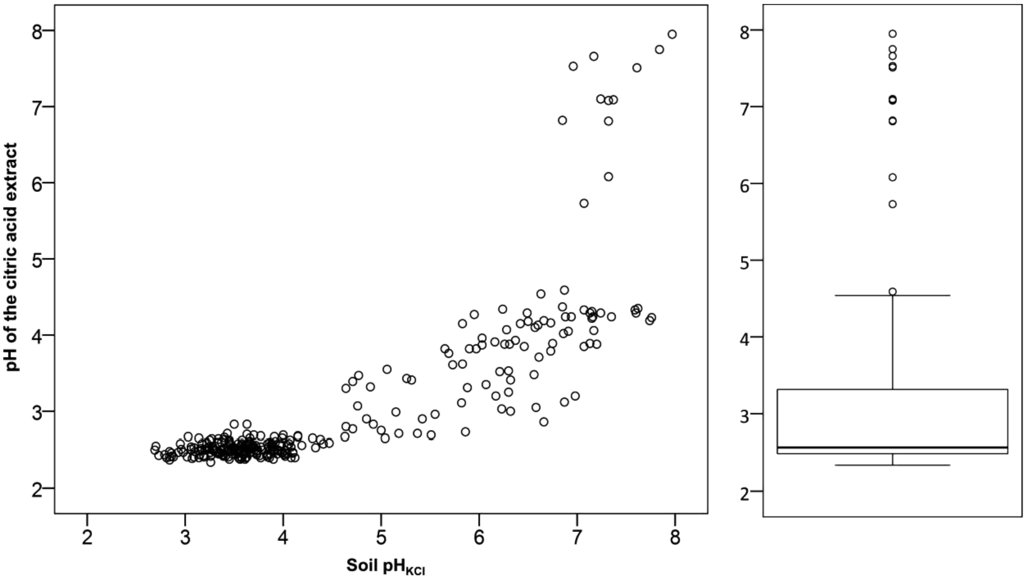

Figure 1: Comparison of the soil pH in KCl and the pH of citric acid after extraction.

4 Conclusions

Our results suggest that in addition to P the nutrients Ca, Mg, K, and Fe should also be measured in the citric acid extracts. Since it is a quite simple method not requiring previous soil pH stratification or elaborate percolation procedures, it would be a suitable standard method for future forest soil inventories. Furthermore, for this soil extract a sampling down to 80 cm is not necessary, since its potential to predict plant-available nutrients, especially in the case of P, is highest in the upper part of the soil (down to 40 cm). With an extensive data set, critical soil values for citric acid-soluble stocks may be derived (analogous to P; *Fäth* et al., 2019) for the elements Ca, Mg, and K to predict local deficiency risks in tree nutrition management.

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