Assessing Nutrient Dynamics in Hydrochar-Amended Soil with Radiogenic ^{87}Sr / ^{86}Sr Isotope Ratios

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Introduction

Hydrochar (HC) amendments can enhance soil health, promote microbial abundance and activity, and support plant productivity. Among their various properties, hydrochars also retain nutrient elements from the original biomass feedstock offering plants an alternative nutrient source.

In this study, we employed radiogenic strontium isotope ratios (^{87}Sr/^{86}Sr) as a geochemical proxy for calcium (Ca)[1-2] to trace nutrient sources in a pot experiment with sunflower cultivation, conducted in the greenhouse facilities of IG-CSIC in Seville. Sr isotopes are particularly advantageous as they are not fractionated during plant uptake or translocation, making them robust tracers for assessing source contributions within the soil–plant continuum.[3-5]
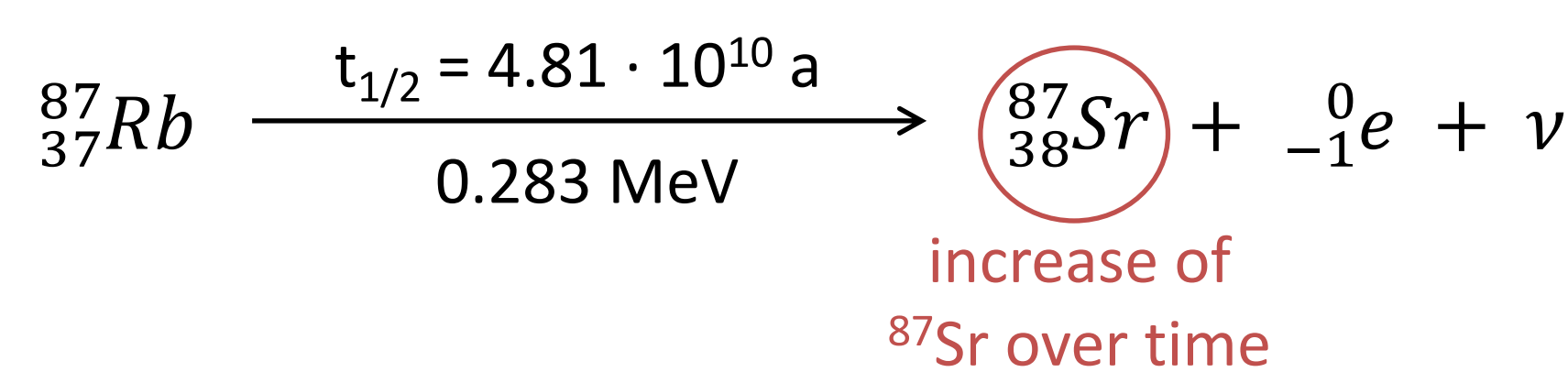
Additionally, we compared two different methods to extract the plant-available Sr-pool.

The radiogenic Sr-isotope system

Four stable Sr-isotopes

^{84}Sr 0.56 %
^{86}Sr 9.86 %
^{87}Sr 7.00 %
^{88}Sr 82.58 %

Radioactive decay of ^{87}Rb

$$^{87}_{37}Rb \xrightarrow[\text{0.283 MeV}]{t_{1/2} = 4.81 \cdot 10^{10}\, a} {}^{87}_{38}Sr + {}^{0}_{-1}e + \nu$$

increase of ^{87}Sr over time

Provenance proxy

⇒ ^{87}Sr/^{86}Sr ratio of primary minerals only depends on its original ratios of ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr, and its geological age

⇒ inorganic and organic matter carries the ^{87}Sr/^{86}Sr ratio of its source

Conclusions

- Contribution of the tested hydrochar as a significant Sr (and by extension Ca) source for short-term plant uptake appears negligible under the tested conditions
- Effective source tracking requires:
  (i) the isotopic Sr ratios of the relevant pools must differ substantially
  (ii) potential contributions to the nutrient pool should exceed 10%
- Method comparison for plant-available fraction revealed that both methods result in identical or near identical results. The quicker method 1 is hence recommended.
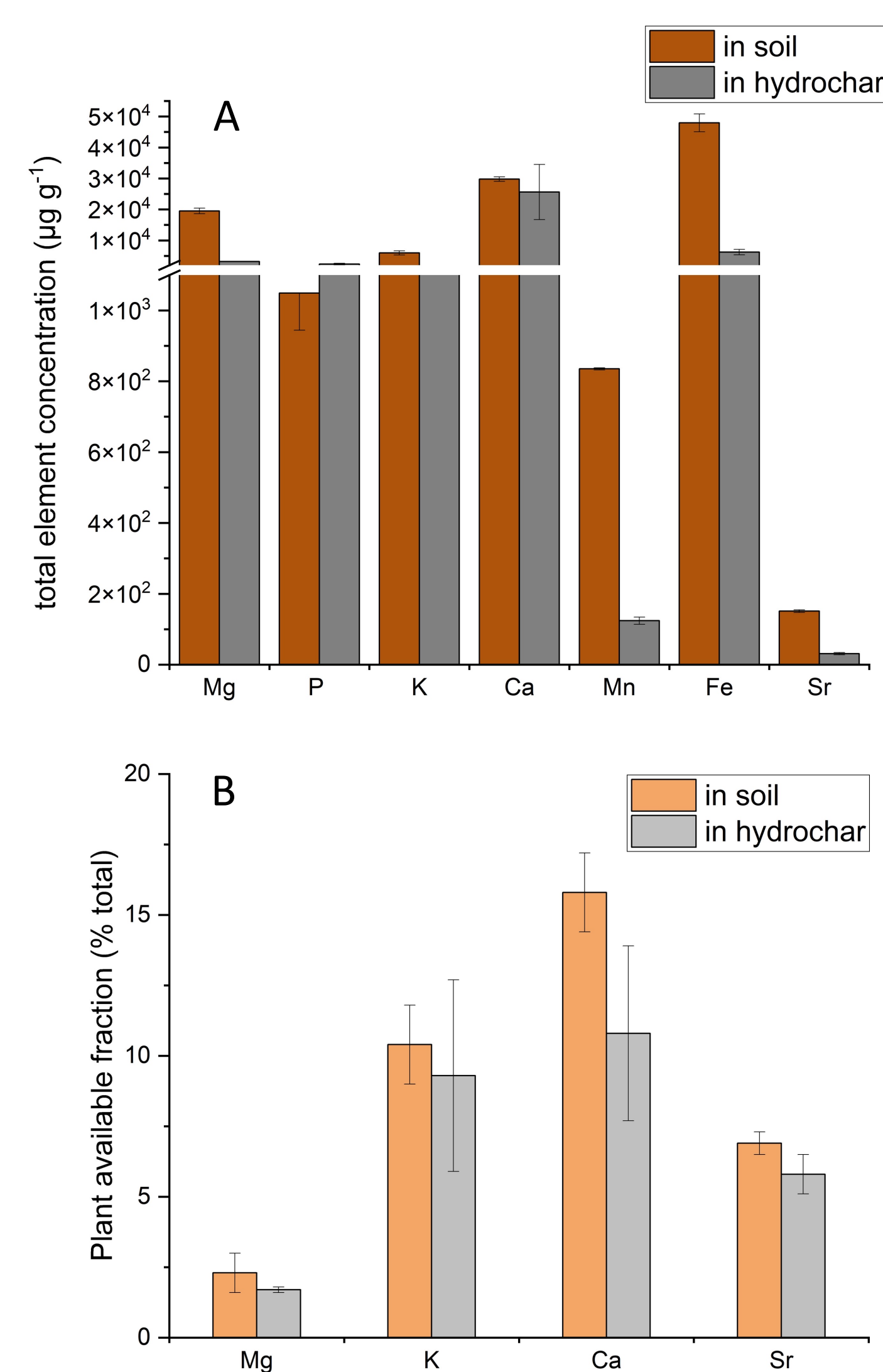
Results

Figure 1: A) Total element concentration in full digests of soil and hydrochar; B) plant-available fraction in soil and hydrochar (method 1).
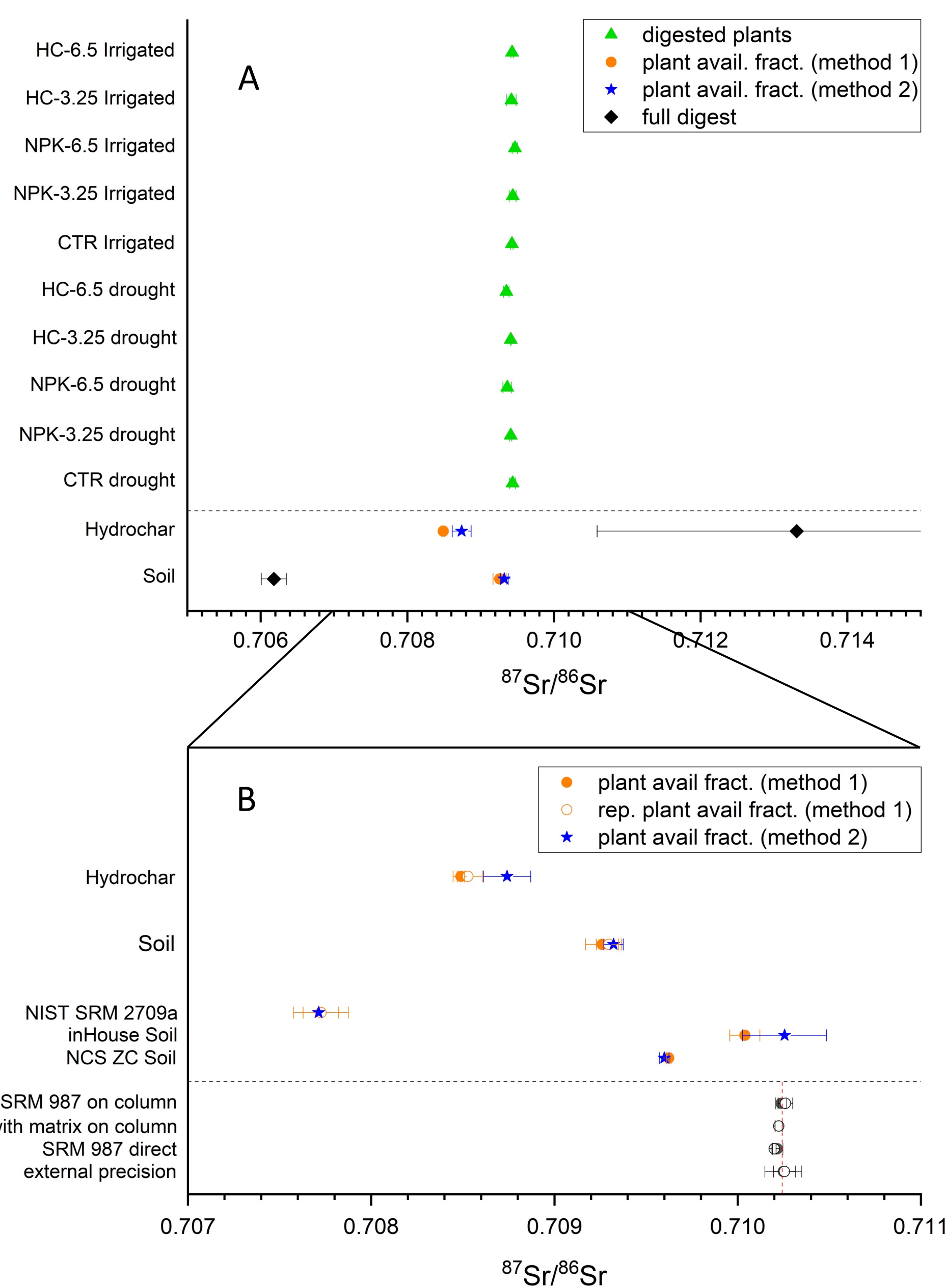

Figure 2: A) ^{87}Sr/^{86}Sr ratios in plant leaves, soil and hydrochar; B) ^{87}Sr/^{86}Sr ratios in plant-available fractions obtained from two different extraction methods. Error bars represent two standard deviations of the mean.

- substantial differences in Sr-isotope ratios of the total Sr pools between source materials:
  0.70618 ± 0.00006 in soil
  0.71331 ± 0.00096 in hydrochar
- Sr-isotope ratios of the plant-available (PA) Sr pools were more closely aligned:
  0.70926 ± 0.00003 in soil
  0.70849 ± 0.00001 in hydrochar

Note: in hydrochar the PA fraction contains much less radiogenic Sr than the total pool, while in soil the PA fraction is shifted towards more radiogenic Sr (possibly due to differences in speciation).

- All ^{87}Sr/^{86}Sr ratios in plant leaves (range: 0.70935 - 0.70947) were indifferent from those in control treatments, regardless of fertilization or irrigation regime.

Comparison of extraction methods for plant available alkali and earth alkaline elements:

- for the tested soils the additional ultrasonication step has no significant influence
- Method 2 extracted slightly more radiogenic Sr from the tested hydrochar

Materials & Methods

Pot experiment

variant	hydrochar	NKP	WHC
HC-6.5 irrigated	6.5 t/ha	–	60 %
HC-3.25 irrigated	3.5 t/ha	–	60 %
NPK-6.5 irrigated	–	TN = „6.5 HC"	60 %
NPK-3.5 irrigated	–	TN = „3.5 HC"	60 %
CTR irrigated	–	–	60 %
HC-6.5 drought	6.5 t/ha	–	30 %
HC-3.25 drought	3.5 t/ha	–	30 %
NPK-6.5 drought	–	TN = „6.5 HC"	30 %
NPK-3.5 drought	–	TN = „3.5 HC"	30 %
CTR drought	–	–	30 %

Plant available fraction

Method 1 (shaking)
- 500 mg of dried soil were gently shaken in 5 mL of 1M NH$_4$OAc for 2h in an end-over-end shaker
- The suspension was centrifuged at 8000*g for 5 min and the supernatant filtered through 0.45 µm
- The supernatant was dried down in teflon vials and then digested in aqua regia, etc.
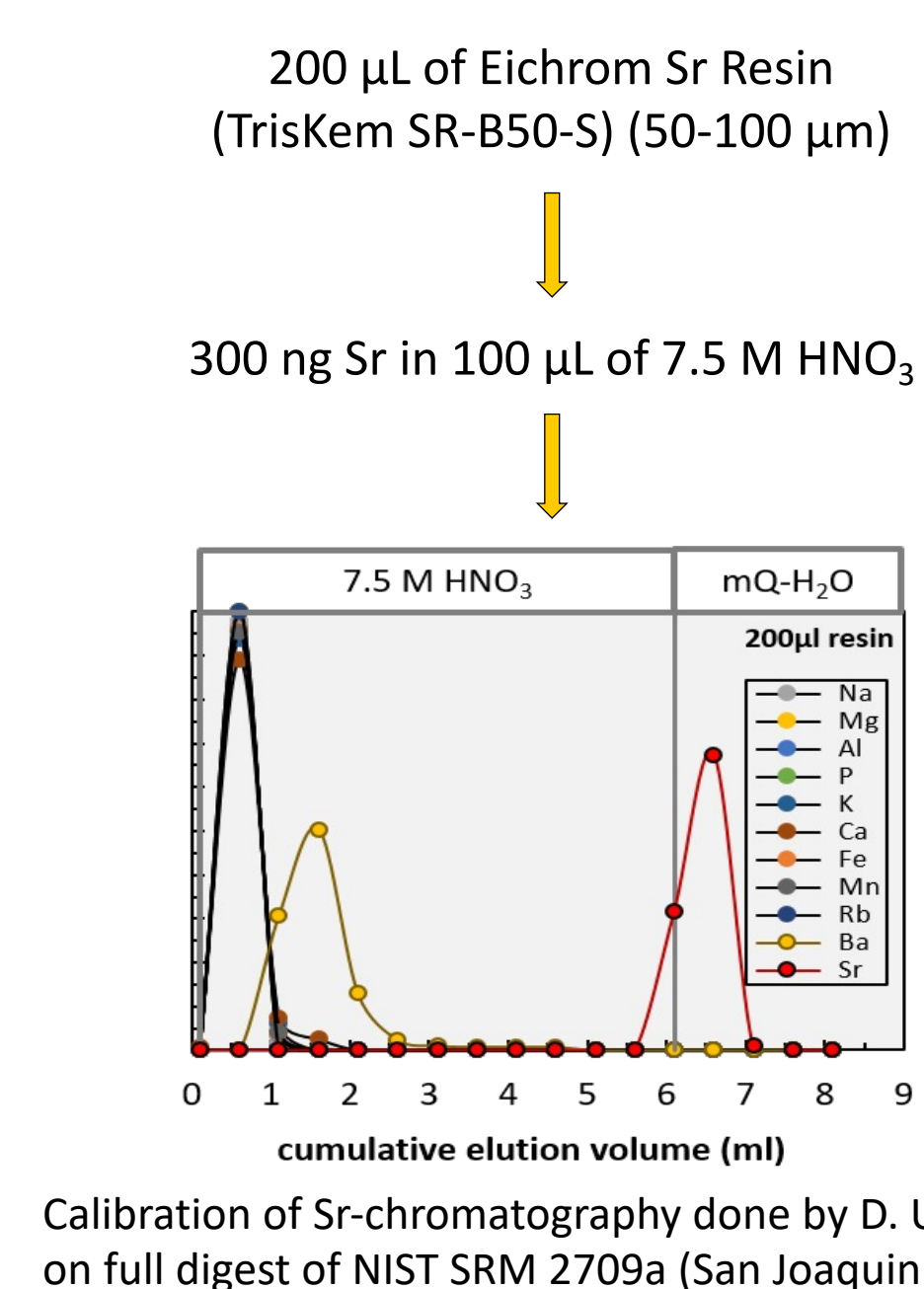
Method 2 (ultrasonication + shaking)
- 500 mg of dried soil were suspended in 5 mL of 1M NH$_4$OAc, subjected to ultrasonication for 1h (0.045 J g^{-1} s^{-1}) and followed by 2h of gentle shaking in an end-over-end shaker
- The suspension was then treated as described under method 1

Sample digestion

Soil and plant samples (full digests)
- 50 mg (dried, sieved soil) or 500 mg (dried, milled plants) digested in 2.5 mL conc. HNO$_3$ + 1.5 mL H$_2$O$_2$ (30%) in MLS turboWAVE (230°C, 40 bar)
- After dry-down, digestion with 3 mL HNO$_3$ conc. + 1 mL HF (40%) in closed teflon vials (48h @ 110°C)
- After dry-down, digestion with 3 mL HCl conc. + 1 mL HNO$_3$ conc. (aqua regia) (4h @ 110°C)
- After dry-down, heated in 3mL H$_2$O + 1 mL HNO$_3$ conc. for 2h @ 120°C (aliquots to determine Sr-conc.)
- After dry-down, samples diluted to 3 ppm Sr in 7.5M HNO$_3$

Sr isotope clean-up in class 5 clean room

200 µL of Eichrom Sr Resin (TrisKem SR-B50-S) (50-100 µm)

⬇

300 ng Sr in 100 µL of 7.5 M HNO$_3$

⬇

Calibration of Sr-chromatography done by D. Uhlig on full digest of NIST SRM 2709a (San Joaquin soil)[5]

Sr isotope ratio determination

- After dry-down of Sr-cuts and ICP-OES for Sr-concentration, sample (and standard) solutions of 50 ppb Sr in 0.3 M HNO$_3$ were prepared
- Ratios were determined on a Nu Plasma II MC-ICP-MS coupled to an Aridus desolvator for sample introduction
- Analyses were carried out in low resolution mode with 80 % transmission
- masses 82, 83 and 85 measured together with Sr masses (84, 86, 87, 88) to correct for Kr and Rb interferences
- correction for natural and instrumental mass-dependent isotope fractionation done by normalizing ^{87}Sr/^{86}Sr ratio to ^{86}Sr/^{88}Sr ratio of 0.1194[6] using an exponential law

References: [1] Capo RC, Stewart BW, Chadwick OA (1998) Geoderma 82:197–225. [2] Bélanger N, Holmden C (2010) Can J Soil Sci 90:267–288. [3] Aguzzoni A, Bassi M, Robatscher P, Scandellari F, et al. (2019) J Agric Food Chem 67:5728–5735. [4] Uhlig D, Amelung W, von Blanckenburg F (2020) Global Biogeochem Cycles 34: e2019GB006513. [5] Uhlig D, Berns AE, Wu B, Amelung W (2023) Plant Soil 489:613–628. [6] Steiger, RH, Jager, E (1977) Earth Planet Sci Letters 36: 359-362.