Commentary: Strontium Is Released Rapidly From Agricultural Lime–Implications for Provenance and Migration Studies

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A Commentary on

Strontium Is Released Rapidly From Agricultural Lime–Implications for Provenance and Migration Studies
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INTRODUCTION

There is an ongoing debate about the potential effect of agricultural lime-sourced strontium (Sr) on surface waters. Strontium isotope signatures of surface waters are being used as one of several proxies to characterize the average bioavailable strontium isotope range (baseline/isoscape) of a specific geographical area. In their article, Andreasen and Thomsen (2021) conclude, based on the study of several soil profiles from a test area in Denmark which received different levels of agricultural liming during the past ∼100 years, that "…Sr is as highly mobile as Ca is, and little is retained in organic-rich topsoils, such that Sr seeps into the underlying groundwater and nearby surface waters" and so contaminates the natural Sr isotope signature of the vadose zone. Their study is a follow up of an earlier study (Thomsen and Andreasen, 2019) in which these authors strongly criticize the use of water-based reference baselines for provenance studies of ancient humans, and go as far as to postulate "…significant overestimation of the degree of pre-historic mobility in an area, as it has in Denmark, where the overall mobility during pre-historic times was likely significantly lower than recently proposed (Frei et al., 2019)."

As outlined below, these and other conclusions are not supported by their data, as they are based on inappropriate mass balance calculations.

A central methodological detail will help the reader understand the below outlined reasoning for this. Andreasen and Thomsen (2021) applied two different procedures to the soils they studied. (1) Acetic acid leaching which releases Sr that is still contained in left over (not yet dissolved) agricultural lime. (2) Ammonium nitrate leaching, which releases exchangeable Sr adsorbed to mineral surfaces and organic matter. The sum of Sr released by both extractions should then be balanced against the total amount of Sr added by agricultural liming.

The crucial mistake lies in the fact that Andreasen and Thomsen (2021) did not balance Sr in their profiles against the amounts of Sr that were actually added over the c. 100 years to the respective soils. The massive loss of 80–100% of Sr they postulate is lost to the vadose zone is solely based on the comparison of acetic acid leachable Sr fractions in 2014 and 2019 (profile C), but does not take into consideration the large amounts of Sr from decades of liming still contained in the organic-rich soils as reflected by the ammonium

TABLE 1 | Strontium retention percentage values in 4 different profiles studied by Andreasen and Thomsen (2021).

Parameters	Quadrant B Extremely over-limed	Quadrant C Extremely over-limed	2019	2014	Quadrant A Normally limed	Farmland F Normally limed
Lime rate in 2012/2013 (2012–2019 for Farmland F); lime [Sr; ppm]; frequency*	36t/ha; 800; once	48t/ha; 800; once				2t/ha; 800; every 4 years
Lime rate in 2012/2013 (2012-2019 for Farmland F); lime [Sr; ppm]; frequency*	36t/ha; 1,000; once	48t/ha; 1,000; once				2t/ha; 1,000; every 4 years
Lime rate in 2012/2013 (2012–2019 for Farmland F); lime [Sr; ppm]; frequency**	36t/ha; 600; once	48t/ha; 600; once				2t/ha; 600; every 4 years
Total Sr added (μg/ha); 800 ppm Sr in lime [+]	2.88E+10		3.84E+10	3.84E+10		3.20E+09
Total Sr added (μg/ha); 1,000 ppm Sr in lime [+]	3.60E+10		4.80E+10	4.80E+10		4.00E+09
Total Sr added (μg/ha); 600 ppm Sr in lime [+]	1.80E+10		2.88E+10	2.88E+10		2.40E+09
Lime rate 1923–2011; [Sr; ppm] in lime; frequency*	2t/ha; 800; every 4 years	2t/ha; 800; every 4 years		2t/ha; 800; every 4 years		2t/ha; 800; every 4 years
Lime rate 1923–2011; [Sr; ppm] in lime; frequency*	2t/ha; 1,000; every 4 years	2t/ha; 1,000; every 4 years		2t/ha; 1,000; every 4 years		2t/ha; 1,000; every 4 years
Lime rate 1923–2011; [Sr; ppm] in lime; frequency**	2t/ha; 600; every 4 years	2t/ha; 600; every 4 years		2t/ha; 600; every 4 years		2t/ha; 600; every 4 years
Total Sr added (μg/ha); 800 ppm Sr lime[++]	3.52E+10		3.52E+10	3.52E+10	3.52E+10	3.52E+10
Total Sr added (μg/ha); 1,000 ppm Sr lime[++]	4.40E+10		4.40E+10	4.40E+10	4.40E+10	4.40E+10
Total Sr added (μg/ha); 600 ppm Sr lime[++]	2.64E+10		2.64E+10	2.64E+10	2.64E+10	2.64E+10
Reference soil volume (m^3) of topmost 50 cm	5.0E+03		5.0E+03	5.0E+03	5.0E+03	5.0E+03
Reference soil weight (g); using soil density of 1.6 t/m^3	8.0E+09		8.0E+09	8.0E+09	8.0E+09	8.0E+09
Calculated [Sr; ppm] in soil; 800 ppm lime[#]	8.0		9.2	9.2	4.4	4.8
Calculated [Sr; ppm] in soil; 1,000 ppm lime[#]	10.0		11.5	11.5	5.5	6.0
Calculated [Sr; ppm] in soil; 600 ppm lime[#]	6.0		6.9	6.9	3.3	3.6
Average [Sr; ppm] measured; NH_4NO_3 [^]	5.5		4.3	4.0	2.8	2.6
SrR% in soil; 800 ppm lime; NH_4NO_3 extract	68		47	43	63	53
SrR% in soil; 1,000 ppm lime; NH_4NO_3 extract	55		37	35	50	43
SrR% in soil; 600 ppm lime; NH_4NO_3 extract	91		62	58	84	71
Average [Sr; ppm] measured; HAc[^]	6.1		2.0	6.6[¤]	1.1	1.2
SrR% in soil; 800 ppm lime; HAc extract	76		22	72	24	25
SrR% in soil; 1,000 ppm lime; HAc extract	61		18	57	19	20
SrR% in soil; 600 ppm lime, HAc extract	101		30	96	32	33
Average [Sr; ppm] measured; NH_4NO_3 + HAc	11.6		6.3	10.6	3.8	3.7

(Continued)

TABLE 1 | Continued

Parameters	Quadrant B Extremely over-limed	Quadrant C Extremely over-limed	2019	2014	Quadrant A Normally limed	Farmland F Normally limed
Combined SrR% in soil; 800 ppm lime[†]	144		69	115	87	78
Combined SrR% in soil; 1,000 ppm lime[†]	116		55	92	69	62
Combined SrR% in soil; 600 ppm lime[†]	**192**		**92**	**154**	**116**	**104**

[*]800–1,000 ppm Sr in lime (Chalk, "Dania," U. Maastrichtian), reported by Thomsen and Andreasen (2019) and used in the mass budget calculations of Andreasen and Thomsen (2021); liming rates reported by Andreasen and Thomsen (2021).

[**]600 ppm Sr used here in addition as the most realistic lime Sr concentration, based on Mg/Ca = 0.042 ± 0.015 (2σ, n = 4) in top 50 cm of profile C (2014; Frei et al., 2020), to account for a dolomitic component in the lime (2.5% Mg-Chalk, "Dankalk Aggersund," Thomsen and Andreasen, 2019).

[+]Total amount of Sr added via agricultural lime in 2012/2013 (during period 2012–2019 for Farmland F).

[++]Total amount of Sr added via agricultural lime during period 1923–2011.

[¤]Assuming 33 ppm of Sr measured by Frei et al. (2020) in the HAc fraction of the 5–15 cm soil interval of untilled quadrant C in 2014, distributed over the 50 cm thick reference soil layer.

[#]Calculated from the total amounts of Sr added via agricultural lime, using respective liming rates, and expressed relative to weight of reference soil volume of 5,000 m^3 assuming a soil density of 1.6 t/m^3.

[^]Calculated as the sum of Sr amounts in individual layers from within the top 50 cm reference soil layer with Sr concentrations and layer thicknesses specified in Table 1 of Andreasen and Thomsen (2021) and in Table S1 of Frei et al. (2020), relative to the weight of the latter.

[†]Combined SrR% values calculated as the sum of SrR% values from NH$_4$NO$_3$ and HAc extracts. A realistic scenario, supported by Mg/Ca = 0.042 ± 0.015 (2σ, n = 4) in top 50 cm of profile C (2014; Frei et al., 2020) is highlighted in red bold letters.

SrR%, Strontium retention percentage; NH$_4$NO$_3$, Ammonium nitrate; HAc, Acetic acid; Sr; ppm, Strontium concentration in ppm.

The average concentration of ~0.1 ppm for Sr in a pristine heathland soil is estimated from the data reported by Andreasen and Thomsen (2021) for individual layers from the top 50 cm of profile N (top 5 cm mor layer excluded). This low concentration has only insignificant effects on the above mass budget calculations.

nitrate leachates. Consequently, their mass balance for profile C is erroneous.

MASS BALANCE CALCULATIONS

Calculations in **Table 1** are based on the soil profile data published by Andreasen and Thomsen (2021) and complemented by data presented in a previous study (Frei et al., 2020) on profile C in the test area representing the situation in 2014. Of the 3 profiles studied from the test area, quadrants B and C received extreme (and hence unrealistic) amounts of agricultural lime in 2012/2013 corresponding to an equivalent of 36 and 48x times, respectively, the amount conventionally added every fourth year (2t/ha) to this farmland. In contrast, profiles A and F represent realistically limed farmland sites which received an average liming rate of 2t/ha every 4th year during the past ~100 years. Elevated exchangeable Mg^{2+} (in the top 50 cm) point to a dolomitic component in the added lime. For this reason, besides using 800 and 1,000 ppm Sr for the lime, a mass budget calculation with the more realistic Sr concentration of 600 ppm typical of a Mg chalk (as measured by Thomsen and Andreasen, 2019) is used. Mass budget values are expressed as strontium retention percentages (SrR%) reflecting the percentages of Sr still present in the top 50 cm of profiles in 2019, relative to the total amount of Sr added during the last ~100 years by agricultural lime (including the massive additions in 2012/2013 to quadrants B and C).

DISCUSSION

Table 1 lists SrR% values calculated on the basis of the sum of Sr released by ammonium nitrate and acetic acid. These clearly imply, unlike postulated by Andreasen and Thomsen (2021), an effective retention of Sr derived from lime added during the last ~100 years in the topmost 50 cm of the studied profiles, even in quadrants that were loaded with extreme amounts of lime. Importantly, SrR% values (using Mg chalk) for realistically limed farmlands represented by profile A and F point to complete retention of Sr.

Tilling of quadrant C, in contrast to no tilling of quadrant B, has led to a faster dissolution of the extreme lime load added in 2012/2013. The somewhat reduced SrR% of this quadrant, compared to the others, likely reflects an oversaturation of lime in the soil and a related saturation of the adsorption capacity of the organic matter due to extreme liming. In this respect, profile C, and likewise profile B with a similarly extreme over-liming, are not representative of common farmland agricultural liming practice.

CONCLUSION

Mass balances show that most of the Sr added over the past ~100 years to the test field quadrants by agricultural lime is still today retained in the topmost 50 cm of the soils. As already concluded in Frei et al. (2020) and shown by Boyer et al. (2018), Sr is effectively and almost irreversibly adsorbed onto organic material in the soils which efficiently prevents loss of Sr into the vadose zone. The adsorptive capacity of organic material for Sr is depicted by the high NH$_4$NO$_3$-based SrR% values for 2019 (**Table 1**). Hence, the conclusion by Andreasen and Thomsen (2021) postulating that Sr is rapidly released from lime into surface waters is not shown by their data. The even more far reaching conclusions that "isoscapes … from surface waters…like Frei

and Frei's (2011) isoscape of Denmark are inappropriate for use in provenance and mobility studies of prehistoric people" are unsupported and up front wrong. Unfortunately these misleading conclusions have caused a great deal of confusion amongst those involved in the construction of meaningful reference baselines, and particularly amongst archaeologists who see themselves thorn between very different interpretations

regarding the origin of some of the iconic prehistoric humans from Denmark.

AUTHOR CONTRIBUTIONS

RF has made mass balance calculations and wrote the commentary.

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