

The effects of culinary processing on lithium from lithiated and reference button mushrooms (*Agaricus bisporus*)



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ABSTRACT

Lithiated products such as button mushrooms that are cultivated in substrates fortified with lithium (Li) salts, have the potential to provide accessible and safe Li dosing as a treatment for some neurological disorders. However, Li losses sustained during culinary processing are not known. This study of commonly used culinary treatments including various combinations of drying, maceration, blanching (of fresh, deep-frozen and re-hydrated mushrooms) and pickling (of fresh and deep-frozen mushrooms) shows that Li is lost from the edible flesh at varying rates depending on the treatment. Blanching of fresh lithiated mushrooms resulted in a 40% loss, increasing to 77–87% when blanching was followed by pickling. Corresponding losses were similar (47–72%) for non-lithiated mushrooms. Higher losses through the combined treatment relative to just blanching appear to be due to chelating and acidifying effects of the vinegar used. This finding has important dose implications for potential future use of lithiated products.

1. Introduction

Lithium (Li) is used in psychiatric medicine to cure some mental disorders. There is ongoing debate about the complexity of this treatment and its side effects in some patients and Tondo et al. (2019) have recently reviewed research on the use of Li to treat mental disorders, with a view to provide guidance for patients and medical practitioners. They concluded that it remained as the standard and most extensively evaluated treatment for bipolar disorder. As a preventive treatment there is continuing discussion on the possible role of supplementary Li in drinking water supplies as a moderating influence in depression and for the prevention of suicides (Eyre-Watt et al., 2021; Gillman, 2022; Ng & Eya, 2019; Vita et al., 2015).

As far as is currently known, Li is not considered as an essential element for human nutrition (EFSA, 2009; Kowalczyk et al., 2022). Its natural occurrence in foods is typically very low. For example, rounded values reported for foods from the Emilia-Romagna Region in Northern Italy (Filippini et al., 2020) ranged from 0.00095 to 0.065 mg kg⁻¹ in many vegetables, 0.00060–0.32 mg kg⁻¹ in cereals and cereal products, 0.0010–0.550 mg kg⁻¹ in dry fruits, nuts and seeds, 0.0012–0.011 mg kg⁻¹ in milk and dairy products, 0.00040–0.013 mg kg⁻¹ in beverages, 0.0010–0.011 mg kg⁻¹ dw in meat and meat products, to 0.0034–0.059 mg kg⁻¹ in fish and seafood. Another recent study reported a concentration of 0.060 ± 0.080 mg kg⁻¹ dry weight (dw) in

fish muscle (Thibon et al., 2021). As far as edible fungi go, Li concentrations very rarely exceeded 1.0 mg kg⁻¹ dw (around 0.10 mg kg⁻¹ fresh weight) in popular mushroom species in the Yunnan region of China and typical levels were below 0.30 mg kg⁻¹ dw (Falandysz et al., 2017; Pankavec et al., 2021b; Zhang et al., 2020). Whole *Boletus edulis* mushrooms from Poland showed a median Li concentration of 0.075 mg kg⁻¹ dw (Falandysz et al., 2022). Reported daily dietary intakes of Li showed correspondingly low values, i.e. 0.01815 mg for individuals in the Emilia-Romagna Region in Northern Italy and 0.0285 mg for adults in France (Filippini et al., 2020; Leblanc et al., 2005).

Chemically, Li has some unique physicochemical features and consequently its use in high-tech industry and in consumer products such as Li batteries (Goonan, 2012), has seen an increasing trend in recent years. The occurrence of Li in river and tap water in the metropolitan Seoul region (Choi et al., 2019) has been linked to the increasing commercial use of Li and density of habitation. However, like other monovalent elements, Li is mobile when in cationic form. It appears unlikely that field crops could be contaminated with Li because of the pollution arising from municipal sewage sludge or drainage water or from the resulting treatment of fields and forest soils.

When raised on a substrate (soil, compost) that is fortified with Li salts, mushrooms can bioconcentrate the element in edible parts at levels that far exceed the concentrations that are usually found in wild or cultivable species that are sold commercially (Falandysz et al., 2022a;

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Table 1
Moisture content (%) of fresh (raw) and processed white *A. bisporus* – data cited or adapted from the literature.

| State and treatment | Moisture (%) | | | | | |
|--|--------------|------------|-------------------------|--|--|--------------------------------------|
| Fresh (raw) | 91.3 | 91.4 ± 0.0 | 92.8 ± 0.4 | 90.8 ± 0.3 ^C / 90.0 ± 0.3 ^S | 92.8 (92.8 ^S) | 92.4 ^C /90.8 ^S |
| Fresh → blanched with water | | | | | | 92.08 |
| Fresh → blanched with sodium metabisulfite ^{BA} | | 82.2 ± 0.1 | | | | |
| Fresh → blanched → braised 10 min. ^{BB} | | 76.3 ± 0.2 | | | | |
| Fresh → blanched → pickled with vinegar | | | | | | 94.9 (94.6–95.2) |
| Deep frozen → blanched with water | | | | | | 92.3 (91.9–92.7) |
| Deep frozen → blanched → pickled | | | | | 69.1–75.8 (66.0–73.3 ^S) ^{BC} | 89.1 (86.7–91.3) |
| Fresh → grilled (for 10 min. without additives) | | | 90.7 ± 0.2 | | | |
| Deep-frozen → grilled (for 10 min.) | | | 94.8 ± 0.3 → 91.8 ± 0.4 | | | |
| Canned → grilled | | | 93.6 ± 0.4 → 91.5 ± 0.1 | | | |
| Reference | A | B | C | D | E | F |

References: A (Jaworska et al., 2008); B (Jaworska et al., 2015); C (Manzi et al. 2001); D (Nasiri et al., 2013); E (Singh et al., 2018); F (this study).

Notes: ^C(caps)

^S (stipes);

^{BA} (blanched in 0.2% sodium metabisulfite at 98 °C for 90 s; the ratio of mushrooms to the blanching solution was 1:5);

^{BB} (braised with a small amount (10%) of 100% rapeseed oil and NaCl (0.5%) for 10 min.);

^{BC} (pickled with natural or synthetic vinegar and spices and stored for a period from 0 to 6 months).

Lopes et al., 2022; Mleczeek et al., 2017). Thus, some lithiated species of cultivable mushrooms (or other vegetables that can be similarly lithiated) are a potential source of Li in the form of an acceptable, easily available product that could be used by individuals who require this supplement. A key consideration for these types of products is whether the achieved level of lithiation (through bio-enrichment/fortification) in these foods would be sufficient to meet the prescribed dosage level required for the pro-medicinal or therapeutic effect. The subsequent consideration if a suitable Li concentration is achieved in such a food, is whether necessary culinary treatments may potentially affect these levels and whether there were recommendations to preserve Li during processing. Further questions in considering this route of administering Li would be digestive tract accessibility and bioavailability from the lithiated edible product.

Dried mushrooms are relatively rich in minerals including a number of elements that are nutritionally essential for humans (K, Mg, P, Se, Zn, Cu) (Falandysz, 2008; Falandysz & Borovička, 2013). This remains true even when the concentrations are based on wet weight (~90% in fungus is moisture). Water is an important determinant of the texture of a fruitbody and its content is associated with efficient absorption and high retention of K due to its essential role in osmoregulation (Stijve, 1996). The moisture content of the white button mushroom, *A. bisporus*, when fresh, freshly-frozen or freshly-canned is 92.81 ± 0.40, 94.76 ± 0.34 and 93.63 ± 0.38%, and when grilled for 10 min (without additives) is 90.70 ± 0.21, 91.85 ± 0.41 and 91.54 ± 0.10%, respectively (Manzi et al., 2001). According to Vetter (2003) the moisture content of fresh *A. bisporus* is 90.51% (from 90.38 to 90.68%), and Nasiri et al. (2013) report 90.76 ± 0.34% in the caps and 90.01 ± 0.27% in the stipes. Jaworska et al. (2015) report the moisture content of fresh *A. bisporus* mushrooms as 91.42 ± 0.01%, reducing to 82.24 ± 0.15% when these were blanched, and reduced further to 76.28 ± 0.22%, when blanched and braised. According to Singh et al. (2018), the moisture content of fresh caps (with a minimal 1 cm stipe) was 92.85% (dry biomass 7.15%); but when blanched in salted water (2%) for 5 min at 85–90 °C and then pickled in natural or synthetic vinegar, reduced to a range from 69.09% to 75.26% (dry biomass from 24.24% to 30.91%) (Table 1). The corresponding content in the stipes (remaining part) was 92.85% (i.e. as in caps), reducing to a range of 66.03% to 77.33% (dry biomass from 26.66% to 38.18%) after being blanched and pickled. The percentages of dry matter for *A. bisporus* collated from older literature by Bernaś et al. were: 7.2, 7.2, 7.7, 8.6, 9.3, 8.2–9.5, 9.4–9.6 and 11.2% (Bernaś et al., 2006a, Bernaś et al., 2006b). Information on the moisture

and dry matter content of raw and processed *A. bisporus* collated from more recent literature and from the present study is summarised in more detail in Tables 1 and 2. The accurate moisture content of edible mushrooms is essential for expressing the intake rates of active constituents on a wet weight basis (whole food) as this allows more realistic nutritional or toxicological assessments (Manzi et al., 2004), while data expressed on a dry weight are useful for normalisation and comparability. The differences in reported moisture content between differently processed mushroom meals are therefore important when assessing the intake rates of mineral constituents (Falandysz et al., 2020a, 2020b).

Among monovalent elements that are present in edible mushrooms, the most important after K is usually rubidium (Rb) (Falandysz & Borovička, 2013). Rubidium occurs in the range from 300 to 320 mg kg⁻¹ dw in caps and from 66 to 120 mg kg⁻¹ dw in stipes of the birch bolete *Leccinum scabrum* (Mędyk et al., 2018). It is anticipated that Rb follows the absorption of K. Following K and Rb, the next abundant monovalent element in mushrooms is sodium (Na) (Falandysz & Borovička, 2013). Sodium tends to be found at greater concentration in the stipe than in the cap of mature fruiting bodies. A similar tendency is observed for Li in studied mushrooms - (*Amanita muscaria*) in Poland (Falandysz et al., 2007 and 2020c), and *Boletus speciosus*, *Boletus umbriniporus* and *Hemileccinum impolatum* in Yunnan, China (Zhang et al., 2020). The Na content in *L. scabrum* ranged from 230 to 270 mg kg⁻¹ dw in caps and from 480 to 710 mg kg⁻¹ dw in the stipes (Mędyk et al., 2018).

The lithium ion is biochemically similar to Na and in biological systems it seem to follow the Na transporters (Thibon et al., 2021). Caesium (stable isotope ¹³³Cs) is a minor element in mushrooms with few published data but there are considerably more reports of the contents of artificial, radioactive Cs (¹³⁴Cs and ¹³⁷Cs) (Falandysz et al., 2022b). Because of the similarity in some properties (monovalent elements but with a large range of ion radius and atomic size), the mechanism of Li, Na, K, Rb and Cs uptake appears to be similar but the distribution in fruiting bodies is different.

Processing methods (drying, blanching, boiling, parboiling, braising, stewing, canning, pickling, frying, roasting, grilling, baking, salting/souring, etc.) of mushrooms generally causes partial breakdown and disintegration of their structures, defragmentation of cell walls, and denaturation of proteins. These processes also break chemical bonds which results in the loss of some solutes including ions and colloids from cell plasma, as well as loss of solids and an easily observable shrinkage of the fruitbody. In the case of essential minerals, the value of a mush-

Table 2Dry matter content (%) of fresh (raw) and processed white *A. bisporus* – data cited or adapted from the literature.

| State and treatment | Dry matter (%) | | | | | | | |
|--|----------------|---------------------------|--------------------|------|--|---|---------------------------------------|--|
| Fresh (raw) | 8.71 ± 0.12 | 8.68 - 8.68 ^{BA} | 8.77 | 8.58 | 8.63 | | 7.2 (7.2 ^S) | 7.60 ^{C*} /9.17 ^{S*} |
| Fresh → blanched (water) | 8.35 ± 0.04 | 8.37 - 8.39 ^{BB} | | 17.8 | 8.39*/8.41 ^S /6.06 ^F | | | 7.92 |
| Fresh → blanched → pickled | | | | | | | | 5.10 ^{vinegar} |
| Raw (fresh, frozen and canned) | | | | | | | 7.19/5.24/6.24 | |
| Grilled (fresh, frozen and canned) ^S | | | | | | | 9.30/8.15/8.46 | |
| Fresh → deep-frozen → blanched → pickled | | | | | | | | |
| Fresh → blanched with an additive ^{BC} | | | | | 8.35/8.37 ^S /6.09 ^F | | | |
| Fresh → blanched with an additive ^{BD} | 8.01 ± 0.02 | 8.40 - 8.40 ^{BB} | | | | | | |
| Fresh → blanched → braised | | | | 23.7 | | | | |
| Fresh → soaked → blanched | 7.52 ± 0.07 | 7.65 - 7.67 ^{BB} | | | | | | |
| Fresh → soaked → blanched with an additive ^{BE} | 7.84 ± 0.10 | 7.93 - 7.96 ^{BB} | | | | | | |
| Fresh → soaked → blanched with an additive ^{BF} | | | | | 7.72*/7.72 ^S /5.66 ^F | | | |
| Fresh → soaked → blanched with an additive ^{BG} | | | | | 7.72*/7.72 ^S /5.68 ^F | | | |
| Fresh → blanched → pickled ^{BH} | | | | | | | 28.36 ^C /33.9 ^S | |
| Fresh → deep frozen → blanched (water) | | | 8.35 | | | | | |
| Fresh → deep frozen → blanched | | | 8.41 ^{BI} | | | | | |
| Fresh → deep frozen → blanched | 8.30 ± 0.03 | 8.39 - 8.39 ^{BB} | 8.37 ^{BJ} | | 8.37*/8.38 ^S /6.08 ^F | | | |
| Fresh → deep frozen → blanched | | | 8.02 ^{BK} | | | | | 7.7 ^{water} |
| Fresh → deep frozen → blanched | | | 7.68 ^{BL} | | | | | |
| Fresh → deep frozen → soaked → blanched | | | 7.56 ^{BM} | | | | | |
| Fresh → deep frozen → soaked → blanched | | | | | | | | 10.9 ^{vinegar} |
| Fresh → deep frozen → blanched → pickled | | | | | | | | |
| Dried → soaked | | | | | | | | |
| Reference | A | A | B | C | D | E | F | G |

References: A (Jaworska et al., 2008); B (Jaworska & Bernaś, 2013); C (Jaworska et al., 2015); D (Jaworska et al., 2003); E (Manzi et al. 2001); F (Singh et al., 2018); G (this study).

Notes: ^C(caps)^S (stipes); Fresh and then blanched*/Deep-frozen and then blanched^S/Canned and then blanched^F^{C*/S*} Fresh from an outlet – bought loose and transported in a plastic bag^S Grilled (without an additive) for 10 min.;^{BA} (stored for a period from 0 to 4 months);^{BB} (stored for a period from 0 to 8 months);^{BC} (blanched in 0.2% sodium metabisulfite at 98 °C for 90 s);^{BD} (blanched in a lactic acid (1.0%) and L-ascorbic acid (0.1%) water solution);^{BE} (soaked in water (1 h) and blanched in a lactic acid (1.0%) and L-ascorbic acid (0.1%) water solution);^{BF} (soaked in a solution of citric and L-ascorbic acids and then blanched in water);^{BG} (soaked in a solution of sodium metabisulphite and then blanched);^{BH} (with natural or synthetic vinegar and spices and stored from 0 to 6 months; blanched for 5 min at 85–90 °C and then pickled in natural vinegar and stored for 2 months);^{BI} (frozen for 12 months and then blanched in solution of sodium metabisulfite (0.2%) and citric acid (0.5%);^{BJ} (frozen for 12 months and then blanched in an aqueous solution of 0.5% citric acid and 0.1% L-ascorbic acid);^{BK} (frozen for 12 months and then blanched in an aqueous solution of citric acid (0.5%), L-ascorbic acid (0.1%), and low methoxyl pectin (0.5%));^{BL} (frozen for 12 months and further soaked in water (1 h) and blanched in an aqueous solution of 0.5% citric acid and 0.1% L-ascorbic acid);^{BM} (frozen for 12 months and then blanched in an aqueous solution of citric acid (0.5%), L-ascorbic acid (0.1%), and low methoxyl pectin (0.5%)).

room meal depends on the identity and extent to which each is retained or lost, e.g. from toxic As, Ag, Cd, Hg, Pb, Sb, Tl or radiocaesium. The partial loss of water following braising, frying and similar treatment of fresh mushrooms may lead to an increase in the content of certain minerals in the whole (wet) mushroom meal (Falandysz et al., 2019c, 2022, 2021a,b; Manzi et al., 2004).

The effect of culinary processing on the Li content of foods including mushrooms is not known. This is an important consideration particu-

larly if mushrooms are to be used for potential therapeutic purposes. This study aimed to characterise the fate of Li captured in the flesh of both, non-lithiated as well as lithiated white button mushrooms that were subjected to several commonly used culinary procedures (Tables 3 and 4). This included the effects of drying, maceration (soaking) and then blanching of re-hydrated mushrooms, blanching of fresh mushrooms, blanching and then pickling of fresh mushrooms, blanching of

Table 3

Concentration levels of Li in fresh non-lithiated *A. bisporus* and after culinary treatment (mean \pm SD and median; mg kg⁻¹ dw and mg kg⁻¹ ww) and estimated effect of treatment (%).

| Type of household treatment and moisture Content in the end product (in %) | Concentration (mg kg ⁻¹ dw) | | | Effect (%) | | | Concentration (mg kg ⁻¹ ww) | | | Effect (%) | | |
|--|--|------------|------------|------------|--------|-------|--|-------------|-------------|------------|--------|-------|
| | Caps | Stipes | Whole** | Caps | Stipes | Whole | Caps | Stipes | Whole** | Caps | Stipes | Whole |
| Fresh \rightarrow dried (90.5%)* | 0.48 \pm | 0.49 \pm | 0.49 | WD | WD | WD | 0.045 \pm | 0.046 \pm | 0.046 | WD# | WD | WD |
| | 0.28 | 0.17 | | | | | 0.027 | 0.029 | | | | |
| | 0.47 | 0.52 | 0.49 | | | | 0.045 | 0.049 | 0.046 | | | |
| Fresh \rightarrow dried \rightarrow macerated \rightarrow blanched (92.1%)# | 0.10 \pm | 0.22 \pm | 0.20 | -79 | -55 | -59 | 0.0079 \pm | 0.017 \pm | 0.016 | -82 | -63 | -65 |
| | 0.09 | 0.11 | | | | | 0.0071 | 0.0087 | | | | |
| | 0.06 | 0.15 | 0.10 | -87 | -71 | -80 | 0.0047 | 0.012 | 0.0079 | -89 | -75 | -83 |
| Fresh \rightarrow blanched (92.1%)# | 0.14 \pm | 0.45 \pm | 0.30 | -71 | -8.2 | -39 | 0.010 \pm | 0.036 \pm | 0.024# | -78 | -22 | -48 |
| | 0.10 | 0.02 | | | | | 0.008# | 0.001# | | | | |
| | 0.17 | 0.44 | 0.29 | -64 | -15 | -41 | 0.014# | 0.035# | 0.023# | -69 | -28 | -50 |
| Fresh \rightarrow blanched \rightarrow pickled (94.9%)## | 0.18 \pm | 0.34 \pm | 0.25 | -62 | -31 | -49 | 0.0092 \pm | 0.017 \pm | 0.013 | -79 | -63 | -72 |
| | 0.02 | 0.02 | | | | | 0.0010 | 0.001 | | | | |
| | 0.19 | 0.34 | 0.26 | -60 | -35 | -47 | 0.0096 | 0.017 | 0.013 | -79 | -65 | -72 |
| Fresh \rightarrow deep frozen \rightarrow blanched (92.3%) [‡] | 0.11 \pm | 0.35 \pm | 0.22 \pm | -77 | -29 | -55 | 0.0085 \pm | 0.027 \pm | 0.017 \pm | -81 | -41 | -63 |
| | 0.01 | 0.02 | 0.01 | | | | 0.0008 | 0.001 | 0.001 | | | |
| | 0.10 | 0.37 | 0.22 | -79 | -29 | -55 | 0.0077 | 0.028 | 0.017 | -83 | -43 | -63 |
| Fresh \rightarrow deep frozen \rightarrow blanched \rightarrow pickled (89.1%) ^{‡‡} | 0.16 \pm | 0.23 \pm | 0.18 | -67 | -53 | -63 | 0.017 \pm | 0.025 \pm | 0.020 | -62 | -46 | -55 |
| | 0.01 | 0.02 | | | | | 0.001 | 0.002 | | | | |
| | 0.18 | 0.24 | 0.21 | -62 | -54 | -57 | 0.020 | 0.026 | 0.023 | -55 | -47 | -51 |

WD (without data).

Notes:

* Calculated from dry biomass data - dry matter content for fresh *A. bisporus* at 9.49%, range from 9.37 \pm 1.43 to 9.62 \pm 1.04% (Vetter, 2003);

** The mean share of the biomass of the caps and stems (percentage by mass) in the whole fruiting bodies was 55:45;

Fresh \rightarrow blanched: calculated from dry weight data - median value of a dry biomass content of *A. bisporus* blanched for 5 min and 10 min in double deionized water at 96-98°C and next drained was 7.92% (own study; equivalent to 92.08% of moisture - values were the same for 5 min and 10 min blanching);

Fresh \rightarrow blanched \rightarrow pickled: calculated from dry weight data - median value of the dry biomass content of *A. bisporus* blanched for 5 min and 10 min in double deionized water at 96-98°C and next drained and pickled was 5.1% (equivalent to 94.9% of moisture) [for 5 min was 4.8% (95.2% moisture) and for 10 min was 5.4% (94.6% moisture)];

‡ Fresh \rightarrow deep frozen \rightarrow blanched: calculated from dry weight data - median value of the dry biomass content of *A. bisporus* blanched for 5 min and 10 min in double deionized water at 96-98°C and next drained and blanched was 7.7% (equivalent to 92.3% of moisture) [for 5 min was 7.3% (92.7% moisture) and for 10 min was 8.1% (91.9% moisture)];

‡‡ Fresh \rightarrow deep frozen \rightarrow blanched \rightarrow pickled - median value of the dry biomass content of the *A. bisporus* blanched for 5 min and 10 min in double deionized water at 96-98°C and next drained and then blanched and pickled was 10.9% (moisture 89.1%) [for 5 min was 8.7% (91.3% moisture) and for 10 min was 13.2% (86.7% moisture)].

deep-frozen mushrooms, and blanching and then pickling of deep-frozen mushrooms.

2. Materials and methods

2.1. Fungal material

An earlier study (Pankavec et al., 2021a) describes the successful cultivation of lithiated *A. bisporus* using compost fortified with different concentrations of Li₂CO₃. In the present study, sub-samples of the cultivated mushrooms were randomly selected from the mushrooms grown in non-fortified compost that acted as a control (Table 3), and from two of the fortified compost groups that showed elevated Li uptake to mushrooms - 50 mg kg⁻¹ dw (experiment A) and 100 mg kg⁻¹ dw (experiment B) added to cultivation substrates, respectively (Table 4). The Li concentrations in these fortified mushrooms showed a median level of 11 \pm 1 mg kg⁻¹ dw (caps), 12 \pm 2 mg kg⁻¹ dw (stipes), 11 \pm 7 mg kg⁻¹ dw (caps) and 15 \pm 10 mg kg⁻¹ dw (stipes), respectively (Table 4). The median concentration levels of Li in pooled samples of the non-lithiated mushrooms (also used as the control/reference material) were 0.47 mg kg⁻¹ dw in caps and 0.52 mg kg⁻¹ dw in stipes (0.49 mg kg⁻¹ dw in whole) (Table 3). The caps and stipes were processed separately. Results for the whole fruiting bodies (relatively young specimens with a cap diameter of 4-6 cm) were calculated by taking into

account the biomass share (%) between caps and stipes (Pankavec et al., 2021a).

Each fruitbody (five sets of 40 lithiated specimens each from experiments A and B, and five sets of 60 non-lithiated specimens from the control groups) was separated into cap and stipe. Each cap and stipe from the lithiated groups was then split into two roughly equal parts (using a ceramic knife) which were separately pooled for each of the experiments. The caps and stipes from the non-lithiated group were divided into six parts each which were pooled (six sets of caps and six sets of stipes). One set (separate pooled caps and stipes) was dried and ground to a powder in a porcelain mortar - this was used as the control/reference material. The second set was first dried, then ground into powder and soaked (macerated) in double deionised water for 12 h, drained of water and blanched. The third set was blanched in double deionised water. The fourth set was blanched in deionised water and then pickled using a vinegar solution. The fifth set was initially deep-frozen for a month, then blanched (without thawing) in double deionised water. The last set was deep-frozen for a month then blanched (without thawing) in deionised water and further pickled in a vinegar solution. Similarly, the divided sets of caps and stipes from the lithiated mushrooms were dried (control) and blanched (fresh) or blanched and then pickled using a vinegar solution. Further details of each treatment are given in the next section.

Table 4

Concentration levels of Li in fresh lithiated *A. bisporus* and after culinary treatment (mean \pm SD and median; mg kg⁻¹ dw and mg kg⁻¹ ww) and estimated effect of treatment (%).

| Type of household treatment and moisture Content in the end product (in %) | Concentration (mg kg ⁻¹ dw) | | | Effect (%) | | | Concentration (mg kg ⁻¹ ww) | | | Effect (%) | | |
|--|--|----------------------|----------------------|------------|--------|-------|--|-------------------------|-------------------------|------------|--------|-------|
| | Caps | Stipes | Whole** | Caps | Stipes | Whole | Caps | Stipes | Whole** | Caps | Stipes | Whole |
| [§] Fresh → dried (90.5%)* | 11 \pm 1 11 | 12 \pm 2 12 | 11 \pm 1 11 | WD | WD | WD | 1.0 \pm 0.1 1.0 | 1.1 \pm 0.2 1.1 | 1.0 \pm 0.1 1.0 | WD | WD | WD |
| [§] Fresh → blanched (92.1%)# | 5.9 \pm 0.9 5.6 | 9.1 \pm 0.9 9.1 | 7.3 \pm 0.9 7.4 | -46 | -24 | -34 | 0.47 \pm 0.07 0.44 | 0.72 \pm 0.07 0.72 | 0.58 \pm 0.07 0.59 | -53 | -34 | -42 |
| ^{§§} Fresh → dried (90.5%)* | 11 \pm 7 15 | 15 \pm 10 19 | 13 \pm 8 17 | WD | WD | WD | 1.0 \pm 0.7 1.4 | 1.4 \pm 0.9 1.8 | 1.2 \pm 0.8 1.6 | WD | WD | WD |
| ^{§§} Fresh → blanched → pickled (94.9%)## | 2.6 \pm 0.5 2.4 | 5.1 \pm 0.8 5.4 | 3.7 \pm 0.6 3.9 | -76 | -66 | -71 | 0.15 \pm 0.03 0.12 | 0.29 \pm 0.05 0.27 | 0.21 \pm 0.03 0.20 | -85 | -79 | -82 |

WD (without data)

Notes:

* Calculated from dry biomass data - dry matter content for fresh *A. bisporus* at 9.49%, range from 9.37 \pm 1.43 to 9.62 \pm 1.04% (Vetter, 2003).

** The mean share of the biomass of the caps and stems (percentage by mass) in the whole fruiting bodies was 55:45;

Fresh → blanched: calculated from dry weight data - median value of a dry biomass content of *A. bisporus* blanched for 5 min and 10 min in double deionized water at 96–98 °C and next drained was 7.92% (own study; equivalent to 92.08% of moisture - values were the same for 5 min and 10 min blanching);

Fresh → blanched → pickled: calculated from dry weight data - median value of the dry biomass content of *A. bisporus* blanched for 5 min and 10 min in double deionized water at 96–98 °C and next drained and pickled was 5.1% (equivalent to 94.9% of moisture) [for 5 min was 4.8% (95.2% moisture) and for 10 min was 5.4% (94.6% moisture)];

^{§/§§} Quantity of Li added to compost (50 mg kg⁻¹ dw)[§]; (100 mg kg⁻¹ dw).

2.2. Conditions of culinary processing

Drying. Separate groups of caps and stipes were sliced and dried at 65 °C for 24 h in an electrically heated commercial dryer (dehydrator for mushrooms, fruits, vegetables and herbs; model: MSG-01; MPM Product, Milanówek, Poland) and then pulverized in a porcelain mortar. The resulting powders were sealed in 50 ml polypropylene self-standing centrifuge tubes (Falcon type) under dry condition and sub-samples were subjected for elemental and other analyses.

Maceration (soaking) and then blanching. Separate groups of caps and stipes were dried as given above and transferred to a glass beaker (250 mL). Double deionised water (150 mL) was poured over the dry mushrooms and the beaker was kept under cover (Parafilm) for 12 h. The fungal materials were then drained (plastic sieve) and blanched in double deionised water at 96–98 °C for 15 min. Blanched materials were drained (filter paper Whatman No. 42), packed into clean sealed polyethylene bags, deep-frozen (-30 °C) and freeze-dried (lyophilizer type LYOVAC GT2; Steris, Germany), then ground into powder using a porcelain mortar. Powdered materials were stored closed in 50 ml polypropylene self-standing centrifuge tubes (Falcon type) under dry condition for elemental and other analyses.

Blanching. Separate groups of caps and stipes were blanched with double deionised water (200 mL) at 96–98 °C for 15 min in 250 mL glass beakers. The materials were drained immediately without allowing the contents to cool. After draining, the fungal materials were cooled at room temperature, packed in sealed polyethylene bags, deep-frozen, lyophilized, ground into powder using a porcelain mortar and stored as powdered material and kept closed in 50 ml polypropylene self-standing centrifuge tubes (Falcon type) under dry condition for elemental and other analyses.

Blanching and then pickling. The fungal materials were blanched in the same way as described above. After draining off the water the materials were placed in glass beakers (250 mL) and pickled with a hot marinade composed of a diluted (1: 3; vol/vol, 150 mL) solution of 10% spirit vinegar (Drewnowska et al. 2017) and double deionized water. The pickles were cooled at room temperature, sealed with para-film and stored in a refrigerator for a period of one month. Following this storage period, the

fungal materials were drained and cooled at room temperature, packed in sealed polyethylene bags, deep-frozen, lyophilized, pulverised as described above and stored closed in 50 ml polypropylene self-standing centrifuge tubes (Falcon type) under dry condition for elemental and other analyses.

Freezing and then blanching. Fresh fungal materials (separately caps and stipes) were packed into brand new sealed polyethylene bags and stored deep frozen (-30 °C) for one month. After this period, the frozen fungal materials were immersed in boiling double deionised water (150 mL) in glass beakers (250 mL) and maintained at 96–98 °C for 15 min. The blanched materials were drained, cooled at room temperature, packed into new bags, deep frozen, lyophilized, pulverised and stored closed in 50 ml polypropylene self-standing centrifuge tubes (Falcon type) under dry condition for elemental and other analyses.

Freezing and then blanching and pickling. Fresh fungal materials (separately caps and stipes) packed into sealed polyethylene bags were deep frozen for a period of one month, then blanched and pickled as described above. Next, the fungal materials were drained, packed into sealed polyethylene bags, deep-frozen, lyophilized, pulverised and stored closed in 50 ml polypropylene self-standing centrifuge tubes (Falcon type) under dry condition for elemental and other analyses.

2.3. Instrumental analysis

The analytical method used for the determination of Li and some other trace elements (not reported here) in fresh and culinary processed mushrooms along with the analytical quality assurance and quality control (QA/QC) procedures and certified reference materials used, have been presented on several occasions earlier in detail (Falandysz et al., 2020; Pankavec et al., 2019; 2021a and; Zhang et al., 2020 and 2022), and is briefly described below.

The nitric acid and microwave oxidized digests of the fungal materials (two 0.5 mg subsamples in parallel for five replicates of each fungal material), were diluted with deionized water up to 10 mL and measured using an ICP-DRC-MS (inductively coupled argon plasma - dynamic reactive cell - mass spectrometer; Perkin-Elmer ELAN DRC II SCIEX, Canada) equipped with a Meinhard concentric nebulizer, cyclonic spray

chamber, Pt cones and a quadruple mass analyser. The methodology was validated through the use of standard procedures (standard solutions, procedural blank samples, duplicates and replicates and calibration of the instrument, with each analytical cycle). These were found to be satisfactory for the reliable measurement of Li as described earlier (Pankavec et al., 2021a and 2021b). The method detection limit (MDL) achieved for Li in the digested fungal solutions was $0.02 \mu\text{g L}^{-1}$. For dehydrated fungal materials an MDL of $0.007 \text{ mg kg}^{-1} \text{ dw}$ was achieved with a limit of quantification at $0.021 \text{ mg kg}^{-1} \text{ dw}$. Moisture content of each pulverised fungal material was determined gravimetrically after laboratory oven dehydration of the sub-samples at 105°C until constant weight and data on Li concentration were calculated both to dry weight and wet weight (ww).

3. Results and discussion

3.1. The effect of drying and maceration of dried mushrooms followed by blanching

The aim of conventional drying (air drying at ambient sunshine condition or oven drying in 45°C to 105°C) or lyophilising mushrooms is to preserve them for culinary storage. An additional effect of this process is to increase the quantity of solids including minerals by around 10-fold relative to the fresh product. The non-lithiated (reference) samples of dried *A. bisporus* when macerated for 12 h followed by blanching, lost on average, 83% of accumulated Li (89% loss for caps and 75% for stipes) on a wet weight (ww) basis (Table 3). There is no other data available in the literature about the effect of maceration alone or for maceration followed by blanching, on retention of Li in processed mushrooms. This may be because maceration of dried mushrooms followed by blanching of a re-hydrated product is a relatively untypical treatment. Dried mushrooms (a whole or sliced) are usually macerated with tap water and both the solids and macerate are then used for cooking (in soups, sauces, etc.). Thus, any accumulated minerals in the mushrooms are maintained within the processed mushrooms or in a prepared meal. On the other hand, maceration of dehydrated mushrooms results in a massive loss of the constitutional dry matter into the water phase, i.e. at around 90% (from our own study with crushed *A. bisporus* and tap water at room temperature) rate, and possibly also minerals. Thus, maceration transfers most of the organic matter and associated material into the macerate which after condensation or dehydration, results in a product that is elevated in the Li, other minerals and organic compounds that were present in the dried mushrooms. Theoretically, the treatment of the dehydrated mushroom (powdering, crushing, or leaving whole) and the maceration temperature and time can affect the efficiency of the maceration process.

Given the lack of any literature data on the effect of maceration for Li, available data for monovalent caesium (radioactive ^{137}Cs) in certain dried and fresh mushrooms may be helpful as a comparator of the effectiveness of maceration. Dried Bay bolete (*Imleria badia*, previous name *Xerocomus badius*) macerated with water or 0.5% saline for 3 h at 20°C was reported to have lost 65% of its accumulated radiocaesium concentration activity, while fresh or deep-frozen mushrooms treated in the same way lost 15% and 29%, and 68% and 71%, respectively (Neukom & Gisler, 1991). Fresh *Cantharellus tubaeformis* when macerated with water alone and with 1% and 5% saline lost radiocaesium at rates of 50%, 50% and 61%, respectively (Stijve, 1994). Dried and powdered King bolete (*Boletus edulis*) macerated with water at room temperature lost monovalent ^{137}Cs and ^{40}K at a rate 95% and 88% (Saba & Falandysz, 2021). Lyophilised, powdered and macerated *B. edulis* lost 43% of the original content of ^{137}Cs and 51% of ^{40}K . The corresponding losses for similarly treated *Leccinum scabrum* and *Leccinum versipelle* were 23% and 24%, and 32% and 29% respectively when calculated on dw (and 43% and 51%, 25% and 24%, and 45% and 29%, when calculated on ww basis, respectively) (Falandysz et al., 2022c).

It appears from these losses that (for Cs at least) the dehydration procedure used (air drying vis. lyophilisation/freeze-drying) and any other treatment (freezing) and perhaps also the type of mushroom (species) can collectively influence the effectiveness of the maceration process. These literature data show a wide variation in the rates at which Cs was extracted. If this behaviour was extrapolated to Li (as it is similarly monovalent), it would indicate that the different maceration techniques used, would most likely result in the transfer of the accessible (and possibly also, the well absorbed) Li into the macerate or its condensed product.

3.2. The Effect of blanching for fresh and deep-frozen mushrooms

When blanched, the measured loss of Li from fresh, lithiated and non-lithiated *A. bisporus* was 42% and 50% ww and 34% and 41% on a dw basis, respectively. The data suggests that the caps appear to be more prone to loss than stipes (Tables 3 and 4). Blanching of the non-lithiated and deep-frozen mushrooms resulted in a decrease of Li content by 63% ww and by 55% on a dw basis. As noted for the fresh mushrooms, the loss was higher in the caps than stipes. Deep freezing is a common way of preserving freshly harvested tubular mushrooms for a short time and is practiced both at home and within the food industry. Domestically however, both tubular and lamellar mushrooms are kept frozen. Blanched or braised mushrooms can be stored deep-frozen for somewhat longer periods.

Lithium, along with other elements from group 1 (monovalent elements) in the s-block of the periodic table, i.e. Na, K, Rb and Cs (not to mention Fr) are all lithophile alkali metals. Ionic Li has an ion radius of 0.76 \AA and covalent radius of 1.23 \AA , followed by Na with 1.02 \AA and 1.54 \AA , K with 1.51 \AA and 2.03 \AA , Rb with 1.61 \AA and 2.16 \AA , and Cs with 1.74 \AA and 2.35 \AA , respectively (www. 2021). Thus, as Li has the smallest ionic radius among singly charged cations it forms relatively stronger bonds with other fungal components and is less water soluble than the other alkali elements, including usually highly bioconcentrated radiocaesium which forms weaker bonds. So, the reported data on the effects of household treatment for Na, K, Rb and Cs (^{133}Cs , ^{134}Cs and ^{137}Cs) could be considered and would be pertinent when examining and discussing the effects for Li.

Fungi that grow in soil absorb nutrition from this substrate through their mycelial network, either storing it in the mycelia or translocating it to the emerging fruiting bodies. Depending on the species, a range of elements may be absorbed more or less efficiently (Falandysz & Borovička, 2013). As mentioned earlier, one of the key elements is K (including ^{40}K with half-life of 1.251×10^9 years) (Međyk et al., 2020). Analogically, many mushrooms that grow on polluted soils and other substrates efficiently absorb radioactive ^{134}Cs and ^{137}Cs (Orita et al. 2017).

There is no published data on the effect of blanching and pickling for Li and Na but some information has been reported on the fate of ^{137}Cs , ^{40}K (total K) and Rb in mushrooms (Daillant et al., 2013; Drewnowska et al. 2017; Falandysz et al., 2020, 2020b, 2021b; Neukom & Gisler, 1991; Saba & Falandysz, 2021; Skibniewska & Smoczyński, 1999; Stijve, 1994). Again, due to a lack of data on Li, available information on the effect of blanching and pickling for ^{137}Cs , ^{40}K (total K) and Rb may be helpful as a comparator of the effectiveness of both techniques for Li.

Due to its vital role in osmoregulation of the water stored in mushrooms, K occurs largely in the intracellular fluid. Lithium and Cs, are very minor elements in mushrooms and do not as yet, have any known biological function in basidiomycetes. In a similar manner to K (and Rb), these elements could also co-occur mostly in the intracellular fluid. Therefore if we extrapolate this behaviour, the effect of culinary treatment on the Li content of mushrooms could be similar to that of K (and ^{40}K), Cs (data are only available for radioactive ^{137}Cs) and Rb, for which there is some available information on the effects of culinary

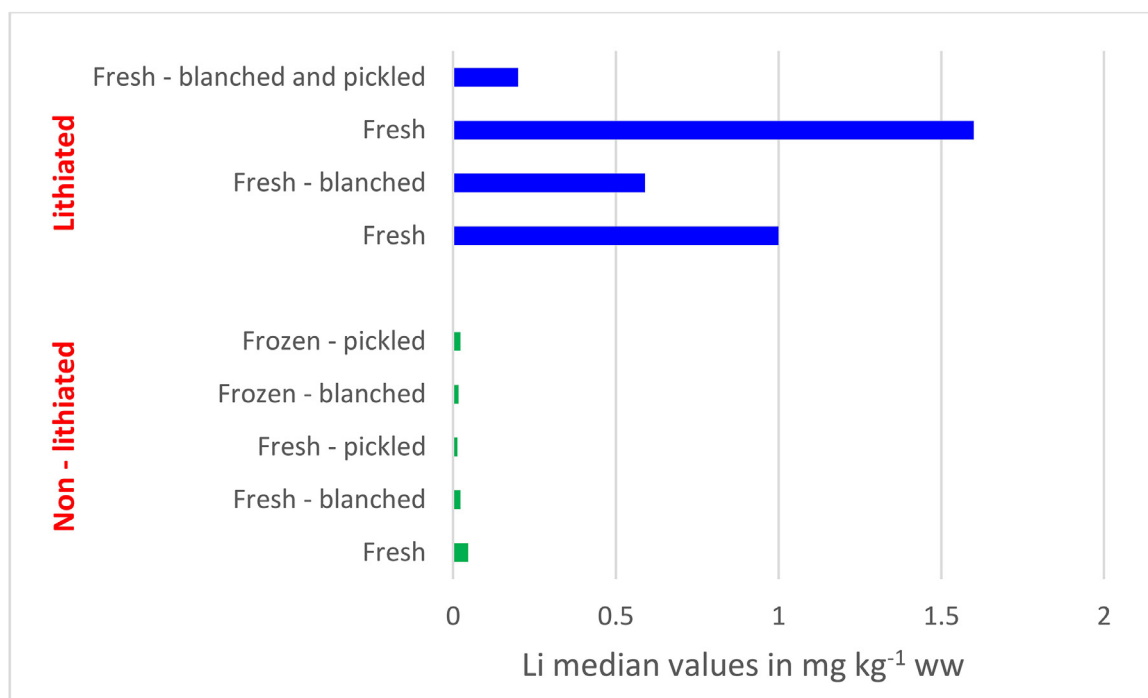


Fig. 1. Median values of Li concentration in whole fruiting bodies of non-lithiated and lithiated *A. bisporus* fresh (raw) and processed culinary products.

processing of wild species. As Li in its physical and chemical features is most similar to sodium, its fate in mushrooms also appears to be similar, e.g. concentrations of both elements in *Amanita muscaria* L. are greater in the caps than stipes, while the opposite is true for K, Rb and Cs (also ¹³⁷Cs) (Falandysz et al., 2007, 2019b, 2020c; Saniewski et al., 2022).

Fresh caps of *Amanita fulva* Fr., blanched under similar condition as the *A. bisporus* in this study, lost 86% of Rb on a dw basis (Drewnowska et al., 2017). Fresh whole fruiting bodies of *Tricholoma equestre* (L.) P. Kumm, *Suillellus luridus* (Schaeff.) Murrill and *I. badia*, when blanched, lost 83%, 70% and 58% ww respectively of the radioactivity arising from ¹³⁴Cs/¹³⁷Cs (Skibniewska & Smoczyński, 1999). When boiled in water for 20 min., fresh *Hydnum repandum* L. lost 51% of accumulated ¹³⁷Cs, while frozen *Boletus edulis* lost only 6.6% on a dw basis when boiled (Dailliant et al., 2013). These reported losses of Rb and ¹³⁷Cs from some species of blanched mushrooms are somewhat higher, similar or lower, respectively, than those obtained for Li loss from *A. bisporus* in this study (Table 3).

The chemical composition of cell walls in mushrooms vary in details between the different species. The structural and intrastructural components however, are composed roughly of aminopolysaccharides (chitin), glucans (α - and β -), proteins, lipids, uronic acids, hydrophobins, sporopollenin, melanins and others (Feofilova, 2010). In an experiment by Stijve (1994), specimens of *Hygrophorus camarophyllus* (Alb. & Schwein.) Dumée, Grandjean & Maire, *Hydnum repandum* L., *Cantharellus tubaeformis* (Fr.) Quél. and *Albatrellus ovinus* (Schaeff.) Kotl. & Pouzar mushrooms, when parboiled (boiling water poured over and cooked until the flesh starts to soften) under the same conditions (100 g parboiled in 0.5 L⁻¹ water for 2 min.), lost ¹³⁷Cs at the rate of 88%, 82%, 51% and 46% ww, respectively.

The texture of the fruitbodies of edible mushrooms varies from a soft type (brittle consistency) to more firm and harder types for around 2000 edible species (not including medicinal polypores, etc.). This difference in texture can be considered as the main factor (along with consideration of the elemental binding to ligands) that influences the fate and rate of

loss of monovalent (and other) elements from the flesh during culinary processing.

3.3. The effect of blanching and then pickling for fresh or deep-frozen mushrooms

The effect of blanching followed by pickling (marinating) on lithiated fresh *A. bisporus* was a loss of 71% of Li dw and 82% ww; non-lithiated mushrooms lost 47% and 72%, respectively. The earlier observation of a higher rate of Li leaching from blanched caps relative to the stipes was maintained after this combined treatment. Acetic acid in the vinegar acts both as a chelator and acidifier in a marinade. This chelating action appears to promote an increased leaching rate of Li from the blanched intermediate product. For non-lithiated mushrooms that were deep-frozen and then blanched and pickled, the corresponding loss was 57% dw and 51% ww. The final pickled product in this case, were relatively higher in dry matter content, at 10.9% (Table 1).

As described above for the other treatments the losses of Li (Table 3) were compared to other monovalent elements for which information on losses from similar treatment is available. The loss of Rb from fresh caps of *Amanita fulva* (the caps are quite fragile) that were blanched and then pickled under similar condition as the *A. bisporus* in this study, was 99% based on a dw basis (Drewnowska et al., 2017). Fresh *T. equestre* and *I. badia* when pickled (without initial blanching) lost ¹³⁷Cs activity concentration at 86% and 58%, wet weight, respectively (Skibniewska & Smoczyński, 1999).

When blanched and then pickled *Boletus edulis* lost 77% of ¹³⁷Cs and 81% of ⁴⁰K activities, and when deep frozen and then blanched and pickled, the losses were around 84% of ¹³⁷Cs and 72% of ⁴⁰K ww (Saba & Falandysz, 2021). In another study, bolete mushrooms such as *B. edulis*, *L. scabrum* and *Leccinum versipelle* (Fr. & Hök) Snell., that were blanched and then pickled, saw ¹³⁷Cs activity decrease from by 55 ± 8% and ⁴⁰K activity decrease by 40 ± 20% ww (Falandysz et al., 2022c).

Data summarising the median concentration levels of Li in whole fruiting bodies of non-lithiated and lithiated *A. bisporus*,



Fig. 2. Effect (%) of culinary processing on the leaching of Li from non-lithiated and lithiated whole fruiting bodies of *A. bisporus* (based on whole weight median values).

and the effects (%) of culinary processing are presented in Fig. 1 and Fig. 2.

4. Conclusions

This study of commonly used culinary treatments of edible mushrooms shows that Li like other monovalent elements is lost from the edible flesh as a result of the processing and that this loss varies depending on the treatment. A valued food with huge economic considerations for growers, retailers and consumers, fresh mushrooms can sometimes be a little difficult to digest and this may also impact on the release of nutrients (or potentially therapeutic components, such as Li in this case) in the gastrointestinal system. Information on the release of these nutrients during culinary processing prior to consumption is therefore important. This study of commonly used culinary treatments including various combinations of drying, maceration, blanching (of fresh, deep-frozen and re-hydrated mushrooms) and pickling (of fresh and deep-frozen mushrooms) shows that Li is lost from the edible flesh at varying rates depending on the treatment.

Blanching of fresh lithiated mushrooms resulted in a 40% loss, increasing to 77–87% when blanching was followed by pickling. Corresponding losses were similar (47–72%) for non-lithiated mushrooms. Higher losses through the combined treatment relative to just blanching appear to be due to chelating and acidifying effects of the vinegar used. In maceration of dried mushrooms is important to include the macerate or residual fluids from other treatments (e.g. braising) in the mushroom meal as is traditionally custom. This is an intermediate stage in understanding how lithiated common mushrooms may provide an enriched source of potentially bioaccessible Li as a pro-therapeutic product. Further studies will investigate *in vitro*, the accessibility of the Li that is potentially available in these enriched mushrooms.

Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors.

Consent to participate

Not applicable. This manuscript does not contain any studies with human participants or animals performed by any of the authors.

Consent to publish

Not applicable. This manuscript does not contain any individual person's data in any form.

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Availability of data and materials

Not applicable.

Declaration of interest statement

The authors declare that they have no conflict of interest.

CRediT authorship contribution statement

Sviatlana Pankavec: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Writing – original draft. **Jerzy Falandysz:** Conceptualization, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Supervision. **Anetta Hanć:** Methodology, Validation, Resources, Formal analysis, Data curation. **Alwyn R. Fernandes:** Data curation, Writing – review & editing.

Data availability

Data will be made available on request.

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