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Authenticating genuine Kakadu plum (*Terminalia ferdinandiana*) powders from fakes using stable isotope analysis and elemental profiling

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A B S T R A C T

Kakadu plum (*Terminalia ferdinandiana*) is a plant species endemic to northern Australia, attracting increasing consumer interest due to its multiple nutritional qualities. As a consumer product at a premium price point, the Kakadu plum may be susceptible to food fraud. This paper determines the prevalence of food fraud in the e-commerce Kakadu plum market. We applied stable isotope analysis (SIA) and elemental profiling using X-ray fluorescence (XRF) through Itrax to evaluate the authenticity of 13 commercially available Kakadu plum powdered samples purchased from Australian and overseas suppliers against four powdered samples directly provided by First Nations harvesters. Overseas and Australian-sourced powders were found to have distinct isotopic and elemental profiles. All overseas powders showed highly enriched $\delta^{13}C$ values indicating they are fakes, not derived from Kakadu plum. Non-metric multi-dimensional scaling (nMDS) of elements also displayed distinct groupings between Australian-sourced and overseas powders, whilst analysis of similarity percentages (SIMPER) differentiated the elemental composition between groups. It was also observed that 89% of overseas products sold as Kakadu plum were deceptively labelled as other products. These results showed food fraud occurred along the supply chain of overseas-sourced product. Given the complexities of multi-national food systems, utilising a combination of stable isotopes and elemental profiling are straightforward applications for detecting fraudulent products.

1. Introduction

Agriculture is important to the Australian economy, accounting for 2.4% of value-added GDP, and an annual farm gate value of AUD$93 billion in 2021–2022 (ABARES, 2023). Demand for native bushfoods is growing with a farmgate value forecasted to increase from $81.5 million currently to $160 million by 2025 (Laurie, 2020). A native food sector led by First Nations enterprises reaps multiple benefits, including the retention of First Nations knowledge, job growth (particularly in remote areas), and improves the economic outcomes for First Nations people. Achieving these multiple benefits rely on protecting the emerging sector, particularly from the proliferation of fake products. Kakadu plum (*Terminalia ferdinandiana*) is the third largest emerging native bushfood, and hence plays an important role in promoting a thriving First Nations-led bushfoods industry in Australia (Laurie, 2020).

T. ferdinandiana (hereafter referred to as Kakadu plum), is a savanna tree growing up to around 7 m tall (Dunlop, Leach, & Cowie, 1995; Gorman, Wurm, Vemuri, Brady, & Sultanbawa, 2020). Also referred to as Gubinge or billygoat plum, the fruit is usually harvested between April to June months, and has a yellow-green flesh when ripe (Dunlop, et al., 1995). Multiple parts of the tree have a history of traditional and medicinal uses for First Nations people (Akter, Netzel, Fletcher, Tinggi, & Sultanbawa, 2018; Gorman et al., 2020; Hegarty, Hegarty, & Wills, 2001; Whitehead, Gorman J., Griffiths A. D., Wightman H., & Massarella H., 2006).

Since the 1990's, Kakadu plum has grown in popularity as a commercial product due to its health benefits, notably its Vitamin C (ascorbic acid) content (Cozzolino, Phan, Netzel, Smyth, & Sultanbawa, 2021). More recent studies on Vitamin C report a range between 14,038 and 15,190 mg per 100 g of fruit dry weight, positioning the Kakadu

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plum as containing the highest levels of ascorbic acid compared to any natural food globally (Brand, Cherikoff, Lee, & Truswell, 1982; Brand Miller, James, & Maggiore, 1993; Konczak, Maillot, & Dalar, 2014; Williams, Edwards, Pun, Chaliha, & Sultanbawa, 2014). An array of more recent additional health benefits have emerged, further contributing to its popularity as a commercially valuable product (Akter, et al., 2018; Konczak et al., 2014; Sirdaarta & Matthews, 2015; Tan et al., 2011). Overall, the nutritional qualities and resultant health benefits of Kakadu plum are attractive to consumers, hence positioning it as a "functional food" (Gorman, et al., 2020).

In addition to the health benefits of Kakadu plum, the fruit contains a wide array of end-consumer applications, including nutraceutical and cosmetic purposes, and as a food ingredient (Laurie, 2020; Richmond, Bowyer, & Vuong, 2019). Generally, Kakadu plum is provided wholesale in powder form, prior to processing into a consumer product. As of 2020, the current farm gate value is $1.6 million annually, with a forecasted farm gate value of $3.5 million by 2025 (Laurie, 2020), driven by research on the health benefits of the fruit, and its diverse applications.

Given the growing demand for functional foods such as the Kakadu plum, it may be susceptible to food fraud, particularly as demand outstrips supply. The health properties of the fruit, and previous intellectual property threats from multinational corporations, has sparked international interest. Further, the superior health benefits of Kakadu plum mean that the fruit is commercially valuable and hence a potential target for fraudsters. Powders marketed as "Kakadu plum" indicate Australian origin and are misleading if these products have been grown and processed elsewhere. There is traditional knowledge inherent in the growth, harvest, and consumption of the fruit, which will be at risk if the industry is overridden with fraudulent product. These nuances surrounding the commercialisation of the Kakadu plum iterate the importance of developing robust controls to protect the industry, and protocols to monitor products marketed as Kakadu plum powder.

Kakadu plum is traditionally a bushtucker food for First Nations communities, and hence is accustomed to relatively short food supply chains. As commercialisation of the product develops and attracts international markets, the food supply chain for Kakadu plum has lengthened and increased in complexity. Kakadu plum is grown and harvested in Australia, and not found anywhere else in the world (Hegarty, et al., 2001). However, without oversight by First Nations people, it could be processed into a powder elsewhere without their involvement. An increased use of intermediaries may confuse consumers around the product's connectedness with First Nations culture, and confounds the return of economic benefits back to First Nations people. More concerningly, long food supply chains are harder to police and are therefore more susceptible to food fraud (Kelly, Heaton, & Hoogewerff, 2005). First Nations-owned companies have made proactive efforts to maintain oversight of the Kakadu plum industry to address these risks. Cooperatives such as the Northern Australia Aboriginal Kakadu Plum Alliance (NAAKPA) streamlines the Kakadu plum supply chain and consolidates efforts to expand the product to overseas markets. NAAKPA have also adopted a collaborative approach by partnering with research bodies such as the Australian Nuclear Science and Technology Organisation (ANSTO). Collectively, the NAAKPA and ANSTO First Nations Kakadu Plum Provenance Project aims to establish a comprehensive food provenance landscape to support businesses owned by First Nations people. Such collaborative partnerships enable genuine producers to maintain oversight of the sector and protect the industry. This study complements this wider initiative, through exploration of Kakadu plum products sourced from overseas providers.

Protection of the nascent Kakadu plum industry requires regulatory instruments capable of intercepting the fraudulent substitution of genuine with fake product. The aim of this research was to determine the extent of fraudulent practices in the international Kakadu plum wholesale market and suggest a reliable protocol capable of distinguishing authentic Kakadu plum powder from adulterated ones. To this end we further sought to characterise the stable isotope and elemental composition of the genuine Kakadu plum product.

A variety of food provenance techniques have emerged, with differing applicability based on factors such as the purpose of testing, cost, timeliness, and accuracy. DNA profiling is a method used extensively as a cost-effective and timely approach in species identification and detecting genetic modification in foods. However, although it is useful in determining the species of a food sample, there are mixed results in determining production methods and geographical origin (Gopi, Mazumder, Sammut, & Saintilan, 2019; Gopi et al., 2019a; Gopi et al., 2019b). The ability to identify species using DNA profiling relies on comprehensive databases employing standardised methods, which can be lacking in premium products. By contrast, a database capturing the elemental composition of Kakadu plum is developing as part of the NAAKPA and ANSTO First Nations Kakadu Plum Provenance Project (Mazumder, Martino, Gopi, Gadd, & Crawford, 2021). This foundation will enable the comparison of overseas product with verified sources from First Nations harvesters. Iso-elemental analyses is useful in determining both geographic origin and production methods of fruits and vegetables by reflecting the environmental and growing conditions of plants (Drivelos & Georgiou, 2012).

Stable isotopes can identify geographic origin in plants, as isotopes reveal soil and climatic conditions (Deng, et al., 2020; Gonzalvez, Armenta, & de la Guardia, 2009). As such, stable isotope analysis (SIA) has emerged as a technique to determine food provenance in a variety of foods. In addition to using SIA to determine geographic origin, differing ratios in the stable isotopes of carbon ($\delta^{13}C$) can indicate the plant type (Kelly, et al., 2005), whether utilising the C_3 Calvin photosynthetic pathway (most shrubs and trees), the C_4 Hatch and Slack photosynthetic pathway (many tropical grasses), or crassulacean acid metabolism (CAM-many succulent plants).

Elemental analysis is an alternative or complementary approach to determining food origin via the detection of multiple trace elements. Plants metabolise nutrients from soil as they grow, thus fruits and vegetables have different elemental profiles based on their geographical origin. Specifically, the Itrax micro X-ray fluorescence (Itrax) core scanner provides rapid analysis of the elemental abundance for a wide range of elements (Gadd, et al., 2018). Although traditionally used for sediment cores, food provenance research has explored the application of Itrax to determine geographical origin (Gopi et al., 2019a; Gopi et al., 2019b). Itrax is a beneficial method because it requires minimal sample preparation and is non-destructive, hence the sample remains intact and can be re-analysed (Gadd, et al., 2018; Gopi et al., 2019b). X-ray fluorescence (XRF) through Itrax has been used to detect the presence of up to 31 elements (Gopi et al., 2019), and hence is a useful indicator for determining the geographical source of food and detecting potential food fraud (Drivelos & Georgiou, 2012; Kelly et al., 2005; Malo et al., 2023; Martino et al., 2023).

We applied both stable isotope analysis and elemental analyses to determine the signature of genuine Kakadu plum powder, sourced from NAAPKA. We also purchased product using e-commerce websites, from Australian suppliers and international wholesalers. From this we sought to (a) determine the prevalence of product substitution in the Australian and international Kakadu plum e-commerce markets and (b) identify the most effective tests to distinguish genuine from commonly substituted products.

2. Methods

2.1. Sample collection

Kakadu plum powders were purchased online from Australian and overseas wholesale suppliers using the search term "Kakadu plum extract". Each powder was advertised as 100% Kakadu plum extract, from the fruit, seed, or unspecified. A total of 17 sets of powders were obtained, which have been grouped under three categories of supplier: "overseas", "NAAKPA" or "commercially acquired Australian powders".

Overseas-sourced powders (9) were purchased through wholesale e-commerce platforms and imported into Australia. The customs documentation for 8 of the powders mentioned products other than Kakadu plum. The product packaging for 6 purchased powders also listed an alternate product, although they were purchased online as Kakadu plum (Table 1). Three powders mentioned Kakadu plum on the product packaging. One powder was labelled as "Kakadu plum" only, with no alternate substances included on either the packaging or customs documentation.

Powders were purchased online from Australian e-commerce suppliers ("AU-CAP", Table 2). Only 4 sets of powders were acquired from 4 commercial suppliers due to time and cost constraints, and the limited availability of the powder. Secondly, 4 sets of powder were also provided from NAAKPA cooperative members located in the Northern Territory (n = 4, Table 2). This product was processed into powder by the respective harvesters, prior to distribution to Kakadu plum wholesalers for sale. One set of powder includes powdered flesh and skin, and three are powdered flesh, skin, and seed ("whole fruit"). These products are verified authentic Kakadu plum powder, as they have been provided directly by NAAKPA. As such, they have been used as a benchmark to compare the authenticity of commercially acquired product.

Potential adulterants underwent SIA and elemental profiling. These potential filler products are C_4 plants and were selected based on their low price point, geographical proximity to overseas-sourced samples, and their availability. Such products are cheaper and may potentially be fillers in fraudulent products. Examples include products derived from corn or sugar, both of which have previously been identified as adulterants in premium functional foods such as honey and spirulina (Rutar, Strojnik, Nečemer, Bontempo, & Ogrinc, 2023; Zhou, Taylor, Salouros, & Prasad, 2018).

Table 2
List of Kakadu plum powders sourced from Australian suppliers either from NAAKPA harvesters, or purchased from Australian providers (AU-CAP). Product information is listed as declared on the product advertisement and packaging. Whole fruit refers to powders containing flesh, skin and seed.

Supplier Category	Sample number	Product name advertised at point of purchase.	Part of plum used in powder	Production location	Quantity provided
NAAKPA	8	Not applicable	Whole fruit powder, seed omitted.	Northern Territory, Australia	30 g
NAAKPA	17	Not applicable	Whole fruit (powder)	Northern Territory, Australia	30 g
NAAKPA	18	Not applicable	Whole fruit (powder)	Northern Territory, Australia	300 g
NAAKPA	19	Not applicable	Whole fruit (powder)	Northern Territory, Australia	300 g
AU-CAP	2	Wild harvested Kakadu plum	Whole fruit (powder)	Western Australia, Australia	30 g
AU-CAP	10	Kakadu plum powder	Whole fruit (powder)	Western Australia, Australia	45 g
AU-CAP	11	Kakadu plum powder	Not provided by supplier (powder)	Western Australia, Australia	15 g
AU-CAP	14	Kakadu plum powder	Whole fruit (powder)	Northern Territory, Australia	30 g

2.2. Sample preparation

Kakadu plum powders were delivered to the Australian Nuclear Science and Technology Organisation (ANSTO) in Sydney, Australia, by NAAKPA, where they were frozen before being unpackaged and divided into labelled glass vials. Each divided glass vial was used for both SIA and elemental analysis through Itrax (XRF).

2.3. Stable isotope analysis

Isotopic analysis was conducted at ANSTO through a continuous-flow isotope ratio mass spectrometer (CF-IRMS). Replicate tests (n = 5) were conducted for each set of powder, to further validate the results and ensure consistency within each sample. A total of 144 measurements were conducted across all replicates. Carbon and nitrogen were analysed in separate sampling rounds, due to the substantially low quantities of $\delta^{15}N$, as expected for plant products. This is due to the large C/N ratios of plants. For example, previous studies have found $\delta^{13}C$ levels between −26.12% and −21.69%, compared to $\delta^{15}N$ values of 1.95% and 7.72% (Chung, et al., 2017). Each replicate was prepared by filling sample powder into tin capsules. Approximately 0.6 mg ± 0.1 mg of each powder was used to analyse $\delta^{13}C$. For the $\delta^{15}N$ analysis, around 12–16 mg of powder was used per replicate so $\delta^{15}N$ levels could be detected. Once filled, each tin capsule was pelletised to remove air, and weighed before proceeding to CF-IRMS. The samples were loaded into an autosampler then fed into an elemental analyser (Thermo Fisher Flash 2000 HT EA, Thermo Electron Corporation, U.S.A.). Each sample was combusted into CO_2 and N_2 at 1020 °C before being transferred with a helium carrier gas into a reduction furnace at 600 °C. Once the CO_2 and N_2 were separated, the gases were transferred into a Thermo Fisher Delta V Plus via the Thermo Fisher Conflo IV interface for analysis (Thermo Scientific Corporation, U.S.A.).

A two-point calibration was utilised to normalise the data, and test for drift, using three standard reference materials (SRM) IAEA USGS-40 L-Glutamic Acid, IAEA USGS-41a L-Glutamic Acid and Elemental

Table 1
List of overseas powders advertised as Kakadu plum extract with product information as declared on the product advertisement, customs and packaging documentation.

Supplier Category	Sample number	Product name advertised at point of purchase.	Part of plum used in powder, advertised at point of purchase.	Product name listed on customs documentation	Product name listed on the label of product packaging	Purchase quantity
Overseas	5	Kakadu plum extract	Fruit (powder)	Aloe vera extract	No product specified	1 kg
Overseas	20	Kakadu plum extract	Other (powder)	Chamomile extract	Chamomile extract	1 kg
Overseas	4	Kakadu plum extract	Fruit (powder)	Devils claw extract	Devils claw extract	1 kg
Overseas	22	Kakadu plum extract	Fruit (powder)	Grapefruit extract	Grapefruit extract	1.5 kg
Overseas	6	Kakadu plum extract	Fruit (powder)	Hawthorn extract	Hawthorn extract (batch number "KakaduPlum")	1 kg
Overseas	1	Kakadu plum extract	Fruit (powder)	Iceland moss	Kakadu Plum extract	1 kg
Overseas	21	Kakadu plum extract	Fruit (powder)	Kakadu plum cosmetic	Kakadu plum cosmetic	500 g
Overseas	3	Kakadu plum extract	Fruit (powder)	Iceland moss extract	Iceland moss extract	1 kg
Overseas	7	Kakadu plum extract	Fruit (powder)	Iceland moss extract	Iceland moss extract	500 g

Microanalysis B2045 Methionine included in each sample run. Additionally, standard substances served as quality control references to "bracket" the analysed samples (Chitin B2160 and Casein Sodium Salt from Bovine Milk B2155). For the potential filler samples, three quality control references were used (Wheat flour B2157, Chitin B2160 and Sorghum flour B2159). Data were reported relative to International Atomic Energy Agency (IAEA) secondary standards, which have been certified relative to Vienna-PeeDee Belemnite (VPDB) for carbon, and air for nitrogen. Results were accurate to 1% for both C% and N%, and ±0.3 parts per million (‰) for $\delta^{13}C$ and $\delta^{15}N$; they were reported in delta (δ) notation in parts per thousand (‰ or per million) determined by the formula:

$$X\ (‰) = \left(\frac{Rsample}{Rstandard} - 1\right) \times 1000$$

Where X can represent the -^{13}C or ^{15}N isotope, and R is -$^{13}C/^{12}C$ or $^{15}N/^{14}N$ respectively. The sample refers to the replicate being analysed, and the standard refers to the relevant SRM.

2.4. Elemental analysis

The relative abundance within each sample was measured for 31 different elements (Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Cd, Sn, Sb, Nd, Hf, Pb, Bi, At, and U) using XRF. The samples were applied to a Perspex panel, which was cleaned with ethanol beforehand. Once cleaned, the middle of the Perspex was lined with double-sided adhesive tape. Intervals of 2 cm were then measured along the adhesive, which was achieved by interspersing each interval with 1 cm tape. The result was a grid of adhesive squares. Each sample had 3 replicates to validate the data, and each replicate was added on the adhesive sections of the grid. The tools were cleaned with ethanol in between samples to prevent cross-contamination. Once each replicate was applied to the tape, they were flattened with a spatula to ensure homogenous thickness, resulting in a grid of approximately 4 cm^2, and 2 mm in height (Gadd, et al., 2018).

The Perspex panel containing the lined powders was then loaded onto the sample stage of the Itrax μXRF high-resolution core scanner at ANSTO for analysis. Scans were set to an exposure time of 10 s, and 1000 μm resolution, with a 55 mA current and 30 kV voltage. The output spectra were reprocessed to the model spectra using Q-Spec 8.6.0 software, which also accounted for elemental inferences and sum peaks. A total of 844 scans were conducted across the Kakadu plum powders and potential adulterants. The average of each sample was used to report the relative elemental abundance.

2.5. Statistical analyses

The mean values of the stable carbon and nitrogen isotopes and elemental replicates were calculated for each sample, and then normalised using min-max scaling. Univariate analysis (Kruskal-Wallis ANOVA) followed by a post hoc Dunn's test, was performed to study the differences in the isotopic ratios of overseas, NAAKPA and commercially available Australian powder (AU-CAP) sample groups ($p < 0.05$). Considering the limited sample size of the Australian powders, a normal distribution was not assumed, hence the Kruskal-Wallis test was used. The isotope ratios are depicted through a stable isotope biplot. The majority of overseas samples listed alternate plant products, despite being ordered as "Kakadu plum" (Table 1). Thus, we compared the isotope values of overseas samples against alternative substances listed on the product labels, and potential adulterants such as corn and sugar. These products were chosen because they are inexpensive and widely available.

Multivariate analysis was used to determine which elements are drivers in distinguishing between the sample groups. In this instance, Non-metric Multi-dimensional Scaling (nMDS), based on Bray-Curtis distances was used. The nMDS is useful for non-normally distributed data, and the stress value determines the quality of nMDS (Clarke, 1993). Then, an analysis of similarity percentages (SIMPER) was used to identify the elements contributing towards significant differences between overseas-sourced and Australian powders (Clarke, 1993). Iso-elemental analyses combine both isotopic and elemental data, with previously successful applications to determine food provenance (Akamatsu et al., 2022; Drivelos & Georgiou, 2012; Gopi et al., 2019b; Kelly et al., 2005). Similarly in this research, iso-elemental analysis was conducted using nMDS to extract the distinguishing isotopes and elements between the sample groups. For both the elemental and iso-elemental analyses, an analysis of similarities (ANOSIM) was performed to understand the significance of the differentiation between groups (R value). Principal component analysis (PCA) is a common chemometric tool for determining food provenance, and previous research has applied PCA to iso-elemental analyses (Akamatsu, et al., 2022; Drivelos & Georgiou, 2012; Gopi et al., 2019b; Kelly et al., 2005). Hence, PCA was also applied to the iso-elemental analyses to determine if this approach also showed differences between sample groups, as presented in the Supplementary Information.

3. Results

3.1. Stable isotope analysis

Kruskal-Wallis ANOVA and Dunn's post hoc test for $\delta^{13}C$ showed a statistically significant difference between overseas and NAAKPA samples ($p = 0.003$). Overseas and AU-CAP did not indicate a significant difference ($p = 0.0632$). This may be attributed to the small sample size of AU-CAP powders, resulting in large variability within the sample group. When NAAKPA and commercially available Australian samples were consolidated into one category ("Australia" powders), they were found to be significantly different from overseas samples ($p = 0.0005$). This is validated in the SIA biplot (Fig. 1), which shows a distinction between the local and overseas samples.

All overseas powders have $\delta^{13}C$ values exceeding the threshold for C_3 plants, indicating they are either CAM or C_4 plants and therefore are not Kakadu plum (Francois, Fabrice, & Didier, 2020; O'Leary, 1988). There is no significant difference between the two Australian powders (NAAKPA and AU-CAP, $p = 1$). By contrast, there were no statistically significant differences observed for $\delta^{15}N$ across all sample groups ($p = 0.437$). Overseas samples were widely dispersed (SD: 4.02), compared to the NAAKPA and AU-CAP samples (SD: 1.81 and 1.65 respectively). Of the overseas samples, 3 were below the limit of detection, however 2 indicated enriched nitrogen. Comparing the NAAKPA samples to the AU-CAP samples, there was no statistically significant difference in both the carbon and nitrogen stable isotopes, and the biplot shows overlap between these sample groups (Fig. 1). Based on the stable isotopes, $\delta^{13}C$ may be considered to be a distinguishing marker between Kakadu plums sourced locally compared to overseas samples.

Packaging information for overseas sourced 'Kakadu plum extract' cited a range of products, including Aloe vera, Chamomile, Devils claw, Grapefruit, Hawthorn, and Iceland moss. When comparing the isotopic composition of these putative sources with those measured for the samples (Fig. 2), we conclude that only the Aloe vera was potentially true to the packaging information. Overseas samples labelled as Chamomile, Devils claw, Grapefruit, Iceland moss and Devils claw are highly enriched in $\delta^{13}C$ compared to these cited source products.

3.2. Elemental analysis

When comparing the elemental analysis between the three groups, there was no statistically significant difference between NAAKPA, AU-CAP and overseas (ANOSIM $p = 0.506$, $R = -0.018$). However, when consolidating the Australian-sourced powders into one group, there was

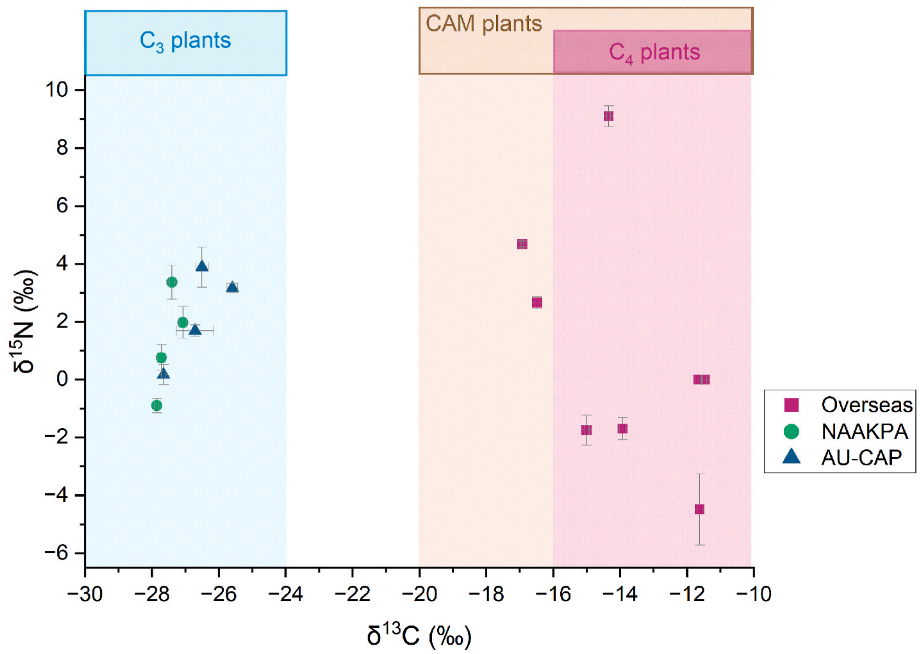

Fig. 1. δ^{13}C and δ^{15}N isotope biplot showing the differentiation between genuine NAAKPA-sourced Kakadu plum powder, and commercially available powders from e-commerce sites in Australia (AU-CAP) and overseas. The expected δ^{13}C isotope range of C_3, C_4 and CAM plants is shown.

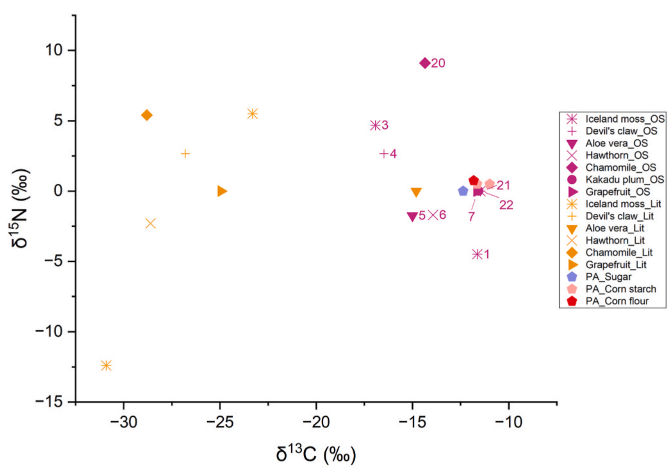

Fig. 2. δ^{13}C and δ^{15}N isotope biplot showing overseas sourced samples (pink), with accompanying legend description denoting the product listed on the packaging. The biplot shows the isotopic composition of Aloe vera (Winter, Aranda, & Holtum, 2005), Iceland moss (Wang & Wooller, 2006), Grapefruit extract (Rossmann, 2001) and remaining products (Khatri, et al., 2021) according to existing literature (orange). Potential adulterants are also included. Outline applied to the overseas sample labelled as aloe vera and genuine aloe vera.

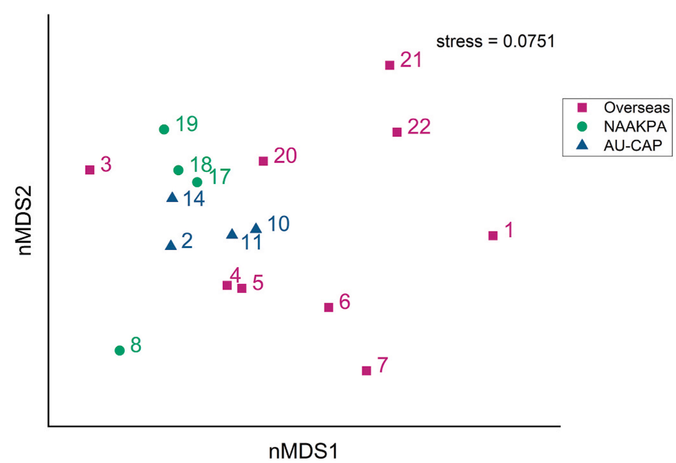

Fig. 3. nMDS differentiation between overseas, NAAKPA and commercially available Australian Kakadu plum samples using elemental composition.

a significant difference observed against the overseas samples (ANOSIM $p = 0.007$, $R = 0.263$). Likewise, nMDS showed a differentiation between Australian and overseas samples based on elemental composition (Fig. 3). The positioning of sample 8 in the nMDS plot (Fig. 3) is explained by the absence of seed in this powder, uniquely amongst the NAAKPA samples. Overseas samples showed high variability in elemental composition, with samples 3, 4 and 5 showing relatively higher levels of Potassium. Nine elements contributed to 39.5% of the differences in elemental composition between Australian and overseas sourced Kakadu plum extract (Table 3), with lower levels of Cadmium and Potassium in the overseas product being the most important difference.

3.3. Iso-elemental analysis

Given the standalone isotope and elemental analyses showed little significant difference between the Australian-sourced powders (NAAKPA and AU-CAP), the iso-elemental analysis consolidated these groups into an "Australia" category. The combination of isotopic and elemental composition shows clustering similar to those derived from the elemental composition (Fig. 4). Similar to Fig. 3, the positioning of sample 3 is explained by high relative abundance of Potassium. The dissimilarity between the Australian and overseas groups is greater using iso-elemental composition, in comparison with using elemental abundance only (ANOSIM $p = 0.001$, $R = 0.391$). Principal components analysis further confirmed the results in Fig. 4 (see Fig. S1).

4. Discussion

The commercial interest in the Kakadu plum presents positive economic opportunities for First Nations harvesters (Gorman, Brad, &

Table 3
Results of SIMPER analysis showing elements contributing most to differences between overseas and Australian-sourced Kakadu powder. Asterisks denote significant differences at $p < 0.05$ *, $p < 0.001$ ** and $p < 0.001$ ***.

Element	Average abundance		Average dissimilarity	Dissimilarity SD	Cumulative contribution %	
	Overseas	Australia				
Potassium	0.259	0.732	0.058	0.013	5.8	**
Cadmium	0.116	0.603	0.053	0.017	11.1	**
Tin	0.264	0.716	0.052	0.015	16.3	**
Copper	0.221	0.674	0.049	0.011	21.2	***
Hafnium	0.316	0.614	0.043	0.011	25.5	*
Arsenic	0.683	0.454	0.038	0.010	29.3	*
Rubidium	0.051	0.377	0.037	0.013	33.0	**
Magnesium	0.245	0.539	0.033	0.009	36.3	**
Chlorine	0.177	0.333	0.032	0.007	39.5	**

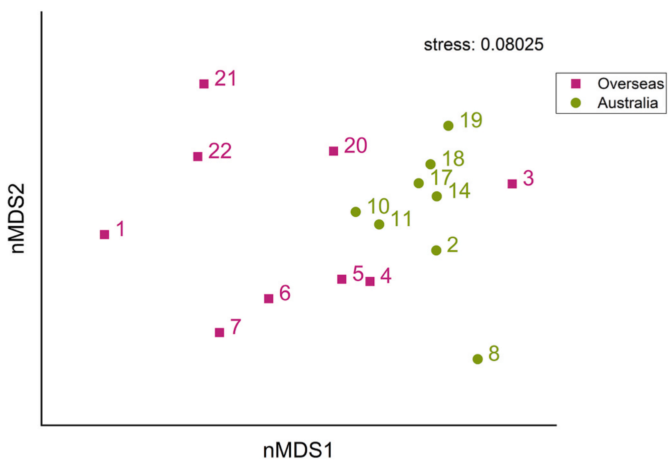

Fig. 4. nMDS differentiating overseas and Australian samples using iso-elemental composition.

Clancy, 2019); however, there are issues to consider to commercialise the fruit. Commercialisation of the Kakadu plum has emerged since the mid-1990's as a consumer product within the nutraceutical, cosmetic, food and beverage sectors (Gorman, et al., 2020). However, as our analysis has demonstrated, the international market in Kakadu Plum extract is rife with fraudulent activity. Of nine samples purchased on e-commerce websites as Kakadu plum, only one was labelled as Kakadu plum in customs information, three labelled as Kakadu plum in packaging, and of these none could possibly have been derived from Kakadu plum, because their $\delta^{13}C$ signatures were consistent with C_4 or CAM plants rather than C_3 plants. Moreover, except for the sample labelled as aloe vera, their $\delta^{13}C$ signatures were not even consistent with the product cited in the customs documentation or package label. Considering that Kakadu plum is uniquely available in Australia, the motive for listing alternate plant products on the product packaging and customs documentation may presumably be employed as a tactic to avoid detection. Overseas samples 7, 21 and 22 were labelled as "Iceland moss", "Kakadu plum", and "Grapefruit" respectively, despite all samples being advertised under the name of "Kakadu plum extract". Regardless of these alternate products mentioned on the product labelling, these three stated powders from overseas suppliers have $\delta^{13}C$ values similar to common, cheaply sourced products such as sugar and corn starch (Fig. 2).

The overseas sourced products were highly deficient in a range of elements characteristic of the genuine product, and elemental analysis also showed a high level of discrimination between genuine and fraudulent products (Table 3, Fig. 3). Potassium, chlorine and rubidium were key differentiators between overseas samples, with potassium contributing the greatest difference between groups (Table 3). This corroborates previous studies demonstrating that genuine Kakadu plum has characteristically high abundance of potassium, chlorine and rubidium (Konczak, et al., 2009; Mazumder et al., 2021). This may be attributed to association between high potassium levels and drought resistance in plants (Li, Yat, Yap, Lim, & Chan, 2011). Overseas sample 3 was an outlier, with potassium abundance similar to Australian powders (Figs. 3 and 4). However, the $\delta^{13}C$ value of sample 3 demonstrates that it cannot be Kakadu plum (Fig. 1). Overall, the SIMPER shows that powders sourced from overseas providers have lower elemental abundance compared to the Australian samples (Table 3). The one exception is arsenic, whereby overseas powders had higher concentrations compared to the Australian powders.

Although standalone elemental composition demonstrated a statistically significant difference between Australian and overseas samples (Fig. 3), our results show that the combination of isotopic and elemental composition shows a stronger statistically significant difference (Fig. 4, Fig. S1). This aligns with previous studies comparing isotope, elemental, and iso-elemental approaches, with the latter approach providing the greatest accuracy (Gopi et al., 2019a). In this instance, $\delta^{13}C$ is a key determinant in distinguishing between Australian and overseas powder, and this variable alone yielded the highest statistical difference between the Australian and overseas groups. Considering the complexity of international food supply chains, and the multiple occurrences of food fraud observed, specific techniques such as DNA profiling could prove difficult, especially without an established database. Therefore, at present $\delta^{13}C$ analysis remains a simple and unequivocal test applicable to the range of samples fraudulently marketed as Kakadu plum internationally. This is applicable regardless of products which have been mislabelled as other C_3 products. As fraudsters develop sophisticated methods to avoid detection, such as the use of C_3 sweeteners, iso-elemental technology will prove useful in identifying products which are not the genuine Kakadu plum.

Several factors have made Kakadu plum susceptible to food fraud. First, it is difficult to distinguish genuine and fraudulent powder by visual inspection (Sammut, Gopi, Saintilan, & Mazumder, 2021), and Kakadu plum is usually sourced wholesale in powder form, then used as an ingredient in nutraceutical products, health supplements, and personal care products (Laurie, 2020). Secondly, limited availability of ripe Kakadu plum fruit can contribute to an undersupply of the genuine product. Kakadu plum is generally wild harvested by hand, and further development of farming methods and labour are required to meet growing consumer demand (Laurie, 2020). In the interim, the outstripping demand over supply makes Kakadu plum a premium and expensive product, with genuine suppliers exposed to being undercut by fraudulent products.

The social and cultural significance of the Kakadu plum means that the observed fraudulent activities have ramifications beyond the financial loss for First Nations harvesters. First Nations communities have been ethically harvesting the fruit for generations and have developed strong traditional knowledge of how to grow and care for Kakadu plum (NAAKPA, n.d.). Overall, food fraud is detrimental to the passing down of intergenerational knowledge and training for First

Nations people. Further, the current legislative landscape is inadequate and is yet to regulate food fraud as a criminal act (Kelly, et al., 2005; Lindley, 2022). This fragmentation is an opportunity for fraudulent activities to occur, and improvements are required to support the commercialisation of Kakadu plum, and the bushfoods sector overall. The nascent First Nations Australian bushfoods industry requires oversight and robust legislation which addresses the concerns and interests of several stakeholder groups, including not only consumers, but also harvesters.

The results of this study demonstrate that overseas suppliers are capable of supplying fake Kakadu plum powders into Australia. Given the complexities of our food systems, a collaborative approach between regulation, and innovative technology via research parties, may be the most appropriate response to prevent food fraud. Our analysis of genuine and fraudulent products suggest that iso-elemental technology is sufficient to easily screen samples, and improved regulation will be required to protect the emerging Kakadu plum industry and ensure the benefits of commercialisation are enjoyed by First Nations communities.

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CRediT authorship contribution statement

Mariel Keaney: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Debashish Mazumder:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **Carol V. Tadros:** Writing – review & editing, Supervision, Software, Data curation, Conceptualization. **Jagoda Crawford:** Writing – review & editing, Supervision, Software, Conceptualization. **Patricia S. Gadd:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Paul Saeki:** Writing – review & editing, Resources, Funding acquisition. **Jesmond Sammut:** Writing – review & editing, Conceptualization. **Neil Saintilan:** Writing – review & editing, Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors of this paper do not have any financial or personal relationships with other people or organisations that could inappropriately influence this manuscript.

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

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References

ABARES. (2023). *Snapshot of Australian agriculture 2023*. Canberra.

Akamatsu, F., Shimizu, H., Hayashi, S., Kamada, A., Igi, Y., Koyama, K., et al. (2022). Chemometric approaches for determining the geographical origin of Japanese Chardonnay wines using oxygen stable isotope and multi-element analyses. *Food Chemistry, 371*, Article 131113.

Akter, S., Netzel, M. E., Fletcher, M. T., Tinggi, U., & Sultanbawa, Y. (2018). Chemical and nutritional composition of Terminalia ferdinandiana (Kakadu plum) Kernels: A novel nutrition source. *Foods, 7*(4), 60.

Brand, J. C., Cherikoff, V., Lee, A., & Truswell, A. S. (1982). An outstanding food source of vitamin C. *The Lancet, 320*(8303), 873.

Brand Miller, J., James, K. W., & Maggiore, P. M. A. (1993). *Tables of Composition of Australian aboriginal foods. Canberra, A.C.T.* Aboriginal Studies Press.

Chung, I. M., Park, S. K., Lee, K. J., An, M. J., Lee, J. H., Oh, Y. T., et al. (2017). Authenticity testing of environment-friendly Korean rice (Oryza sativa L.) using carbon and nitrogen stable isotope ratio analysis. *Food Chemistry, 234*, 425–430.

Clarke, K. R. (1993). Non-parametric multivariate analyses of changes in community structure. *Australian Journal of Ecology, 18*(1), 117–143.

Cozzolino, D., Phan, A. D. T., Netzel, M. E., Smyth, H., & Sultanbawa, Y. (2021). The use of vibrational spectroscopy to predict vitamin C in Kakadu plum powders (Terminalia ferdinandiana Exell, Combretaceae). *Journal of the Science of Food and Agriculture, 101*(8), 3208–3213.

Deng, X., Liu, Z., Zhan, Y., Ni, K., Zhang, Y., Ma, W., et al. (2020). Predictive geographical authentication of green tea with protected designation of origin using a random forest model. *Food Control, 107*, Article 106807.

Drivelos, S. A., & Georgiou, C. A. (2012). Multi-element and multi-isotope-ratio analysis to determine the geographical origin of foods in the European Union. *TrAC, Trends in Analytical Chemistry, 40*, 38–51.

Dunlop, C. R., Leach, G. J., & Cowie, I. D. (1995). Combretaceae. In *Flora of the Darwin region* (Vol. 2, pp. 142–150). Darwin: Conservation Commission of the Northern Territory.

Francois, G., Fabrice, V., & Didier, M. (2020). Traceability of fruits and vegetables. *Phytochemistry, 173*, Article 112291.

Gadd, P., Gopi, K., Sammut, J., Saintilan, N., Crawford, J., & Mazumder, D. (2018). Itrax micro X-ray fluorescence (µXRF) for soft biological tissues. *MethodsX, 5*, 1267–1271.

Gonzalvez, A., Armenta, S., & de la Guardia, M. (2009). Trace-element composition and stable-isotope ratio for discrimination of foods with Protected Designation of Origin. *TrAC, Trends in Analytical Chemistry, 28*(11), 1295–1311.

Gopi, K., Mazumder, D., Sammut, J., & Saintilan, N. (2019). Determining the provenance and authenticity of seafood: A review of current methodologies. *Trends in Food Science & Technology, 91*, 294–304.

Gopi, K., Mazumder, D., Sammut, J., Saintilan, N., Crawford, J., & Gadd, P. (2019a). Combined use of stable isotope analysis and elemental profiling to determine provenance of black tiger prawns (Penaeus monodon). *Food Control, 95*, 242–248.

Gopi, K., Mazumder, D., Sammut, J., Saintilan, N., Crawford, J., & Gadd, P. (2019b). Isotopic and elemental profiling to trace the geographic origins of farmed and wild-caught Asian seabass (Lates calcarifer). *Aquaculture, 502*, 56–62.

Gorman, J. T., Brad, C., & Clancy, T. F. (2019). Management Program for Terminalia ferdinandiana in the northern territory of Australia 2019-2023. In *Darwin*.

Gorman, J. T., Wurm, P. A. S., Vemuri, S., Brady, C., & Sultanbawa, Y. (2020). Kakadu plum (Terminalia ferdinandiana) as a sustainable indigenous Agribusiness. *Economic Botany, 74*(1), 74–91.

Hegarty, M. P., Hegarty, E. E., & Wills, R. B. H. (2001). *Food safety of Australian plant bushfoods*. Canberra: RIRDC.

Kelly, S., Heaton, K., & Hoogewerff, J. (2005). Tracing the geographical origin of food: The application of multi-element and multi-isotope analysis. *Trends in Food Science & Technology, 16*(12), 555–567.

Khatri, P. K., Larcher, R., Camin, F., Ziller, L., Tonon, A., Nardin, T., et al. (2021). Stable isotope ratios of herbs and spices commonly used as herbal infusions in the Italian market. *ACS Omega, 6*(18), 11925–11934.

Konczak, I., Maillot, F., & Dalar, A. (2014). Phytochemical divergence in 45 accessions of Terminalia ferdinandiana (Kakadu plum). *Food Chemistry, 151*, 248–256.

Konczak, I., Zabaras, D., Dunstan, M., Aguas, P., Roulfe, P., & Pavan, A. (2009). Health benefits of Australian native foods: An evaluation of health-enhancing compounds. In *Canberra*.

Laurie, S. (2020). *Australian native foods and botanicals 2019 20 market study*.

Li, A., Yat, Y. W., Yap, W. K., Lim, C. W., & Chan, S. H. (2011). Discriminating authentic Nostoc flagelliforme from its counterfeits by applying alternative ED-XRF and FTIR techniques. *Food Chemistry, 129*(2), 528–532.

Lindley, J. (2022). Food regulation and policing: Innovative technology to close the regulatory gap in Australia. *Journal of Consumer Protection and Food Safety*, 1–10.

Malo, N., Mazumder, D., Crawford, J., Gadd, P., Gopi, K., Saintilan, N., et al. (2023). Evaluating the application of portable handheld X-ray fluorescence (XRF) scanner for determining seafood provenance: A case study on Penaeus monodon. *Foods, 12*(15), 2874.

Martino, J. C., Crawford, J., Gadd, P., Sammut, J., Saintilan, N., & Mazumder, D. (2023). A novel use of a handheld elemental scanner for authenticating prawn provenance. *Food Control, 151*, Article 109813.

Mazumder, D., Martino, J., Gopi, K., Gadd, P., & Crawford, J. (2021). *Kakadu plum provenance: Pilot study Project report*. Report prepared for the Indigenous Land and Sea Corporation.

NAAKPA. (n.d.). About us. In.

O'Leary, M. H. (1988). Carbon isotopes in photosynthesis. *BioScience, 38*(5), 328–336.

Richmond, R., Bowyer, M., & Vuong, Q. (2019). Australian native fruits: Potential uses as functional food ingredients. *Journal of Functional Foods, 62*, Article 103547.

Rossmann, A. (2001). Determination of stable isotope ratios in food analysis. *Food Reviews International, 17*(3), 347–381.

Rutar, J. M., Strojnik, L., Nečemer, M., Bontempo, L., & Ogrinc, N. (2023). Determining the authenticity of spirulina dietary supplements based on stable isotope and elemental composition. *Foods, 12*(3), 562.

Sammut, J., Gopi, K., Saintilan, N., & Mazumder, D. (2021). Facing the challenges of food fraud in the global food system. In C. M. Galanakis (Ed.), *Food authentication and traceability* (pp. 35–63). Academic Press.

Sirdaarta, J., & Matthews, B. (2015). Kakadu plum fruit extracts inhibit growth of the bacterial triggers of rheumatoid arthritis: Identification of stilbene and tannin components. *Journal of Functional Foods, 17*, 610–620.

Tan, A. C., Hou, D. X., Konczak, I., Tanigawa, S., Ramzan, I., & Sze, D. M. Y. (2011). Native Australian fruit polyphenols inhibit COX-2 and iNOS expression in LPS-activated murine macrophages. *Food Research International, 44*(7), 2362–2367.

Wang, Y., & Wooller, M. (2006). The stable isotopic (C and N) composition of modern plants and lichens from northern Iceland: With ecological and paleoenvironmental implications. *Jökull Journal, 56*, 27–38.

Whitehead, P. J., Gorman, J., Griffiths, A. D., Wightman, H., Massarella, H., & A, J. (2006). Feasibility of small scale commercial native plant harvests by indigenous communities. In *Canberra*.

Williams, D. J., Edwards, D., Pun, S., Chaliha, M., & Sultanbawa, Y. (2014). Profiling ellagic acid content: The importance of form and ascorbic acid levels. *Food Research International, 66*, 100–106.

Winter, K., Aranda, J., & Holtum, J. A. (2005). Carbon isotope composition and water-use efficiency in plants with crassulacean acid metabolism. *Functional Plant Biology: FPB, 32*(5), 381–388.

Zhou, X., Taylor, M. P., Salouros, H., & Prasad, S. (2018). Authenticity and geographic origin of global honeys determined using carbon isotope ratios and trace elements. *Scientific Reports, 8*(1), Article 14639.