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Metals in New Zealand *Undaria pinnatifida* (Wakame)

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Abstract

***Undaria pinnatifida*, Wakame is a popular edible seaweed in its native Asia and was first recorded in New Zealand in Wellington Harbor in 1987. It is classified as an unwanted species under the Biosecurity Act 1993, but there is growing interest in harvesting this seaweed for human consumption. The aim of this study was to evaluate the concentrations of metals in *U. pinnatifida* from several locations (Marlborough Sounds and Wellington harbor) and across seasons. In brief, the highest monthly mean concentration of metals found in New Zealand wild *U. pinnatifida* was Ca (16.97g·kg^{-1}), K (48.48 g·kg^{-1}), Mg (9.47 g·kg^{-1}), P (12.05 g·kg^{-1}), Cr (1.04 mg·kg^{-1}), Cu (3.78 mg·kg^{-1}), Mn (14.61 mg·kg^{-1}), Ni (2.78 mg·kg^{-1}), Se (0.83 mg·kg^{-1}), Zn (35.03 mg·kg^{-1}), As (46.71 mg·kg^{-1}), Cd (2.91 mg·kg^{-1}), Hg (0.042 mg·kg^{-1}) and Pb (0.31 mg·kg^{-1}). These results showed that New Zealand *U. pinnatifida* is a good source of the nutritionally important minerals calcium, magnesium, potassium and phosphorus. They also contained trace amounts of minerals such as chromium, copper, manganese, nickel, selenium and zinc. Contaminants such as arsenic, cadmium, mercury and lead were found at very low, safe, levels.**

Keywords

Metals, *Undaria pinnatifida*, Wakame

1. Introduction

The importance of health foods is becoming widely acknowledged and as a result the consumption of seaweed in Western countries has gradually increased. Seaweeds have been employed as food and medicines for a long period of time in many Asian countries such as Japan, Korea, China, Vietnam, Indonesia and Taiwan [1]. Seaweed is an excellent source of nutrients such as fiber, polyunsaturated fatty acids, vitamins, proteins, and miner-

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als [2]. Seaweeds bio-accumulate essential elements for example Cr, Ni, Se, Mg, Ca, K and Zn at higher rates than terrestrial vegetation [3]. But seaweed can also contain non-essential elements, such as As, Pb Cd or Hg due to environmental pollution [3]. In brief, metal uptake occurs in two steps: The first is passive uptake; a surface reaction, where metals are absorbed by algal surfaces through electrostatic attraction to negative sites [4] [5]. This is independent of factors which influence the metabolism such as temperature, light, pH or age of the plant, but it is influenced by the relative abundance of elements in the surrounding water [4]. The second way metals can be taken up into seaweeds is a slower active uptake in which metal ions are transported across the cell membrane into the cytoplasm and is more dependent upon metabolic processes [4] [5].

Wakame, *U. pinnatifida*, is the most popular edible seaweed in Asia. It has a sweet flavour and is most often served in soups and salads [6]. Japan Korea and China are the main suppliers and use the most *U. pinnatifida* and related products and have already successfully developed cultivation techniques and commercialisation of *U. pinnatifida* related products. The current aquaculture production is between 450,000 and 500,000 tonnes in Japan and Korea respectively with China producing a few hundred tonnes [7]. The global harvest of wild *U. pinnatifida* was 2742 tonnes in 2011 [8].

Raw Wakame contains substantial amounts of essential trace elements such as manganese, copper, cobalt, iron, nickel and zinc, similar to Kombu (kelps from the Family Laminariaceae) and Hijiki (*Sargassum fusiforme*) [9]. Processed Wakame is used for various instant foods such as noodles and soups [6] [9]. The most common dried Wakame product is made from blanched and salted Wakame which is washed with freshwater to remove salt, cut into small pieces, dried in a flow-through dryer and passed through sieves to sort the different sized pieces [9] [10]. It has a long storage life and has a fresh green colour when rehydrated [6] [9]. In addition to human consumption as a regular food item, there is growing interest of *U. pinnatifida* in the health food and pharmaceutical markets [11]. *U. pinnatifida* has proved to be a very useful source of Fucoidan [12], a fucose-containing sulfated polysaccharide found in brown algae and proven to have numerous health benefits including: anticoagulant anti-thrombotic, immunomodulation, anti-inflammation, antitumor/anti-proliferation/anticancer, angiogenesis, cardioprotection, antivirus, gastric mucosal protection and neuroprotection [13]. Antioxidant compounds such as Fucoxanthin, have also been extracted from *U. pinnatifida* [14].

The population of *U. pinnatifida* has been extended by accidental introductions and translocations for aquaculture from China and to Atlantic France and Mediterranean France however most movement of *U. pinnatifida* has been by unintentional introductions to Europe, USA, Australia, New Zealand, Mexico and Argentina [9] [15] [16]. *U. pinnatifida* was first recorded in New Zealand in Wellington Harbor in 1987 [17] and were most likely transported in the ballast of foreign fishing vessels [18]. At present, *U. pinnatifida* in New Zealand has been reported from Great Barrier Island, Auckland (Waitemata Harbor), Coromandel, Tauranga, Gisborne, Napier, Port Taranaki, Wellington and the Wellington region of Cook Strait in the North Island, in the Marlborough Sounds, Nelson, Golden Bay, Kaikoura, Lyttelton, Akaroa, Timaru, Oamaru, Dunedin Harbor, Bluff in the South Island and also from Stewart Island and the Snares Islands [18]. Unlike more tropical climates where there is significant dieback in warm conditions, *U. pinnatifida* seems to persist year long in New Zealand waters [18].

In 2000 *U. pinnatifida* was classified as an unwanted species under the Biosecurity Act 1993 under section 164c [19]. However, by 2004 a policy was developed that allowed the commercial harvest of the seaweed in two situations: where it was taken as a by-product of another activity, for example, the clearing of mussel farming lines or as part of a control or eradication programme [19]. In 2010 the government reviewed the policy and allowed the harvest of *U. pinnatifida* from artificial structures and farming in some defined areas which already had high levels of infestation [20].

Given that *U. pinnatifida* is regularly consumed by humans and it is now able to be harvested or farmed as a commercial product in some parts of New Zealand, it is important to examine the nutritional quality of this seaweed in New Zealand. This research focused on metals components in *U. pinnatifida* as these metals have been shown to have impact on human health. Fourteen metals, Ca, K, Mg, P, Cr, Cu, Mn, Ni, Se, Zn, As, Cd, Hg and Pb were investigated in this study.

2. Material and Methods

2.1. Sampling Sites

Sampling for this research focused on four different sites. *U. pinnatifida* was collected from two mussel farms from Port Underwood, South Island, New Zealand. The two farms were designated as PE 327 (41˚20'36.89"S, 174˚07'50.17"E) and 106 (41˚19'35.05"S, 174˚08'56.71"E) (**Figure 1**). Sampling of PE 327 was carried out on a monthly basis from April to October 2011. Sampling of 106 was carried on monthly basis from July to October 2011. Every month six plants were collected from each farm. The license to harvest the *U. pinnatifida* was issued by MAF Biosecurity New Zealand, Biosecurity Act 1993 Section 52 Permission granted to Wakatu Seafoods Ltd.

The two additional sites were integrated into this study from August to November 2011. They were located on the eastern and western side of Miramar Peninsula in Wellington Harbour, New Zealand. The eastern sampling site was designated as Wellington site A, located in Shelley Bay (41˚17'38.082"S, 174˚49'16.110"E), the western sampling site is designated as Wellington site B, located in Worser Bay (41˚18'46.207"S, 174˚49'49.678"E) (**Figure 1**). Six replicate plants were collected from each farm. The license to harvest the *U. pinnatifida* was issued by MAF Biosecurity New Zealand Biosecurity Act 1993 Section 52 Permission granted to Sustainable Seafood NZ Ltd.

2.2. Seaweed Pre-Treatment

The samples collected from PE 327 and 106 were rinsed to remove debris and epiphytic organisms from the thallus. The blade was separated from the sporophyll, frozen, lyophilized, ground to a fine powder and stored in polyethyene bottles to await analysis.

The samples collected from Wellington harbor were rinsed to remove debris and epiphytic organisms from the thallus. The blades were separated from the sporophylls. The samples were dried to constant weight at 60˚C in a Sanyo MOV-112 laboratory oven, ground to fine powder and stored in polystyrene bottles to await analysis.

2.3. Metals Analysis

In brief, the dried, ground samples of *U. pinnatifida* were digested in acid, filtered, diluted and measured on a Varian Liberty ICP AX Sequential inductively coupled plasma atomic emission spectroscopy (ICP-AES). Acid digestions were carried out by adding an 0.5 g of sample to 10 mL of concentrated Laboratory Analytical Grade 70% HNO_3 in acid digestion block (VELP Scientifica DK20 heating digester). The reaction mixture was heated at 90˚C for 30 minutes and then 110˚C for 2 hours. 5 mL of 80% $HClO_4$ was then added and heating discontin ued when dense white fumes appeared. After cooling, the mixture was filtered through what man number 42 filter paper. The resulting solution was finally made up to 50 mL with deionized water in a volumetric flask. Each blade and sporophyll sample from a single plant harvested was subjected to two replicate metals analysis experiments. The ICP AES was running at Power of 1.2 kW, plasma flow at 15.0 L/min, auxiliary flow at 1.5 L/min, nebulizer Pressure at 200 kPa, replicate time at 1 second, stability time of 15 seconds and PMT Voltage of

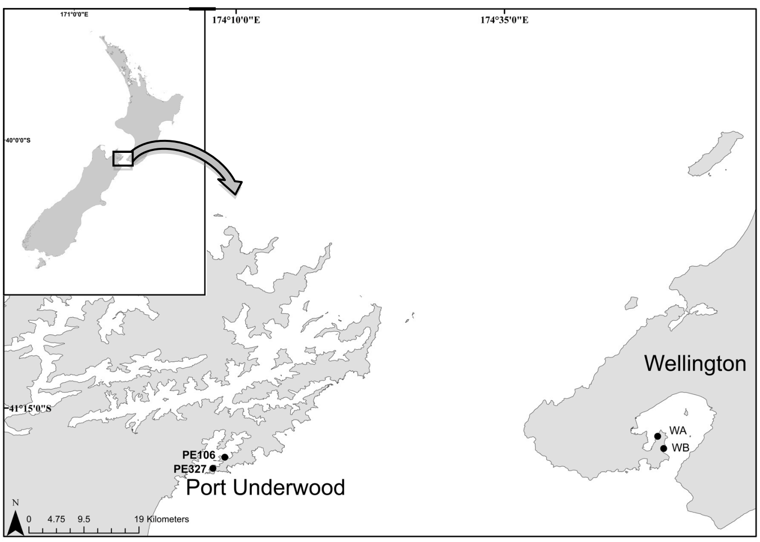

Figure 1. Location of *Undaria pinnatifida* samples.

650 V. The ICP AES sample introduction settings was set at default, sample uptake of 30 seconds, rinse time of 10 seconds and pump rate at 15 rpm.

3. Results and Discussion

Our results demonstrate that *U. pinnatifida* contained variety of minerals and heavy metals and that these varied in content across the time period investigated. Essential minerals for human health such as Ca, K, Mg and P were the most abundant minerals while Cr, Cu, Mn, Ni, Se and Zn contents existed in trace amounts. **Table 1** shows the range of metal contents of *U. pinnatifida* collected from four different sites in New Zealand.

Various agencies e.g. the World Health Organisation (WHO) and the National Health and Medical Research Council of Australia (NHMRC) have recommended daily intake (RDI), upper level of intake (UI), tolerable daily intake (TDI) and adequate intake (AI) for some of the metals in this study. In addition, the WHO has also provided guidelines of provisional tolerable weekly intakes (TWI) for some of the more harmful heavy metals in this study. We have determined the amount of each metal contained in an average serving of Wakame seaweed salad. This is based on 40 g (wet weight) serving (approximately 4 g dry weight). These quantities are compared to the WHO and NHMRC guidelines in **Table 2**. Mean data across all sites from October 2011 was used, because most metals displayed the highest concentration in that month and October is the most likely harvesting period due to the large size of the plants at that time. A comparison of arsenic was not carried out because available guidelines only govern inorganic arsenic levels, while total arsenic level was measured in this study.

3.1. General Patterns

There were significant differences between metal contents in the blade and sporophyll tissues, with the blade generally containing higher concentration of metals than the sporophyll. This distribution may be able to be explained by the following mechanism. Absorption of elemental ions into the algal cells first occurred in the blade when the division and enlargement of the cells occurred, and the elements can be secondarily transferred to the sporophyll by active transport though inner hyphae in kelp species [20]-[22]. Therefore, the lower metal concentrations in the sporophyll can be explained by the difference of transfer tendency of the metals through the transport system.

3.2. Calcium

There was an increase in the blade tissue content of calcium in 327 between May and June, and then it became relatively stable. In general the blade tissue contents of Ca in 327 were slightly higher than the other three sites. A similar pattern of fluctuations for the sporophyll tissue content of Ca had been observed for all four sites. PE 327 had slightly higher sporophyll tissue content of Ca than the other three sites. The blade values were comparable with previous research of *U. pinnatifida* e.g. 12.8 $g\cdot kg^{-1}$ from New Zealand [23], 9.31 $g\cdot kg^{-1}$ recorded in Spain [24] and 9.5 $g\cdot kg^{-1}$. [25]. The World Health Organisation recommends the daily intake (RDI) of Ca is between 1 g/day and 1.3 g/day for adult [26]. Whereas the nutrient reference values for Australia and New Zealand states that the upper level of intake (UI) for Ca is 2.5 g/day and the recommended daily intake for adult is 1 g/day [27].The Australia/New Zealand food standards code suggests the Care commended dietary intake for adult is 0.8 g [28]. Consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Port Underwood would contribute 2.8% and 3.6% of the RDI by WHO/FAO and NHMRC respectively while the same sample from Wellington would contribute 3.1% and 4.1% of the RDI by WHO/FAO and NHMRC respectively.

3.3. Potassium

There were steady increases of blade content of potassium in PE 327 from April to October, a similar trend also observed along the sampling period in farm 106 and both Wellington sites between August and October. A similar pattern of fluctuations of the sporophyll tissue content of K had been observed for all four sites but the sporophyll content of K in 106 had noticeable lower concentration than the other three sites. The blade values were lower than in previous research e.g. 71.2 $g\cdot kg^{-1}$ from New Zealand [23], 86.99 $g\cdot kg^{-1}$ recorded in Spain [24] and 56.91 $g\cdot kg^{-1}$ [25]. The World Health Organisation do not have a recommended intake of K but the nutrient reference values for Australia and New Zealand states that the adequate intake (AI) for K is 2.8 g/day and 3.8g/day for adult women and men respectively [27]. Consumption of 40 g (wet weight) *U. pinnatifida* obtained in October

Table 1. Metal contents of *Undaria pinnatifida* collected from four different sites in New Zealand (see methods for locations). Values are the range of the monthly means ± standard error (n = 6). Sampling months are indicated by superscript numbers (Jan = 1, Feb = 2, etc.).

Metal	Site	Blade	Sporophyll
Ca (g·kg^{-1})	PE 327	9.77 ± 0.148^{4} - 16.97 ± 0.45^{6}	7.88 ± 0.24^{4} - 8.75 ± 0.35^{6}
	106	8.26 ± 0.08^{8} - 9.07 ± 0.34^{10}	6.37 ± 0.13^{7} - 7.03 ± 0.39^{10}
	Wellington Site A	8.89 ± 0.17^{8} - 10.13 ±0.20^{10}	6.72 ± 0.17^{8} - 7.03 ± 0.055^{10}
	Wellington Site B	8.76 ± 0.20^{8} - 10.31 ± 0.40^{10}	7.20 ± 0.39^{8} - 7.41 ± 0.23^{10}
K (g·kg^{-1})	PE 327	19.42 ± 0.26^{5} - 45.86 ± 0.91^{10}	27.25 ± 0.27^{5} - 28.69 ± 0.86^{6}
	106	32.85 ± 0.33^{8} - 42.14 ± 0.59^{10}	15.18 ± 0.54^{7} - 16.10 ± 0.44^{10}
	Wellington Site A	29.49 ± 0.62^{8} - 44.68 ± 0.52^{10}	27.12 ± 0.88^{7} - 28.97 ± 0.29^{10}
	Wellington Site B	27.92 ± 0.62^{8} - 48.48 ± 0.56^{10}	26.21 ± 0.49^{11}- 27.08 ± 0.52^{10}
Mg (g·kg^{-1})	PE 327	6.83 ± 0.14^{4} - 9.21 ± 0.36^{10}	4.58 ± 0.36^{4} - 6.64 ± 0.32^{10}
	106	8.20 ± 0.16^{7} - 9.47 ± 0.31^{10}	5.75 ± 0.045^{8} - 6.16 ± 0.37^{10}
	Wellington Site A	8.34 ± 0.32^{8} - 9.23 ± 0.33^{10}	5.45 ± 0.14^{11}- 5.72 ± 0.11^{8}
	Wellington Site B	8.26 ± 0.21^{8}- 9.47 ± 0.22^{10}	7.30 ± 0.22^{8} - 7.59 ± 0.14^{10}
P (g·kg^{-1})	PE 327	9.28 ± 0.19^{7} - 12.05 ± 0.23^{10}	7.89 ± 0.16^{5} - 9.41 ± 0.30^{10}
	106	10.41 ± 0.19^{7} - 11.62 ± 0.26^{10}	6.60 ± 0.42^{7} - 7.76 ± 0.73^{10}
	Wellington Site A	9.09 ± 0.19^{8} - 10.31 ± 0.66^{10}	8.24 ± 0.053^{11}- 8.54 ± 0.13^{10}
	Wellington Site B	8.60 ± 0.43^{8} - 10.61 ± 0.43^{10}	7.99 ± 0.16^{8} - 8.71 ± 0.11^{10}
Cr (mg·kg^{-1})	PE 327	0.69 ± 0.094^{4} - 1.04 ± 0.21^{10}	0.76 ± 0.065^{4} - 0.92 ± 0.024^{6}
	106	0.74 ± 0.077^{8} - 0.78 ± 0.053^{7}	0.70 ± 0.027^{9} - 0.77 ± 0.016^{7}
	Wellington Site A	0.80 ± 0.093^{9} - 0.84 ± 0.020^{10}	0.68 ± 0.031^{8} - 0.74 ± 0.026^{10}
	Wellington Site B	0.64 ± 0.060^{8} - 0.73 ± 0.029^{10}	0.57 ± 0.06^{11} - 0.69 ± 0.019^{10}
Cu (mg·kg^{-1})	PE 327	3.08 ± 0.16^{7} - 3.78 ± 0.23^{10}	1.64 ± 0.16^{9} - 1.85 ± 0.11^{7}
	106	2.97 ± 0.22^{7} - 3.77 ± 0.23^{10}	1.84 ± 0.092^{8} - 2.44 ± 0.16^{10}
	Wellington Site A	2.28 ± 0.21^{8} - 2.62 ± 0.15^{10}	2.21 ± 0.10^{8} - 2.40 ± 0.12^{10}
	Wellington Site B	2.48 ± 0.27^{9} - 2.66 ± 0.12^{10}	2.33 ± 0.091^{9} - 2.64 ± 0.11^{10}
Mn (mg·kg^{-1})	PE 327	8.73 ± 0.58^{7} - 10.39 ± 2.45^{10}	4.79 ± 0.26^{7} -7.72 ± 0.85^{4}
	106	8.25 ± 0.67^{8} - 9.99 ± 1.26^{10}	5.59 ± 0.38^{7} - 6.26 ± 0.40^{10}
	Wellington Site A	12.57 ± 0.78^{9} - 14.61 ± 1.23^{10}	6.86 ± 0.59^{11} - 7.68 ± 0.24^{10}
	Wellington Site B	8.36 ± 0.17^{11}- 8.57 ± 0.19^{10}	7.46 ± 0.28^{11} - 7.93 ± 0.13^{10}
Ni (mg·kg^{-1})	PE 327	1.54 ± 0.39^{4} - 2.78 ± 0.12^{10}	1.14 ± 0.16^{5} - 1.62 ± 0.35^{4}
	106	1.81 ± 0.13^{7} - 2.24 ± 0.12^{10}	1.36 ± 0.045^{8} - 1.62 ± 0.18^{10}
	Wellington Site A	1.78 ± 0.11^{11} - 1.95 ± 0.067^{10}	1.50 ± 0.078^{11} - 1.69 ± 0.056^{8}
	Wellington Site B	1.91 ± 0.12^{8} - 2.10 ± 0.057^{10}	1.53 ± 0.27^{11} - 1.70 ± 0.050^{10}
Se (mg·kg^{-1})	PE 327	0.54 ± 0.017^{4} - 0.61 ± 0.016^{10}	0.18 ± 0.0173^{6} - 0.33 ± 0.030^{7}
	106	0.40 ± 0.02^{7} - 0.53 ± 0.056^{10}	0.37 ± 0.041^{9} - 0.40 ± 0.021^{10}

Continued

	Wellington Site A	0.80 ± 0.049^{9} - 0.83 ± 0.14^{8}	0.48 ± 0.039^{11} - 0.52 ± 0.03^{9}
	Wellington Site B	0.65 ± 0.11^{8} - 0.81 ± 0.078^{10}	0.38 ± 0.03^{8} - 0.48 ± 0.025^{10}
Zn (mg·kg^{-1})	PE 327	20.52 ± 1.63^{5} - 26.11 ± 2.71^{10}	14.18 ± 1.28^{5} - 18.60 ± 0.92^{10}
	106	22.60 ± 0.76^{7} - 27.30 ± 2.78^{10}	21.16 ± 1.70^{8} - 23.60 ± 2.33^{10}
	Wellington Site A	30.24 ± 1.64^{9} - 33.39 ± 3.99^{10}	13.70 ± 1.06^{8} - 15.41 ± 0.53^{10}
	Wellington Site B	29.41 ± 1.66^{9} - 35.03 ± 2.05^{10}	15.10 ± 1.03^{11} - 16.01 ± 0.49^{10}
As (mg·kg^{-1})	PE 327	40.54 ± 2.00^{10} - 46.71 ± 0.75^{5}	23.84 ± 1.49^{4} - 29.47 ± 1.75^{7}
	106	30.41 ± 1.52^{8} - 31.89 ± 2.22^{7}	23.94 ± 1.45^{8} - 29.23 ± 2.27^{7}
	Wellington Site A	34.79 ± 2.25^{11} - 42.88 ± 2.56^{8}	28.46 ± 5.87^{10} - 32.84 ± 2.30^{8}
	Wellington Site B	32.12 ± 1.77^{11} - 36.41 ± 3.30^{8}	30.03 ± 2.40^{8} - 31.27 ± 7.38^{9}
Cd (mg·kg^{-1})	PE 327	2.33 ± 0.21^{10} - 2.91 ± 0.097^{6}	1.82 ± 0.26^{10} - 2.19 ± 0.17^{5}
	106	1.57 ± 0.088^{8} - 1.74 ± 0.19^{10}	1.51 ± 0.059^{8} - 1.68 ± 0.11^{7}
	Wellington Site A	2.11 ± 0.13^{9} - 2.24 ± 0.17^{8}	1.97 ± 0.21^{10} - 2.10 ± 0.17^{8}
	Wellington Site B	1.82 ± 0.29^{11} - 2.21 ± 0.21^{8}	1.67 ± 0.32^{10} - 2.20 ± 0.4^{9}
Hg (mg·kg^{-1})	PE 327	0.023 ± 0.015^{5} - 0.040 ±0.017^{9}	No values
	106	0.024±0.0086^{7} - 0.040± 0.0026^{9}	No values
	Wellington Site A	0.021±0.010^{8} - 0.042± 0.020^{11}	No values
	Wellington Site B	0.021 ±0.0034^{8} - 0.037 ± 0.026^{11}	No values
Pb (mg·kg^{-1})	PE 327	0.22 ± 0.024^{10} - 0.29 ± 0.044^{4}	0.14 ± 0.0047^{4} - 0.29 ± 0.048^{5}
	106	0.24 ± 0.022^{10} - 0.30 ± 0.019^{7}	0.21 ± 0.015^{10} - 0.27 ± 0.017^{7}
	Wellington Site A	0.28 ± 0.018^{9} - 0.31 ± 0.022^{8}	0.23 ± 0.026^{10} - 0.25 ± 0.016^{9}
	Wellington Site B	0.25 ± 0.032^{11} - 0.29 ± 0.029^{9}	0.167±0.021^{10} - 0.174±0.0167^{8}

ber from Port Underwood and Wellington would contribute 4.8% and 5.1% of the AI recommended by NHMRC respectively.

3.4. Magnesium

There was an increasing trend for the blade tissue content of Mg in PE 327 between April and October. The blade tissue contents of Mg from August to October were very similar between the four sites. There was also an increasing trend between April and October for the sporophyll tissue content of Mg in PE 327. The other three sites showed some fluctuations of sporophyll tissue content of Mg, in which Wellington B site had slightly higher concentration than the other three sites between August and November. The blade values were similar to what had been found in previous research of *U. pinnatifida* e.g. 8.33 g·kg^{-1} [28] but lower than 11.81 g·kg^{-1} [24]. World Health Organisation recommends the daily intake (RDI) of Mg were 0.22 g/day and 0.26 g/day for adult women and man respectively. Whereas the nutrient reference values for Australia and New Zealand states that the upper level of intake (UI) for adult Mg is 0.35 g/day and the RDI for adult is between 0.31 and 0.42 g/day [27]. The Australia New Zealand food standards code suggests the Mg recommended dietary intake for adult is 0.32 g [28]. Consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Port Underwood and Wellington would both contribute 9% of the NHMRCRDI.

3.5. Phosphorus

There were fluctuations without noticeable trend for the blade tissue content of phosphorus at all four sites. A

Table 2. Consumption of 40 g (wet weight) of *Undaria pinnatifida* (blade tissues) obtained in October 2011. RDI = recommended daily intake; AI = adequate intake; UI = upper level of intake; TDI = tolerable daily intake (per 70 kg body weight); TWI = tolerable weekly intake (based on 70 kg body weight); WHO = World Health Organisation; FAO = Food and Agriculture Organisation of the United Nations; NHMRC = National Health and Medical Research Council of Australia.

Metal	WHO/FAO guidelines	NHMRC guidelines	% of WHO/FAO guidelines Port Underwood	% of NHMRC guidelines Port Underwood	% of WHO/FAO guidelines Wellington	% of NHMRC guidelines Wellington
Calcium (Ca)	1 - 1.3 g RDI	1 g RDI	2.8% of RDI	3.6% of RDI	3.1% of RDI	4.1% of RDI
Potassium (K)		2.8 - 3.8 g AI		4.8% of AI		5.1% of AI
Magnesium (Mg)		0.32 - 0.42 g RDI		9% of RDI		9% of RDI
Phosphorus (P)		1 g RDI		4.8% of RDI		4.2% of RDI
Chromium (Cr)		0.025 - 0.035 mg AI		11.8% of AI		9.6% of AI
Copper (Cu)		10 mg UI		0.15% of UI		0.11% of UI
Manganese (Mn)		5 - 5.5 mg AI		0.8% of AI		1.06% of AI
Nickel (Ni)	0.84 mg TDI		1.3% of TDI			1% of TDI
Selenium (Se)	0.026 - 0.034 mg RDI	0.06 - 0.07 mg RDI	7.1% of RDI	3.5% of RDI	9.5% of RDI	4.6% of RDI
Zinc (Zn)		8 - 14 mg RDI		0.78% of RDI		1% of RDI
Cadmium (Cd)	0.49 mg TWI		1.9% of TWI			1.8% of TWI
Mercury (Hg)	0.112 mg TWI		0.13% of TWI			0.12% of TWI
Lead (Pb)	1.75 mg TWI		0.054% of TWI			0.064% of TWI

similar pattern was also observed for the sporophyll tissue content of P. The blade values were higher than what had been found in previous research of *U. pinnatifida* e.g. 4.79 g·kg^{-1} [23] but lower than 4.50 g·kg^{-1} [25]. The nutrient reference values for Australia and New Zealand states that the upper level of intake (UI) of Pare 4 g/day for adult between 19 to 70 years old and 3 g/kg for adult above 70 years old and the recommended dietary intake (RDI) for adult is 1 g/day [27]. The Australia New Zealand food standards code suggests the P recommended dietary intake for adult is 1 g [28]. Consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Port Underwood and Wellington would contribute 4.8% and 4.2% of the NHMRC RDI respectively.

3.6. Chromium

There was an increasing trend between April and June for the blade tissue content of chromium in PE 327, it became relative stable until September and ended with another small increase in October. The blade tissue content of Cr from the other three sites showed some fluctuations across the sampling period. There was also an increasing trend between April and June for the sporophyll tissue content of Cr in farm PE 327, which became relative stable to the end of its sampling period. The sporophyll tissue contents of Cr in the other three sites were steady across the sampling period. The blade values were similar to previous research e.g. 0.74 mg·kg^{-1} [23] and 0.72 mg·kg^{-1} [25]. The nutrient reference values for Australia and New Zealand states that the adequate intake (AI) is 0.035 mg/day and 0.025 mg/day for adult men and women respectively [27].The Australia New Zealand food standards code suggests the Cr estimated safe and adequate daily dietary intake recommended for adult is 0.2 mg [28]. Therefore consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Port Underwood and Wellington would contribute 11.8% and 9.6% of the NHMRC recommended AI respectively.

3.7. Copper

The blade tissue contents of copper in the sites of Port Underwood were similar to each other and were higher than the Wellington sites. There was a decreasing trend of the blade tissue content of Cu between April and July in farm PE 327, and the trend became positive between July and October. The blade tissue content of Cu in the other three sites had small fluctuations but were relative stable cross the sampling period. The sporophyll tissue content of Cu from all four sites showed some fluctuations across the sampling period with no noticeable trend observed. The blade values were lower than in previous research e.g. 9.76 mg·kg^{-1} [23] but high than 1.8 mg·kg^{-1} [25]. The nutrient reference values for Australia and New Zealand state that the upper level of intake (UI) for adult of Cu is 10 mg/day and the AI is 1.7 and 1.2 mg/day for adult men and women respectively [27]. Therefore consumption of less than 1 kg of wild *U. pinnatifida* would enough to delivery adequate amount of Cu to human. Consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Port Underwood and Wellington would contribute 0.15% and 0.11% of the NHMRC recommended UI respectively.

3.8. Manganese

There were small fluctuations for the blade tissue content of manganese across all four sites across the sampling period. The blade from Wellington site A had higher Mn content than the other three sites while both Wellington sites were higher in the sporophyll. The blade values were comparable to previous research e.g. 10.1 mg·kg^{-1} [23] and 8.7 mg·kg^{-1} [24]. The Australia New Zealand food standards code for Mn states estimated safe and adequate daily dietary intake recommended for adult is 5 mg [28]. The nutrient reference values for Australia and New Zealand states that the adequate intakes (AI) are 5.5 mg/day and 5 mg/day for adult men and women respectively [27]. Consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Port Underwood and Wellington would contribute 0.8% and 1.06% of the NHMRC recommended Ai respectively.

3.9. Nickel

In farm PE 327, there was a steady increase of the blade tissue content of nickel between April and June, which was followed by small drop between June and July, and ended with another small increasing trend. The blade tissue contents of Ni in Port Underwood sites were slightly higher than sites from Wellington. The sporophyll tissue contents of Ni in all four sites were relatively stable with some fluctuations and no noticeable trend. The blade valueswere similar to previous research e.g. 2.65 mg·kg^{-1} [25]. The World Health Organisation/Food and Agriculture Organization of the United Nations (WHO/FAO) state that the Ni tolerable daily intake (TDI) is 12 µg/kg of body weight [29]. Assuming an adult with 70 kg the level would be 0.84 mg per 70 g person per day. Consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Port Underwood and Wellington would contribute 1.3% and 1% of the WHO/FAO recommended TDI respectively.

3.10. Selenium

The blade tissue contents of selenium in all four sites showed patterns of fluctuation. The blade and sporophyll from Wellington had higher Se content than Port Underwood. The blade values were higher than what had been found in previous research e.g. 0.070 mg·kg^{-1} [23] and 0.5 mg·kg^{-1} [25]. The World Health Organisation has RDI for adult of Se are 0.026 and 0.034 mg/day respectively for adult women and men [26]. Whereas the nutrient reference values for Australia and New Zealand states that upper level of intake (UI) for adult of Se is 0.4 mg/day and the recommended daily intake (RDI) are 0.06 and 0.07 mg/day for women and men respectively [27].The Australia New Zealand food standards code suggests the Se recommended dietary intake for adult is 0.07 mg [28]. Consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Port Under wood would contribute 7.1% and 3.5% of the WHO/FAO and NHMRCRDI respectively while seaweed from Wellington would contribute 9.5% and 4.6%respectively

3.11. Zinc

The blade tissue contents of zinc in all four sites showed small fluctuations. Wellington sites had slightly higher content of blade tissue Zn than Port Underwood sites. The sporophyll tissue content of Zn in all four sites also showed small fluctuations. Site 106 had slightly higher sporophyll tissue content of Zn than the other three sites. The blade values differed from previous research e.g. 22.9 mg·kg^{-1} [23], 17.4 mg·kg^{-1} [24] and 9.44 mg·kg^{-1} [25]. The nutrient reference values for Australia and New Zealand states that the upper level of intake (UI) for Zn is 40 mg/day and the recommended daily intake (RDI) is 14 and 8 mg/day for adult men and women respectively [27]. The Australia New Zealand food standards code suggests the Zn recommended dietary intake for adult is 12 mg [28]. Consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Post Underwood and Wellington would contribute 0.78% and 1% of the NHMRCRDI respectively.

3.12. Arsenic

The blade tissue content of arsenic between May to October in farm PE 327 showed a slow decreasing trend and a similar trend also been noticed in Wellington Site A between August and November. The blade tissue content of As from the other two sites showed small fluctuations and were relatively stable during their sampling period. The sporophyll tissue content of As between April and July in farm PE 327 showed a slow increasing trend and small fluctuations had been identified in the other three sites. The blade values differed from previous research e.g. 35.62 $mg \cdot kg^{-1}$ [23] and seaweed product in Spain contained total As could ranged from 0.031 - 149 $mg \cdot kg^{-1}$ [30]. Marine algae could contain high levels of arsenic, but most were bound into organic molecules such as arsenosugars, which were not acutely toxic like the inorganic forms [31]. In New Zealand, the only regulation applying to seaweed foods is inorganic arsenic. In the New Zealand Food Standards Code, the limit for inorganic arsenic in seaweeds is 1 $mg \cdot kg^{-1}$ where the material is adjusted to 85% moisture [32].However, there was no evidence that consumption of organic arsenic at levels up to 50 mg/kg/bw per day, through high levels of seafood consumption had led to adverse effects [33]. Therefore, the total arsenic detected in seaweeds was unlikely to contribute health problems.

3.13. Cadmium

Both the blade and sporophyll tissue contents of cadmium in all four sites showed small monthly fluctuations with no clear trends identified. The blade values differed from previous research e.g. 0.13 to 1.9 $mg \cdot kg^{-1}$ (Almela*et al.*, 2002) [34]. The World Health Organisation/Food and Agriculture Organization of the United Nations (WHO/FAO) states that the Cd provisional tolerable weekly intake (TWI) is 7 µg/kg of body weight [35]. Assuming an adult with 70kg the level would be 0.49 mg per week. Consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Port Underwood and Wellington would contribute1.9% and 1.8% of the WHO/FAO recommended TWI respectively.

3.14. Mercury

The blade tissue content of mercury in all four sites was very low. No statistical analyses performed for sporophyll tissue content Hg as no reliable values recorded. The blade values were comparable to previous research e.g. 0.03 mg/kg [23].The World Health Organisation/Food and Agriculture Organization of the United Nations (WHO/FAO) states the Hg provisional tolerable weekly intake (TWI) is 1.6 µg/kg of body weight [36]. Assuming an adult with 70 kg the level would be 0.112 mg per 70 g person per week. Consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Port Underwood and Wellington would contribute 0.13% and 0.12% of the WHO/FAO recommended TWI respectively.

3.15. Lead

The blade tissue content of lead in all four sites showed small fluctuations across months. There was an increase of the sporophyll tissue content of Pb level between April and May in farm PE 327, which leveled out for the rest of the sampling period. The blade values differed from previous research e.g. 0.23 $mg \cdot kg^{-1}$ [23] and 0.79 $mg \cdot kg^{-1}$ [25]. The World Health Organisation/Food and Agriculture Organization of the United Nations (WHO/FAO) states the Pb provisional tolerable weekly intake (TWI) is 25 µg/kg of body weight [37]. Assuming an adult with 70 kg the level would be 1.75 mg per 70 g person per week. Consumption of 40 g (wet weight) of *U. pinnatifida* obtained in October from Port Underwood and Wellington would contribute 0.054% and 0.064% of the WHO/FAO recommended TWI respectively.

4. Conclusion

Despite its long coastline, there has historically been little seaweed utilisation in New Zealand [38] [39]. This is likely to change with the availability of *U. pinnatifida* as a resource. This study investigated the metal contents of *U. pinnatifida* harvested from New Zealand waters and found that *U. pinnatifida* is rich in Ca, Mg, K and P with small amounts of Cr, Cu, Mn, Ni, Se and Zn. The concentrations of the above elements when compared to World Health Organisation/Food and Agriculture Organization of the United Nations (WHO/FAO) guidelines and nutrient reference values for Australia and New Zealand, show that *U. pinnatifida* is safe for human consumption and the results for As, Cd, Hg and Pb when compared with WHO/FAO guidelines show that New Zealand *U. pinnatifida* contains no heavy metals in levels that would be of any concern.

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