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The Medical Geology and Discovery of Taranjebin Manna as a Hyper Selenium Accumulator; Biomedical and Ethno-Medical Efficacy Links to Calc-alkaline and Alkalic Tethyan Magmatic Arcs

Ziarati P[1,2*] **and Hochwimmer B**[3]

[1]*Nutrition and Food Sciences Research Center, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran*

[2]*Department of Medicinal Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran*

[3]*Hochwimmer B and Associates Pty Ltd, Consultant Geologists: Mineral Exploration; Mining; Environmental Geology, Albury, Australia*

[*]**Corresponding author:** Ziarati P, Nutrition and Food Sciences Research Center, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran, Tel: +982122640051; Fax: +982122633986; E-mail: ziarati.p@iaups.ac.ir

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Abstract

Taranjebin Manna, a rare specific gum exudate from Fabaceae genera (Alhagi), screened for selenium content. These were from some 90 samples complied into 14 bulk samples, representing three regional centres of Iran. Previous multidisciplinary studies had suggested selenium in an exudate chemical species context was the likely active component. The present study supports this contention and explains Taranjebin Manna's very high ethno-medical demand in Iran, and for its export. Several proposed biochemical hypotheses introduced here support selenium as the active constituent in context of Manna's glycoprotein content. Research into Manna seleno polysaccharides and selenoglycoproteins is likely to reveal novel compounds of high medical interest. It is argued Taranjebin Manna ethno-medical indication for neonatal hyper-bilirubinemia and thyroid issues is related to these selenium compounds. The mean content of selenium was consistently very high, averaging 492 mg Se/100 g (dry weight of Manna) in the range of 482 to 513 mg Se/100 g. As a result, important traditional medical Manna efficacy is inferred from these findings. Possible reason for this hyper-accumulation was investigated by conducting a review of selenium geogenic factors and Investigation into Taranjebin Manna's distribution. This concluded biogeochemical factors such as specific local geogenic conditions combined with specific geological terrains contributed to Manna selenium mobility within specific Alhagi genera species, *Apersarum boiss*, *A. bushe* and *A. mannifera Desf*Climatic, biological and geogenic-geological factors all contribute to high content of selenium in Taranjebin.

Keywords: Manna; Taranjebin; Iran; Selenium; Medical geology

Introduction

Taranjebin is a semi liquid resinous sweet substance that exudes onto the leaves and branches of the Manna producing camel's thorn species (genus Alhagi within Fabaceae, the legume family). Taranjebin hardens into white granules which gradually turn to yellow and brown colours [1-7]. Among various Manna which have been observed in Iran, only Taranjebin has a tear like shape [8]. Taranjebin, Shir-Khesht, Bid-Khesht and Gaz-Alafi are very much used Iranian Manna among others. Taranjebin (TA) or Persian Manna is specifically formed on the camel's thorn shrubs (genus Alhagi). Etymology of Taranjebin shows this word is derived from the Persian word "Tar-angabin" meaning wet honey. In traditional Persian and Islamic medicine, it is also referred to as Asal al nada (Dew honey), Oshtorangebin (Camel thorn honey) and honey of rose. In addition, Taranjebin as a Persian Manna, is also known as Merniabin Manna, Alhagi Manna (from the plane genus), Hedysarum Manna and Caspian Manna in English and Manne de Perse, Manne d' hedysarum and Manne d' alhagi in French [7,9].

Taranjebin Manna forms on *Alhagi persarum* Boiss, and *A. bushe* and *A. mannifera Desf.* Surprisingly, these species do not yield Taranjebin everywhere they grow. This phenomenon seems to relate to temperature, soil conditions, and existence of an insect from the genus Larinus inhabiting the Alhagi shrubs [10]. Recent studies show a strong relationship between Taranjebin production and a specific 'froghopper' insect; Poophilus nebulosus Leth [9]. Significantly, Camel's thorn shrubs yield manna only in certain areas of Khorasan, Tabriz, Tabas, Zarand, Tegerood (near Qom) and Booshehr in Iran during the hot season [11-13]. Consequently, it is proposed these factors are combined with geology as determinates for Ethno-medical active Taranjebin Manna, as discussed in the following Manna Medical Geology section on calc-alkaline to alkalic provinces of the Tethyan magmatic arcs.

Given wide usage and terminologies of various Manna, terminology is an important aspect summarised here. Diverse manna's have been used as laxatives, antipyretics, expectorant and forms in the treatment of hyperbilirubinemia in Iranian traditional medicine including neonatal hyperbilirubinemia [1,2]. Characteristics of Manna have been attributed to its sacchariferous compound [5]. Notably glycoprotein's and other therapeutic compounds are likely to be discovered and act in concert with nutritionally diverse Iranian 'Mannas.' Of the well-known 'gum' exudates elsewhere, gum Arabic, the original discovery source of arabinose and ribose sugars, is an exudate from the Gondwana genus, Acacia, generally *A. Senegal* or *A. vachellia* species, also within the Fabaceae family. Like Manna, it has a complex mixture of glycoprotein's and polysaccharides. Amongst numerous uses it was traditionally used as an anti-inflammatory. There is still much to be discovered from gum exudates, particularly from the Fabaceae, which is interesting as certain species define selenium flora biogeographically and have been the most successful bio-mineral exploration indicators.

Taranjebin is the most economically valuable Manna in the Persian herbal markets and the most economically exported Manna from Iran's herbal markets. Nowadays, Taranjebin is mainly used as a mild laxative and treatment of neonatal jaundice in Persian Ethnomedicine. Studies have shown a lowering bilirubin effect with no observed toxicity in mice [12-14]. Ethanolic extract of herbal products containing this manna have been shown to have inhibitory effects on cell growth and synthesis of cellular proteins, DNA, and RNA [15,16]. In addition, traditional Persian Ethnomedicine uses for Taranjebin include - fever, rubella, health maintenance, cough, pectoral aches, nausea-vomiting and thirst [9,11-14].

Whilst selenium is an essential nutrient, different animals have variable adaptive requirements biochemically. This is presumably due to a combination of physiological and nutritional stress and lifestyle demands that may be dependent on ecological availability and ecological behavioral adaptations to acquire selenium concentrations to match deficiency or overcome toxicity stress in novel ways. Nutritionally, some native animal diets such as the marsupial sugar gliders (Australia-Indonesia) preferentially utilize sap exudates, including gums, nectar, manna and honeydew. These animals typically have poor protein quotas [17], which they partially make up with pollen and other sources. Depending on geogenic conditions of selenium mobility, even with potentially hyper selenium accumulators such as the Fabaceae species, shortages may occur if geological conditions are depleted in selenium or if unsuitable when hyper selenium accumulation ability against geochemical gradient, as is the case with many flowering plant species, is unremarkable. Therefore, it is possible animals such as sugar gliders supplement with pollen for selenium in addition to protein. Pollen and nectar can concentrate selenium in some plant species to high levels than leaf or stem tissue.

Geogenic factors largely control levels of selenium in plants, even for accumulating Fabaceae species and others which may have adaptive tolerance. For example, under appropriate selenium supply in waste waters with around 0.4 to 0.7 ppm Se, certain plant such as radish and mustard pollen and nectar have been shown to concentrate selenium to high levels, (around 400 to 800 ppm in pollen and 60 ppm in nectar). Whilst selenium is essential for proper nerve cell health, excess levels disrupt this function, evident in dysfunctional honey bee communications. Selenium is an essential micronutrient, potentially; excessively high geogenic circumstances for small animals, such as insects may impose adaptive selenotoxic pressures. The Taranjebin Manna insect; *Poophilus nebulosus Leth*, perhaps has adaptive tolerance, and this needs to be tested. Taranjebin Manna's can exceed the geogenic driven high selenium in mustard pollen and nectar by an order of magnitude, as this study now demonstrates, forming an ideal nutritional supplement for deficient wild animals and humans alike. Hyper accumulation biotic potentials against selenium geochemical gradients aside, this indicates special geogenic and geological conditions contribute to such very high selenium levels in Taranjebin Manna.

Selenium proteins [16] and glycoproteins appear to be essential in preventing various diseases. Of the eight essential trace elements, selenium is an important antioxidant, essential for thyroid, brain function, and metabolism and in the right molecular form appears to act as a chemo preventative, notably, for colon, breast, prostate, and possibly liver, pancreatic and other cancers. As Manna is a known DNA synthesis retardant, it may act against pathogens (and cancers) by retarding bacterial DNA syntheses, in analogy to certain antibiotics not affected by resistance including methotrexate, a folate decoy normally used in leukemia chemotherapy. Thereby, Manna may reduce live pathogen induced jaundice and bilirubin levels in liver disease as well as secondary infection to neonatal hyperbilirubinemia shock, countering inflammation, septicemia and necrosis. Furthermore, selenium can be a bacterial bio-film retardant and one such study found that selenium retarded *Staphylococcus* by 90% [17]. Should significant Se occur in sap or honeydew exudates, (particularly in mutual plant/insect benefit) this would benefit both plant and insect during the plant injury, and this micro-ecosystem selected in an evolutionary sense for the presence of a selenium geogenic-biotic context, that also possibly confer natural toxic resistance of Fabaceae plants.

Another factor could be Manna mediated resilience against insufficient competency of red blood corpuscle in a neonatal context of this excess red blood cell hematopoiesis. For as noted below, selenium is an essential component in antioxidant enzyme glutathione peroxidase in mammalian red blood corpuscles [18].

Furthermore, selenium is essential in thioredoxin reductase, deiodinase enzymes, in the conversion between thyroid hormones. Thyroid insufficiency is known in Iran and perhaps selenium is an additional factor on top of Hashimoto disease vectors in combating insufficiency. Indeed, selenium can reduce excess anti-thyroid receptor antibodies [19]. Conversely, conceivably, if such insufficiency persists from selenium shortage dependency hormone conversion, over compensating hormone production may occur if thioredoxin reductase, deiodinase enzymes are not functioning optimally. Inflammation can occur through multiple ways, including those. Indirectly these enzymes reduce oxidative species in both animals and plants, for which selenium requirements vary. Manna selenium may therefore, not only avert neonatal hyperbilirubinemia shock, but inflammation generally. Common sources of selenium (Se) are fish, shellfish, meat, particularly organ meats [15], milk, eggs and some nuts such as South American Brazil nuts which provide good sources of selenium. Other sources include cereals, other grains and dairy product. Iranian nuts such as almonds may also provide good sources of selenium. Selenium concentrations in plant-based foods vary widely by geographic location [13,15,16,20,21]. For example, according to the US Department of Agriculture Food Composition Database, Brazil nuts may average 544 mcg selenium/ounce, yet analyses vary widely. Likely this reflects geogenic conditions.

Based on USDA National Nutrient Database for Standard Reference's Recommended Dietary Allowance (RDA), average daily level of intake sufficiently meets the nutrient requirements of nearly all (97%-98%) healthy individuals. Adequate Intake (AI) are established when evidence is insufficient to develop an RDA and is set at a level assumed to ensure nutritional adequacy. Estimated Average Requirement (EAR) is the average daily level of intake estimated to meet the requirements of 50% of healthy individuals. It is usually used to assess the adequacy of nutrient intakes in population groups but not individuals. Tolerable Upper Intake Level (UL) is maximum daily intake unlikely to cause adverse health effects [22].

Generally, selenium content of soil can affect selenium content in plants, so the quantities of selenium in animal products also vary [13-16], though not as much as in plant-based foods due to homeostatic mechanisms. Formulated livestock feeds also generally contain constant levels of selenium. Plants are therefore an important source of selenium, and soils generally reflect bedrock and source geology: low and more rarely high selenium bioregions, including base metal sulphides, precious metal minerals such as telluride

mineralization associated with selenium, coal fired power stations, fly ash disposals, may therefore be reflected in plants, animal and human health. The range of beneficial selenium, however, is narrow, excess selenium can lead to selinosis. Biologically, a wide range of tolerances exist, including, importantly, in bacteria involved in bio oxidation and reduction of selenium compound in rocks and soils. In bacteria, selenium and tellurium resistance is mediated by different genes, for tellurium by the arsenical ATPase efflux pump resident in plasmids [23]. Superoxide or H_2O_2 production is implicated in selenium toxicity by antioxidant production more than cell needs [22-25].

A literature survey has revealed that there are a few studies that have touched on the essential elements of Manna, more specifically for Selenium on rare Iranian Manna. In the present study, we focus on biogeochemical studies of interesting and little studied Manna exudates, hosted by specific Iranian Fabaceae species within the genus Alhagi, termed Taranjebin from eastern and central Iran. Taranjebin Manna is purported to have very high traditional ethno-medical value; therefore, the main goal of current study was to determine sodium, potassium, lithium, calcium, magnesium and importantly selenium in Taranjebin Manna, to investigate biochemical and potential geogenic reasons for the very high demand of Taranjebin in Iran and its high export demand.

Materials and Methods

Sampling method

Manna was carefully selected for its traditional efficacy judged by knowledgeable, experienced and reputable herbal collectors.

Ninety different samples Manna Taranjebin (Figure 1) were prepared from 3 provinces in different parts of studied locations in Iran, namely Khorasan-e-razavi, southern Khorasan and Yazd in July 2016. Samples were given specific codes i.e., T1-T5 for samples from Yazd (central south Iran), T6-T10 for samples from southern Khorasan (central east Iran), and T11-T14 for samples from Khorasan-e-razavi (North east Iran) as illustrated in Table 1. The provinces where these three groups of samples were collected are shown (Figures 2 and 3).

Figure 1: Taranjebin Manna.

Growing location and sample codes	Part used	Local Ethno-medical name	English Common name	Family	Botanical name
Iran: Yazd: (T1-T5)	Manna	Taranjebin	Camel's Thorn Manna	Fabaceae	Alhagi Camel's Thorn fisch Or Alhagi pseado Alhagi
Southern Khorasan: (T6-T10)					
Khorasan-e-razavi: (T11-T14)					

Table 1: Botanical, local and English name and growing location of studied Manna, Taranjebin.

Analytical method

For mineral elements analysis, each sample was oven dried at 450°C to a constant weight. Each oven-dried sample was ground in a mortar until it could pass through a 60-mesh sieve. The studied samples according to international protocols were stored in clean, dry, high density polyethylene bottles of 100 ml capacity with screw caps.

Figure 2: Map of growing location of studied Manna, Taranjebin.

All glassware and plastic containers used in the study were washed with liquid soap, rinsed with water, soaked in 10% HNO_3 v/v for 48 h, cleaned thoroughly with distilled water and dried in such a manner to ensure no contamination.

Each powdered sample split of 2.00 grams was separately placed in a 100 ml digestion flask with approximately 15 ml of digestion mixture added, then heated on a hot plate in the fuming chamber for wet digestion. The digestion mixture comprised concentrated HNO_3, H_2SO_4 and HCl in the ratio of 6:1:1. Samples in flasks were firstly heated slowly, then vigorously till a white residue was obtained. The residue was then dissolved and made up to 10 ml with 0.1 N HNO_3 and NH_4 solution in a volumetric flask [13,24]. Blanks and samples were processed and analyzed in duplicate, simultaneously. All chemicals used in the study were of analytical grade (AR) and all necessary precautions were taken to avoid any possible contamination of the sample as per the AOAC guidelines [26,27].

Sample element concentrations were determined as means ± SE of three replicates in each test and determined based on sample dry weight (DW). The measurements were performed using a Perkin Elmer Pin An Acle 900 T atomic absorption (AA) spectrophotometer,

employing an air-acetylene flame for lithium, sodium, potassium, calcium and magnesium using six standard solutions for each metal. The calibration curve correlation coefficient was examined to ensure an r^2=0.996 before initiating sample analysis.

Coefficient of variations (%CV) in determination of the elements in all samples was less than 2%. The temperature of the air-acetylene flame was about 2,300°C. An air- acetylene flame can be used with all Perkin-Elmer burner heads. The operating instructions for use of the air-acetylene flame were as per the appropriate instrument manual. For the air-acetylene flame, the acetylene flow is about 4 litres/minute, or 8.5 cubic feet/hour, using a heat combustion value of 1450 BTU per cubic foot. The heat given off would be approximately 12,300 BTU per hour.

Application of concentrated HNO_3 along with 30% hydrogen peroxide H_2O_2 (Merck) for mineralization of samples to complete sample digestion [25-30], following Environmental Protection Agency (EPA) Method 3052 was carried out. Digested samples were read directly by the atomic absorption spectrophotometer, at a wavelength of 766 nm - K, Ca nm- 422.7 and 285 nm - Mg, 589.0 nm - Na. Chemical analyses were performed in three replications and the mean values are presented.

Selenium determination

Stock standard solutions for selenium were 1000 µg/mL solution. All reagents and standards were of analytical grade (Merck, Germany). The palladium matrix modifier solution was prepared by the dilution (10 g/L) Pd $(NO_3)_2$ and iridium AA standard solution, 1000 g/mL in 20% HCl, 0.1% V/V nitric acid prepared by dilution trace pure 65% nitric acid and 0.1% Triton X-100 were used. Doubly distilled water was used in all operations. Analyses were performed according to Analytical Method ATSRD 2003 [31].

Results and Discussion

The geological, biological and medical reviews and hypotheses derived from them pertaining to Taranjebin Manna are presented above.

The mean value for Selenium contents of Taranjebin from 3 different provinces (Figure 3) averaged selenium content of 492 mg/100 g Se (0.492%) in the range of 482 to 513 mg/100 g Se (N: 14, STD 8.2), dry weight. Given the combined medical and geological importance of the present studies demonstration of high selenium in Taranjebin Manna a broad range of geological, biological and medical reviews on selenium were conducted. Thus, we demonstrate for the first time very high quantities of selenium for a Fabaceae species hosted Manna, a specific gum exudate termed Taranjebin from central, east and northeast Iran.

The very carefully regionally selected Manna for its traditional efficacy provides a good avenue to geochemically reflect geological provenance. Such geo-biogenic factors alongside traditional medicinal and nutritional potential on review and hypotheses presented were discussed above. This connectivity was found particularly for neonatal hyperbilirubinemia and thyroid issues that could be explained by this studies demonstration of high selenium Manna levels in geogenic and geological context.

Efficacy hypothesis regarding selenium biogeochemistry for this Manna considered in the sections reasonably explain the traditional uses and support our result that a high selenium content in Manna is the active component to ethno-medical efficacy specifically for Taranjebin Manna. Further research into the specific active compounds of selenium in manna, particularly selenoglycoproteins and selenopolysaccharides are likely to reveal novel compounds of high medical interest. It is argued that Taranjebin Manna ethno-medical indication for neonatal hyper bilirubinemia and thyroid issues is related to these likely novel selenium compounds. Indeed, selenoglycoprotein's are also indicated in certain cancer chemo preventions. Conversely inorganic selenium supplementations have been proven to have negative effects, (in context of adequate nutrition). This may also point to the need for selenosis amelioration strategies by host plants from inorganic selenium sources, Manna production being one of them.

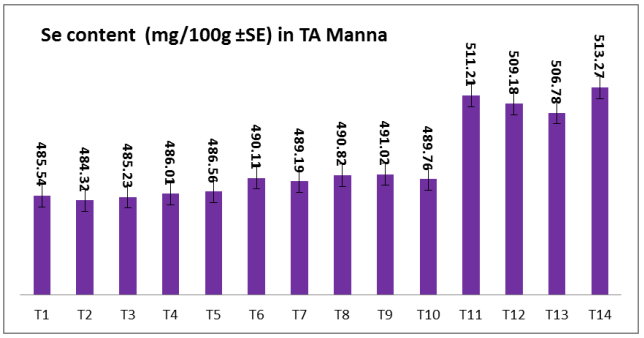

Figure 3: Selenium content in different studied Taranjebin samples.

Code	Mineral Elements (mg/100 g)		Mineral Elements (mg/100 g)			
	Li	Na	K	Ca	Mg	Se
T1	0.08b ± 0.26	1.399b ± 0.076	33.33a ± 0.77	16.867c ± 0.342	63.228b ± 1.003	485.54b ± 8.23
T2	0.07b ± 0.24	1.288b ± 0.043	33.76a ± 0.76	16.382c ± 0.318	64.878b ± 1.006	482.15b ± 10.11
T3	0.07b ± 0.17	1.325b ± 0.012	33.35a ± 0.90	16.660c ± 0.402	63.098b ± 0.976	491.56b ± 7.67
T4	0.08b ± 0.16	1.307b ± 0.043	32.08a ± 0.86	16.248c ± 0.328	63.667b ± 0.889	488.34b ± 5.24
T5	0.08b ± 0.12	1.348b ± 0.053	33.88a ± 0.90	16.111c ± 0.445	64.912b ± 0.902	486.72b ± 9.17
T6	0.03c ± 0.20	1.928a ± 0.065	30.66b ± 1.002	18.562b ± 0.328	c46.887 ± 0.623	490.11b ± 9.76

T7	0.03c ± 0.23	1.956a ± 0032	30.46b ± 0.875	18.456b ± 0.362	45.200c ± 0.562	489.19b ± 8.44
T8	0.04c ± 0.23	1.998a ± 0.025	30.26b ± 0.56	18.456b ± 0.316	45.677c ± 0.516	493.2b ± 8.25
T9	0.04c ± 0.17	1.876a ± 0.042	29.70b ± 0.453	19.888b ± 0.306	46.450c ± 0.529	491.02b ± 8.09
T10	0.04c ± 0.28	2.010a ± 0.087	b30.20 ± 0.76	b18.567± 0.301	47.331c ± 0.518	b487.56 ± 11.23
T11	0.09a ± 0.28	1.994a ± 0.065	a34.47 ± 0.54	23.465a ± 0.376	72.740a ± 1.433	487.64b ± 12.56
T12	0.08a ± 0.20	1.835a ± 0.049	a34.30 ± 0.87	23.115a ± 0.343	72.765a ± 1.245	502.76a ± 12.05
T13	0.07a ± 0.24	1.936a ± 0.028	a34.47 ± 0.90	23.986a ± 0.352	71.333a ± 1.652	500.07a ± 10.44
T14	0.07a ± 0.25	1.973a ± 0.063	34.83a ± 0.73	23.867a ± 0.326	71.210a ± 1.703	513.27a ± 9.05

Table 2: East (T1-5), Central East (T6-T10) and Northeast (T11-14) Iranian Taranjebin Manna sample analytical result for lithium, sodium, potassium, calcium, magnesium and selenium. Values with different letters within each parameter were significantly different ($P<0.05$).

Medical geology of manna host and related selenium hyperaccumulators

Table 2 presents a soil fractionation analysis of a Manna collection area which reveals less than 11.5% Clay or silt, the texture being sandy loams, which would aid selenium mobility through oxygen access. Low clay and low soil organic carbon content are known to aid selenium mobility, as the geogenic review of selenium mobility illustrates, especially for the Alhagi genus with very deep roots.

Of the Fabaceae Alhagi genus (i.e., Camelthorns or Manna trees) few species exist, primarily in the old world. Geogenically, they can sample very deep substrates, as a small bush they may have roots exceeding around 15 m, utilising ground waters in arid environments. Larva of the *Coleophora argyrella*, Lepidoptera species feeds exclusively on *Alhagi maurorum*. The genus apparently gets its name from the Arabic meaning pilgrim. Selenium absorption would be aided in this environment of deep water tables by the fact selenium concentration mobility is associated with high pH, further aided by low sulphuration mineral systems and environs, lateral to higher sulphides and selenium sources.

Precipitation leads to leaching of selenium from the soil. Normally wet conditions favour oxygen and low pH, but in deep friable soils this may not be the case for oxygen or pH where carbonates buffer acidity. In terms of mineralization associated with selenium geoindicator flora generally, these are often selenium floras lateral to mineralization, reflecting proximal positions to distal sulphides which characteristically have low pH soils, or acid rock drainage (ARD) in wet conditions. In dry conditions, such as in Iran, this may be more proximal and carbonates buffer acidity. Some researchers consider climate change to affect available selenium negatively [32,33]. Other sulphide systems associated with selenium are less ARD producing, ranging to alkaline.

Medical Geology supports high selenium Taranjebin Manna findings in the central east Iranian Tethyan metallogene belts (Figure 3), a restricted distribution, that reflects selenium's rarity and association with lower sulphidation hydrothermal systems. These feature lower levels of acid producing sulphides such as iron sulphides relative to acid buffering minerals by dissociating carbonates, alkali oxides, hydroxides and silicates. Arsenic may be present, but it is not a particular acid producing sulphide. These sulphide systems water trend toward neutral or alkaline, favouring selenium mobility. Sulphate and bicarbonate are the principal anions compared to ARD waters where the main anion is sulphate and cations iron, magnesium and aluminium. However, carbonate base metal and telluride gold mineralization associations of selenium often carry appreciable sulphates and other metals including Cd, Cu, Hg, Mn, Mo, Ni, U, Zn, Au, Ag Pb, and metalloids As, Sb, Sc, Te, Bi, In. Bar the precious most leach into oxidizing neutral to slightly alkaline mine waters [34]. It is as well to be aware of toxicities in ethno medical products or other beneficial micronutrients.

From the geogenic discussions, these are Neo-Tethyan arc systems in central sector and the eastern arc systems influenced by western Pakistan known for widespread alteration Cu ± Mo ± Au, epithermal gold and base metals also evident in the Lut block, a former continental fragment. Molybdenum contents may reflect intra compression extension and be associated with the low sulphidation suites mentioned above as selenium associates. In higher concentration within extensional systems, such Se associated base metal hydrothermal mineralization may form giant deposit lateral to the porphyry and epithermal systems where magmatic and meteoric waters mix. The Porphyry and higher sulphidation types contain less selenium and being prone to ARD/AMD less conducive for selenium bio mobility in soils. It is possible stronger rift basins have not yet been more widely recognised in Iran, with the more alkaline differentiated magmatism series that can be associated with low sulphur and higher selenium metallogenesis one suspects indicative of the very high Manna selenium results from NE Iran reported here (Table 3).

Soil Dial	Sample Depth cm	Sand %	Silt %	Clay %	Soil Texture	Sand/Clay
Meddle Voucher	0-30	83	8.5	8.5	Loamy Sand	9.76
Terminal Voucher	0-30	82	10.5	7.5	Loamy Sand	10.93
Initial Braid	0-30	81	11.5	7.5	Loamy Sand	10.8
Meddle Braid	0-30	79	10.5	10.5	Sandy Loam	7.52

Terminal Braid	0-30	80	10.5	9.5	Loamy Sand	8.42

Table 3: Soil fractionation studies of Manna source area Studied soil samples from Jajarm City in North Khorasan Province. Note the loamy Sand textures with minor clay and silt, suitable for selenium mobility.

Arcs and back arc extensional systems display temporal and geochemical evolution to calc- alkaline an alkaline intrusive, generally in later stages of volcanism. It should be noted that selenium may also concentrate in altered volcanic rock with disseminated sulphides and as inclusion in rock forming minerals, more widely disseminated, not necessarily requiring mineral deposits (an economic definition of high grade) to form significant mineralization that will be reflected as more widespread selenoflora within volcanic arc formations, particularly in alkalic domains.

Orogenic links

Mineralization in the Lut block of eastern Iran was formed in the middle Eocene, at the end of a period of extensive Palaeocene-Eocene volcanism; whilst Cu-Mo deposits in the Kerman belt of central Iran formed in the middle Miocene at the end of a period of voluminous Eocene- Oligocene volcanism. It has been proposed that these late differentiated stages of volcanism are represented by relatively high Sr/Y and La/Yb ratios magmas, indicative of arc maturity high magmatic water content [35]. These hydrous phases, represented by hydrous amphiboles and biotite, and suppression of plagioclases, are prerequisites for porphyry Cu ± Mo ± Au potential required in shallow crustal arc magma emplacements and general ore-forming sub-volcanic magmatic-hydrothermal systems. These potentials may also be largely unmapped in the east of Iran.

In this context, it is notable that the eastern and northern zones are slightly higher in Manna selenium results (Table 2) than that of Yarzd district. Perhaps this reflects the lower geographical distribution and strength of more differentiated forms of cal-alkaline rock trending to alkalic suite of minerals (Figure 3). Calc alkaline suite, replete with porphyry and gold mineralization occur SE of Yazd in the Kerman sector. It would be interesting to further study if Manna efficiency, as judged by selenium content, could be correlated with favourable regional rock Sr/Y and La/Yb ratios reflecting hydrous fertile magma origin of these volcanic arc formations of the UDMZ arc and Khorasan calc-alkaline volcanic and plutonic arcs. Another general rough field guide might be visually gained with amphiboles and biotite, though the rare earth's elemental ratios will discriminate more hydrous minerals in otherwise pathologically identical appearing terrains. Conversely, Ethno-medical manna may be an indication of mineralization extent of higher selenium content and proportions of A-type differentiated magma sources suspected in east and north central to northeast sectors around Khorasane- Razavi.

The calc-alkaline volcanic and plutonic arc ages are relatively young and coincide broadly with Late Eocene-Oligocene and Miocene-Pliocene mineralization associated volcanism in the American cordillera. Porphyry Cu-Au mineralization in the Chagai belt of western Pakistan formed in four pulses during the Eocene, early Miocene, middle-late Miocene, and late Miocene-Pliocene, after a prolonged period of arc magmatism that began in the Late Cretaceous. It is still active, and reflects the long evolutionary development, as for the American Laramide orogeny, though terminating in late Eocene. The subduction angle of The Arabian plate under Iran however is not as shallow as that under Colorado, well into the back arc. So, one can expect 'Selenium floras' may be protracted across the Iranian metallogene belts, including back arc extensional elements suspected in NE Iran suspected from high selenium manna here. Therefore, one hypothesis might be that this contributes to the restricted geographical distribution of medically effective Manna exudates that relate to selenium and mineralization distribution.

Given these Mid to late Cainozoic ages, it is interesting to speculate if the plant genus Alhagi that host Manna arose in the late Cainozoic due to palaeogeographical and the late stage Tethyan arc geochemical evolution culminating in hydrous calc-alkaline to alkalic magmatism. For it seems in a similar way *Fabacian oxytropis* genus selenium hyperaccumulators diverged from Astragalus about 16-12 Ma, around the Langhian to Tortonian stage of the Miocene, after the main initial Oligocene metallogene events in the American cordillera. Given the discourse with the West Pakistan arc mineralizing magmatism over a longer period, it is also interesting to speculate a parallel evolutionary sequence in Fabaceae selenium hyper accumulators, such as *Alhagi manna* broadly from East to West and if the hyper accumulating genome had its origins in west Pakistan as a result.

It suggests that 'selenium floras' can tolerate high selenium geological terrains globally. 'Selenium floras' as widely noted [36] are related to geology, and prominently so in western USA, due to continental convergence of the pacific plate. Globally 'selenium floras' include Canada, Columbia and Queensland Australia [37]. Geologically, these are subduction related and transitions to ensialic rifts. Once again, the Fabaceae family are noted here as 'selenium floras' including the vetches or species of the Astragalus genus globally. Our results presented in Iran for Manna selenium contents reflect similar geological tectonic and metallogenic evolution in the cratonisation of Iran. Significantly also this reflects similar prospectivity of Iran, it is proposed here for alkalic series of selenium associated mineralization.

Convergence of the Arabian plate under Iran has a similar effect, as reflected in Manna selenium content, along the suture inboard of the Zargros Fold and Thrust Belt and Sanandaj-Sirjan Metamorphic Belt. The geographic distribution of Manna selenium may be of interest geogenically in terms of efficiency of traditional health benefits since, as noted in Table 2, the selenium content is higher in eastern and northern Iran Manna. In the American Cordillera high selenium flora is strong in the back arc extensional province of more evolved calc-alkaline suites to alkalic magmas which based on these results presented, relate to the Alborz sector of northern Iran. This suggests why selenium content in Manna may be highest in the Northern Alborz Takab arcs. This would point to a more evolved arc influence from the longer calc-alkaline geological evolutionary influence of the West Pakistan arcs, from central east of Iran to north east alkalic geology and metallogenic belt orogenesis.

In conclusion, this supports a strong Medical geology link between Manna selenium contents with degree of alkaline volatiles in more differentiate volcanic and plutonic arcs of Iran.

Further geological evidence for internal arc differentiation of this kind is evident from reviewing metallogeny of the northern Alborz arcs, in the central north sector. This appears to be an evolved calc-alkaline to mildly alkaline arc. For example, in the Alborz, Sari Gunay epithermal gold deposit, this system is located within a mildly alkaline latitic to trachytic volcanic complex in central-northwest Iran, with younger volcanic hosts of Mid Miocene age around 11.7 and 11.0 Ma.

The late stage is suggestive of a post collisional subduction phase, compared to the Urumieh-Dokhtar Arc calc-alkaline rocks, SE of Yarzd in Kerman hosting large porphyry copper mineralization (e.g., Sar Cheshimeh, Meiduk) resulting from 'normal' calc-alkaline arc subduction tectonic mineralization's. Rather it is reflective of post continental collisional extension system for the Takab arc belt of Iran, comprised of structurally controlled, middle Miocene, mildly alkaline volcano-plutonic complexes [38].

Therefore, in terms of Orogenesis, it is concluded higher Manna selenium at Khorasane- Razavi is due to such higher evolved continental collision-alkalic-types, somewhat more ensialic in nature compared to the Urumieh-Dokhtar arc hosting normal type porphyry Cu deposits, and though extensive deposits occur here, (e.g., Sar Cheshimeh, Meiduk) indicative of being less effective in Manna Medical Geology efficacy terms. In a way the northeast east of Iran reflects potential for epithermal and porphyry like the Rio Grande Rift of California, and other rifts host to more evolved alkalic magmatism. Indeed, there is a crustal wide structural jog with the east of Iran. Rift Jog basins are important focal factors in the Rio Grande Rift, and the Cravensville arc of Australia associated with the Tumut-Mitta trough extensions rift jog along the Gilmore Suture Zone of the Lachlan belt in south eastern Australia including the Unicorn Mo-Cu-Ag climax hybrid of the Saltpetre Metallogene [39,40]. However, the central north Takab arc belt of Iran appears less alkaline than classic base metal associated gold deposit terrains such as Porgera (Australia) Emperor (Fiji), and Cripple Creek post collisional or back-arc extension. On the contrary, the central Alborz sector of the Takab arc may host early post syncollisional systems in terms of the Neogene closure of a Neo-Tethys ocean, between the Afro-Arabian and Eurasian plates, and perhaps more evolved in the north east, based on Manna selenium results presented here perhaps vectoring prospectivity.

Geogenic selenium mobility factors: Geomicrobiological activity; global medical geology

Not all forms of selenium are available to plants, such as bacterially reduce metalloid forms. These are dependent on geogenic and geomicrobiological conditions, but generally a selenium cycle ensures availability, though some processes lead to depletion. Selenium, being a volatile element, is strongly subjected to climactic and geological factors. Selenium hyper accumulator plants may accumulate more than 1% Se, usually in arid environments with some calcium carbonates. In high concentration 'selenium flora' plants may exhibit characteristic garlic like odour. Often these are in geobotanical indicator plants such as Astragalus species of the Fabaceae family, first noticed on the Colorado Plateau in terms of mineralised geology. High selenium geologically is associated with mineralization, specifically metallic sulphides but can also be pervasively and widely disseminated within minerals throughout certain geological units as low grade and broad hydrothermal alteration.

As a group IV element, selenium behaves similarly to sulphur and tellurium. Though both selenium and tellurium, as metalloids, have some metal like properties, selenium between sulphur and tellurium reflects its position in the periodic table. These metalloids are lower in abundance than sulphur; estimated crustal abundance are around 0.05-0.14 ppm selenium and 10^{-5} to 10^{-2} ppm tellurium [41]. Selenium is in association with metal sulphides where it may partially replace sulphur and more commonly in high levels with unusual sulphides including tellurium, such as base metal associated gold and silver telluride deposit. Cripple Creek Colorado and similar environments are well known areas, including Nevada and Harz Mountains, Saxony-Anhalt, Germany.

Globally, the historical geogenic biota selenium surveys have been marred by historical analyses with poor precision at DL's around 0.1 ppm by conventional ICP-MS [36]. Furthermore, Se being volatile means losses occur if samples are ashed. However, analyses employing nitric acid hydrogen peroxide have generally yielded sufficiently refined results and from this biota, geological selenium strata have been outlined from tree top leaf selenium analysis surveys [36].

Synchrotron work on Astragalus [24] indicates that selenium and species distribution to be mostly leaf bound rather than in twigs and this is in accordance with conifers and deciduous trees in North America [32,36]. However, elsewhere in the genus Combretum (bush weed in Sahara Africa and South America), selenium is equally distributed in leaves and stems.

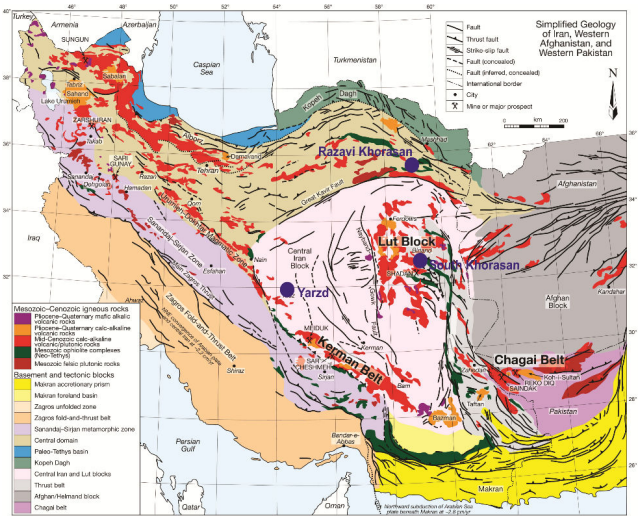

Figure 4: Distributions of Manna Sources in Iran (blue dots).

As seen in the Figure 4, blue dots represent Manna exudates market source areas and superimposed on the Simplified Geology of Iran, and surround [40]. Selenium prospective Mid Cainozoic calc-alkaline magmatic arcs are shown south of Yazd, along with Mesozoic plutonic rocks and Pliocene-Quaternary clac-alkaline in the Chagai-South Khorasan in the east, and similar series in the NE of Iran around Khorasane- Razavi.

The Astragalus genus, or vetch genus are common hyper selenium accumulators worldwide. They have wide prevalence of beta-nitropropionic acid (3-NPA), a mitochondrial inhibitor and the free acid 3-NPA and isoxazlin-5-one, derivatives. Leaf beetle insects have developed a defence mechanism to them. Some species of insects are brightly coloured, displaying warnings of their toxic contents to predators. It is an open question for the Alhagi genus of Manna production and if selenium is involved in a defence mechanise in symbiosis of Larinus insects. Mitochondrial inhibition is one of the mechanisms of cell apoptosis dealing with cancers. Possibly some cancers are averted before they rise in this way. This hypothesis should be tested in terms of Manna benefits, should low plasmid level inhibition be augmented by known Manna DNA retardation, given the

Fabaceae family connection with hyper selenium accumulation capacity.

Closely related genera to Astragalus, Oxytropis also includes selenium flora species, such as loco weed on the Colorado Plateau, a well-known back arc pull apart basin extension province. This imparted sulphide mineralization of molybdenum, rare metal minerals and tellurium sulphides, scandium and selenium are notable (e.g., Cripple Creek). The Oxytropis genus diverged from Astragalus about 16-12 Ma, around the Langhian to Tortonian stage of the Miocene, after the main Oligocene metallogene events in the American cordillera.

Indeed, Astragals are a very widely used traditional medical herb by many cultures. Coincidently, they are one of the most reliable prospecting plants, first noted in 1957, clearly having Medical Geology links. With concentration of selenium flora reaching around 1% Se dry weight [36]. This study shows Manna has similar order selenium concentration and as this study suggests similar vectoring potential, and significantly considerable scope for novel medically active compound discovery.

Conclusion

As some elements such as calcium, magnesium, selenium, lithium, sodium and potassium contents have not been determined in Taranjebin to date, our study focused on them, especially calcium and selenium, due to high nutritional value in Iranian context. Manna nutritional observations need to be viewed in the context of regional food bowl, in terms geological environments and anthropogenic inputs. These factors include irrigation, fertiliser and historical cultural life styles changes, with nutritional adequacy reflected in responding ethnomedicine practices. Historically, traditional uses of Manna were for inflammation and disease, particularly for liver and systemic inflammation expressed as neonatal hyperbilirubinemia, as noted. Recent Iranian Manna observational research concluded Manna not only possess valuable medicinal properties but may also comprise good sources of essential mineral elements beneficial in treatment of various deficiency disorders. In terms of poor malnourished communities in Iran, gaps may be present for adequate essential selenium micronutrient.

Taranjebin Manna, a rare specific gum exudate from Fabaceae genera Alhagi, was screened for its high ethno-medical quality and, for the first time, it was found to have a very high selenium content that is indicative of a likely active component. This work has shown, for the first time, selenium exists in high quantities in the Manna type Taranjebin. Biogeochemical results are reported here along with reviews on Manna terminology, selenium geochemistry, mobility and geogenic links along with soil fractionation studies from a Manna producing area. We discuss these results in terms of Medical Geology of the highly specialized Taranjebin Manna ethnomedical product. Considering these results, we have reviewed traditional medical efficacy of Manna and proposed biomedical efficacy hypotheses for its high demand and linking efficacy to selenium biochemistry and geogenic attributes with the Ethno-medical Geology distribution of Taranjebin Manna in Iran. Several biochemical hypotheses were discussed for this potential activity, in the context of Mann's glycoprotein content as a plausible explanation for Taranjebin Manna's high ethno-medical demand. Its use for neonatal hyperbilirubinemia and thyroid issues is highly suggestive of high selenium species contents as the active component. The average selenium content was consistently high, averaging 492 mg/100 g Se in the range of 482 to 513 mg/100 g Se (N: 14, STD 8.2), dry weight. Important traditional medical Manna efficacy is inferred because of this finding. Investigation into Taranjebin Manna distribution reveals biogeochemical factors, such specific local geogenic conditions which contribute to Manna selenium content derived from specific Alhagi genera species, *Apersarum Boiss*, *A. bushe* and *A. mannifera Desf.* Therefore, it was concluded that Medical Geology explains the traditional efficacy of Taranjebin Manna. Soil texture studies point to sandy loam textures with clay and silt equally around 11%. Our studies reveal suitable sandy loams for these plants Manna Selenium accumulation. Other mobility factors are discussed in terms of calcareous higher pH within regions of disseminated sulphide mineralization from specific host rocks. The distribution channels of such active Taranjebin Manna reveal Medical Geology of Manna to central south, eastern and north eastern Neo-Tethyan volcanic and pluton arc systems hosting metallogene zones. These are known for hydrous calc alkaline trends, towards stronger alkalic (higher volatile element content) magmatism, within the Urumieh-Dokhar arc, Chagai arcs of western Pakistan and the north eastern Alborz arcs respectively. The studies on higher Manna selenium sourced in Rasavi Khorasan concluded that they are result of younger post collisional extension systems that correlate with higher Manna selenium. Other potential sources of selenium are amongst sulphides of the ophiolite suite that accompany these terrains along sutures, these may also provide suitable basic conditions with carbonates. However, since average Manna selenium content increases in the earlier calc alkaline to post collisional alkalic trends, this points to differentiate volcanic and plutonic arcs of Iran for both a source and quality Manna product in terms of selenium content. A possible symbiotic insect relationship is considered from the genus Larinus habiting the Alhagi shrubs generating the Manna exudates. Findings are also discussed in context of global Fabaceae species, such as, Astragalus, in terms of selenium hyper accumulation evolution in geologically selenium enriched mineral terrains, with differentiated volatile magma sources, some displaying base metal associated gold terrains.

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Conflict of Interest

None of the authors have any conflicts of interest associated with this study.

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