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NEWER TRACE ELEMENTS MEASURED BY RNAA AND AAS

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ABSTRACT: Very recently, quite attention has been made on a few more trace elements in foodstuff as newer essential for animal and human health in certain ranges of concentration or intakes. These traces are namely: Aluminum, Nickel, Vanadium and Tin. Al and Ni have been measured by Atomic Absorption Spectroscopy (AAS), and two latter ones measured by Radiochemical Neutron Activation Analysis (RNAA) in few references laboratories. Here also scandium was analyzed by Instrumental Neutron Activation Analysis (INAA) as well. These measurements were made for the most of the Iranian diets and other participant countries' diets in frame of coordinated research project (CRP) led by International Atomic Energy Agency (IAEA) in period of 1986–1994, but practically it took more years. Here in this work the daily dietary intakes of above mentioned trace elements are given and discussed while the results of other 20 more nutritionally important trace elements were appeared somewhere else.

Introduction

In a few recent decades numerous research works have been performed for importance of minerals to human health in many countries in all over the world. This is true that these minor and trace elements are some structurally, nutritionally and even radiologically important. Among these, nutritional importance trace elements some may be essential trace elements with certain definitions (Valkavic, 1975; Skalny, 1999) and some other trace elements may be toxic. Meantime there have been controversial dispute whether essentiality and toxicity is under the influence of elemental characteristic or concentration. Though the forms of species, compound and valance state of metals are quite significant (Valkavic, 1975; Skalny, 1999; WHO, 1996; Panel, 2002; Ebdon et al., 2001; IAEA, 1980), but there are some trace or ultra-trace elements which in certain ranges of concentrations or intakes that play as an essential and in higher level pretend to be toxic element.

Therefore the terms of requirement level or recommended allowances and etc. are the matter of importance and consideration. But these definitions with some added word make rather different meaning such as basal requirement, normative requirement or safe range of intakes for individual/population, even lower/upper level of requirement and tolerable level which all make sense that one never can say a certain element is an essential and another one is non essential or it is purely toxic. Because the most of trace elements in lower ranges may be at the risk of deficiency and in higher range at the risk of toxicity and meantime in medium range may act as an essential element so called sometime "safe range of intake for individual or safe range of population mean intakes in larger study group" (WHO, 1996; Panel, 2002). This meaning, comes from the statement saying that "there are no toxic substances but toxic doses" which is in contradiction to some extent with simplified statement that "trace essential is very low amount of the element but biologically very significant and effective in health maintaining" (Valkavic, 1975; IAEA, 1980; Oberleas et al., 1999).

On the light of reasonably enough research work, there are some certain elements in certain ranges of concentration or intakes as essential elements and usually they are not occurring toxic or fatal in normal dietary at all (e.g. Fe, Zn, Cr, Co, Cu, Mo, Se, I) and there are some toxic trace elements that from very low level about ìg quantity (e.g. As, Cd, Pb, Hg) with possibly some pharmacological essentialities (Valkavic, 1975; Skalny, 1999; WHO, 1996; Panel, 2002; Ebdon et al., 2001; IAEA, 1980; Oberleaset al., 1999; Underwood, 1977; Bowen, 1966). However, controversial elements are Al, Ni, V, Sn and some more that the function of their essentiality is not as much as previous elements so called essentials. Also the toxicity of these elements are potentially far less than the toxic elements even in higher quantity. This is likely due to abnormalities in dietary, drinking, environmental condition or unless some excessive exposure somehow. However the latter elements are so called Newer or Possibly essential elements. The aspect of this matter is the interest of this work in particular their analysis in daily diet of Iranian study groups.

Materials and methods

The procedure for diet preparation and relevant study groups were described in previous papers (Gharib et al., 2001a,b). Here it is to be summarized briefly.

Study groups

The study groups were selected among common healthy people from five major regions in accordance with their various food habits in Center, North, East, West and South indicating by C, N, E, W and S respectively. Then, three classes of the population (study groups) were chosen: Literate Illiterate and Rural indicating by numbers1, 2 and 3 respectively .All Iranian study groups are prefixed with IR abbreviation of Iran. Since the central study groups have to be representative for larger population ,then, each study group (1, 2, 3) were forming from 6 study groups composed of the families from 2, 3, 4, 5, 6, and 7 members and then all put into one study group to be comparable with others. However, here in this study, the representative man out of each study group is an adult person aged 20–65 years and weight of 50–65 kg.

Sampling method

Total mixed diet prepared on the basis of dietary recording method. This method was chosen since a) no statistic data were available on the food consumption in national or regional level, b) no common understanding would let one for duplicate diet preparation in a large study group in regional level and c) no marketing basket method could be implemented in the mid of 1980's when this program planned, as the result of uneasiness/unpopular whole food marketing. Therefore, this job was assigned on a few trained nutrition students. However these volunteers who were familiar with the regions and food habits of the people, made questioning the appropriate selected test subjects (study groups) and recording what ever they eat (in accordance with their detailed food items and all forms of cookings or non cooked items) every day for 4–5 consequent days. Also individual habit of eating, drinking and additives were questioned and recorded.

Diet reconstitution/Reformulating

The recording data of food consumption in laboratories of Nutrition Institute were processed and converted to the appropriate food composition either cooked or raw. Then, this composite transferred to special blender with titanium blade, mixed, homogenized, freeze dried and powdered. This material was aliquoted to a few samples to be sent to different local or reference laboratory by International Atomic Energy Agency (IAEA) to be taken up for analysis.

Measurement

As it was mentioned in earlier publication in more detail (Gharib et al., 2001a,b), this project was an international one and many countries participated as collection centers (for daily diet sampling) and reference analytical centers(for analytical purposes) or some may be for both. Therefore, the diets were to be analyzed in a few references laboratories and back up laboratories along with the appropriate quality assurance criteria.

The elements of the interest of this work were of Al, Ni, V, Sn and Sc. The first two elements are analyzed by Atomic Absorption Spectroscopy, AAS, in Medical Physical Laboratory of Toronto and in Agriculture Research Center of Jokioinen in USA respectively. Meantime, Both Vanadium and Tin analyzed by Radiochemical Neutron Activation Analysis, RNAA, in Institute "Jozef Stefan" in Ljubljana, former Yugoslavia. Scandium measured by Instrumental Neutron Activation Analysis in Siebersdorf Laboratory of IAEA in Vienna. Meantime a few measurements were made locally by different method as well (Gharib et al., 2001a). The main participants were of:

AU: Australia, BR: Brazil, CA: Canada, CH: China, **IR: Iran**, IT: Italy, JA: Japan, NO: Norway, PO: Portugal, SP: Spain, SU: Sudan, SW: Sweden, TH: Thailand, TU: Turkey and US: USA. These countries are namely collection centers but some more countries participated as analytical centers or for both.

The reason to perform this analysis in different laboratories was due to speciality and being of them as a reference laboratory for above mentioned elements. A very strict quality assurance program was applied on this project as a whole by IAEA.

Results and discussion

The results for interested elements are given in Tables 1 and 2 for different regions and different main study groups respectively. Table 3 shows the more results

Table 1. Intakes of some newer trace elements of Iranian daily diet in terms of different regions (mg/day/person).

	Dry wt., gr/day	Al	Ni	V	Sn	Sc
IR-C-1	806	28.4	0.51	0.063	0.381	0.0054
IR-C-2	921	27.1	0.55	0.070	–	0.0079
IR-C-3	906	25.6	0.56	0.048	–	0.0042
IR-C	**878**	**27.0**	**0.54**	**0.061**	**0.381**	**0.0058**
IR-N-1	1019	43.7	1.75	0.106	–	–
IR-N-2	1540	42.7	0.15	0.073	–	–
IR-N-3	1413	29.6	1.16	–	–	–
IR-N	**1324**	**38.7**	**1.02**	**0.090**	–	–
IR-E-1	633	15.5	0.45	0.048	–	–
IR-E-2	674	25.6	0.51	–	–	–
IR-E-3	1007	28.1	0.67	0.073	–	–
IR-E	**762**	**23.1**	**0.54**	**0.061**	–	–
IR-W-1	1005	24.9	0.70	0.059	–	–
IR-W-2	1116	36.5	0.69	–	–	–
IR-W-3	816	14.8	0.50	–	–	–
IR-W	**979**	**25.4**	**0.63**	**0.059**	–	–
IR-S-1	691	–	0.50	–	–	
IR-S-2	699	–	0.55	–	–	
IR-S-3	1040	–	0.78	–	–	
IR-S	**810**	–	**0.61**	–	–	
IR av.	**951**	**28.5**	**0.67**	**0.067**	**0.381**	**0.0058**

Table 2. Intakes of some newer trace elements of Iranian daily diet in terms of main study groups (mg/day/person).

	Dry wt., gr/day	Al	Ni	V	Sn	Sc
IR-C-1	806	28.4	0.51	0.063	0.381	0.0054
IR-N-1	1019	43.7	1.75	0.106	–	–
IR-E-1	633	15.5	0.45	0.048	–	–
IR-W-1	1005	24.9	0.70	0.059	–	–
IR-S-1	691	–	0.50	–	–	–
IR1	**831**	**28.1**	**0.78**	**0.069**	**0.381**	**0.0054**
IR-C-2	921	27.1	0.55	0.070	–	0.0079
IR-N-2	1540	42.7	0.15	0.073	–	–
IR-E-2	674	25.6	0.51	–	–	–
IR-W-2	1116	36.5	0.69	–	–	–
IR-S-2	699	–	0.55	–	–	–
IR2	**990**	**33.0**	**0.49**	**0.072**	–	**0.0079**
IR-C-3	906	25.6	0.56	0.048	–	0.0042
IR-N-3	1413	29.6	1.16	–	–	–
IR-E-3	1007	28.1	0.67	0.073	–	–
IR-W-3	816	14.8	0.50	–	–	–
IR-S-3	1040	–	0.78	–	–	–
IR3	**1036**	**24.5**	**0.74**	**0.061**	–	**0.0042**
IR av.	**952**	**28.5**	**0.67**	**0.067**	**0.381**	**0.0058**

Table 3. Intakes of dietary newer trace elements in central region of Iran (mg/day/person).

	Dry wt., gr/day	Al	Ni	V	Sn	Sc
IR-C-12	851	20.8	0.539	0.076	0.323	0.0059
IR-C-13	730	23.9	0.477	0.031	0.433	0.0042
IR-C-14	639	15.8	0.504	0.047	0.388	0.0059
IR-C-15	664	25.0	0.605	0.047	–	0.0048
IR-C-16	873	31.0	0.408	0.060	–	0.0037
IR-C-17	1082	53.7	0.555	0.119	–	0.0079
IR-C-1 av.	**806**	**28.4**	**0.515**	**0.063**	**0.381**	**0.0054**
IR-C-22	1194	35.5	0.493	0.161	–	0.0410
IR-C-23	902	27.9	0.563	0.063	–	0.0069
IR-C-24	896	27.7	0.849	0.056	–	0.0048
IR-C-25	819	35.9	0.347	0.034	–	0.0025
IR-C-26	964	24.9	0.590	0.067	–	0.0028
IR-C-27	752	10.7	0.453	0.041	–	0.0041
IR-C-2 av.	**921**	**27.1**	**0.549**	**0.070**	–	**0.0079**
IR-C-32	997	31.4	0.610	0.071	–	0.0064
IR-C-33	694	23.5	0.413	0.053	–	0.0031
IR-C-34	657	18.5	0.535	0.033	–	0.0030
IR-C-35	1220	19.8	0.933	0.040	–	0.0034
IR-C-36	913	17.3	0.440	0.053	–	0.0026
IR-C-37	862	42.8	0.446	0.040	–	0.0064
IR-C-3 av.	**906**	**25.6**	**0.563**	**0.048**	–	**0.0042**
IR-C av.	**878**	**27.0**	**0.542**	**0.061**	**0.381**	**0.0058**

Table 4. The daily diet content of some newer trace elements in various countries (ppm).

	Al	Ni	V	Sn	Sc
AU	14.80	0.593	–	–	–
BR	19.03	0.691	0.033	–	0.003
CA	–	–	–	–	–
CH	27.67	0.259	0.047	–	–
IR	29.98	0.707	0.040	0.381	0.0058
IT	13.27	0.262	–	–	–
JP	6.34	0.356	0.024	–	–
NO	8.33	0.544	–	–	–
PO	14.52	0.240	–	–	–
SP	10.41	0.274	0.052	–	0.001
SU	39.72	0.546	0.125	–	0.008
SW	–	0.607	–	–	–
TH	13.92	0.341	0.019	–	–
TU	24.09	0.764	0.046	–	0.005
US	27.62	0.341	–	–	0.001
Ave.	**19.61**	**0.462**	**0.048**	**0.381**	**0.0040**

Table 5. Some further relevant data on this work for interested trace elements (WHO, 1989, 1996; Oberleas et al., 1999).

Elements	Al	Ni	V	Sn	Sc
	AAS		RNAA		INAA
Normal requirement mg/day	3–14	0.1	0.01	0.01	–
Tolerable level mg/day	65	0.6	10	15–30	–

raising from smaller study groups in central region which each of six is being represented as IR-C-1, IR-C-2and IR-C-3. The daily diet content of newer trace elements are shown in Table 4 for various countries participated in this work. The normative requirement/level and tolerable level for discussed trace elements as well as the analytical methods are given in Table 5. These data are all illustrated in Figures 1–4 which may be more useful.

Aluminum. There are no quite enough evidences or data to prove the essentiality of Al in any species of plants, animal or microorganisms as yet. In vitro, Al has

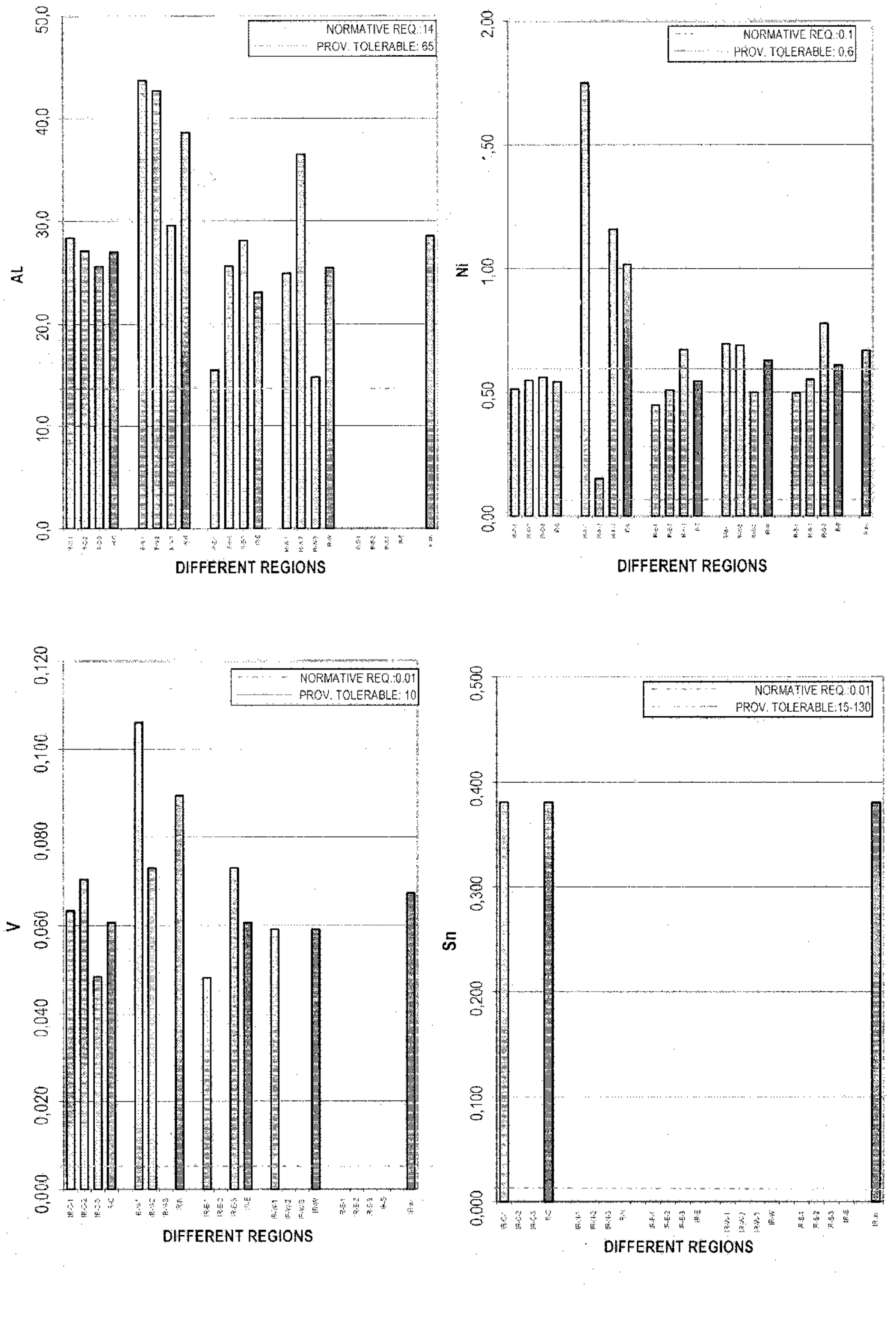

Fig. 1. Comparative intakes of newer trace elements in different regions study gropus (mg/day/person).

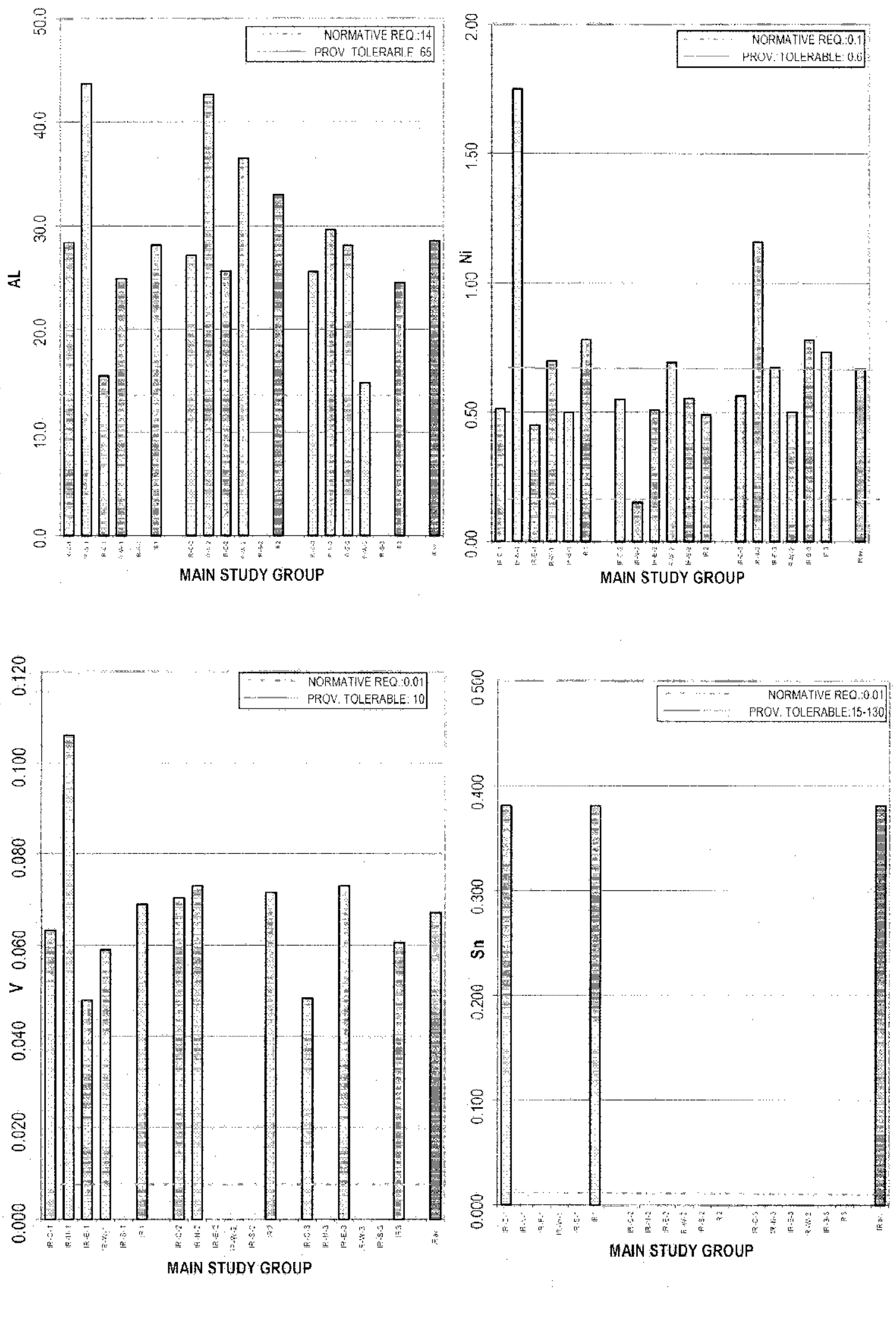

Fig. 2. Comparative intakes of newer trace elements in main study groups (mg/day/person).

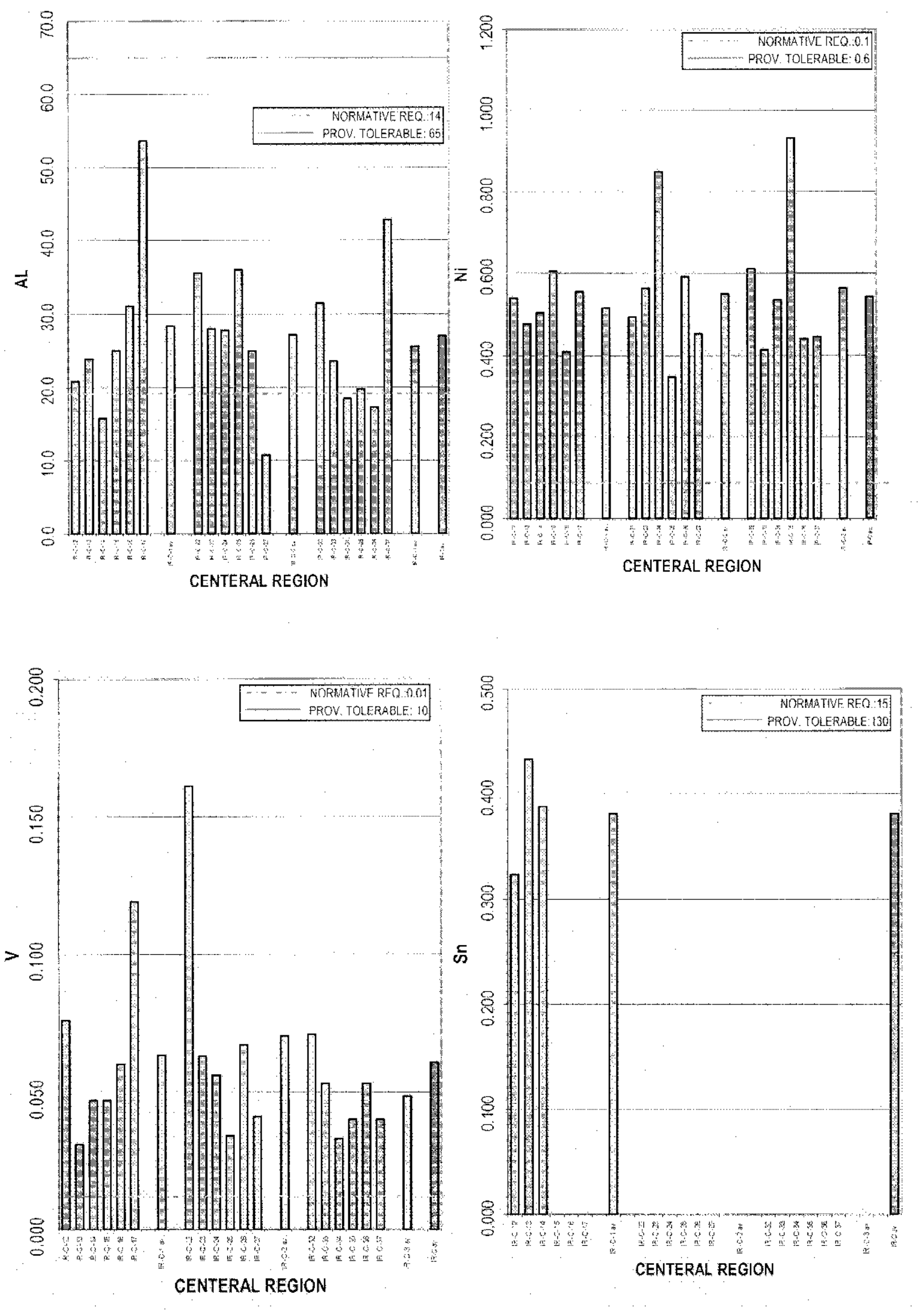

Fig. 3. Comparative intakes of newer trace elements in main study groups (mg/day/person).

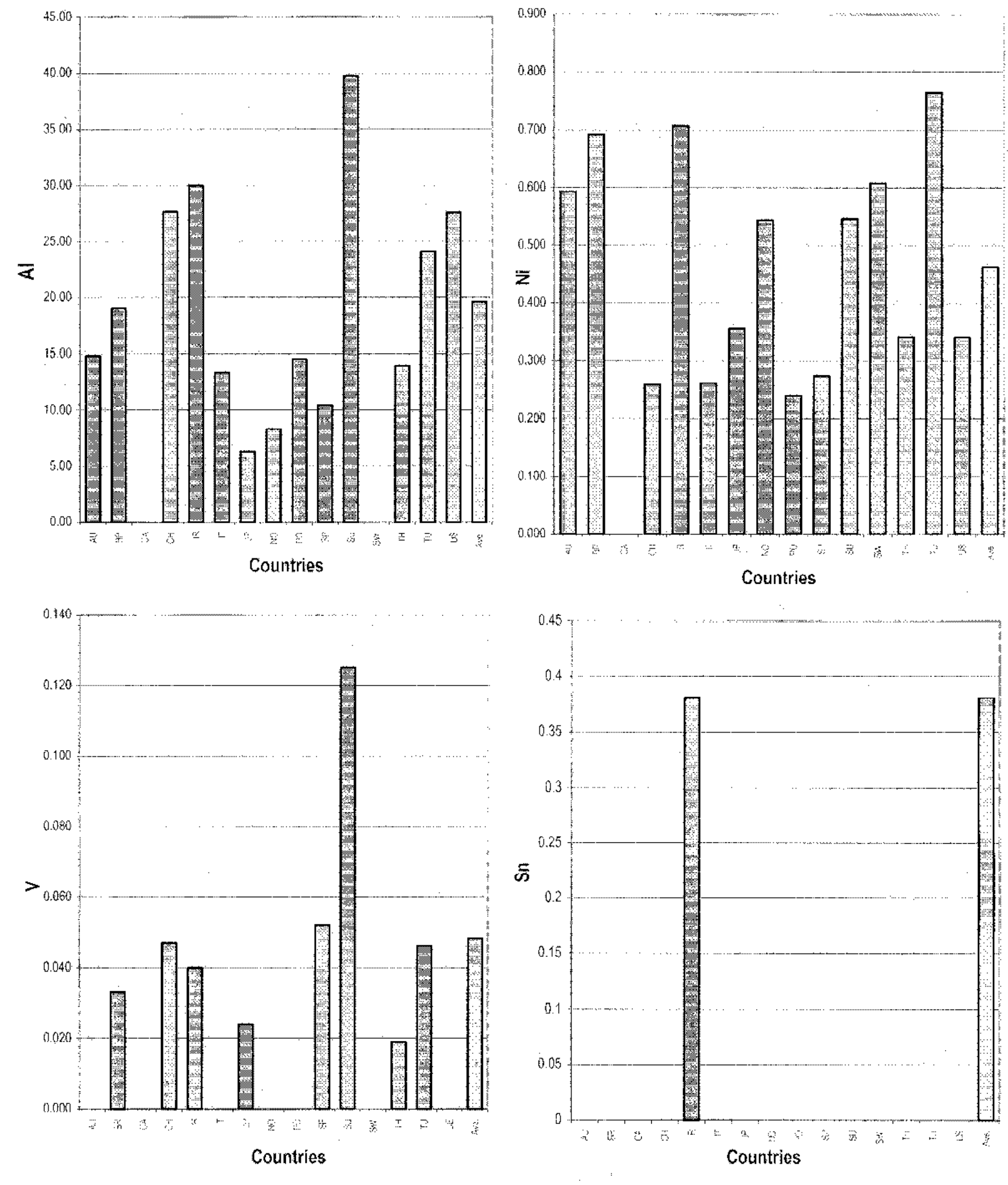

Fig. 4. Comparative concentration of newer trace elements in various countries (ppm).

been shown to stimulate a few enzyme systems (Oberleas et al., 1999; Underwood, 1977). However, low aluminum semi synthetic ration in goats' diet for four years exhibited some differences and less life expectancy as compared with that of control goats (WHO, 1996). Ingested Al is poorly absorbed about 2–4%. Aluminum may also be inhaled from atmosphere whose absorption by this route is more efficient. Soluble salts such as $AlCl_3$ are better absorbed than the more insoluble salts. The excessive exposure and inhalation of aluminum powder may cause, Less motility in the gastrointestinal tract, Hypo chromic anemia (not associated with Fe deficiency), Bone formation, Pulmonary fibrosis mostly in dialysis when the Al content of some water used for the preparation of dialysates. The most important contribution to Al intakes comes from antacid medications that provide several grams of metal per day. Aluminum interacts with many elements such as Ca, F, Fe, Mg, P and Sr when ingested in excess and can reduce their absorption. It has also been shown that Al interferes with variety of biological and enzymatic processes (e.g. displace Mg from ATP, with resulting stabilization of ATP and bone formation) (Oberleas et al., 1999). The estimates of average daily intakes have ranged from 3–14 (WHO, 1996) or 4–51 (Oberleas et al., 1999) mg/day depending on geographical location, pH of soils, cookware, aluminum sulfate baking powder, water and industries. At this levels and lower, there would be no risk of interactions or toxicity. Provisional tolerable intake of aluminum is approximately 1 mg/kg of body weight or 65 mg/day/adult (WHO, 1996; Oberleas et al., 1999; Alfrey, 1986; Bogden et al., 1982).

Nickel. There are some direct evidences that nickel, the same as other metals in the first transition series of periodic table, is essential to microorganisms and animals. The existence of this metal in metalloprotein of human serum and its presence in a few enzymes, RNA and evidence that nickel function similarly in human, then the possible nickel essentiality for man is quite high (Valkavic, 1975; WHO, 1996; Oberleas et al., 1999). Pathological signs consistent with nickel deficiency have been produced in chicks, rats, swine and goats. Dietary nickel is poorly absorbed in the range of 1–10% even at high intakes. This absorption is enhanced by Iron deficiency, pregnancy and lactation. Excessive nickel exposure may be led to dermatitis and eczema .Nickel has been reported to increase in blood and relevant tissues with cancer, myocardial infarction. The concentration of nickel has been reported 4.8 µg/L in whole blood and 1.7–4.4 µg/L in human serum. Available information for animal and its extrapolation to human, may suggest a basal nickel requirement of less than 100 µg?/day/adult. Threshold level for toxicity/provisional tolerable level may be less than 600 ìg daily (WHO, 1996).

Vanadium. The essentiality of vanadium was first suggested in 1971 by three laboratories, stating that in chicks or rats causing reduced growth of wing and tail feathers and reduced body growth respectively (Oberleas et al., 1999). Also it is believed that vanadium does have a role in hormone, glucose, tooth metabolism and inhibit the cholesterol synthesis which is stimulated by manganese (Valkavic, 1975; WHO, 1996). It is hypothesized that vanadium regulates the Na^+/K^+ ATPase as the sodium pump and phosphoryl-Transfer enzymes. The absorption of vanadium is rather poor and a great amount that can be absorbed from gastrointestinal tract under some conditions (Bogden et al., 1982). The V^{+5} ion is absorbed 3–5 times more efficient than V^{+4}. Serum vanadium level is about 0.15 ng/ml and more than 1.0 ng/ml may consider as excessive exposure. The studies suggest a daily intake of 10 ìg daily as a basal vanadium requirement. A daily intake of 10 mg/day indicates the signs of toxicity in humans. Thus less than above intake may assume as threshold toxicity/ tolerable level. Vanadium concentration of diet more than 25 mg/kg for rat and 50mg/kg for animals result depressed growth, diarrhea and mortality. Vanadium appears to be more toxic when added to highly purified diets and completely prevented by EDTA by inhibiting its absorption or increasing the dietary chromium (Underwood, 1977).

Tin. Tin could function at the active site of metalloenzymes and proteins. The oxidation-reduction potential of $Sn^{+2} \leftrightarrows Sn^{+4}$ is 0.13 volts which is well within the range of physiological oxidation- reduction and very close to the potential of the flavin enzymes. Essentiality of tin is established and it is responsible for growth, less efficiency of food utilization, alopecia and depressed response to sound (Underwood, 1977; Alfrey, 1986; Bogden et al., 1982; Schwarz, 1971). Inorganic tin has a low order of toxicity because its poor absorption in particular when the dietary intake is high. Tin human poisoning symptoms include nausea, abdominal cramps, diarrhea, vomiting and its chronic exposure to excessive intake lead to group depression, anemia and affect several enzymes and interfere with metabolism of Zn, Cu, Ca and alter the tissue concentrations of a few other elements. Organic tin compounds are appreciably more toxic and attack the central nervous system (Barrens, Stroner, 1959). The recent study suggest average basal and normative requirement about 0.01 mg /day/adult, but not yet confirmed. Provisional tolerable intake for tin is 2 mg /kg of body weight or 130 mg/day/adult (WHO, 1989; Yokoi et al., 1990).

Scandium. Since Sc is the first element of first series of transition elements which are most of them essential, hence it may be in order of some essentiality too. Meantime it is just next element to Ca, then, perhaps it may have some biological behavior similar to alkaline earth metals. But there is not much work or literature about this element to prove it. In this work, the intakes or diet's content of scandium also measured and given in tables where any results was available.

Conclusion

In accordance with the recent literature (WHO, 1989, 1996; Oberleas et al., 1999; Ebdon et al., 2001; Panel, 2002) and considering the previous section as well as Table 5, the following observation may be drawn out. The results shows that the alteration of these elements in Iranian daily diet is rather in wider ranges and all apparently meet almost the normal requirement if they are to play an essential role .Among these, nickel content or intakes in particular for certain study groups seems to be higher than tolerable level, this is while no symptoms has been reported epidemiologically. Nickel content of diets in some other countries is more or less similar to Iran. Therefore no particular contaminations might have been likely occurred to Iranian diets. This is to be added to the epidemiological study which partly has been carried out for deficiency of certain essential elements and relevant diseases in Iran. In this regard one has to consider a further points to be important:

Aluminum content of the body tissues and its intake are considered that may alter to some extent with environmental pattern while essential elements have more symmetrical distribution (Oberleas et al., 1999). Therefore body tolerance is not confined as long as the minimum amount should be accessible via diet.

The interaction of this trace element with other essential or non essential are more important when the imbalances are occurred and absorption and retention (biological half life) is drastically changed as the result of various species or compounds of micronutrient. Though homeostatic control may be applicable by biochemical mechanism.

However another matter concerning the newer trace elements is their poor absorption. Since, the absorption of these traces in ideal condition mostly is less than 10% in particular when the intake of element is higher the percentage of absorption is lower.

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