Presence of Arsenic in Pesticides used in Sri Lanka: A Preliminary Analysis

M.A.C.S. Jayasumana

Department of Pharmacology, Faculty of Medicine and Allied SciencesRajarata University of Sri Lanka

P.A. Paranagama

Department of Chemistry, Faculty of Science, University of Kelaniya

M. Amarasinghe & S.I. Fonseka

Department of Botany, Faculty of Science, University of Kelaniya

and

D.V.K.Wijekoon

Water Resources Board, Colombo 07

ABSTRACT

World Health Organization classifies pesticides with arsenic compounds as active ingredients to be highly hazardous. Arsenic (As)-containing pesticides are thus banned in Sri Lanka since 1995 and it has been officially notified in the extraordinary gazette notification no 1190/24 of the Democratic Republic of Sri Lanka of 6th June, 2001. Arsenic is not even prescribed to include as an inert ingredient, except for six types of pesticides in which it is allowed (within limits) as an impurity and in Sri Lanka, copper-based pesticides only are legally allowed to contain (within limits) arsenic.

Present study is an attempt to test the pesticides available in the Sri Lankan market for presence of arsenic. Despite the fact that importation of As- containing pesticides is illegal, results of the present study revealed that twenty nine (29) out of the 31 available pesticide brands belong to 20 active ingredients in the local market tested, contained As in the range of $180\pm14-2586\pm58$ µg/kg and it varied depending on the type of active ingredient, brand, batch of pesticides, importer and the area that it is used.

Using arsenicals in augmenting toxicity of pesticides is speculated a potential means through which As enters the natural environment, especially in the areas where rice cultivation is predominant. Chemical waste produced by a variety of industries is a cheap and a readily available source of arsenic.

Results of the present study therefore highlight the potential magnitude of an environmental pollution issue that has not been hitherto received due attention. It is an urgent need therefore to divert more resources to consolidate these findings and to plan and implement strategies to prevent/ abate pollution of Sri Lankan environment with arsenic derived from agrochemicals. Chronic arsenic poisoning

evidently leads to many health hazards and it has been proved beyond doubt that the entry of minute quantities of As to human body in microgram levels over several years can cause many non communicable diseases. A multipronged approach with input from different specialties will be needed to make inroads into this national problem.

INTRODUCTION

Arsenic compounds have been used as pesticides for centuries. The oldest records indicate use of arsenic sulfide in China as early as AD 900 (Shepard, 1939). The poisonous properties of arsenic trioxide were well known during the middle ages and it was a favorite instrument of murder as practiced by the Borgias. This knowledge of the poisonous properties of arsenic compounds probably led to their use as insecticides. The first insecticidal use of arsenic in recent times has been reported in 1867 in Colorado potato beetle in the USA (Peryea, 1998). In that occasion, copper aceto arsenite (Paris green) was used as an insecticide. Thereafter, Paris green has been used in many countries for mosquito abatement. Lead arsenate was the most extensively used arsenical insecticide which has been introduced in 1892 for use against gypsy moth in Massachusetts, USA. Lead arsenate initially was prepared by farmers at home by reacting soluble lead salts with sodium arsenate. Lead arsenate was the principle pesticide used in Western world until Dichloro Diphenyl Trichloroethane (DDT) was introduced by Paul Muller in 1939 (Benson et al., 1969).

Arsenic trioxide, As₂O₃ is a white crystalline material sometimes referred to as white or gray arsenic. It is the starting material in the commercial manufacture of arsenical compounds used as insecticides and weedicides. The calcium arsenate that was sold commercially as an insecticide is a complex mixture of several calcium arsenates and an excess of calcium hydroxide. Commercial calcium arsenate generally is colored pink and is alkaline in reaction. It is a finely divided powder. It has been used extensively against certain insects affecting field crops, especially cotton.

Following the use of arsenical pesticides for 2-3 decades several ill effects of human exposure to arsenic has been identified. As arsenic is accumulated in environment and in biological systems there were many serious concerns of continuation of arsenical pesticides. With the time, more serious health impact has been detected due to chronic arsenic poisoning (Kapaj et al., 2006). This not only affects the user of pesticides but also the population in general by entering the food chain and polluting the water table and surface water. It has serious environmental impacts like the destruction of fish, bird wildlife and the quality of the habitat. The increase of cancer, chronic kidney disease, diabetes mellitus, heart diseases suppression of the immune system, sterility among males and females, neurological and behavioral disorders, especially among children, have been attributed to chronic arsenic poisoning. (Tchounwou et al., 2003. Tseng et al., 2003; Rahaman et al., 2003; Meliker et al., 2007; Kozul et al., 2009; Vahter, 2009). These effects probably extend to farm and other animals. With the expansion of knowledge about the fate

of arsenic in environment and adverse health effect of chronic arsenic poisoning, many countries have restricted or banned the usages of arsenic containing pesticides.

Termination of lead arsenate use in USA, started in state of Washington in 1948 was declared on 1st of August 1988 and all insecticidal uses of lead arsenate were officially banned in USA. Due to harmful effects on human health, physical removal of arsenic contaminated topsoil by excavation has been carried out in USA (Peryea, 1998). Arsenical pesticide use in Germany was banned in 1974 (Nagy, 1974). Calcium arsenate, lead arsenate, copper arsenate and sodium arsenite have been classified as highly hazardous (class 1b) technical grade active ingredients according to the classification introduced by WHO in 2009 (WHO guidelines of pesticides, 2009).

Arsenic in drinking water, usually in its inorganic form, is known as the silent, slow killer because its presence is not revealed by taste, odour or colour of the water. Groundwater is the main source of drinking water in many countries around the world. In rural areas of Bangladesh and India (West Bengal), the presence of arsenic in groundwater has endangered tens of millions of people (Chakraborti et al., 2010). Apart from ground water, elevated arsenic levels in rice have been identified as a significant source of inorganic arsenic in south east Asian region (Abedin et al., 2002; Meharg, 2004). Rice is particularly susceptible to arsenic accumulation compared to other cereals. There are many controversies over the primary source of arsenic in ground water and rice in the south east Asian region. Some scientists are arguing this is naturally occurring while some are showing pesticides as the main source (Jamal, 2000).

Although presence of arsenic in locally-grown rice has been reported from Sri Lanka (Jayasekara and Freitas, 2004; Yamily et al., 2008 and Chandrajith et al., 2010) presence of arsenic in pesticides has hitherto not been investigated. The Control of Pesticides Act No. 33 of 1980 in Sri Lanka regulates imports, licensing, packing, labeling, storage, formulation, transport, sale, use thereof and other concerns of pesticides. The Registrar of Pesticides (ROP) is the sole authority implementing the laws and regulations under this Act. The Pesticides Technical Advisory Committee advises Registrar of Pesticides on policy and technical matters. The use of WHO class 1a and 1b pesticides for pest control in Sri Lanka was banned since 1995 and it has been officially notified in the extraordinary gazette notification no 1190/24 of the democratic republic of Sri Lanka of 6th June 2001 which states that use of pesticides containing arsenic or arsenic compounds as the active ingredient, is banned within Sri Lanka.

Jayasumana et al. (2011) reported the presence of arsenic in drinking water, rice grown in the area, hair and urine of patients of Chronic Kindney Disease of unidentified etiology (CKDu) as well as in body parts of diseased CKDu patients from Sri Lanka's largest rice cultivation areas in the North-Central Province. This led to the hypothesis that presence of arsenic compounds in drinking water and food may be a potential cause of CKDu and the pesticides containing arsenicals may be the potential source of it.

Objective of the present study therefore is to determine presence of arsenic in pesticides imported and used within the country.

MATERIALS AND METHODS

Pesticide sample collection

Sealed samples of pesticides (insecticides, weedicides and fungicides) were purchased from the major sales outlets in Padaviya and Anuradhapura town in Anuradhapura District, Padavi-Sripura in Trincomale District, Galewela in Kurunegala District and from company show rooms in Colombo. These sales outlets are the major centres through which agrochemicals are distributed in the adjacent areas. Brand names of pesticides to be sampled were selected to include - those that have the same active ingredient (according to the labels on the containers). nevertheless, distributed by different companies. Samples of the same pesticide brand collected from different areas belonged to different batches. Out of the 31 brands of pesticides tested for arsenic, seven were solids and the rest were liquids and they were contained in bottles (taken as samples in this study) of 100 ml in volume except for Glyphosates, of which some brands were contained in bottles of 500 ml in volume. Table 01 presents the number of samples used in this study from each brand with different active ingredients. Information provided with the pesticide containers (by the producers and distributors) did not state about presence of arsenic either as an active ingredient or an impurity.

Detection of arsenic in pesticides

Presence and content of arsenicals in pesticides was determined after digesting one gram samples of pesticides (either solid or liquid) using concentrated nitric acid (Analar grade) and then heating the mixture to 120°C on a hot plate. Since the boiling point of arsenic acid that is formed through the reaction of arsenic compounds and nitric acid is 130°C, maintaining the temperature below that is essential to retain the arsenic acid without being evaporated. This process is carried out in a fume hood. Concentrated Nitric acid was added in 10 ml aliquots to the digesting solution until it becomes transparent and colourless. This process took approximately three hours to complete, depending on the constitution of the pesticide. Once a colourless or a pale yellow transparent solution is obtained, 10 ml of a mixture of sulphuric and nitric in the ratio of 1:4 was added then and it was heated to 120°C until the volume is reduced to about 5 ml. In instances where a white or off-white precipitate was formed with the addition of the acid mixture, the flask was removed from heat.

Table 01: Number of samples tested for Arsenic from each brand of pesticides with different active ingredients collected from different areas.

No	Active ingredient	T	C	Bran	Physi	Place of	No	Total
		У	O	d No.	cal	purchase	of	No. of
		p	m		natur		samp	sampl
		e	pa		е		les	es
			ny					
01	Carbofuran	I	Α	01	S	Colombo	04	
			A	01	S	Padaviya	08	
			A	01	S	Anuradhapura	10	1000
			В	02	S	Colombo	08	36
			В	02	S	Anuradhapura	06	
02	Imidacloprid	I	Α	03	L	Colombo	05	10
			Α	03	L	Padaviya	05	
03	Methoxyfenozide	I	Α	04	L	Colombo	05	10
			Α	04	L	Anuradhapura	05	
04	Tubuconazole	F	Α	05	L	Colombo	04	08
			A	05	L	Galewela	04	
05	Etofenprox	I	С	06	L	Colombo	04	08
			C	06	L	Anuradhapura	04	
06	Fenoxaprop-p-	W	С	07	L	Colombo	04	08
	ethyl +Ethoxysulfuron		С	07	L	Padaviya	04	
07	Diazinon	I	С	08	L	Colombo	03	06
07	Diuziioii	1	C	08	L	Padaviya	03	
08	Quinalphos	I	C	09	L	Colombo	04	08
00	Quintiplies		C	09	L	Padaviya	04	
09	Thiamethoxam	I	D	10	S	Colombo	05	10
			E	11	S	Anuradhapura	05	
10	Pretilachlor+	W	D	12	L	Colombo	04	08
	Pyribenzoxim		D	12	L	Anuradhapura	04	
11	Oxyfluorofen	W	D	13	L	Anuradhapura	04	04
12	Bispyribac Na	W	Е	14	L	Colombo	03	06
	201		Е	14	L	Anuradhapura	03	
13	Glyphosate	W	A	15	L	Colombo	08	
			A	15	L	Padaviya	08	
			A	15	L	Anuradhapura	06	
			В	16	L	Colombo	06	
			В	16	L	Galewela	06	82
			В	16	L	Anuradhapura	08	
			D	17	L	Colombo	08	
			D	17	L	Anuradapura	06	

			D	17	L	Galewela	06	
	_		F	18	L	Colombo	08	
			F	18	L	Anuradhapura	06	
			F	18	L	Galewela	06	
14	Methomyl	1	F	19	S	Colombo	04	08
			F	19	S	Anuradhapura	04	
15	Chlophyriphos	1	В	20	L	Colombo	05	
			В	20	L	Anuradhapura	05	20
			C	21	L	Colombo	05	
			C	21	L	Padaviya	05	
16	MCPA	W	Α	22	L	Colombo	04	
-175	1000000		A	22	L	Anuradhapura	04	
	1		C	23	L	Colombo	04	
			C	23	L	Padaviya	04	
			D	24	L	Colombo	04	
			D	24	L.	Anuradhapura	04	40
			D	24	L	Galewela	04	
			F	25	L	Colombo	04	
			F	25	L	Padaviya	04	
			F	25	L	Anuradhapura	04	
17	Carbendazim	F	A	26	S	Colombo	05	10
			C	27	S	Colombo	05	
18	Penthoate	I	E	28	L	Colombo	04	
-	A A A A A A A A A A A A A A A A A A A		E	28	L	Padaviya	04	12
			E	28	L	Anuradhapura	04	
19	Dimethoate	1	В	29	L	Colombo	04	08
			В	29	L	Anuradhapura	04	
20	Profenofos	I	A	30	L	Colombo	05	
20			A	30	L	Anuradhapura	05	
			C	31	L	Colombo	05	25
			C	31	L	Anuradhpura	05	
			C	31	L	Padaviya	05	

Presence of mercury in pesticides leads to the formation of this precipitate. If precipitate is formed, next step (adding of percloric acid) was not be performed. This precipitate was well soluble in water. This mixture was added 5 ml of perchloric acid and heating was continued until the volume reduces to about to 5 ml and the solution was allowed to cool to room temperature. The resultant solution was transferred into a volumetric flask, diluted to 100 ml and used to measure arsenic and mercury content at µg/kg levels, using an Atomic Absorption Spectrometer equipped with hydride generator (AAS-HG).

Investigations were carried out at the analytical chemistry laboratory in University of Kelaniya using GBC 932 plus AAS-HG, Australia and results were confirmed by repeating the tests using aliquots from the same pesticide samples at the Water Resources Board, Sri Lanka using Shimadzu AAS-HG, Japan. The reading from AAS-HG was then multiplied by 100 to calculate the amount of arsenic present in a kg of pesticides. Each pesticide was analysed using the above method in triplicate samples. In order to determine the accuracy of the method, blank solutions without pesticides were prepared according to the above procedure and arsenic content was determined using the AAS-HG. Spiked samples (10 µg/Kg) in triplicates were also digested to confirm the methodology.

RESULTS AND DISCUSSION

Arsenic content in micrograms per kg in the pesticide samples investigated along with that of the blanks as well as the As measurements made at the laboratory of Water Resources Board of Sri Lanka are presented in Table 02.

A pesticide is composed of two main components, active and the inert ingredients. The active ingredient is the specific compound designed either to kill or debilitate the pest. In general, the active ingredient forms a certain percentage of the pesticide mixture and the rest comprises the inert ingredients that improve their storage, handling, application, effectiveness, or safety. Besides, there may be some chemical compounds present as impurities.

Table 02: Arsenic content in tested pesticide samples

A A B B A A A	Colombo Padaviya Anuradhapura Colombo Anuradhapura Colombo Padaviya Colombo	0114007 0307034 0315845 214574 245125 12018106 12145364	331 ±12 2458 ±78 554 ±16 854 ±21 1654 ±35	355±18 2574±86 624±25 811±32 1558±48
A A A	Padaviya		180 ±14	
Α	Colombo		359 ±12	220±17 410±25
A	Anuradhapura	1210108 1242156	911 ±24 872 ±18	887±35 950±25
A	ubuconazole A Colombo A Galewela		288 ±23 214±3 680 ±14 635±2	
C Anuradhapura		128051 154247	757 ±18 2584 ±28	782±12 2487±32
enoxaprop-p- C Colombo hyl Ethoxysulfur C Padaviya		EFKP000 62814254 EFKP000 62815445	1254 ±26 2578 ±39	1311±34 2490±45
iazinon C Colombo C Padaviya		171041 124152	625 ±42 995 ±21	689±52 1005±30
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		134129 928 ±08 134011 1893 ±15		952±18 1725±24
Thiamethoxam D Colombo E Anuradhan		CHK90215 25884544	542 ±19 1024 ±25	569±24 996±45
Pretilachlor+ D Colombo		SJS12058 SJS10G15	415 ±18 655 ±20	476±24 685±32
Oxyfluorofen D Anura		SA050B16	788 ±32	759±14
ribac Na E Colombo		B2111132 B2111130	721 ±21	718±29 1524±42
A A B B B	Colombo Padaviya Anuradhapura Colombo Galewela Anuradhapura Colombo	145225 142558 125478 35269 34986 35128 52487	233 ±15 858 ±24 1452 ±35 ND ND ND ND ND 785 ±17	245±21 847±36 1398±48 ND ND ND ND 765±21
	C C C C C D E D D E E A A B B B B	C Colombo C Padaviya C Colombo C Padaviya C Colombo C Padaviya C Colombo C Padaviya D Colombo E Anuradhapura D Colombo D Anuradhapura E Colombo E Anuradhapura A Colombo E Anuradhapura B Colombo A Padaviya A Anuradhapura B Colombo B Galewela B Anuradhapura D Colombo	C Anuradhapura 154247 C Colombo EFKP000 62814254 EFKP000 C Padaviya EFKP000 62815445 C Colombo 171041 C Padaviya 124152 C Colombo 134129 C Padaviya 134011 D Colombo CHK90215 E Anuradhapura 25884544 D Colombo SJS12058 D Anuradhapura SJS10G15 D Anuradhapura SA050B16 E Colombo B2111132 E Anuradhapura B2111130 A Colombo 145225 A Padaviya 142558 A Anuradhapura 125478 B Colombo 35269 B Galewela 34986 B Anuradhapura 35128 D Colombo 52487 <td>C Anuradhapura 154247 2584 ±28 C Colombo EFKP000 1254 ±26 C Padaviya EFKP000 2578 ±39 C Colombo 171041 625 ±42 C Padaviya 124152 995 ±21 C Colombo 134129 928 ±08 C Padaviya 134011 1893 ±15 D Colombo CHK90215 542 ±19 E Anuradhapura 25884544 1024 ±25 D Colombo SJS12058 415 ±18 D Anuradhapura SJS10G15 655 ±20 D Anuradhapura SA050B16 788 ±32 E Colombo B2111132 721 ±21 E Anuradhapura B2111130 1458 ±36 A Padaviya 145225 233 ±15 A Padaviya 142558 858 ±24 A Anuradhapura 125478 1452 ±35 B Colombo 35269</td>	C Anuradhapura 154247 2584 ±28 C Colombo EFKP000 1254 ±26 C Padaviya EFKP000 2578 ±39 C Colombo 171041 625 ±42 C Padaviya 124152 995 ±21 C Colombo 134129 928 ±08 C Padaviya 134011 1893 ±15 D Colombo CHK90215 542 ±19 E Anuradhapura 25884544 1024 ±25 D Colombo SJS12058 415 ±18 D Anuradhapura SJS10G15 655 ±20 D Anuradhapura SA050B16 788 ±32 E Colombo B2111132 721 ±21 E Anuradhapura B2111130 1458 ±36 A Padaviya 145225 233 ±15 A Padaviya 142558 858 ±24 A Anuradhapura 125478 1452 ±35 B Colombo 35269

	D	Galewela	53658	1462 ±24	1511=29
	F	Colombo	B0411070	865 = 29	860±32
	F	Anuradhapura	B0411258	2586 ±58	2570=48
	F	Galewela	B0411356	853 ±24	850±30
Methomyl	F	Colombo	A2411033	1112 ±29	1058±38
	F	Anuradhapura	A2411145	1458 ±35	1395±45
Chlophyriphos	В	Colombo	179011	1365 ±42	1286=38
	В	Anuradhapura	179145	654 = 09	670±35
	C	Colombo	A41525	865 ±31	874±38
	C	Padaviya	A45244	1008 ±24	1110±62
MCPA	Α	Colombo	1130024	858 ±15	856±24
	A	Anuradhapura	1130147	458 ±12	480±24
	C	Colombo	UCF20K19	895 ±11	890±14
	C	Padaviya	UCF20K28	478 ±13	472±18
	D	Colombo	0252146	1258 ±18	1288±42
	D	Anuradhapura	0252654	1496 ±24	1428±28
	D	Galewela	0248756	789 ±20	768=28
	F	Colombo	00256398M	ND	ND
	F	Padaviya	00256329M	ND	ND
	F	Anuradhapura	00256353M	ND	ND
Carbendazim	A	Colombo	991110	1458 ±23	1566±28
	C	Colombo	KJ2544	1163 ±25	1176±36
Penthoate	E	Colombo	A7010194	698 ±36	676::40
	E	Padaviya	A7010254	565 ±31	586±44
	E	Anuradhapura	A7010568	1258 ±44	1120±82
Dimethoate	В	Colombo	150110	965 ±25	984±32
	В	Anuradhapura	151256	2457 ±59	2380±72
Profenofos	A	Colombo	10051102	1452 ±45	1468±52
	A	Anuradhapura	10051265	865 ±21	880=26
	C	Colombo	HG12544	458 ±12	426±20
	C	Anuradhpura	HG12578	569 ±22	588=36
	C	Padaviya	HG12654	987 ±32	1010±42

(Total no of brands tested-31,

Arsenic was detected in 29 brands.

Arsenic was not detected in 02 brands.

Total no of active ingredients that were in the 31 brands tested -20.)

Since As-based pesticides are banned in Sri Lanka, presence of it as an active ingredient is a direct violation of the regulations based Pesticide Control Act of Sri Lanka. Inert compounds play a key role in increasing effectiveness of the pesticide formulation. The current list of approved inert ingredients of pesticides for agricultural use is listed in electronic code of federal registrations (e-CFR, EPA-

USA, 2011) and it clearly states that arsenic or arsenic related compounds cannot be used as inert ingredients in pesticides. The regulation is such that if As is present as an inert ingredient in the imported pesticides, it should be declared to the ROP of Sri Lanka.

Impurities in pesticide formulations too should be reported, whether they were present in the raw/starting material, formed during synthesis, storage or handling. According to the IUPAC technical report of pesticide impurities-(2003) arsenic is reported or likely to be present only in 6 pesticides even as an impurity. Those are Aluminium phosphide, Copper oxychloride, DSMA, MSMA, Zinc phosphide and Zineb. Out of those six compounds, only copper compounds are registered and allowed to use in Sri Lanka. So ideally arsenic cannot contain as an active ingredient, inert ingredient or as an impurity in any of the pesticide available in Sri Lanka except copper compounds.

Arsenic content was also shown to vary according to the active ingredient, brand and the batch number as well as the location where these pesticides are in wide use.

Presence of As in pesticides

According to the provisions available in the Control of Pesticides Act No. 33 of 1980, importation of pesticides that contain As or Hg as active ingredients is prohibited. Present study however was able to reveal that 29 out of 31 pesticide brands that are widely used in Sri Lanka contain As in significant amounts ranging from 180 $\pm 14~\mu g/Kg$ (in Imidacloprid collected from Colombo) to 2586 \pm 58 $\mu g/Kg$ (in Glyphosate collected from Anuradhapura) per kg of pesticide.

Since no information is given by the producer about the presence of As as the active ingredient in the pesticides tested, it could either be due to the fact that importer's certificate is erroneously prepared to conceal deliberately the presence of As as an active ingredient or that As is present as an impurity.

Arsenic content in weedicides are relatively high and the highest was recorded in the Glyphosate samples collected from Anuradhapura. Among the insecticides tested, As content was highest (2584 \pm 28 μ g/Kg) in Etofenprox collected from Anuradhapura. All samples of Glyphosate from one importer (B) and MCPA from importer F were not detected to contain Arsenic. Moreover, Glyphosates distributed by three other importers contained Arsenic as high as 2586 \pm 58 ppb/kg.

Active ingredients

Active ingredients of the pesticides subjected to present study are organic compounds (according to the information provided by the importing companies) and as such they should be less hazardous to human and the environmental health. However, presence of As transforms them to potential pollutants of soil and particularly groundwater..

Most of the inorganic arsenic compounds which were in use as pesticides in early 1900s were reported to possess similar properties to these organic compounds.

Inorganic arsenic compounds however are not innocent and they have a tendency to bio-accumulate and produce a wide range of adverse health effects on humans It was the main reason to abandon arsenical pesticides from the world (Peryea, 1998). When compared to organic active ingredients, inorganic arsenic compounds are very cheap and abundantly available as a waste product in mining and electronic industries. For example 260000 metric tones of arsenic rich dust containing an average of 76% As₂O₃ were stored underground at the giant mine in USA (Riveros et al., 2001). Even with the same active ingredient, pesticides have revealed to contain varying amounts of As, indicating that the composition is altered in the production process.

A most plausible explanation for the presence of arsenic in pesticide is that it may be added to enhance the toxicity of pesticides. Arsenic combines easily with carbon to form a variety of organic compounds with one or more As-C bonds. Organoarsenic compounds were largely used as herbicides and fungicides before the replacement from organophosphates (Crompton, 1998). Many countries have banned organo-arsenic pesticides as a result of increased awareness of their detrimental effects on the human health and environment. Admisite (10-chloro-9-10-dihydrophenarsazine), Clark 1(Diphenyl arsine chloride), Clark 2 (Diphenyl arsine cyanide) and Lewisite (2-chloro-ethenyl dichloro arsine) are some of the most toxic chemical compounds ever produced by mankind and those have been used as chemical warfare agents. (Henriksson et al., 1995)

Geographical distribution of As-containing pesticides

Except for Methoxyfenozide, Chlophyriphos and Profenofos sold by Company A, in all other instances, the As content of the pesticides used in out-of Colombo locations was greater than that was available in Colombo.

As content of the insecticide Etofenprox and weedicide Glyphosate collected from Anuradhapura was as thrice as much as that collected from Colombo,

If As is present as an active ingredient without being declared, it should be present in equal amounts in samples collected from different areas. On the contrary, presence of relatively high contents of As in pesticides collected from paddycultivating areas in the North Central Province imply that it is present in pesticides either as an integral part of the active ingredient and/or as an impurity. Although it appears that the importers abide by the Control of Pesticides Act No. 33 of 1980, which prohibits importation of pesticides containing Arsenic or Mercury as an active ingredient by producing a certificate from the producers to that effect, results of the present study reveal that As is imported along with pesticides most probably as an impurity, in considerable amounts. Present study is the first of this kind in Sri Lanka which tested for presence of As in pesticides and it highlights the necessity to develop protocols for a formal procedure to screen pesticides for presence of As either as an active ingredient or as an impurity. High bio-accumulation capacity of this carcinogen in human bodies have proven to cause a number of health hazards in areas polluted with As (Kapaj et al., 2006) and the amount of pesticides imported by Sri Lanka escalates annually (Jayasumana et al., 2011).

Importers of pesticides with As

It is apparent that presence of As in pesticides with the same active ingredient, for instance, Glyphosate or MCPA, vary considerably in the pesticide samples tested from different importers. Since arsenicals are cheaper than the organo-chemicals used as pesticides, it is not incomprehensible that importers may tend to substitute less harmful, nevertheless more expensive organo-pesticides of short life spans with cheaper inorganic arsenicals to bring about the same effect more intensely.

This state of affairs demands strengthening current procedures in importing, registering and distribution of pesticides within the country. Apparently more As in the form of impurities are added to the pesticides distributed to the North Central Province where mass-scale paddy farming takes place. Besides, Chronic Kidney Disease of unknown etiology (CKDu) is endemic to this area and it has been hypothesized recently (Jayasumana et al., 2011) that presence of relatively high content of As in groundwater that most of the rice farmers in these areas consume on a daily basis is the cause of renal failure and untimely death of members of these farmer communities. Continuous monitoring of quality of pesticides in terms of type and quantity of As present has thus become an essential means in reducing groundwater and soil pollution in these areas.

CONCLUSIONS AND RECOMMENDATIONS

Importing pesticides with As or As- related compounds is illegal under the current law of Sri Lanka. As can enter the pesticide formulations either at the manufacturers end abroad or added after importation, prior to distribution within the country. More investigations therefore are needed to identify the point-sources of As into pesticides and also to environment as it has the potential to cause massive human health problems.

Since no reported work is available as to the presence of arsenic in the bedrocks below Sri Lankan land mass, pesticides that are excessively used in paddy farming were attributed as one of the most likely source of arsenic in groundwater and soils in Rajarata area.

Thus, it is an urgent need to divert more resources to consolidate these findings and to plan and implement strategies to contain environmental pollution, particularly of groundwater, soil and plants with arsenic derived from agrochemicals. Rainwater harvesting for drinking purposes, promoting natural and traditional methods for pest control, public awareness over chronic toxicity of arsenic and potential risks in agrochemical—based agriculture and phytoremediation to remove arsenic in groundwater and soil may be prudent immediate measures in addressing this issue. Although there are some laws and regulations to prevent importation of arsenic containing pesticides to Sri Lanka those are not adequately implemented to prevent importation of AS-containing pesticides or other agrochemicals. Thus it is the prime duty of relevant authorities to take immediate measures to implement those laws and regulations and protect Sri Lanka and Sri Lankans from this accumulative non threshold carcinogen.

ACKNOWLEDGEMENT

Invaluable contribution of Mrs. Priyantha Senanayake in conveying the divine guidance for the present study is gratefully acknowledged. Sincere gratitude is extended to Prof. Nalin de Silva, Dean of the Faculty of Science, University of Kelaniya for his kind guidance.

REFERENCES

Abedin, M.J., M.S.Cresser, and A.A.Meharg. (2002). Arsenic accumulation and metabolism in rice (*Oryza sativaL.*). *Environ. Sci. Technol* 36(5): 9628.

Benson, N.R., R.D.Bartram, C.D.Moodie, W.A.Starr, E.Blodgett, D.R.Heinicke, H.M.Reisenauer, and F.G. Viets. (1969). Re-establishing apples orchards in the Chelan-Manson area. Report to the U.S. Bureau of Reclamation, Denver, CO, USA.

Chakraborti, D. (2010). Status of groundwater arsenic contamination in Bangladesh: A 14-year study report, *Water research* 44:5789-802.

Chandrajith, R., S. Nanayakkara., K.Itai, T.N.C.Athuraliya, C.B. Dissanayake, and T.Abeysekera. (2010). Chronic kidney disease of uncertain etiology in Sri Lanka: Geographic distribution and environmental implications. *Environ Geo chem. Health* DOI10.1007/s10653-0109339-1.

Crompton, T. (1998). Occurrence and analysis of organometallic compounds in the environment, Chichester, West Sussex John Wiley and Sons.

EPA-USA, (2011). Inert Ingredients Permitted for Use in Non food Use Pesticide Products. http://www.epa.gov/opprd001/inerts/inert_nonfooduse.pdf

Henriksson, J., A., P.A.Bergqvist, and L.Norrgren. (1995). The toxicity of Organoarsenic based warfare agents: In vitro and in vivo studis, *Toxicol* 30:213-9.

IUPAC technical report. (2003). Significance of impurities in the safety evaluation of crop protection products, Pure Appl. Chem. 75(7):937-973.

Jamal, A.(2000). Arsenic poisoning in Bangladesh-end of a civilization, Dhaka, Bangladesh, Palash media and publisher.

Jayasekara, R., and M.C.Freitas. (2005). Concentration levels of major and trace elements in rice from Sri Lanka as determined by the k₀ standardization method *Biological trace element research* 103:83-96.

Jayasumana, M.A.C.S., P.Paranagama, and M.Amarasinghe. (2011). Chronic kidney disease of unknown etiology and arsenic in ground water in Sri Lanka. Paper presented in workshop on challenges in groundwater management in Sri Lanka, March 15, in Colombo, Sri Lanka.

Kapaj, S., H.Peterson, K.Liber and P.Bhattacharya. (2006). Human health effects from chronic arsenic poisoning, a review *Journal of Environmental science and health* 41:2399-2428. Kozul, C.D., H.E.Kenneth, R.I. Enelow, and J.W.Hamilton. (2009). Low-Dose Arsenic Compromises the Immune Response to Influenza A Infection in Vivo. Environ Health Perspect117:1441-1447.

Meharg, A.A. (2004). Arsenic in rice understanding a new disaster for south east asia. Trends in plant science (9)9:415-417.

Meliker, J.R., R.L.Wahl, L.L.Cameron, and J.O.Nriagu. (2007). Arsenic in drinking water and cerebrovascular disease, diabetes mellitus, and kidney disease in Michigan: a standardized mortality ratio analysis, *Environmental Health* 6:4.

Nagy, V.M. (1974). Deutsche Lebensmittel-Rundschau 70:173-175.

Peryea, F. (1998). Historical use of lead arsenate insecticides, resulting soil contamination and implications for soil remediation. paper presented at the 16th world congress of soil science, August 20-26, in Montpellier, France.

Prasad, G.V.R., and N.F.Rossi. (1995). Arsenic intoxication associated with tubulointerstitial nephritis. *Am J Kidney Diseases* 26(2):373-376.

Rahman, M.M., B.K. Mandal, T.R. Chowdhury, M.K. Sengupta, U.K. Chowdhury, D.Lodh, C.R. Chana, G.K. Basu, S.C. Mukherjee, and K.C. Saha. (2003). Arsenic ground water contamination and sufferings of people in North 24-Parganas, one of the nine arsenic affected districts of West Bengal, India. J. Environ. Sci. Health A38: 25–59.

Riveros, P.A., J.E.Dutrizac and P.Spencer. (2001). Arsenic disposal practices in the metallurgical industry, Canadian metallurgical quarterly 40(4):395-420.

Shepard, H.H.(1939). The chemistry and toxicology of insecticides. Burgess, Minneapolis, MN, USA.

Tchounwou, B.P., A.K.Patlolla and J.A.Centeno. (2003). Carcinogenic and systemic health effects associated with arsenic exposure—a critical review. *Toxicol. Pathol* 31:575–588.

Tseng, C., T.Ching-Ping, C.Hung Yi, H.YuMei, C.Choon Khim, and C.ChienJen. (2002). Epidemiologic evidence of diabetogenic effect of arsenic, *Toxicology Letters* 133:69–76.

Tseng, C., T.Ching-Ping, C.Hung-Yi, H.Yu-Mei, C.Hung-Yi, and C.Chien-Jen. (2003). Long-term arsenic exposure and ischemic heart disease in arseniasis-hyperendemic villages in Taiwan, *Toxicology Letters* 137: 15-21.

Vahter, M. (2009). Effects of Arsenic on Maternal and Fetal Health. Annual Review of Nutrition 29: 381-399.

WHO. (1995). Guidelines for drinking water quality. Health criteria and other supporting information. Geneva:940–94.

WHO. (2009). The WHO recommended classification of pesticides by hazards and guidelines to classification. Geneva 27, Switzerland. Yamily, J.Z., and J.M.Duxbury. (2008). Arsenic in rice - Estimating normal levels of total arsenic in rice grain, Environmental science and technology 42(10): 3856-3860.