

Heavy Metal Contamination and Allicin in Shallots and Garlic in Srisaket Province, Thailand

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Received: March 14, 2022; Revised: May 31, 2022; Accepted: June 17, 2022

Abstract

Heavy metal (HM) contamination in economic crops is a recognized global concern, causing serious health hazards for consumers and having negative impacts on national economies. This study aimed to investigate HM contamination levels of crops of shallots and garlic around Srisaket Province, reputed to be the best quality grown in Thailand. Their functional groups of allicin were studied using Fourier-transform infrared spectroscopy, and the concentrations of HMs for commonly consumed shallots and garlic in 7 districts of Srisaket Province with a total of 38 samples, were determined using atomic absorption spectroscopy. The results found that their functional groups comprised hydroxyl, carbonyl, carboxylic and organosulfur compounds, and the concentrations of Pb, Cd, Cu, and Zn in shallots and garlic were at safe levels for the permissible limits set by the Ministry of Public Health in Thailand, Codex Alimentarius Commission, and Ministry of Health of the People's Republic of China. The concentrations ranged from 0.013-0.061 mgPb/kg, 0.001-0.003 mgCd/kg, 1.268-4.365 mgCu/kg, and 5.585-11.265 mgZn/kg. This is the first pilot study and report on concentrations of HMs in edible shallots and garlic in Srisaket Province, Thailand. The data can be used as preliminary information for both Thai and overseas consumers to consider the measurement of safe consumption of both crops.

Keywords: Heavy metals; Adsorption; Allicin; Health hazards; Garlic; Shallots

1. Introduction

Environmental pollutants have significantly increased due to a wide range of factors, including industrialization and economic globalization (Tóth *et al.*, 2016). Food safety and security issues are seen by many countries as key factors for sustainable development (Rai *et al.*, 2019). In the past decade, environmental pollutants have greatly threatened both food security and human health (Selahvarzi and Sobhan Ardakani, 2020).

In particular, research has shown that various types of heavy metals (HM) and metalloids can adversely affect human metabolism and may contribute to increased mortality rates worldwide (Bibi *et al.*, 2021).

In Thailand, a relatively developing country, agriculture is a major part in its domestic economy. Also, the possibility of HM contamination in crops grown for export has serious economic consequences.

In most developing countries, the usage of sewage sludge as fertilizer and inadequately treated wastewater as water supply are also contributing to increased bioaccumulation levels in food crops (Gebeyehu and Bayissa, 2020).

Shallot (*Allium ascalonicum* Linn.) and garlic (*Allium sativum* Linn.) have long been used for both culinary and medicinal purposes in Asia. Both plants are important in human nutrition and commonly used as seasonings in many Thai cuisines. Additionally, Thai people use these plants as herbal medicines and skin treatments. Fresh shallots and garlic contain several sulfur compounds, i.e. allicin, diallyl disulfide, diallyl trisulfide, methyl allyl trisulfide, dithiols, ajoene and alliin. Thai people believe that allicin, for example, has many medicinal properties such as inhibiting the growth of many bacteria and fungi, controlling blood cholesterol levels, dissolving blood clots in blood vessels, preventing blood vessels from rupturing, lowering blood pressure, widening blood vessels and inhibiting progression of cancer cells.

Besides, shallots and garlic are important economic crops in Thailand, creating income for local farmers. In 2021, the production of shallots and garlic was 77,515 tons and 15,7604 tons, respectively (Department of International Trade Promotion in Thailand, 2021). The shallots and garlic grown in many districts of Srisaket Province are famous and are considered by many consumers and reputed to be the best quality in Thailand. This is especially so in the Yangchumnoi district, which is referred and complimented to be the best quality in the world because of their special features of oily skin, dried head, bright red color for shallots and white color for garlic, small neck, slender and strong odor. Because of these qualities, both foods can be preserved for 5-6 months. They are exported to many countries including Japan, Cambodia, Lao PDR and China. At present, Yangchumnoi district has approximately 14,000 rai (5,534 acres) of shallot and garlic planting areas, yielding 42,000 tons per year and generating income to local farmers in Srisaket Province at least 200-300 million Thai Baht (\$US 5,987,398 - 8,981,097) per year (Technologychaoban, 2021).

Nowadays, pesticides and chemical fertilizers have been increasingly applied globally in agricultural areas because of their labor-saving and convenience and perceived increased production and therefore income returns. Even though they increase productivity, they can cause health and environmental problems in human and animals. Shallots and garlic are plants that store nutrients in the roots of bulb, which are sources of nutrients. Importantly, after pesticides and chemical fertilizers are applied in order to protect crops from pests, supply nutrients in soil and control diseases, there is contamination in other environmental compartments, i.e. air, soil, water and organism. Besides, unpurified pesticides and fertilizers usually contain several impurities, especially HMs. Cd, Pb, and Zn were found in high levels of pesticides and herbicides, and As, Cu, Cd, Pb, and Zn were reported to be major impurities in chemical fertilizers (Kuziemska *et al.*, 2016). If entering the human body, they may interfere with the functioning of cells, such as inhibiting the activity of certain enzymes, causing enzymes to work less, and altering the structure of biomolecules in the human body. Additionally, Pb and Cd are considered as potential carcinogens and associated with the etiology of a number of diseases, especially cardiovascular, kidney, blood, nervous, and bone diseases (Järup, 2003; Sandeep *et al.*, 2019). Although Cu and Zn are essential elements, their excessive concentrations in food and agricultural products are of great concerns because of their toxicity to humans and animals (Kabata-Pendias and Mukherjee, 2007). Cultivation of edible crops in soil contaminated with HMs can lead to the uptake and accumulation of them in crops resulting in a risk to human and animal health (Lim *et al.*, 2008). Serious, systemic health problems can occur as a result of the excessive dietary accumulation of HMs such as Cd and Pb in the human body (Zhuang *et al.*, 2009).

There have been no the studies on concentrations and possible health effects of various HMs in the widespread growing and consumption of crops of shallots and

garlic in Srisaket Province, Thailand. We are concerned of possible adverse effects on human health because of the large consumption of shallots and garlic by many Thai people as spices and seasonings in plentiful Thai cuisines.

The present study aimed to investigate and to quantify the concentrations of contamination of HMs in shallots and garlic in these two economic crops in Srisaket Province, Thailand. The findings of this study, we believe, will provide a foundation for quality assessment and safety management of agricultural products especially shallots and garlic in Thailand. We also aim to raise awareness of farmers and consumers about quantities of HMs and their potential for both domestic and export harm.

2. Materials and Methods

2.1 Study area

Srisaket Province (14°92'11.7"N 104°39'21.8"E) is located in Northeastern Thailand (Figure 1). Most areas of Srisaket Province are plateau alternating with agricultural areas and rice fields. There are mountains and forests in the south, adjacent to the Phanom Dong Rak mountain range, forming the boundary line between Thailand and Cambodia. It is considered as the origin of many rivers, with most of the areas having a slope to the north and west, forming many large and small rivers. These rivers converge at the Mun and Chi rivers to form complex sediments with poor drainage. Soil characteristics of the lowland area are caused by sediments being accumulated over a long period, resulting in fertile soil suitable for growing shallots and garlic with high quality.

2.2 Sampling and sample preparation

Shallot and garlic samples were collected from planting sites with farmers' permission from November 2019 to January 2020 in their harvesting season by random sampling in seven districts of Srisaket Province namely: Mueangsrisaket (MD), Rasisalai

(RD), Yangchumnoi (YD), Kanthararom (KD), Uthumphonphaisai (UD), Wanghin (WD) and Phayu (PD). Nineteen samples of each type of plants were collected, ranging from 2-4 samples with a total of 38 samples. Sampling sites, codes of shallot (S1-S7) and garlic samples (G1-G7) are represented in Table 1. Shallot and garlic samples were collected and briefly stored in polyethylene bags in the field, and transferred to the laboratory immediately for analysis. All samples were properly washed with tap water, followed by a rinse with distilled water. Then, the samples were sliced and kept in an electric oven at 70 - 80 °C for 48 h for drying (Bibi *et al.*, 2021; Yang *et al.*, 2011). Oven dried samples were ground to a fine powder using ceramic mortar and pestle. Pulverized samples were stored in pre-cleaned and accurately labeled bottles, and then stored in desiccators at room temperature until further analysis.

2.3 Chemical analysis

Shallot and garlic samples were ground following the methods as reported earlier and partially divided to detect the functional groups of allicin in the samples with a Fourier-transform infrared spectrometer (Shimudsu FTIR-8900) in wavenumbers, ranging from 4000 to 450 cm⁻¹. Pulverized samples of each plant (~1.0 g) were added in labeled conical flasks (50 mL), and 10 mL nitric acid (conc. HNO₃) was mixed. This mixture was kept overnight at room temperature and subsequently heated on a hot plate until the appearance of brown fumes, then kept at room temperature to cool. Next, 10 mL perchloric acid was added. This mixture was heated again until a clear solution was obtained. Digested samples were diluted to 50 mL using 2% HNO₃ prior to analysis (Bibi *et al.*, 2021; Parveen *et al.*, 2020). The total concentrations of Pb, Cd, Cu and Zn were determined using an atomic absorption spectrometer (Perkin Elmer Analyst 400). Percent recovery values of the laboratory control sample were in the ranges of 110.0 - 88.9% for shallots and 108.7 - 97.1% for garlic.

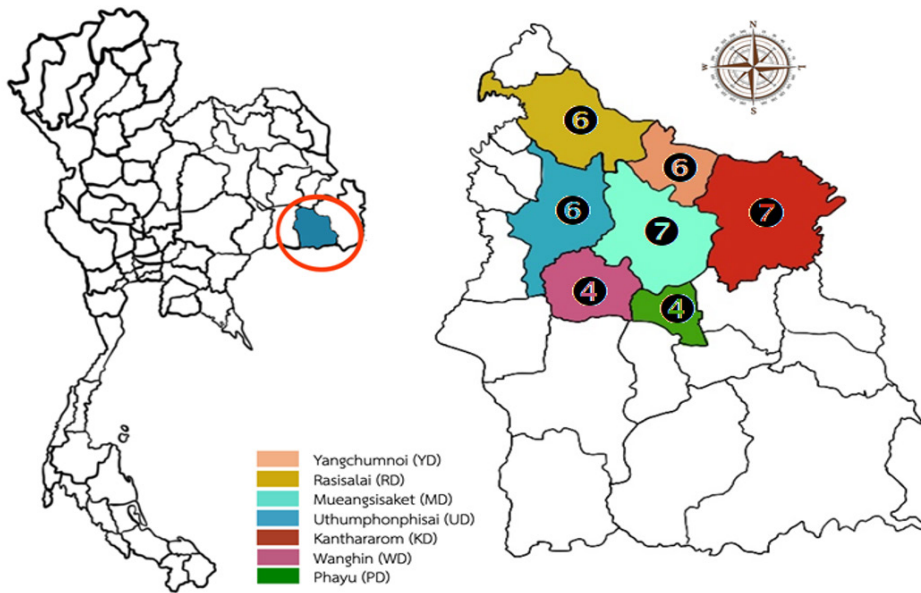


Figure 1. Map of Thailand and sampling sites in Srisaket Province. Number symbols representing the sampling numbers

Table 1. Symbols of sampling sites and samples

Sampling sites	Symbols of samples							Total
	MD	RD	UD	YD	KD	WD	PD	
Number of samples	7	6	4	6	7	4	4	38
Number of shallots	4	3	2	3	3	2	2	19
Number of garlic	3	3	2	3	4	2	2	19
Code of shallots	S1	S2	S3	S4	S5	S6	S7	
Code of garlic	G1	G2	G3	G4	G5	G6	G7	

3. Results and Discussion

3.1 Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectrum of shallot and garlic showed the presence of functional groups: hydroxyl, carbonyl, carboxylic and organosulfur compounds (Table 2 and Figure 2) which are alliin constituents in shallot and garlic. Broad peak at 3363 cm^{-1} is due to the O-H stretching of a hydroxyl group which indicates the presence of polyhydroxy compounds such as flavonoids and saponins. The peak at 2931 cm^{-1} is due to the asymmetric stretching of C-H groups of aromatic compounds. The peak at 1643 cm^{-1}

is corresponding to C = O and -COO- stretching of peptide linkages, and C = O and -COO- stretching of carbonyl and carboxylic groups. The peak at 1411 cm^{-1} indicates the O-H bond of carboxylic acids (Rastogi and Arunachalam, 2011), which in turn reveal the presence of flavonoids, tannins, saponins, and glycosides. The split peaks at 1041 and 1157 cm^{-1} indicates the S = O group revealing the presence of organosulfur compounds including alliin, alliin and diallyl disulfide (Divya *et al.*, 2017; Songsungkan and Chanthai, 2014). It can be seen from Table 2 and Figure 2a that the vibration position of the C = O group was shifted, and the numbers of vibration peaks of the S = O group were split comparing with the alliin extract of garlic,

extracted from methanol, which appears only the main peak at 1036 cm⁻¹ (Divya *et al.*, 2017). Thus, it is evident that gluten indicating the internal structure of allicin was influenced by HM ions contaminating the shallot samples. The contribution of the ions within the sample influenced the peak intensity, peak number, and position of functional groups. This behavior occurs in both shallot and garlic. The FT-IR spectrum of garlic are similar as shown in Figure 2b.

3.2 Heavy metal content in shallot and garlic samples

The concentrations of HMs of shallots and garlic around Srisaket Province are presented in Figure 3. Their concentrations were compared with the permissible limits of the Notification of Ministry of Public Health in Thailand, (1986), which are equal to Codex Alimentarius Commission (World Health Organization, 2011).

Table 2. FT-IR peak values and functional groups of shallot and garlic methanolic extracts

Shallot	Frequency (cm ⁻¹)		Bonds	Functional groups
	Garlic	Allicin extract		
3363	3355	3265	O-H	Hydroxyl
2931	2931	2926	C-H	Aromatic compounds
2380	2381	2384	S-H	Sulfhydryl
1643	1643	1619	C=O	Carbonyl and Carboxylic
1411	1411	1395	O-H	Carboxylic
1041, 1157	1026, 1134	1036	S=O	Organosulfur

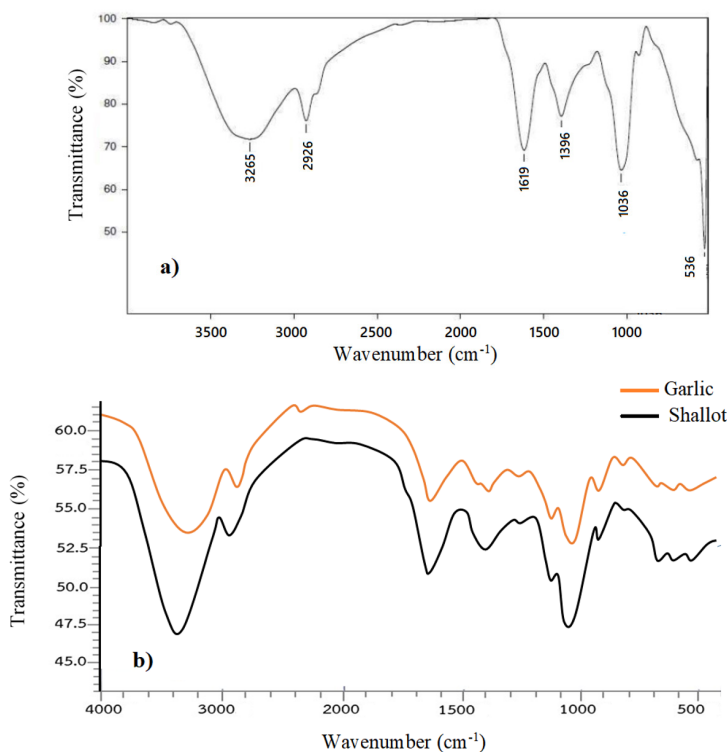


Figure 2. FT-IR spectra for a) allicin methanolic extract, and b) shallot and garlic samples

The maximum allowable HM concentrations for Pb, Cd, Cu and Zn were 0.2 mg/kg, 1.0 mg/kg, 20 mg/kg, 100 mg/kg, respectively. The concentrations of HMs found in both crops were Pb (0.013 - 0.056 mg/kg), Cd (0.001 - 0.002 mg/kg), Cu (1.268 - 3.383 mg/kg) and Zn (5.585 - 9.169 mg/kg) for shallot samples, and Pb (0.020 - 0.610 mg/kg), Cd(II) (0.001 - 0.003 mg/kg), Cu (1.730 - 4.369 mg/kg) and Zn (5.768 - 11.265 mg/kg) for garlic samples. The average concentrations of HMs in shallot and garlic samples were in the descending order: Zn > Cu > Pb > Cd. The concentrations of HMs were compared with the maximum permissible level of contaminants recommended for vegetables in China (Ministry of Health of the People's Republic of China, 1991, 1994, 2005). The maximum allowable HMs concentrations for Pb, Cd, Cu and Zn were 0.2 mg/kg, 0.3 mg/kg, 10 mg/kg, 20 mg/kg, respectively. It can be seen that these maximum allowable HMs concentrations are lower than those standards of Thailand, except Pb are equal at 0.2 mg/kg. Hence, these results indicated that the shallots and garlic from Srisaket Province were safe for consumers. They were also implied that farmers apply fertilizers and pesticides at appropriate levels.

Overall, the measured levels of HMs were slightly higher in the garlic than in shallot samples as illustrated in Figure 3. However, this study was analogous to the previous reports that the levels of HMs in the leave were higher than those in the bulb samples. Higher levels of HMs in leaves were found when compared in bulbs, specifically shallot leaves, which have more exposure routes than bulbs. We believe that this is due to HMs may pass to leaves through stomata along with contaminated air and via transportation through xylem vessels from contaminated soil and water (Bibi *et al.*, 2021; Demirezen and Aksoy, 2006). In this study, it was likely due to garlic absorbing HMs from the water into their tissues. Additionally, the absorption of HMs of into garlic depends on specific transfer factors of the plant itself (Kladsomboon *et al.*, 2020). According to previous studies, it is possible that the high accumulation of HMs found in plants may be associated with high concentrations in soil (Bibi *et al.*, 2021;

Demirezen and Aksoy, 2006). For this reason, the HMs detected in shallot bulbs were less compared with those detected in garlic bulbs.

In addition, Zn and Cu levels of shallots and garlic in MD and KD sites were higher than in the other sites. According to this preliminary survey of sampling sites, both sites are large urban communities mainly manufacturing shallots and garlic with higher production quantities when compared with other sites because the demand of shallots and garlic is increasing both inside Thailand and for export. Then, farmers accelerate their production to the market by applying chemicals such as pesticides, chemical fertilizers and plant growth hormones in high quantities, causing chemical residues contaminated in soil and crops. For this reason, it may result in higher levels of HMs found when compared with the other sites. When applying pesticides and chemical fertilizers in food crops, which are the source of many essential human nutrients (Hirschi, 2009), local farmers should be concerned with risks of contamination with HMs because crops can absorb metals via soil, water, and air from environments, and metals can be bioaccumulated in different parts of plants (Srinivas *et al.*, 2009).

3.3 Comparison of HMs concentrations in shallots and garlic

From this study and literature reviews, HM concentrations in shallots, garlic and onions were compared as shown in Table 3. In this study, HMs in garlic were found higher than those in shallots. This may be due to the physical characteristics of garlic with a single bulb; each bulb consists of several cloves stacked together and has a hard shell that can retain water. Shallots, by comparison, have thin skins and were expected to contain a lot of water as the main ingredient inside the bulb, which were compared by weight after drying from the same weight of fresh plants. Therefore, it is possible that garlic stores higher number of HMs when compared with shallots. This trend is similar to previous reports (Amin *et al.*, 2013; Filimon *et al.*, 2021; Wu *et al.*, 2011), which found that HMs levels in garlic were higher than those

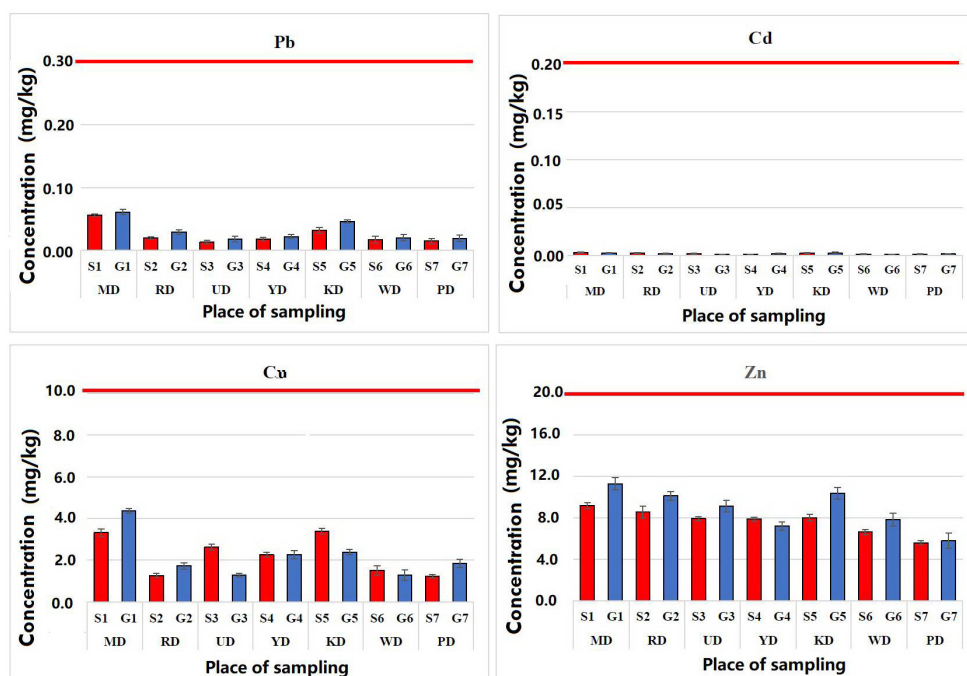


Figure 3. Average concentrations of heavy metals in shallot and garlic samples. The horizontal lines show the limit of permissible values from Ministry of Health of the People’s Republic of China

in onions as shown in Table 3. This may be because aerial plant parts specifically onion leaves have more exposure routes than bulbs. In this study, all HM concentrations were below the permissible levels in food crops. However, if they were found in high concentrations, they can adversely affect metabolic activity in the human body, causing anemia, obesity and diarrhea, and harming the reproductive, circulatory and immune systems.

Many studies have shown that HMs are often examined in onions, especially in Europe, and few studies have examined HMs in shallots and garlic. The HM concentrations of shallots in this study are consistent with findings in shallots grown in Indonesia (Purbalisa *et al.*, 2021), indicating that shallots can also accumulate Pb at safe levels. Pb levels in garlic of the present study were similar to those reported in Eastern Serbia (Filimon *et al.*, 2021). The Pb concentrations in shallots and garlic from Indonesia and Eastern Serbia were reported for 0.420 - 0.4739 mg/kg

and 0.43 mg/kg, respectively. However, the HM concentrations in garlic were lower than those obtained in Pakistan (Amin *et al.*, 2013) and China (Wu *et al.*, 2011). The HM concentrations in garlic from Pakistan were reported for Pb (4.94 - 8.3 mg/kg), Cu (6.7 - 14.5 mg/kg) and Zn (6.2 - 11.2 mg/kg).

Comparative assessments revealed that shallots and garlic were much lower than the permitted levels. Therefore, consumers can consume them safely. Interestingly, the average concentrations of all HMs in the shallot and garlic samples were lower than those reported in Table 3 because the study sites were not as close to industrial and mining areas as other studies. Besides, during the planting season, the atmosphere, time and temperature are suitable for planting. These conditions help to decrease the large amounts of chemical pesticides and fertilizers, resulting in concentrations within the acceptable limits of these metals in crops (World Health Organization, 2011).

Table 3. Comparison of HM concentrations (mg/kg) in shallots, garlic and onions

Crops	Country	Metal concentration (mg/kg)										Reference	
		Pb	Cd	Cu	Zn	Mn	Fe	Ni	Others				
Shallots	Thailand	0.013 - 0.056	0.001 - 0.002	1.268 - 3.383	5.585 - 9.169	-	-	-	-	-	-	-	This study
Garlic	Thailand	0.020 - 0.610	0.001 - 0.003	1.730 - 4.369	5.768 - 11.265	-	-	-	-	-	-	-	This study
^a Shallots	Indonesia	15.350	nd	4.255	-	-	-	-	-	-	-	-	(Priyadi et al., 2021)
Shallots	Indonesia	0.420 - 0.473	-	-	-	-	-	-	-	-	-	-	(Purbalisa et al., 2021)
Garlic	Nigeria	Nd	0.45	4.65	-	-	51.0	-	-	-	-	-	(Olusakin O and Olaoluwa J, 2016)
Garlic	China	-	-	7.8 - 9.7	-	-	-	-	-	-	-	-	(Wu et al., 2011)
Garlic	Pakistan	4.94 - 8.3	-	6.7 - 14.5	6.2 - 11.2	2.0 - 5.75	5.9 - 15.75	1.45 - 2.55	Co = 0.45 - 1.65	-	-	-	(Amin et al., 2013)
Garlic	Eastern Serbia	0.43	-	6.76	11.53	3.82	7.40	-	-	-	-	-	(Filimon et al., 2021)
Onions	China	-	-	5.9 - 7.3	-	-	-	-	-	-	-	-	(Wu et al., 2011)
Onions	Pakistan	2.7 - 11.2	-	6.05 - 22.6	11.4 - 25.5	0.55 - 28.05	6.15 - 26.15	0.5 - 2.0	Co = 0.35 - 1.55	-	-	-	(Amin et al., 2013)
Onions	Eastern Serbia	0.45	-	3.94	5.48	9.96	6.68	-	-	-	-	-	(Filimon et al., 2021)
Onions	South Africa	nd	0.20	8.70	61.97	27.09	-	-	-	-	-	-	(Bvenura & Afolayan, 2012)
Onions	Pakistan	0.208	0.043	0.377	1.539	1.108	4.587	-	Co = 0.174	-	-	-	(Bibi et al., 2021)
Onions	Nigeria	0.53 - 0.95	-	4.20 - 7.50	10.33 - 18.89	1.45 - 1.98	-	-	-	-	-	-	(Audu & Lawal, 2009)
Onions	United Kingdom	7.5	3.6	2.8	64.4	-	-	-	-	-	-	-	(Alexander et al., 2006)
Onions	Slovak Republic	0.05 - 0.21	0.02 - 0.04	0.67 - 1.06	1.32 - 2.32	-	-	0.05 - 0.31	-	-	-	-	(Bystrická et al., 2015)
Onions	Ghana	Nd	0.05	0.06	0.08	0.11	3.76	-	Cr = 0.32	-	-	-	(Ametepey et al., 2018)
Onions	Brazil	0.49	0.02	-	-	-	-	0.06	Co = 0.09	Cr = 0.07	-	-	(Guerra et al., 2012)
Onions	Bangladesh	0.52	0.22	2.4	-	-	-	0.92	Cr = 1.1	-	-	-	(Islam et al., 2017)
Onions	Romania	0.13	-	1.37	2.01	1.34	4.65	-	-	-	-	-	(Harmanescu et al., 2011)
Onions	Algeria	39.33	-	18.33	37.67	-	-	-	Cr = 16.33	-	-	-	(Cherfi et al., 2014)
Onions	Ethiopia	-	0.05	-	-	-	-	-	-	-	-	-	(Bekele Bahiru, 2021)
Onions	Nigeria	nd	0.45	4.36	-	-	33.5	-	-	-	-	-	(Olusakin and Olaoluwa , 2016)
Onions	Nigeria	0.460 - 0.533	-	-	-	-	-	-	-	-	-	-	(Orisakwe et al., 2017)
^b Onions	Nigeria	1.276 - 1.305	0.057 - 0.058	-	0.503 - 0.978	0.215 - 0.250	0.935 - 1.796	nd	Cr = nd	-	-	-	(Yaradua et al., 2020)
^b Onions	Saudi Arabia	3.15 - 4.38	0.93 - 1.13	3.29 - 10.03	11.36 - 23.15	7.84 - 19.05	31.9 - 66.9	-	-	-	-	-	(Ali & Al-Qahrani, 2012)
^b Onions	Turkey	6.0	0.61	37.5	115.97	-	-	3.6	-	-	-	-	(Demirezen and Aksoy, 2006)

nd = not detected, detection limit (0.01 ppm), a = ppm, b = ug/g

3.4 Adsorption mechanism

There is no evidence in literatures on studies of HM transmission in shallots and garlic, then this is a novelty of this study. To propose an ion adsorption mechanism of HMs in shallots and garlic, it can be verified using an FT-IR analysis (Figure 2). Fresh shallots and garlic contain various sulfur compounds: allicin, diallyl disulfide, diallyl trisulfide, methyl allyl trisulfide, dithiins, ajoene, and alliin. For example, the structure of allicin is composed of S - H (sulfhydryl) and S = O groups. In the present study, a mechanism based on the negatively charged S - O and SH groups of allicin expressed allicin binding to the positively charged ions of HMs transmitted from soil via roots. The S - H and S = O groups at the active site can adsorb HM ions very well as shown in Figure 4. As a result, these groups are capable of bonding ions of surrounding HMs through the dissociation of a hydrogen cation.

3.5 Transportation of heavy metals into shallot or garlic

HM contaminants in soil exist as a variety of chemicals in dynamic equilibrium, which are governed by physical, chemical and biological properties of soil (Chaney, 1988). Owing to the nature of insoluble HMs, it is difficult for them to be transported to roots, possibly only slightly. The transportation of HM ions across the root cell membrane allows HMs to enter the plant tissue. HMs are first introduced into the apoplast and then directed to the root xylem. After that, HMs are translocated apo-plastically into the plant tissue due to the continuum of root epidermis and cortex. HMs in root cells have

to cross the endodermis and casparian strip to reach the xylem (Sandeep et al., 2019). The processes involved the uptake and sequestration of HMs because they are taken up to roots from where they are translocated to bulbs and shoots, respectively by means of apoplast and symplast pathways. HMs are transported through the xylem into the bulb, which the cell wall contains a large number of active sites of allicin that binds or bonds to the HM ions, and then accumulated in the plant parts. From the shoots, HMs are transported by xylem into and loaded in the leaves; then, they are stored in vacuoles (Figure 5). For this reason, the leaves have a higher concentration of HMs than the bulbs.

For translocation of metals from roots to shoots, HM transporters carry HM ions from root symplast into xylem apoplast (Marschner et al., 1996) and are probably driven by transpiration pump (Salt et al., 1995). Physiological concentrations of HMs in the plant cell are regulated by tonoplast as well as metal transporters on the plasma membrane. It is well known that different types of membrane proteins are involved in the process of metal uptake in plants, but lacuna is also used in understanding the molecular transportation of HMs through plant membranes (Ghori et al., 2016; Sandeep et al., 2019). Therefore, complete knowledge about the transportation processes within plants is very important to agriculture, especially about the creation of transgenic plants. This key principle can be applied that farmers can choose crop types to grow, which are capable of transporting and storing metals well. This is to improve the process of decontamination and soil remediation that has an important effect on HM contamination in economic crops.

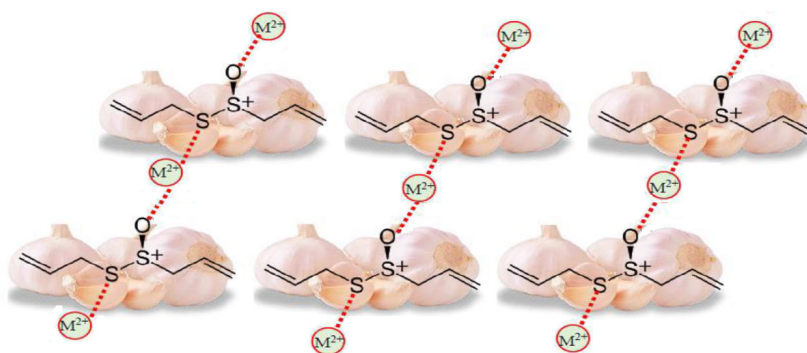


Figure 4. Mechanism for the adsorption of heavy metal ions on allicin of garlic

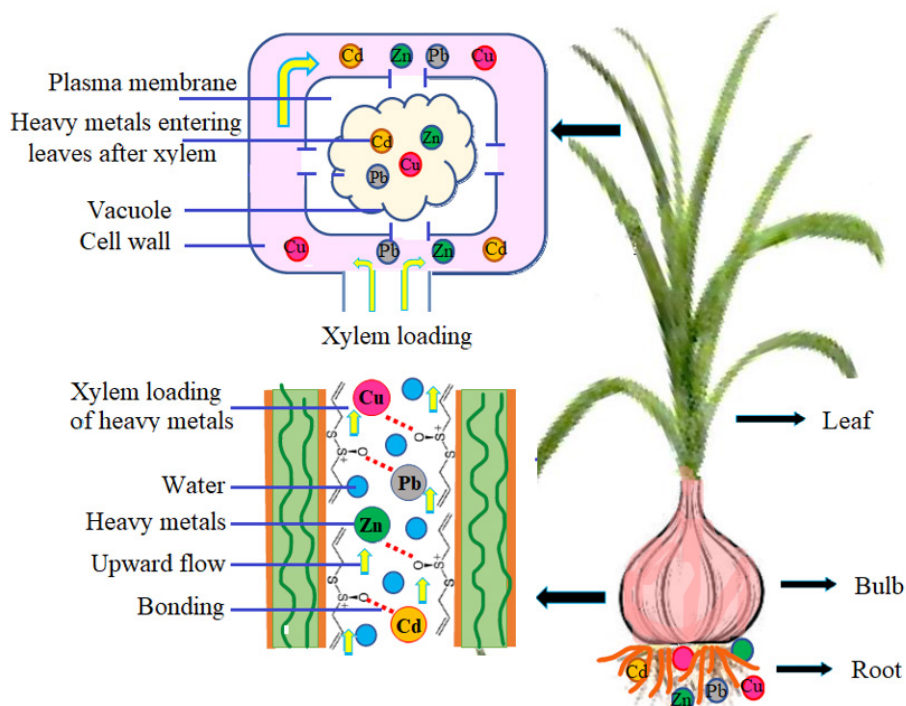


Figure 5. Schematic mechanism of transportation of heavy metals into garlic

Moreover, if food crops are contaminated with these HM pollutants, they inevitably affect living organisms. However, plants can be applied to treat HMs. The most efficient and economical way in this aspect has been found to be bioremediation. Plants have been found to be quite efficient in the process, commonly known as phytoremediation. Phytoremediation is the process of removal of HMs through plants. These absorbed HMs are bio-accumulated in the plant tissue. Based on the accumulation of HMs, it is mainly classified as hyperaccumulators and non-hyperaccumulators. Hyperaccumulators can take up HMs from soil through roots and translocate them to shoots and leaves. Contrastingly, non-hyperaccumulators are those plant species that can accumulate HMs in their below-ground parts and cannot translocate them to shoots and leaves (Ghori *et al.*, 2016; Sandeep *et al.*, 2019).

3.6 Impact of heavy metals on humans

Both shallot and garlic were selected based on their utilizations as food and for medicinal purposes. Moreover, the shallot bulb is used to treat many health disorders,

precisely food poisoning, cholera, indigestion and to cure dermal infections because of its antimicrobial properties, which are mainly due to the presence of organo-sulfur compounds (Abbasi *et al.*, 2012). The usages of pesticides and chemical fertilizers to increase agricultural yields with ignoring their potential effects can be a problem of HM contaminants in the environment because of HM residues in soil and crops. When considering the part of the crops grown for consumption, there is a risk of HM transfer from soil to humans. Plants absorb higher concentrations of HMs from soil and accumulate them in plant tissues. These HMs enter the human body through the food chain. The body is unable to metabolize HMs and it then accumulates in human soft tissues causing metabolic dysfunction and death if taken in excess (Sandeep *et al.*, 2019; Sobha *et al.*, 2007). Excessive exposure to HMs has undesirable effects on humans, and associated harmful effects are only noticeable after years of exposure (Khan *et al.*, 2008). Therefore, this is a problem that should be realized and given much importance. Though some HMs such as Co, Cu, Fe, Mn, Mo, Ni and Zn are essential elements for normal growth and plant metabolism, Pb and Cd

are not essential for plant growth. Generally, these elements are toxic to the human body when their concentrations exceed optimal (Rascio and Navari-Izzo, 2011), and the daily intake of metals (DIM) for Pb, Cd, Cu and Zn was 0.004, 0.001, 0.04 and 0.3 mg/kg/day, respectively (Ramteke *et al.*, 2016). The uptake of HMs by plants and their subsequent accumulations along the food chain can pose a threat to human health as well as animals. Absorption by plant roots is one of the main routes of HM entry in the food chain. The absorption and accumulation of HMs in plant tissues depends on many factors, including temperature, humidity, organic matter, pH and nutrient availability (Kumar Sharma *et al.*, 2007).

4. Conclusion

This pilot study indicates that heavy metal (HM) levels in shallots and garlic from all sampling sites Srisaket Province, Thailand, were below the permissible safe levels set by the Ministry of Public Health in Thailand, Codex Alimentarius Commission, and Ministry of Health of the People's Republic of China. Agricultural soil in sampling sites was suitable for agriculture because it was not contaminated with toxic HMs, especially Cd and Pb. The HM contamination in food crops as a result of the usages of pesticides and chemical fertilizers is a serious concern. It also affects the soil used for farming and can be a health hazard owing to the dietary consumption of contaminated vegetables. Food plants are essential to the human diet and, in particular, provide nutrients to maintain normal health. Therefore, prolonged usage of pesticides and chemical fertilizers results in the accumulation of HMs, especially in plants, and poses a risk to the human body. Therefore, special attention must be paid to monitor the residual HM content in plants as well as the toxicity levels of many metals. Especially, shallot and garlic are food crops that are popular in Thailand and Asian countries with based on their utilizations as culinary and medicinal purposes. Appropriate approaches and remedial options should focus on reducing HMs in soil and food

crops to prevent potential health risks to consumers. It is thus proposed that HM contamination survey should be conducted on all food commodities on a regular basis for food crop safety for consumer's health concerns.

Acknowledgments

This study was partially financially supported by Chevron Enjoy Science Project, Thailand. The authors wish to acknowledge the staffs and administrative board of the Chemistry Department and Applied Science and Science Center of the Faculty of Science and Technology, Surindra Rajabhat University, for providing experimental equipment and laboratory. Thank Dr. Warren Prior, Formerly Professor at Deakin University, Australia for editing English of the manuscript.

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