

ASSOCIATION OF ARSENIC FRACTIONS TO ARSENIC IN RICE PLANTS

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Abstract

Arsenic in rice fields of district Tando Mohammad Khan is a concern, most likely originating from long term canal irrigation water receiving significant quantities of wastewater. Evaluation of available soil arsenic through fractionation schemes can help understand the chemical association with elements and its transformation to rice. In this study 120 soil samples, from 24 rice fields and associated rice shoots were collected from intensive rice cultivated area of the district. Fractionation schemes illustrated that most of the arsenic in soils was calcium-bound and available arsenic (water soluble + exchangeable), with some as iron and aluminum bound arsenic, contributing 38, 29, 17 and 10 percent to total soil arsenic. The regression equations further confirmed the significant contribution of each calcium-bound ($r = 75$), available ($r = 65$), iron-bound ($r = 49$) and aluminum-bound arsenic ($r = 0.42$) to rice grain. The same was true for straw + husk, however, the relationships were significant only in case of calcium-bound ($r = 0.79$) and available arsenic (0.48). Only 4 out of 24 sites were contaminated by soil arsenic (5.47-59.77 mg kg⁻¹) and 01 by grain arsenic (0.15-1.00 mg kg⁻¹), but concentration in straw + husk was more (0.30-1.29 mg kg⁻¹) than that in grain. In order to avoid further arsenic increase in rice soils, regular monitoring of arsenic in soil, rice grain and straw + husk may be carried out.

Key words: Fractionation, Rice grain, Straw + husk, Calcium-bound-arsenic, Iron-bound-arsenic, Hydride generation assembly.

Introduction

Rice is main meal portion of Asian people taken in larger quantities and arsenic concentration in rice has become a big issue worldwide. The crop is cultivated all over Sindh (i.e. upper, middle and lower) province. The study area is part of lower Indus Plain and is amongst main districts of the province growing rice. The rice in this area relies on the irrigation water of Indus-Basin-system. The river water carries drainage and wastewater of "Indus" at Punjab and Sindh (Anon., 2007). About 1.5 million gallons of poisonous spill of industries and sewerage from Hyderabad is discharged into sub-distributary canals on daily basis (Wattoo *et al.*, 2006). The wastewater of sugar mills, laundries, plastic factories and domestic sewage of district Tando Mohammad Khan is part of these canals irrigating rice fields (Guriro, 2009) and contain relatively more arsenic than that initially present in River Indus at Kotri Barrage (Chohan *et al.*, 2020a). The same has been reported for wastewater of district Badin (Chohan *et al.*, 2020b). The chemical constituents are relatively low in domestic wastewater (Memon *et al.*, 2019). The left bank outfall drain (LBOD) was constructed in the area to deal with the issue of water logging and also collect the extra water from floods or otherwise. But instead, it carries the industry and municipality based run-off, which falls into sub-distributary canals and ultimately in river. Rice in the area is normally grown under flooded conditions, and there is possibility of arsenic accumulation in soil environment (Gupta *et al.*, 2002). Continuous irrigation, even with low arsenic concentration in water, can in the long run buildup the arsenic level in rice fields, rice grain and enter the food chain (Abedin *et al.*, 2002; Jamali *et al.*, 2006; Wattoo *et al.*, 2006; Anon., 2007; Bhattacharya *et al.*, 2009).

Arsenic is not included under the list of plant-essential nutrients. Presence of arsenic concentration in plant parts is subject to the overall and available arsenic concentration (water-soluble + exchangeable) in soil. Which relies on the chemical forms i.e., arsenite and arsenate. However, these forms in soil are continuously interconverted (Martinez-Sanchez *et al.*, 2011) and therefore, a more reliable approach is to determine arsenic concentration in soil using fractionation testing methods. Alkaline soils have significant amounts of calcium carbonate or calcium salts, which lead to calcium-bound, exchangeable, including water soluble (available), and also little aluminum-bound and iron-bound arsenic (Norra *et al.*, 2005; Fayiga *et al.*, 2007). Fractionation schemes extract chemical fractions from soil using mild (i.e. water) to moderate (i.e. NH₄Cl) and severe (i.e. H₂SO₄) extractants (Onken & Adriano (1997), based on increased binding strength of a metal. The quantity of different arsenic fractions, their relationship with the concentration in plant can be beneficial in understanding the arsenic dynamics in soil plant system. The most common schemes include those of Onken & Adriano (1997), Jiang *et al.*, (2014); Wan *et al.*, (2017).

Research related to the impact of arsenic fractions in soil and their association to arsenic in rice parts and contamination level are scarce and is rather a new-fangled issue in the area. The regional studies generally relate to cereals like wheat and maize, and some vegetables (Arain *et al.*, 2009; Baig *et al.*, 2011) or are related to total arsenic enrichment in soils (Jamali *et al.*, 2006; Rasool *et al.*, 2016). There is very scanty data reported on soil pertaining to various fractions as well as the arsenic concentration in rice grain and straw. This study aims to: 1) evaluate inorganic arsenic fractions in rice growing sites of district Tando Mohammad Khan; 2) Compare the total arsenic concentration in soil and rice shoot with the established permissible limits; 3) Use regression models to find out the contribution of inorganic fractions to rice grain and straw + husk.

Material and Methods

Study area: District Tando Muhammad Khan (latitude: 24°11' to 23°09' N, longitude: 60°19' to 62°15' E) is located in the South East of Sindh, Pakistan on the left bank of Indus River. The study area is part of the lower Indus plain formed by the quaternary alluvial-deltaic sediments deposits of the Indus River through the ancient Hakra, Nullah and Gungra water courses. Being a vast alluvial plain, its land is highly uniform in character and is not diversified by hills or rivers (Baig *et al.*, 2009; District Government Tando Mohammad Khan, 2009). The climate of the study area is semi-arid and subtropical continental, with temperatures between 4.5-46°C and mean rainfall of <200 mm.

Sample collection and processing: One hundred twenty five samples from surface (0-15 cm) and sub-surface (15-30 cm) were obtained from 24 rice growing fields using screw type auger (stainless steel). Soil samples transported to the laboratory were spread using plastic trays in fume cupboard. The samples were first air-dried at room temperature for ten days, followed by grinding and reducing the particle size to 2 mm. Associated plants were collected from the same fields at the time of rice harvest. These plants were decontaminated by rinsing it first with normal tap water, followed by double washing using distilled water. The straw + husk and grain were kept separately. These parts were washed thrice with ultrapure water and air dried separately in an electric oven at 65°C for 48 h (Ryan *et al.*, 1996). The samples were homogenized using agate-mill, passed through a nylon sieve of <75 µm mesh. Before analysis samples were labeled and stored in plastic containers and kept at ambient temperature.

Analytical procedures: Soil arsenic fractionation: Extraction of inorganic arsenic fractions was achieved by the test-scheme of Onken & Adriano (1997). The fractions were namely available, aluminum-bound, iron-bound and calcium-bound arsenic. Plastic tubes of 50 ml volume having 2 g soil and 40 ml of 1M NH₄Cl were shaken on an orbital shaker (180 rpm) for 30 minutes. After centrifuging the contents (2000 rpm) for 10 minutes, the clear extract was decanted in separate plastic vial and analysed for available-arsenic. The residue in plastic tube was extracted with 0.5M NH₄F for 30 minutes and tested for aluminum-bound-arsenic. Likewise, the remaining two fractions were correspondingly extracted with 0.1M NaOH and 0.5M H₂SO₄ for 17 hours and tested for iron and calcium bound arsenic. In between each extraction, saturated NaCl (25 ml) was used. All the arsenic fractions were passed through 0.45 µm cellulose membrane, capped before running on hydride generation.

Arsenic in soil and rice shoot: Concentration of total arsenic in soil and rice shoots was separately determined by placing 2 g of each in specific digestion tubes with HCl and HNO₃ (3:1) mixture and kept for 12 hours. This was followed by heating the contents starting from low temperature of 50°C and slowly increased to 200°C. This took about 70 minutes before the digestion could start. The process continued for four hours and the digested samples turned into thickened material. The digested samples were tightly stoppered, and kept in refrigerator (Anon., 1998).

All the arsenic analyses was carried out on absorption-spectrometry (Shimadzu-AA6300, Japan) coupled with Hydride-Vapour Assembly (Shimadzu-HVG1, Japan). Arsenic cathode lamp generated radiation at a wavelength of 193.7nm and a slit width of 0.7nm. The vapour assembly used HCl (10%) solution as carrier at a flow-rate of 10 ml m⁻¹. Whereas, NaBH₄ (0.5%) in NaOH (0.05%) solution was used as reducing medium at 5 ml m⁻¹ flow rate. Both HCl and NaBH₄ were driven by the reaction-coil and gas-liquid divider. These solutions reached the flame with the flow (0.32 MPa) of nitrogen gas. Before the sample analysis the instrument was run with standards solutions contained varying amount of arsenic concentrations and the deduction limit of arsenic was 0.1 µg kg⁻¹.

Statistical analysis and interpretation of the data:

Descriptive statistics of arsenic in soil (total and fractions) and plant parts (grain and straw + husk), and linear regression among soil and plant arsenic was carried out using Statistix 8.1. Percent contamination of arsenic in soil and plant parts (i.e. grain) was assessed according to the permissible limits as given by Anon., (1992) and Anon., (2010). While, the standard values for straw + husk arsenic are not available, therefore, these values were only discussed in the light of available literature (Bhattacharya *et al.*, 2009).

Results and Discussion

Soil arsenic fractions: The calcium-bound-arsenic was the most dominant fraction, found in the range of 1.35-25.66 mg kg⁻¹ in surface and 1.01-15.71 mg kg⁻¹ in subsurface rice field soils, contributing 38% and 31% (Table 1) of total arsenic (5.47-59.77 mg kg⁻¹ in surface and 7.32-38.55 mg kg⁻¹ in sub-surface soils). The next fraction i.e. available-arsenic ranged from 1.23-21.11 mg kg⁻¹ and 0.87-10.67 mg kg⁻¹ contributing 29% and 25% of total arsenic present in the soil. The iron-bound-arsenic fraction contributed 17% (0.97-11.31 mg kg⁻¹) and 29% (0.63-8.2 mg kg⁻¹) of the total arsenic correspondingly in surface and subsurface soils. The lowest concentration present in rice field soils was that of aluminum-bound-arsenic (0.68-5.87 mg kg⁻¹ in surface and 0.71-6.20 mg kg⁻¹ subsurface) contributing only 10% and 16% in total arsenic concentration. The individual fractions of surface soil are presented in Fig. 1. The available-arsenic fraction typically adsorbs on the clay separates and is generally released from the mineral surfaces by ligand-exchange (Zhang *et al.*, 2013). The calcium-bound-arsenic fraction ought to be the prevailing fraction in these soils. Fractionation schemes allow partitioning into various fractions (i.e. exchangeable, Al, Fe, or Ca bound forms) based on chemical alteration of the ions in a soil system, therefore, one fraction may complement the other. However, these schemes have proved the high availability and transport of arsenic in calcite rich soils (Yolcubal & Akyol, 2008). The results reported by Adriano (1986) also support this fraction to be dominant due to sorption of calcium minerals. Major oxides and hydroxides of iron and aluminum occur in acidic soils,

therefore play major role in the retention and transport of arsenic in acidic environment. Nonetheless, even lower quantities of iron oxides are responsible for arsenic adsorption (Taggart *et al.*, 2004). The occurrence of iron oxides i.e., goethite and hematite in calcareous soils of Pakistan have already reported by Memon *et al.*, (2009). As rice cultivation is carried out under flooding conditions, the quantity of iron-bound-arsenic may be more than other crops. Poorly crystalline iron oxides associated with arsenic are more prevalent in rice soils than in wheat soils, due to larger quantities of iron minerals where rice is cultivated under flooded conditions (Norra *et al.*, 2005).

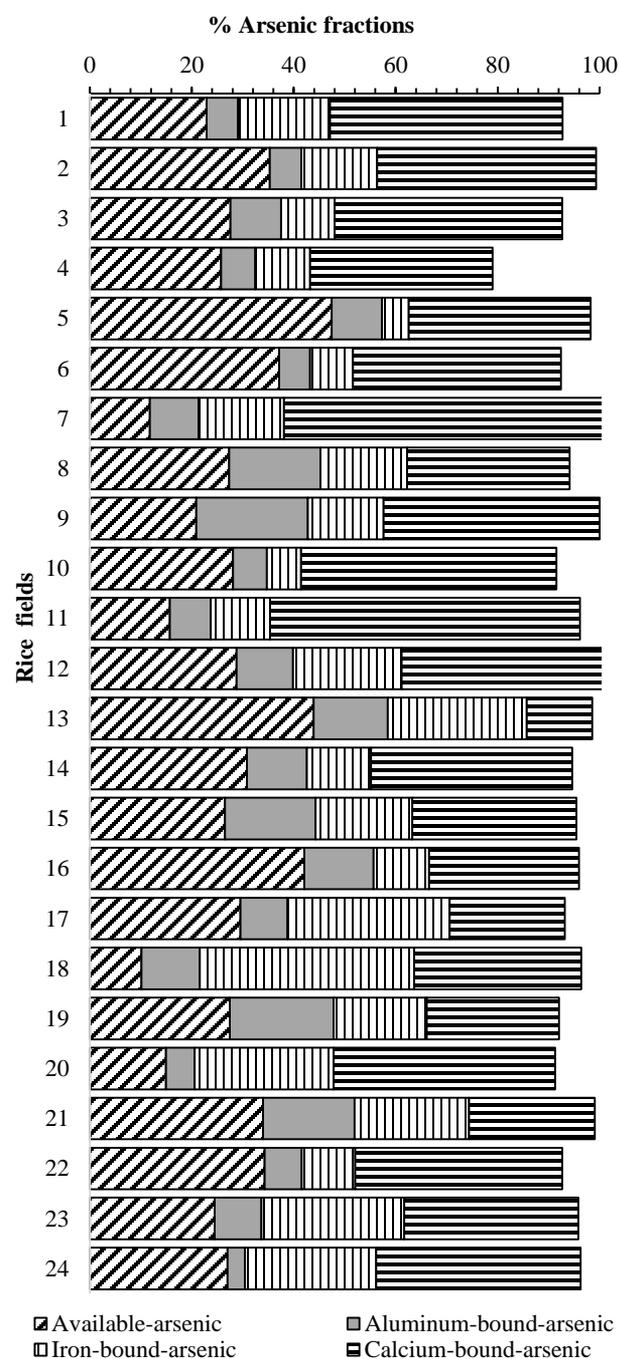


Fig. 1. Results of arsenic fractionation i.e., available, aluminum-bound, iron-bound and calcium-bound arsenic in rice growing sites of surface soils.

Total arsenic in soil and rice and their comparison with permissible limits: Total arsenic concentration (Table 1) was higher in surface (5.47-59.77 mg kg⁻¹) than that in sub-surface (7.32-38.55 mg kg⁻¹) and was in agreement with the concentrations reported by Cappuyns *et al.*, (2002) and Luo *et al.*, (2008). Based on mean values, arsenic decreased from surface to sub-surface by 36%. However, the standard deviation values show wide variability in arsenic concentration of surface soils. This variability was under sites 2, 3, 12 and 17 due to four rice growing sites ranging from 51.59 to 59.77 mg kg⁻¹. The arsenic concentration in these sites was relatively more due to low sand and pH and high clay, silt and Fe and is in agreement with the results of Fayiga *et al.*, (2004) and (2007). Similar total arsenic concentrations have been reported (8.7-46.2 mg kg⁻¹) for agricultural soils irrigated with drainage mixed water of Manchar Lake, Sindh-Pakistan (Arain *et al.*, 2009). Silva Junior *et al.*, (2019) reported similar arsenic (0.98-41.71 mg kg⁻¹) concentration in Amazon, Biome-Brazil. Regarding rice shoots (Table 1), straw + husk had more arsenic concentration (0.30-1.29 mg kg⁻¹) than that in grain (0.15-1.00 mg kg⁻¹). Looking at mean arsenic concentrations (straw + husk - 0.79 mg kg⁻¹ and grain - 0.43 mg kg⁻¹), straw + husk had about two times higher arsenic concentration over that in grain. This is because, arsenic moves from rhizosphere to rice shoots by means of xylem which further distributes to other aerial parts, thus, the buildup of arsenic drops from roots to stem, leaves and grain, and is in line with the studies by Liu *et al.*, (2004).

The arsenic concentration in soil, grain, and straw + husk obtained in this study was compared with available standard permissible limits of arsenic set by different organizations (Table 2) as there are no standard limits locally established for total arsenic in soil or rice grain. Majority of the scientists use a limit of 50 mg kg⁻¹ arsenic in soil as given by Anon., (1992). Which seems much higher compared to a limit (30 mg kg⁻¹) given by Anon., (2005). Permissible limits of total arsenic by other countries are even lower than these values. According to action level of arsenic for agricultural soils set by Anon., (1992) only 17% rice sites (surface soils) were above the permissible limit of 50 mg kg⁻¹ arsenic. The percent contaminated rice sites increased (29% at surface and 8% at subsurface) when compared with 30 mg kg⁻¹ arsenic limit given by Chinese Food standards Agency (2005). The situation was worse and the arsenic contaminated rice sites further increased to 63% and 17% when the arsenic limit of 20 mg kg⁻¹ was considered (Anon., 2015). Considering the permissible limits of rice by Anon., (2010), only one sample was above the limits of 1.0 mg kg⁻¹. In contrast, 100% rice grain samples were above the prescribed limit of 0.15 mg kg⁻¹ by Chinese Food standards Agency (2005) and 0.10 mg kg⁻¹ by Anon., (2015) and Anon., (2016) norms. In case of straw + husk, it is mostly used for animal feed and there are no arsenic limits on the record. However, the data can be discussed on the basis of previous values reported in literature. Among straw + husk, straw has main quantity of arsenic. Literature reports variable arsenic concentration of straw i.e. 1.15-4.15 mg kg⁻¹ (Bhattacharya *et al.*, 2009), 0.077 to 5.139 mg kg⁻¹ (Chakma *et al.*, 2012) and even up to 92 mg kg⁻¹ (Abedin *et al.*, 2002). All these studies (Bhattacharya *et al.*, 2009; Chakma *et al.*, 2012) report concern over the use of arsenic contaminated straw as feed

and that more likely, this concentration will increase in milk products, meat, etc. of cow, buffalo. Nonetheless, the values obtained in this study (0.3-1.29 mg kg⁻¹) are much lower than those already reported.

Contribution of soil fractions to rice through regression models: In order to find out the contribution of each soil arsenic fraction to rice grain and straw + husk, regression analysis was carried out. Arsenic concentration present in each soil fractions (calcium-bound, available, iron-bound and aluminum bound arsenic) of surface soil showed a linear, positive and significant relationship ($p < 0.05$ – < 0.001) with the arsenic concentration in rice grain (Table 3). The coefficient of correlation (r) values varied from 0.42 for aluminum-bound-arsenic to 0.75 for calcium-bound-arsenic. The regression equation ($Y = a + bx$) along with coefficient of determination (R^2) explained that accumulation in rice grain was mainly contributed from calcium-bound-arsenic (56%), followed by available-arsenic (43%), iron-bound (26%) and aluminum-bound arsenic (18%). As for subsurface soil, the contribution mainly came from calcium-bound (r = 0.66) and available arsenic (r = 0.53) and the arsenic accumulation in grain from these fractions was respectively 0.44% and 0.28%. The regression equation ($Y = a + bx$) along with coefficient of determination (R^2) explained that accumulation in rice grain was mainly contributed from calcium-bound-arsenic (56%), followed

by available (43%), iron-bound (26%) and aluminum-bound arsenic (18%). The relationship between arsenic in each fraction and straw + husk as presented in Table 4 showed linear, positive and significant ($p < 0.05$ – $p < 0.001$) relationship for calcium-bound (r = 0.79 and 0.66) and available arsenic (r = 0.48 and 0.54), correspondingly.

The regression analysis illustrated that calcium-bound-arsenic fraction contributed 62% and 44% and available-arsenic as 23% and 29% to the arsenic concentration present in straw + husk, correspondingly in surface and subsurface soils. The available-arsenic fraction is the one that is available to plant at any given time and is dependent on the calcium-bound, iron-bound and aluminum-bound arsenic fractions, with the former one contributing the most and the later one, the least (Fayiga *et al.*, 2007). The available-arsenic fraction is therefore continuously altered depending on the change in chemical species. The calcium-bound-arsenic fraction contributes the most to bioavailable fraction with limited iron-bound and aluminum-bound arsenic. This is because, in calcareous soil conditions, the arsenate-outer sphere complexes of arsenate govern over the inner surface bound ones (Adriano, 2001 and Yolcubal & Akyol, 2008) with no or little arsenite. This also conveys the quick desorption of arsenic from calcium-bound-arsenic and its entry to available-arsenic. This also means that the calcium-bound-arsenic is not a permanent part of crystal lattice.

Table 1. Arsenic in soil (fractions and total) and plant parts (grain and straw + husk) of rice.

Variable	Range	Mean ± Std.	Range	Mean ± Std.
	0-15 cm		15-30 cm	
Soil arsenic (mg kg⁻¹)				
Available-arsenic ⁺	1.23-21.11	7.66 ± 4.98	0.87-10.63	4.22 ± 2.01
Aluminum-bound-arsenic ⁺⁺	0.68-5.87	2.61 ± 1.51	0.71-6.20	2.71 ± 1.53
Iron-bound-arsenic ⁺⁺⁺	0.97-11.31	4.48 ± 2.92	0.63-8.20	3.18 ± 2.06
Calcium-bound-arsenic ⁺⁺⁺⁺	1.35-25.66	9.94 ± 6.41	1.01-15.71	5.10 ± 3.85
Total arsenic	5.47-59.77	26.29 ± 14.74	7.32-38.55	16.85 ± 7.46
Plant arsenic (mg kg⁻¹)				
Rice grain	0.15-1.00	0.43 ± 0.24		
Straw + husk	0.30-1.29	0.79 ± 0.28		

+Exchangeable arsenic fraction

++Aluminum bound arsenic fraction

+++Iron bound arsenic fraction

++++Calcium bound arsenic fraction

Table 2. Arsenic contamination in soil and rice grain.

Parameter	Soil depth (cm)		Permissible limit (mg kg ⁻¹)	References
	0-15	15-30		
Total arsenic in soil	17 (04)	0	50.0	FAO (1992)
Total arsenic in rice grain	4 (1)		1.0	FAO/WHO (2010)

Table 3. Regression analysis of soil arsenic fractions (0-15 and 15-30 cm) with arsenic in rice grain.

Soil arsenic fractions	Coefficient of correlation (r)		Coefficient of determination (R ²)		Regression equation (Y = bx + a)	
	0-15	15-30	0-15	15-30	0-15	15-30
Available	0.65**	0.53**	0.43	0.28	0.032 x + 0.19	0.064 x + 0.17
Aluminum-bound	0.42*	0.26 ^{NS}	0.18	0.07	0.07 x + 0.26	0.041 x + 0.32
Iron-bound	0.49**	0.39 ^{NS}	0.24	0.15	0.040 x + 0.26	0.045 x + 0.29
Calcium-bound	0.75***	0.66***	0.56	0.44	0.03 x + 0.15	0.04 x + 0.22

NS – Non-significant, *, ** and *** - Significant at p 0.05, 0.01 and 0.001 HSD test

Table 4. Regression analysis of soil arsenic fractions (0-15 and 15-30 cm) with arsenic in straw + husk of rice plant.

Soil arsenic fractions	Coefficient of correlation (r)		Coefficient of determination (R ²)		Regression equation (Y=bx+a)	
	0-15	15-30	0-15	15-30	0-15	15-30
Available	0.48*	0.54**	0.23	0.29	0.03 x + 0.59	0.075 x + 0.47
Aluminum-bound	0.1 ^{NS}	0.10 ^{NS}	0.01	0.01	0.02 x + 0.75	0.045 x + 0.67
Iron-bound	0.32 ^{NS}	0.37 ^{NS}	0.10	0.14	0.031 x + 0.65	0.052 x + 0.68
Calcium-bound	0.79***	0.66**	0.62	0.44	0.04 x + 0.45	0.05 x + 0.54

NS – Non-significant, *, ** and *** - Significant at p 0.05, 0.01 and 0.001HSD test

Conclusion

Fractionation schemes resulted in higher availability and transport for calcium-bound and available arsenic, based on the carbonate rich nature of these soils with arsenate as a dominant ion. The soils showed limited presence of iron and aluminum bound arsenic fractions. About 94-97% of total arsenic was in the form of inorganic fractions. Although the results of this study are not indicative of any critical hazard, the accumulation of arsenic in soil and mainly in rice grain needs to be evaluated on regular basis. This is particular for straw + husk, which had more arsenic than that in rice grain. When utilized as a feed for animals, can enter in the food chain, transfer to human via meat, milk products, etc. and be a threat to human.

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