

ASSESSMENT OF HEAVY METALS AND THERMAL PROPERTIES OF SOIL-RICE-HUSK SYSTEM COLLECTED FROM THREE DISTRICTS OF BANGLADESH

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Abstract: This study was conducted to evaluate the contamination of heavy metals and their thermogravimetric properties in the soil-rice-husk system. Heavy metals concentration was determined by Atomic Absorption Spectroscopy (AAS) and thermal property was also analyzed by using Thermo Gravimetric Analyzer (TGA). Metals uptake in rice crop grown in soils of three different areas (Savar, Chapainawabganj and Gazipur) in Bangladesh was studied. Soil, rice husk and rice samples were analyzed after microwave acid digestion. Heavy metals concentration detected in rice samples decreases in the following order as Fe > Mn > Zn > Cu > Ni > Co > Cd > Pb. The metal content in husk was higher than in corresponding rice. Fe concentration was higher than other metals in soil, husk and grain samples. The concentrations of Cd and Pb in the soil were found to be below the detection limit and the order of the other heavy metals as Fe > Mn > Zn > Cu > Ni. The thermal properties of the soil-rice-husk system did not show any significant visible variation during this experiment except for the soil of the Gazipur areas. The residual mass obtained from the TG thermogram helps to make a relation between the quality of soil and the rate of uptake of heavy metals by rice or its husk.

Introduction

Rice is one of the most important and widespread cereals in the world. It is the staff of life for 3 billion people, mainly in Asia⁽¹⁾, contributing over 70% of the energy and 50% of the protein provided by their daily food intake. Rice (*Oryza sativa*, Poaceae) provides the bulk of the human diet throughout Asia. In the last report of European Commission, India was presented as the first country for rice production with 19% of export. It is the staple food of Bangladesh, which has significant uses of human nutrition⁽²⁾. The economy of Bangladesh depends on the agriculture, mainly rice. As of 2016, it employs 47% of the total labor force and comprises 16% of the country's GDP. Bangladesh is the fourth largest rice producing country in the world⁽³⁾. Different types of rice (Aush, Aman or Boro) are cultivated in Bangladesh throughout the year. Aman (broadcast and transplanted) is generally cultivated in December-January, Boro in March - May and Aus

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in July-August cropping seasons. Among these cropping transplanted Aman is most important and occupied about 46% of the rice cultivated land in 2009 - 2010⁽⁴⁾.

Heavy metals may have a serious impact if they are released into the environment even in trace quantities⁽⁵⁾. These can enter into the food chain from aquatic and agricultural ecosystems and threaten human health indirectly⁽⁶⁾. Whereas food crops may be exposed to heavy metal through contaminated soil or atmospheric dispersal of such metals from industrial areas, human beings may be exposed to heavy metals through consumption of contaminated foods such as rice⁽⁷⁾. Heavy metals like Fe, Cu, Zn, Ni and other trace elements are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders⁽⁸⁾.

On this basis the presence of toxic heavy metals in rice, which may raise the metal daily intake, should be strongly avoided in order to prevent negative effects on human health. The following elements are considered macronutrients in rice and their content is usually in some percentage of P, S, K, Ca and Mg. Other elements, like Mn, Fe, Cu, Zn, Se, and Ni are considered to be useful micronutrients to plants when used in amounts which facilitate the physical growth and development of plants⁽⁹⁾ and they are present in lower amount, while As, Cr, Pb and Cd are undesirable elements because of their toxic effects even in very low quantity. As a consequence, it is crucially necessary to reduce possible accumulation effects in rice grains from the environment for safe food production⁽¹⁰⁾. When these metals exceed maximum acceptable limits they become toxic to the plants. Just like in plants - Fe, Cu, Mn and Zn are useful in humans when used in trace amounts. When these metals exceed the acceptable limits in the body, they pose health problems⁽¹¹⁾. Some of these health problems are cancer, hypertension, fever, kidney disorder and DNA damage in living cells⁽¹²⁾. Heavy metals are non-degradable and stay longer in the soil⁽¹³⁾. Crops such as rice that are grown in submerged conditions are even more exposed to heavy metal sources both from the soil and water. Rice being the second most consumed crop in the world may in turn expose the majority of its consumers to the heavy metals⁽¹⁴⁾.

Heavy metals and trace elements are also a matter of concern due to their non-biodegradable nature and long biological half-lives. Wastewater from industries or other sources carries sufficient amounts of toxic heavy metals such as Cd, Cu, Zn, Cr, Ni, Pb, and Mn in surface soil which create a problem for safe rational utilization of agricultural soil⁽¹⁵⁾. Long-term use of industrial or municipal wastewater in irrigation is known to have a significant contribution to the content of trace and heavy elements such as Cd, Cu, Zn, Cr, Ni, Pb, and Mn in surface soil ^(15, 16). As a result, excessive accumulation of trace elements in agricultural soils through wastewater irrigation may not only result in soil contamination but also affect food quality and safety⁽¹⁷⁾. Karim *et al.* 2008⁽¹⁸⁾ conducted a study on the arsenic and heavy metal concentration in surface soils and vegetables of Feni district.

The thermal decomposition reactions play an important role during different processes of the biomass utilization. Thermogravimetric analysis (TGA) is a quite precision method for the study of pyrolysis at control heating rates, under well-defined conditions in the kinetic system. It also provides information about the partial process and reaction kinetics. The thermal degradation patterns of lignocellulose biomass are strongly affected by their chemical composition such as cellulose, hemicellulose and lignin. A physical and thermo-chemical property of rice husk varies depending on the types of variety and geographical location of the cultivated crop. Physical properties such as particle size, moisture content and bulk density are important factors of any biomass. Transportability, flow ability and combustion characteristics are dependent on the physical properties.⁽¹⁹⁾

There are a few information regarding heavy metal concentrations and thermo-gravimetric analysis of soil-rice-husk system of the three different districts of Bangladesh. The aim of the present study was to determine the concentrations of heavy metals in soil, rice husk and rice grains produced in the three different districts (Gazipur, Savar and Chapainawabganj) of Bangladesh and to study the thermal properties of soil-rice-husk system. The metal contents of soils of the three districts were also correlated with the metals found in the crops grown the respected area which also supported by the TGA data.

Materials and Methods

Study areas: Soil and rice samples were collected from paddy fields of the districts in Bangladesh namely Savar, Chapainawabganj and two areas of Gazipur. Among these, two districts were selected from the industrial area near Dhaka city and other was apart from the industrial area in the north-western part of the Bangladesh, beside the Padma River.

Sample collection: Sampling of soil and paddy rice was conducted in January-February 2016 just before harvesting time. Soil samples were collected from 0 to 15 cm depth from corresponding rice samples cultivated paddy fields by random selection of the field at a specific distance. The collected soil samples were dried in air for a few days by spreading on a clean piece of paper. Visible roots and debris were removed from the soil samples and discarded. After air drying, a portion of the soils was ground by a wooden hammer. Ground samples were screened to pass through a 0.5 mm stainless steel sieve. Soils were preserved in plastic containers with proper labeling. Rice samples were collected from corresponding paddy fields for ensuring the original locations of samples. Paddy rice (rice grains with husks) was air dried to constant weight and husks were removed using mortar and pestle. The rice grain (paddy rice without husks) and husks were then separately ground to a fine powder.

Digestion of samples: Well homogenized soil, rice grain and husk samples were weighed (0.5 g each) and taken into separate teflon vessel, then 10 ml concentrated HNO₃ was added in each digestion tube. The tubes were tightly closed with a cap provided with a hole to pass away of gases formed during the digestion. This procedure was performed according to US-EPA 3050B method⁽²⁰⁾. The samples were placed in a CEM MARS XPRESS microwave and digested at 180°C for 20 minutes at 200 psi with a microwave power of 1600W⁽²¹⁾. Both the digested samples of rice grain and rice husk were diluted with de-ionized water up to 25 ml and digested soil samples were diluted up to 100 ml in volumetric flasks. Powdered samples were preserved in a plastic container for thermogravimetric analysis at 600°C.

Measurement of heavy metals: The concentrations of Mn, Fe, Ni, Cu, Zn, Cd and Pb in the samples of rice grain, husk, and soil were determined by flame Atomic Absorption Spectrophotometer (AAS) (AAS 200, PerkinElmer). Standard solutions of corresponding metals were used to calibrate the instrument. Concentrations of all metals in soil, rice grain and husk samples are expressed on dry weight basis.

Thermogravimetric analyses: Thermogravimetric analyses (TGA) were carried out to measure the change in mass of samples as a function of time or temperature for characterization of multicomponent materials and thermal decomposition. TGA (TGA-50H, Shimadzu) was performed from room temperature to 600°C in the presence of atmospheric nitrogen gas with a flow rate of 10 ml/min and temperature increase rate of 10°C/min, using aluminium crucibles and samples masses of ~5 mg. The measurements were repeated at least three times for each sample.

Results and Discussion

Heavy metals concentrations in the soil, rice and husk samples were analyzed by AAS and are shown in Figs 1 - 5. The soil sample collected from Savar was found to be rich in Mn, Fe, Ni, Cu and Zn. The paddy grown in such soil might have absorbed these elements from the soil, and therefore, the husk and rice were also found to contain higher amount of these elements (Fig. 1). Cd and Pb were found to be below detection level (BDL) for soil and Cd was in a very low concentration in rice and husk.

The soil sample collected from Chapainawabganj was found to be rich in Mn, Ni, Cu and Zn; whereas Fe was in very abundance in amount (Fig. 5). But the husk and rice obtained from corresponding paddy field contained comparatively lower amount of these elements than husk or soil (Fig. 2). Cd and Pb were also found at below detection level.

Likewise Savar and Chapainawabganj, soil samples of Gazipur region (Gazipur-1, Gazipur-2) were found to be rich in Mn, Ni, Cu and Zn; whereas Fe was in abundance in amount. But the rice obtained from corresponding paddy field also contained

comparatively lower amount of these elements than husk or soil (Figs 3, 4). Cd and Pb were also found at below detection level.

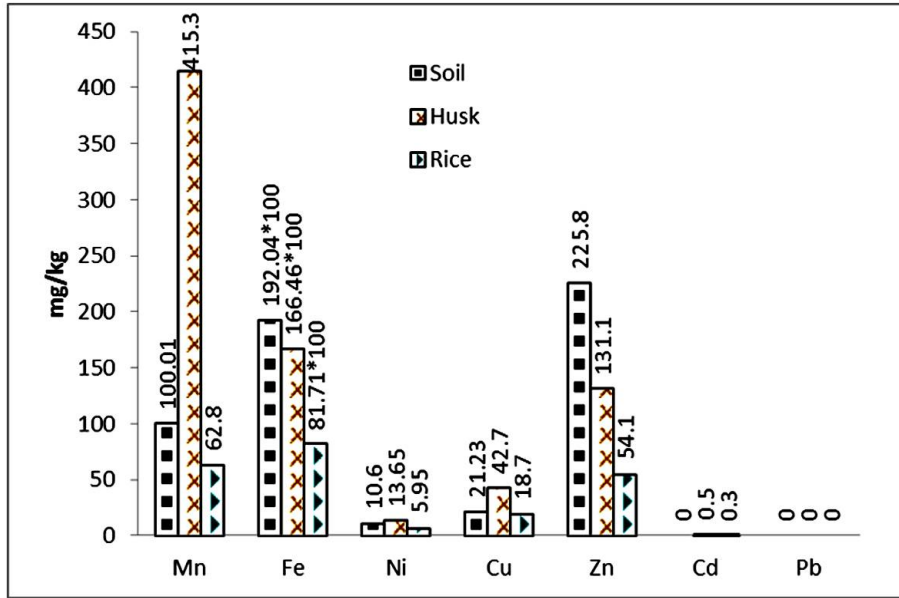


Fig. 1. Heavy metals content (mg/kg) of the samples collected from Savar.

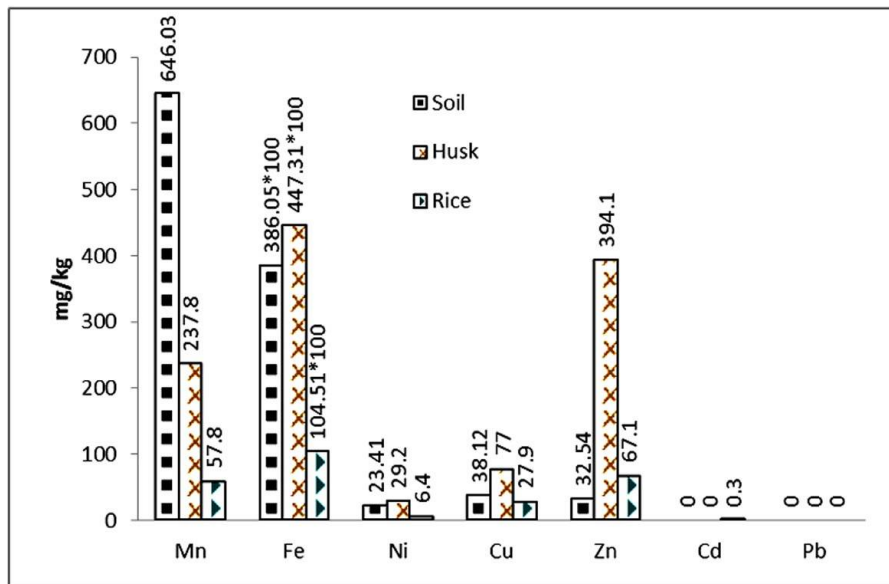


Fig. 2. Heavy metals content (mg/kg) of the samples collected from Chapainawabganj.

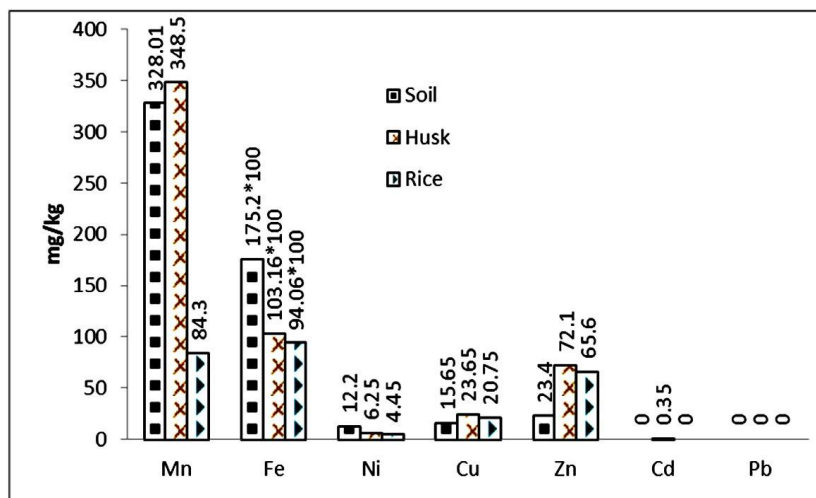


Fig. 3. Heavy metals content (mg/kg) of the samples collected from Gazipur-1.

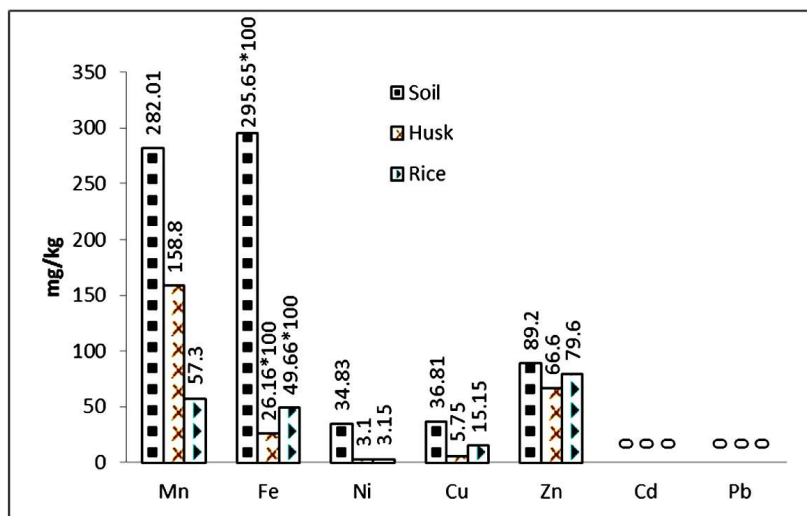


Fig. 4. Heavy metals content the samples collected from Gazipur-2.

Table 1. Heavy metals content acceptable limits (mg/kg) according to USEPA⁽²²⁾ guidelines for sediments.

Category	Mn	Fe	Ni	Cu	Zn	Cd	Pb
Non polluted	< 300	< 17000	< 20	< 25	< 90	*	< 40
Moderate polluted	300-500	17000-25000	20-50	25-50	90-200	*	40-60
Heavily polluted	>500	>25000	>50	>50	>200	>6	>60

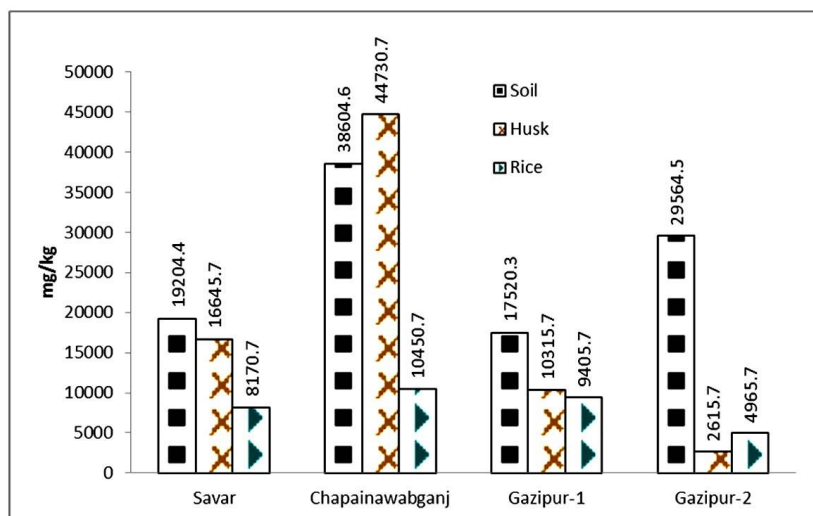


Fig. 5. Iron (Fe) content (mg/kg) of the samples.

According to the US Environmental Protection Agency (USEPA) guidelines (Table 1) soil of Chapainawabganj was found to be heavily polluted with Mn element whereas soil of Savar was non-polluted. The soils of Chapainawabganj and Gazipur-2 were heavily polluted with Fe than the other two sites (Savar and Gazipur-1), which were found to be moderately polluted. The element Ni and Cu of Savar and Gazipur-1 were found in non-pollution level, but Chapainawabganj and Gazipur-2 were moderately polluted. We also observed that in Savar, the Zn in soil was heavily polluted than that of the other three sites. Higher concentration of Zn in Savar area might be due to industrial activities, such as textiles, paints, battery, milling and chemical industries which might contaminate or introduce heavy metals into the soil⁽⁹⁾.

From the Figs 1 - 5 it was seen that the descending order of the average contents of metals in rice as: Fe > Mn > Zn > Cu > Ni > Co > Cd > Pb. From results it was also observed that the concentration of Pb element in soil, husk and rice grain was below detection limit. Whereas the amount of Cd and Pb were in the soil below the detection limit but Cd element found in rice husk and rice grain. This was due to the rice grown in contaminated soil or through irrigation using groundwater or municipal wastewater⁽¹³⁾ and use of heavy metals containing agrochemicals such as pesticides, herbicides and fertilizers⁽¹²⁾. Heavy metals from the contaminated paddy soils may take place by the rice plant and accumulated in the grain⁽²³⁾. According to the Codex Alimentarius Commission 2014⁽²⁴⁾, heavy metal contamination in rice should not exceed the maximum limit of 0.4 mg/kg for Cd. The Cd concentration of rice grain from Savar and Chapainawabganj was found to be 0.3 mg/kg, but the maximum tolerance level for Cd is 0.2 mg/kg for rice as stated by National Food Safety Standard 2012. This may be because of Cd from the

industries and vehicle exhaust can pollute air which then can be absorbed directly by the rice grains⁽²⁵⁾.

Fig. 6 shows thermograms (TG) for soil, husk and rice grain in (a) Chapainawabganj; (b) Gazipur-1; (c) Gazipur-2; and (d) Savar. A typical weight loss against temperature curve for the dehydration/pyrolysis of soil, rice and husk in nitrogen atmosphere under non isothermal conditions at heating rate of 10 C/min from room temperature (RT) to 600°C was chosen as it produced highest degradation of the samples. The TG curve can be divided into three regions. The first region is drying zone, second is devolatilization zone and the third one is char formation zone ⁽²⁷⁾. In all rice, husk and soil samples, a mass loss within the temperature range from RT to 200°C was observed as a result of dehydration. The drying of the sample mainly occurred up to temperature 80-100°C, where moisture released was 1.91, 9.45, 3.57 and 36.92% for soil of Savar, Chaapai-nawabganj, Gazipur 1 and Gazipur 2, respectively. Similarly moisture released as 7.87, 8.18, 8.11 and 8.24% for rice and 7.95, 6.89, 5.12 and 5.66% for husk of the four respective places were found. From Fig. 6 it is seen that the dissociation patterns are almost same except for the thermogram of Gazipur 2 area. In this thermogram a rapid decrease of water in the soil was observed. It might be due to the higher initial moisture percentage of the soil sample (Table 2). The initial moisture could be higher in Gazipur 2 because of sampling just a few hours after rainfall.

Table 2. Moisture percentage of soil, rice grain and husk samples.

Area	Soil (%)
Savar	3.12
Chapainawabganj	18.22
Gazipur-1	20.34
Gazipur-2	46.36

The 63.65 - 67.48% mass loss occurs at 200 - 400°C for rice, for husk it was 53.64 - 56.70%, while for soil it was 1.26 - 3.20%. Degradation within this temperature range could be attributed to the combustion of carbohydrates and other aliphatic compounds. The greater mass loss was observed in this temperature range for rice and husk. 3.2, 1.26, 2.79 and 2.26% of soil mass was loss at 200 - 400°C for Savar, Chapainawabganj, Gazipur 1 and Gazipur 2, respectively. The loss of mass could be an indicator of soil organic matter (SOM) present in that area. As a result it could be concluded that soil sample of Savar was rich in SOM, while soil of Chapainawabganj contained very low amount of SOM. Soil organic matter supplies necessary nutrient for the plant. So rich in soil organic matter may indicate the good fertility and productivity of the soil. The char yield occurred in the 400 - 600°C where could be the thermal degradation of carbonate and more stable aromatic structures occurred⁽²⁶⁾. The residual mass was found 1.55 -

2.57% for soil, 18.14 - 20.65% for rice and 17.34 - 21.18% for husk in the four places of the three districts which was found to be similar for residual mass of 13.82% observed for rice husk in Tanzania by Said *et al.* 2014⁽²⁷⁾.

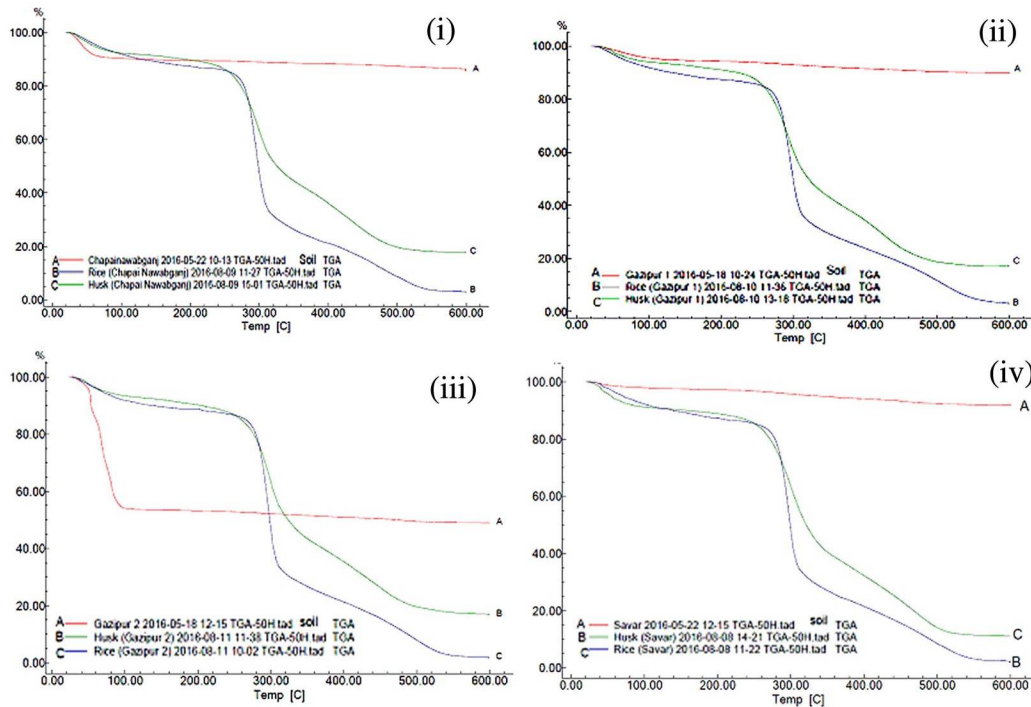


Fig. 6. TG curves for soil, husk and rice grain in (i) Chapainawaganj; (ii) Gazipur 1; (iii) Gazipur 2; and (iv) Savar.

The residual mass of the TG analysis could indicate the stable form or inorganic part of soil, rice and husk which would have supportive of heavy metal contents in the samples determined with AAS. The heavy metal content was relatively higher for rice and husk than found in the respected soil samples.

Conclusion

Soil is a great geochemical reservoir for contaminant as well as a natural buffer for transportation of chemical materials and elements in the atmosphere, hydrosphere, and biomass. In this paper, it was found that the metal composition of the soils of different regions were different in amount. It was also found that the accumulation of the metals in the crops corresponded to such metallic contents of the respected soils. It indicated if the soil contained high amount of iron; the crops also contained high content of iron, and so on.

It is obvious that the heavy metal contamination in the environment is of more concern worldwide. For this, it is the most important component of the human biosphere. The knowledge on the sources of heavy metals contamination in agricultural soils and rice is necessary in order to improve food safety by minimizing the possibility of food insecurity as well as human health problems. The most adverse effect of heavy metals is that they can be introduced into the food chain and threaten human health. Agricultural products growing on soils with high metal concentrations are represented by metal accumulations at levels harmful to human and animal health as well as to the bio-environment. Therefore, the levels of heavy metals in rice should be monitored as rice is considered a source of energy for the large population in Bangladesh. The present National environmental policies should be reinforced to ensure that heavy metals contaminations in agricultural soils and in food crops are minimized. This will help in reducing health risk to the population at large.

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