Transfer of elements from paddy soils into different parts of rice plants (Oryza sativa L.) and the resulting health risks for the Vietnamese population

Su vân chuyển các nguyên tố từ đất vào các phần của cây lúa (Oryza sativa L.) và đánh giá các rủi ro sức khỏe đối với người dân Việt Nam

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The uptake of elements from paddy soils into shoot, husk, and unpolished grain of rice plants was investigated in Mekong, Huong, and Red River areas in Vietnam. The transferability of most studied soil elements into plant parts decreases in the order: shoot > husk > grain. Exceptions are Mg, S, Cd, Cu, Zn, and Mo, whose transfer drops in the order: shoot > grain > husk, the transfer of P falls in the order: grain > shoot > husk. The translocation of the most health relevant elements into the different plant parts is affected by soil parameters like pH, organic matter, Fe- and Mn-phases, and clay minerals. Health risk assessment approaches for the average daily rice consumption are performed for non-cancer risk (Hazard Index - HI) including the elements As, Cd, Pb, Co, Cu, Mn, Mo, and Ni as well as for cancer risk for the elements As and Pb (Incremental Lifetime Cancer Risk - ILCR). All rice studied grain samples exceed the safe HI-index of below 1. 81% of the grain samples were within the level of concern ranging between 1.4 < HI < 5, 18% varied between 5 < HI < 8.4, although their corresponding soils showed only a little pollution. Cd, As, Mn, and Pb were the most important elements causing non-cancer risks for rice-consuming people. The cancer-risk values ILCR were mean 2.2 x 10^{-3} and are considerably higher than the safe threshold of 10^{-4} to 10^{-6}. Arsenic is the dominant factor for cancer risk. Rice-eating people living in Red River and Huong River areas face mainly health risks of exposure to As and Cd in the Mekong River area in addition to Pb.

Keywords: rice; paddy soil; element transfer; health risk; Vietnam

1. Introduction

Rice is the principal energy and protein supplying source for most of the Asian population in a daily basis. However, rice can be a prominent intake of harmful elements such as As, Cd, and Pb. Rahman and Hasegawa (2011) stated that, compared to other agricultural products, rice is the food with the highest content of As. High concentration of As in rice and drinking water is recognized as one of the main reasons for serious chronic diseases affecting millions of inhabitants in Bangladesh and West Bengal, India (Bhattacharya et al., 2010; Abedin et al., 2002; Khan et al., 2009). Due to the uncomplicated uptake of Cd into rice plants, rice consumption can also cause illnesses (Rizwan et al. 2016). A 50% of rice samples, collected in Cd-polluted paddy soils in Tak Province, Thailand, exceeded...
the concentration of 0.4 mg Cd kg\(^{-1}\) and up to 90% surpassed the permissible threshold of 0.2 mg Cd kg\(^{-1}\) (Sripachote et al. 2012; Simmons et al. 2005). Lead may also have a potential health risk in different rice-producing areas as recognized by Norton et al. (2014), Shraim (2017), and Fakhri et al. (2018). Chronic exposure to these elements causes deleterious health effects resulting in harmful impacts on heart, bones, skin, kidney, neurological disorders, and different cancer types (EFSA 2009, 2010; Smith et al. 2006; Kumarathilaka et al. 2018; Jaishankar et al. 2014).

Soils enriched with potentially toxic elements are often assumed to cause higher accumulation in plants. The growth and yield of rice plants can be negatively affected when exposed to high concentrations of trace metals (Marquez et al. 2018). Element concentrations in paddy soils are determined by their parent material, but also by anthropogenic contamination like mining and industrial operations, air pollution, agricultural practices (fertilizer and pesticides), and/or using contaminated wastewater for irrigation. However, the accumulation of an element in a plant depends on the plant species or cultivars, it’s irrigation. However, the accumulation of an element in a plant depends on the plant species or cultivars, it’s irrigation. The growth and yield of rice plants can be negatively affected when exposed to high concentrations of trace metals (Marquez et al. 2018).

According to Greger (2004), the fluid-transporting process within the root zone (a depth of 10 cm). The analysis was executed in the laboratory of the Geoscience Center of Göttingen University, Germany.

Vietnam is one of the world’s largest rice producers (FAO 2018). The biggest granaries of the country are the Mekong River Delta in the south and the Red River Delta in the north where abundant water boosts irrigation. In addition, annual flooding events deliver fertile suspended material that settles in the riverine areas, including rice fields. As a result, parent material of paddy soils is mainly alluvial sediment, rich in organic matter. Some of the paddy soils in Vietnam are polluted by heavy metal(loid)s such as As, Cd, Cr, Cu, Pb, and Zn from industrial and mining activities leading to the contamination of rice grains (Huong et al. 2008; Phuong et al. 2010; Ha 2011; Vinh et al. 2012). However, most of the As contamination in paddy soils and rice grains comes from natural sources, strongly influenced by redox processes as described by Seyfferth et al. (2014) and Nguyen et al. (2020a, b). Around 11% of the Mekong River soils and 92% of Red River soils exceeded the Vietnamese As limit of 15 mg kg\(^{-1}\) for agricultural soils. Different soil conditions of these areas may be a reason for toxic element enrichments within the grains.

Similar investigations on the transfer of a broad variety of toxic elements into different rice plant parts are widely lacking in the literature. Understanding the influence of soil factors on element translocation, to and within the rice plant, is crucial to mitigate their uptake and protect human health. For Vietnam, as an important rice producing, consuming and exporting country, there are some information on the daily risk exposure to toxic metal(loid) intake by eating rice (Nguyen et al. 2020a, b). However, a corresponding chronic risk assessment for the population is still missing.

The goals of this research are: 1) to evaluate the translocation of a wide range of elements from paddy soils into the rice plant parts of under the influence of soil parameters such as pH, organic material, Al-, Fe-, and Mn-oxides/hydroxides; 2) to characterize the element concentration in the differing parts of rice plants (shoot, husk, grains); 3) to get information on long-term cancer and non-cancer health risks from rice consumption in Vietnam.

2. Materials and methods

2.1. Sampling, digestion, analysis and quality control

Rice plants and their corresponding soil samples were collected along three river systems in Vietnam including the Red River Delta in the north (19 sites), the Huong River in the center (4 sites), and the Mekong River Delta in the south (78 sites). The sample locations are shown in Fig. 1 (coordinates of the sampling sites are listed in Table S2 in the supplementary material). All samples were taken within 10 days before harvesting time. The 23 rice plant samples of the Red River and Huong River areas were separated into shoot (stalk and leaves combined), husk, and unpolished rice grain. Roots and stubbles were left in the fields. The 78 rice samples of the Mekong River area were split into husks and grains. The soil samples were taken within the root zone (a depth of 10 cm). The analysis process was executed in the laboratory of the Geoscience Center of Göttingen University, Germany.
The plant samples were dried at 60 °C and the soil samples at 105 °C. All samples were pulverized into grain sizes <63 µm by a Frisch® agate ball mill before analysis. Soils’ pH-values were determined in a 1:2.5 (w/v) ratio of air-dried unground soils to 0.01 M CaCl₂ solution by using the glass electrode ProfiLine pH/mV-Meter 197.

The Loss on Ignition (LOI), representative for organic matter and structural water in the soil samples, was determined as the percentage weight loss after heating the samples to 530 °C for 24 hours. The milled plant and soil samples were completely digested in a mixture of ultrapure concentrated acids HNO₃ (65%), HF (40%) and HClO₄ (72%) in closed ultra clean PTFE vessels (PicoTrace®, Göttingen, Acid Sample Digestion System DAS 30). For the soil samples, about 1 ml of 37% HCl was added in the last step of the soil digestion procedure. The clear digestion solutions were then measured by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) Agilent 5100 VDV and by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) Thermo Scientific iCAP Q to get the total element concentrations.

2.2. Exposure and long-term health risk calculations for rice consumption

The chronic risk exposure from rice consumption affecting human health can be evaluated on the basis of indices of Lifetime Cancer Risk and of Lifetime Non-cancer Risk (Järup, 2003; Mulware, 2013). These indices are based on the Chronic Daily Intake (CDI) in mg per kg body weight per day (USEPA 1989) which can be determined as follows:

\[
CDI = \frac{(CF \times IR \times EF \times ED)}{(BW \times AT)}
\]

where \( CF \) is the harmful element concentration in rice (mg kg⁻¹); \( IR \) is the average daily rice consumption of 0.398 kg day⁻¹ for Vietnamese adults (Nguyen et al. 2020); \( EF \) is the exposure frequency (365 days year⁻¹); \( ED \) is the exposure duration (70 years); \( BW \) is the Vietnamese average body weight (b.w.) of 52 kg for an adult (Nguyen et al. 2020); \( AT \) is the average period of exposure days to hazardous element intake.

2.2.1. Chronic non-cancer risks

The chronic non-cancer risk approach is used to evaluate non-carcinogenic health effect of harmful elements from different sources. For rice, As, Cd, Pb, Mn, Co, Ni, Cu, and Mo are considered as the most critical and potentially harmful elements causing adverse health effects. The
Target Hazard Quotient (THQ) describes the exposure to an element and can be reckoned as follows:

\[ THQ = \frac{CDI}{RfD} \]

\( RfD \) is the chronic Reference Dose in mg kg\(^{-1}\) b.w. day\(^{-1}\) of a harmful element and represents the maximum permissible element amount taken up from all sources (food, water, air etc.). The \( RfD \) values of elements for this paper are taken from previous research (Nguyen et al. 2020a, b).

The Chronic Hazard Index (HI) for non-cancer factors is the sum of the THQ for each relevant element and represents the total non-carcinogenic hazard attributable to exposure:

\[ HI = \sum_{n=1}^{m} THQ \]

At HI \( \geq 1 \), potential health effects should be concerned even if the exposure for every single element is below its RD (USEPA 1989). Nordberg et al. (2015a) noticed that the HI-approach is simple but limited in its scope because it may either under- or over-estimate the risk from multiple chemical exposures.

### 2.2.2. Chronic cancer risks

Incremental Lifetime Cancer Risk (ILCR) is an index to estimate the incremental probability of an individual cancer progression over a lifetime (USEPA 1989). The ILCR of a harmful substance is computed as follows:

\[ ILCR = CDI \times SF \]

where \( SF \) is the Slope Factor. It represents an upper estimate of increased cancer risk from a lifetime exposure to a carcinogenic substance by ingestion, inhalation or dermal contact in \([\text{mg } / \text{kg b.w. day}]^{1}\) (USEPA 1989). The three elements As, Cd, and Pb are considered as key carcinogenic risk factors for low dose element intakes. However, there is insufficient information about the slope factor of oral Cd intake, therefore, Cd was excluded. In this study, the ILCR of As and Pb are estimated for eating unpolished rice with slope factors \( SF_{\text{As}} = 1.5 \) and \( SF_{\text{Pb}} = 0.0085 \) \([\text{mg } / \text{kg b.w. day}]\) (OEHHA 2011).

Cumulative cancer risk (\( \sum ILCR \)) is the sum of single lifetime cancer risks, which are restricted to the carcinogens As and Pb:

\[ \sum ILCR = ILCR_{\text{As}} + ILCR_{\text{Pb}} \]

USEPA (1989), proposed a healthy safe level where \( \sum ILCR \) is below \( 10^{-6} \). The acceptable suggested level falls in the range from \( 10^{-6} \) to \( 10^{-4} \).

### 3. Results and discussion

#### 3.1. Element distribution in parts of rice plants

After being taken up, primarily by the root surface, ions are translocated by the xylem sap to the different plant parts. During the transport, many elements are enriched at cell walls (Greger 2004; Meharg and Zhao 2012). In general, the element transferability to plant parts depends on element species, plant genotypes/cultivars, and external factors. The translocation of elements in the plant takes place by the phloem and/or xylem sap. Essential elements fulfill different biological functions such as osmoregulation. The water and nutrient mass flow within the plant is driven by stomatal aperture, energy transfer, membrane permeability and electrochemical potentials. Furthermore, some of the elements serve as cell wall and membrane stabilizers and are necessary constituents of amino and nucleic acids, proteins, enzymes, coenzymes, and chlorophyll (Marschner 2012).

The elements Ba, Na, Ca, Mn, Pb, Co, As, K, Cd, Fe, Ni, Mg, Zn, and S are more concentrated in shoot than in unpolished grains (Sh/Gr 84 to 2). Meanwhile, the Cu and Mo concentrations in shoot are approximate to those in unpolished grain. Especially, the P concentration is enriched threefold in unpolished grains in comparison to shoot. The concentration of most elements (except Ni and P) in shoot is higher than that in husk, especially for Na, Cd, Mg, and K. Most elements show higher concentrations in husk compared to those in grain, except for Cu, Cd, S, Zn, P, Mo, and Mg. Preferential transfer of some elements to grains may be explained by ion charges or the formation of organic complexes (Marschner 2012). The negative ions phosphate, molybdate and sulfate are repelled by the negatively charged cell walls allowing the more distant transport to the grains. Elements such as Cu, Zn, Mg, Ni and presumably some other metals may be transported within the plant as soluble organic complexes.

Following a general trend, most element concentrations decrease in the order: shoot > husk > grain; Cd, Mg, Zn, S, Cu, and Mo concentrations in the order: shoot > grain > husk, and P concentration in the order: grain > shoot > husk. Meng et al. (2018) found comparable results for the Cd distribution in rice plant parts.

On average, the masses portions of the plant parts to the whole aboveground plants are 0.42 of shoot, 0.46 of grain, and 0.12 of husk (Table 1). The relative mass portions of elements in different parts are shown in Fig. 2. A large load of most elements is stored in the shoot, holding more than 50% of the total element uptake. In contrast, 50% - 80% of the P, Mo, Ni, and Cu uptake is accumulated in the grain. The storage of elements in husk is below 10% except for Pb, Bi, and Sb.
There is a great difference among mean concentrations of potentially harmful elements in soils and related rice plant parts among other regions in Asia as compiled in Table 2. Arsenic concentrations in Japanese and Vietnamese soils are similar, but two times lower in soils from India, Malaysia, Thailand, and China. However, husk and grain samples from India and Malaysia contain 2 - 3 times more As. This can be explained by the very high As concentration, up to 700 µg L$^{-1}$, in the irrigation water (Biswa et al. 2014). Surprisingly, the As concentrations in shoots in India are about 3 times lower than those in China and Vietnam. The Cd concentrations in soils and grains in China, Japan, and Vietnam are remarkably higher than those in other countries. Concentrations of other potentially harmful elements are approximate among rice grains in China, Japan, and Vietnam. Rice grains in India and Malaysia have high contents of As, Cr and Pb. Korea shows heavy metal concentrations in soils remarkably low compared to China, Japan, and Vietnam. Nearly all elements within the different areas show decreasing concentrations in the order soil > shoot > husk > grain.
Table 1. Average physiologcal concentrations of element in soils and rice plant parts collected in Red River (RR), Huong River (HR) and Mekong River (MR) (mg kg⁻¹, except for LOI in wt. % and pH). Ratio represents the mass ratio of shoot, husk, or unpolished grain to the whole aboveground plant.

| Element | Soil (n = 101) | Shoot (n = 23) | Husk (n = 101) | Grain (n = 101) |
|---------|---------------|---------------|---------------|---------------|
|         | RR | HR | MR | Mean | RR | HR | MR | Mean | RR | HR | MR | Mean | RR | HR | MR | Mean |
| pH      | -  | -  | -  | -    | 0.41 | 0.47 | 0.42 | 0.12 | 0.11 | 0.12 | 0.12 | 0.47 | 0.43 | 0.46 | 0.46 |
| LOI     | 6.5 | 6.4 | 10.3 | 9.3  | -    | -    | -    | -    | -    | -    | -    | -    | -    | -    | -    |
| Al      | 75850 | 74854 | 87130 | 84522 | <4  | <4  | <4  | <4  | <4  | <4  | <4  | <6  | <4  | <4  | <4  | <4  |
| Ca      | 5689 | 2180 | 3725 | 4033 | 5219 | 3915 | 4992 | -    | -    | -    | -    | 1099 | 1388 | 749 | 840 | 134 | 139 | 87 | 98 |
| Fe      | 44221 | 34523 | 34773 | 36541 | 70 | 163 | 86  | -    | -    | -    | -    | 238 | 28.6 | 20.0 | 21 | 10.8 | 12.9 | 10.3 | 10.5 |
| K       | 20081 | 19786 | 19680 | 19760 | 35711 | 22842 | - | 33473 | - | 10 | 34 | 10 | 34 | 10 | 34 | 10 | 34 |
| Mg      | 8142 | 5772 | 6460 | 6750 | 2671 | 3013 | 2731 | -    | -    | -    | -    | 311 | 415 | 324 | 325 | 1384 | 1240 | 1290 | 1305 |
| Mn      | 526 | 254 | 304 | 344 | 696 | 848 | 723 | -    | -    | -    | -    | 256 | 252 | 177 | 195 | 22 | 24 | 21 | 21 |
| Na      | 5295 | 2991 | 4587 | 4657 | 346 | 541 | 380 | -    | -    | -    | -    | 201 | 8.6 | 52.5 | 44.7 | 4.2 | 5.5 | 7.6 | 6.9 |
| P       | 865 | 487 | 780 | 785 | 1139 | 1493 | -    | 1200 | - | 1308 | 1104 | 1411 | 1380 | 3545 | 3235 | 3269 | 3319 |
| S       | 651 | 516 | 930 | 861 | 1635 | 2352 | -    | 1760 | - | 690 | 554 | 625 | 634 | 1089 | 1051 | 880 | 926 |
| Ti      | 4854 | 4856 | 4808 | 4819 | 0    | 0    | 0    | -    | -    | -    | -    | 192 | 21.5 | 7.1 | 10.0 | 124 | 151 | 0.5 | 0.69 |
| As      | 22.5 | 13.6 | 12.6 | 14.8 | 2.7 | 3.2 | 2.82 | 0.41 | 0.78 | 0.30 | 0.34 | 0.21 | 0.27 | 0.18 | 0.19 | -    | -    | -    |
| Ba      | 417 | 460 | 394 | 402 | 93 | 125 | 99  | -    | -    | -    | -    | 19.2 | 21.5 | 7.1 | 10.0 | 1.24 | 1.51 | 0.51 | 0.69 |
| Bi      | 0.88 | 0.56 | 0.40 | 0.51 | 0.010 | 0.008 | 0.009 | 0.0058 | 0.0035 | 0.0006 | 0.0017 | <0.0004 | 0.0017 | <0.0004 | <0.0004 | -    | -    | -    |
| Cd      | 0.37 | 0.25 | 0.27 | 0.29 | 0.44 | 0.45 | 0.44 | 0.103 | 0.155 | 0.028 | 0.047 | 0.120 | 0.085 | 0.037 | 0.055 | -    | -    | -    |
| Ce      | 0.90 | 0.83 | 0.81 | 0.83 | 0.123 | 0.202 | 0.137 | 0.0714 | 0.0537 | 0.0230 | 0.0333 | <0.0009 | 0.0058 | <0.0007 | <0.001 | -    | -    | -    |
| Co      | 15.7 | 13.3 | 13.2 | 13.8 | 0.17 | 0.79 | 0.28 | 0.063 | 0.126 | 0.045 | 0.052 | 0.016 | 0.083 | 0.025 | 0.026 | -    | -    | -    |
| Cr      | 69 | 39 | 94 | 86 | 0.97 | 0.71 | 0.92 | 0.38 | 0.39 | 0.17 | 0.22 | <0.1 | <0.1 | <0.1 | <0.24 | -    | -    | -    |
| Cu      | 48 | 27 | 30 | 34 | 3.52 | 3.51 | 3.52 | 2.23 | 2.21 | 1.99 | 2.04 | 3.35 | 3.58 | 3.26 | 3.29 | -    | -    | -    |
| Mo      | 0.98 | 1.07 | 0.94 | 0.95 | 0.52 | 0.71 | 0.55 | 0.10 | 0.06 | 0.17 | 0.16 | 0.64 | 0.69 | 0.41 | 0.47 | -    | -    | -    |
| Ni      | 39.9 | 28.5 | 36.3 | 36.4 | 0.37 | 0.85 | 0.45 | 0.58 | 0.44 | 0.42 | 0.45 | 0.36 | 0.95 | 0.30 | 0.34 | -    | -    | -    |
| Pb      | 50.5 | 29.7 | 28.6 | 33.5 | 0.73 | 0.13 | 0.63 | 0.90 | 0.74 | 0.44 | 0.54 | <0.02 | <0.02 | 0.17 | 0.17 | -    | -    | -    |
| Sb      | 2.01 | 1.58 | 2.06 | 203 | 0.033 | 0.008 | 0.029 | 0.0234 | 0.0095 | 0.0028 | 0.0070 | <0.0006 | <0.0006 | <0.0006 | <0.0007 | -    | -    | -    |
| Sn      | 4.81 | 4.56 | 4.15 | 4.32 | <1.16 | <0.06 | 0.94 | <0.69 | <0.06 | 0.32 | <0.38 | <0.06 | <0.06 | <0.16 | <0.14 | -    | -    | -    |
| U       | 3.74 | 4.53 | 4.45 | 4.30 | 0.0096 | 0.0042 | 0.0087 | 0.0062 | 0.0032 | 0.0025 | 0.0032 | <0.0001 | 0.0006 | <0.0001 | <0.0001 | -    | -    | -    |
| Zn      | 110 | 83 | 90 | 94 | 40.1 | 62.6 | - | 44 | 11.5 | 9.5 | 15.9 | 14.8 | 23.1 | 26.9 | 19.6 | 20.5 | -    | -    | -    |
As concentration in 10 grain samples of rice cultivars is 0.14 mg kg$^{-1}$. The transfer of elements was evaluated and the results are displayed in Table 3. These influences can be explained by the fact that each soil parameter has a different impact on element availability. Thus, the element concentration in the plant reflects the combined effects of all soil parameters as mentioned in literature (Blume et al. 2016). Some effects of soil parameters on the transfer of elements are summarized as follows:

- The negative correlation trends of the transfer of elements Ca, Mn, P, Cd, Co, Cu, and Ni with soil pH-value may be explained by higher plant-available element concentration in soil solution at lower pH-value. In an acidic environment, H$^+$ ions can replace sorbed cations at the surfaces of soil phases and release them into solution. This facilitates the element uptake by the plant.

- Opposite to cations, Mo shows an increased uptake trend towards higher pH-value. Under reducing conditions, Mo is able to form complexes with organic matter, presumably with sulphur groups. Increasing soil pH-values lead to more biological destruction of organic matter, releasing Mo into the soil solution.

- The transfer of Cr and Mo are negatively correlated with soil Fe and Al. Chromium and Mo are less sorbed at low Fe and Al concentrations in soil, facilitating their plant uptake.

- The positive correlations among the transfers of As, Bi, and Sb suggest similar availability trends in the soil and comparable uptake mechanisms by the plant.

- The transfer of Mg, S, As, Bi, Cr, Mo, Ni, Sb, and Zn show negative trends with the soil Fe and Al. Chromium and Mo are less sorbed with soil Fe and Al. The OM content influences positively the transfer of As. The OM may form soluble As organic complexes, facilitating the As transport into the plant. In contrast, increasing OM content leads to decreasing transfer of S, Cr, Cu, and Mo. While Sulphur is a compound of the OM, other elements may be sorbed. Under oxidizing conditions and/or at higher pH-value, organic compounds are degraded and release these elements into solution facilitating their plant uptake.
3.3. Health risk assessment

Potentially harmful elements such as As, Cd, Pb, Co, Cu, Mn, Mo, and Ni were selected to estimate the non-cancer risk by means of Target Hazard Quotients (THQ), for single elements, and chronic cumulative Hazard Index (HI) for all selected elements (USEPA 1989; Nordberg et al. 2015a).

Table 3. Influences of soil parameters and soil element concentrations on transportability of elements to aboveground rice plants from the Red River and Huong River areas, listed in decreasing order of importance

| Element | Soil factors |
|---------|-------------|
| Ca      | -Ca, -pH > Mn > +Al |
| Mg      | -Mg, -Fe > Mn |
| Mn      | -Mn > -pH |
| Na      | -Na, +Fe > +LOI > +Al |
| P       | -P > -pH > Mn |
| S       | -LOI, S > +Al, +Fe |
| As      | -As > +LOI, -Fe, +pH |
| Bi      | -Bi > -Fe |
| Cd      | -pH > -Mn |
| Co      | -pH > -Mn |
| Cr      | +Cr, -Fe > +Al, -LOI |

+ positive correlation trends (mostly linear); - negative correlation trends (mostly exponentially decreasing)

Fe, K, Ba, Li, Sn, and U show no visible correlation with soil factors or their soil concentration.

Table 4. Indexes for health risk assessment for harmful elements including non-cancer risk and cancer risk

| Index | Area | Statistics | As | Pb | Cd | Co | Cu | Mn | Mo | Ni | HI | ILCR |
|-------|------|------------|----|----|----|----|----|----|----|----|----|-----|
| RD1   | Red  | Min-Max    | 0.8-2.6 | <0.2 | 0.02-7.4 | 0.03-0.24 | 5.5-65 | 88-348 | 1.4-9.9 | 0.2-7.8 | - | - |
|       | Mean |            | 1.6   | <0.2 | 0.92  | 0.12  | 26   | 170  | 49   | 2.8  | - | - |
|       |     | Huong      | 1.0-2.6 | <0.2 | 0.33-0.96 | 0.48-1.02 | 21-36 | 163-202 | 3.7-7.0 | 2.9-17 | - | - |
|       | Mean |            | 2.1   | <0.2 | 0.63  | 0.63  | 27   | 181  | 53   | 7.3  | - | - |
|       |     | Mekong     | 0.6-4.3 | 0.02-7.1 | 0.06-0.88 | 0.06-0.88 | 8.4-78 | 101-219 | 0.8-7.8 | 0.2-23 | - | - |
|       | Mean |            | 1.4   | 1.3  | 0.19  | 0.19  | 25   | 158  | 3.2  | 3.1  | - | - |
|       |     | Mean       | 1.5   | 1.0  | 0.42  | 0.20  | 25   | 161  | 3.6  | 3.2  | - | - |
| THQ   | Red  | Min-Max    | 0.1-1.3 | <0.1 | 0.05-0.33 | 0.04-0.74 | 0.03-0.28 | 0.01-0.29 | 1.4-24 | - | - |
|       | Mean |            | 0.8   | <0.1 | 0.26  | 0.08  | 0.13 | 0.85  | 0.12  | 0.14  | 4.7 | - |
|       |     | Huong      | 0.5-1.3 | <0.1 | 0.03-0.96 | 0.32-0.68 | 0.11-0.18 | 0.81-0.91 | 0.09-0.18 | 0.4-0.51 | 3.7-6.1 | - |
|       | Mean |            | 1.04  | <0.1 | 1.86  | 0.42  | 0.14 | 0.91  | 0.13  | 0.37  | 4.9 | - |
|       |     | Mekong     | 0.29-2.1 | 0.1-1.4 | 0.04-0.59 | 0.04-0.39 | 0.5-0.19 | 0.02-0.20 | 0.3-0.11 | 1.6-8.4 | - | - |
|       | Mean |            | 0.70  | 0.87 | 0.81  | 0.13  | 0.12 | 0.79  | 0.08  | 0.15  | 3.7 | - |
|       |     | Mean       | 0.73  | 0.69 | 1.19  | 0.13  | 0.13 | 0.81  | 0.09  | 0.16  | 3.9 | - |
| ILCR  | Red  | Min-Max    | 12.39 | <0.01 | - | - | - | - | - | - | 12-39 |
|       | Mean |            | 24 | <0.01 | - | - | - | - | - | - | 24 |
|       |     | Huong      | 15-39 | <0.01 | - | - | - | - | - | - | 15-39 |
|       | Mean |            | 31 | <0.01 | - | - | - | - | - | - | 31 |
|       |     | Mekong     | 9-64 | 0.01-0.6 | - | - | - | - | - | - | 9-64 |
|       | Mean |            | 21 | 0.1 | - | - | - | - | - | - | 21 |
|       |     | Mean       | 22 | 0.09 | - | - | - | - | - | - | 22 |

RD: Reference Dose of an element represents its maximum permissible level for daily intake per kg human body weight in mg kg⁻¹ b.w. day⁻¹ (Nguyen et al. 2020);

CDI: Chronic Daily Intake of an element from rice consumption in mg kg⁻¹ b.w. day⁻¹;

THQ: Target Hazard Quotients; HI: chronic cumulative Hazard Index for non-cancer risk;

ILCR: Incremental Lifetime Cancer Risk; ILCR: Incremental Cumulative Cancer Risk

3.3.1. Non-cancer risks

Chronic cumulative Hazard Indexes (HI) for the intake of the elements As, Cd, Pb, Co, Cu, Mn, Mo, and Ni from rice consumption were calculated. All samples have HI values ≥ 1.4, surpassing the safe level of 1 as suggested by USEPA (1989). A 39% of the samples show HI values ranging between 1.4 and 3.44% ranges between 3 and 5, and 18% ranges between 5 and 8.4. Rice consumption poses health hazards of concern with HI > 5 in 26% of the Red River samples, in 2 of 4 samples from the Huong River, and 14% of the Mekong River samples. Cadmium, As, Pb, and Mn are the most prominent harmful elements by rice consumption and contribute in 64 – 97% (average 86%) to
In some samples, the THQs of Cd, Pb, As, and Mn are very high, reaching up to 21, 4.7, 2.1, and 1.7 respectively. The elements Ni, Cu, Co, and Mo cause a much lower risk. For lacking data, other sources for harmful element intake such as other food, drinking water or air pollution were not included in this study, but should be also considered to assess the real danger arising from these contaminants.

For arsenic, 3 of 4 samples from the Huong River, 26% of the Red River samples and 14% of the Mekong River samples have THQ_{As} > 1. On the average, As contributes in 22% to the HI value in the three river areas. For cadmium, 39% of the Red River and 29% and Mekong River samples show THQ_{Cd} > 1. Especially, samples HN10 and HN9, collected close to a brick manufactory, have THQ_{Cd} of 21 and 7 respectively. Cadmium contributes in 23% on average to the total hazard index (HI) in the three river areas. All of the Red River and Huong River grain samples have very low Pb concentrations < 0.02 mg kg\(^{-1}\) corresponding to CDI_{Pb} < 0.2 mg kg\(^{-1}\) b.w. day\(^{-1}\) and THQ_{Pb} < 0.1. Lead is responsible for less than 2% of the HI-value in these two river areas. In contrast, the Mekong River grain samples contain at least 10-times more Pb than the samples from the other river areas. Lead contributes in 3 - 69% (average 21%) to the total hazard risk in the Mekong River area. Manganese is usually not considered as a harmful element. In fact, on the average, Mn holds 24% of the HI values. Manganese surpasses THQ = 1 in 10% of the samples, but 99% of the samples have THQ > 0.5.

3.3.2. Cancer risk

The index of Incremental Lifetime Cancer Risk (ILCR) for As and Pb from rice consumption, as well as the Cumulative Cancer Risk (ΣILCR) is calculated and shown in Table 6 and Fig. 5. The ILCR depicts the probability of causing cancer, for example ILCR \(10^{-4}\) indicates that 1 in 10,000 individuals develops cancer. All samples exceed the threshold of acceptable cancer risk which should range from \(10^{-4}\) to \(10^{-6}\) according to USEPA (1989). In the ΣILCR \(10^{-4}\) - \(10^{-3}\), health risk management should take action. The ΣILCR values fluctuate from \(9 \times 10^{-4}\) to \(64 \times 10^{-4}\) (average \(22 \times 10^{-4}\)), revealing a high level of cancer risk. The mean ΣILCR levels are \(21 \times 10^{-4}\) of the Mekong River rice, \(24 \times 10^{-4}\) of the Red River rice, and \(31 \times 10^{-4}\) of the Huong River rice. The slightly greater risk of the Huong River samples might be due to the strongly acidic condition of the soils (Nguyen et al. 2020). Of these two elements, As contributes 96% to the ΣILCR while Pb only holds 4%. Cadmium represents an important cancer risk factor for the Red River and the Huong River rice. However, the cancer risk of Cd is mainly by inhalation while the oral intake may be overlooked.
The system helps to get a relative risk contribution of every harmful substance and allows to compare the risk for different rice samples.

4. Conclusion

Elements are transported within the plant through charge interactions on the cell walls. As a result, concentrations of most cationic elements gradually decrease with an increasing distance from the root in the order: shoot > husk > grain. Exceptions are Cd, Mg, Zn, S, Cu, and Mo, whose concentrations decrease in the order: shoot > grain > husk. In particular, the P concentration decreases in the order grain > shoot > husk. The preferential transfer of S, Mo, and P into the grain is probably due to their anionic character and their electrostatic repulsion at the negative loaded cell walls. The easily transport of Cu, Zn and Ni into the grains may be due to the formation of soluble organic complexes in the sap.

Health risk calculations on basis of the daily intake of As, Cd, Pb, Cu, Mn, Mo, and Ni by rice consumption indicate that, all unpolished rice grains are within unsafe levels of non-cancer risk with a chronic cumulative Hazard Index (HI) ranging between 1.4 and 8.4 (with one sample even exceeding 21). The risk level of HI = 1 should not be exceeded. A 18% of all samples surpass the high-risk level of HI = 5: in Huong River area in 50%, Red River area in 26%, and the Mekong River area in 14%. The elements Cd, As, Mn, and Pb are the main contributors to the HI-value contributing in 64 - 97% of the HI (average 86%). These elements should be included into any health risk study for rice consumption. Further possibilities to lower their uptake by rice grains should be explored.

The cancer risk index (ΣILCR) of As and Pb fluctuates from $9 \times 10^{-4}$ to $64 \times 10^{-4}$ (mean $22 \times 10^{-4}$). It is considerably higher than the acceptable cancer risk threshold between $10^{-6}$ and $10^{-4}$. The mean ΣILCR values are $21 \times 10^{-4}$ of Mekong River grain, $24 \times 10^{-4}$ of Red River grain, and $31 \times 10^{-4}$ of Huong River grain. Arsenic is the most potential carcinogenic risk factor for rice consumption in Vietnam.

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6. References

[1] Abedin, M. J., Feldmann, J, Meharg, A. A. (2002). Uptake kinetics of arsenic species in rice plants. Journal of Plant Physiology, 128, 1120-1128. https://doi.org/10.1104/pp.010733

[2] Bhattacharya, P., Samal, A. C., Majumdar, J., Santra, S. C. (2010). Arsenic contamination in rice, wheat, pulses, and vegetables: A study in an arsenic affected area of West Bengal, India. Water Air Soil Pollution, 213, 3-13. https://doi.org/10.1007/S11270-010-0361-9

[3] Biswas, A., Biswas, S., Santra, S. C. (2014). Arsenic in irrigated water, soil, and rice: perspective of the cropping seasons. Paddy and Water Environment, 12, 407-412. https://doi.org/10.1007/S10333-013-0396-9

[4] Blume, H.P., Brümmer, G. W., Fleige, H., Horn, R., Kandeler, E., Kögel-Knabner, I., et al. (2016). Soil Science (16th edn). Springer, Germany.

[5] FAO (2018). Rice market monitor, Vol XXI No. 1. http://www.fao.org/3/i9243en/i9243EN.pdf. Accessed 16 July 2020.

[6] EFSA (2009). Cadmium in food - Scientific opinion of the Panel on Contaminants in the Food Chain. EFSA Journal, 7:980. https://doi.org/10.2903/j.efsa.2009.980

[7] EFSA (2010). Scientific Opinion on Lead in Food - EFSA Panel on Contaminants in the Food Chain (CONTAM). EFSA Journal, 8:1570. https://doi.org/10.2903/j.efsa.2010.1570

[8] Fakhri, Y., Bjerklund, G., Bandpei, A. M., Chirumbolo, S., Keramati, H., Hosseini, P. R., et al. (2018). Concentrations of arsenic and lead in rice (Oryza sativa L.) in Iran: A systematic review and carcinogenic risk assessment. Food and Chemistry Toxicology, 113, 267-277. https://doi.org/10.1016/j.fct.2018.01.018

[9] Greger, M. (2004). Metal availability, uptake, transport and accumulation in plants. In Prasad MNV (Ed.), Heavy Metal Stress in Plants - From Biomolecules to Ecosystems. Springer, Berlin, pp 1-27.

[10] Ha, C.T.T. (2011). Survey on heavy metals contaminated soils in Thai Nguyen and Hung Yen provinces in Northern Vietnam. Journal of Vietnam Environment, 1, 34-39. https://doi.org/10.13141/jve.vol1.no1.pp34-39

[11] Herawati, N., Suzuki, S., Hayashi, K., Rivai, I. F., Koyama, H. (2000). Cadmium, copper, and zinc levels in rice and soil of Japan, Indonesia, and China by soil type. Bulletin of Environmental Contamination and Toxicology, 64, 33-39. https://doi.org/10.1007/s001289910006

[12] Huong, N.T.L, Ohtsubo, M., Li, L., Higashi, T., Kanayama, M., Nakano, A. (2008). Heavy metal contamination of soil and rice in wastewater-irrigated paddy field in a suburban area of Hanoi, Vietnam. Communications in Soil Science and Plant Analysis, 13, 205-215. https://doi.org/10.11362/jcssjclayscience1960.13.205

[13] Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., Beeregowda, K. N. (2014). Toxicity, mechanism and health effects of some heavy metals. Interdisciplinary
toxicology, 7, 60-72. https://doi.org/10.2478/intox-2014-0009

[14] Khan, N. I., Owens, G., Bruce, D., Naidu, R. (2009). Human arsenic exposure and risk assessment at the landscape level: a review. Environmental Geochemistry and Health, 31, 143-166. https://doi.org/10.1007/S10653-008-9240-3

[15] Kumarathilaka, P., Seneweeru, S., Meharg, A., Bundschuh, J. (2018). Arsenic speciation dynamics in paddy rice soil-water environment: sources, physicochemical, and biological factors - A review. Water Research, 140, 403-414. https://doi.org/10.1016/j.watres.2018.04.034

[16] Kunhikrishnan, A., Go, W. R., Park, J. H., Kim, K. R., Kim, H. S., Kim, K. H., et al. (2015). Heavy metal(loid) levels in paddy soils and brown rice in Korea. Korean Journal of Soil Science and Fertilizer, 48. https://doi.org/10.7745/KJSSF.2015.48.5.515

[17] Kuramata, M., Abe, T., Matsumoto, S., Ishikawa, S. (2011). Arsenic accumulation and speciation in Japanese paddy rice cultivars. Soil Science and Plant Nutrition, 57, 248-258. https://doi.org/10.1080/00380768.2011.565479

[18] Mao C, Song Y, Chen L, Ji J, Li j, Yuan X, et al. (2019) Human health risks of heavy metals in paddy rice based on transfer characteristics of heavy metals from soil to rice. CATENA 175:339-348. https://doi.org/10.1016/j.catena.2018.12.029

[19] Marquez J., Pourret O., Facon, M-P, Weber, S., Bich, T., Hoang, H., et al. (2018). Effect of cadmium, copper and lead on the growth of rice in the coal mining region of Quang Ninh, Cam-Pha (Vietnam). Sustainability, 10. https://doi.org/10.3390/su10061758

[20] McCauley, A., Jones, C., Olson-Rutz, K. (2017). Soil pH and organic matter. Nutrient Management 8. http://landresources.montana.edu/nm/documents/NM8.pdf. Accessed 27 March 2019

[21] Meharg, A. A., Zhao, F. J. (2012). Arsenic & Rice. Springer, Dordrecht, Heidelberg, London, New York.

[22] Meng, J., Zhong, L., Wang, L., Liu, X., Tang, C., Chen, H., et al. (2018). Contrasting effects of alkaline amendments on the bioavailability and uptake of Cd in rice plants in a Cd-contaminated acid paddy soil. Environmental Science and Pollution Research, 25, 8827-8835. https://doi.org/10.1007/S11356-017-1148-y

[23] Nguyen, T. P., Ruppert, H., Sauer, B., Pasold, T. (2020a). Harmful and nutrient elements in paddy soils and their transfer into rice grains (Oryza sativa) along two river systems in northern and central Vietnam. Environmental Geochemistry and Health, 42, 191-207. https://doi.org/10.1007/S10653-019-00333-3

[24] Nguyen, T. P., Ruppert, H., Pasold, T., Sauer, B. (2020b). Paddy soil geochemistry, uptake of trace elements by rice grains (Oryza sativa) and resulting health risks in the Mekong River Delta, Vietnam. Environmental Geochemistry and Health, 42, 2377-2397. https://doi.org/10.1007/S10653-019-00456-7

[25] Nordberg, G. F., Gerhardtsson, L., Mumtaz, M. M., Ruiz, P., Fowler, B. A. (2015b). Interactions and mixtures in metal toxicology. In Nordberg, G. F., Fowler, B. A., Nordberg, M. (ed), Handbook on the Toxicology of Metals (pp. 213-238). Elsevier, UK.

[26] Norton, G. J., Williams, P. N., Adomako, E. E., Price, A. H., Zhu, Y., Zhao, F. J., et al. (2014). Lead in rice: Analysis of baseline lead levels in market and field collected rice grains. Science of the Total Environment, 485-486:428-434. https://doi.org/10.1016/j.scitotenv.2014.03.090

[27] OEHHA - Office of Environmental Health Hazard Assessment, 2009. Technical Support Document for Cancer Potency Factors: Methodologies for derivation, listing of available values, and adjustments to allow for early life stage exposures. https://oehha.ca.gov/media/downloads/crnr/tsdencerpotency.pdf. Accessed 22 June 2020

[28] Phuong NM, Kang Y, Sakurai K, Iwasaki K, Kien CN, Noi NV, et al. (2010) Levels and chemical forms of heavy metals in soils from Red River Delta, Vietnam. Water, Air, & Soil Pollution 207:319-332. https://doi.org/10.1007/s11270-009-0139-0

[29] Rahman, M. A., Hasegawa, H. (2011). High levels of inorganic arsenic in rice in areas where arsenic-contaminated water is used for irrigation and cooking. Sci Total Environ, 409, 4645-4655. https://doi.org/10.1016/j.scitotenv.2011.07.068

[30] Rizwan M, Ali S, Adrees M, Rizvi H, Zia-ur-Rehman M, Hannan F, et al. (2016) Cadmium stress in rice: toxic effects, tolerance mechanisms, and management: a critical review. Environmental Science and Pollution Research 23:17859-17879. https://doi.org/10.1007/s11356-016-6436-4

[31] Seyfferth, A. L., McCurdy, S., Schaefer, M. V., Fendorf, S. (2014). Arsenic concentrations in paddy soil and rice and health implications for major rice-growing regions of Cambodia. Environmental Science & Technology, 48, 4699-4706. https://doi.org/10.1021/es405016t

[32] Shraim, A. M. (2017). Rice is a potential dietary source of not only arsenic but also other toxic elements like lead and chromium. Arabian Journal of Chemistry, 10, S3434-S3443. https://doi.org/10.1016/j.arabjc.2014.02.004

[33] Simmons, R. W., Pongsakul, P., Saiyasitpanich, D., Klinphoklap, S. (2005). Elevated levels of cadmium and zinc in paddy soils and elevated levels of cadmium in rice grain downstream of a zinc mineralized area in Thailand: Implications for public
health. Environmental Geochemistry and Health, 27, 501-511. https://doi.org/10.1007/S10653-005-7857-z

[34] Smith, A. H., Marshall, G., Yuan, Y., Ferreccio, C., Liaw, J., von Ehrenstein, O., et al. (2006). Increased mortality from lung cancer and bronchiectasis in young adults after exposure to arsenic in utero and in early childhood. Environmental Health Perspectives, 114, 1293-1296. https://doi.org/10.1289/ehp.8832

[35] Sriprachote, A., Kanyawongha, P., Ochiai, K., Matoh, T. (2012). Current situation of cadmium-polluted paddy soil, rice and soybean in the Mae Sot District, Tak Province, Thailand. Soil Science and Plant Nutrition, 58, 349-359. https://doi.org/10.1080/00380768.2012.686435

[36] Suriyagoda, L. D. B., Dittert, K., Lambers, H. (2018). Mechanism of arsenic uptake, translocation and plant resistance to accumulate arsenic in rice grains. Agriculture, Ecosystems & Environment, 253, 23-37. https://doi.org/10.1016/j.agee.2017.10.017

[37] USEPA (1989). Risk Assessment Guide for Superfund (RAGS): volume I, Human Health Evaluation Manual-Part A, baseline risk assessment. https://www.epa.gov/sites/production/files/2015-09/documents/rags_a.pdf. Accessed 19 March 2019

[38] Vinh, N. C., Oborn, I., Ha, P. Q., Minh, N. D., Hough, R., L., Khai, N. M., et al. (2012). Potential environment and public health risk due to contamination of heavy metals from industrial waste water in Lam Thao, Phu Tho, Vietnam. American Journal of Environmental Sciences, 8, 71-78.

[39] Wan, Y., Camara, A. Y., Yu, Y., Wang, Q., Guo, T., Zhu, L., et al. (2018). Cadmium dynamics in soil pore water and uptake by rice: Influences of soil-applied selenite with different water managements. Environmental Pollution, 240, 523-533. https://doi.org/10.1016/j.envpol.2018.04.044

[40] Xiao, L., Guan, D., Peart, M. R., Chen, Y., Li, Q., Dai, J. (2017). The influence of bioavailable heavy metals and microbial parameters of soil on the metal accumulation in rice grain. Chemosphere, 185, 868-878. https://doi.org/10.1016/j.chemosphere.2017.07.096

[41] Zarcinas, B. A., Ishak, C. F., McLaughlin, M. J., Cozens, G. (2004a). Heavy metals in soils and crops in Southeast Asia. Environmental Geochemistry and Health, 26, 343-357. https://doi.org/10.1007/S10653-005-4669-0

[42] Zarcinas, B. A., Pongsakul, P., McLaughlin, M. J., Cozens, G. (2004b). Heavy metals in soils and crops in Southeast Asia 2. Thailand. Environmental Geochemistry and Health, 26, 359-371. https://doi.org/10.1007/S10653-005-4670