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Combining magnet-assisted soil washing and soil amendment with zero-valent iron to restore safe rice cultivation in real cadmium-contaminated paddy fields

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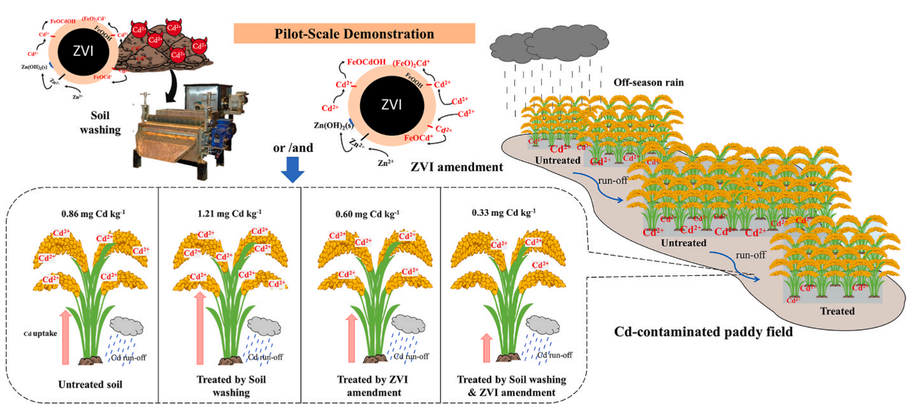
HIGHLIGHTS

- Magnet-assisted soil washing by ZVI removed all bioavailable Cd in a paddy soil.
- Yet, the soil washing alone failed to restore safe rice cultivation.
- Off-season flood re-contaminated the treated soil with Cd from untreated areas.
- Using ZVI amendment after the soil washing help alleviate Cd re-contamination.
- Combining the two techniques provided safe rice production under climate fluctuation.

GRAPHICAL ABSTRACT



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ABSTRACT

Local villagers in Mae Sot District, Tak Province, Thailand are at risk of diseases related to cadmium (Cd) due to excessive consumption of rice contaminated with Cd due to zinc mining. This study verifies the hypothesis that to achieve safe rice cultivation, magnet-assisted soil washing followed by soil amendment using zero-valent iron (ZVI) is required not only for rapid remediation of the existing Cd contamination but also for the prevention of Cd recontamination caused by contaminated run-off from an upgradient contaminated paddy. Accordingly, this study conducted a pilot-scale demonstration of the combined technique to restore a real Cd-contaminated paddy

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Zero-valent iron
Food safety

(41.02 ± 5.47 mg/kg^{-1}) and compared it with remediation using only soil amendment with ZVI or only magnet-assisted soil washing. The Cd concentration in rice grains from the contaminated rice field without treatment was 0.86 ± 0.01 mg/kg^{-1}, and thus higher than the acceptable level of 0.4 mg/kg^{-1}. Even though the use of magnet-assisted soil washing without amendment initially removed all the bioavailable Cd from the soil, it failed to reduce Cd uptake by the rice plants. This failure was caused by heavy off-season rain, which flooded and re-contaminated the experimental fields with Cd-contaminated run-off from an upgradient contaminated field, leading to a Cd concentration in rice grains of 1.21 ± 0.01 mg/kg^{-1}. Similarly, the use of ZVI as a soil amendment without magnet-assisted soil washing could not ensure safe rice cultivation during the off-season flood, as Cd concentration in the rice grains was still 0.60 mg/kg^{-1}. However, magnet-assisted soil washing followed by soil amendment using ZVI successfully removed Cd from soil and sequestered Cd from Cd-contaminated run-off, resulting in protection against Cd re-contamination in soil and the reduction of Cd content in rice grains to 0.33 mg/kg^{-1}, representing a 60% removal efficacy. Also, this combined technique remained positive for rice growth compared to non-treatment.

1. Introduction

The cadmium (Cd) content in soil that results from anthropogenic activities is an important cause of human exposure to Cd via the food chain (Kubier et al., 2019; Zou et al., 2021). This issue is an extensive problem in Asian countries such as Korea (Moon et al., 2021; Shin et al., 2019) and China (Zou et al., 2021). Similarly, in Mae Sot District of Tak Province, Thailand, Cd contamination in agricultural area is caused by human activity: zinc mining at the top of the Mae Tao creek results in leaching of Cd to the creek, which is used for downstream paddy irrigation (Khum-in et al., 2020; Kosolsaksakul et al., 2014). In Mae Sot, the Cd concentration in soil ranges from 0.5 to 284 mg/kg^{-1}, which is 95 times the Cd level in agricultural soil required by the European Economic Commission's standard (1.0–3.0 mg/kg^{-1}) (IWMI, 2005; Suwatvitayakorn et al., 2020). This level of contamination poses health risks to humans, as they eventually consume Cd-contaminated rice grain. Cd affects the kidneys and skeleton of humans, and is classified as a carcinogen because occupational or environmental Cd exposure can cause lung, prostate, kidney, and liver cancer (Cui et al., 2021; Fatima et al., 2019; Zhu and Costa, 2020). The maximum permissible Cd level in polished rice grain is 0.4 mg/kg^{-1}(Codex Alimentarius Commission, 2018).

Soil remediation techniques such as soil amendment can reduce metal availability in metal-contaminated soil (Qiao et al., 2018; Khum-in et al., 2020; Kosolsaksakul et al., 2018). However, the effect may only be temporary because contaminants remain in the soil. Soil washing, on the contrary, may be a more attractive alternative for the remediation of highly metal-contaminated soil that requires prompt and permanent metal removal. Soil washing can be performed *ex situ* or *in situ,* depending on the physical and/or chemical processes used to extract metal contaminants from the soil (Tack and Bardos, 2020). The extracted contaminants are then sent to a secure landfill or further treated using physicochemical or biological processes. The treated soil can then be reused.

Zero-valent iron (ZVI) has a high sorption capacity and magnetic characteristics, making it an ideal candidate for soil washing to remove phyto-accessible copper (Cu) (Feng et al., 2016). Also, an *ex-situ* sediment-washing process using ZVI powder and magnetic recovery has been found to be successful in removing substantial portions of mercury (Hg) (72.6%), zinc (Zn) (42.4%), and copper (Cu) (23.5%) from sandy and organic sediment. The process also reduced sediment toxicity by 80%–99.8% for organic sediment and 99% to >99.98% for sandy sediment (Feng et al., 2018). In the laboratory, magnetic separation can effectively remove up to 78% of total Cd and up to 93% of exchangeable and carbonate Cd fractions from soil, potentially resulting in a reduction of Cd in rice grain of 97%, making it safe for consumption. Moreover, this technique has no unacceptable effects on the germination of rice seeds or the supply of plant nutrients (Phenrat et al., 2019). Nevertheless, no field-scale demonstration of this innovative soil washing technique using ZVI has yet been performed.

Although bench-scale experiments have demonstrated the effectiveness of magnet-assisted soil washing, implementation of this technique in the field presents several challenges. One of the major concerns is the potential for re-contamination of the washed soil by upgradient contamination sources in the rainy season and by off-season rain. For instance, in the case of Cd contamination in Mae Sot District in Tak Province, no treatment of the Cd source in the uphill mine has yet been carried out. Moreover, due to the large area of contaminated paddy fields (2.14 × 10^{7} m^{2}), it may not be feasible to restore all the paddy fields simultaneously. In the event of heavy rain caused by climate change, Cd-contaminated runoff from the upgradient untreated paddy fields or Cd sources in the uphill mine could lead to the re-contamination of already washed paddy fields.

Therefore, this study verifies the hypothesis that to achieve safe rice cultivation, magnet-assisted soil washing followed by soil amendment using ZVI is required not only for rapid restoration of the existing Cd contamination but also for prevention of Cd recontamination caused by contaminated run-off from an upgradient contaminated paddy. Pilot-scale experiments were conducted, utilizing ZVI as a soil amendment and a magnet-assisted soil washing machine (see Fig. 1). As a soil amendment, ZVI was mixed with paddy soil before rice transplantation. ZVI aids in Cd adsorption from the soil and reduces Cd uptake by roots. For soil washing, ZVI was mixed with a paddy-soil slurry *ex situ*. Cd was desorbed from the soil and adsorbed by ZVI. Then, the ZVI which had adsorbed the ZVI was separated from the soil slurry with a magnet-assisted soil washer (see Fig. 1). The washed soil was then returned to the paddy for rice cultivation. The soil washing experiments were the most crucial pilots, followed by soil amendment to evaluate the necessity of using soil amendment after soil washing for real field-scale applications. In addition to analyzing the soil, we quantified the uptake of pollutants, Cd, and essential nutrients such as Fe and Zn by rice grown in soil treated using the different approaches.

2. Materials and methods

2.1. Properties of soil and ZVI

Field testing was performed in a Cd-contaminated paddy area of Phatat Pha Daeng Subdistrict, Mae Sot District, Tak Province, Thailand. The soil was clayey with a slightly alkaline pH of 7.67 and a total organic carbon content of 4.52% (Khum-in et al., 2020). The Cd concentration in the field was 41.02 ± 5.47 mg/kg^{-1}, which was higher than the allowable amount for cropland by both EU (3.0 mg/kg^{-1}) and Thai (37 mg/kg^{-1}) standards. The bioavailable Cd fraction (i.e., the exchangeable and carbonate fractions) in this area was 25.69% (8.85 ± 0.05 mg/kg^{-1}), while the Fe–Mn oxide, organic, and residual fractions were 64.49%, 8.47%, and 1.34% (22.22 ± 0.31 mg/kg^{-1}, 2.92 ± 0.59 mg/kg^{-1}, and 0.46 ± 0.07 mg/kg^{-1}), respectively (Khum-in et al., 2020). Concentrations of Fe and Zn, were 38,223.92 ± 7240.11 mg/kg^{-1} and 1535.62 ± 283.55 mg/kg^{-1}, respectively (Khum-in et al., 2020). The details of the soil sampling method used here, the techniques used to measure total Cd, Fe and Zn in soil, and the Cd sequential extraction protocol have been previously described (Khum-in et al., 2020). The ZVI material used in this study was a by-product of bearing manufacture, and the same protocol as the previous study (Khum-in et al., 2020) was used. The ZVI was cleaned three times using detergent and water, and its physicochemical characteristics, such as particle size, morphology, mineralogy, and surface area, were examined using the same techniques described in the previous study (Khum-in et al., 2020). The ZVI properties are shown in Data S1 in the Supporting Information (SI).

2.2. Magnet-assisted soil washing

A prototype of the magnet-assisted soil washing equipment used in this study is shown in Fig. 2. It consists of two major parts: soil slurry mixing tanks and a magnetic separator (for details, see **Method S1** in **SI**). This machine was patented in 2019 in Thailand (petty patent number 15261). The washing process is shown in **Method S2** in **SI**. Noticeably, wash water from the soil washing process was released to a creek nearby without any treatment because the total Cd concentration was lower than the acceptable level for surface water (<5 μg/L). This is because Cd dissolved from the soil into the wash water was effectively sorbed onto the ZVI, which was magnetically recovered by the magnetic separator of the magnet-assisted soil washing unit (Phenrat et al., 2019).

2.3. Field experiment

The field experiment consisted of two main steps. First, soil amendment, soil washing, or both were applied to treat the Cd-contaminated paddy soil (soil between the surface and a depth of 15 cm was sampled). Secondly, rice plantlets were cultivated and te Cd and

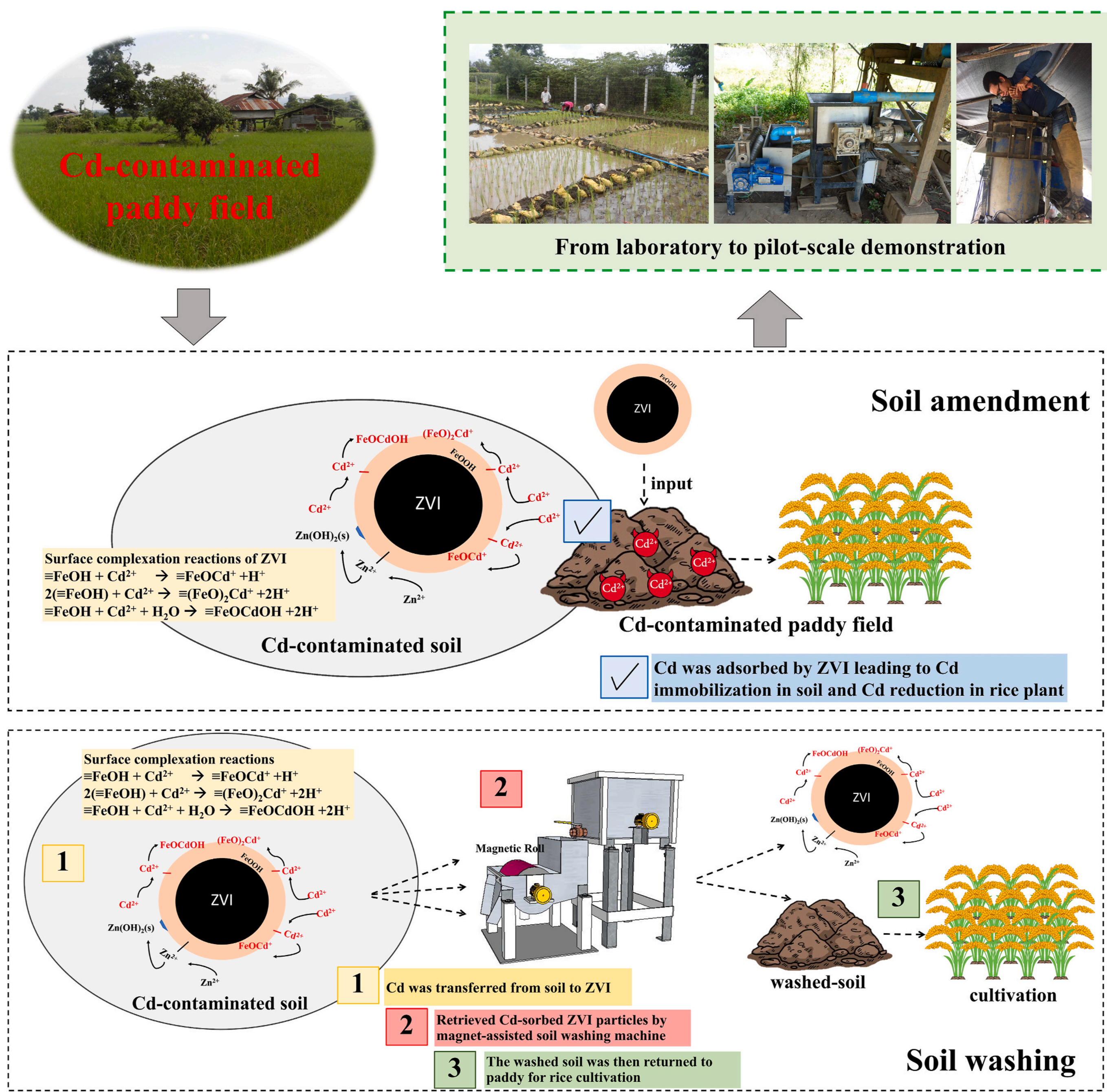

Fig. 1. Zerovalent iron for stabilizing cadmium via soil amendment and for removal from soil via magnet-assisted soil washing.

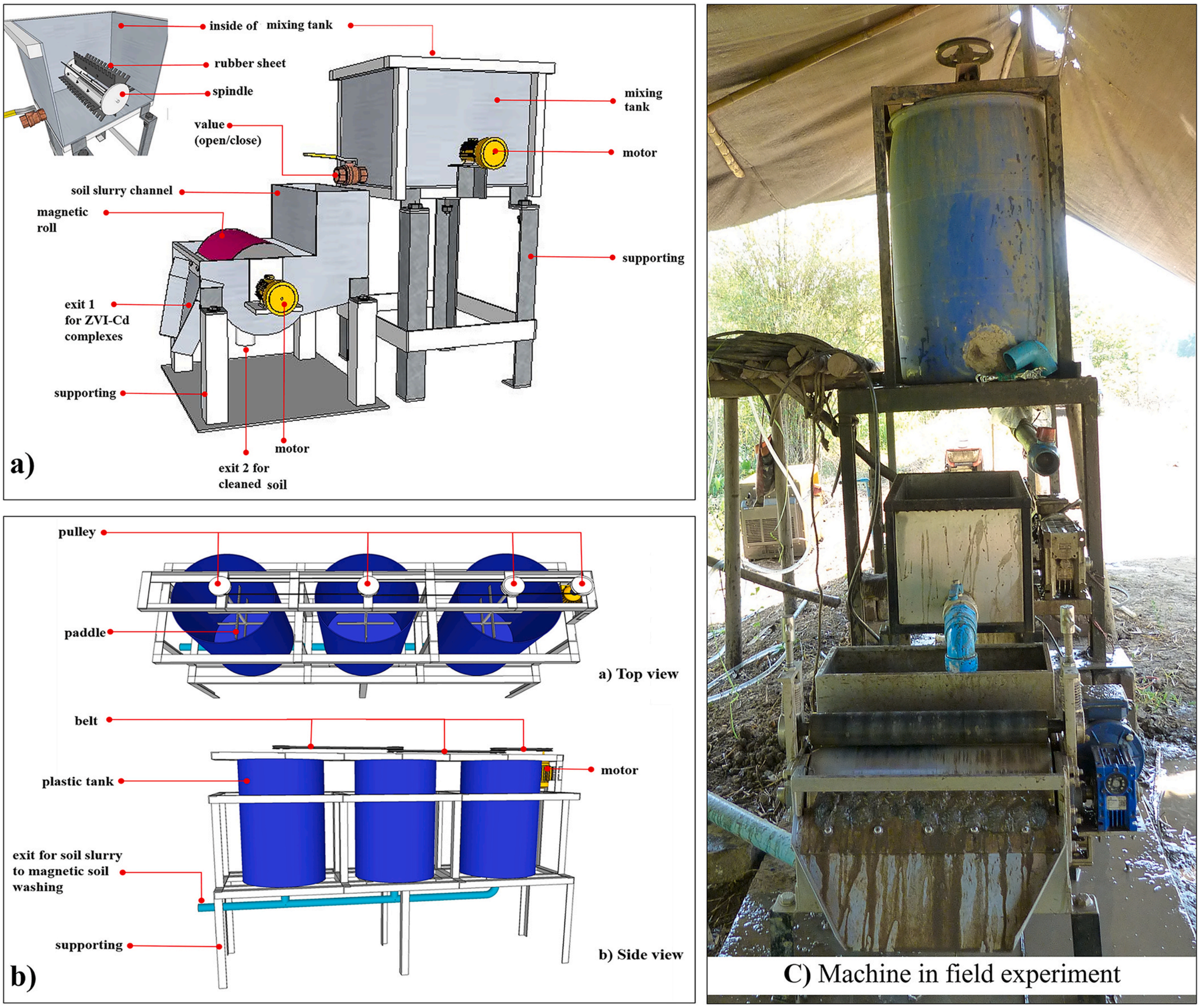

Fig. 2. a) Magnet-assisted soil washing and b) soil slurry mixing tank prototype in c) field experiments.

nutrient contents of soil and parts of the rice plants were quantified from samples collected from treated and untreated pilot rice fields at various phases of rice growth. A reduction of Cd in rice grain to below the safe threshold for polished rice served as the primary indicator of remediation success. Each pilot experiment was performed in duplicate plots, each of which measured 2 m × 4 m (see Figure S1).

This field experiment was conducted from January 2017 to May 2017, spanning from winter to the beginning of the summer season. At each pilot field boundary, a 30 cm high soil barrier was built to retain water and prevent unintentional mixing of treatments (Figure S1a) (Khum-in et al., 2020). The pilot experiment remained unflooded for the majority of the time due to seasonal conditions, in line with actual local practice during this period of time. The pilot fields were irrigated by Mae Tao Creek. Magnet-assisted soil washing was applied to soil slurry (at a soil-to-water ratio of 1:2 and a ZVI concentration of 10 g/kg^{-1}) for 6 h. Various conditions and combinations of soil washing and soil amendments for field experiments were investigated (Table 1): i) ZVI application as a soil amendment, ii) magnet-assisted soil washing alone and iii) ZVI application as an amendment to the magnet-assisted washed soil. These three pilot studies were compared to determine whether soil amendment is required following soil washing when upgradient soil, irrigation water, and run-off remain polluted with Cd. An untreated field without soil washing or amendment was also used in this study as a control experiment (CE).

Table 1
Amendment dose in each treatment.

Treatment	Soil treatments
Control (CE)	Untreated soil
ZVI 0.5%	0.5% ZVI (5.3 t acre^{-1}) for amendment
Washing 1%	1% ZVI (10.58 t acre^{-1}) for washing
Washing + ZVI 0.5%	1% ZVI (10.58 t acre^{-1}) for washing followed by 0.5% ZVI (5.3 t acre^{-1}) for soil amendment after washing

*ZVI dose developed from laboratory experiment (Phenrat et al., 2019).

To prepare for the pilot study, 187 rice plantlets (*Oryza sativa* L.; cv. Khao Dawk Mali 105) were seeded in uninfluenced areas for 4 weeks before being transplanted into each pilot field. The Cd concentrations in transferred plantlets in the field started at 0.0484–0.1248 mg kg^{-1} in the root, 0.0486–0.1244 mg kg^{-1} in the stem, and 0.0484–0.1245 mg kg^{-1} in the leaf. Every 21 days until harvest, soil samples were taken at a depth of 0–15 cm. Similarly, rice samples were taken at the seedling stage (first 4 weeks), 60 days later (when the plants were in a heading state), and at the time of harvest (when the plants were in a mature state). Soil and rice plant samples were kept at 4 °C and delivered to the laboratory for preparation and chemical analysis, which will be discussed in the next chapter (Khum-in et al., 2020). Furthermore, we investigated the impact of soil amendment and washing on crop growth and stress by measuring rice plant height at each stage. More importantly, as a part of our community citizen science program, we trained community researchers to perform soil washing, soil amendment, and rice and soil sampling (Fritz et al., 2019; Khum-in et al., 2020). The community researchers then collected samples and shipped them to the laboratory for analysis.

2.4. Chemical analysis

The soil samples collected during the pilot experiments were oven-dried at 105 °C for 24 h prior to being ground by mortar and sieved through a 2 mm sieve to remove gravel. Cd, Zn and Fe concentrations in the soil samples were determined using atomic absorption spectroscopy (AAS) after microwave-assisted acid digestion by 65% nitric acid, as described in the previous paper (EPA method 3051a) (Khum-in et al., 2020). Rice samples were divided into root, stem, leaf, husk, and grain. The rice stem and roots were washed thoroughly in tap water and rinsed with deionized water to remove soil. All parts of the rice plants were dried at 70 °C for 72 h and ground to a fine powder, which was subsequently digested using microwave-assisted acid digestion with 2 mL of 30% H_2O_2 and 65% nitric acid according to EPA method 3051a(Khum-in et al., 2020). The digested samples were then analyzed to determine Cd, Zn, Fe concentrations using AAS.

2.5. Calculation of Cd fate factors

To understand the impact of soil washing, soil amendment and their combined use on Cd distribution and accumulation in different parts of rice plants, Cd fate factors including the enrichment factor, accumulation factor, and translocation factor were calculated. First, the accumulation of Cd, Zn, and Fe in rice roots, stems, leaves, or grain at different growth stages was reported as the enrichment factor (*EF*), using the initial metal level in the rice sample at the seedling stage for standardization (Eq. (1)) (Chattaong and Jutamas, 2020; Khum-in et al., 2020):

$$EF^{i} = C \text{ in } i \text{ at a stage of interest} / C \text{ in } i \text{ at seedling stage} \tag{1}$$

where i identifies a specific rice tissue, C is the Cd, Zn, or Fe concentration, and the *EF* values for each growth state of interest were determined and compared to the seedling state.

To assess the relative translocation and accumulation of Cd, Zn, and Fe from contaminated soil to different parts of rice plants at the harvesting stage, the accumulation factor (*AF*) and translocation factor (*TF*) were also evaluated. These factors were calculated based on Eqs. (2) and (3) (Chattaong and Jutamas, 2020; Khum-in et al., 2020):

$$AF_{tissue/soil} = C_{tissue} / C_{soil} \tag{2}$$

$$TF_{tissue1/tissue2} = C_{tissue1} / C_{tissue2} \tag{3}$$

where C_{tissue} is the concentration of Cd, Zn, or Fe in a rice tissue (grain, stem, or root), and C_{soil} is the concentration of Cd, Zn, or Fe in the corresponding soil. If the assessed plant tissue is the leaf, the concentration of Cd, Zn or Fe in the lower part of the rice plant (i.e., the stem) is used as the denominator. In contrast, if the assessed plant tissue is the root, the concentration of Cd, Zn or Fe in soil is used as the denominator.

2.6. Statistical analysis

To assess the impact of soil washing, soil amendment and their combined use on Cd concentration in rice grain and Cd fate factors, Student's t-test was performed using SPSS Student Version 16.0 (SPSS Inc. , Chicago). The Cd concentrations in rice and Cd fate factors in rice after different soil treatments were compared with the control (untreated) sample. The least significant difference (LSD) was used for the comparison of means. The level of significance used for the *t*-test and comparison of means was $p < 0.05$.

3. Results and discussion

3.1. Accumulation of Cd, Fe and Zn in the control experiment

Concentrations of Cd in the control experiment (CE) soil were generally steady with slight variations during the initial 84 days (31.33 ± 1.56 to 38.92 ± 1.99 mg/kg^{-1}). Nevertheless, Cd unexpectedly peaked at 50.62 ± 3.67 mg/kg^{-1} during harvest time (see Figure S4); this was the result of off-season heavy rain that produced run-off and caused flooding in the pilot fields after the 90th day. Obviously, after the off-season flooding, the total Cd in the soil increased by 43%, confirming the addition of Cd from the flood to the field. This increase of Cd in the soil had an important effect on Cd in rice, which will be discussed later in the paper. Meanwhile, Fe in the soil slightly increased from 40,608 ± 1060 mg/kg^{-1} to 41,494 ± 803 mg/kg^{-1} after 21 days, and gradually declined to 32,886.47 ± 1725.99 mg/kg^{-1} by the end of cultivation. Finally, the initial concentration of Zn in soil was 1712 ± 144.25 mg/kg^{-1}, but by 63 days, this Zn concentration had reached a high of 3111.75 ± 1099.35 mg/kg^{-1} and then declined to 1976.48 ± 131.27 mg/kg^{-1} during harvest (see Figure S5). The dynamics of Fe and Zn concentrations in soil toward the end of the cultivation were presumably also governed by the run-off and flooding caused by the off-season heavy rain after the 90th day. This hypothesis is supported by a recent study (Yang et al., 2019) revealing that water incubation of soil (similar to run-off and flooding in this study) changed soil Eh and pH, causing reductive dissolution of crystalline iron oxides and formation of new amorphous iron oxides as well as precipitation of metal sulfide, all of which caused changes in metal speciation which either released typical heavy metals (Cu, Zn, Cd and Pb) to water or immobilized waterborne metals in the soil.

The accumulation of Cd in the CE rice plants during the four stages of rice growth (transplanting, tillering, heading, and mature stages) for each part of the plant is shown as *EF* in Fig. 3a. Notably, the Cd content in each rice tissue at the transplant stage was fixed as the initial value. Therefore, any subsequent increase of Cd accumulation was caused by Cd uptake from the soil to the rice. At the tillering, heading and mature stages, respectively, the accumulation of Cd in the CE rice plants was in the order of root (EF^{root} = 90.24 ± 0.00, 91.17 ± 1.48 and 190.61 ± 8.00) > stem (EF^{stem} = 26.28 ± 0.00, 21.34 ± 0.904 and 24.35 ± 0.812) > leaf (EF^{leaf} = 11.25 ± 0.00, 14.67 ± 0.03 and 12.28 ± 0.062).

However, presumably due to the increase of Cd in the soil due to the off-season flood, the Cd concentrations in the rice grain were 0.86 ± 0.01 mg/kg^{-1}, which is higher than the acceptable level set by the Codex Alimentarius Commission (2018) (Fig. 4a). The amount of Cd translated (*TF*) from soil to root, root to stem, stem to husk, and stem to grain were 0.47 ± 0.014, 0.13 ± 0.001, 0.32 ± 0.0008, and 0.28 ± 0.012, respectively (Fig. 4b). Zn and Fe accumulations in different parts of rice plants are presented as *EF* values in Fig. 3b and c. At the tillering, heading, and mature stages, respectively, the highest Zn accumulation was found in the roots (EF^{root} = 4.80 ± 0.00, 5.60 ± 0.11 and 5.56 ± 0.142), followed by the stem (EF^{stem} = 3.70 ± 0.00, 2.67 ± 0.06 and 2.09 ± 0.08) and the leaves (EF^{leaf} = 1.34 ± 0.00, 1.34 ± 0.00 and 0.95 ± 0.01). However, Fe accumulation exhibited a different pattern. Fe accumulation was highest in the leaves and stem at the tillering stage (EF^{leaf} = 0.76 ± 0.00 and EF^{stem} = 0.76 ± 0.00, EF^{root} = 0.35 ± 0.00), followed by the roots at the heading stage (EF^{root} = 0.52 ± 0.02, EF^{leaf} = 0.35 ± 0.01, EF^{stem} = 0.176 ± 0.012) and the leaves in the mature stage (EF^{leaf} = 0.45 ± 0.02, EF^{root} = 0.33 ± 0.02, EF^{stem} = 0.123 ± 0.04). Comparatively, Cd accumulated at a higher rate in the rice plants during cultivation than Zn and Fe.

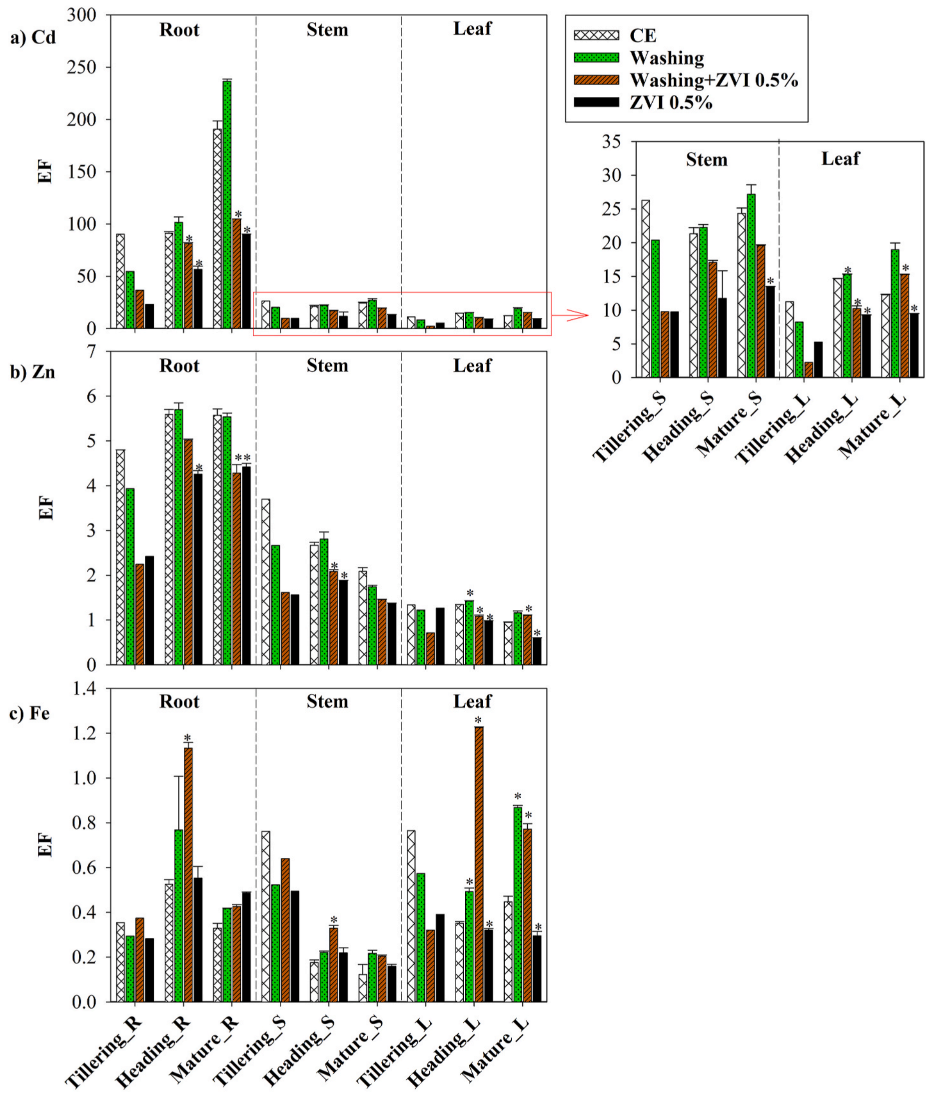

Fig. 3. The *EF* change of a) Cd b) Zn and c) Fe in rice plants during cultivation under different treatments. Statistical significance (p value < 0.05) for each treatment vs. CE, or between conditions, is indicated by an asterisk (*).

In addition, Zn and Fe accumulation factors at harvest time were highest in the roots ($AF_{root/soil} = 0.20 \pm 0.008$) followed by the stem ($AF_{stem/soil} = 0.07 \pm 0.007$) and the grains ($AF_{grain/soil} = 0.037 \pm 0.003$) for Zn, and in the roots ($AF_{root/soil} = 0.11 \pm 0.001$) followed by the stem ($AF_{stem/soil} = 0.01 \pm 0.004$) and the grains ($AF_{grain/soil} = 0.01 \pm 0.001$) for Fe. The rice roots accumulated more Cd ($AF_{root/soil=}0.47$) than Zn (0.20) and Fe (0.11). The rice stem and grain accumulated metals in the order of Zn ($AF_{stem/soil} = 0.07$ and $AF_{grain/soil} = 0.037$) followed by Cd (0.06 and 0.02) and Fe (0.01 and 0.01), respectively (Figure S6).

For Zn and Fe translocation behaviors, the *TF*s of Zn were 0.20 ± 0.008 ($TF_{root/soil}$), 0.36 ± 0.023 ($TF_{stem/root}$) and 0.52 ± 0.01 ($TF_{grain/stem}$). In contrast, the translocation behaviors of Fe were 0.114 ± 0.001 ($TF_{root/soil}$), 0.08 ± 0.03 ($TF_{stem/root}$) and 1.09 ± 0.37 ($TF_{grain/stem}$) (Fig. 4b). Comparatively, the translocation relations from stem to husk and grain were the highest for Fe, followed by Zn and Cd; these results are similar to those of a recent study (Khum-in et al., 2020).

Zn and Fe accumulations in rice grains were found to be 73.35 ± 0.69 and 294.05 ± 5.76 mg/kg^{-1}, respectively (see Fig. 4a). Notably, Zn and Fe concentrations in brown rice grains in this field experiment were higher than the average Zn and Fe levels in brown rice grains in Thailand, which are 25.30 ± 5.24 and 8.62 ± 2.82 mg/kg^{-1}, respectively. However, the Zn and Fe concentrations in the brown rice grains in this study are similar to those found by previous studies conducted in the same districts (54.57 ± 3.13 mg/kg^{-1} for Zn and 211.42 ± 146.01 and 1209.72 ± 195.55 mg/kg^{-1} for Fe) (Khum-in et al., 2020; Thongsri et al., 2010). This demonstrates that the local geochemistry of the paddy soil causes higher Zn and Fe contents in rice.

3.2. Accumulation of Cd in samples using magnet-assisted soil washing and soil amendment

Changes in Cd level following magnet-assisted soil washing treatments (washing only, and washing plus amendment with ZVI 0.5%, respectively) are illustrated in Fig. 5a. These treatments will be compared with treatment using ZVI (0.5%) amendment without soil washing. Immediately after the washing process, magnet-assisted soil washing reduced the concentration of Cd from 42.97 ± 0.44 mg/kg^{-1} to 34.33 ± 1.78 mg/kg^{-1} (i.e., a removal efficacy of 21% of the total Cd). Notably, while a recent laboratory experiment was able to remove 78% of the total Cd from the soil (Phenrat et al., 2019), this study could remove only around 21% of the total Cd; this is presumably due to the use of different chemical fractions of the soil in the two studies. In a recent laboratory experiment, the sum of exchangeable and carbonate fractions of the untreated soil was 50.15% (Phenrat et al., 2019), whereas the sum of the two fractions of the untreated soil in this study was 25.69%. Thus, the Cd fraction removed by magnet-assisted soil

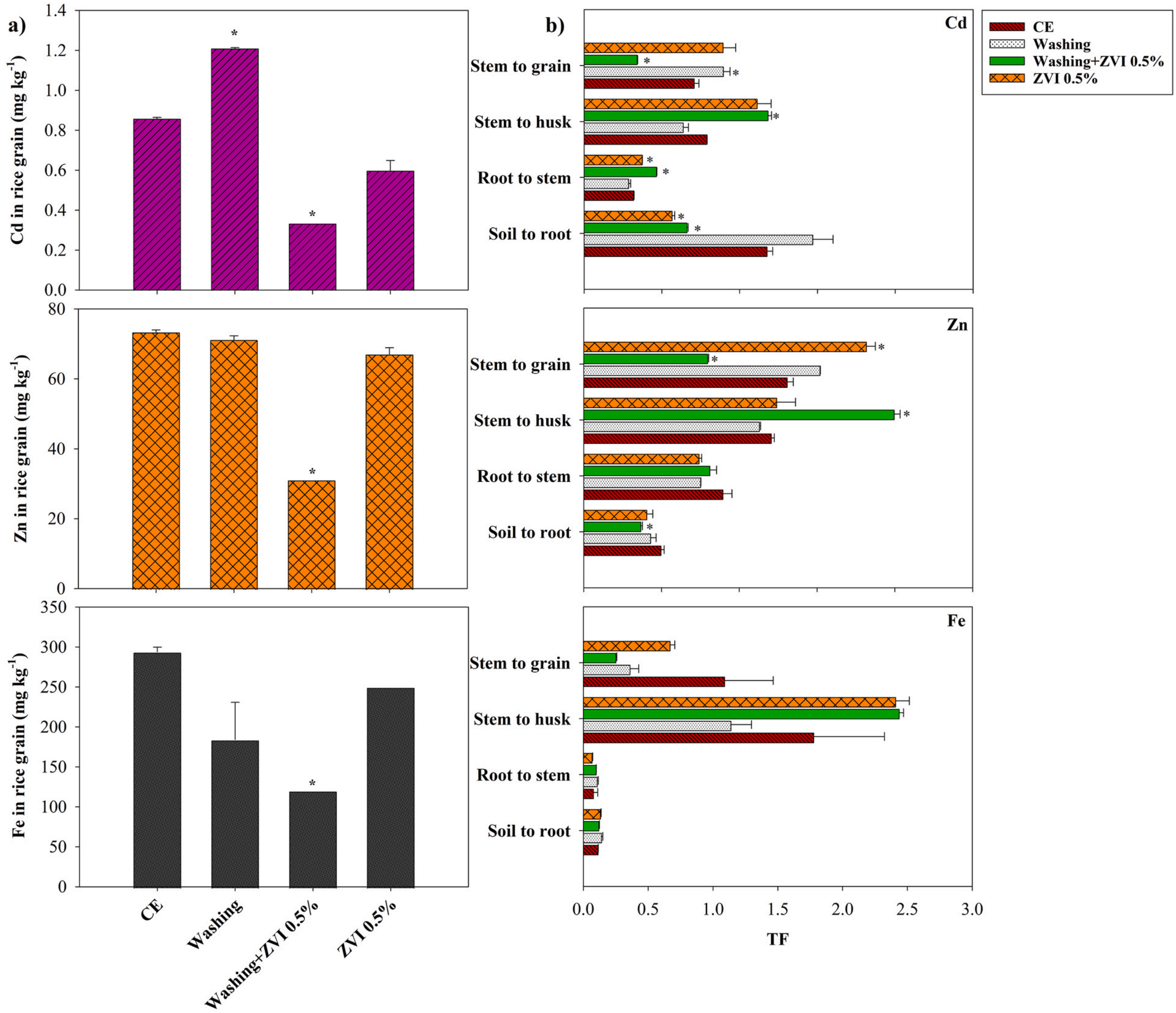

Fig. 4. Results of the experiments including a) cadmium level and b) *TF* in rice grain at harvest time in soil. Statistical significance (p value < 0.05) for each treatment vs. CE, or between conditions, is indicated by an asterisk (*).

washing using ZVI in this pilot experiment was 1.36 times the two mobile fractions, which is similar to the Cd fraction removed by magnetic-assisted soil washing in laboratory experiments in a previous study (1.55 times the two mobile fractions) (Phenrat et al., 2019).

Similar to the CE experiment, during the cultivation period Cd level varied due to the flooding events. Initially, in the soil-washing experiment, Cd levels remained relatively stable, increasing slightly from 34.33 ± 1.78 mg/kg^{-1} to 37.45 ± 0.94 mg/kg^{-1} after 21 days, and decreasing to 35.71 ± 0.74 mg/kg^{-1} after 84 days. Similarly, in the soil washing and amendment experiment, Cd levels in the soil remained reasonably steady, increasing from 32.40 ± 2.18 to 35.52 ± 5.92 mg/kg^{-1} after 21 days and reducing to 33.63 ± 0.57 mg/kg^{-1} after 84 days. However, in the ZVI amendment experiment without soil washing, Cd in the soil increased from 18.90 ± 0.17 mg/kg^{-1} to 27.39 ± 0.22 mg/kg^{-1} after 21 days, and further increased to 32.21 ± 3.02 mg/kg^{-1} after 84 days. Nonetheless, at the mature stage (Fig. 5a) the off-season heavy rain that created run-off and prompted flooding in the pilot fields after the 90th day caused the Cd levels in the soil from the two soil-washing treatments to rise to 50.36 ± 4.05 mg/kg^{-1} (washing) and 49.41 ± 0.52 mg/kg^{-1} (washing + ZVI 0.5%), which represents increases of 41% and 47%, respectively, following the flooding. Unsurprisingly, the ZVI amendment was also affected by the heavy rain, resulting in an elevated Cd concentration in the soil (49.43 ± 0.99 mg/kg^{-1}). In summary, off-season heavy rain, contaminated run-off, and contaminated flood floods had important effects on Cd accumulation in both soil and rice in all pilot testing conditions.

Cd accumulation in rice tissues during the heading and mature stages (*EF*) for all experiments is represented in Fig. 3. At the heading stage, the *EF* of Cd in the soil washing (EF^{root} = 101.61 ± 5.20, EF^{stem} = 22.29 ± 0.41, and EF^{leaf} = 15.36 ± 0.01), washing and amendment (EF^{root} = 81.21 ± 1.10, EF^{stem} = 17.07 ± 0.31, and EF^{leaf} = 10.25 ± 0.40), and ZVI amendment (EF^{root} = 56.63 ± 3.01, EF^{stem} = 11.76 ± 4.09, and EF^{leaf} = 9.27 ± 0.023) samples were mostly lower than those of the CE (EF^{root} = 91.17 ± 1.48, EF^{stem} = 21.34 ± 0.904, and EF^{leaf} = 14.66 ± 0.03) samples, except for the *EF* values found in the soil washing experiment. This finding implies that soil washing removed the phytoavailable Cd fraction and decreased the accumulation of Cd in the rice sections; this is similar to the findings of Phenrat et al. (2019) and Makino et al. (2019). In addition, the combination of soil washing and soil amendment enhanced the Cd reduction from soil to rice, especially at the tillering stage (as shown in Fig. 3a). This was presumably a result of Cd removal by washing (Phenrat et al., 2019) and ZVI immobilizing processes (Guo et al., 2021). However, due to excessive rain following the 90th day causing contaminated run-off, when the *EF* were calculated at the mature state, the *EF values* of the rice plants in the soil washing experiment (EF^{root} = 236.55 ± 1.98, EF^{stem} = 27.17 ± 1.42, and EF^{leaf} = 18.96 ± 1.00) were higher than those of the rice plants in the CE (EF^{root} = 190.61 ± 7.99, EF^{stem} = 24.35 ± 0.90, and EF^{leaf} = 12.28 ± 0.06).

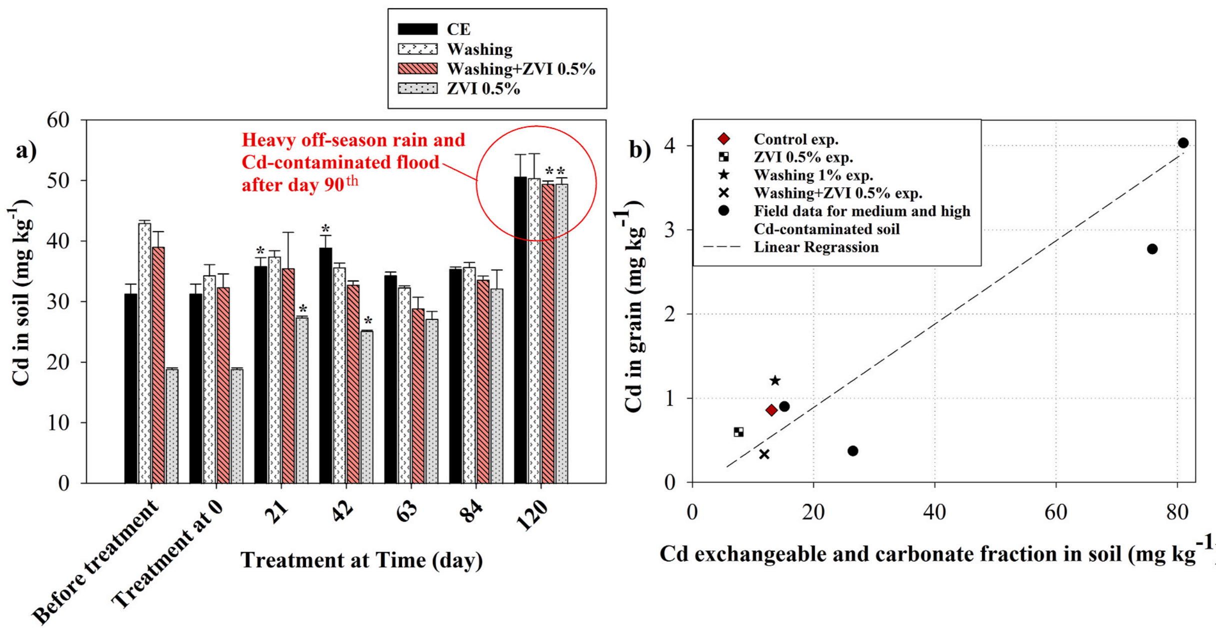

Fig. 5. Results of the experiments including a) change in cadmium concentration in soil and b) hypothetical cadmium concentration in treatment with/without soil amendment and soil washing. Statistical significance (p value < 0.05) for each treatment vs. CE, or between conditions, is indicated by an asterisk (*).

Meanwhile, the *EF* values of rice plants in the soil washing with ZVI amendment experiment ($EF^{root} = 104.80 \pm 0.01$, $EF^{stem} = 19.67 \pm 0.11$, and $EF^{leaf} = 15.30 \pm 0.04$) and the amendment-only experiment ($EF^{root} = 89.64 \pm 0.75$, $EF^{stem} = 13.44 \pm 0.08$, and $EF^{leaf} = 9.42 \pm 0.10$) were lower than those of the CE rice plants, except for the *EF* values for rice leaves in the soil washing with ZVI amendment experiment. This indicates that ZVI amendment was necessary after soil washing or without soil washing to adsorb immobile Cd, which may be present in contaminated run-off following excessive heavy rain. This reveals that soil washing alone is insufficiently robust to recover paddy soil if upgradient soil remains polluted with an available Cd fraction. The preferred solution is to use soil amendment after cleaning the soil.

At the harvesting stage, the Cd concentration in rice grains produced by plants in the soil-washing experiment was 1.21 ± 0.01 mg/kg^{-1}, whereas the Cd concentration in rice grains from plants in the soil washing and amendment experiment was reduced to 0.33 ± 0.00 mg/kg^{-1}. Both these concentrations should be compared to that found in the control experiment (0.86 ± 0.01 mg/kg^{-1}; Fig. 4a). The uptake of Cd in rice grains from plants in soil-washing experiment was 141.69% of the CE, whereas the soil washing and amendment treatment reduced the accumulation of Cd to 39.82% of the CE (100%) (see Table S2). This is presumably due to available Cd being mobilized by polluted run-off from the upgradient soil to the experimental fields. Nonetheless, after soil washing and amendment, the Cd level in rice grains was lower than the permitted threshold. It is worth noting that applying only ZVI (0.5%) as a soil amendment led to rice grains with a Cd concentration of 0.60 ± 0.05 mg/kg^{-1}. This suggests that applying magnet-assisted soil washing before adding ZVI (0.5%) as an amendment further reduces Cd accumulation in rice grain by 45%. The efficacy and necessity of using this combined technique rather than using soil amendment by ZVI alone is summarized in Table 2 by comparing the results of this study with those of other recently published articles. Noticeably, the four recent studies using ZVI for soil amendment alone in Table 2 cannot provide safe Cd level in rice (<0.4 mg kg^{-1}).

These findings are also supported by an analysis of the relationship between the combination of exchangeable and carbonate fractions of Cd in the soil and the Cd concentration in rice grain from the same contaminated area (Kosolsaksakul et al., 2014). The sum of exchangeable and carbonate fractions of Cd in the soil was 8.37 mg/kg^{-1} immediately after soil washing. As a result, assuming no additional Cd contamination from Cd-contaminated run-off had entered the treated paddy, the concentration in the rice grain could potentially have been 0.31 mg/kg^{-1} (Fig. 5b). However, Cd-contaminated run-off swamped the area, resulting in re-pollution of the soil. This raised the sum of exchangeable and carbonate fractions of Cd in the soil-washed experiment to 13.66 mg/kg^{-1}. This should promote a Cd concentration in the rice grain of 0.57 mg/kg^{-1}, which partially explains the elevated Cd content measured in rice grain (1.21 ± 0.01 mg kg^{-1}). This implies that Cd-contaminated run-off raised the concentration of Cd in the soil, which was then taken up by the rice plants.

While treatment by soil washing combined with ZVI amendment was also impacted by the Cd-contaminated run-off, the sum of exchangeable and carbonate fractions of Cd in the soil only slightly increased to 11.87 mg/kg^{-1} because the ZVI immobilized the more mobile Cd. This should promote a Cd concentration in rice grain of 0.48 mg kg^{-1}, which is higher than the measured content (0.33 ± 0.00 mg/kg^{-1}; Fig. 5b) and similar to the predicted concentration (0.31 mg/kg^{-1}). This shows that applying a low dose of ZVI (0.5%) as a soil amendment following magnet-assisted washing supported the sorption of Cd from Cd-contaminated run-off and reduced Cd mobilization in the rice, regardless of the finding that the amendment did not help to reduce Cd in the soil.

The results of the study were also examined using *TF* values, which are shown in Fig. 4b. The experiment involved soil-washing, and the results show that the Cd content transferred to the rice tissue after soil washing appeared to be in the order of root ($TF_{root/soil} = 0.588$) > grain ($TF_{grain/stem} = 0.419$) > stem ($TF_{stem/root} = 0.114$). Similarly, the values of soil washing and amendment were in the order of root ($TF_{root/soil} = 0.265$) > stem ($TF_{stem/root} = 0.186$) > grain ($TF_{grain/stem} = 0.155$). For the ZVI amendment experiment, the values were in the order of grain ($TF_{grain/stem} = 0.435$) > root ($TF_{root/soil} = 0.226$) > stem ($TF_{stem/root} = 0.149$). These findings help to explain the Cd content and its uptake by the rice grain.

The *TF* values for the soil washing experiment were similar to those for the CE, which was influenced by heavy rain and followed the order of root (i.e., root ($TF_{root/soil} = 0.47$) > grain ($TF_{grain/stem} = 0.42$) > stem ($TF_{stem/root} = 0.13$). Therefore, it can be concluded that using ZVI amendment, with or without washing, can reduce Cd translocation from

Table 2
Cd removal from soil and rice via magnet-assisted soil washing and/or soil amendment using ZVI in this study in comparison to recently published articles.

Techniques	Experiment type	ZVI Dose (%w/w)	Cd in soil (mg kg^{-1})		Removal in soil (%)	Cd in rice (mg kg^{-1})		Removal in rice (%)	Reference
			Untreated	Treated		Untreated	Treated		
Soil washing	Field	1%	42.98 (total Cd)	34.33 (total Cd) (after washing)/50.36 (after off-season rain and flood)	20% (after washing)/-17% (after off-season rain and flood)	0.86	1.21	−40.7%	This study
	Pot	10% (MZVI)	211.62 (total Cd), 92.65 (Exchangeable Cd)	39.16, (total Cd),2.34 (Exchangeable Cd)	81% (total Cd), 97% (F1&F2)	No rice cultivation in treated soil			Phenrat et al. (2019)
	Pot	10% (NZVI)	211.62 (total Cd), 92.65 (Exchangeable Cd)	44.67, (total Cd),4.75 (Exchangeable Cd)	78% (total Cd), 95% (F1&F2)				Phenrat et al. (2019)
Soil amendment	Field	0.5%	50.62 (total Cd), 13.08 (F1&F2)	49.43 (total Cd), 7.65 (F1&F2)	2.35 (total Cd), 41% (F1&F2)	0.86	0.6	30.2%	This study
	Field	5%	30.12 (total Cd), 7.67 (F1&F2)	34.82 (total Cd), 5.74 (F1&F2)	−15.6% (total Cd), 25% (F1&F2)	0.84	0.58	30.95%	Khum-in et al. (2020)
	Pot	0.05%	2.7 (total Cd)	–	–	2.0	1.9	5%	Qiao et al. (2018)
	Pot	0.05%	2.0 (total Cd)	–	–	0.66	0.52	21.21%	Qiao et al. (2019)
Soil washing &amendment	Field	1% (washing), 0.5% (amendment)	39.05 (total Cd),	32.40 (total Cd) (after washing)/49.41 (total Cd) (after off-season rain and flood)	17% (after washing)/−26% (total Cd) (after off-season rain and flood)	0.86	0.33	61.63%	This study

the soil to the roots of rice plants. This indicates that ZVI-based amendment immobilizes Cd through co-precipitation and the formation of iron oxyhydroxide/oxide structures in the soil, as previously reported (Qiao et al., 2018; Khum-in et al., 2020; Phenrat et al., 2019).

The results of the sequential extraction experiment (Figure S7) support the conclusion that ZVI amendment, especially at 0.5%, transforms bioavailable Cd to the Fe–Mn oxide fraction, leading to a decline in Cd uptake by roots.

3.3. Accumulation of Zn and Fe in soil and rice after magnet-assisted soil washing and soil amendment

The study compared Zn and Fe accumulation in the soil during cultivation after magnet-assisted soil washing treatments with and without ZVI (0.5%) amendment (see Figure S5). The dynamics of Zn in magnet-assisted soil washing (washing and washing with ZVI 0.5% amendment, respectively) showed an increase after 42 days of treatment (from 1893 ± 114.55 to 2934 ± 247.03 mg/kg^{-1} and from 1760 ± 172.53 to 2464.91 ± 69.05 mg/kg^{-1}) and then a slight decrease at harvest time (2274 ± 221.71 and 2048.46 ± 38.56 mg/kg^{-1}). However, when ZVI (0.5%) amendment was applied without soil washing, Zn concentrations gradually increased from 954 ± 56.57 to 1921.68 ± 146.86 mg/kg^{-1}. The concentration of Fe in the treated soil showed a slight change during cultivation. At harvest time, the concentration of Fe in the treated soils was 33,860 ± 2060 mg/kg^{-1} for the washing treatment, 40,428 ± 602.69 mg/kg^{-1} for the washing + ZVI 0.5% amendment treatment, and 41,518 ± 1029.70 mg/kg^{-1} for the ZVI 0.5% amendment treatment without washing.

The Zn and Fe concentrations in rice plants during the four states of growth are presented in Fig. 3. Zn was found to accumulate more in the lower part of plant tissue in the treated soil, which is similar to the Cd accumulation pattern. The results reveal that during the tillering, heading, and mature stages, respectively, the *EF* values of Zn were ranked in the order of root (EF^{root} = 3.93 ± 0.00, 5.70 ± 0.15, and 5.54 ± 0.09) > stem (EF^{stem} = 2.67 ± 0.00, 2.81 ± 0.16, and 1.74 ± 0.03) > leaf (EF^{leaf} = 1.22 ± 0.00, 1.42 ± 0.01, and 1.16 ± 0.04) with soil washing. With soil washing and ZVI 0.5% amendment, the *EF* values were ranked in the order of root (EF^{root} = 2.25 ± 0.00, 5.02 ± 0.06, and 4.28 ± 0.20) > stem (EF^{stem} = 1.62 ± 0.00, 2.08 ± 0.04, and 1.45 ± 0.01) > leaf (EF^{leaf} = 0.72 ± 0.00, 1.09 ± 0.025, and 1.10 ± 0.01). Finally, with ZVI 0.5% amendment without soil washing, the *EF* values were in the order of root (EF^{root} = 2.42 ± 0.00, 4.26 ± 0.08, and 4.42 ± 0.08) > stem (EF^{stem} = 1.56 ± 0.00, 1.88 ± 0.002, and 1.37 ± 0.006) > leaf (EF^{leaf} = 1.26 ± 0.00, 0.98 ± 0.003, and 0.59 ± 0.02).

The Zn accumulation factor in systemic soil-rice issues at harvest time is represented in Figure S6. The application of the soil washing and amendment reduced Zn deposition affinity in the rice plants. The Zn accumulation affinity reduced in the order 0.15 (washing + ZVI 0.5%) < 0.16 (ZVI 0.5%) < 0.17 (washing) < 0.20 (CE) for roots ($AF_{root/soil}$), 0.05 (washing) ~ 0.05 (ZVI 0.5%) ~ 0.05 (washing + ZVI 0.5%) < 0.07 (CE) for stems ($AF_{stem/soil}$), and 0.015 (soil washing + ZVI 0.5%) < 0.03 (soil washing) < 0.035 (ZVI 0.5%) < 0.037 (CE) in grains ($AF_{grain/soil}$). This is confirmed by the trend of Zn translocation affinity from soil to root as $TF_{root/soil}$, which followed the order 0.147 (washing + ZVI 0.5%) < 0.16 (ZVI 0.5%) < 0.17 (washing) < 0.20 (CE). Nevertheless, Zn translocation from root to stem ($TF_{stem/root}$) also slightly declined in the order 0.30 (washing), ~0.30 (ZVI 0.5%), ~0.32 (washing + ZVI 0.5%) < 0.35 (CE). There was less Zn translocation from stem to rice grain when using soil washing and ZVI 0.5% ($TF_{grain/stem}$ = 0.33) and soil washing ($TF_{grain/stem}$ = 0.68) than when using ZVI (0.5%) amendment ($TF_{grain/stem}$ = 1.06). Moreover, the Zn level in the rice grain was 71.18 ± 1.13 mg/kg^{-1} with soil washing only, 31.10 ± 0.00 mg/kg^{-1} with soil washing and ZVI 0.5%, and 67.06 ± 1.84 mg/kg^{-1} with ZVI (0.5%) amendment only (see Fig. 4). These results show that the final Zn content in rice grain under the different treatments decreased in comparison to that of rice grains in the CE (Zn concentration = 73.35 ± 0.69 mg/

kg^{-1}).

Interestingly, the concentration of Zn in rice grain was reduced by 57.61% through soil washing and ZVI amendment (31.10 ± 0.00 mg/kg^{-1}), by 8.58% through ZVI (0.5%) amendment (67.06 ± 1.84 mg/kg^{-1}) and by 2.95% through soil washing (71.18 ± 1.13 mg/kg^{-1}) compared to the CE (73.35 ± 0.69 mg/kg^{-1}). Using ZVI amendment has been shown to reduce Zn in rice plants, with one recent study reporting that ZVI (5%) can reduce Zn in rice plants by 19%, likely due to the removal of Zn ions in the soil-water mixture through surface precipitation (Khum-in et al., 2020; Suponik et al., 2015). Additionally, a higher dose of ZVI can increase Zn sorption due to the higher number of sorption sites (Houben and Sonnet, 2010).

Regarding Fe behavior, the application of soil washing and soil amendment increased Fe accumulation in the root ($AF_{root/soil}$) in the order of 0.14 (washing) > 0.13 (ZVI 0.5%) > 0.12 (washing + ZVI 0.5%) > 0.11 (CE). Fe accumulation in the stem ($AF_{stem/soil}$) followed the order of 0.015 (washing) > 0.012 (washing + ZVI 0.5%) > 0.009 (ZVI 0.5%) > 0.0088 (CE). Meanwhile, treatments had a slight effect on Fe accumulation in rice grain, as follows: 0.0054 (washing), 0.003 (washing + ZVI 0.5%), 0.006 (ZVI 0.5%), and 0.009 (CE).

Translocation from soil to root ($TF_{root/soil}$) was in the order of 0.14 (washing) > 0.133 (ZVI 0.5%) > 0.12 (washing + ZVI 0.5%) > 0.11 (CE). On the other hand, Fe translocation from the rice root to the rice stem ($TF_{stem/root}$) also slightly increased in the order of 0.11 (washing), ~0.10 (washing + ZVI 0.5%) > 0.078 (CE), except when using ZVI 0.5% amendment (0.068). However, the translocation of Fe from rice stem to rice grain ($TF_{rice/stem}$) declined after treatments, especially when soil washing was used: 0.165 (washing + ZVI 0.5%) < 0.22 (washing) < 0.52 (ZVI 0.5%) < 0.565 (CE). Using ZVI amendment and soil washing apparently reduced Fe content in rice grain. Presumably, ZVI at the rice root sequestered much more of the Fe^{2+} and Fe^{3+} released from the soil than the Fe^{2+} and Fe^{3+} released due to oxidative dissolution (Khum-in et al., 2020).

Eventually, these treatments affected the Fe content in the rice grain, resulting in 184.35 ± 46.46 mg/kg^{-1} with soil washing, 120.42 ± 0.00 mg/kg^{-1} with soil washing + ZVI (0.5%), and 250.05 ± 0.00 mg/kg^{-1} with ZVI (0.5%) amendment.

In conclusion, using soil washing and ZVI amendment together resulted in a reduction of both Zn and Fe concentrations in the rice plant to 31.10 mg/kg^{-1} and 120.42 mg/kg^{-1}, respectively. These values are lower than the provisional maximum tolerable daily intake (FAO/WHO, 2011), as shown in Table S3.

3.4. *Effect of magnet-assisted soil washing and soil amendment on rice growth*

Figure S8a illustrates the relative growth of rice under different treatments during cultivation. The results show that the growth of rice in the treatment experiments was similar to that of rice in the CE. Daily rice growth rates (see Figure S8a and Table S4) were measured during the experiments. The daily growth rate in the CE was 1.024 cm per day, while the daily growth rate was 1.278 cm per day for soil washing, 1.077 cm per day for soil washing with amendment (ZVI 0.5%), and 1.140 cm per day for ZVI 0.5% amendment. These results suggest that the growth rates of plants under the with soil washing and/or ZVI 0.5% treatments were slightly higher than the growth rate of plants in the CE (1.024 cm), which is consistent with the findings of a recent study (Phenrat et al., 2019).

4. Conclusion

This pilot experiment evaluated the Cd restoration efficiency of using magnet-assisted soil washing followed by ZVI soil amendment and compares this with the restoration efficiency of using only ZVI soil amendment or only soil washing in real Cd-contaminated paddy fields. The goal is the cultivation of safe rice grain with lower Cd concentration than the maximum acceptable level. In untreated paddy soil, the concentration of Cd in rice grain was 0.86 ± 0.01 mg/kg^{-1} higher than the threshold (0.4 mg kg^{-1}). Even though magnet-assisted soil washing alone can remove 1.36 times the bioavailable Cd, it did not reduce Cd uptake by rice (1.21 ± 0.01 mg/kg^{-1}) due to Cd-contaminated runoff and flooding caused from heavy rain during the experiment. Using soil amendment with ZVI (0.5%) after magnet-assisted soil washing successfully sequestered Cd from heavy rain in soil and reduced the Cd concentration in rice grain to 0.33 mg/kg^{-1} (60%). Moreover, the treatments with soil washing followed by soil amendment with ZVI (0.5%) had positive effects on rice growth but reduced the Fe and Zn content in rice grain by 58% and 59%, respectively. When considering the growth rate of rice, Fe and Zn uptake, and the Cd uptake of each treatment (as shown in Figure S8b), the best restoration option for systematic, permanent Cd removal from the soil appears to be the use of magnet-assisted soil washing followed by ZVI amendment (0.5%). This method also provides effective protection from Cd re-contamination by Cd-contaminated runoff, while maintaining appropriate levels of Fe and Zn in rice grain.

Credit author statement

Vinita Khum-in: Conceptualization, Methodology, Investigation, Writing - Original Draft, Visualization.; **Jirapon Suk-in, Papop In-ai, Kitsanateen Piaowan, Yarnnapat Praimeesub, Kusuma Rintachai**: Methodology; **Wisa Supanpaiboon**: Methodology, Validation; **Tanapon Phenrat:** Conceptualization, Methodology, Formal analysis, Resources, Writing - Original Draft, Visualization, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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