



Evaluation of oil sludge vermicompost for integrated nutrient management in rain fed wetland rice (*Oryza sativa* L.): SAMOE, FIAM and Fuzzy TOPSIS approach

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ABSTRACT

In present study, the *Periyonix excavate* and *Eisenia fetida*-mediated oil sludge-vermicompost was used for crop trial by taking rice (*Oryza sativa* L.) as a tested crop. An improved soil quality with significant improvement in nutrient status was resulted, furthermore, significant reduction in solubility of toxic metals (Cr, Ni, Pb) and minuscule amount of metal was detected in the root portion part of rice plant. Cr, Ni and Pb was detected in edible parts under raw oil sludge treatment. The FIAM modelling ensures positive transport of grain uptake of toxic metal (Cr, Ni, Pb) in presence of oil sludge. The SAMOE risk thermometer indicated a high-risk hazard in oil sludge treatment. Fuzzy-TOPSIS analysis also predicted the highest synergetic performance score and rank for the concentration of heavy metals in oil sludge treatment. Moreover, the composite treatment (VC 50%+NPK50%) attributed profuse yield of rice hence could be an alternative agronomic practice.

Keywords: Crop uptake, FIAM, Fuzzy-TOPSIS, metal, oil sludge-vermicompost, *Oryza sativa* L.

Rice (*Oryza sativa* L.) serves as the primary food source for a large proportion of the world's population (Sabah *et al.*, 2020). In order to sustain rice production, excessive use of synthetic fertilizers and pesticides is common practice within the rice ecosystem, resulting in increased greenhouse gas emissions and environmental pollution (Desmedt *et al.*, 2022). The global food production system has become increasingly complex due to the challenges posed by climate change, as well as shortages in land and water resources. Besides its economic significance, the rice ecosystem has attracted worldwide interest due to its distinctive feature of transitioning from flooded to wetland, and ultimately to a terrestrial environment as it reaches maturity (Dash *et al.*, 2011). This ecosystem is additionally impacted by a variety of agronomic practices, such as transplanting, tillage, and the use of nitrogen-based fertilizers.

Green Revolution has revolutionized modern agriculture practices over the last five decades, with the inclusion of various modern techniques (increased area under farming, applying double cropping system, adoption of HYV of seeds, and applying more inorganic fertilizers and pesticides) (Brainerd and Menon, 2014). However, in order to meet the increasing demand of the growing population, agriculture practices have become more reliant on inorganic amendments to achieve high productivity in a shorter time. This extensive use of

agrochemicals results in the accumulation of residues in the soil, leading to nutrient depletion. Improper use of imbalanced mineral fertilizers by farmers, without integrated nutrient management, leads to soil health deterioration, loss of beneficial microorganisms, negative impact on soil biodiversity, soil acidification, reduction in organic matter, loss of soil carbon, nitrogen leaching, and soil compaction (Gupta *et al.*, 2022; Banerjee *et al.*, 2023). The growth of industrialization is also a significant factor that affects agriculture, as it produces toxic waste by-products that are harmful to ecosystems. Some industries even dispose of their waste near agricultural land, which can result in the accumulation of toxic metals in the soil (Ghosh *et al.*, 2022). As a result, polluted soil is considered a significant source and sink of toxic metals in the environment.

In this scenario, the edible oil industry's role in generating a significant amount of waste, both in liquid and solid form, can have a detrimental effect on the soil ecosystem (Uroko and Njoku, 2021). These pollutants harbour high concentrations of fats, oils, sodium, phosphorus, sulphate and various other pollutants like Pb, Zn, Mn, Cu, Cr, Cd, Ni, As, and Hg (Alvarenga *et al.*, 2022). The release of large quantities of pollutants into the sewer from edible oil refinery units can contaminate water and soil resources to a significant extent. While the edible oil industry is a major

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contributor to economic growth and development, the production of large amounts of by-products from the oil extraction process has a detrimental impact on environmental health. Therefore, there is an urgent need for a sound and efficient management system to treat these by-products in a sustainable manner. Composting and vermicomposting technologies are ahead increasing interest for remediating various types of solid waste in this context (Sahariah *et al.*, 2015). Composting and vermicomposting are excellent sustainable waste management options for the biological waste generated by edible oil mills. Vermicomposting, which uses worms to convert organic substances into stabilized humus-like byproducts, is a cost-effective and efficient biotechnological process. Earthworms play a significant role in accelerating the decomposition process, reducing waste volume, and resulting in value-added products. However, there is currently no available data on vermicomposting the wastewater and sludge generated by the edible oil industry. Earthworms' guts contain microbes that release enzymes such as lipases, amylase, proteases, and cellulases that help with biodegradation (Medina-Sauza *et al.*, 2019). In order to cope with metal stress, earthworms release antioxidants, metallothionein proteins, and cytochrome P450 enzymes. Earthworms have been used in several studies to demonstrate industrial waste such as oil slag management (Yadav and Garg, 2009). The harmful effects of oil industrial waste on the environment are widely recognized, and crops grown on soil contaminated with toxic waste offer insight into the potential risks to the ecosystem and human health. There is evidence indicating that crops grown on metal (Pb, Zn, Mn, Cu, Cr and Cd)-contaminated soil may contain concentrations of heavy metals that exceed permissible limits.

Rice, wheat, maize, vegetables, and other major crops, when grown on waste dumping sites, considerably collect a high concentration of heavy metals (Ni, Cr, and Pb) in their plant parts (root, shoot, and grain), which poses a possible hazard to the food chain. To interpret metal uptake by crops growing on waste-contaminated soil, solubility-free ion activity model (FIAM) can be applied (Banerjee *et al.*, 2023). A severity-adjusted margin of exposure (SAMOE) can be used to comprehend the increasing risk of exposure to HMs from consuming dietary products in a contaminated area (Golui *et al.*, 2021). The Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) is a useful method for ordering potential solutions according to their Euclidean distances. Using information entropy, TOPSIS is able to discover the scenario that is closest to the positive ideal solution (Si+) and the scenario that is farthest from the negative ideal

solution (Si-) (Sianaki *et al.*, 2018). The Fuzzy-TOPSIS method was utilized in order to calculate the synergetic performance score as well as the risks associated with each treatment.

There is currently a lack of information regarding the use of vermicomposted edible oil waste slag as compost for agricultural purposes, despite its potential benefits. To address this gap, we conducted a two-year consecutive field experiment involving rice crop. The experiment involved using a combination of this vermicomposted oil waste slag and inorganic fertilizers. Our study focuses on two key objectives: (i) assessing the efficacy of vermicomposted oil waste slugs as an organic fertilizer in agriculture and evaluating the potential risks associated with direct application of waste oil slag to the soil, including changes in chemical, microbial, and heavy metal concentrations (Cr, Pb, Ni, Fe, Cd, and Cu) over time, using multi-criteria decision-making techniques like Fuzzy-TOPSIS to identify the most suitable solutions for minimizing health risks among ten treatments, and (ii) evaluating the level of metal transferred from oil waste slag treatment to (*Oryza sativa* L.) and the associated risks of consuming rice crops using FIAM and SAMOE risk thermometer models. Additionally, we will assess the quality and yield of rice crops from an agronomist's perspective.

MATERIALS AND METHODS

Processing of vermicompost (VC)

Oil sludge is a mixture of oil, water (50% of the total mass), solid particles, organic hydrocarbons (both light hydrocarbons: gasoline or diesel and heavier components: asphalt or tar) and various contaminants (Pb, Hg, and Cd) that accumulate as a byproduct in oil refineries, storage tanks, or during oil extraction processes (USEPA, 1999). Oil industry sludge (OIS) was collected from oil refinery at Haldia, West Bengal in the year 2019. Vermicompost (VC) was prepared from using two earthworm species (*Perionyx excavatus* and *Eisenia fetida*) at the vermicompost unit of the Indian Statistical Institute, Giridih, Jharkhand. Cow dung (CD) was used as a bulking agent and collected from local cattle houses. Different feedstock combinations were introduced to *P. excavates* and *E. fetida* with one positive control (only cow dung) and one negative control (only OIS) and left for 90 days for conversion of waste to compost. The ratios (OIS: CD) of the feedstock were (1:1) where 10 worms (healthy, non-ciliated, 35-40 days old) were employed per kg of substrate. Due to the fact that worms introduced to OIS died within one day, we maintained only OIS for up to 90 days. At the end of 90 days, the prepared VC was withdrawn from composting unit, sieved and preserved for crop trial.

Experimental setup

Field experiments were conducted for two consecutive years in the wet seasons (June – September) of 2019-2020 on rice (*Oryza sativa* L.) at the Agriculture Experimental Farm, Indian Statistical Institute, Giridih, Jharkhand, India. In this region, rice-based cropping systems are followed. The main season for growing rain fed rice is the monsoon (June-September). The cultivators in this area follow mostly mono-cropped rice with sporadic vegetable crops. Urea is the most widely used N supplement. Sometimes, cow dung manure is used as an organic supplement, subject to the availability after its use in other domestic purposes. In the field experiments oil sludge vermicompost, well rotten cow dung manure (CDM), raw oil sludge, and inorganic fertilizers (urea, single superphosphate and muriate of potash to supply N, P and K, respectively) were used. Recommended dose of fertilizer for Jharkhand state i.e., 80:60:40 (N:P: K) ha⁻¹ was opted for the trial. The characteristics of vermicomposts were given in Table 1.

The experiments were conducted in a randomised block design with 10 treatments, in fixed plots for two consecutive years. Each treatment was replicated 4 times in 5 m x 4 m plots. The treatment details were given in Table 2. The organic supplements were applied seven days prior to and fertilizers at transplanting. Rice variety Khanika was transplanted. At harvest the yield components were recorded from 10 randomly selected plants, leaving 2 border rows from each plot. Grain and straw yields were recorded from 1 m² area of each plot and converted in to t ha⁻¹. Other agronomic practices like watering, drainage of excess water, weeding, and application of pesticides were followed uniformly for all the treatments recommended by the Department of Agriculture, Government of Jharkhand.

Soil sampling and analysis of soil and plant sample

The field moist samples were collected at four different stages of crop i.e., 0, 30, 60 days and post-harvest for analysis of microbial parameters like microbial biomass C, soil respiration, enzymatic activities. Soil samples were kept in a sterile plastic bag from each replicate of ten treatments. The 0-day sample was taken just before the transplanting and post-harvest samples were drawn ten days after rice harvesting. Soil microbial biomass C was estimated by ninhydrin reactive nitrogen method as prescribed by Jenkinson (1994). Fluorescein diacetate (FDA) hydrolyzing activity was measured by the method of Schnürer and

Rosswall (1982). Dehydrogenase activity was determined by the method of Casida *et al.* (1964). To assess the physicochemical parameters, viz., pH, total organic carbon, available phosphorus (P) and exchangeable potassium (K), soil samples were drawn from each replicate before sowing and after harvesting. Reaction (pH) of soil samples was determined by Systronic pH meter model No. 335 with a glass electrode using sample–water suspension in the ratio of 1:2.5. The soil total organic carbon was estimated using methods was described by Walkley-Black methods. The available P was determined using Bray’s I extractant and exchangeable K of soil samples were determined using 1(M) ammonium acetate extraction methods and data was observed using a flame photometer (Systronic, Model No- 130). The methods used here were derived from Page *et al.* (1982).The samples were air-dried, sieved through 2 mm sieve and preserved for analysis. All the parameters were analyzed following the methods described by Page *et al.* (1982). Likewise, the vermicompost and cow dung samples were also undergone for the measurement of available nutrients (N, P, K). Straw and grain yield of the rice were recorded at harvest.

Sequential extraction of metal fractions in soil and total metal content of plant samples

Bioavailable (water soluble and exchangeable) metal concentration was measured following the methods of Tessier *et al.* (1979) using air-dried, 0.2 mm (Ghosh *et al.*, 2022) sieved sample. For water-soluble fractions, 1.0 g of air-dried soil samples were extracted sequentially with 50 mL deionized water, shaking (120 r/min) for 30 min at room temperature; 0.5 mol/L Mg (NO₃)₂ in 50 mL with shaking (120 r/min) for 30 min at room temperature for an exchangeable fraction. Quantification of phytoaccumulated metal was done by digesting the dried root, shoot and grain in a 4:1 ratio (HNO₃:HClO₄) acid mixture. Concentrations of metal in the digests were measured using atomic absorption spectrophotometer (Systronics AA S-816) and expressed in terms of dry weight basis. Standard solutions of the metals (Pb, Cr, Ni) were made from the stock solution (1000 mg/L, Merck grade) in 1% (v/v) HNO₃ for calibration. For quality checking, certified reference materials 2710 and blank extract were used.

Metal removal ratio and metal mobility assessment

The metal removal ratio was calculated following Eq. 1 (Sahariah *et al.*, 2015; Chakraborty *et al.*, 2022).

$$\text{Metal removal ratio} = \frac{\text{Concentration of metal at OD} - \text{Concentration of metal at after harvest}}{\text{Concentration of metal at OD}} \dots\dots\dots (1)$$

Apart from nutritional factors, presence of toxic components like heavy metals and their plausible movement towards plant systems was assessed and represented as bio-concentration factors (BCF), translocation factors (TF) and bioaccumulation factors (BAF) (Islam *et al.*, 2020). The formulae are given below

$$\text{Bioconcentration factors (BCF)} = \frac{C_{\text{root}}}{C_{\text{soil}}} \dots (2)$$

$$\text{Translocation factor (TF)} = \frac{C_{\text{shoot}}}{C_{\text{root}}} \dots (3)$$

$$\text{Bioaccumulation factor (BAF)} = \frac{C_{\text{grain}}}{C_{\text{soil}}} \dots (4)$$

Prediction models (FIAM) for HMs accumulated by rice plant and risk assessment by FIAM-HQ

Without assessing the soil-free ion activity, FIAM can be utilized to forecast the transfer of HMs from soil to rice grain. The ratio of the metal content of the plant [M_{plant}] to the activity of the metal ions in the soil pore water [$M^{(n-)}$], as shown in Equation (1), is used to compute the transfer factor (TF). (Golui *et al.*, 2017).

$$TF = \log \frac{[M_{\text{plant}}]}{[M^{(n-)}]} \dots (5)$$

HMs' free ion activity can be calculated using the Freundlich equation, which is a simplistic pH-dependent technique.

$$p(M^{(n-)}) = \{p[M_C] + k_1 + k_2 \text{pH}\} / n_F \dots (6)$$

where ($M^{(n-)}$) is the free HMs ions activity in the soil; M_C is the easily displaceable soil bioavailable HMs content;

k_1 and k_2 are experimental metal-specific constants; and

n_F is the power term from the Freundlich equation.

By combining Equations (1) and (2), the expression for predication of HMs uptake by plants can be represented as:

$$p[M_{\text{plant}}] = C + \beta_1 p[M_C] + \beta_2 \text{pH} \dots (7)$$

where $C = k_1/n_F - \log TF$, $\beta_1 = 1/n_F$, $\beta_2 = k_2/n_F$ and C , β_1 and β_2 are empirical metal and plant-specific coefficients (Mandal *et al.*, 2019). Equation (3) was parameterized by using the "SOLVER" addon facility in Microsoft Excel 365.

Rice grown in HMs-contaminated soil poses a health risk to humans, which can be quantified using the hazard quotient (HQ). The average daily intake (ADI) of HMs divided by their reference dose (RfD) could be used to calculate HQ. For the purpose of calculating the HQ, it was assumed that each person consumed 0.2 kg of rice per day (Golui *et al.*, 2017) and weighed an average of 68 (Kumar *et al.*, 2021). RfD values were determined

according to IRIS (2020). Therefore, the HQ was calculated by:

$$HQ = \frac{M_{\text{plant}} \times W}{RfD \times 68} \dots (8)$$

Where M_{plant} is HM content of rice grain cultivated on coal mine contaminated land; W_W is the weight of rice grain consumed daily; and RfD is the reference dose for different HMs.

Risk assessment of HMs through dietary exposure (SAMOE, Risk thermometer, and SAMOE-TCR) in different treatments

The Swedish National Food Agency has presented Risk Thermometer, a novel approach for risk characterization (Chowdhury *et al.*, 2020). Equation (5) can be used to determine SAMOE for various heavy metals.

$$SAMOE = \frac{TDI}{(AFBMR \times AF \times SF \times E)} \dots (9)$$

Where, TDI is provisional tolerable daily intake (PTDI), AFBMR is non-linear relation in dose range (1/10; BMR is the benchmark response), AF is assessment factor taken as 10, SF is severity factor taken as 100, and E is the exposure factor (concentration of HMs).

The target cancer risk (TCR), which estimates a person's lifetime exposure to carcinogenic HMs, is a crucial tool for evaluating dietary risks. It can be estimated using Equation (6) (Sengupta *et al.*, 2021).

$$TCR = \frac{E_{Fr} \times ED \times FIR \times C \times CSF}{BW \times AT} \times 10^{-3} \dots (10)$$

Where E_{Fr} is the frequency of exposure to various HMs, ED is the duration of exposure. FIR is rate of ingestion of food. C is HM content in rice grain, CSF is the oral cancer slope factor for HMs, BW is the average body weight. AT is the average carcinogenic exposure time, 10^{-3} is unit conversion factor

Evaluation of probable health Risks from different treatments using Fuzzy-TOPSIS

One of the traditional methods for solving multi-criteria decision-making (MCDM) problems with precise numbers is the "Technique for Ordering Preference by Similarity to Ideal Solution (TOPSIS)" because it has an easy computation process, a methodical procedure, and sound logic that resembles human decision-making. The TOPSIS approach involves the use of entropy in order to determine which alternatives are the closest to the S_i^+ and which alternatives are the farthest away from the S_i^- . This technique has been widely employed in decision-making evaluation, including health risk assessment (Singh *et al.*, 2018).

The “alternatives” (treatments) and “criteria” (Bioavailable metals) were established for different treatments, with rankings to be assigned based on the level of health risk. Assuming “b” viable alternatives, $P = \{P_1, \dots, P_b\}$, are to be estimates alongside “c” criteria. $Q = \{Q_1, \dots, Q_c\}$

A matrix O was used in allocating ratings to the criteria, where z_{ij} indicates the alternative P_i ' value for criterion Q_j .

$$O_{b \times c} = \begin{bmatrix} z_{11} & z_{12} & \dots & z_{1c} \\ \vdots & \dots & z_{ij} & \vdots \\ z_{b1} & \dots & \dots & z_{bc} \end{bmatrix} \dots\dots\dots (11)$$

Using entropy, the criteria weights were calculated as follows:

$$r_{ij} = \frac{z_{ij}}{z_{1j} + \dots + z_{bj}}; \forall j \in \{1, \dots, c\}, \text{ and} \dots\dots\dots (12)$$

$$G_j = -\frac{1}{\ln b} \sum_{i=1}^b r_{ij} \ln r_{ij}; \forall j \in \{1, \dots, c\} \dots\dots\dots (13)$$

Where $0 \leq G_j \leq 1$ and indexes with higher entropy have maximum variation. Therefore, the criteria's weight may be estimated as:

$$w_j = \frac{w_j}{a_1 + \dots + a_c} \dots\dots\dots (14)$$

Where, $a_j = 1 - w_j$; All the weights were aggregated into the w_{cxc} matrix.

Construction of normalized matrix as follow:

$$\bar{Y}_{ij} = \frac{y_{ij}}{\sqrt{\sum_{i=1}^n y_{ij}^2}} \dots\dots\dots (15)$$

Weighted normalized matrix was determined using this formula,

$$U_{ij} = \bar{Y}_{ij} \times W_j \dots\dots\dots (16)$$

Calculate the ideal best (S_i^+) and ideal worst value (S_i^-)

$$S_i^+ = \left[\sum_{j=1}^b (V_{ij} - V_j^+)^2 \right]^{0.5} \dots\dots\dots (17)$$

$$S_i^- = \left[\sum_{j=1}^b (V_{ij} - V_j^-)^2 \right]^{0.5} \dots\dots\dots (18)$$

Evaluation of Performance Score and rank of each treatment as follow

$$P_i = \frac{S_i}{S_i^+ + S_i^-} \dots\dots\dots (19)$$

Statistical analysis

All the statistical analysis were done by using r statistical package.

RESULTS AND DISCUSSION

Background of oil sludge based vermicompost

Changes of chemical parameters over time (0 days and after harvest) in the field experiment was given in Fig. 1. The vermicompost generated from oil sludge was observed to comprise a substantial quantity of advantageous nutrients. At the start of the experiment, i.e., at 0 days, the mean pH values of all the treatments were in proximity to the standard range (6.10 - 6.40) that is mildly acidic in character. Following the post-harvest period of 90 days, the pH values across all treatments exhibited an increase, leading to a moderate shift towards the neutral range of 6.33 - 6.60. There was a statistically significant temporal fluctuation in pH observed across all treatments. The rise in pH levels was found to be beneficial for the plants as they thrive in a neutral pH environment for optimal metabolic activity, leading to an improved nutrient uptake. The observed increase in increment may be attributed to the gradual rise in pH resulting from the addition of organic amendments over time. A comparable outcome was reported by Zeb *et al.* (2020) in their study on rice cultivation using vermicompost based on fly-ash. Organic carbon content (mean: 0.62 ± 0.05) exhibited an increase in all treatments from the day of transplant to post-harvest (mean: 0.65 ± 0.055), and the variation across treatments was found to be statistically significant. The available phosphorus (P) and potassium (K) content exhibited a statistically significant difference (p for D = 0.003, LSD = 1.55; p for T = 0.004, LSD = 2.11) and (p for D = 0.006, LSD = 5.63; p for T = 0.007, LSD = 6.81) respectively, increased substantially from the initial stage to post-harvest, in the vermi-amended treatments. The balanced mineralization of nutrients and enzymatic activity in vermicompost, when used in combination with inorganic fertilizers, results in a high concentration of available potassium (K) and phosphorus (P). According to Das *et al.* (2019), the soils in Giridih are comparatively abundant in potassium and phosphorus, but these nutrients are primarily present in an insoluble form, leading to a deficiency of plant-available potassium in the soil. The beneficial bacteria present in vermicompost have the ability to solubilize phosphorus and potassium, fix nitrogen, and synthesize substances such as indole acetic acid (IAA), Gibberellic acid (GA), Hydrogen cyanide (HCN), Ammonia, and Siderophore production that promote plant growth, thereby providing a rich source of nutrients to plants (Choudhary *et al.*, 2022; Ghosh *et al.*, 2023). Additionally, these microbes improve the soil nutrient cycle, promote decomposition, and maintain soil fertility by enhancing soil organic matter (Adhikari *et al.*, 2017).

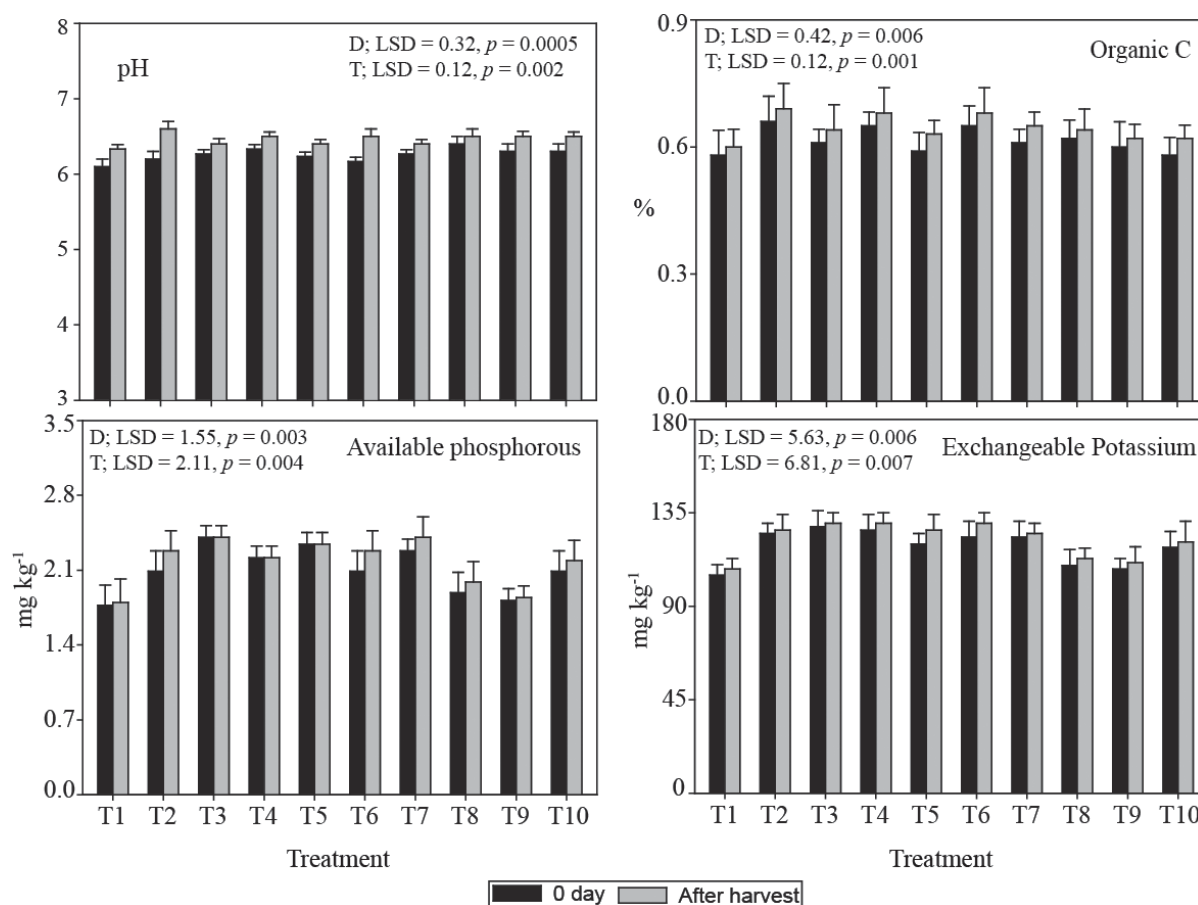


Fig. 1: Temporal variation of some soil properties amended with vermicomposted oil sludge and cow dung manure (two years mean data \pm standard error)

Impact on temporal variation of soil microbial attributes

To ensure soil health, it is crucial to maintain the soil organic carbon derived from microbial sources for sustainability. An assessment of soil microbial biomass C under varying soil amendments provides a concise understanding of soil microbial activity. However, the Giridih soil, which is sandy and acidic in nature, is deficient in humus content, resulting in low intrinsic microbial activity. The principal role of microorganisms in the cycling of carbon and nitrogen is often considered as an indicative measure of soil health and quality (Nannipieri *et al.*, 2003). While microbial biomass carbon (MBC) is an inherent constituent of organic matter, a decrease in MBC can significantly affect nutrient cycling and the availability of minerals for plants (Tang *et al.*, 2017). In this study, the temporal variation of microbial attributes such as MBC, FDA, and DHG in different treatments was represented (Fig. 2a – 2c). The MBC values were higher at the beginning

(0 d) of all treatments except T2 (OSA; 1:1) and gradually decreased up to 60 d, then increased at 90 d (post – harvest) Fig. 2a. The promotion of plant growth is facilitated by the initial increase in microbial activity, which provides nutrition to the plant. Nevertheless, the observed contrast between increased plant growth and decreased microbial biomass could be due to competition for nutrients between plants and microorganisms (Ghosh *et al.*, 2022). Regardless of the treatments, a substantial rise in MBC following cropping could be attributed to the plant residues remaining in the soil, which restore microbial activity. After post – harvest, the highest MBC were observed in T7 (CD+F) and T3 (OSA (1:1)+F) as compared to rest of the treatments and rank wise distributed T7 > T3 > T5 > T6 > T2 > T10 > T4 > T1 > T9 > T10. This may be due to the quality of organic components and their decomposition process and this observation is in line with Bhattacharyya *et al.* (2003). The ANOVA test revealed that treatment wise periodic variations (p for T

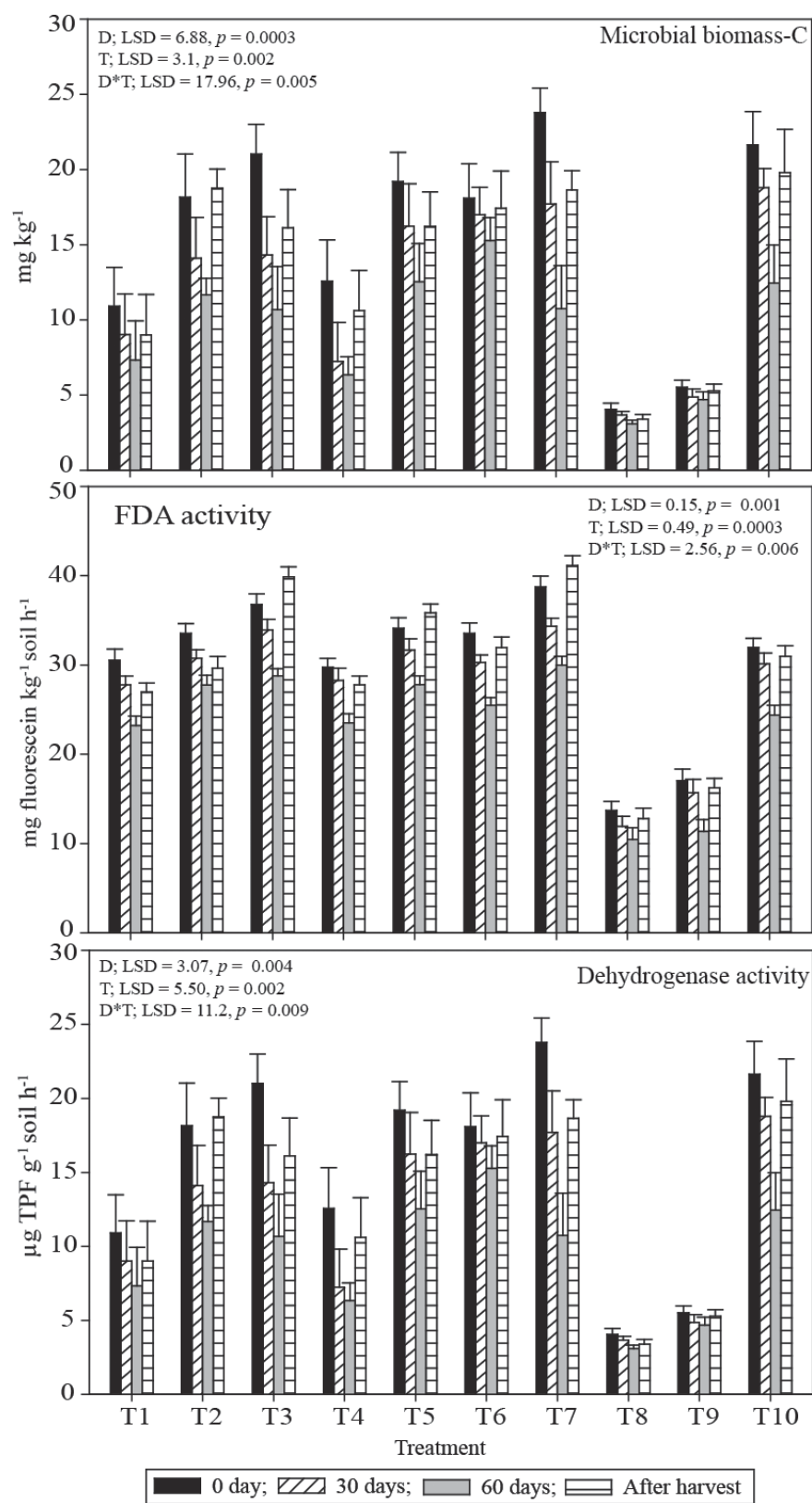


Fig. 2: Temporal variation of microbial biomass C and enzyme activities in rice soil amended with vermicomposted oil sludge and cow dung manure (two years mean data ± standard error)

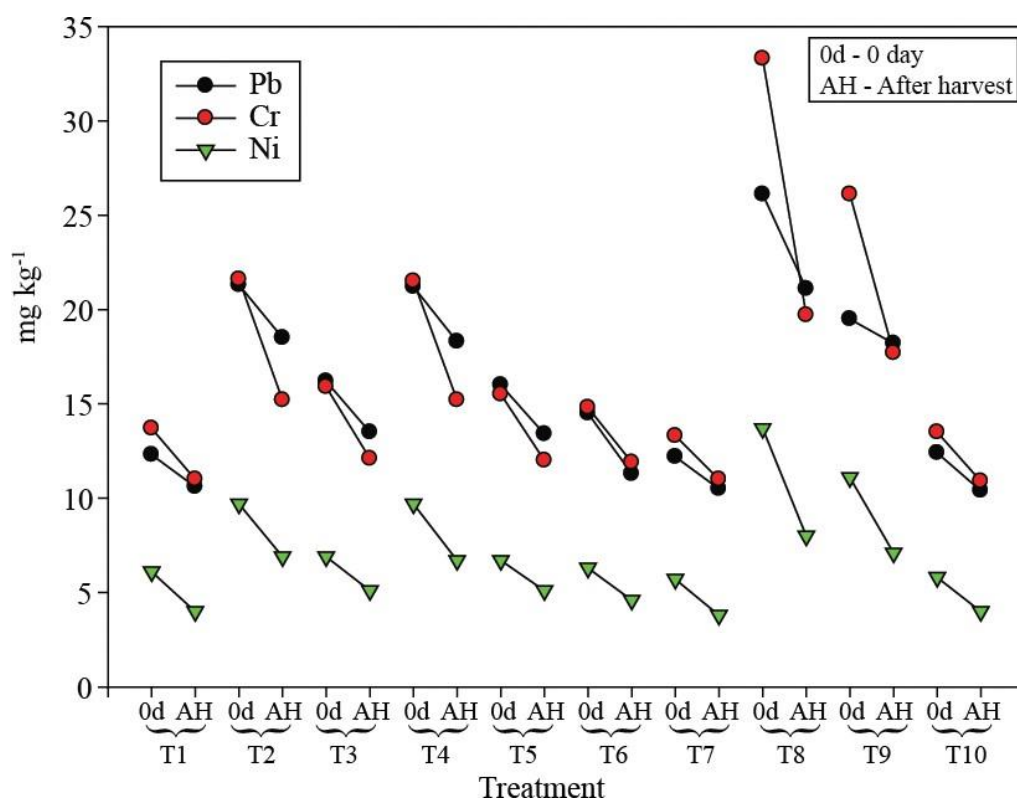


Fig. 3: Changes in bioavailable fractions [water soluble (W) and exchangeable (E)] of different metals during rice cultivation amended with vermicomposted oil sludge and cow dung manure

=0.0003; LSD =6.88; p values D = 0.002; LSD = 3.1; p values T X D = 0.005; LSD = 17.96). As compared to T2 (OSA; 1:1) + earthworm (*Periyonix excavates*) and T4 (OSA; 1:1) + earthworm (*Eisenia fetida*), T2 showed the best result. Compared to the other treatments, the application of cow dung with or without inorganic fertilizer (T7 and T3) resulted in the highest MBC. This finding is consistent with a previous study by Bhattacharyya *et al.* (2003) and Sharma *et al.* (2022).

The activity of fluorescein diacetate hydrolysis (FDA) is commonly used as a measure of overall enzymatic activity in soil microorganisms. This assay provides a comprehensive overview of the total enzymatic activity present in the soil. This hydrolysis process is facilitated by various biological enzymes including lipase, protease, and esterase, which operate optimally under favourable conditions (Tian *et al.*, 2015). At the start of the experiment, the fluorescein diacetate hydrolysis (FDA) activity was considerably greater at day 0 in all treatments, except for T3, T5, and T7 (Fig. 2b). However, during the post-harvest period, T7 and T3 exhibited the most favourable outcomes compared to all other treatments. The difference in treatment-day interactions was significant (Fig. 2b.) The divergent behavior observed in the fluorescein diacetate

hydrolysis (FDA) activity may be attributed to the presence of active enzymes within deceased biomass, as well as to cellular fragments associated with active cells (Bhattacharyya *et al.*, 2003).

The main roles of the intracellular enzyme dehydrogenase (DHG) include facilitating the transfer of electrons and hydrogen ions between various elements (Nannipieri *et al.*, 2003). Enzyme dehydrogenase is significantly found maximum in treatments T7 and T10, and T3 followed by rest of all treatments (Fig. 2c). The observed trend could be attributed to elevated levels of organic matter in the soil, which subsequently led to increased production of enzymes. Another crucial factor that influences the production of dehydrogenase enzymes is the quality of organic matter present in the soil (Fontaine *et al.*, 2003) and the combination of organic and inorganic fertilizers increased the nutrient content of soil (Soto *et al.*, 2020). T8 and T9 exhibited lower levels of dehydrogenase activity, possibly because of the impact of the fertilizer on the population of soil microorganisms (Romero *et al.*, 2010) and which may have been caused by a heavy metal's interaction with the enzyme-substrate complex, denaturing the protein enzyme and affecting both enzyme synthesis and activity (Ghosh *et al.*, 2022).

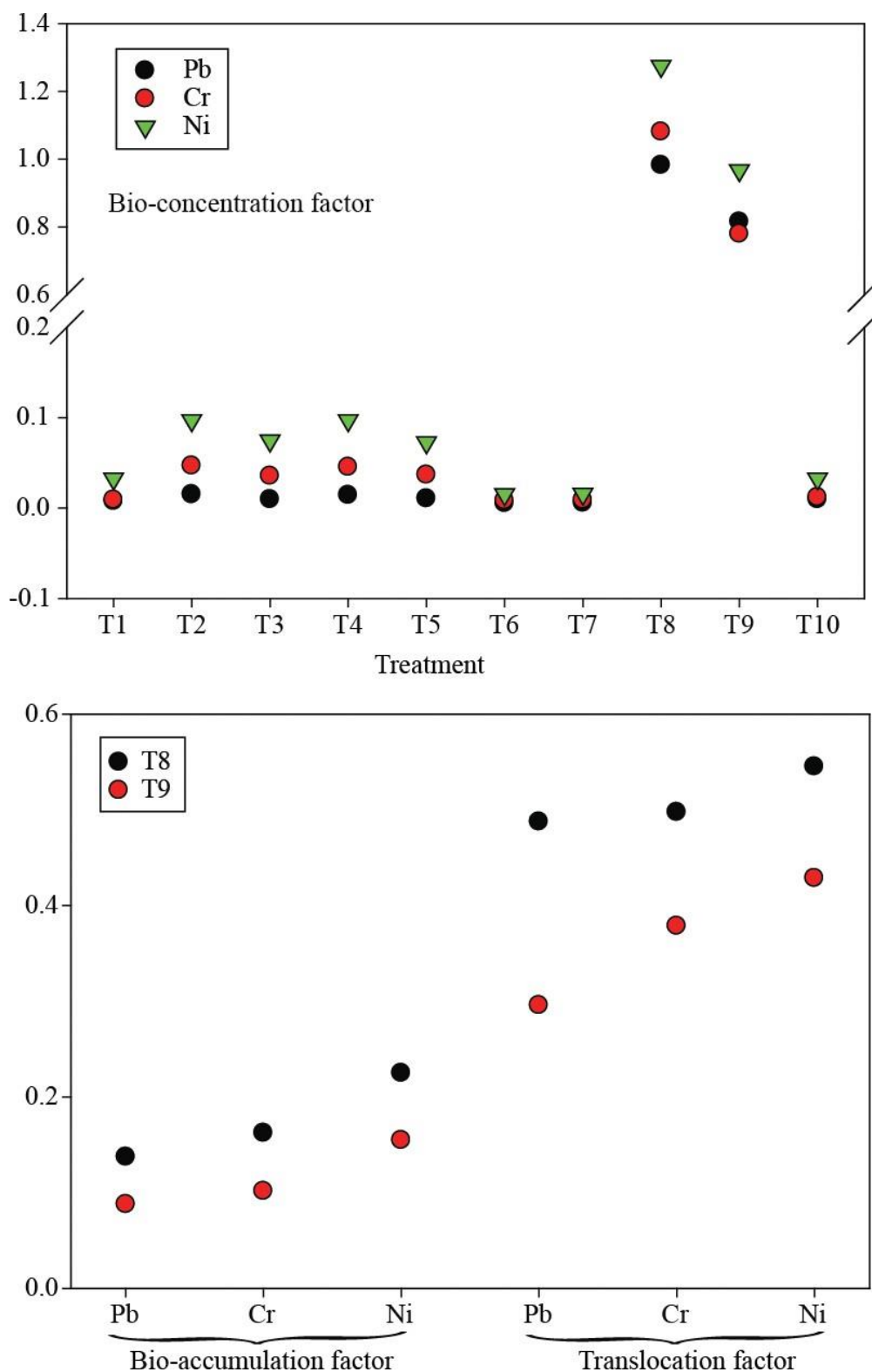


Fig. 4: Bio-concentration factor, translocation factor and bioaccumulation factor during rice cultivation amended with vermicomposted oil sludge and cow dung manure

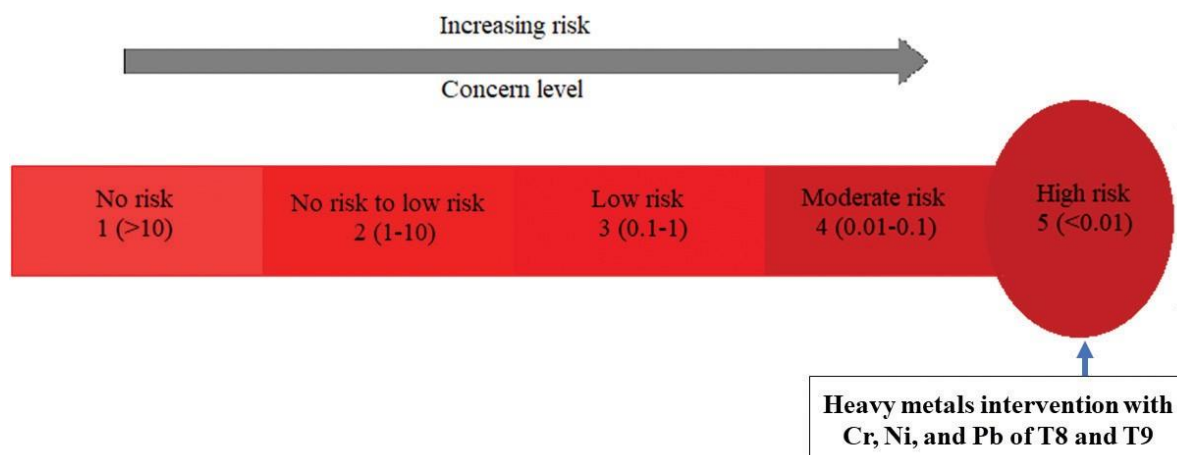


Fig. 5: Risk thermometer scale shows heavy metals (Cr, Ni, Pb) uptake potential in rice grain grown on oil sludge waste contaminated treatments (T8 and T9)

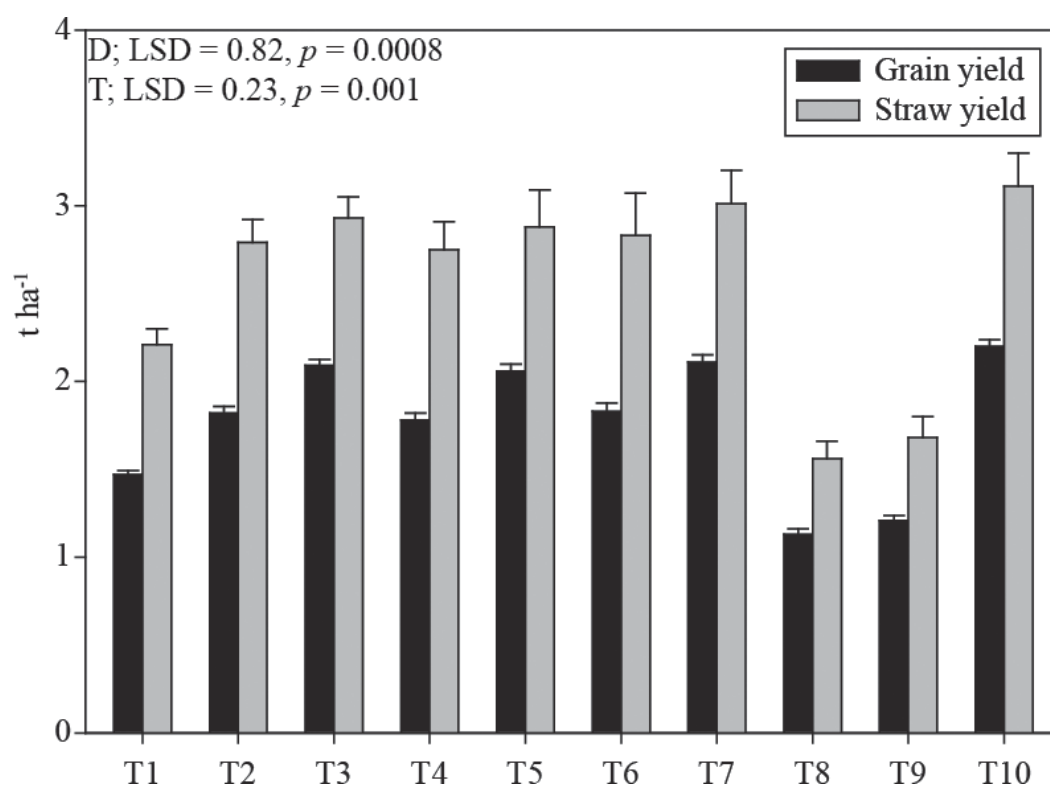


Fig. 6: Straw and grain yield of rice amended with vermicomposted oil sludge and cow dung manure before-sowing (seedlings) and post-harvest soil

The effect of vermicomposted oil sludge and cow dung manure amendments on the straw and grain yield of rice was evaluated both before sowing (during seedling stage) and after harvesting the crop, focusing on their impact on the soil. (Two years mean data \pm standard error)

Table 1: Some properties of vermicomposts (mean ±SE data)

Parameters	Vermicompost (<i>Perionyx excavates</i>)	Vermicompost (<i>Eisenia fetida</i>)
pH	7.22±0.3	7.26±0.2
EC (mS/cm)	1.34±0.9	1.39±0.7
TOC (%)	3.3±0.5	3.2±0.5
Available N (mg kg ⁻¹)	1031±16.7	1026±13.9
Available P (mg kg ⁻¹)	397±11.8	378±12.1
Exchangeable K (mg kg ⁻¹)	1501±13.2	1482±12.7

Table 2: Treatment combinations for two-year rice crop trial

Treatment	Treatment details
T1	Control (No amendment)
T2	Oil sludge vermicompost (<i>Perionyx excavates</i>) (1:1) 100%
T3	Oil sludge vermicompost (<i>Perionyx excavates</i>) (1:1) 50%+ fertilizer (NPK) 50%
T4	Oil sludge vermicompost (<i>Eisenia fetida</i>) (1:1) 100%
T5	Oil sludge vermicompost (<i>Eisenia fetida</i>) (1:1) 50%+ fertilizer (NPK) 50%
T6	Cow dung manure 100%
T7	Cow dung manure 50% + fertilizer (NPK) 50%
T8	Raw oil sludge 100%
T9	Raw oil sludge + fertilizer (NPK) 50%
T10	Fertilizer (NPK)100%

Oil sludge vermicompost, cow dung manure and raw oil sludge 100% = 10t/ha

Oil sludge vermicompost, cow dung manure and raw oil sludge 50% = 5t/ha

Table 3: Prediction of HMs transport (FIAM) and risk analysis in diet (SAMOE) of oil sludge amended rice grains

Heavy metals (Treatments)	Constant	β 1	β 2	R ²	FIAM- HQ	SAMOE- TCR	SAMOE
Cr (T8)	0.694	-0.206	0.039	0.996	0.54	1.12E-02	0.0005
Ni (T8)	-6.558	-0.088	4.113	0.999	0.26	1.88E-02	0.0020
Pb (T8)	-6.211	-0.005	3.210	0.998	2.40	1.47E-04	0.0024
Cr (T9)	-1.397	-0.082	1.119	0.997	0.41	8.53E-03	0.0006
Ni (T9)	-5.047	-0.643	5.344	0.995	0.18	1.26E-02	0.0023
Pb (T9)	-1.335	-0.169	1.192	0.992	1.37	8.40E-05	0.0027

Table 4: Risk evaluation through performance score (Fuzzy-TOPSIS) values and rank of different treatments in pot experiment

Treatment	Si+	Si-	Pi	Rank
T1	0.098	0.082	0.457	6
T2	0.075	0.072	0.489	4
T3	0.079	0.065	0.450	8
T4	0.069	0.073	0.515	3
T5	0.080	0.065	0.446	9
T6	0.092	0.070	0.435	10
T7	0.098	0.086	0.468	5
T8	0.086	0.099	0.535	1
T9	0.072	0.077	0.516	2
T10	0.099	0.082	0.453	7

Sequential extraction and bio-accessible of heavy metals

The presence of metals such as Pb, Cr, and Ni in soil can lead to a variety of interactions with soil components, resulting in different forms of metal occurrence, ranging from easily extractable to highly resistant. The water-soluble and exchangeable fractions of these metals are particularly hazardous, as they are readily available for biological uptake (Banerjee *et al.*, 2023). Fig. 3, illustrates how these two stages contribute to the accumulation of heavy metals in both soil and plants. At the outset, all metal concentrations were higher in cumulatively water-soluble and exchangeable forms. However, over time, the concentration of these metals gradually decreased in the days following harvesting. In the beginning, the concentration of Pb, Cr, and Ni in the water-soluble and exchangeable phase was highest in treatment T8, with chromium showing the greatest reduction during the post-harvest period compared to rest of all treatments. Compared to the other treatments, higher concentrations of bio-accessible metals were observed in the case of Pb (T8, T2, T4, and T9), Ni (T8, T9, T2, and T4), and (T8, T9, T2, and T4) respectively. The lower availability of metals in treatments such as T10 suggests that vermicomposting of oil sludge may have had a beneficial impact on soil fertility. The observed pattern of metal reduction provides valuable insights into the initial metal concentrations, their reduction over the course of the study, the morphology of the metal substrates, and the extent of metal reduction in different treatments (He *et al.*, 2019).

Accumulation of metal in the rice plant parts

The uptake of metals in various parts of plants is a crucial consideration when recommending agronomic practices for long-term sustainability. In this study, we evaluated the accessibility of metals in rice plant roots and their potential translocation to the shoot and grain (Fig. 4). The use of vermicomposted oil waste in soil cultivated with rice plants resulted in a reduction in the bioavailability of metals like Pb, Cr, and Ni. The translocation of metals from soil to plants is influenced by various plant-specific activities such as the rhizosphere nature of the plant, the selective nature of its roots, and its uptake capacity. Regardless of the treatments applied, metal accumulation in the grain was found to be zero in all treatments except T8 (OS) and T9 (OS + F). The uptake of three metals (Pb, Cr, and Ni) was significantly lower in plants grown in soil containing these metals, regardless of the rice plant parts (root, shoot, or grain), compared to plants grown in the control soil. The distribution pattern of the three metals varied among the different parts of the plant. Regarding

accumulation, the root had the highest levels of Pb, followed by the shoot and grain. In contrast, the grain had the highest uptake of Cr, followed by the root and shoot. As for Ni, greater accumulation was observed in the shoot of rice than in the root and grain. All the metals (Pb, Cr, Ni) in grain are significantly low compared to control ($p < 0.0003$). Such restrictions in metal migration to plant in oil sludge-treated soil might be due to presence of increased organic matter which likely forms an organometallic complex thus reducing transfer. As compared to bioavailable metal accumulation from soil to rice root part, T2 ((V + OS) + *Periyonix excavates*) showed the highest metals uptake as compared to T4 ((V + OS) + *Eisenia Fetida*) treatment. Contrary to the findings of Trentin *et al.* (2019), who observed that excessive manganese (Mn) amelioration induced phytotoxicity, our study suggests that vermicompost-induced phytotoxicity occurs. However, it is worth noting that such contradictions can arise due to variations in composting technology, feedstock composition, soil type, and other environmental factors. The translocation of metals from soil to plant is influenced by several plant attributes, including root selectivity, plant uptake physiology, and rhizospheric nature (Mondal *et al.*, 2020). Root accumulation occurs due to direct exposure to soil metal, while shoot uptake is the result of translocated metal. Furthermore, the results of our study clearly demonstrate that the incorporation of oil sludge into the soil system retards metal translocation from soil to plant, possibly due to the formation of humic complexation, rhizospheric modification, or microbial modification. This finding is consistent with the results of a study by Goswami *et al.* (2017), who conducted a comparative analysis of cropping systems using vermicompost and drum compost.

Plants employ various mechanisms, such as accumulation, stabilization, chelation, and volatilization, to cope with metal toxicity (Islam *et al.*, 2020). Calculative measures such as bioconcentration factor, translocation factor, and bioaccumulation factor are used to assess the distribution pattern of metals among different plant parts under various treatments (Fig. 4). The bioconcentration factor (BCF) majorly deals with root metal uptake, where the trend was Pb > Ni > Cr. Typically, high concentrations of Pb facilitate easy movement to the xylem and phloem for better translocation. However, the minimal concentration of plant-available metal ($2-7 \text{ mg kg}^{-1}$) across the treatments may hinder its migration, as evidenced by an inconsequential translocation rate ($\text{TF} < 1$). The root accumulation of Cr is dependent on its oxidation state. Typically, Cr (VI) is soluble and can be readily absorbed by roots, although lower translocation ($\text{TF} < 1$) was

beneficial for the tested crop. As noted by (Page and Feller, 2015), Cr is retained in roots due to immobilization in the vacuoles of root cells or compartmentalization in cells to prevent its release through the xylem. A high translocation factor (TF) i.e., >1 concludes greater mobility from root to aerial parts. The T8 treatment (OS) exhibited the highest BAF and TF values for all metals compared to the T9 treatment (OS + F). No BAF and TF values were observed for the other treatments. Pb utilizes the symplastic pathway for its translocation, and it forms a metal complex with nicotianamine that gets translocated towards developing organs and matured seeds (Chakdar *et al.*, 2022; Wang *et al.*, 2022). The mobilization of metals (Pb, Cr, and Ni) is critical when it comes to bioaccumulation, which was found to be lower for T9, in the tested crop.

Risk assessment through FIAM (Free ion activity model) and FIAM-HQ of HMs in Treatments

In our experiment, for the purpose of predicting the uptake of HMs (Ni, Cr and Pb) by rice grains, the solubility-free ion activity model was implemented after post-harvest. The rice grain HMs variability may be explained by the solubility-free ion activity model (FIAM), which takes into account soil pH, soil organic carbon (OC), and a bioavailable component of HMs and the model parameters were represented in Table 3. Soil pH and soil organic carbon have been identified by Meena *et al.* (2016) as the primary factors influencing the solubility of HMs in polluted area. In our experiment, maximum accumulation of HMs Ni, Cr, and Pb in rice grain occurs only at T8 and T9 (post-harvest), hence only these two treatments were implemented in this model analysis. According to Table 3, β_1 values in the FIAM model are negative for all the HMs (Ni, Cr, and Pb). The model's parameters β_1 (negative value) show that pH and OC have an impact on the movement of heavy metals from the soil to rice grains in a favourable way. Therefore, the metal content of rice grains will also increase as pH or OC rise. As compared to 0-day, post-harvest pH and OC levels were substantially higher. As a result, the model proposed that rice grains may exhibit the absorption of nickel (Ni), chromium (Cr), and lead (Pb) by heavy metals (HMs). Numerous studies relate soil pH, the mobility of bioavailable forms of HMs, and soil OC to similar conclusions. (Mandal *et al.*, 2019, Banerjee *et al.*, 2023).

This study calculated the hazard quotient (HQ) of the FIAM model to determine the risk of HMs uptake in rice grains to human health. The highest limit of FIAM-acceptable HQ has been set to 0.5. When FIAM-HQ > 0.5, rice grains are considered as a threat to human health (Raj *et al.*, 2022). During post-harvest, the mean value of HQ represented in Table 3. These findings

showed that, with the exception of T8Ni, T9 Ni and T9 Cr, the hazard quotient values for T8Cr, T8Pb, and T9 Pb are greater than the safe level (FIAM-HQ 0.5). T8 and T9 treatments were amend with toxic oil sludge and rice grown on this treatment possess serious health hazard due to presence of toxic HMs (Cr and Pb) as obtained from HQ (FIAM) analysis. Our findings were supported by Golui *et al.* (2021) and Banerjee *et al.* (2023)

Target cancer risk assessment (SAMOE) and risk thermometer in different treatments

In order to comprehend potential health hazards, the daily exposure of people to HMs is evaluated. Human health risk from post-harvested rice has been calculated through the use of a "Risk thermometer." The risk category and level of concern for the "Risk thermometer" for HMs in rice grains are shown in Fig. 5.

To evaluate the toxicity of heavy metals (Ni, Cr, and Pb) in rice grains from treatments T8 and T9, the Risk Thermometer scale was employed. The findings from Table 3 indicate a significant health risk (Class 5) associated with rice grain consumption [T8Ni_{SAMOE}: 0.0020, T8Cr_{SAMOE}: 0.0005, T8Pb_{SAMOE}: 0.0024; T9Ni_{SAMOE}: 0.0023, T9Cr_{SAMOE}: 0.0006, T9Pb_{SAMOE}: 0.0027] for humans. Due to the addition of harmful waste oil sludge, it seems that eating rice in T8 and T9 could be harmful for health. The target cancer risk (TCR) of (SAMOE model) rice grain value was for T8Ni (1.88E-02), T8Cr (1.12E-02), T8Pb (1.47E-04); T9 Ni (1.26E-02), T9Cr (8.53E-03), and T9Pb (8.40E-05) above than prescribed limit (10^{-4}) (Li *et al.*, 2020). The experiment results show that intake of rice may not be safe for humans and that long-term use of these rice grains may cause Ni, Cr, and Pb toxicity in the near future.

Analysis of probable risk on various treatments of experiment using Fuzzy-TOPSIS

Employing the fuzzy-TOPSIS-MCDM (multi-criteria decision-making process), the most suitable alternative (bioavailable-metals) for heavy metals (HMs) concentrations in various treatments was determined. Based on the criteria of "Ni, Cr, and Pb," alternatives "P = treatments" were investigated for this research. (Table 4) displays the ideal best and ideal worst values and the parameters The entropy technique is used to calculate the criteria-weights ($W_j = 0.371, 0.253, \text{ and } 0.380$ respectively) of the predicted risk from concentration of HMs of ten treatments. According to the table T8 > T9 > T4 > T2 > T7 > T1 > T10 > T3 > T5 > T6 represents the order of HMs accumulation in treatments. The result showed that T8 and T9 were nearest from ideal best solution and T6 was the closest

worst ideal solution. Therefore, in ten different treatments, T8 and T9 showed the highest risk and least risk was observed in T6, T5, and T3. This observation was occurred in T8, and T9 due to the mixing of toxic oil sludge waste to the treatments, while T6, T5 and T3 exhibited the least risk due to presence of organic components (cow dung, vermicompost) in the experiment after -harvest. Our results were coinciding with Saif-Ud-Din *et al.* (2022) where risk was evaluated based on the accumulation of metals in different food resources.

Translocation and bioaccumulation in grain

Evaluation of yield and yield characteristics

The application of different vermicompost compositions and inorganic fertilizer (F) doses led to significant variations in yield components at harvest (Fig. 6). The crops treated with F (T10) showed the highest dry matter accumulation, followed by those treated with vermicompost and the untreated control (T1). However, for both rice grain and straw yield, crops treated with fertilizer and vermicompost with fertilizer showed significantly higher yields than control soil crops (Bhattacharyya *et al.* 2003). The use of inorganic fertilizers (T10) can quickly provide necessary nutrients for plant growth, leading to increased dry matter accumulation and crop yield compared to untreated (T8 and T9) plants. Furthermore, vermicompost containing humic acid substances and their decomposition products can also have a positive impact on plant growth, indirectly promoting dry matter accumulation and crop yield compared to untreated plants (Goswami *et al.* 2017).

The research study investigated the effects of vermicomposted oil sludge, as well as organic and inorganic amendments, on soil characteristics and plant health. The application of experimental vermicompost at realistic doses for submerged rice cultivation over a short-term did not demonstrate any adverse effects on the investigated soil quality indicators or crop yield parameters. Compost with a low concentration of oil sludge was found to be a more dependable organic amendment. However, compost with a high concentration of oil sludge may pose a risk of heavy metal bio-accumulation, albeit at a very low level, upon application. This study shed light on various scientific insights, such as monitoring microbial enzyme activity, conducting health risk evaluations using SAMOE and Fuzzy-TOPSIS, and assessing how microbial communities respond to metal-induced stress in vermicompost amended treatments. The study highlights the importance of maintaining a sustainable soil micro-ecosystem and managing industrial waste. Vermicomposting is a promising avenue for researchers

to explore in order to transform industrial waste into valuable organic fertilizers for agricultural use.

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