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# Biotransfer, bioaccumulation and detoxification of nickel along the soil - faba bean - aphid - ladybird food chain

Mohd Irfan Naikoo [a,*], Fareed Ahmad Khan [a], Ahmed Noureldeen [b], Jörg Rinklebe [c,d], Christian Sonne [e], Nishanta Rajakaruna [f,g], Parvaiz Ahmad [h,*]

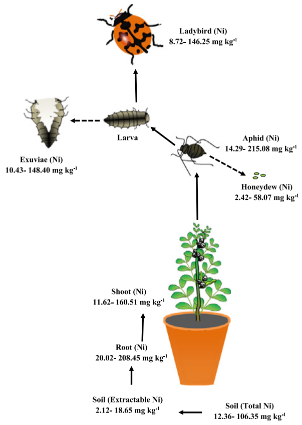
[a] Plant Ecology and Environment Laboratory, Department of Botany, Aligarh Muslim University, Aligarh, Uttar Pradesh 202002, India
[b] Department of Biology, College of Sciences, Taif University, P.O. Box 11099, Taif 21944, Saudi Arabia
[c] University of Wuppertal, School of Architecture and Civil Engineering, Institute of Foundation Engineering, Water- and Waste-Management, Laboratory of Soil- and Groundwater-Management, Pauluskirchstraße 7, 42285 Wuppertal, Germany
[d] Department of Environment, Energy and Geoinformatics, Sejong University, Seoul 05006, Republic of Korea
[e] Department of Bioscience, Arctic Research Centre (ARC), Aarhus University, Faculty of Science and Technology, Frederiksborgvej 399, PO Box 358, DK-4000 Roskilde, Denmark
[f] Biological Sciences Department, California Polytechnic State University, San Luis Obispo, CA, United States
[g] Unit for Environmental Sciences and Management, North-West University, Potchefstroom 2520, South Africa
[h] Department of Botany, S.P. College Srinagar, Jammu and Kashmir, India

## HIGHLIGHTS

- Nickel (Ni) concentration increased in a dose-dependent manner along the food chain.
- Ni biomagnified in faba bean roots and aphids while biominimized in ladybirds.
- Ni is eliminated through honeydew of aphids.
- Ni is eliminated by shedding of pupal exuviae during metamorphosis of ladybirds.

## GRAPHICAL ABSTRACT

The range of Ni content (mg $kg^{-1}$ dry weight) in the components of the soil-broad bean- aphid-ladybird food chain exposed to soil contaminated with varying doses of Ni (0–100 mg $kg^{-1}$ soil). Dashed arrows indicate the routes of elimination of Ni from the food chain.



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## ABSTRACT

Nickel release from anthropogenic and natural sources into the environment has resulted in biomagnification in terrestrial ecosystems. Here, we studied the biotransfer and toxicokinetics of nickel (Ni) along the soil < faba bean < aphid-ladybird food chain. The soil was spiked with the following Ni concentrations (in mg $kg^{-1}$ soil ww); T0 (0), T1 (25), T2 (50), T3 (75), and T4 (100). Our results revealed a significant elevation of Ni transfer with increasing Ni doses. The transfer coefficients (TC) indicate Ni biomagnified in soil to root and shoot to aphid >1 while the TC of the biominimisation of Ni in the aphid to ladybird was <1. The Ni removal from aphids through honeydew (excreta) and pupal exuviae during metamorphosis suggests a possible detoxification mechanism operating at two distinctive trophic levels, controlling the bioaccumulation of Ni along the examined food

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* Corresponding authors.
*E-mail addresses:* mdirfanmsbo@gmail.com (M.I. Naikoo), parvaizbot@yahoo.com (P. Ahmad).

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chain. Such toxicokinetics is not reported elsewhere and emphasize the need for future studies aiming to elaborate the possible mechanisms, potential components and physiological pathways associated with the bioaccumulation of Ni across food chains of the ecosystem.

## 1. Introduction

The increase in industrialization and urbanization has increased soil pollution by toxic heavy metals, which globally exacerbating environmental deterioration (Nascimento et al., 2014; Palansooriya et al., 2020). An upsurge in nickel (Ni) contamination levels in soil due to reckless industrial setups has also seriously damaged ecosystems (Antoniadis et al., 2019). Nickel exists naturally in soil derived from ultramafic rocks (Rajakaruna and Boyd, 2014), but anthropogenic actions lead to Ni pollution in non-ultramafic-derived soils (Dar et al., 2019; Tsadilas et al., 2019). Ni is a heavy metal, i.e., relentless, non-degradable and remaining in soil and accumulating consistently in soil horizons in higher than acceptable thresholds (D'Amore et al., 2005; Antoniadis et al., 2019). According to Kumar et al. (2019), Ni in Indian agricultural soils exceeds its limit for Indian natural soil guidelines. Various studies demonstrate that most metals are reactive and frequently poisonous, even at lower fixation rates that accumulate in individual organisms and thereby ecosystems (Dar et al., 2015; Gall et al., 2015; Antoniadis et al., 2017; Dar et al., 2017). The substantial increases of Ni in soil escalate the concerns of Ni transfer and biomagnification in food webs (Meindl and Ashman, 2013), and this may be especially problematic in developing countries (Butt et al., 2018; Morris et al., 2019). Nickel is required by organisms in trace amounts but become toxic if their limits of accumulation exceed the toxicity thresholds (Kabata-Pendias, 2010; Chaffai and Koyama, 2011; Shahzad et al., 2018). In 2008, Ni was categorized as “allergen of the year” (Gillette, 2008).

Plant species absorb and bioaccumulate Ni to varying degrees (Naikoo et al., 2019b; Tsadilas et al., 2019; Ferrero et al., 2020). Those plants that tend to withstand high Ni concentrations may pose a greater health risk to consumer organisms than the sensitive and adversely affected ones (Alloway, 1995; Dar et al., 2018). The Ni uptake in accumulator or hyperaccumulator plants increases its concentrations in plant shoot tissues (van der Ent et al., 2017) and enhances its accumulation in food chains and webs (Srivastava et al., 2005; Zhou et al., 2012; Dar et al., 2015; Naikoo et al., 2019a). Excessive concentrations of Ni reduce germination, retard shoot and root growth, interfere with absorption of other useful cations, and limit photosynthetic capacity (Ahmad and Ashraf, 2011).

Toxic concentrations of Ni can also influence cross-kingdom interactions such as plant-arthropod interactions (Walker et al., 2001; Boyd, 2009; Meindl and Ashman, 2014). Arthropods are ecologically and economically important component of terrestrial ecosystems. Arthropods are the indicators of environmental quality, principal consumers of primary production, linking lower trophic to higher trophic levels, including the transfer of heavy metals to upper trophic levels (Dallinger and Rainbow, 1993; Dar et al., 2017). Nickel transfer in plant-insect food chains has received little attention. In agroecosystems, the predatory arthropods are important natural biological pest control agents; Ni exposure may harm predatory ladybirds, often used in biological pest control, thus affecting pest management (Green et al., 2010; Gospodarek and Kafel, 2014; Kozlov, 2015; Dar et al., 2017; Naikoo et al., 2019a).

So far there are no studies available concerning the bioaccumulation of Ni in aphid-ladybirds nor on Ni soil contamination in subtropical and tropical agroecosystems. Thus, this study aims to investigate the current gap in knowledge of biotransfer and toxicokinetics of Ni along the soil - plant - arthropod food chain (soil < faba bean < aphid-ladybird). The food chain model consisted of *Vicia faba* L, having a large biomass and widespread geographic cultivation, black bean aphid - *Aphis fabae*, which is a severe pest of *Vicia faba*, and the aphid predatory ladybird-*Coccinella transversalis* as the third trophic level.

## 2. Material and methods

Soil (sandy loam) procured from agricultural farm fields of Aligarh Muslim University (AMU) was used in this study. The obtained soil was used to fill experimental pots spiked with different Ni concentrations and labelled as treatments (T0 = 0, T1 = 25, T2 = 50, T3 = 75 and T4 = 100 mg $kg^{-1}$ soil (w/w). Each treatment was replicated four times. Nickel stock solution of 10 mg $ml^{-1}$ (10 $gl^{-1}$) was created by dissolving Ni in nitrate form (Ni $(NO_3)_2$) in double-distilled water (DDW) and added to the soil treatment as described above. The pots containing 5.5 kg of soil were then incubated for 21 days to equilibrate (Naikoo et al., 2019a), followed by soil analysis for various chemical properties, including Ni concentration (both total and bioavailable fractions).

Post soil incubation, faba bean seeds (six seeds per pot) were sown at 0.5 cm depth. The pots were placed in a randomised block design (RBD) at the AMU Glass House (set to 16:8 h day-night system and 26 °C ± 1 °C) and sprinkled with DDW at regular intervals. Under each pot, plastic trays were kept to collect the leachate and percolated water and reused when watering. At 5 to 6 leaf seedling stage, three *Vicia faba* seedlings were retained and allowed to grow in each pot following thinning.

To examine the effects of Ni on faba bean growth, 30 and 60 days old *V. faba* plants and leaves were sampled for chlorophyll content and dry mass, respectively. At the flowering stage, two hundred laboratory-cultured adult faba bean aphids (*Aphis fabae*) free from Ni contamination were transferred and allowed to infest the faba bean plants for three weeks. Each pot was subsequently covered with sleeve cages of fine netting for preventing aphid movement among Ni treatments (Dar et al., 2017). After infesting, aphids were collected from each pot and separated into two groups, one for Ni estimation and other to be stored in a deep freezer (Model: DW 40L6226, Haier Bio-medical, China) at -18° C to feed the fourth instar larvae of ladybirds (*Coccinella transversalis*).

Faba bean plants were also sampled for determining the amount of Ni in tissue. Nickel content in aphid honeydew was estimated by modifying the methodology of Crawford et al. (1995). Fresh, clean honeydew was challenging to collect in sufficient quantity from the feeding aphid colonies for Ni analysis. Most of it becomes trapped on the leaf or stem surfaces. Plant stem and leaves, on which aphids fed, were collected from all pots and were divided into two equal groups. One group of plant samples were washed with distilled water to remove the honeydew and then dried. Plant samples from another group were dried without washing. The Ni content present in the honeydew was calculated by subtracting the Ni concentrations between washed and unwashed plant parts (Crawford et al., 1995).

The aphid feeding to predator ladybird larvae was done as described by Dar et al. (2017). Twenty larvae (fourth instar) of the ladybirds were equally divided into five treatments. Each larva was reared separately and fed fresh frozen aphids collected from one of the pot cultures in a petri dish (diameter = 10 cm) containing filter paper moistened with double distilled water. All petri dishes were covered by fine nettings fixed with rubber bands. These petri dishes containing larvae were then placed in a controlled environment cabinet (set to 25 °C and 16:8 h day-night regime). The larva was reared individually (to disallow cannibalism and to assess the consumption precisely). Consumption of aphids by individual larva was measured daily, and fresh (frozen) aphids were added to the petri dishes following Dar et al. (2017). The feeding of ladybird larvae continued until the emergence of adult ladybirds. The newly developed adult ladybirds were weighed and kept in a deep freezer at −18 °C to measure the Ni content.

### 2.1. Soil property analysis

Soil pH was determined with a digital pH meter (M-182, India) in a soil: water suspension (1:2.5 w/v). Soil carbon and nitrogen content were measured by Walkley, and Black's titration (Jackson, 1958) and Micro-Kjeldahl (Bremner, 1960) methods, respectively.

### 2.2. Nickel analysis

Nickel content in plant, aphid and ladybird samples was determined by modifying the methodology of Allen et al. (1986). Three soil samples from each pot were collected and air dried, mashed and sieved through a fine 2 mm mesh. 1 g of each soil sample was digested at 80 °C using a mixture of concentrated tri acid ($HNO_3/H_2SO_4/HClO_4$; 5:1:1 v/v). The extract was brough to room temperature and filtered through a Whatman #42 filter paper, and brought to 50 ml by diluting with DDW. Each filtrate was analysed for total Ni using Atomic Absorption Spectrometry (AAS) (model: GBC,932 plus - GBC Scientific Instruments, Braeside, Australia). The bioavailable fraction of Ni in soil was determined by following the diethylene triamine pentaacetic acid (DTPA) extraction method of Lindsay and Norvell (1978). The AAS with an air/acetylene flame, containing a Ni cathode lamp running at settings; current 4.2 mA, wavelength 232.0 nm and slit width 0.2 nm was used for Ni analysis. Prior to the analysis of the samples, AAS was calibrated by Milli-Q water for zeroing the instrument. From a standard solution of Ni (1000 $\mu g/ml^{-1}$), three different known concentrations in increasing order were run, with blank in between standards, to ensure the baseline zero point. Linear graph of calibration (absorbance vs concentration) was then produced followed by the analysis of samples.

The shoots and roots of faba bean plants were washed with DDW, and dried in a forced draft oven at 75 °C for 3 days. The dried samples were finely powdered using a kitchen grinder and then sieved under a 2 mm mesh size. The finely powdered root and shoot samples (0.3 g) were digested at 80 °C using a mixture of concentrated tri acid ($HNO_3/H_2SO_4/HClO_4$; 5:1:1 v/v). The samples prepared were analysed for Ni by using Atomic Absorption Spectrometry (AAS) (model: GBC, 932 plus Braeside, Australia). The methodology of Dar et al. (2015) was followed for the digesting samples of aphid, ladybird and their exuviae (from each treatment). Samples of aphids (20 mg), individual ladybirds and exuviae of ladybird pupa (0.5 mg) were prepared and digested as described above. The final volume of digested solution was brought to 5 ml by diluting with DDW. Nickel was quantified using AAS after proper calibration as defined earlier (model: GBC,932 plus Braeside, Australia; Ni Detection Limit, 0.1 ppm). The analytical quality grade chemicals and reagents supplied by Sigma-Aldrich were used in the study. To confirm the analytical quality, Certified Reference Material (CRM)- GBW - 07402 for soil, NIM - GBW- 10048 (Celery plant) for plants samples and CRM-GBW - 008552 (pork muscles) for insects was used with mean recoveries for Ni recorded at 96.7%. Process contamination was also checked by digesting procedural blanks.

### 2.3. Calculations and data analysis

The analyses of the data were done through SPSS statistical software (IBM 20). Duncan's multiple range test (DMRT) was applied to data to check the significance of differences at $p < 0.05$ between various treatments. Origin 2019 software was used for generating graphs. The Ni transfer coefficients were determined by calculating the concentration of Ni at the receiving end to Ni content at source. Nickel content in ladybird pupa before the emergence of its adult ladybird was determined by adding the Ni content obtained in the exuviae to that of the newly emerged ladybird. Percentage of Ni removal via exuviae of pupa was calculated as:

$$\text{Percentage of Ni removal through pupal exuvia} = \frac{\text{Ni content in an individual ladybird}}{\text{Ni content in an individual pupa}} \times 100$$

## 3. Results

### 3.1. Effect of Ni on soil properties

Soil amended with varying Ni levels had no statistically significant ($p > 0.05$) effect on the pH and organic C (%). The nitrogen content significantly ($p < 0.05$) increased at higher Ni doses (Table 1). The concentration-dependent and significant ($p < 0.05$) increase of soil total and DTPA extractable Ni levels were recorded (Table 1).

Different Ni treatments applied to the soil did not change the percent organic C content of the soil. The increase in the soil nitrogen is attributed to soil Ni application as nitrate salt ($Ni(NO_3)_2$). The soil Ni content (both soil total and DTPA extractable fraction) increased considerably with different Ni amendments but were below the Permissible Limits of Indian standards (75–150 mg $kg^{-1}$; Awashthi, 1999; Nicholson and Chambers, 2008) as well as International Standards (e.g., Austria ~60 mg $kg^{-1}$, France ~65 mg $kg^{-1}$, UK ~230 mg $kg^{-1}$) (Antoniadis et al., 2019).

### 3.2. Nickel effects on faba bean growth

Significant reduction in chlorophyll *a* and b content was recorded in a dose dependent manner as compared to the control ($p < 0.05$)

**Table 1**
Chemical properties and Ni concentrations (total and extractable) of soil treated with different doses of Ni (mean ± SE, n = 4). Values with different small superscript letters in each group are significantly different from each other at $p < 0.05$ as per DMRT.

| Parameters | T0 | T1 | T2 | T3 | T4 |
|---|---|---|---|---|---|
| pH | $7.81 \pm 0.04^a$ | $7.77 \pm 0.03^a$ | $7.74 \pm 0.05^a$ | $7.74 \pm 0.04^a$ | $7.72 \pm 0.03^a$ |
| Organic C (%) | $0.72 \pm 0.04^a$ | $0.71 \pm 0.03^a$ | $0.71 \pm 0.03^a$ | $0.73 \pm 0.03^a$ | $0.74 \pm 0.03^a$ |
| Total N (%) | $0.17 \pm 0.02^b$ | $0.19 \pm 0.02^b$ | $0.22 \pm 0.02^{ab}$ | $0.24 \pm 0.02^{ab}$ | $0.28 \pm 0.03^a$ |
| Total nickel in soil (mg $kg^{-1}$) | | | | | |
| Ni | $12.36 \pm 0.44^e$ | $36.82 \pm 1.64^d$ | $59.78 \pm 2.05^c$ | $82.23 \pm 3.07^b$ | $106.35 \pm 9.51^a$ |
| DTPA extractable nickel in soil (mg $kg^{-1}$) | | | | | |
| Ni | $2.12 \pm 0.08^e$ | $6.36 \pm 0.21^d$ | $10.58 \pm 0.34^c$ | $14.36 \pm 0.40^b$ | $18.65 \pm 0.44^a$ |

T0: control soil; T1: 25 mg $kg^{-1}$; T2: 50 mg $kg^{-1}$; T3: 75 mg $kg^{-1}$; T4: 100 mg $kg^{-1}$ Ni treatments.

(Fig. 1a, b). The dry weight of faba bean decreased significantly at higher doses of Ni ($p < 0.05$) (Fig. 1c). However, for treatment T1 chlorophyll *a* and b content as well as dry weight of faba beans were statistically ($p > 0.05$) similar. The Ni content in the roots of faba bean growing in soils treated with increasing levels of Ni enhanced significantly ($p < 0.05$). The maximum Ni content of 208.45 mg kg$^{-1}$ dry matter was reported for T4, while the control (T0) contained Ni content of 20.02 mg kg$^{-1}$ dry roots (Fig. 2a). The Ni transfer coefficient from soil to faba bean roots showed an increasing trend, ranging from 1.62 to 1.96 for soil total Ni to root total Ni and 9.44 to 11.18 for Ni extractable fraction (DTPA) to root Ni concentration (Table 2).

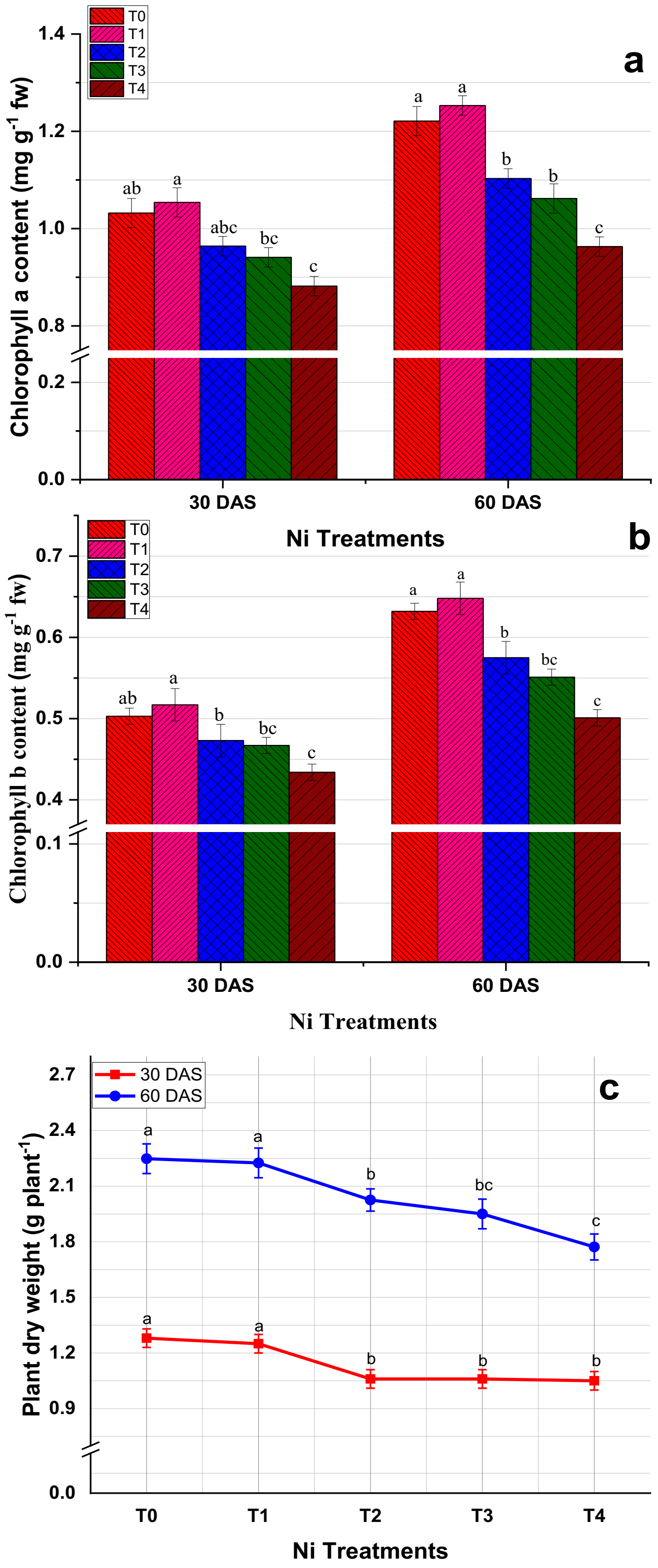

**Fig. 1.** Impact of different concentrations of Ni on the content of (a) chlorophyll *a*, (b) chlorophyll *b* and (c) dry weight in *Vicia faba* at 30 and 60 days after sowing (Mean ± SE; $n = 4$). Different letters indicate significant difference at $p \le 0.05$ as per DMRT.

### 3.3. Biotransfer of Ni in food chain

#### 3.3.1. Nickel transport from roots to shoots

The amount of Ni moved to faba bean shoots varied significantly ($p < 0.05$) among Ni treatments. The maximum Ni content of 160.51 mg kg$^{-1}$ dry shoots was calculated for higher Ni treatment whereas in control, 11.62 mg kg$^{-1}$ Ni in dry shoots was noted (Fig. 2b). The Ni transfer coefficient for roots to shoots of faba bean was calculated <1 (~0.77), in all the Ni treatments (Table 2).

#### 3.3.2. Nickel transport from shoots to aphids

The statistically significant increases of Ni levels with respect to treatments were observed in aphids feeding Ni contaminated faba bean shoots ($p < 0.05$). Aphids feeding on T4 faba bean shoots accumulated highest Ni content of 215.08 mg kg$^{-1}$ dry matter whereas the Ni amount in aphids raised on faba bean of control treatment was only 14.29 mg kg$^{-1}$ dry matter (Fig. 2c). Transfer coefficient of Ni (Table 2) for faba bean shoots to aphids showed a steady increase (from 1.23 to 1.34) as compared to the TCs of root to shoot (from 0.58 to 0.77).

#### 3.3.3. Nickel transport from aphids to ladybirds

Nickel accumulated significantly in newly emerged adult ladybirds feeding on Ni contaminated aphids ($p < 0.05$) (Fig. 2d). The maximum Ni accumulated in adult ladybirds was recorded for T4 (146.25 mg kg$^{-1}$) while for control it was only 8.72 mg kg$^{-1}$ (Fig. 2d). The transfer coefficients of Ni from aphids to ladybirds showed a steady decrease as compared to transfer coefficients of the shoot to aphid and were valued below 1 (~0.68) in all Ni treatments (Table 2).

### 3.4. Nickel elimination with honeydew of aphids

The aphids excrete some amount of accumulated Ni via honeydew. Nickel levels in aphid honeydew increased in relation to the Ni concentrations applied in the soil. The ratio of the amount of Ni in honeydew to that of aphid showed striking variations and increased with increasing metal exposure, ranging from 0.15 to 0.26 (Table 3). The concentration of Ni in aphid honeydew in control (T0) treatment was 2.42 mg kg$^{-1}$ dry weight while in T4, it was 58.07 mg kg$^{-1}$ dry matter. The amount of Ni excreted with honeydew was positively correlated with Ni content transferred to aphids via faba bean shoots (Fig. 3a).

### 3.5. Nickel sequestration in exuviae of ladybirds

Ladybirds minimized their metal body burden by sequestering some of the Ni content in pupal exuviae. Significant Ni elimination through ladybird pupal exuviae was observed in a concentration-dependent manner ($p < 0.05$) (Table 3). The amount of Ni eliminated via exuviae in control was 10.43 mg kg$^{-1}$ dry matter, while for the higher treatment (T4), it reached up to 148.40 mg kg$^{-1}$ dry matter. The extent of Ni sequestration through the exuviae of pupa shows a strong and positive correlation with Ni accumulated in the pupal body (Fig. 3b).

### 3.6. Effects of Ni on the ladybird predation rate

The mean feeding rate of aphids by ladybirds, i.e., the predation rate, showed no statistical difference when feeding on aphids contaminated with Ni up to T3 level ($p > 0.05$). However, the average aphid

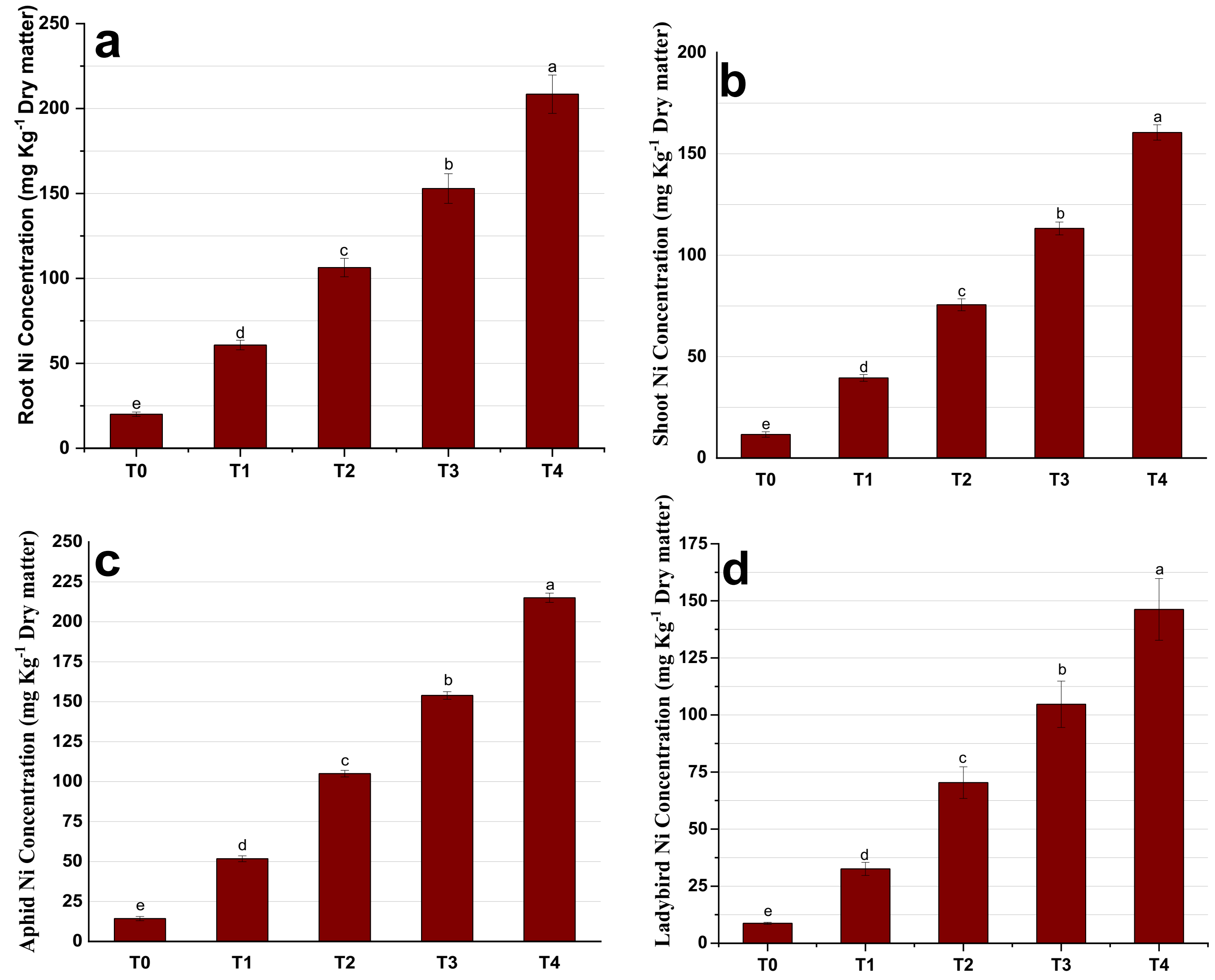

**Fig. 2.** Influence of different Ni concentrations on Ni accumulation in (a) roots of *Vicia faba*, (b) shoots of *Vicia faba*, (c) aphids and (d) ladybirds (Mean ± SE; $n = 4$). Different letters indicate significant difference at $p \le 0.05$ as per DMRT.

consumption by the larvae of fourth instar predatory ladybirds reduced statistically at T4 Ni level ($p < 0.05$) (100 mg Ni kg$^{-1}$ soil) (Fig. 3c). No statistical difference in the biomass of aphids and ladybirds was observed ($p > 0.05$) (Table 4).

## 4. Discussion

### 4.1. Nickel effect on growth of faba bean

The decrease in chlorophyll pigment in present study corroborates with the findings of Shahid et al. (2014) and Piršelová et al. (2016)

**Table 2**
Transfer coefficients of Ni concentrations between various components of the soil – plant – aphid – ladybird food chain on amendment of soil with various levels of Ni.

| Food chain components | T0 | T1 | T2 | T3 | T4 |
|---|---|---|---|---|---|
| Total soil to root | 1.62 | 1.65 | 1.78 | 1.86 | 1.96 |
| Extractable soil to root | 9.44 | 9.55 | 10.06 | 10.65 | 11.18 |
| Root to Shoot | 0.58 | 0.65 | 0.71 | 0.74 | 0.77 |
| Shoot to aphid | 1.23 | 1.31 | 1.39 | 1.36 | 1.34 |
| Aphid to ladybird | 0.61 | 0.63 | 0.67 | 0.68 | 0.68 |

T0: control soil; T1: 25 mg kg$^{-1}$; T2: 50 mg kg$^{-1}$; T3: 75 mg kg$^{-1}$; T4: 100 mg kg$^{-1}$ Ni treatments.

**Table 3**
Ni content (mg kg$^{-1}$ dry weight) excreted via honeydew of aphids and in pupal exuviae of predatory ladybirds exposed to varying levels of Ni concentration (mean ± SE; $n = 4$). Values with different superscript letters in each group are significantly different from each other at $p < 0.05$ as per DMRT.

| Treatments | Honeydew | Pupal exuviae |
|---|---|---|
| T0 | 2.42 ± 0.38$^{e}$<br>(0.17) | 10.43 ± 1.54$^{e}$<br>(14.25) |
| T1 | 9.82 ± 0.98$^{d}$<br>(0.19) | 37.76 ± 1.91$^{d}$<br>(14.12) |
| T2 | 22.05 ± 1.38$^{c}$<br>(0.21) | 78.75 ± 3.76$^{c}$<br>(13.87) |
| T3 | 38.48 ± 1.75$^{b}$<br>(0.25) | 112.36 ± 5.85$^{b}$<br>(13.29) |
| T4 | 58.07 ± 2.58$^{a}$<br>(0.27) | 148.40 ± 9.45$^{a}$<br>(12.67) |

T0: control soil; T1: 25 mg kg$^{-1}$; T2: 50 mg kg$^{-1}$; T3: 75 mg kg$^{-1}$; T4: 100 mg kg$^{-1}$ Ni treatments.
Values within parenthesis in honeydew columns are the ratios of Ni content in honeydew vs Ni content in aphids.
Values within parenthesis in exuviae columns are percentages of total Ni content lost via exuviae.

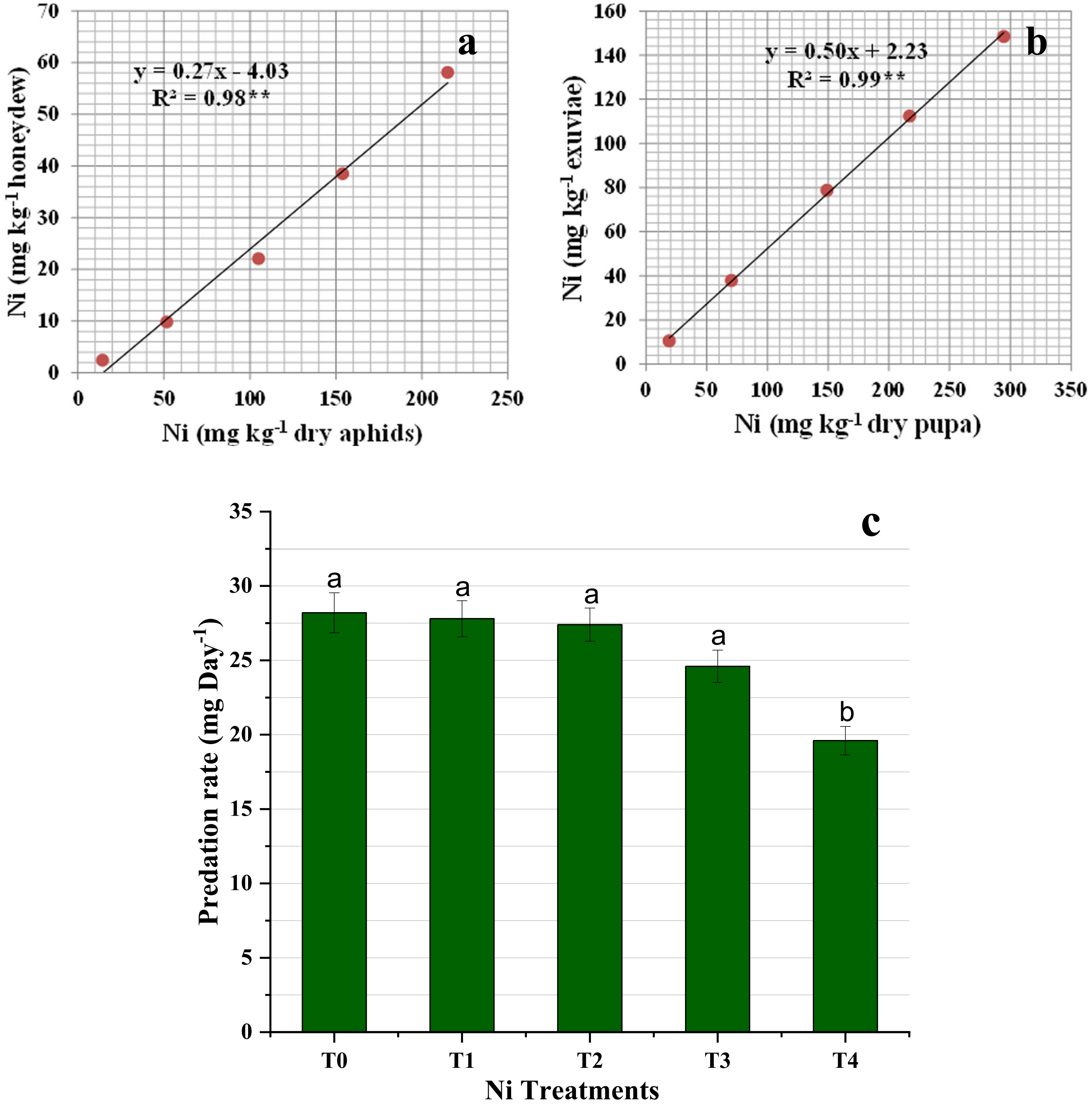

**Fig. 3.** Equation of linear regression and square of correlation coefficients ($R^2$) plotted between 2 variables. (a) Ni in independent variable, aphid vs dependent variable honeydew, (b) Ni in independent variable ladybird pupa vs dependent variable pupal exuviae, (c) Impact of different concentrations of Ni on the consumptions of aphids by ladybird larvae (mean SE; n=4). Different letters indicate significant difference at $p \leq 0.05$ as per DMRT.

who also showed the reduction in chlorophyll pigments in *Vicia faba* leaves under heavy metal stress. Exposure of excessive Ni to plants can disrupt chloroplast structure, block synthesis of chlorophyll pigments and electron transport reactions, reduce enzyme activity in Calvin Cycle, alter the composition plasma membrane and limit the intake of $CO_2$ due to stomatal closure, eventually hampering photosynthetic activity (dos Reis et al., 2017; Chatzistathis et al., 2019). A likely mechanism for such changes may be Ni induced decline of $H_2O$ content or oxidative stress due to peroxidation of membranes (Chatzistathis et al., 2019; Nazir et al., 2020). Nickel is an essential plant micronutrient (Taiz and Zeiger, 2010), however, when it exceeds the critical limit, it becomes toxic and hampers growth and development of plants (Shahzad et al., 2018; Morris et al., 2019). The Ni induced decrease in plant growth parameters may be due to alteration in one or many factors, including inhibition of mitotic cell divisions in root meristems (Morris et al., 2019; Tsadilas et al., 2019). In addition, a decline in transpiration rate and water balance disruption and increases in the level of endogenous abscisic acid that promotes stomatal closure may also play a role (Chen et al., 2009; Sreekanth et al., 2013; Chatzistathis et al., 2019). Ni inhibits shoot elongation through the suppression of cell division and through necrosis and

**Table 4**
Variation in fresh and dry mass (mg individual$^{-1}$) of aphids and newly emerged adult ladybirds exposed to various application rates of Ni (mean ± SE; $n = 4$). Values with different superscript letters in each group are significantly different from each other at $p < 0.05$ as per DMRT.

| Amendments | Fresh mass (mg) | | Dry mass (mg) | |
|---|---|---|---|---|
| | Aphid | Adult ladybird | Aphid | Adult ladybird |
| T0 | $0.22 \pm 0.02^{a}$ | $33.15 \pm 1.37^{a}$ | $0.033 \pm 0.003^{a}$ | $6.91 \pm 0.28^{a}$ |
| T1 | $0.22 \pm 0.02^{a}$ | $32.25 \pm 1.29^{a}$ | $0.033 \pm 0.002^{a}$ | $6.79 \pm 0.23^{a}$ |
| T2 | $0.21 \pm 0.01^{a}$ | $31.68 \pm 1.18^{a}$ | $0.032 \pm 0.003^{a}$ | $6.68 \pm 0.20^{a}$ |
| T3 | $0.19 \pm 0.02^{a}$ | $30.65 \pm 1.02^{a}$ | $0.030 \pm 0.002^{a}$ | $6.52 \pm 0.17^{a}$ |
| T4 | $0.19 \pm 0.01^{a}$ | $30.15 \pm 0.94^{a}$ | $0.030 \pm 0.001^{a}$ | $6.49 \pm 0.19^{a}$ |

T0: control soil; T1: 25 mg kg$^{-1}$; T2: 50 mg kg$^{-1}$; T3: 75 mg kg$^{-1}$; T4: 100 mg kg$^{-1}$ Ni treatments.

chlorosis due to the interruption in the uptake and metabolism of Fe (Chatzistathis et al., 2019; Shahzad et al., 2018).

## 4.2. Biotransfer of Ni in food chain

### 4.2.1. Nickel transport from soil to roots

The roots of faba bean accumulated maximum Ni content in the studied food chain (Fig. 2a). The transfer coefficients of Ni were also highest for soil to root transfer in the food chain. Our findings corroborate with previous findings of Nadgórska-Socha et al. (2013), reporting increased Ni concentrations in *Vicia faba* roots when grown in heavy metal amended soil. Likewise, roots of various plant species accumulated more heavy metals as compared to aboveground parts (Shaheen and Rinklebe, 2015; Shaheen et al., 2015; Dar et al., 2017; Naikoo et al., 2019b). The entry of Ni in the plant roots is through symports with zinc present in plasma membranes of epidermal root cells (Deng et al., 2014). Dalir and Khoshgoftarmanesh (2014) suggested that amino acids regulate Ni uptake in plants by forming complexes with it in root apoplasm and/or symplasm after being absorbed by root cells in the free hydrated cationic form (Dalir and Khoshgoftarmanesh, 2014, 2015). The amino acid, histidine, shows a strong affinity towards $Ni^{2+}$ ions (Krämer et al., 1996; Kerkeb and Krämer, 2003). These Ni-chelates complexes are believed to be either absorbed by the cells of roots or transported via plasmalemma and, once inside the root cells, Ni is disassociated from the ligand and taken up by the plant, (Dalir and Khoshgoftarmanesh, 2014; Dalir and Khoshgoftarmanesh, 2015). Additionally, organic acids (malate and citrate) form complexes with Ni and assist in Ni uptake (Schaumlöffel et al., 2003; Montargès-Pelletier et al., 2008; Naicker et al., 2016). Moreover, it is believed that the mechanisms involved in plant Mn, Fe, and Zn uptake is responsible for Ni hyperaccumulation as well (Chatzistathis et al., 2019; Ferrero et al., 2020).

### 4.2.2. Nickel transport from root to shoot

Nickel translocation from roots to the shoots of *Vicia faba* increased in a concentration-dependent manner while their transfer coefficients were lower than that of soil-root transfer. Several studies have reported similar findings in *V. faba* and other plants (Probst et al., 2009; Nadgórska-Socha et al., 2013; Piršelová et al., 2016). Once taken up by the roots, Ni ions are translocated to the aboveground parts of the plants through xylem transpiration stream (Peralta-Videa et al., 2002; Gong et al., 2003). This transport is regulated through various chelators such as phytochelatins and metallothioneins, organic acids (malic and citric acids), amino acids and some peptides (nicotianamine and histidine) that bind metals in cytosol and other subcellular organelles for their passage and accumulation in the plants (Krämer et al., 1996; Douchkov et al., 2005; Dalir and Khoshgoftarmanesh, 2014, 2015). The Ni transport from roots to shoots via xylem and aided by transpiration stream is believed to be tightly regulated by metal ligands, such as nicotianamine (Pianelli et al., 2005), histidine (Kerkeb and Krämer, 2003) and organic acids like citric and malate acid (van der Ent et al., 2017). These metal ligands act as intracellular chelators, binding Ni in the cytosol or subcellular components for its transportation and accumulation in plants. Moreover, ZIP/IRT family transporters (Ferrero et al., 2020) and Oligopeptide transporters (OPT) are also believed to translocate Ni in plants (Deng et al., 2018; Schaaf et al., 2004).

### 4.2.3. Nickel transport from shoot to aphid

The TC of Ni from broad bean shoots to aphids >1 indicate biomagnification of Ni in aphids. Earlier reports document Ni bioaccumulation in phytophagous arthropods and biomagnification in *Melanotrichus boydi* feeding on Ni hyperaccumulator *Streptanthus polygaloides* (Schwartz and Wall, 2001; Peterson et al., 2003; Wall and Boyd, 2006). The TC of Ni decreased in aphids feeding on faba bean plants grown at higher Ni levels due to minimal feeding of aphids on the faba bean shoots accumulating higher amounts of Ni. The significant amount of Ni excreted via honeydew seems to be an important pathway of Ni detoxification in aphids. Crawford et al. (1995) reported copper and cadmium excretion via honey dew of *Aphis fabae*. The elimination of Cd, Pb and Zn via honeydew of mustard aphid and beetle exuviae has been reported in our earlier studies (Dar et al., 2015, Dar et al., 2017 and Naikoo et al., 2019a), however, the mechanisms of metal detoxification were not confirmed. After tapping into plant shoots and sucking phloem sap, the Ni enters midgut epithelial cells of arthropods and binds with metallothioneins and become metabolically inactive (Zhou et al., 2015a; Zhou et al., 2015b). The metallothionein - metal complexes are fused into granules formed by cell lysosomes and become insoluble (Luoma and Rainbow, 2008; Naikoo et al., 2019b). Thus, Ni is localized in the midgut and is prevented from entering into the tissues of organisms (Zhou et al., 2015a; Zhou et al., 2015b). These granules may be retained or excreted by organisms (Hare, 1992). If retained, Ni will be biomagnified and, if excreted, bio-minimized (Dallinger and Rainbow, 1993; Zhou et al., 2015b).

### 4.2.4. Nickel transport from aphids to ladybirds

The TC of Ni from aphids to adult ladybirds were lower than the TCs of the shoot to aphid, pointing to Ni biominimization in predator ladybirds. Ladybirds feed voraciously for its faster growth during fourth instar larval stage (Naikoo et al., 2019a) and therefore the majority of metal accumulation may happen in the 4th instar larval stage (Gintenreiter et al., 1993). During metamorphosis, the ladybirds eliminate part of the accumulated metals by shedding pupal exuviae during the pupation process (Dar et al., 2015; Dar et al., 2017; Naikoo et al., 2019b). Thus, the Ni content in the newly emerged ladybirds is subsequently lower than that of larvae. Studies by Dar et al. (2017) showed the elimination of Cd, Pb and Zn via pupal exuviae during the metamorphosis of *Coccinella septempunctata*. Similarly, Pb excretion through exuviae of ladybirds was observed by Naikoo et al. (2019a).

The amount of Ni in adult ladybirds was lower than in its pupal exuviae, indicating loss of Ni during metamorphosis as also shown earlier by Sang et al. (2018). Nickel is generally a non-essential element, and only a single enzyme in eukaryotes is known which needs Ni as a cofactor, but that protein is lacking in arthropods (Green and Walmsley, 2013). Insect species have evolved numerous morphological, physiological, and behavioral adaptations to regulate Ni body burden. The direct elimination from the gut is the primary defensive strategy of insects as described in *Epilachna nylanderi* against excess dietary Ni (Mesjasz-Przybyłowicz et al., 2014). In arthropods, Ni is accumulated in midgut epithelium cells as granular concretions and subsequently eliminated through both apoptotic or necrotic pathways (Klag et al., 2002; Przybyłowicz et al., 2004; Przybyłowicz et al., 2005) or excreted by organisms during epithelial cell renewal or by apocrine and holocrine secretions (Ludwig and Alberti, 1988; Przybyłowicz et al., 2004; Nakonieczny, 2007). It is believed, that arthropods also eliminate Ni from the anterior part of midgut into the hindgut through transmembrane transport via malpighian tubules as described in *Chrysolina clathrate* (Przybyłowicz et al., 2005; Nakonieczny, 2007).

## 4.3. Impact of Ni on aphids and ladybirds

The aphid biomass (fresh and dry mass) did not alter statistically as also reported by Boyd and Martens (1999) for biomass of pea aphids (*Acyrthosiphon pisum*) feeding on Ni-hyperaccumulating plant (*Streptanthus polygaloides*). Their results suggest that aphids may be relatively insensitive to their Ni hyperaccumulating host plant (Boyd and Martens, 1999; Konopka et al., 2013).

The reduction in consumption of aphids (at T4 levels of heavy metal treatments) by predatory ladybirds appears to be due to Ni accumulation at higher amounts in aphid bodies. It may be concluded that Ni accumulated in the bodies of aphids (*Aphis fabae*) at lesser concentrations did not deter their predator (*Coccinella transversalis*). But, the aphids of

T4 treatment may have strategically reduced their palatability and thereby limiting the consumption by the ladybirds. This suggests that Ni may be sub-lethal for ladybirds even in the lack of any biomagnification. Thus, it is crucial to understand the effects of sub-lethal amounts of Ni accumulation in aphids and its eventual impact on the well-being of natural biological control agents such as ladybirds for more effective integrated pest management practices.

Nickel treatments had no significant influence on the biomass (fresh and dry mass) of ladybirds. Also, the Ni accumulation was not lethal for ladybirds, however, the reduction of ladybird biomass points towards sub-lethal effects occurring at higher Ni accumulation levels. Arthropods can store and detoxify heavy metals (Crommentuijn et al., 1995) to a certain threshold. Beyond this limit, it becomes impossible for arthropods to detoxify Ni effectively and the consistent increase in heavy metals concentration may enhance the toxicity in arthropods, thereby turning sublethal concentrations to lethal levels (Crommentuijn et al., 1995; Dar et al., 2017; Naikoo et al., 2019a).

## 5. Conclusion

Nickel biomagnified in aphids at the second trophic level although aphids excreted a proportionate amount of Ni with increasing Ni exposure levels. The accumulation of Ni in newly emerged ladybirds increased proportionately with Ni levels in the soil. We observed no biomagnification of Ni in ladybirds at the third trophic level which is due to effective Ni elimination mechanism via pupal exuviae. These elimination strategies by arthropods suggest possible detoxification mechanisms operating at different trophic levels. The mobility of Ni in different trophic levels and their resulting ecotoxicological effect is a matter of concern. Furthermore, this information of tri-trophic transfer of Ni in the plant-arthropod food chain may be of significance for bioremediation of Ni contaminating soils.

## CRediT authorship contribution statement

MIN and FAK designed and performed the experiments. AN and NR analysed the data and helped in paper writing. JR, CS and PA revised the manuscript to the present form. All authors agree to submit this manuscript.

## Declaration of competing interest

The author declares no conflict of interest regarding the publication of this paper.

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