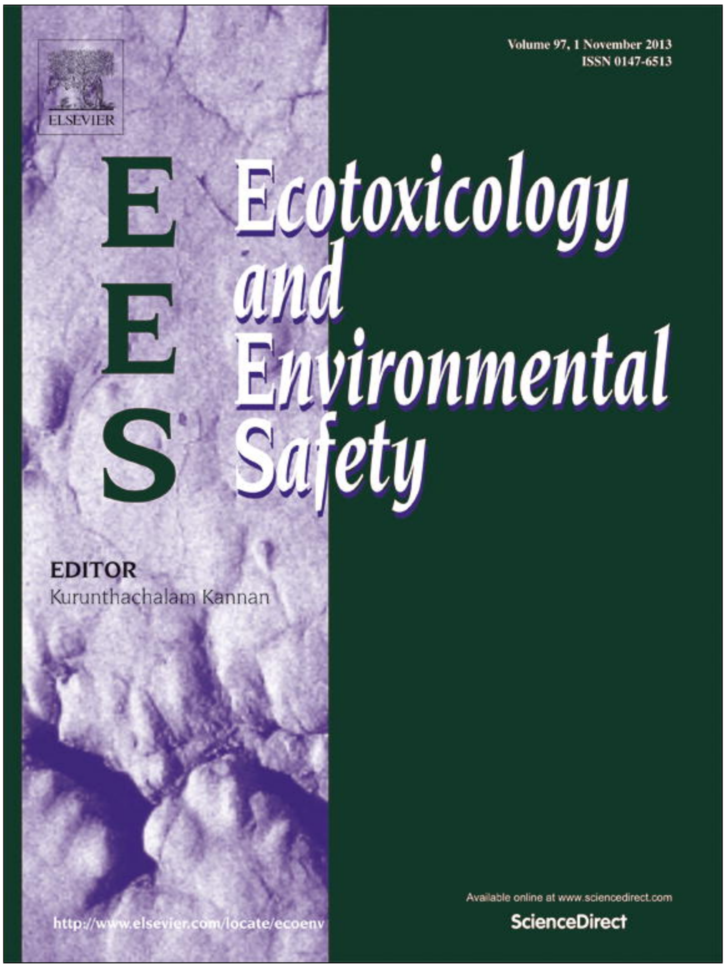
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Diet composition as a cause of different contaminant exposure in two sympatric passerines in the Middle Urals, Russia

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A B S T R A C T

Contaminant exposure can vary between species but primary causes of it are often unclear. In order to estimate heavy metal intake of two sympatric passerines – *Ficedula hypoleuca* Pall. and *Parus ater* L. – we studied nestling diet and metal concentrations in prey invertebrates, near the Middle Ural copper smelter and in an unpolluted area. Diet of *P. ater* contained more Cu, Cd and Zn compared to *F. hypoleuca* and the same amount of Pb. Contribution of different prey taxa to bird metal intake was not equal to their dietary proportion. Proportion of Cu, Zn, Pb and Cd provided to birds by spiders and molluscs, as well as Cd and Pb provided by ants and imagoes Diptera, exceeded their dietary fraction by several times. In contrast, the contribution of Lepidoptera and sawfly larvae to bird metal intake was less than their dietary proportion. Pollution-related changes in the diet modified bird contaminant exposure along with pollutant concentrations in preys.

1. Introduction

Contaminant exposure is one of the key factors determining toxic effects. Researchers use different measures of exposure including pollutant concentrations in food, faeces and organs of birds (Berglund et al., 2010, 2011; Eeva and Lehikoinen, 1996; Janssens et al., 2003; Nyholm, 1995; Schipper et al., 2008). Studies of pollutant intake of birds are scarce and usually deal with one species (Morrissey et al., 2005; Schipper et al., 2012), which does not allow comparisons between species.

The aim of the study was to estimate contaminant exposure in two forest passerines in the Middle Urals, Russia, both near a metallurgy complex and in an unpolluted area, and to estimate the contribution of different food components to bird metal intake. We tested two hypotheses. (1) Different bird species can experience different contaminant exposure within the same habitat due to differences in diet structure. (2) Alteration of the diet of insectivorous birds induced by transformation of the invertebrate community can affect contaminant exposure in two ways. Elevated exposure in the polluted area (as a result of total contamination of the environment) can either increase additionally (if the proportion of food objects with high pollutant concentrations grow) or decrease (if the proportion of less toxic preys increases).

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2. Material and methods

2.1. Study area

This study was performed in the year 2000 in vicinities of the Middle-Ural copper smelter (Russia, Revda, 56°51′N, 59°53′E). It is a strong source of sulphur dioxide and polymetallic dust. Total emissions in the year 2000 equalled 63100 t including 56300 t sulphur dioxide (GSO, 2001). A geochemical anomaly with soil metal concentrations exceeding 10–100 times background levels has formed around the smelter since being put into operation in 1940 (Vorobeichik et al., 1994). Zones with different levels of pollution and degradation of forest ecosystems were distinguished in vicinities of the plant based on complex investigations (Vorobeichik et al., 1994). The zone of high pollution (impact zone) extends westwards up to 2.5 km from the smelter. Cu and Pb concentrations in the soil (horizon A1) exceed regional background levels by 43.4 and 9.5 times respectively (Belskii et al., 2005). The relatively unpolluted (background) zone is situated ≥16 km to the west of the smelter.

Plots with nestboxes were established in two forest types along the pollution gradient. One type was aspen-birch forest with some admixture of conifers; in the other, spruce and fir dominated with admixture of pine, birch and aspen. In the impact zone, the forest was rarefied due to the long-term effect of pollution. For this study, we used two plots in the impact zone and two plots in the background zone, so that impact plots corresponded to background plots by vegetation type. Impact plots were situated 1 km to the west of the smelter (deciduous forest, area 41 ha with 81 nestboxes) and 1.5 km to the southwest of the smelter (conifer forest, 23 ha, 46 nestboxes). Background plots were situated 16 km to the west of the smelter (deciduous forest, 21 ha, 42 nestboxes) and 20 km to the west of the smelter (conifer forest, 32 ha, 64 nestboxes).

2.2. Model species

Nestboxes were commonly occupied by pied flycatchers *Ficedula hypoleuca* Pall. and coal tits *Parus ater* L. The pied flycatcher is larger than the coal tit with body mass (± SE) during breeding in the study area 13.04 ± 0.02 g (n = 1840) and 9.20 ± 0.06 g (77), respectively (Belskii, unpublished). Both species are insectivorous but differ in foraging habitats and techniques. Pied flycatchers catch invertebrates in tree crowns, on the ground and in the air when taking off from a perch. Coal tits forage mainly in crowns of conifers but also use deciduous trees in the west of the species range. The pied flycatcher is a long-distant migrant with winter grounds in West Africa, south of the Sahara. Coal tits winter in the forest zone (Cramp and Perrins, 1993).

2.3. Sampling and measurements

Nestling diet was studied using neck collars. Samples were collected in 14 nests of *F. hypoleuca* from 21st June to 10th July at nestling age 4–13 days (hatching day 0, 177 boluses containing 325 specimens of invertebrates) and in 8 nests of *P. ater* from 31st May till 11th July at nestling age 5–15 days (205 boluses, 412 specimens of invertebrates). Food boluses were kept individually in Eppendorf tubes in 70% ethanol. In the laboratory, boluses were placed on filter paper and invertebrates were separated carefully. Invertebrates were dried on filter paper until the liquid disappeared from integuments and mass stabilised. Each specimen was weighed using electronic scales, Kern 770 with accuracy 0.1 mg. Differences between species and study sites in diet structure based on number of food objects (Appendix 1) were tested with χ^2-test.

Invertebrates belonging to bird preys were sampled for chemical analyses. Invertebrates were caught by hands and an entomological net in plots with nestboxes in both zones. The invertebrates were dried in a muffle furnace at 70 °C for 3 days. The objects were weighed before and after drying in order to calculate conversion factor between wet and dry mass (Appendix 2). Since no molluscs were sampled from vegetation in the impact zone shells dropped by birds in nests were analysed. The shells were not swallowed by nestlings and contained dry soft tissues inside. It is known that shells, together with soft tissues, dissolve in acidic medium of the nestling stomach, and so their analysis is appropriate when estimating metal intake in birds. These shells were washed in distilled, deionised water with a brush to remove superficial dirt.

2.4. Chemical analyses and data processing

Mass of samples for chemical analyses varied from 20 to 100 mg, and one sample usually contained several specimens of invertebrates. Samples were digested in a microwave oven in Teflon vessels in a mixture of 1 ml nitric acid and 4 ml double-distilled, deionised water, at pressure 900 kPa. Metal (Cu, Pb, Cd, Zn) concentrations were measured with an AAS 6 Vario atomic absorption spectrometer (Analytik Jena, Germany) at the Institute of Plant and Animal Ecology (Yekaterinburg, Russia). Standard tissue of bovine liver CRM-185 R was used as a control sample. Calibration solutions were prepared from liquid standards produced by the Urals plant for chemical reagents. In total, 142 samples were analysed.

Because of differences in feeding type within the order Hymenoptera, we distinguished groups of herbivores (sawflies Symphyta) and polyphages (ants Formicidae). Imagoes and larvae of butterflies and sawflies were analysed separately since insects of different developmental stages differ in caloric value and metal concentrations. Differences between zones in metal concentrations were tested with Mann–Whitney U test.

Contaminant exposure of nestlings before leaving the nest was calculated as daily metal intake per unit of body mass as follows. Average weighted metal concentrations in food were multiplied by daily food intake and divided by bird body mass. Average weighted metal concentrations in food were calculated based on metal concentrations in different preys and diet structure (proportions of different components in food dry mass) (Tables 1–3, Appendix 3). Daily food intake was calculated on the basis of daily energy of maintenance (DEM) and assimilable energy density of invertebrate preys (Dolnik and Postnikov, 1990; Appendix 2). DEM for passerine fledglings reaching adult body mass (m_f) is:

$DEM_f = 6.12 * m_f^{0.688}$ kJ/day (Dolnik and Dolnik, 1994). Body mass of the species is shown in Section 2.2. Assimilable energy content of food in *F. hypoleuca* equalled 16.2 kJ/g dry mass in the background zone and 16.3 kJ/g in the impact one, and in *P. ater* 14.8 kJ/g and 16.1 kJ/g respectively. Contribution of invertebrate groups to intake of each metal to birds was calculated in % of metal intake with 1 g of food (Tables 1 and 2, Appendix 4).

Standard errors of composite indices (dietary average weighted metal concentrations and daily metal intake) were calculated as described in Taylor (1982). Significance of differences between species and areas was tested with Student's *t*-test.

3. Results

The diet of *F. hypoleuca* in the background zone was more diverse compared to *P. ater* (11 and 5 orders of invertebrates, Shannon diversity index 1.79 and 0.99 respectively) (Tables 1 and 2). In the background zone, Lepidoptera larvae prevailed among preys of *F. hypoleuca* and together with Araneae in the diet of *P. ater.* Proportion of Lepidoptera increased in diets of both bird species in the impact zone compared to the background zone; the same was true for Araneae in the diet of *F. hypoleuca*. Diet diversity decreased in polluted area compared to background one both in *F. hypoleuca* and *P. ater* (Shannon diversity index 1.02 and 0.80 respectively). Differences between zones by number ratio of food objects (Appendix 1) were significant in *F. hypoleuca* ($\chi^2 = 40.7$, $df = 5$, $p < 0.001$) and *P. ater* ($\chi^2 = 17.5$, $df = 3$, $p < 0.001$).

In the background zone, the highest concentrations of Cu and Zn were registered in Araneae, and Pb and Cd in Mollusca (Table 3). The lowest concentrations of Cd and Zn were observed in sawfly larvae, Cu in Lepidoptera larvae, and Pb in Lepidoptera imagoes. In the impact zone, the highest concentrations of all metals were registered in molluscs. The lowest concentrations of Cu and Pb were observed in Lepidoptera larvae, Cd in sawfly larvae, and Zn in Hemiptera (Table 3). Concentrations of metals in most invertebrate taxa were higher in the impact zone compared

Table 1
Nestling diet (% air-dry mass) and contribution (%) of invertebrate taxa to dietary metal intake of *F. hypoleuca* in two zones near the Middle-Ural copper smelter.

Taxon, developmental stage	Background zone					Impact zone				
	Dietary proportion	Contribution to dietary metal intake				Dietary proportion	Contribution to dietary metal intake			
		Cu	Zn	Cd	Pb		Cu	Zn	Cd	Pb
Lepidoptera, i *	3.0	2.6	3.1	1.0	1.8	4.0	2.9	4.1	2.8	4.1
Lepidoptera, l *	34.8	14.0	27.4	6.5	22.0	66.5	26.7	42.2	16.6	35.1
Diptera, i	19.6	19.5	27.3	51.6	28.1	5.7	4.9	5.4	11.0	9.3
Hymenoptera, Symphyta, i	4.4	4.8	2.4	2.2	3.5	1.2	1.6	0.6	0.8	3.3
Hymenoptera, Symphyta, l	7.7	3.9	3.5	0.9	8.9	2.3	1.1	1.5	0.4	2.1
Hymenoptera, Formicidae, i	1.8	1.4	2.4	5.3	2.9	0.7	0.8	1.8	3.3	2.6
Araneae	7.4	29.1	19.5	22.4	9.7	15.1	57.1	42.3	62.9	38.3
Coleoptera, i	6.2	5.0	2.3	2.2	8.2	2.2	2.5	1.5	1.2	4.3
Coleoptera, l	0.3	n.a. **	n.a.	n.a.	n.a.	0	0	0	0	0
Homoptera, i	6.1	9.4	9.0	3.4	7.2	0.3	0.9	0.2	0.3	0.3
Hemiptera, i	6.1	9.6	2.5	3.6	6.3	1.0	1.5	0.4	0.7	0.6
Opiliones	1.6	n.a.	n.a.	n.a.	n.a.	0	0	0	0	0
Megaloptera, i	0.6	n.a.	n.a.	n.a.	n.a.	0.3	n.a.	n.a.	n.a.	n.a.
Mollusca	0.3	0.7	0.6	0.9	1.4	0	0	0	0	0
Raphidioptera, i	0.1	n.a.	n.a.	n.a.	n.a.	0	0	0	0	0
Trichoptera, i	0	0	0	0	0	0.7	n.a.	n.a.	n.a.	n.a.

* i – imagoes, l – larvae
** n.a. – not analysed

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Table 2
Nestling diet (% air-dry mass) and contribution (%) of invertebrate taxa to dietary metal intake of *P. ater* in two zones near the Middle-Ural copper smelter.

Taxon, developmental stage	Background zone					Impact zone				
	Dietary proportion	Contribution to dietary metal intake				Dietary proportion	Contribution to dietary metal intake			
		Cu	Zn	Cd	Pb		Cu	Zn	Cd	Pb
Lepidoptera, i *	0.4	0.2	0.2	0.1	0.2	3.1	1.8	2.7	1.8	3.0
Lepidoptera, l *	41.5	7.6	19.0	4.5	25.7	68.9	22.4	38.1	14.3	35.3
Diptera, i	6.1	2.8	4.9	9.2	8.5	0.4	0.3	0.4	0.7	0.7
Diptera, l	0.1	n.a. **	n.a.	n.a.	n.a.	0	0	0	0	0
Hymenoptera, Symphyta, i	0	0	0	0	0	0.3	0.4	0.1	0.2	0.9
Hymenoptera, Symphyta, l	0	0	0	0	0	1.9	0.8	1.1	0.3	1.6
Araneae	49.5	88.6	75.2	85.8	63.2	23.1	70.7	56.3	80.0	56.9
Coleoptera, i	1.4	0.5	0.3	0.3	1.9	0	0	0	0	0
Coleoptera, l	0.6	n.a.	n.a.	n.a.	n.a.	0.4	n.a.	n.a.	n.a.	n.a.
Homoptera, i	0.4	0.3	0.4	0.1	0.5	1.3	3.0	0.6	1.0	1.0
Mollusca	0	0	0	0	0	0.1	0.6	0.7	1.7	0.6
Trichoptera, i	0	0	0	0	0	0.5	n.a.	n.a.	n.a.	n.a.

* i – imagoes, l – larvae
** n.a. – not analysed

to the background zone (Table 3). Concentration ratios (impact/background) for Cu varied from 1.7 to 5.2, Zn 1.2–5.2, Cd 1.4–9.0, and Pb 2.4–14.

According to calculated average weighted concentrations the diet of *P. ater* in the background zone contained greater amounts of Cu, Cd and Zn (1.7–2.2 times) compared to *F. hypoleuca* and the same amount of Pb (Table 4). In the impact zone dietary metal concentrations were similar in different bird species. Differences between zones in dietary average weighted Pb concentrations were significant in both species and equalled 4.1 times (Table 4). At the same time impact/background ratios of Cu, Zn and Cd in *F. hypoleuca* diet (2.0, 1.8 and 1.8 respectively) were greater than in *P. ater* diet (1.1, 1.2 and 1.3 respectively).

The calculated daily metal intake of nestlings per unit of body mass was greater in *P. ater* than in *F. hypoleuca* for Cu and Cd, only in background area. Exposure to Pb was greater in the impact zone than in the background zone in both species (Table 5). Metal intake in most cases exceeded tolerable daily intake (TDI) for birds but was lower than the lowest-observable-adverse-effect level (LOAEL) (Sample et al., 1996; Morrissey et al., 2005).

Contribution of different prey taxa to metal intake of nestlings was not equal to their dietary proportion due to different concentrations of chemical elements (Tables 1 and 2). In the background zone, contribution of spiders to metal intake of *F. hypoleuca* was 1.3–3.9 times and of *P. ater* 1.3–1.8 times greater than their dietary proportion. In the impact zone, the proportion of metals provided by spiders to birds was 2.5–4.2 times greater than their dietary fraction. The contribution of molluscs to dietary metal intake exceeded 2–17 times their proportion in the bird diet. Ants and imagoes Diptera provided disproportionately high amounts of Cd and Pb. In contrast, the contribution of Lepidoptera larvae to metal intake of *F. hypoleuca* was 1.3–5.3 times and *P. ater* 1.6–9.2 times less than their dietary mass fraction. The same was true for sawfly larvae in the case of Cu, Zn and Cd.

4. Discussion

Our data on bird diet accord with previous studies in that *P. ater* has greater trophic specialisation than *F. hypoleuca* (Cramp and Perrins, 1993). Diet of *F. hypoleuca* was more diverse than in *P. ater* in all sites. Diet diversity decreased near the smelter, and the effect in *F. hypoleuca* was greater than in *P. ater*. Surprisingly, both species consumed more caterpillars in the polluted area despite their abundance on trees not differing from that in the background zone (Belskii and Belskaya, 2009). Increased mass proportion of caterpillars is partly due to their greater body mass (Belskii and Belskaya, 2009). Bird breeding starts later in the polluted area and nestlings receive caterpillars of older instars as a result.

Our calculations showed that contaminant exposure can differ in different bird species even within the same habitat. The main reasons for this are differences in bird diets since ingestion is the main pathway of pollutant intake in birds (Smith et al., 2007). Calculated values of daily metal intake of birds may underestimate real exposure since we did not take into account contribution of soil and dust presumably ingested by birds with food. However, these sources of contamination seem to be of minor importance for birds foraging on vegetation, in air and only partly on ground. It should be mentioned that for both species an averaged diet (young and older nestlings combined) was presented. Since diet of small and larger nestlings could differ exposure may depend on age. Moreover, we were not able to estimate contribution of every diet component to metal concentrations in bird body since data on metal absorption from different preys were lacking. In fact we calculated gastrointestinal transit of metals and contribution of different prey taxa to this flow.

Daily metal intake of birds in this study exceeded the TDI but was less than the LOAEL (Sample et al., 1996; Morrissey et al., 2005). Values of TDI and LOAEL are based on laboratory experiments and may be not applicable to wild animals because of the complexity of factors affecting exposure in nature. We observed decreased breeding success of both species in the impact zone with dietary metal concentrations below LOAELs (Belskii et al. 2005).

Contribution of different prey taxa to bird metal intake was not equal to dietary proportion of these invertebrates. Proportions of Cu, Zn, Pb and Cd provided to birds by spiders and molluscs, as well as Cd and Pb provided by ants and imagoes Diptera, exceeded by several times their dietary fraction. In contrast, the contribution of Lepidoptera and sawfly larvae to metal intake of birds was less than their dietary proportion. This fact reflects differences in metal concentrations in invertebrates. Among taxa consumed by birds molluscs, spiders and ants are known to accumulate high amounts of metals (Bengtsson and Rundgren, 1984; Coughtrey and Martin, 1977; Hopkin, 1989; Hunter et al., 1987; Rabitsch, 1995). Lepidoptera and sawfly larvae usually have the lowest metal concentrations (Eeva et al., 2005; Hopkin, 1989). In short, bird species using spiders, molluscs and ants for food experience greater exposure compared to caterpillar specialists.

Pollution-related changes in the bird diet result in an altered ratio of prey species with high and low metal concentrations. We tried to determine in what way alteration of bird diet along the pollution gradient can affect contaminant exposure. We calculated

Table 3
Metal concentrations (mg/kg dry mass) in invertebrates in background and impact zones near the Middle-Ural copper smelter, arithmetic mean ± SE (n samples). Concentrations significantly different ($p < 0.05$) from background values are shown in bold (Mann-Whitney U test, *z* (*p*) are values of *z*-adjusted and significance level *p*).

Taxon, developmental stage	Cu			Zn			Cd			Pb		
	back-ground	impact	z (p)	back-ground	impact	z (p)	back-ground	impact	z (p)	back-ground	impact	z (p)
Lepidoptera, i *	15.9 ± 1.6 (8)	26.8 ± 6.3 (5)	−1.61 (0.107)	117.1 ± 19.6 (7)	209.0 ± 54.2 (5)	−1.87 (0.062)	1.1 ± 0.5 (8)	**4.4** ± **2.5** (5)	−2.34 (0.019)	2.5 ± 0.9 (8)	**17.7** ± **8.2** (5)	−2.49 (0.013)
Lepidoptera, l *	7.5 ± 0.7 (5)	14.8 ± 4.5 (5)	−0.94 (0.347)	91.5 ± 32.1 (5)	132.2 ± 37.1 (5)	−0.73 (0.465)	0.6 ± 0.2 (5)	1.6 ± 1.0 (5)	−0.52 (0.601)	2.7 ± 0.7 (5)	**9.3** ± **1.6** (5)	−2.61 (0.009)
Diptera, i	18.6 ± 1.0 (13)	**31.5** ± **4.6** (9)	−3.04 (0.002)	161.2 ± 35.9 (11)	197.4 ± 36.0 (7)	−0.77 (0.441)	9.1 ± 0.7 (12)	12.3 ± 2.9 (6)	−0.66 (0.512)	6.2 ± 0.9 (13)	**28.9** ± **7.6** (8)	−3.48 (0.0005)
Hymenoptera, Symphyta, i	20.5 ± 2.1 (4)	48.9 ± 12.0 (3)	−1.85 (0.064)	63.0 ± 8.2 (4)	95.9 ± 45.0 (3)	0.00 (1.000)	1.7 ± 0.6 (4)	4.0 ± 1.8 (3)	−1.85 (0.064)	3.4 ± 1.1 (4)	49.6 ± 17.8 (3)	−1.85 (0.064)
Hymenoptera, Symphyta, l	9.6 ± 1.3 (8)	**18.6** ± **1.4** (5)	−2.63 (0.008)	52.9 ± 6.7 (7)	**139.7** ± **27.0** (5)	−2.52 (0.012)	0.4 ± 0.1 (8)	**1.2** ± **0.3** (5)	−2.34 (0.019)	5.0 ± 0.6 (7)	**16.0** ± **2.7** (5)	−2.84 (0.004)
Hymenoptera, Formicidae, i	14.9 ± 3.1 (6)	**42.9** ± **2.3** (5)	−2.74 (0.006)	159.2 ± 54.4 (6)	**548.8** ± **70.3** (5)	−2.74 (0.006)	10.4 ± 4.1 (6)	**29.7** ± **2.7** (5)	−2.74 (0.006)	7.1 ± 2.4 (6)	**64.6** ± **6.7** (5)	−2.74 (0.006)
Araneae	73.4 ± 10.2 (6)	**139.6** ± **9.5** (5)	−2.56 (0.011)	303.7 ± 37.9 (6)	**583.5** ± **36.9** (5)	−2.74 (0.006)	10.4 ± 1.0 (6)	**26.4** ± **1.5** (5)	−2.74 (0.006)	5.6 ± 1.1 (6)	**44.8** ± **11.4** (5)	−2.74 (0.006)
Coleoptera, i	15.1 ± 1.6 (12)	**41.8** ± **5.2** (13)	−3.92 (0.0001)	42.0 ± 6.2 (12)	**145.8** ± **11.6** (13)	−4.14 (0.00003)	1.2 ± 0.1 (12)	**3.5** ± **0.**7 (13)	−2.45 (0.014)	5.6 ± 0.5 (12)	**35.3** ± **5.0** (13)	−4.24 (0.00002)
Homoptera, Cicadinea, i	28.9 ± 1.0 (5)	**109.4** ± **19.3** (4)	−2.45 (0.014)	170.0 ± 12.4 (5)	112.6 ± 36.4 (4)	1.22 (0.220)	1.9 ± 0.1 (5)	**6.0** ± **1.6** (4)	−2.20 (0.027)	5.1 ± 0.9 (5)	**14.0** ± **3.2** (4)	−2.45 (0.014)
Hemiptera, i	29.6 ± 1.5 (6)	**55.0** ± **2.6** (6)	−2.88 (0.004)	46.9 ± 16.8 (6)	93.0 ± 25.1 (6)	−1.28 (0.201)	2.0 ± 0.5 (6)	**4.1** ± **0.2** (6)	−2.24 (0.025)	4.5 ± 1.1 (6)	10.7 ± 3.2 (6)	−1.92 (0.055)
Mollusca	45.1 ± 9.6 (5)	**233.1** ± **59.8** (4)	−2.45 (0.014)	269.7 ± 54.2 (5)	**1395.4** ± **114.4** (4)	−2.45 (0.014)	11.8 ± 1.5 (5)	**106.0** ± **6.6** (4)	−2.45 (0.014)	22.1 ± 3.7 (5)	**87.2** ± **14.4** (4)	−2.45 (0.014)

* i – imagoes, l – larvae.

Table 4
Average weighted metal concentrations ± SE (mg/kg air-dry mass) in the diet of *F. hypoleuca* and *P. ater* in two zones near the Middle-Ural copper smelter.

Bird species	Zone	Metals			
		Cu	Zn	Cd	Pb
Ficedula hypoleuca	background	18.7 ± 1.7 [+]	115.8 ± 30.5	3.5 ± 0.7	4.3 ± 0.9 *
	impact	37.0 ± 8.7	208.3 ± 49.2	6.3 ± 3.0	17.6 ± 3.6 *
	predicted concentration in the impact zone if birds in the impact zone had the same diet as in the background zone	40.1 ± 7.3	184.6 ± 43.6	7.0 ± 2.4	21.3 ± 4.7
Parus ater	background	41.0 ± 4.6 [+]	199.8 ± 44.8	6.0 ± 1.1	4.4 ± 1.0 *
	impact	45.5 ± 10.7	239.1 ± 54.2	7.6 ± 3.5	18.2 ± 3.7 *
	predicted concentration in the impact zone if birds in the impact zone had the same diet as in the background zone	78.2 ± 13.4	358.8 ± 58.2	14.5 ± 4.4	28.4 ± 6.2

* Differences between zones are significant at $p < 0.05$ (Student's t-test)
[+] Differences between species within the same zone are significant at $p < 0.05$ (Student's t-test)

Table 5
Calculated dietary daily metal intake ± SE (mg/kg body mass) to fledglings of *Ficedula hypoleuca* and *Parus ater* in two zones near the Middle-Ural copper smelter.

Species	Zone	Mean daily food intake per nestling, g dry mass	Daily metal intake			
			Cu	Zn	Cd	Pb
Ficedula hypoleuca	background	2.21 ± 0.02	3.19 ± 0.29 [+]	19.69 ± 5.20	0.59 ± 0.12 [+]	0.73 ± 0.16 *
	impact	2.20 ± 0.02	6.22 ± 1.48	35.16 ± 8.33	1.07 ± 0.50	2.97 ± 0.61 *
Parus ater	background	1.90 ± 0.05	8.48 ± 1.07 [+]	41.36 ± 9.54	1.24 ± 0.24 [+]	0.91 ± 0.21 *
	impact	1.75 ± 0.05	8.68 ± 2.10	45.60 ± 10.64	1.45 ± 0.68	3.46 ± 0.72 *
Tolerable daily intake, mg/kg body mass/day [a, b]			5.39	4.36	0.54	0.64
Lowest-observable-adverse-effect level, mg/kg/day			61.7 [c]	131 [d]	20.03 [e]	11.3 [f]

[a] Sample et al., 1996
[b] Morrissey et al., 2005
[c] Mehring et al., 1960 (from: Morrissey et al., 2005)
[d] Stahl et al., 1990 (from: Morrissey et al., 2005)
[e] White, Finley, 1978 (from: Morrissey et al., 2005)
[f] Edens et al., 1976 (from: Morrissey et al., 2005)
* Differences between zones are significant at $p < 0.05$ (Student's t-test)
[+] Differences between species within the same zone are significant at $p < 0.05$ (Student's t-test)

the average weighted metal concentrations in bird food in the impact zone for the case of birds in the impact zone that had the same diet as in the background zone. In this case, metal concentrations in the diet of *F. hypoleuca* in the impact zone would be 9% greater for Cu, 10% greater for Cd, 21% greater for Pb, and 11% less for Zn in comparison with the actual diet of the birds (Table 4). Metal concentrations in food of *P. ater* would also be greater: 72% for Cu, 91% for Cd, 57% for Pb and 50% for Zn. Thus, the observed contaminant exposure was less than that predicted provided that the background diet remained. The decrease of exposure is due to the increased dietary proportion of caterpillars that accumulate heavy metals below the average level. In contrast, a higher dietary proportion of spiders increases exposure. The role of molluscs is contradictory. It was shown that Ca-diminished diet may increase intestinal absorption of Cd and Pb (Scheuhammer, 1996; Dauwe et al., 2006). Lack of molluscs with Ca-rich shells in the nestling diet in the impact zone on the one hand reduces metal intake to birds but on the other hand may increase absorption of toxic metals. Thus dietary shifts in the polluted area can modify contaminant exposure produced by increased pollutant concentrations in food.

5. Conclusion

Our results show that: (1) contaminant exposure can differ in different bird species even within the same habitat; (2) contribution of different food components to bird metal intake is not equal to their dietary proportion because of different metal content. Contribution of spiders and molluscs (Cu, Zn, Pb and Cd), ants and imagoes Diptera (Cd and Pb) to bird metal intake exceeded their dietary proportions. At the same time, contribution of Lepidoptera and sawfly larvae to metal intake was less than their dietary fraction; (3) environmental pollution affects contaminant exposure in two ways: both changing pollutant concentrations in preys and shifting the diet structure. As a result, contaminant exposure of the species in question can change along the pollution gradient disproportionately to pollutant level in the environment.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2013.07.014.

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