

Supplementary material

Organic farming reduces pesticide load in a bird of prey

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Table S1. Pesticides detected in the blood of 55 Montagu's harrrier (*Circus pygargus*) chicks. Method to quantify pesticides was either liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) or automated thermal desorption gas chromatography coupled with tandem mass spectrometry (ATD-GC-MS/MS); LOD = limit of detection; LOQ = limit of quantification; N = number of individuals in which the compound was detected and if quantified (>LOQ) used to obtain mean, SD = Standard Deviation, and range (minimum–maximum), all concentrations are given in $\mu\text{g}\cdot\text{g}^{-1}$ (=ng.g⁻¹ = ppb).

Compound	Method ¹	LOD	LOQ	N	Mean \pm SD ⁵	Minimum	Maximum
Herbicides							
BifenoX	ATD-GC-MS/MS	0.0012	0.0038	10	<LOQ	-	-
Carbetamide	LC-MS/MS	0.0053	0.0176	1	29.75	-	-
Chloridazon	ATD-GC-MS/MS	0.0213	0.0709	17	121.02 \pm 125.90	35.96	563.10
2,4-MCPA	ATD-GC-MS/MS	0.1579	0.5263	2	2020.12 \pm 176.57	1895.27	2144.98
Mecoprop-P	ATD-GC-MS/MS	0.0500	0.1667	3	799.35 \pm 369.40	409.93	1144.79
Metamitron	ATD-GC-MS/MS	0.0577	0.1923	8	25.01 \pm 28.29	3.28	88.34
Oxadiazon	ATD-GC-MS/MS	0.0086	0.0286	1	71.68	-	-
Propyzamide	ATD-GC-MS/MS	0.0021	0.0071	1	339.07	-	-
Sulcotrione	LC-MS/MS	0.0021	0.0071	53	1111.78 \pm 540.67	312.42	3184.67
Tebutam	ATD-GC-MS/MS	0.0526	0.1754	24	64.62 \pm 49.77	13.81	180.24
Fungicides							
Boscalid	ATD-GC-MS/MS	0.0005	0.0016	3	1369.09 \pm 819.48	791.50	2307.00
Carbendazim	LC-MS/MS	0.0042	0.0140	7	97.50 \pm 81.21	0.216	258.29
Cyproconazole	ATD-GC-MS/MS	0.0192	0.0639	3	70.04 \pm 69.82	13.65	148.13
Cyprodinil	ATD-GC-MS/MS	0.0011	0.0036	2	41.34 \pm 42.91	11.00	71.68
Difenoconazole	ATD-GC-MS/MS	0.0359	0.1196	15	240.02 \pm 317.74	31.68	1213.55
Dimethomorph	ATD-GC-MS/MS	0.0072	0.0242	3	241.49 \pm 94.27	163.33	346.19
Dimoxystrobin	ATD-GC-MS/MS	0.0038	0.0128	2	171.79 \pm 16.87	159.86	183.72
Epoxyconazole	LC-MS/MS	0.0027	0.0091	1	51.05	-	-

Flusilazole	ATD-GC-MS/MS	0.0144	0.0481	1	137.63	-	-
Myclobutanil	ATD-GC-MS/MS	0.0214	0.0714	1	142.12	-	-
Prochloraze	ATD-GC-MS/MS	0.0170	0.0568	1	1292.89	-	-
Quinoxifen	ATD-GC-MS/MS	0.0048	0.0161	3	39.93 ± 38.73	9.73	83.59
Insecticides							
Bifenthrin	ATD-GC-MS/MS	0.0035	0.0116	1	18.46	-	-
Clothianidin	LC-MS/MS	0.0103	0.0344	3	929.30 ± 1268.76	189.92	2394.32
Cypermethrin	ATD-GC-MS/MS	0.0013	0.0042	2	204.34 ± 46.88	171.19	237.49
Indoxacarb	ATD-GC-MS/MS	0.0069	0.0231	3	<LOQ	-	-
Piperonyl butoxide	ATD-GC-MS/MS	0.0004	0.0015	5	36.30 ± 22.48	12.60	70.67
Thiacloprid	LC-MS/MS	0.0014	0.0048	1	87.48	-	-

Table S2. Main properties of pesticides detected in blood samples of Montagu's harrier nestlings. The DT50 ranges (detection time 50% = time to detect a 50% decrease in pesticide concentration) provided show the minimum and maximum values from field studies or from general literature (when field data were not available) and can vary greatly depending on the sources (for more details see Lewis et al., 2016). Model species corresponds to the birds for which the LD50 (lethal dose 50% = quantity of pesticide killing 50% of the test animals) was obtained: *Colinus virginianus* (Cv), *Coturnix japonica* (Cj), *Anas platyrhynchos* (Ap), and *Serinus canaria* (Sc). Main crops, DT50, Bird LD50, and model species were compiled from the Pesticide Properties DataBase (PPDB) of the University of Hertfordshire (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>, accessed on 21 August 2023; Lewis et al., 2016). Type and mode of action were obtained from the Herbicide, Fungicide, and Insecticide Resistance Action Committees' online posters (available at <https://www.hracglobal.com/>, <https://www.frac.info/>, <https://irac-online.org/> accessed on 21 August 2023). "Ban" corresponds to prohibition years in France; data obtained from legislative texts (available at <https://www.legifrance.gouv.fr/> accessed on 21 August 2023). NA: not applicable when not considered as an active substance of plant protection products in Europe.

Main crops	Ban	DT50 range (days)	Bird LD50 (mg.kg ⁻¹)	Model species	Mode of Action
2,4-MCPA	Yes	25	377	Cv	Auxin mimicking
Bifentox	Yes	8.3–32.1	>2000	Cv	Inhibition of protoporphyrinogen oxidase
Bifenthrin	No (2019)	65–125	1800	Cv	Sodium channel modulation
Boscalid	Yes	196–312.2	>2000	Cv	Inhibition of succinate dehydrogenase
Carbendazim	No (2014)	20–40	>2250	Cv	Tubulin polymerization
Carbetamide	No (2021)	8	>2000	Cv	Inhibition of microtubule organization
Chloridazon	No (2018)	3–105	>2000	Cv	Inhibition of photosynthesis at PS II
Clothianidin	No (2018)	13.3–1386	430	Cv	Competitive modulation of nicotinic acetylcholine receptor (nAChR)
Cypermethrin	Yes	9.3–31.2	>9520	Ap	Sodium channel modulation
Cyproconazole	No (2021)	62.1–501.2	94	Cv	Inhibition of demethylation
Cyprodinil	Yes	11–98	>500	Ap	Inhibition of methionine biosynthesis
Difenoconazole	Yes	20–265	>2150	Ap	Inhibition of demethylation
Dimethomorph	Yes	34–54	>2000	Cv	Interference with cellulose synthase.

Dimoxystrobin	Wheat, oilseed rape	Yes	2–39	>2000	Cv	Inhibition at Quinone outer binding site
Epoxiconazole	Cereals, sugar beet, coffee, banana	No (2019)	52–226	>2000	Cv	Inhibition of demethylation
Flusilazole	Cereals, sugar beet, oilseed rape, fruits	No (2008)	63–240	>1590	Ap	Inhibition of demethylation
Indoxacarb	Corn, vegetables, fruits, cotton	No (2021)	4.9–7.5	73.5	Cv	Voltage-dependent sodium channel inhibition
Mecoprop-P	Cereals, sports fields, lawns	Yes	21	>500	Ap	Auxin mimicking
Metamitron	Sugar beet, beets	Yes	11.1	1302	Cj	Inhibition of photosynthesis at PS II
Myclobutanil	Turfs, ornamentals, orchards, vineyards	No (2021)	9–66	510	Cv	Inhibition of demethylation
Oxadiazon	Turfs, sports fields, ornamentals, vineyards	No (2018)	90–330	>2150	Cv	Inhibition of protoporphyrinogen oxidase
Piperonyl butoxide	NA	Yes	NA	NA	NA	Synergistic action
Prochloraz	Cereals, oilseed rape, fruits, turfs, avocado	No (2021)	28.6–245	662	Cv	Inhibition of demethylation
Propyzamide	Alfalfa, oilseed rape, beans, fruits, ornamentals	Yes	13.9–271.3	6578	Cj	Inhibition of microtubule assembly
Quinoxifen	Cereals, grape, cucurbits, tomato	No (2019)	13–190	>2250	Cv	Inhibition of signal transduction
Sulcotrione	Cereals, corn, sunflower, oilseed rape, soybean, cotton	Yes	10.8–89.7	>1350	Ap	Inhibition of hydroxyphenyl pyruvate dioxygenase
Tebutam	Oilseed rape, sunflower, peanut, soybean, cotton	No (2002)	60	>5000	Ap	Inhibition of microtubule assembly
Thiacloprid	Vegetables, turfs, sod farms, landscape plants, ornamentals	No (2018)	5.95–16.8	35	Sc	Competitive modulation of nicotinic acetylcholine receptor (nAChR)

Table S3. Estimate, standard error (SE), statistic value (z), and significance (p) of each effect tested on the number of pesticides detected in Montagu's harrier chicks using generalized linear mixed-effects models fitted with a negative binomial distribution

Parameter	Estimate	SE	z	p
Intercept	1.40	0.16	8.72	< 0.001
% Organic farming (300 m)	-0.38	0.13	-2.98	< 0.01
Intercept	1.07	0.22	4.90	< 0.001
Sex M	-0.38	0.33	-1.15	0.25
Rank 2	-0.18	0.27	-0.65	0.51
Rank 3	0.09	0.44	0.20	0.84
Rank 4	0.25	0.38	0.65	0.52
Sex M \times Rank 2	0.60	0.47	1.28	0.20
Sex M \times Rank 3	0.39	0.55	0.71	0.47
Sex M \times Rank 4	0.94	0.71	1.31	0.19

Table S4. Estimate, standard error (SE), statistic value (t), and significance (p) of each effect tested on the sum of concentrations of pesticides (log-transformed) in Montagu's harrier chicks using linear mixed-effects models

Parameter	Estimate	SE	t	p
Intercept	7.28	0.23	31.71	<0.001
Sex M	-0.21	0.36	-0.59	0.55
Rank 2	-0.13	0.32	-0.39	0.69
Rank 3	-0.48	0.51	-0.94	0.35
Rank 4	0.25	0.61	0.41	0.68
Sex M \times Rank 2	-0.73	0.54	-1.35	0.18
Sex M \times Rank 3	0.58	0.63	0.91	0.37
Sex M \times Rank 4	0.34	1.04	0.33	0.74

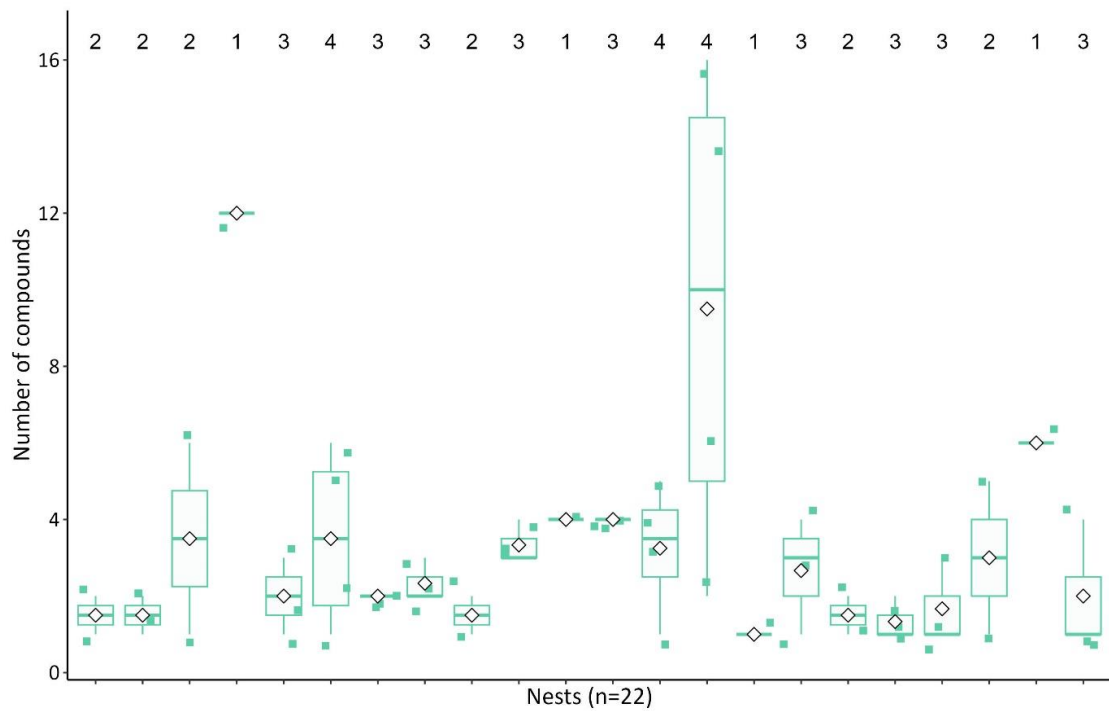


Figure S1. Variation in the number of pesticides detected in Montagu’s harrier chicks according to the nest they belonged to. The bottom and top lines of the boxes correspond to the first and third quartiles, the middle line corresponds to the median, and the whiskers correspond to the lower and higher values included in the 95% confidence interval. All values were plotted with a small degree of random variation to the location of each point; therefore, they do not correspond to a round number. Blank diamonds depict the mean; sample sizes are specified above the boxes.

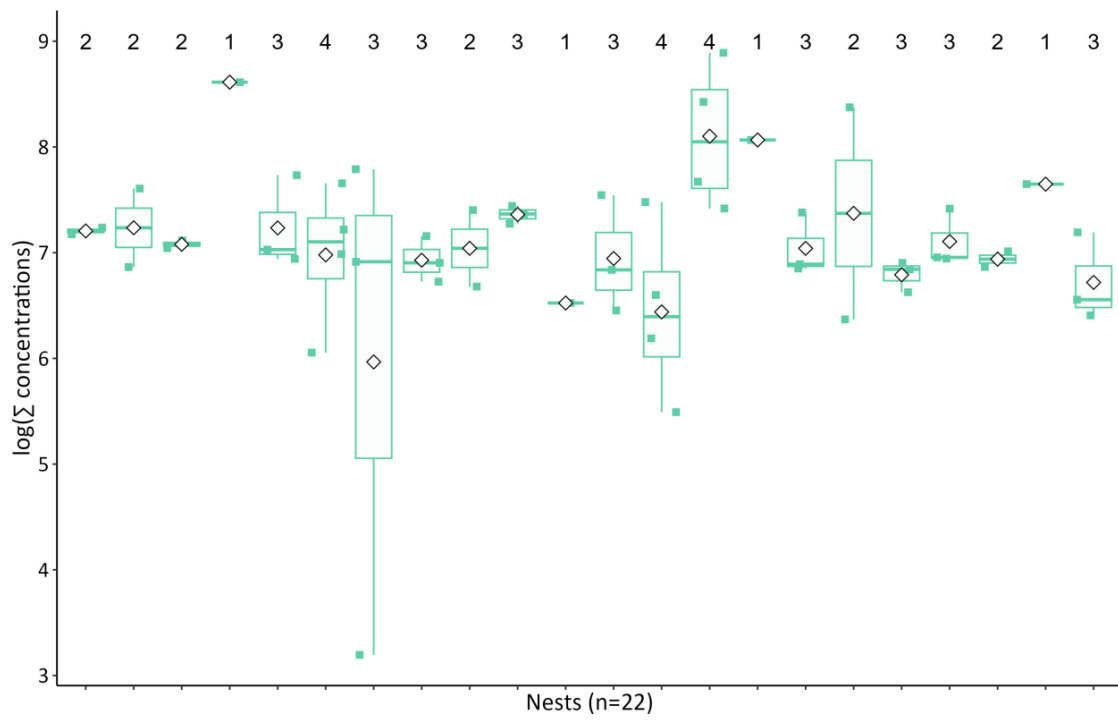


Figure S2. Variation in the sum of concentrations (log-transformed) of pesticides detected in Montagu's harrier chicks according to the nest they belonged to. For legend details, see Figure S1.

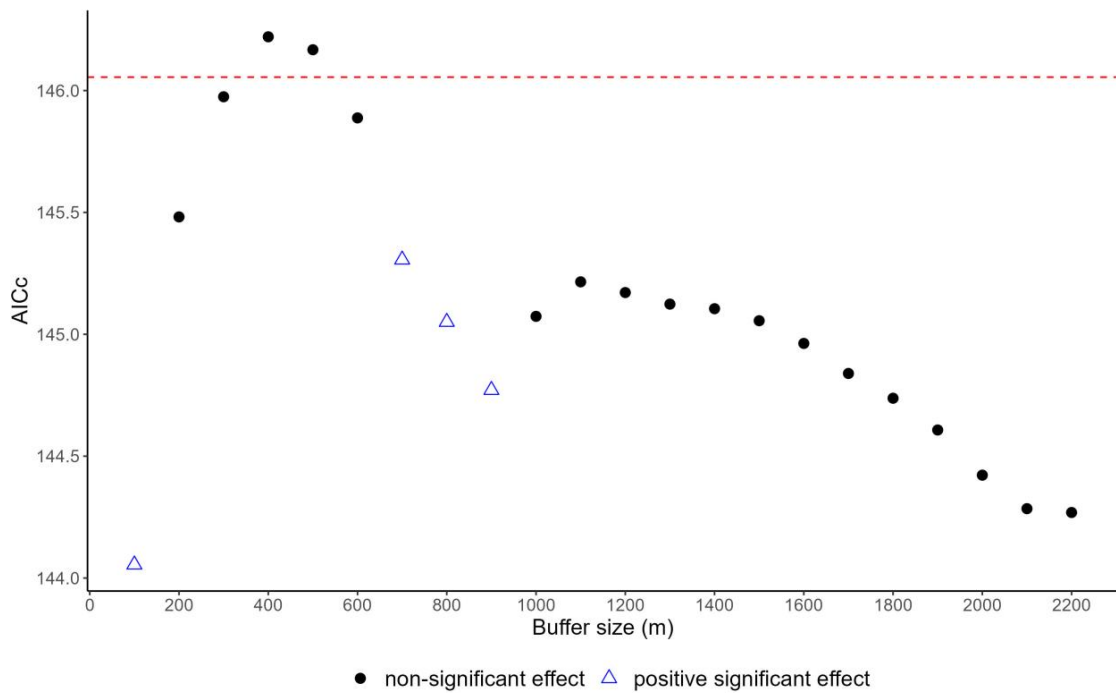


Figure S3. Model selection using AICc to assess the response of the total concentration (log-transformed) of pesticides detected in Montagu's harrier chicks to the effect of the percentage of organic farming around the nests at different distances (buffer sizes ranging from 100 m to 2200 m radius). AICc = Akaike Information Criterion corrected for small sample sizes. The red dotted line corresponds to the lowest AICc of candidate models + 2. Red triangles indicate a negative significant effect of organic farming (i.e., a negative model estimate and assorted 95% confidence interval not crossing 0). Black dots represent a non-significant effect of organic farming (i.e., the 95% confidence interval of model estimate crosses 0).

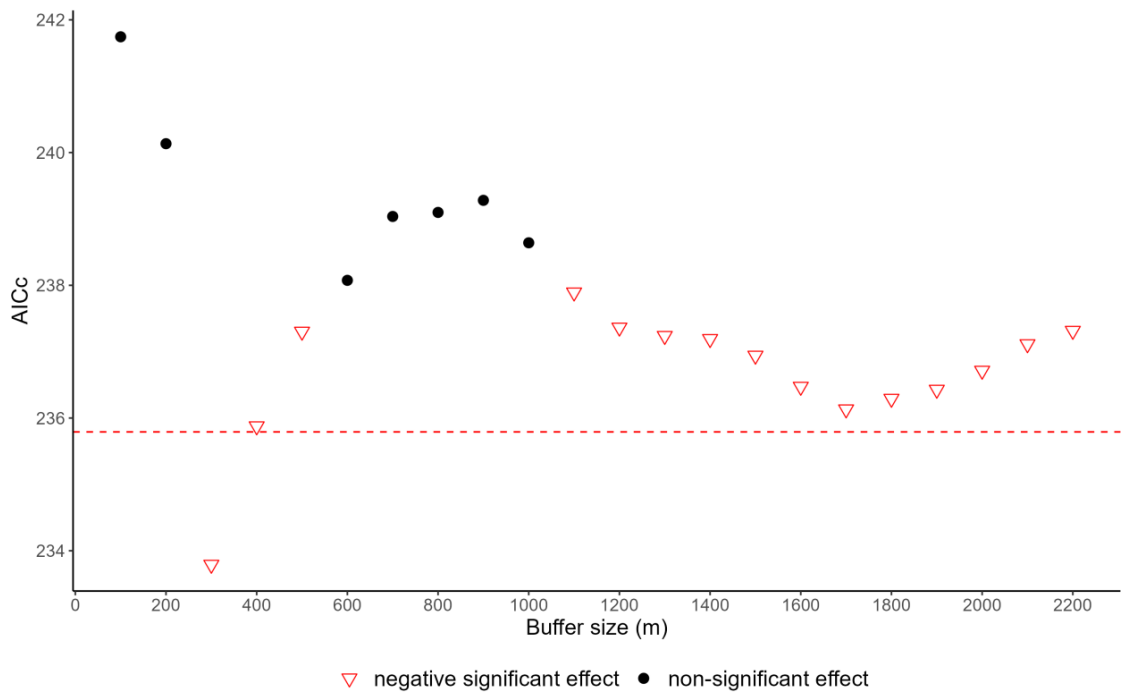


Figure S4. Model selection using AICc to assess the response of the number of pesticides detected in Montagu’s harrier chicks to the effect of the percentage of organic farming around the nests at different distances (buffer sizes ranging from 100 m to 2200 m radius). For legend details, see Figure S3.

References

Lewis, K.A., Tzilivakis, J., Warner, D., Green, A., 2016. An international database for pesticide risk assessments and management. *Hum. Ecol. Risk Assess.* 22, 1050-1064.
<https://doi.org/10.1080/10807039.2015.1133242>