

Feeling the Heat: Gulls as Bioindicators of Flame Retardant Emissions from UK Landfill

Tongue ADW¹, Drage DS¹, Harrad S¹, Reynolds SJ^{2,3}, Fernie KJ⁴

¹School of Geography, Earth and Environmental Sciences, University of Birmingham, UK B15 2TT axt571@bham.ac.uk; ²School of Biosciences, University of Birmingham, UK B15 2TT; ³Army Ornithological Society (AOS), Aldershot, UK GU11 1PS; ⁴Ecotoxicology & Wildlife Health, Environment & Climate Change Canada, Canada L7S 1A1

Introduction

Waste streams are important reservoirs of several persistent organic pollutants (POPs), including legacy brominated flame retardants (BFRs)¹. Landfill is often an important foraging substrate for birds (e.g., gulls *Larus* spp.)². Because of their widespread distribution, broad foraging niches, and the fact that contaminants often sequester in eggs and other tissue compartments, birds can be important bioindicators of environmental POPs contamination^{3,4,5}. Studies demonstrate correlations between bird use of landfill and elevated avian BFR burdens^{6,7,8}. However, in Europe, few studies have examined BFR contamination in birds; ours is the first to investigate BFR burdens and profiles across a UK landfill species-assemblage. We examined legacy BFRs, including: polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD), plus novel BFRs (NBFRs) in the eggs of five species: black-headed gull *Chroicocephalus ridibundus*, common gull *Larus canus*, great black-backed gull *L. marinus*, European herring gull *L. argentatus* and lesser black-backed gull *L. fuscus*.

Materials and methods

During 2016–2018, eggs were collected under licence in Argyll, western Scotland (UK) from gull colonies located within 3 km of the same mainland municipal solid waste landfill facility, following the methodology used in the North American Great Lakes Herring Gull Monitoring Program (i.e., collection of one randomly-selected pre-embryonated egg per nest from 10–13 individual nests per species, per site⁹). In addition, and where possible for each species, two full clutches (i.e., an additional six eggs) were obtained in order to analyse intra-clutch flame retardant burdens and profiles. Aliquots (1 g.) of egg samples were spiked with internal standards prior to pressurised liquid extraction, combined with an in-cell multi-silica clean-up. Clean extracts were concentrated to near-dryness and reconstituted in toluene containing recovery determination standards. Target compounds were: BDEs –28, –47, –99, –100, –153, –154, –183, –209; NBFRs: (1,2-bis(2,4,6-tribromophenoxy) ethane [BTBPE], decabromodiphylethane [DBDPE], 2-ethylhexyl-2,3,4,5-tetrabromobenzoate [EHTBB], pentabromobenzene [PBB], and pentabromoethylbenzene [PBEB]), and three HBCDD diastereoisomers (α , β and γ). PBDEs and NBFRs were determined via GC-EI/MS. HBCDD was measured using LC-MS/MS.

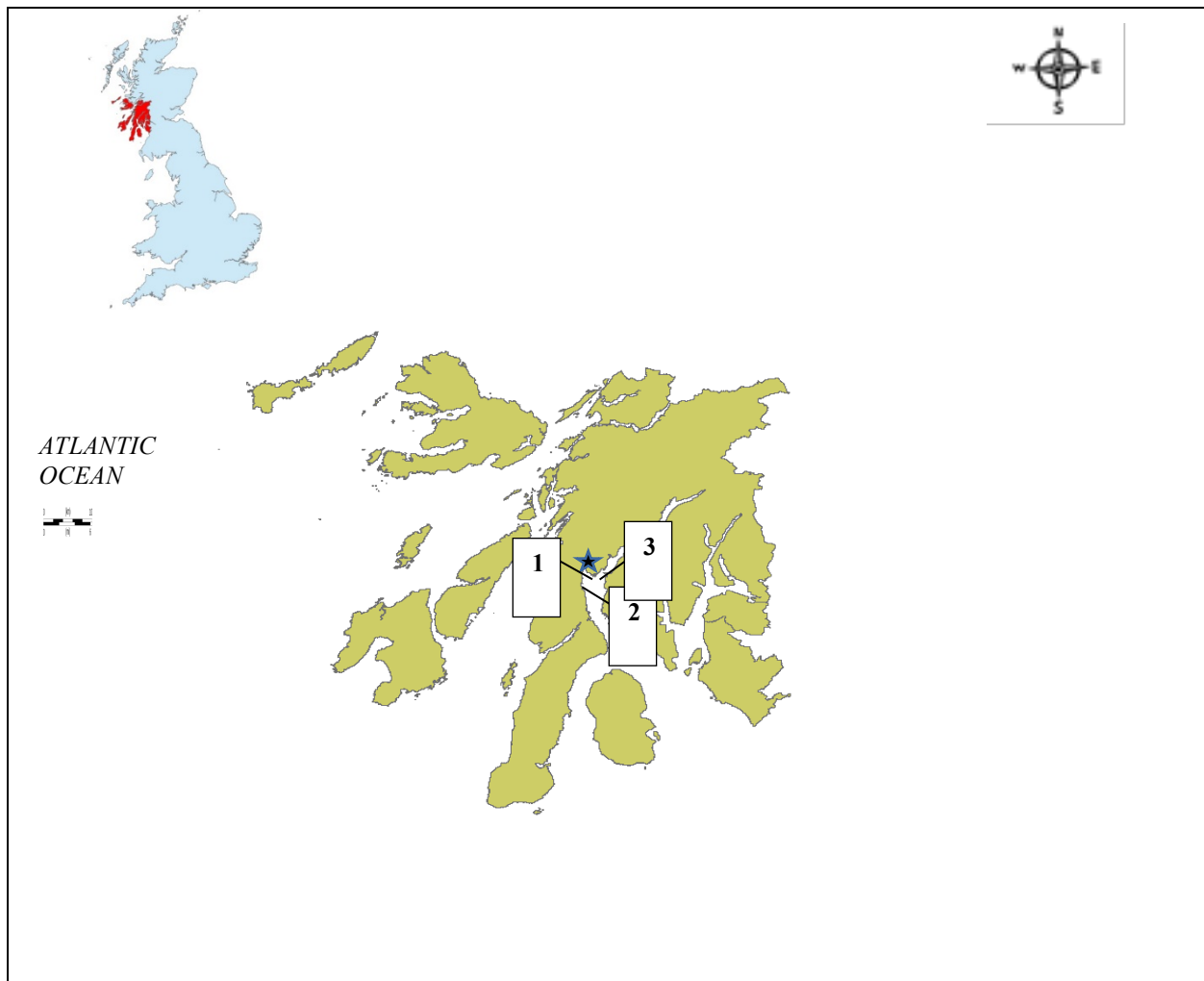


Figure 1: The locations of study sites, including the landfill (denoted by star) in western Scotland (Argyll), where five gull species provided eggs that were collected under licence for flame retardant analysis. Sites as follows:

1. Black-headed gull colony (Duncuan islet);
2. Common gull colony (Ardrishaig);
3. Great black-backed gulls, European herring gulls and lesser black-backed gull colonies (Liath Eilean islet).

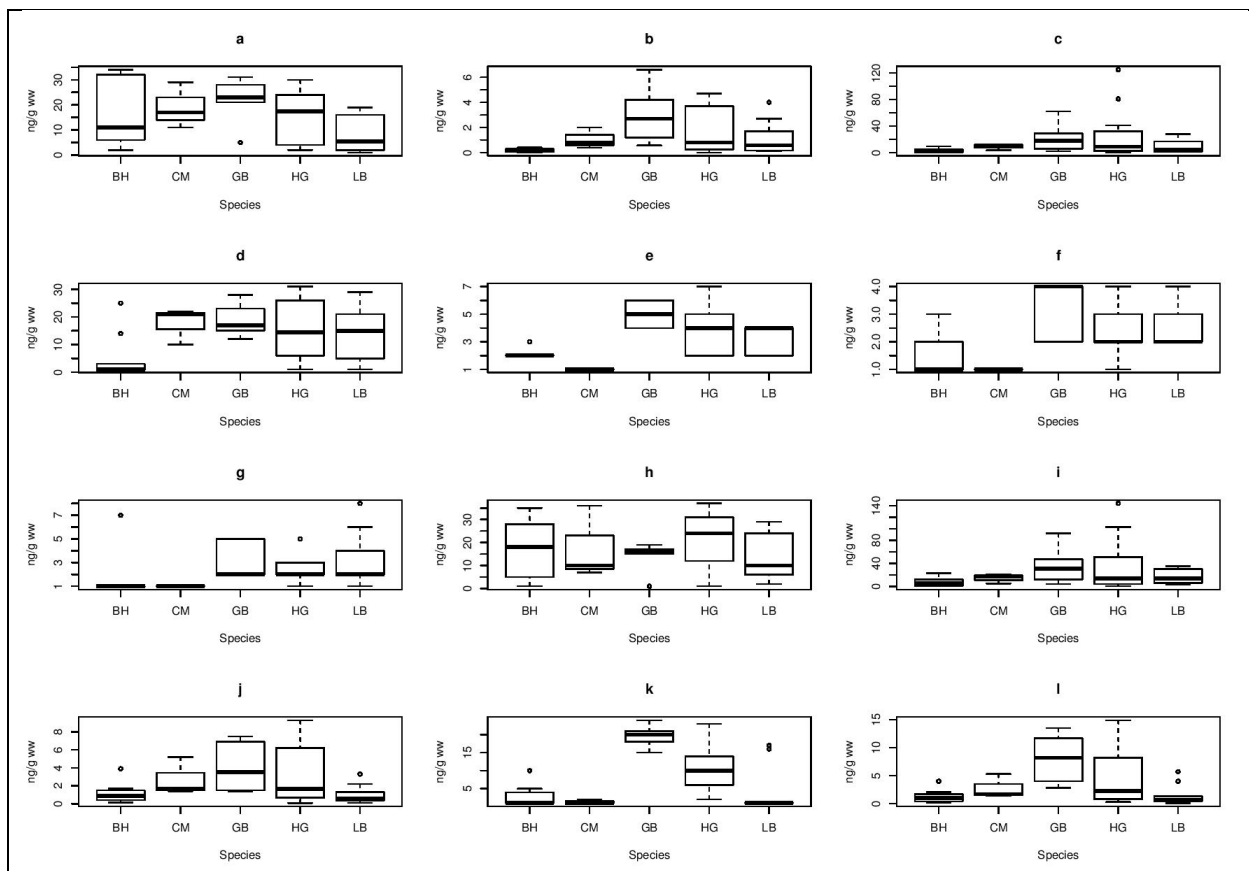


Figure 2: Boxplots (i.e., displaying minimum, first-quartile, median, third-quartile and maximum concentrations in ng/g wet weight [ww]) of PBDEs (eight congeners: [a] BDE-28; [b] BDE-47; [c] BDE-99; [d] BDE-100; [e] BDE-153; [f] BDE-154; [g] BDE-183; [h] BDE-209; [i] Sum-PBDEs) and HBCDD ([j] α -HBCDD; [k] γ -HBCDD; [l] Total HBCDD) detected in egg homogenates of five gull *Larus* spp. species collected under licence from colonies located within 3 km of a landfill in western Scotland (UK), in 2016. Species are: black-headed gull (BH); common gull (CM); great black-backed gull (GB); herring gull (HG) and lesser black-backed gull (LB).

Results and discussion

A total of 42 eggs from all five species at landfill-situated colonies has been analysed for BFR and NBFR concentrations (black-headed gull $n=10$, common gull $n=3$, great black-backed gull $n=5$, European herring gull $n=14$, lesser black-backed gull $n=10$) (Figure 2). To the best of our knowledge, this is the first study worldwide to report flame retardants in common gulls. This is also the first study of BFRs in UK-breeding great black-backed gulls, European herring gulls and lesser black-backed gulls. Comparatively high arithmetic mean BFR

concentrations in the eggs of great black-backed gulls (Σ_8 PBDEs: 46.4 ng/g ww; HBCDD: 8.04 ng/g ww) and European herring gulls (Σ PBDEs: 37.2 ng/g ww; HBCDD: 4.5 ng/g ww) may be related to their relatively wide foraging niches and abundance at the landfill study site, respectively (ref. ¹⁰; personal observations). Black-headed gulls (Σ PBDEs: 5.71 ng/g ww; HBCDD: 1.24 ng/g ww) and common gulls (Σ PBDEs: 14.3 ng/g ww; HBCDD: 2.8 ng/g ww) were not observed foraging on this particular landfill (although both species are known to use landfill

elsewhere as a foraging substrate ¹⁰), possibly explaining their relatively lower mean BFR egg burdens. Lesser black-backed gulls, observed using the landfill in small numbers, exhibited mean Σ PBDEs of 16.5 ng/g ww and mean HBCDD of 1.44 ng/g ww.

In general, Σ PBDE concentrations were somewhat lower than those recently reported for Great Lakes American herring gulls *Larus smithsonianus* (i.e., Σ_{14} PBDE range: 244–657 ng/g ww; HBCDD: 7.17–19.8 ng/g ww ¹¹) However, total HBCDD concentrations in these Scottish-breeding great black-backed gulls (range: 4.0–13.5 ng/g ww) are comparable with such data. Among NBFs, we have detected only DBDPE at concentrations >1 ng/g ww, in five individual eggs of four species (i.e., black-headed gull [42 ng/g ww], common gull [27 ng/g ww], great-black-backed gull [484 ng/g ww] and European herring gull [two eggs: 3.3 and 4.8 ng/g ww]). The relatively high concentrations in black-headed and common gulls (that were not observed on the study landfill) might suggest that landfill is not yet a major source of environmental DBDPE concentrations, although the extent to which these individuals may have used landfill in the non-breeding season is unknown. We believe that the DBDPE concentration reported in the great black-backed gull egg (484 ng/g ww) is the highest reported in wildlife to date.

References:

1. Danon-Schaffer MN, Mahecha-Botero A, Grace JR, et al. (2013); *Sci. Total Environ.* 290: 461-62.
2. Belant JL, Seamans TW, Gabrey SW, et al. (1995); *Am. Midl. Nat.* 134: 30-40.
3. Chen D, Hale RC (2010); *Environ. Int.* 36: 800-11.
4. Furness RW, Greenwood JJD (1993); *Birds as Monitors of Environmental Change*. Chapman & Hall, London.
5. Ratcliffe DA (1967); *Nature* 215: 208-10.
6. Chen D, Martin P, Burgess NM, et al. (2013); *Environ. Sci. Technol.* 47: 12238-47.
7. Polder A, Venter B, Skaare JH, et al. (2008); *Chemosphere* 73: 148-54.
8. Tang W-b, Huang K, Zhao J-h, et al. (2015); *Chemosphere* 126: 25-31.
9. de Solla SR, Weseloh DVC, Hughes K, et al. (2016); *Waterbirds* 39 (1): 166-79.
10. *Birds of the Western Palearctic interactive* (BWPi) (2009); Birdguides, London.
11. Su G, Letcher RJ, Moore JN, et al. (2015); *Environ. Res.* 142: 720-30.

Acknowledgements:

We gratefully acknowledge the Natural Environment Research Council (NERC) for funding ADWT via a PhD studentship (NERC ref NE/L002493/1). We are also grateful to have received funding awards from the Waterbird Society and the Seabird Group.