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Dacthal and chlorophenoxy herbicides and chlorothalonil fungicide in eggs of osprey (*Pandion haliaetus*) from the Duwamish–Lake Washington–Puget Sound area of Washington state, USA

Shaogang Chu [a], Charles J. Henny [b], James L. Kaiser [b], Ken G. Drouillard [a], G. Douglas Haffner [a], Robert J. Letcher [a,*]

[a] *Great Lakes Institute for Environment Research, University of Windsor, 401 Sunset Avenue, Windsor, ON N9B 3P4, Canada*
[b] *U.S. Geological Survey, Forest and Rangeland Ecosystem Science Center, 3200 SW Jefferson Way, Corvallis, OR 97331, USA*

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Osprey eggs from the Puget Sound area contain the herbicide dacthal and its analogue.

Abstract

Current-use chlorophenoxy herbicides including 2,4-dichlorophenoxyacetic acid, dicamba, triclopyr, dicamba, dimethyl tetrachloroterephthalate (DCPA or dacthal), and the metabolite of pyrethroids, 3-phenoxybenzoic acid (3-PBA), and the fungicide, chlorothalonil, were investigated in the eggs of osprey (*Pandion haliaetus*) that were collected from 15 sites from five study areas Puget Sound/Seattle area of Washington State, USA. DCPA differs from acidic chlorophenoxy herbicides, and is not readily hydrolyzed to free acid or acid metabolites, and thus we developed a new method. Of the 12 chlorophenoxy herbicides and chlorothalonil analyzed only DCPA could be quantified at six of these sites (2.0 to 10.3 pg/g fresh weight). However, higher levels (6.9 to 85.5 pg/g fresh weight) of the unexpected DCPA structural isomer, dimethyl tetrachlorophthalate (diMe-TCP) were quantified in eggs from all sites. diMe-TCP concentrations tended to be higher in eggs from the Everett Harbor area. As diMe-TCP is not an industrial product, and not commercially available, the source of diMe-TCP is unclear. Regardless, these findings indicate that DCPA and diMe-TCP can be accumulated in the food chain of fish-eating osprey, and transferred in ovo to eggs, and thus may be of concern to the health of the developing chick and the general reproductive health of this osprey population.

Keywords: Chlorophenoxy herbicide; Chlorothalonil fungicide; Dimethyl tetrachloroterephthalate (DCPA); Osprey eggs; Puget Sound

1. Introduction

The osprey (*Pandion haliaetus*) is a fish-eating bird with a holarctic breeding distribution. Osprey feed almost exclusively on live fish (>90%) although the fish species comprising the diet depends on availability in the area. During breeding, these birds catch fish at relatively short distances from the nest. Ospreys are considered an avian sentinel species of persistent and bioaccumulative organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and other organochlorine (OC) contaminants (e.g., pesticides) (Henny et al., 2004). OC contaminants in eggs reflect local exposure in breeding areas. POPs in osprey have traditionally focused on these ‘‘legacy’’ OC pesticides (e.g., DDTs, chlordanes and hexachlorocyclohexanes (HCHs)) and other OCs (e.g., PCBs and PCDDs) (Elliott et al., 2000, 2001). In osprey from the Williamette River in western Oregon in the United States, biomagnification factors of 87 and 4.3 were reported for *p,p′*-DDE and chlordane pesticides, respectively, in eggs relative to the fish diet (90% large-scale sucker (*Catostomus macrocheilus*) and northern pikeminnow (*Ptychocheilus*

* Corresponding author. National Wildlife Research Centre, Canadian Wildlife Service, Environment Canada, Carleton University (Raven Road), Ottawa, ON K1A 0H3, Canada. Tel.: +1 613 998 6696; fax: +1 613 998 0458.
E-mail address: robert.letcher@ec.gc.ca (R.J. Letcher).

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oregonensis) (Henny et al., 2003). However, there are currently very few data on potentially bioaccumulative, current-use herbicides, pesticides or fungicides in this apical, fish-eating predator.

Current-use, chlorophenoxy herbicides are manufactured as free acids, as alkaline salts (e.g., potassium or dimethylamine salts) or as esters (e.g., methyl, butoxyethyl, isooctyl or 2-ethylhexyl esters) (Santos-Delgado et al., 2000). Aquatic herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) and triclopyr are widely used to selectively control broadleaf and woody plants in various waterways. 2,4-D is one of the oldest and most commonly used herbicides. Once in water, 2,4-D is readily degraded to 2,4-dichlorophenol (Crosby and Tutass, 1996), which is estrogenic (Jobling et al., 1995). Microbial degradation is also important, and Armbrust (2000) predicted that degradation of 2,4-D acid by bacteriophytoplankton was greater than by photolysis. Triclopyr has a similar chemical structure to 2,4-D and photochemically decomposes to trichloropyridinol within hours once it is in water (Petty et al., 2003). Other chlorophenoxy acid herbicides have similar environmental behavior, as they have relatively high water solubility and are readily metabolized to free acid forms under environmental conditions.

One of the heavily and currently used chlorophenoxy herbicides is the neutral dimethyl tetrachloroterephthalate (DCPA), commonly known as dacthal (James and Hites, 1999). DCPA is a pre-emergent herbicide that is used to control numerous annual grasses and broadleaf weeds in the crop production of onions, strawberries and other agronomic crops, turf and ornamental plants. During the 1990 s about 5×10^5 kg of DCPA was applied to crops in the U.S. every year, and half was used for onions and broccoli production (James and Hites, 1999). In fact, according to the US EPA, DCPA was number 10 among the pesticides in current use in the U.S. in 1998–99. DCPA is frequently detected in air, soil, sediment, surface water, and ground water in North America where this herbicide is widely used (Cox, 1991; Monohan et al., 1995; Carpenter et al., 1997; Rostad, 1997; Rawn and Muir, 1999; Muir et al., 2004). Due to the wide use and application of DCPA, air and precipitation concentrations in the Great Lakes basin have been reported as high, or higher than those of other OC pesticides, such as DDT and HCH (James and Hites, 1999). Although chlorophenoxy herbicides and pesticides do not readily appear to have high bioaccumulation potential, some compounds have been reported in aquatic biota and abiotic samples. DCPA was reported in sediment and carp fish samples from east-central Washington State at irrigated farming sites. Whole body carp concentrations were 8.6–67 ng/g wet weight and comparable to *p*,*p*′-DDT, dieldrin and chlordane concentrations (Munn and Gruber, 1997). DCPA was also reported in fish samples from the Great Lakes basin (Clark et al., 1984). Abiotic adsorption and aquatic food web bioconcentration of DCPA is presumably due to bioavailability in water and apparent biotic stability and relatively long half-life (Ross et al., 1990; Wettasinghe and Tinsley, 1993; Carpenter et al., 1997). DCPA has a log K_{OW} value of 4.48 and thus has a bioaccumulative potential in aquatic food webs.

Pyrethroids are widely applied as insecticides throughout the world. Although they appear to be of low toxicity to humans and mammals, their heavy industrial and commercial usage is of environmental concern (Leng et al., 1997; Allan et al., 2005). Pyrethroids such as cypermethrin, deltamethrin and permethrin can be metabolized rapidly by cleavage of the central ester linkage and oxidation of the resulting alcoholic component, yielding carboxylic acids. Therefore, the carboxylic acids, such as 3-phenoxybenzoic acid (3-PBA), can be used as valuable diagnostic analytes for the monitoring of exposure of biota to pyrethroids (Angerer and Ritter, 1997). 2,4,5,6-Tetrachloroisopthalonitrile, or chlorothalonil, is a current-use, broad-spectrum fungicide (log $K_{OW} = 2.88$), and is used agronomic crops such as vegetables, small fruit, turf and ornamental plants.

Concern is high for exposure of wildlife to current-use pesticides, e.g., effects on hormone-dependent processes (Andersen et al., 2002). In the present study, we investigated several potentially bioaccumulative, current-use and chlorinated herbicides, pesticides and fungicides, including DCPA, in eggs of osprey, which are highly contaminated with legacy POPs such as PCBs and DDTs, from the Puget Sound area in northwestern Washington state, USA (Henny et al., 2004). DCPA is generally determined along with other acidic herbicides, as it is thought that its chemical properties for ultratrace isolation are similar with other acidic herbicides. However, the methodologies used have not validated this assumption (Clark et al., 1984; Ngan and Ikesaki, 1991; US EPA 515.1, 1995; US EPA 515.2, 1995; James and Hites, 1999; Rawn and Muir, 1999). To measure ultra trace levels of these acidic herbicides and pesticides, we also developed and compared two analytical methodologies for their determination in the osprey eggs.

2. Materials and methods

2.1. Chemicals and materials

Dimethyl tetrachloroterephthalate (DCPA), (2,4-dichlorophenoxy)acetic acid (2,4-D), 4-(2,4-dichlorophenoxy)butanoic acid (2,4-DB), (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T), 3,6-dichloro-*o*-anisic acid (dicamba), 2-(2,4,5-trichlorophenoxy)propanoic acid (Silvex), 3,5,6-trichloro-2-pyridyloxyacetic acid (triclopyr), and chlorothalonil were purchased from AccuStandard Inc. (CT, USA). Also purchased from AccuStandard were 4-chloro-*o*-tolyloxyacetate (MCPA, methyl derivative of 4-chloro-*o*-tolyloxyacetic acid) and 2-(4-chloro-2-methylphenoxy)propanoate (MCPP, methyl derivative of 2-(4-chloro-2-methylphenoxy)propanoic acid. 3-phenoxybenzoic acid (3-PBA), as one of the main pyrethroids metabolites, tetrafluoroterephthelic acid and 2-phenoxybenzoic acid (2-PBA) were purchased from Aldrich Inc.(WI, USA). All standards had a purity of >97% as indicated by the manufacturer. Dimethyl tetrafluoroterephthalate (DFPA) was synthesized in our laboratory by methylating tetrafluoroterephthelic acid using diazomethane. DFPA was used as internal standard because it is not present in environmental samples, and its chromatographic behavior is similar to DCPA. Dimethyl tetrachlorophthalate (diMe-TCP) was also synthesized in our laboratory by reaction of tetrachlorophthalic anhydride (Aldrich) with methanol. The reaction product was liquid–liquid partitioned and purified by silica column. The purity of diMe-TCP was >97% as indicated by GC/MS (EI source) analysis.

All solvents [hexane, acetone, methanol, isooctane, dichloromethane (DCM), *tert*-butyl methyl ether (MTBE)] were OMNISOLV® grade solvent and purchased from VWR International Inc. (ON, Canada). Distilled