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Review of anthraquinone applications for pest management and agricultural crop protection

Shelagh T DeLiberto* and Scott J Werner



Abstract

We have reviewed published anthraquinone applications for international pest management and agricultural crop protection from 1943 to 2016. Anthraquinone (AQ) is commonly found in dyes, pigments and many plants and organisms. Avian repellent research with AQ began in the 1940s. In the context of pest management, AQ is currently used as a chemical repellent, perch deterrent, insecticide and feeding deterrent in many wild birds, and in some mammals, insects and fishes. Criteria for evaluation of effective chemical repellents include efficacy, potential for wildlife hazards, phytotoxicity and environmental persistence. As a biopesticide, AQ often meets these criteria of efficacy for the non-lethal management of agricultural depredation caused by wildlife. We summarize published applications of AQ for the protection of newly planted and maturing crops from pest birds. Conventional applications of AQ-based repellents include preplant seed treatments [e.g. corn (*Zea mays* L.), rice (*Oryza sativa* L.), sunflower (*Helianthus annuus* L.), wheat (*Triticum* spp.), millet (*Panicum* spp.), sorghum (*Sorghum bicolor* L.), pelletized feed and forest tree species] and foliar applications for rice, sunflower, lettuce (*Lactuca sativa* L.), turf, sugar beets (*Beta vulgaris* L.), soybean (*Glycine max* L.), sweet corn and nursery, fruit and nut crops. In addition to agricultural repellent applications, AQ has also been used to treat toxicants for the protection of non-target birds. Few studies have demonstrated AQ repellency in mammals, including wild boar (*Sus scrofa*, L.), thirteen-lined ground squirrels (*Ictidomys tridecemlineatus*, Mitchell), black-tailed prairie dogs (*Cynomys ludovicainus*, Ord.), common voles (*Microtus arvalis*, Pallas), house mice (*Mus musculus*, L.), Tristram's jirds (*Meriones tristrami*, Thomas) and black rats (*Rattus rattus* L.). Natural sources of AQ and its derivatives have also been identified as insecticides and insect repellents. As a natural or synthetic biopesticide, AQ is a promising candidate for many contexts of non-lethal and insecticidal pest management.

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Supporting information may be found in the online version of this article.

Keywords: 9,10-anthraquinone; agricultural depredation; biopesticide; non-lethal; repellent; wildlife damage management

1 INTRODUCTION

1.1 Background

Attempts to protect agricultural crops from vertebrate and invertebrate pests date back to the beginning of agricultural systems (ca 11 500 years ago). From forest gardening and subsistence farming to increased mechanization and global marketing, vertebrate and invertebrate pests have kept pace with our production efficiencies. Methods to manage agricultural pests have included myriad toxicants and non-lethal strategies (e.g. chemical, biological and physical control techniques). As early as the mid-1700s, Native Americans were using *Veratrum* spp. extract as a chemical repellent to protect corn seed from avian predators.¹

Many natural and synthetic chemicals have been evaluated for their feeding repellency in wild birds, mammals and insects. Criteria for evaluation of effective chemical repellents include: efficacy, potential for wildlife hazard, phytotoxicity and environmental persistence.² One substance that has been thoroughly evaluated in many pest species and application contexts is anthraquinone, or 9,10-anthraquinone (AQ).

Anthraquinone is the quinone derivative of anthracene which is commonly found in dyes, pigments and many plants and organisms. Anthraquinone refers to the diketone structure of 9,10-anthraquinone. Mass synthesis of AQ from anthracene, a fraction of anthracene oil obtained in the distillation of coal tar, began

in the late 1800s.³ Synthetic forms of AQ enabled the production of AQ-based dyes in the early 1900s.

Early repellents primarily comprised dye products that had a noxious odor or taste.⁴ Commonly used products included Prussian blue, red iron oxide, carbon black, coal tars and starch.^{2,4} The literature indicates that anthracene and AQ repellent research began in the 1940s. In a review of avian repellents, Neff and Meanley² reported that anthracene was successfully tested with European green finches (*Carduelis chloris* L.) in 1941. Avery *et al.*⁵ concluded that 0.5% anthracene on rice seed (*Oryza sativa* L.) was the least effective repellent tested with red-winged blackbirds (*Agelaius phoeniceus* L.). No other repellent testing of anthracene has been published. In contrast, AQ has been extensively evaluated for pest management and agricultural crop protection.

Anthraquinone was first patented as a bird repellent in 1943. Heckmanns and Meisenheimer submitted the German patent (No. 743517)⁶ that fostered the first commercial formulation of an AQ-based repellent (i.e. Morkit). A subsequent US patent enabled

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the importation and distribution of Morkit in the United States.^{4,7} Anecdotal data from Neff and Meanley² indicate that AQ was being tested as a bird repellent around the world in the 1940s. For example, in 1948, researchers in Israel reported the protection of AQ-treated grasses and clovers from Israeli sparrows (Family: Passeridae) and larks (Family: Alaudidae), and researchers in France reported ineffective results of AQ applied to corn seed.² Anthraquinone has continued to be studied as a chemical repellent in each decade since 1940.

The mode of action of AQ is to cause post-ingestional distress in birds. Several studies have described the behavior of birds following ingestion of AQ.^{5,8,9} The emetic response is produced through irritation of the gut, but the actual mechanism is unclear. The post-ingestional distress that occurs from eating AQ-treated food results in a conditioned avoidance to that food type.^{5,10}

The United Nations Economic and Social Council (UN ECOSOC) developed and adopted the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) in July 2003. The GHS seeks to harmonize the major existing systems for chemicals in transport and in the workplace, pesticides and consumer products, without lowering the level of protection afforded by existing systems. Other international parties, including the European Union (EU), the Codex Alimentarius Commission (Codex) and the North American Free Trade Agreement (NAFTA), have sought to harmonize pesticide legislation by providing maximum residue limits (MRLs).¹⁰ With this rise in emphasis on MRLs, we provide a novel review of AQ applications for international pest management and agricultural crop protection, including recommended concentrations based upon available testing data, from 1943 to 2016. This synthesis serves to illustrate the relevant concentrations of AQ needed for various agricultural pest management needs. We have divided AQ applications into four categories: avian seed treatments, avian foliar treatments, miscellaneous avian applications and non-avian applications (Tables 1 to 4). We have summarized the testing of AQ-based products in various species, and the patents and registrations currently available for international AQ applications.

1.2 Review methods

We have reviewed the scientific and gray literature for AQ repellent studies conducted up to and including 2016. We have searched anthraquinone, 9,10-anthraquinone, avipel, morkit and repellent, along with various combinations of bird(s), mammals, rodents, etc., using various literature search engines (AGRIS, AGRICOLA, BIOSIS, CAB, Google Scholar and Zoological Record). We have also utilized backward reference searching to identify and examine references in an article that related to anthraquinone. Most papers, both peer reviewed and gray literature, have been included in this review for the purposes of a complete record of species tested with AQ repellents.

2 AVIAN SEED TREATMENTS

Most pest management uses of AQ include preplant seed treatments for the protection of newly planted crops from wild birds. Bird damage to agricultural seeds begins immediately after planting. Granivorous birds can damage pre- and post-emergent seedlings by exhuming and/or consuming the seed coat, hypocotyl and cotyledon(s). Seed treatments are used to protect pre- and post-emergent seedlings from avian depredation without negatively affecting the germination of treated seeds.

2.1 Corn

Corn (*Zea mays* L.) seed treatments have been tested with ring-necked pheasants (*Phasianus colchicus* L.),^{11–13} sandhill cranes (*Grus canadensis* L.),^{14,15} Canada geese (*Branta canadensis* L.),¹³ house crows (*Corvus splendens* Vieillot),⁹ rooks (*C. frugilegus* L.)¹⁶ and rock pigeons (*Columba livia* Gmelin),¹⁷ with varying results (supporting information Table S1). Early testing with ring-necked pheasants and AQ-treated corn had inconclusive results; none of the repellents tested, including AQ, reduced damage relative to untreated controls.¹¹ Treatment concentrations were not indicated, thus prohibiting the interpretation of results. In general, recent laboratory efficacy and field experiments with ring-necked pheasants demonstrate that AQ is an effective repellent for pre- and post-emergent seedlings (Table 1).^{12,13}

Among other birds evaluated with corn seed treatments, sandhill cranes and Canada geese both demonstrated reduced consumption of corn treated with relatively low levels of AQ.^{13,14} Recent testing with house crows in Pakistan demonstrated a 45% reduction in consumption of corn seed treated with 10 000 mg AQ kg⁻¹ relative to untreated corn.⁹ Rooks in Great Britain, however, consumed corn treated with up to 100 000 mg AQ kg⁻¹, though corn damage was relatively low (i.e. 3.5–9.0%).¹⁶

Esther¹⁷ evaluated the repellency of corn seed treated with a plant-extracted formulation of AQ. Pigeons were offered corn seed treated with 0.16, 1.6 or 4.8 mL natural AQ kg⁻¹ and corn treated with 0.5 and 1.0 mL synthetic AQ kg⁻¹. Corn treated with 1.0 mL synthetic AQ kg⁻¹ was preferred over untreated seeds. Although significant repellency for corn treated with 4.8 mL natural AQ kg⁻¹ was observed on day 1, repellency was not observed on days 2 to 4.¹⁷ Previously, the repellency of 10 000 mg AQ kg⁻¹ offered in solution in the drinking water of rock pigeon demonstrated a 50% reduction in water intake. AQ is insoluble in water, which may have contributed to the lower efficacy compared with other tested compounds.¹⁸

2.2 Rice

Testing of rice seed treatments has largely focused on *Icteridae* species found in the United States, primarily red-winged blackbirds. Testing has included no-choice and choice experiments and a variety of AQ-based products. Red-winged blackbirds have consistently demonstrated repellency to AQ-treated rice seed. Repellency has been positively associated with AQ concentrations as low as 50 mg AQ kg⁻¹ and up to 20 000 mg AQ kg⁻¹, regardless of the tested product.^{5,13,19–25} A threshold concentration of 4921 mg AQ kg⁻¹ on rough rice was predicted for 80% repellency in red-winged blackbirds;¹³ this concentration also causes conditioned avoidance in investigations of sensory cues.²³ Red-winged blackbirds preferred untreated rice to rice treated with 2325 mg AQ kg⁻¹ in preference testing.¹³ Common grackles (*Quiscalus quiscula* L.), boat-tailed grackles (*Q. major* Vieillot), great-tailed grackles (*Q. mexicanus* Gmelin) and brown-headed cowbirds (*Molothrus ater* Boddaert) have demonstrated repellency to AQ-treated rice seed at 5000–20 000 mg AQ kg⁻¹ in no-choice trials.^{5,19,20,22,24,26}

Field testing of AQ-treated rice seed in water-seeded field tests in Louisiana demonstrated that rice seed treated with 7100–8800 mg AQ kg⁻¹ at planting was effective for blackbird repellency.^{19–21,27} Anthraquinone-treated plots had higher plant density than control plots at the conclusion of the study, and bird activity within control plots was twice that observed within treated plots.^{19–21,27} Anthraquinone residues on treated rice seed decreased up to 50% 1–3 days post-planting without affecting blackbird repellency.^{19–21,27} Attempts to soak rice seed with an

Table 1. Recommended concentration of anthraquinone (mg kg⁻¹) for avian seed treatments. Recommended concentration is stated in mg AQ kg⁻¹ seed type

Crop	Species	Scientific name	Recommended concentration (mg AQ kg ⁻¹) ^a
Corn	Canada goose	<i>Branta canadensis</i>	1450
Corn	Ring-necked pheasant	<i>Phasianus colchicus</i>	n/a
Corn	Sandhill crane	<i>Grus canadensis</i>	2500
Corn	Rock pigeon	<i>Columba livia</i>	None
Corn	House crow	<i>Corvus splendens</i>	10 000
Corn	Rook	<i>Corvus frugilegus</i>	None
Rice	Dickcissel	<i>Spiza americana</i>	>5000
Rice	Red-winged blackbird	<i>Agelaius phoeniceus</i>	5000
Rice	Common grackle	<i>Quiscalus quiscula</i>	20 000
Rice	Boat-tailed grackle	<i>Quiscalus major</i>	10 000
Rice	Great-tailed grackle	<i>Quiscalus mexicanus</i>	2000
Rice	Brown-headed cowbird	<i>Molothrus ater</i>	5000
Sunflower, confectionary	Common grackle	<i>Quiscalus quiscula</i>	9200
Sunflower, oilseed	Red-winged blackbird	<i>Agelaius phoeniceus</i>	1994
Sunflower, hulled	Ring-necked pheasant	<i>Phasianus colchicus</i>	>1310
Sunflower, oilseed	Ring-necked pheasant	<i>Phasianus colchicus</i>	15 800
Wheat	Horned lark	<i>Eremophila alpestris</i>	3010
Wheat	House sparrow	<i>Passer domesticus</i>	800–10 000
Wheat	Mallard	<i>Anas platyrhynchos</i>	170
Wheat	Ring-necked pheasant	<i>Phasianus colchicus</i>	Unknown
Wheat	Rook	<i>Corvus frugilegus</i>	>2250
Oak spp.	Wild birds		3.32 kg ha ⁻¹
Pine spp.	Wild birds		150 000
Millet	Brown-headed cowbird	<i>Molothrus ater</i>	5000
Millet	Northern bobwhite	<i>Colinus virginianus</i>	1180
Millet	European starling	<i>Sturnus vulgaris</i>	1131
Millet	Red-winged blackbird	<i>Agelaius phoeniceus</i>	>1000
Oats	Wild turkey	<i>Meleagris gallopavo</i>	4000–5300
Sorghum	Brown-headed cowbird	<i>Molothrus ater</i>	None
CUBC ^b	European starling	<i>Sturnus vulgaris</i>	33 300
Poultry pellets	European starling	<i>Sturnus vulgaris</i>	>35 000
Poultry feed	Chicken	<i>Gallus gallus</i>	20 000

^a Recommended concentration based on available testing data; see supporting information Table S1 for citations.

^b CUBC: CU bird carrier is a high-protein and high-fat feed.

AQ suspension yielded low AQ residues (1300 mg AQ kg⁻¹) at planting and no repellency to blackbirds.²⁷ Anthraquinone was retained on drill-seeded rice up to 19 days post-planting, and residues averaged 5993 mg AQ kg⁻¹ during the test period.²⁵

Internationally there has been one additional species evaluated with AQ-treated rice seeds. Rice treated with 5000 mg AQ kg⁻¹ reduced consumption by dickcissels (*Spiza americana* Gmelin) in no-choice trials, while rice treated with 500 and 1000 mg AQ kg⁻¹ was ineffective. In choice trials, dickcissels consumed more untreated millet (*Panicum* spp.) than AQ-treated rice seed.²⁸

2.3 Sunflower

Bird damage to sunflower (*Helianthus annuus* L.) is largely an issue during the ripening phase of plant growth owing to passerine damage to sunflower achenes. In addition, ground feeding birds such as ring-necked pheasants can damage newly planted sunflower fields. Testing with AQ as a sunflower seed treatment has been conducted with red-winged blackbirds, common grackles and ring-necked pheasants. Red-winged blackbirds exhibited greater than 80% repellency for sunflower treated with 1994 mg

AQ kg⁻¹ in concentration–response experiments.¹³ When AQ was applied to sunflower seed in combination with registered insecticides or registered fungicides, a threshold concentration of 1475 mg AQ kg⁻¹ was predicted to elicit 80% repellency for oilseed sunflower in blackbirds. This is the same threshold concentration as sunflower treated with AQ alone.^{13,29} When an ultraviolet visual cue was added to the AQ seed treatment, synergistic repellency was observed at 200 mg AQ kg⁻¹ and 350 mg AQ kg⁻¹ (i.e. 45–115% increase in repellency).³⁰ Interestingly, common grackle testing with AQ-treated confectionary sunflower demonstrated a much higher threshold concentration, with predicted 80% repellency at 9200 mg AQ kg⁻¹.³¹

Ring-necked pheasant testing with AQ-treated sunflower hearts (i.e. hulled sunflower) demonstrated a maximum repellency of 66% at 1310 mg AQ kg⁻¹.¹³ In a later study, oilseed sunflower treated with 15 800 mg AQ kg⁻¹ was planted and allowed to sprout to seedling stage before being offered to pairs of ring-necked pheasants. Results indicated less damage to emergent seedlings from AQ seed treatments (12% damage) than untreated seedlings (54% damage).³¹

Table 2. Summary of pen and field trials assessing avian foliar treatments with anthraquinone. Efficacy of foliar applications is described using a (+) for treatments that demonstrated a decrease in damage or a (-) for treatments that demonstrated no decrease in damage. Treatment tested is stated in litres of formulated anthraquinone product per hectare, and in milligrams of anthraquinone applied per seed type. Residue is stated in milligrams of anthraquinone per kilogram of crop type

Crop	Species	Scientific name	Treatment tested (L ha ⁻¹)	Treatment tested (mg kg ⁻¹)	Residue(mg kg ⁻¹)	Efficacy of foliar application (+/-)	Country	Original citation
Rice, post-emergent seedling	Red-winged blackbird	<i>Agelaius phoeniceus</i>	9.3, 23.3, 37.2		n/a	+	USA (Florida)	Avery <i>et al.</i> , 2000 ⁵⁵
Rice, post-emergent seedling	Red-winged blackbird	<i>Agelaius phoeniceus</i>	18.6		n/a	+	USA (Florida)	Avery <i>et al.</i> , 2000 ⁵⁵
Rice, post-emergent seedling	Red-winged blackbird	<i>Agelaius phoeniceus</i>	9.3, 18.6		72–131, 274–467	-	USA (Louisiana)	Avery <i>et al.</i> , 2000 ⁵⁵
Rice, ripening	Red-winged blackbird	<i>Agelaius phoeniceus</i>	9.3		209–337	+	USA (Louisiana)	Avery <i>et al.</i> , 2002 ⁵⁶
Rice, wild	Red-winged blackbird	<i>Agelaius phoeniceus</i>	18.6, 55.8		430	+	USA (California)	Avery <i>et al.</i> , 2000 ⁵⁷
Rice, wild, ripening	Red-winged blackbird	<i>Agelaius phoeniceus</i>	18.6, 55.8		430, 800–1000	-	USA (California)	Avery <i>et al.</i> , 2000 ⁵⁷
Sunflower, oilseed, ripening	Red-winged blackbird	<i>Agelaius phoeniceus</i>	4.7, 9.4		481 decreasing to 385, 978 decreasing to 952	+	USA (North Dakota)	Werner <i>et al.</i> , 2014 ²⁹
Sunflower, oilseed, ripening	Red-winged blackbird	<i>Agelaius phoeniceus</i>	18.7 applied twice 3 days apart		167 (bracts), 4 and 7 (achenes)	-	USA (North Dakota)	Niner <i>et al.</i> , 2015 ⁶⁰
Sunflower, oilseed, ripening	Wild birds		4.7		1.4–15.7	-	USA (North Dakota)	Kandel <i>et al.</i> , 2009 ⁵⁹
Sunflower, oilseed, ripening	Red-winged blackbird	<i>Agelaius phoeniceus</i>	4.7, 9.4, 18.7		45, 141, 320	+	USA (Colorado)	Werner <i>et al.</i> , 2014 ²⁹
Sunflower, confectionary, ripening	Common grackle	<i>Quiscalus quiscula</i>	18.7		6001	+	USA (Colorado)	Werner <i>et al.</i> , 2011 ³¹
Lettuce seedlings	Horned lark	<i>Eremophila alpestris</i>	10		103–570	+	USA (California)	Cummings <i>et al.</i> , 2006 ⁶²
Lettuce seedlings	Horned lark	<i>Eremophila alpestris</i>	2.79		n/a	+	USA (California)	York <i>et al.</i> , 2000 ⁶¹
Turf	Canada goose	<i>Branta canadensis</i>	1.9 ^a		n/a	+	USA (Colorado)	Devers <i>et al.</i> , 1998 ⁶⁵
Turf	Canada goose	<i>Branta canadensis</i>	4.5		2.02 L ha ⁻¹ , 0.22 L ha ⁻¹ 7 days post-spray	+	USA (Ohio)	Dolbeer <i>et al.</i> , 1998 ⁴⁶
Turf	Canada goose	<i>Branta canadensis</i>	2.3		1.2 L ha ⁻¹ , 0.4 L ha ⁻¹ 7 days post-spray	+	USA (Ohio)	Blackwell <i>et al.</i> , 1999 ⁶⁴
Turf	Canada goose	<i>Branta canadensis</i>	4.7		n/a	+	USA (Oregon)	Gordon and Lyman, 2000 ⁶⁶
Turf	Canada goose	<i>Branta canadensis</i>	9.4		n/a	+	USA	Knauer <i>et al.</i> , 2000 ⁶⁷
Turf	Canada goose	<i>Branta canadensis</i>	9.4		n/a	+	USA (North Carolina)	Ayers <i>et al.</i> , 2010 ⁶³

Table 2. Continued

Crop	Species	Scientific name	Treatment tested (L ha ⁻¹)	Treatment tested (mg kg ⁻¹)	Residue(mg kg ⁻¹)	Efficacy of foliar application (+/-)	Country	Original citation
Sugar beet	House sparrow	<i>Passer domesticus</i>	8.8 – 16.3 ^a	n/a	n/a	+	England	Dunning, 1974 ⁶⁸
Wheat	House sparrow	<i>Passer domesticus</i>		2500, 5000, 7500, 10 000	n/a	+	Pakistan	Ahmad <i>et al.</i> , 2015 ⁸
Soybean	Canada goose	<i>Branta canadensis</i>		833 applied every 7 days	n/a	+	USA (South Dakota)	Dieter <i>et al.</i> , 2014 ⁶⁹
Corn	House crow	<i>Corvus splendens</i>		250, 500, 750, 1000	n/a	+	Pakistan	Saleem <i>et al.</i> , 2015 ⁹
Sweet corn	European starling	<i>Sturnus vulgaris</i>		1000, 2500, 5000, 7500, 10 000, 20 000	327, 429, 700, 1574, 2770, 4805	-	USA (Colorado)	Tupper <i>et al.</i> , 2014 ⁴⁹
Sweet corn	Red-winged blackbird	<i>Agelaius phoeniceus</i>		1000, 2500, 5000, 7500, 10 000, 20 000	341, 1020, 2347, 2600, 4912, 9619	+	USA (Colorado)	Carlson <i>et al.</i> , 2013 ⁷⁰
Blueberries	European starling	<i>Sturnus vulgaris</i>		1000, 2000, 3000, 4000, 5000	n/a	-	USA (Colorado)	Tupper <i>et al.</i> , 2014 ⁴⁹
Holly berries	American robin	<i>Turdus americanus</i>		50, 250, 400, 500, 1000	n/a	+	USA (Colorado)	Poche, 1998 ²²
Almonds	American crow	<i>Corvus brachyrhynchos</i>		5000, 10 000, 20 000, 40 000	2980, 7380, 14 700, 31 500	+	USA (Colorado)	Werner <i>et al.</i> , 2015 ²⁶

^a Units for these treatment applications are kg AQ ha⁻¹.

Table 3. Summary of pen and field trials assessing miscellaneous avian treatments with anthraquinone. Efficacy of miscellaneous avian treatments is described using a (+) for treatments that demonstrated a decrease in consumption or a (–) for treatments that demonstrated no decrease in consumption

Crop	Species	Scientific name	Application	Treatment tested (mg kg ⁻¹)	Efficacy of application (+/–)	Country	Original citation
Granular pesticide	Northern Bobwhite	<i>Colinus virginianus</i>	Surface	1000, 2000, 5000, 8000, 10 000	+/–	USA (Colorado)	Poche, 1998 ²²
Rodenticide bait	Canada Goose	<i>Branta canadensis</i>	Surface	1000, 10 000, 50 000	+	USA (Colorado)	Werner <i>et al.</i> , 2011 ⁷³
Rodenticide bait	Canada Goose	<i>Branta canadensis</i>	Surface	10 000, 26 000	+	USA (Colorado)	Werner <i>et al.</i> , 2011 ⁷³
Rodenticide bait	Ring-necked pheasant	<i>Phasianus colchicus</i>	Surface	10 000, 20 000	+	USA (Colorado)	Werner <i>et al.</i> , 2011 ⁷³
Rodenticide bait	Horned lark	<i>Eremophila alpestris</i>	Surface	10 000, 20 000	+	USA (Colorado)	Werner <i>et al.</i> , 2011 ⁷³
Toxic pest baits	Kea	<i>Nestor notabilis</i>	Unknown	Unknown	+	New Zealand	Orr-Walker and Roberts, 2010 ⁷⁹
Toxic pest baits	Kea	<i>Nestor notabilis</i>	Incorporated	1000	+	New Zealand	Orr-Walker <i>et al.</i> , 2012 ⁸⁰
Toxic pest baits (dough/carrot)	North Island robin	<i>Petroica australis longipes</i>	Surface	450, 900	+	New Zealand	Clapperton <i>et al.</i> , 2014 ⁷⁵
Toxic pest baits	North Island robin	<i>Petroica australis longipes</i>	Surface	20 000 (with d-pulegone)	+	New Zealand	Day and Matthews, 2005 ⁷⁶
Toxic pest baits	North Island robin	<i>Petroica australis longipes</i>	Surface	10 000 (with d-pulegone)	+	New Zealand	Day <i>et al.</i> , 2003 ⁷⁴
Structure	Rock pigeon	<i>Columba livia</i>	Surface	9.4 L ha ⁻¹	+	USA	Knauer <i>et al.</i> , 2000 ⁶⁷
Poultry feed	Chicken	<i>Gallus gallus</i>	Incorporated	15 000, 20 000, 30 000, 70 000	+	USA (Florida)	Damron and Jacob, 2001 ⁸²
Fruit, wild	Blackbirds	(<i>Turdus</i> spp.)	Incorporated	Unknown	+	England	Sorensen, 1983 ⁸³
Chrysolimid larvae	Tits	<i>Parus</i> spp.	Incorporated	400, 600	+	Germany	Hilker and Kopf, 1994 ⁸⁴

2.4 Wheat

As mentioned previously, Heckmanns and Meisenheimer submitted supporting experiments to the US Patent Office in 1944. There were two experiments with crows: (1) cage testing of a mixture of 250 000 mg AQ kg⁻¹ and 750 000 mg talcum kg⁻¹ on wheat (*Triticum* spp.) seed; (2) post-emergent wheat seed treatment of 250 000–100 000 mg AQ kg⁻¹ mixed with varying levels of talcum. Both of these experiments demonstrated crow repellency and no negative effects to wheat germination.^{4,6} A more recent study demonstrated minimal repellency among rooks offered post-emergent wheat seedlings from 2250 mg AQ kg⁻¹ seed treatments (label rate). Rooks plucked seeds prior to germination and otherwise ate only above-ground phytomass. Plant density relative to the control was marginally improved.³²

Among other birds evaluated with wheat seed treatments, mallards (*Anas platyrhynchos* L.) and horned larks (*Eremophila alpestris* L.) both demonstrated reduced consumption of wheat treated with relatively low levels of AQ.^{26,33} Pheasants were effectively repelled by unknown concentrations of five commercially available AQ-based wheat seed treatments.³⁴ Recent testing in New Zealand demonstrated varying repellency of house sparrows (*Passer domesticus* L.) to wheat treated with 323–860 mg AQ kg⁻¹; AQ-treated wheat was consumed less than untreated wheat in each test.^{35,36} Testing with house sparrows in Pakistan at higher AQ levels (2500–10 000 mg AQ kg⁻¹) demonstrated up to an 80%

reduction in consumption of wheat seed treated with AQ relative to untreated wheat.⁸

2.5 Direct seeding of forest tree species

Historically, AQ has been registered for the protection of forest tree seed, including longleaf pine (*Pinus palustris* Mill.), Eastern white pine (*P. strobus* L.) and oak (*Quercus* spp.), from wild birds.^{37–40} Anthraquinone seed treatments have also been used in reforestation as a bird damage prevention method for black pine (*P. nigra*, Arnold), shortleaf pine (*P. echinata*, Mill.) and loblolly pine (*P. taeda* L.) in Europe and the United States as recently as 2005.^{41–44} Defauce and Enriquez⁴⁵ successfully tested AQ seed treatments to protect pine and eucalyptus (*Eucalyptus* spp.) seeds from wild birds in Spain.

2.6 Miscellaneous seed treatments

The repellency of AQ-based seed treatments for millet has been tested with four bird species: red-winged blackbirds, brown-headed cowbirds, European starlings (*Sturnus vulgaris* L.) and Northern bobwhite quail (*Colinus virginianus* L.). Red-winged blackbirds exhibited moderate (approximately 69%) repellency for 500–1000 mg AQ kg⁻¹ treated millet.²² European starlings and Northern bobwhite quail exhibited 90% repellency for millet treated with 1131 and 1180 mg AQ kg⁻¹ in cage testing.²²

Table 4. Summary of pen and field trials assessing non-avian treatments with anthraquinone. Efficacy of non-avian treatments with anthraquinone is described using a (+) for treatments that demonstrated a decrease in damage or a (–) for treatments that demonstrated no decrease in damage

Crop	Species	Scientific name	Application	Treatment tested (mg kg ⁻¹)	Efficacy of application (+/–)	Original citation
Corn	Wild boar	<i>Sus scrofa</i>	Seed	8000	+	Santilli <i>et al.</i> , 2005 ⁸⁹
Loblolly pine	Deer mouse	<i>Peromyscus maniculatus</i>	Seed	150 000 (with 20 000 Endrin 25 W)	–	Langdon and LeGrande, 1965 ⁹⁰
Corn	Thirteen-lined ground squirrel	<i>Spermophilus tridecemlineatus</i>	Seed	4826	–	Hodne-Fischer, 2009 ¹²
Corn	Black-tailed prairie dog	<i>Cynomys ludovicianus</i>	Seed	5000, 10 000, 20 000, 40 000	+	Werner <i>et al.</i> , 2011 ⁷³
Wheat	Common vole	<i>Microtus arvalis</i>	Odor	50 000	+	Hansen <i>et al.</i> , 2015 ^{92,94}
Wheat	Common vole	<i>Microtus arvalis</i>	Odor	150 000	–	Hansen <i>et al.</i> , 2016 ⁹³
Wheat	House mouse	<i>Mus musculus</i>	Odor	50 000	–	Hansen <i>et al.</i> , 2015 ^{92,94}
Wheat	House mouse	<i>Mus musculus</i>	Odor	150 000	–	Hansen <i>et al.</i> , 2016 ⁹³
Carrot	Pocket gopher	<i>Thomomys bottae</i>	Seed	Unknown	–	Hansen <i>et al.</i> , 2015 ⁹⁴
Barley	Gunther's vole	<i>Microtus guntheri</i>	Seed	Unknown	–	Hansen <i>et al.</i> , 2015 ⁹⁴
Barley	Tristram's jird's	<i>Meriones tristrami</i>	Seed	Unknown	+	Hansen <i>et al.</i> , 2015 ⁹⁴
Cereal pellet bait	Roof rat	<i>Rattus rattus</i>	Incorporated	1000, 2500 (with 1080 rodenticide)	+	Cowan <i>et al.</i> , 2015 ⁹⁶
Cereal pellet bait	Roof rat	<i>Rattus rattus</i>	Incorporated	1000 (with 1080 rodenticide, 1700 d-pulegone and green dye)	+	Crowell <i>et al.</i> , 2016 ⁹⁷
Cereal pellet bait	Brush-tailed possum	<i>Trichosurus vulpecula</i>	Incorporated	1000, 2500 (with 1080 rodenticide)	–	Cowan <i>et al.</i> , 2015 ⁹⁶
Cereal pellet bait	Brush-tailed possum	<i>Trichosurus vulpecula</i>	Incorporated	1000 (with 1080 rodenticide, 1700 d-pulegone and green dye)	–	Crowell <i>et al.</i> , 2016 ⁹⁷

Brown-headed cowbirds needed 5000 mg AQ kg⁻¹ for sustained repellency, although lower concentrations were also repellent.⁴⁶

There have been few tests of AQ repellency in gallinaceous birds. Two experiments evaluated the repellency of AQ-treated whole oats (*Avena sativa* L.) with wild turkeys (*Meleagris gallopavo* L.). Results predicted 80% repellency at 4000 and 5300 mg AQ kg⁻¹ in male and female wild turkeys respectively.⁴⁷

Although previous tests with brown-headed cowbirds have indicated AQ repellency among various seeds, sorghum (*Sorghum bicolor* L.) seed treatments including 5000 and 10 000 mg AQ kg⁻¹ provided no repellency within Oklahoma fields. Cowbirds consumed all of the AQ-treated sorghum during the field study. The authors suggested that the AQ sourced for this test may have been old and therefore may have lost its repellency.⁴⁸

Two experiments conducted with European starlings utilized pelletized baits to determine threshold repellency. One experiment utilized poultry pellets with AQ incorporated into the pellet mix prior to formation of pellets. Even at concentrations up to 35 000 mg AQ kg⁻¹, only 77% repellency was observed.⁴⁹ European starling tests utilizing CU bird carrier, a high-protein and high-fat feed, predicted 80% repellency at 6275 mg AQ kg⁻¹.⁴⁹ The formulation of the AQ treatment (i.e. homogeneous baits versus surface application) can therefore influence repellent efficacy.

2.7 Discussion

Anthraquinone seed treatments have been shown to protect pre- and post-emergent seedlings from depredation in laboratory efficacy experiments with a variety of avian species. This review highlights the variability in concentrations of AQ needed to protect seeds from different avian species and even within species to protect various seed types. Red-winged blackbirds demonstrated greater than 80% repellency to sunflower treated with 1700 mg AQ kg⁻¹, whereas common grackles required 12 200 mg AQ kg⁻¹.^{29,31} Red-winged blackbirds demonstrated 79% repellency to 4921 mg AQ kg⁻¹ treated rice seed, several thousand mg kg⁻¹ more than needed for sunflower.¹³ These results still require field validation as recommended laboratory concentrations are transitioned to use in field settings. For example, environmental conditions (i.e. irrigation, planting methods) will affect how AQ is retained on seeds. Field tests of AQ-treated rice had varying results, depending on whether the rice seed was drill seeded or water seeded.^{25,27} Another factor affecting transition of laboratory efficacy concentrations to field settings is how birds forage. Laboratory efficacy studies with Canada geese demonstrated repellency to AQ-treated corn seed; however, geese feed by grazing and would not have contact with the treated seed once planted. Species-specific laboratory efficacy experiments and field residue studies are recommended at AQ concentrations sufficient for the protection of pre- and post-emergent seedlings from avian depredation.⁵⁰

Anthraquinone is not toxic to red-winged blackbirds or European starlings at 100 mg kg⁻¹.^{51,52} There have been no reported

avian or mammalian mortalities related to the ingestion of pre- or post-emergent seedlings from AQ seed treatments, thus indicating limited wildlife hazard.²² Testing has also demonstrated a lack of acute toxicity in crayfish (*Procambarus clarkii* Girard) associated with AQ treatments within rice–crayfish crop rotations.⁵³ Anthraquinone has been shown to have negligible effects on the germination of various agricultural crop seeds.^{17,21,31} Sunflower seed treatments comprising AQ and a registered fungicide or AQ and a registered insecticide demonstrated no decrease in avian repellency or seed germination.²⁹ Moreover, AQ residues from 10 000 mg AQ kg⁻¹ rice seed treatment were 0.1 mg AQ kg⁻¹ at harvest.²⁵

Based upon the promising repellency of AQ seed treatments, several patents have been filed subsequent to the original German patent in 1943 (German Patent No. 743517).⁶ A patent was filed in each of the United Kingdom (GB1601226; 1981), Japan (JP62-43961; 1987) and the United States (US005885604; 1999).⁵⁴ All three of these patents described the use of AQ for the protection of seeds from birds, and in some cases have led to the registration of products for the protection of seeds from birds (supporting information Table S3).

3 AVIAN FOLIAR TREATMENTS

Foliar treatments are applied directly to emergent seedlings and to maturing and preharvest crops via ground or aerial spray applications. Foliar pesticide applications are most commonly used for the application of insecticides, fungicides, herbicides and molluscicides on agricultural crops. Herbivorous birds can damage emergent seedlings and above-ground phytomass. Granivorous birds can damage maturing seeds prior to harvest. Foliar applications have demonstrated some success in cage testing, but the efficacy of foliar repellent applications is often limited by insufficient repellent residues on the surface used by wild birds. The use of AQ as a foliar treatment is not as widely found in the literature as seed treatments. Anthraquinone-based repellents have been tested in foliar applications for the protection of emergent seedlings and maturing and preharvest agricultural crops (Table 2).

3.1 Rice

Several studies have evaluated foliar applications of AQ to prevent rice damage by blackbirds. Presoaked rice seed that was hand sprayed post-planting with greater than 18.6 L ha⁻¹ of a formulated AQ product (50% AQ) repelled red-winged blackbirds from small test plots (300 m²). However, a field test of this method utilizing two 5 ha fields aerially water seeded with rice was not successful at 9.3 and 18.6 L ha⁻¹ of an aerially applied formulated AQ product.⁵⁵ Anthraquinone residues on treated rice seedlings from the field trial ranged from 72 to 131 mg AQ kg⁻¹ and from 274 to 467 mg AQ kg⁻¹ at 1 h post-spray and were thus insufficient for avian repellency.⁵⁵ A field trial conducted in Louisiana using 18.7 L ha⁻¹ of a formulated AQ product (50% AQ) aerially applied on a 4 ha ripening rice field decreased bird activity in the treated plot by 80% in the first 24 h and resulted in complete blackbird abandonment after day 2. Anthraquinone residues on rice panicles averaged 337 mg AQ kg⁻¹ upon application and declined to 209 mg AQ kg⁻¹ 14 days post-treatment.⁵⁶

Wild rice (*Zizania palustris* L.) is grown in California and Minnesota. Ripening wild rice treated with 18.6 and 55.8 L ha⁻¹ of a formulated AQ product (50% AQ) was ineffective at preventing damage from blackbirds, despite residues of 430–1000 mg AQ kg⁻¹.

Large numbers of blackbirds remained in wild rice fields, despite the AQ concentrations associated with this study.⁵⁷

3.2 Sunflower

More than 75% of annual blackbird damage to ripening sunflower occurs within the first 18 days after flowering.⁵⁸ Field enclosure experiments demonstrated lower damage and higher yield of oilseed and confectionery sunflower that were hand sprayed with 4.7 and 9.4 L ha⁻¹ of a formulated AQ product (50% AQ) for red-winged blackbirds and common grackles respectively.^{29,31} The backs of mature sunflower heads were hand sprayed with 4.7–18.7 L ha⁻¹ of a formulated AQ product (50% AQ) in cage testing with red-winged blackbirds. Results demonstrated less damage among blackbirds exposed to sunflower heads treated with 18.7 L ha⁻¹ of the formulated product (i.e. 320 mg AQ kg⁻¹ residues on treated sunflower achenes) compared with untreated sunflower heads.²⁹ Ground applications of an AQ-based repellent (50% AQ) on ripening sunflower at 9.4 and 37.4 L ha⁻¹ have failed to deliver sufficient AQ residues on sunflower heads for adequate prevention of bird damage.^{59,60}

3.3 Lettuce

Enclosure trials of an AQ-based formulation (50% AQ) sprayed on lettuce (*Lactuca sativa* L.) seedlings at 2.79 kg ha⁻¹ did not prevent damage from horned larks (i.e. 60% damage was observed).⁶¹ An AQ-based formulation (50% AQ) sprayed on lettuce seedlings at 10 L ha⁻¹ effectively repelled horned larks within experimental enclosures (i.e. 8.5% damage within treated and 68% damage within untreated enclosures).⁶² However, in a field test of three 1.2 ha test sites sprayed with 10 L ha⁻¹ of an AQ-based formulation (50% AQ), differences between treated and untreated plots were inconclusive owing to low bird abundance.⁶²

3.4 Turf

Numerous studies have demonstrated the effectiveness of AQ for the reduction of goose damage to turf grasses.^{46,63–67} Application rates from 4.7 to 9.3 L ha⁻¹ of an AQ-based product (50% AQ) yielded chemical residues of 0.22–0.4 kg ha⁻¹ 7 days post-application.^{46,64} Thus, AQ applications have been particularly useful for airports to reduce goose–aircraft strike hazards.⁶⁷

3.5 Miscellaneous foliar applications

Single trials of AQ as a foliar treatment for seedlings have been conducted with sugar beets (*Beta vulgaris* L.), wheat, soybeans (*Glycine max* L.) and corn. Sugar beet seedlings sprayed at 8.8–16.3 kg AQ ha⁻¹ demonstrated no significant decrease in grazing damage by house sparrows.⁶⁸ Recent testing in Pakistan of wheat and corn seedlings sprayed at 1000 mg AQ kg⁻¹ demonstrated marginal decreases in grazing damage by house sparrows and house crows respectively.^{8,9} However, foliar applications of AQ on soybeans demonstrated promising repellency against Canada geese.⁶⁹

Sweet corn is a high-value commodity that is difficult to protect owing to the husk surrounding the corn kernels. Cage testing demonstrated a positive concentration–response relationship for red-winged blackbirds offered sweet corn treated with 341–9619 mg AQ kg⁻¹.⁷⁰ European starlings offered sweet corn treated with 327–4805 mg AQ kg⁻¹ and untreated sweet corn in a choice test within cages ate similar amounts of AQ-treated and untreated sweet corn as concentration increased. Whereas birds repelled by anthraquinone would typically increase untreated

corn consumption, starlings ate less overall, potentially owing to the high sucrose concentration in sweet corn and starlings' inability to process sucrose.⁴⁹

Novel uses for AQ as a foliar treatment have also been evaluated. Defauce and Enriquez⁴⁵ described foliar applications of AQ to protect branches and buds of young trees in nurseries. This idea has been extended to the potential protection of ripening fruit. Anthraquinone is registered for use in Uruguay as a bird repellent for grapes.⁷¹ Cage testing of American robins (*Turdus migratorius*, L.) with holly berries (*Ilex* spp.) treated with AQ showed modest results (33.5–69.7% repellency).²² In European starling cage testing with blueberries (*Vaccinium* spp.), 5000 mg AQ kg⁻¹ was not sufficient to deter feeding, although untreated blueberries were preferred over blueberries treated with 2500 mg AQ kg⁻¹ in choice tests.⁴⁹ An additional foliar application of AQ involves protection of nut crops from crow damage. Anthraquinone-treated raw almonds were evaluated in cage testing with American crows (*Corvus brachyrhynchos* Brehm) to determine the concentration–response relationship. These experiments demonstrated that 5200 mg AQ kg⁻¹ is needed to repel American crows from treated almonds.²⁶

3.6 Discussion

Foliar applications of AQ for ripening crops are limited by the methods currently available for applying chemical repellents to emergent and ripening crops. Small-scale field testing of foliar applications applied using hand-held spray equipment (i.e. backpack sprayers) has demonstrated repellent efficacy in rice⁵⁵ and sunflower.²⁹ But larger-scale field testing of foliar applications applied using aerial-spray or ground-spraying methods (i.e. tractor based) in rice and sunflower has failed reliably to provide blackbird repellency.^{56,60} More effective application methods for treating ripening crops with AQ repellents are needed. In addition, methods to reduce the amount of AQ required for repellency of ripening crops are also needed. A study has demonstrated the synergistic effect of an ultraviolet feeding cue with AQ-based repellents.^{30,72} A patent related to this synergistic application strategy (US Patent No. 9 131 678 B1) involves the use of visual cues that exhibit spectral characteristics sufficiently similar to the repellent so as to reduce the amount of AQ needed for avian repellency.⁷² This ultraviolet strategy for avian repellency may enable the registration and commercial development of AQ-based products for foliar applications and the protection of emergent and ripening agricultural crops at decreased AQ concentrations.

4 MISCELLANEOUS AVIAN APPLICATIONS

In addition to plant protection, AQ has been found to protect non-target birds from accidental poisoning and to deter wild birds from perching in unwanted places (Table 3). In cage testing of Northern bobwhite quail, Poche²² determined that AQ-treated granular pesticides successfully protected quail chicks from mortality. Testing to protect non-target bird species, including Canada geese, ring-necked pheasants and horned larks, indicated that AQ-treated rodenticide baits prevented consumption of 20 000 mg zinc phosphide kg⁻¹ baits.⁷³ Further testing of AQ-treated toxic pest baits has been conducted in New Zealand^{74,75} to protect the endangered North Island robins (*Petroica longipes*, Garnot). Day and Matthews⁷⁶ applied for both international and US patents based upon these data. Later risk assessments of aerially applied toxic pest baits demonstrated that kea (*Nestor notabilis*, Gould), an endemic New Zealand mountain

parrot, was potentially at risk.^{77,78} Captive testing of kea and tomtits (*Petroica macrocephala*) has shown promise for the use of AQ to prevent consumption of toxic pest baits by endemic New Zealand bird species.^{75–81}

Flocks of birds on structures such as docks or eaves of industrial buildings can also cause damage through fecal contamination. Knauer *et al.*⁶⁷ described the successful use of AQ as an avian perch deterrent for European starlings at a metropolitan airport.

Natural sources of AQ have been identified for their behavioral modifications in wild birds. The seeds of common weeds, including sicklepod (*Senna obtusifolia*, L.) and coffee senna (*Cassia occidentalis*, L.), can contaminate the feed of domestic animals. These seeds contain sufficient concentrations of AQ to be toxic to poultry.⁸² Blackbirds (*Turdus* spp.) avoid buckthorn fruits, presumably owing to their emodin content (an AQ derivative).⁸³ Similarly, Hilker and Kopf⁸⁴ observed that tits (*Parus* spp.) significantly avoided larvae that contained 1,8-dihydroxylated 9,10-anthraquinone.

4.1 Discussion

Several studies have demonstrated the efficacy of AQ for the protection of non-target birds from mortality owing to consumption of toxic pest baits or rodenticide baits. Additional research is needed to develop species-specific pest baits, including AQ applications, for the protection of non-target species that exhibit AQ repellency relative to target species. There is a patent application in the United States (No. EP20030733670) and an international patent (WS 2004/000014 A1) for a bird repellent that combines AQ and a visual cue or AQ and d-pulegone or AQ, a visual cue and d-pulegone to provide increased avian repellency to toxic pest baits.^{76,81}

Structural application of AQ is a growing field of study. US Patent No. 6 328 986 B1 involves the use of AQ for deterring birds from perching, roosting or loafing on plant and structural surfaces (supporting information Table S3).⁸⁵ An additional US patent application (No. US14/607 567) describes the use of various quinones to protect building materials from bird, pest and/or fungal damage.⁸⁶

5 NON-AVIAN APPLICATIONS

Relatively few studies have evaluated AQ as a mammalian repellent (Table 4; supporting information Table S2). Wild boar (*Sus scrofa*, L.) cause extensive damage to agricultural crops in the United States and Europe.^{87,88} Santilli *et al.*⁸⁹ demonstrated the efficacy of 6400 mg AQ kg⁻¹ as a corn seed treatment with wild boar. In choice testing, AQ reduced wild boar consumption of treated corn by 86.5%. In no-choice testing, AQ reduced wild boar consumption by 40%.⁸⁹

Several studies have evaluated AQ repellency in rodents. Anthraquinone has been regularly applied to coniferous and other tree species in direct seeding applications throughout the mid-south of the United States. Although applied primarily as a bird repellent, the effects of AQ as a rodent repellent are unclear. In two field tests, 150 000 mg AQ kg⁻¹ failed to protect loblolly pine seed⁹⁰ and white oak (*Quercus alba* L.), cow oak (*Quercus michauxii* Nutt.) and cherrybark oak (*Quercus pagoda* Raf.) acorns³⁷ from bird and rodent damage. Thirteen-lined ground squirrels (*Ictidomys tridecemlineatus*, Mitchell) damage newly seeded corn.⁹¹ In field testing of corn treated with 4826 mg AQ kg⁻¹, thirteen-lined ground squirrels ate similar amounts of AQ-treated and untreated

corn.¹² In tests with black-tailed prairie dogs (*Cynomys ludovicainus*, Ord.), 24–37% repellency was observed for corn treated with 5000–40 000 mg AQ kg⁻¹. Black-tailed prairie dogs consumed more untreated oat baits than any other treatment, including 10 000 and 20 000 mg AQ kg⁻¹ treated oat baits and 10 000 and 20 000 mg AQ kg⁻¹ plus 20 000 mg zinc phosphide kg⁻¹ treated oat baits.⁷³ Rodenticide baits (20 000 mg zinc phosphide kg⁻¹) treated with 10 000–20 000 mg AQ kg⁻¹ resulted in 30% mortality among black-tailed prairie dogs.⁷³

In Europe, several tests have been conducted for the protection of agricultural crops from wild rodents, including common voles (*Microtus arvalis*, Pallas) and house mice (*Mus musculus*, L.). These studies evaluated the effect of odor on rodent consumption of wheat. Male common voles demonstrated no difference in wheat consumption in the presence of AQ, while female common voles exhibited a 47% reduction in wheat consumption in the presence of AQ.^{92,93} Female house mice demonstrated no difference in consumption of wheat in the presence of AQ, while male house mice preferred wheat in the presence of AQ.^{87,88} Feeding trials with Gunther's voles (*M. guentheri*, Danford & Alston), Tristram's jirds (*Meriones tristrami*, Thomas) and Botta's pocket gophers (*Thomomys bottae*, Eyndoux & Gervais) offered AQ-treated carrots [*Daucus carota* subsp. *sativus* (Hoffm.) Schubl. & G. Martens] and barley (*Hordeum vulgare* L.) illustrated AQ repellency in Tristram's jirds only. Gunther's voles and pocket gophers consumed similar amounts of AQ-treated and untreated food.⁹⁴

Extensive testing has been conducted in New Zealand to ensure brush-tailed possum (*Trichosurus vulpecula*, Kerr) and black rat (*Rattus rattus*, L.) kills remain high when AQ treatments are used to protect birds. Baits treated with 400–1000 mg AQ kg⁻¹ generally did not prevent consumption of lethal or non-lethal baits by possums.^{95–97} However, rats (*Rattus rattus* L.) have demonstrated some repellency for AQ-treated baits and thus decreased mortality in lethal baiting programs.^{96,97}

As a biopesticide, natural sources of AQ have been identified as insecticides and insect repellents. For example, the heartwood of teak (*Tectona grandis*, L.f.) is known for its durability against termites owing largely to the presence of various AQs. Osbrink *et al.*⁹⁸ observed little termiticidal activity of AQ in Formosan subterranean termites (*Coptotermes formosanus*, Shiraki). Gupta and Sen-Sarma⁹⁹ also evaluated AQ and derivatives of AQ for toxicity to termites (*Neotermes bosei* and *Microcerotermes besoni*). Chryso-phanol, an AQ derivative, had the highest termite resistance, while AQ was only effective at higher doses.⁹⁹

Emodin, an AQ derivative, has been evaluated as a feeding deterrent with eastern tent caterpillars (*Malacosoma americana*, Fabricius). Trial and Dimond¹⁰⁰ observed a reduction in feeding by caterpillars on pin cherry branches (*Prunus pensylvanica*, L.f.) sprayed with a solution of 4 mg of emodin in 1 mL of chloroform when compared with untreated branches. Emodin can also cause mortality in various mosquito larvae.^{101,102}

Several other researchers have conducted insecticidal trials using natural AQs. Ateyyat and Abu-Darwish¹⁰³ conducted laboratory tests using extracts of Sinai buckthorn (*Rhamnus dispermus*) bark on peach trunk aphid (*Pterochloroides persicae*). Adult aphids died after a 24 h exposure to 10 000 mg AQ kg⁻¹ extracts. Ba *et al.*¹⁰⁴ also demonstrated insecticidal activity of plant extracts (*Cassia nigricans*, Vahl) containing AQs on cowpea pod sucking bug (*Clavigralla tomentosicollis*, Stål), and they recommend use of extracts for controlling cowpea insect pests in Nigeria.

Additional implications of AQ include feeding deterrence in Dover sole (*Solea solea*, L.),¹⁰⁵ other fishes¹⁰⁶ and ants,¹⁰⁷ stress

reduction in common carp (*Cyprinus carpio*, L.)¹⁰⁸ and reduction in methane gas production in sheep.¹⁰⁹

5.1 Discussion

The extensive use of AQ in diverse areas from insects to wild boar illustrates the many additional uses of this compound beyond avian repellency. Worldwide there is considerable need for rodent and small mammal repellents owing to harvest loss and damage to infrastructure.⁹² Additional testing is needed to evaluate mammalian repellency of AQ-treated agricultural products. Multiple patents exist for feed containing AQ for reduction in stress in fish production (e.g. black carp *Mylopharyngodon piceus* J. Richardson and Wuchang bream *Megalobrama amblycephala* P.L. Yih; China Patents No. 101810258 and No. 101810259; 2010).

6 CONCLUSIONS

We reviewed more than 100 publications regarding AQ applications for international pest management and agricultural crop protection. Criteria for evaluation of effective chemical repellents include: efficacy, potential for wildlife hazard, phytotoxicity and environmental persistence. As a biopesticide, AQ often meets these criteria of efficacy for the non-lethal management of agricultural depredation caused by pest wildlife. Anthraquinone and its derivatives have been identified as a chemical repellent, perch deterrent, insecticide and feeding deterrent in many wild birds, mammals, insects and fishes.

Research needs for AQ-based products include species-specific efficacy data among all target animals as well as the efficacy of crop-specific applications. This is especially true of rodents and other pest mammal species (i.e. rabbits) that cause millions of dollars of damage to agricultural crops and infrastructure worldwide.^{110,111} Additionally, application strategies are needed to improve the efficacy of foliar AQ applications for the protection of emergent and ripening agricultural crops. For example, the synergistic effect of the addition of an ultraviolet feeding cue to AQ-based repellents is one such tool that may enable registration of AQ-based products for foliar applications. Future research should evaluate this strategy with candidate avian and mammalian species and crops.

Although the mode of action of AQ as a post-ingestive repellent is known, the mechanism behind the emetic nature of AQ in birds and mammals is still unclear. Future research should attempt to elucidate this mechanism. A further understanding of the mode of action of AQ in pest species will enable more reliable use of AQ in pest management.

Because relatively few AQ-based products are currently available for international pest management, cost-benefit analyses would enable the commercial development of necessary non-lethal and insecticidal products. Additional research regarding insect and mammalian repellency and bird-repellent and target-specific pesticides is warranted.

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SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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