RESPONSE OF MALLARDS TO CHEMICALLY CONTAMINATED DRINKING WATER

By

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Fisheries and Wildlife

1982

ABSTRACT

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Response of mallards (Anas platyrhynchos) to water supplies contaminated with hydroquinone, copper sulfate or simazine when simultaneously offered nontreated water was observed. Mallards, when confined to a small cage, developed patterns in drinking and treatment was sufficient to overcome the ritualization of a drinking location. Treatments did not distrupt total water intake, only the ritual in which drinking occurred. Ducks detected and avoided hydroquinone treated water. The opposite was apparent with copper sulfate treated water where ducks preferred the treatment. No preference or avoidance of simazine was observed. A second experiment was conducted to observe the effects of hydroquinone on mallard ducklings. At unavoided concentrations of hydroquinone by adult mallards, enlarged livers and sex selective toxicity affecting growth occurred in ducklings. Although the presence of hydroquinone in water systems has the potential to be toxic to mallards, their ability to detect the chemical makes it more likely that they would attempt to avoid contaminated areas.

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Dr. Harold Prince for his support, guidance and numerous critiques of this manuscript. Additional thanks are extended to Drs. Robert Ringer, Howard Johnson and Niles Kevern for their assistance in planning this project and for providing final draft refinements. Glenn Dudderar deserves thanks for contributing numerous suggestions. Charles Rewa provided help in designing this study and collecting data for which I am grateful. I am indebted to my husband, Richard, for his unceasing guidance, support and inspiration needed to carry out this task.

The McGraw Wildlife Foundation donated the mallards and the Michigan State University Agricultural Experiment Station helped fund this project.

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INTRODUCTION

Avian behavioral response to environmental pollutants is an important topic of study. Spillage of industrial chemicals often leads to severe contamination of waterways. Many reports of waterbird mortality due to water-borne pollutants illustrate a nonavoidance or possibly a non-detection response by these birds. For example, in February, 1976, a spill of 250,000 gallons of fuel oil in the Chesapeake Bay resulted in the death of 30,000-50,000 water-birds representing over 31 species (Reiger 1977). Although some birds appear to avoid oil slicks (Casement 1966, Bourne 1968), the above statistics suggest that this behavior is not common to all avian species. Other cases include a Kepone ® (chlordecone) spill which seriously contaminated the James River and Chesapeake Bay. Also, the Ohio River was the site of a carbon tetrachloride spill due to an accidental dumping of this hepatotoxic agent by a chemical plant (Menzer and Nelson 1980).

Although severe chemical spills do not occur regularly, there are also many permanent water systems that may contain hazardous substances such as industrial settling ponds, sewage treatment ponds and heated water systems. Boag and Lewin (1980) describe collecting 87 dead or moribund waterbirds at a tailings pond associated with an oil sands extraction plant in Alberta. These birds were collected prior to a deterrent effectiveness study. Avoidance or detection of water-borne contaminants by waterbirds in permanent water systems is not easily observed or confirmed.

Avoidance response by birds to contaminated foodstuffs is varied. Although bioaccumulation of persistent pesticides such as DDT and dieldrin that have been incorporated into foodstuffs is well documented (Edwards 1970), there is no evidence that birds or mammals are able to detect the contaminants. Some chemicals added or coated onto feed can be detected and avoided by birds. Hill (1972) found that house sparrows (*Passer domesticus*) detected pesticides in their diet and selected nontreated food if an alternative existed. If there was no alternative, food consumption decreased even though they still consumed lethal levels of pesticides. Bennett and Prince (1981) observed similar results with ring-necked pheasants (*Phasianus colchicus*). They found that pheasants would shift from eating treated, preferred foods and revert to original food preferences if treatment ceased. Ridsdale and Granett (1969) found that although common grackles (*Quiscalus quiscalus*) could detect the toxicant DRC-1339, they still consume lethal amounts of contaminated foods which was similar to results of Schwab (1964) for starlings (*Sturnus vulgaris*).

Does this observed detection and often avoidance response of contaminated feed by terrestrial birds imply similar behavior in waterbirds? Flickinger *et al*. (1980) observed mortality of shorebirds due to Furadan 3G, which is an insecticide formulation of carbofuran, sprayed onto flooded rice fields. They noted that Furadan did not repell birds. Waterbirds are also unable to detect aldrin (Flickinger and King 1972). Prior to Furadan usage, aldrin was used extensively on rice fields but was found to be toxic to birds and waterfowl such as the fulvous tree duck (*Dendrocygna bicolor*) (Tucker and Crabtree 1970). Custer and Albers (1980) showed that caged mallards (*Anas platyrhynchos*) subjected to heavily oiled water avoided the oil after initial contact. These investigators suggest that ducks may avoid oiled water if unoiled water is available.

Lipicus *et al*. (1980) found that mallards avoided water dyed orange and were possibly attracted to black-colored water. Visual stimuli appeared to be responsible for avoidance or hesitancy towards usage of orange water. In a preliminary water preference study, Rewa (pers. comm.) showed that mallards preferred distilled water over tap or pond water. Research suggests that if given adequate stimuli, waterbirds may be able to detect certain compounds in aquatic systems. It appears that both visual and taste stimuli can be involved. The present study was designed to determine if some of the potentially hazardous chemicals that occur in Michigan waters can be detected and avoided by mallards.

EXPERIMENT I

Chemicals Studied

Hydroquinone (purified grade), copper sulfate granules (cupric sulfate pentahydrate) and simazine (2-chloro-4, 6-bis (ethylamino)-s-triazine) as the product Aquazine® Algicide were utilized for this study (see Appendix A for structural formulas).

Hydroquinone is an ingredient of developing solutions (Sussman 1973) and discharged by the printing and press industry (Windholz 1976). It is presently on the U.S. Environmental Protection Agency's priority list of environmental pollutants and is in the beginning stages of testing to determine present discharge concentrations and future limitations. Woodard et al. (1949) found the acute oral LD_{50} of hydroquinone in rats to be 320 mg/kg and in pigeons 300 mg/kg. In a preliminary test to the present study, concentrations of 2500 and 5000 ppm of hydroquinone in the drinking water for 10 days, were lethal to mallards. Labored breathing, trembling and lack of coordination was observed at 1000 ppm. Based on these observations, concentrations of 100, 500 and 1000 ppm were used in the present study.

Copper sulfate is used an an algicide and molluscicide at concentrations from 0.25-100 ppm in aquatic systems (McIntosh 1974, Wall 1976, Malek 1974). Depending on the chemical formulation and medium of ingestion, copper sulfate has a wide range of effects on birds. It can promote the growth of chicks at concentrations up to about 250 ppm (Mayo et al. 1956, King 1975). Smith (1969) concluded that copper supplement concentrations above 300 ppm will depress growth in chicks. Copper sulfate at 600 ppm in an artificial pond caused acute copper toxicosis in Canada geese (Branta canadensis) which exhibited necrosis of the proventriculus and gizzard (Henderson and Winterfield 1974). In adult mallards, concentrations close to 400 ppm in water can begin to cause toxic effects (Hurst 1926). Based on toxicity concentrations and its utilization in natural systems 30, 60 and 100 ppm copper sulfate were used in the present study.

Simazine, marketed as Aquazine® 80W, is used to control a variety of algae and submerged aquatic macrophytes (Ellis et al. 1976). Control of the latter group includes plants such as Chara sp., Potamogeton sp. and Vallisneria americana. Simazine has a LC_{50} of >5000 ppm for mallards, ring-necked pheasants and bobwhites (Colinus virginianus) (Hill et al. 1975) and a very low solubility of approximately 5 ppm in water (Weed Science Society of America 1979). Aquazine® is used in natural waterways at concentrations of 5 ppm as recommended by Ciba-Geigy. Aquazine® is in the form of a wettable powder so concentrations of 5, 20 and 50 ppm were used for the present study.

Materials and Methods

Male game farm mallards, donated by the McGraw Wildlife Foundation, Dundee, Illinois were housed in individual compartments each measuring 68 by 70 by 28 cm in a Petersime finishing battery. Room temperature varied between 18 to 26°C during each chemical experiment. Water consumption was measured for 12 birds given a choice between distilled water and distilled water containing one of three concentrations of hydroquinone, copper sulfate or simazine based on % active ingredient. Daily water consumption was recorded and corrected for water loss via evaporation. Each chemical was offered for a 15 day treatment period which followed a 10 day acclimation period. Treatment solutions were prepared daily. Body weights were taken at the beginning and end of the acclimation and treatment periods. Food was available *ad libitum* and there was continuous light. Watering cups constructed of plexiglass and specially designed to minimize spillage and food contamination (Purol 1975) were utilized. During the treatment period, watering cups were randomly switched to decrease position bias. Fecal trays were examined and cleaned daily and data were not utilized for birds on days when excessive water spillage occurred.

Statistical comparisons of water consumption for individual mallards were made with a Scheffe interval test (Gill 1978) and a Mann-Whitney test was used for individual birds with heterogeneous variance (Conover 1971). Comparisons of body weights were made using a paired t-test (Gill 1978). A 2-way analysis of variance with ducks and concentrations as main effects was used to analyze water consumption for each treatment (Gill 1978). All levels of significance are reported as ≤ 0.05.

Results

During the initial experiment, 2 out of 12 birds never acclimated to the watering cups during the hydroquinone acclimation period which resulted in lethal dehydration. In the following acclimation periods, when copper sulfate and simazine were used, the birds were introduced to the watering cups at the beginning of the acclimation period and no further dehydration occurred. A total of 7 of 36 ducks were excluded from the data analysis due to excessive water spillage.

The mallards' body weights varied from 1.25 ± 0.15 kg to 1.11 ± 0.11 kg during the acclimation period (Table 1). Treatments however, did not affect body weights.

Mallards developed drinking preferences based on 33 individual records (Figure 1). Sixteen birds showed a preference for left or right watering cups. A treatment

Table 1. Mean body weights (kg) ± S.D. of mallards consuming drinking water treated with one of three concentrations of hydroquinone, copper sulfate or simazine, measured prior to acclimation (Preaccl) and treatment (Pretrt) and after treatment (Posttrt).

Treatment	Concentrations (ppm)	n	Mean Body Weights (kg)		
			Preaccl	Pretrt	Posttrt
Hydroquinone	100	3	1.20±0.17	1.15±0.13	1.20±0.13
	500	3	1.20±0.15	1.07±0.25	1.17±0.19
	1000	3	1.12±0.06	1.12±0.03	1.15±0.05
Copper Sulfate	30	3	1.40±0.15	1.10±0.09[a]	1.20±0.09
	60	2	1.35±0.21	1.22±0.11	1.25±0.07
	100	4	1.29±0.19	1.12±0.06	1.09±0.08
Simazine	5	3	1.15±0.10	1.02±0.08	1.02±0.08
	20	2	1.25±0.14	1.12±0.11	1.12±0.11
	50	4	1.30±0.13	1.11±0.10	1.12±0.06

[a] significantly different from Preaccl weight ($P \leq 0.05$).

Figure 1. Number of mallards demonstrating a preference for a position (L=left, R=right), treatment (nontreated or treated water) or dual (both position and treatment) during a 10 day period.

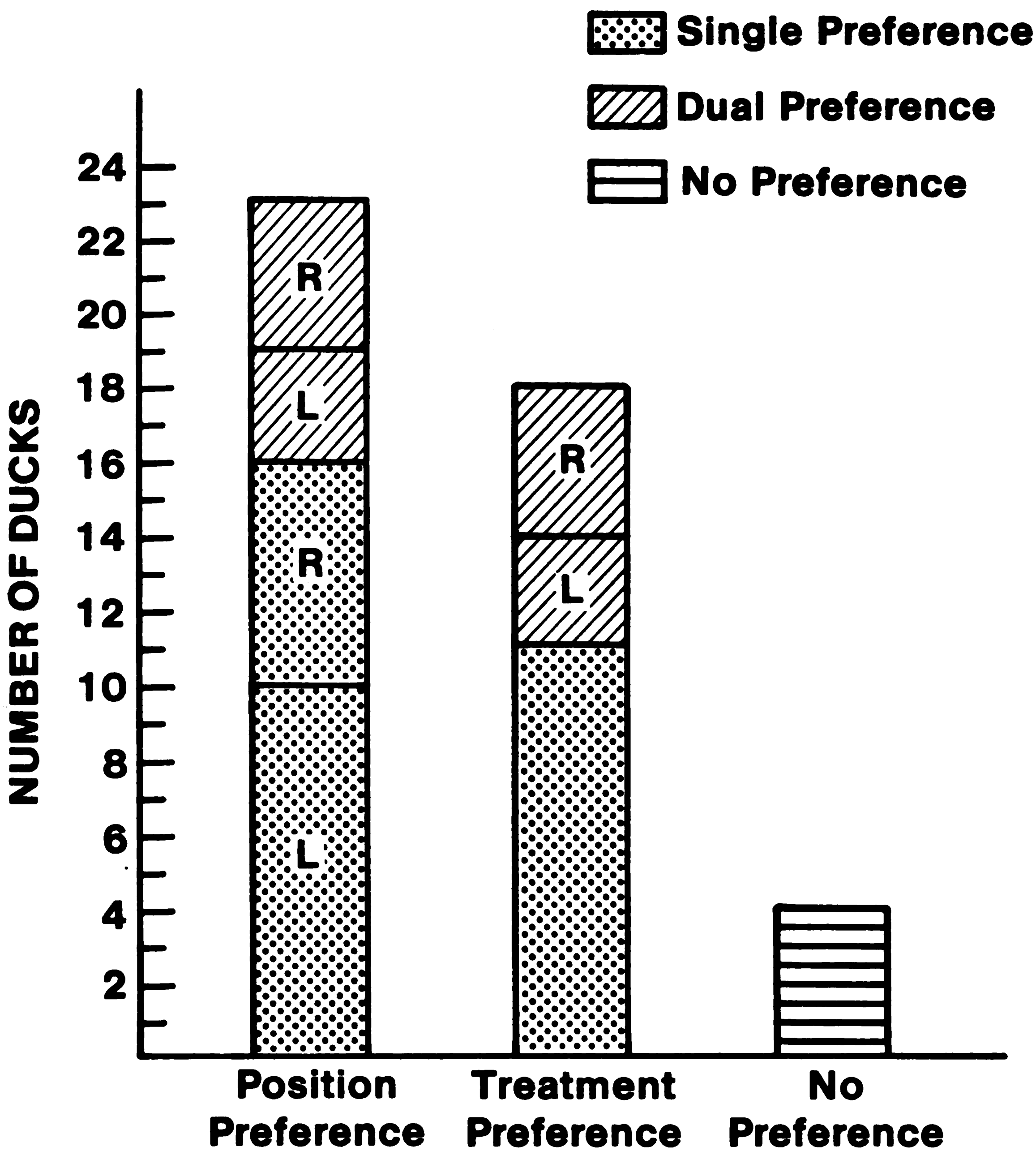

Single Preference
Dual Preference
No Preference
NUMBER OF DUCKS
24
22
20
18
16
14
12
10
8
6
4
2
R
L
R
L
R
L
Position Preference
Treatment Preference
No Preference

Figure 1.

Figure 1. Number of mallards demonstrating a preference for a position (L=left, R=right), treatment (nontreated or treated water) or dual (both position and treatment) during a 10 day period.

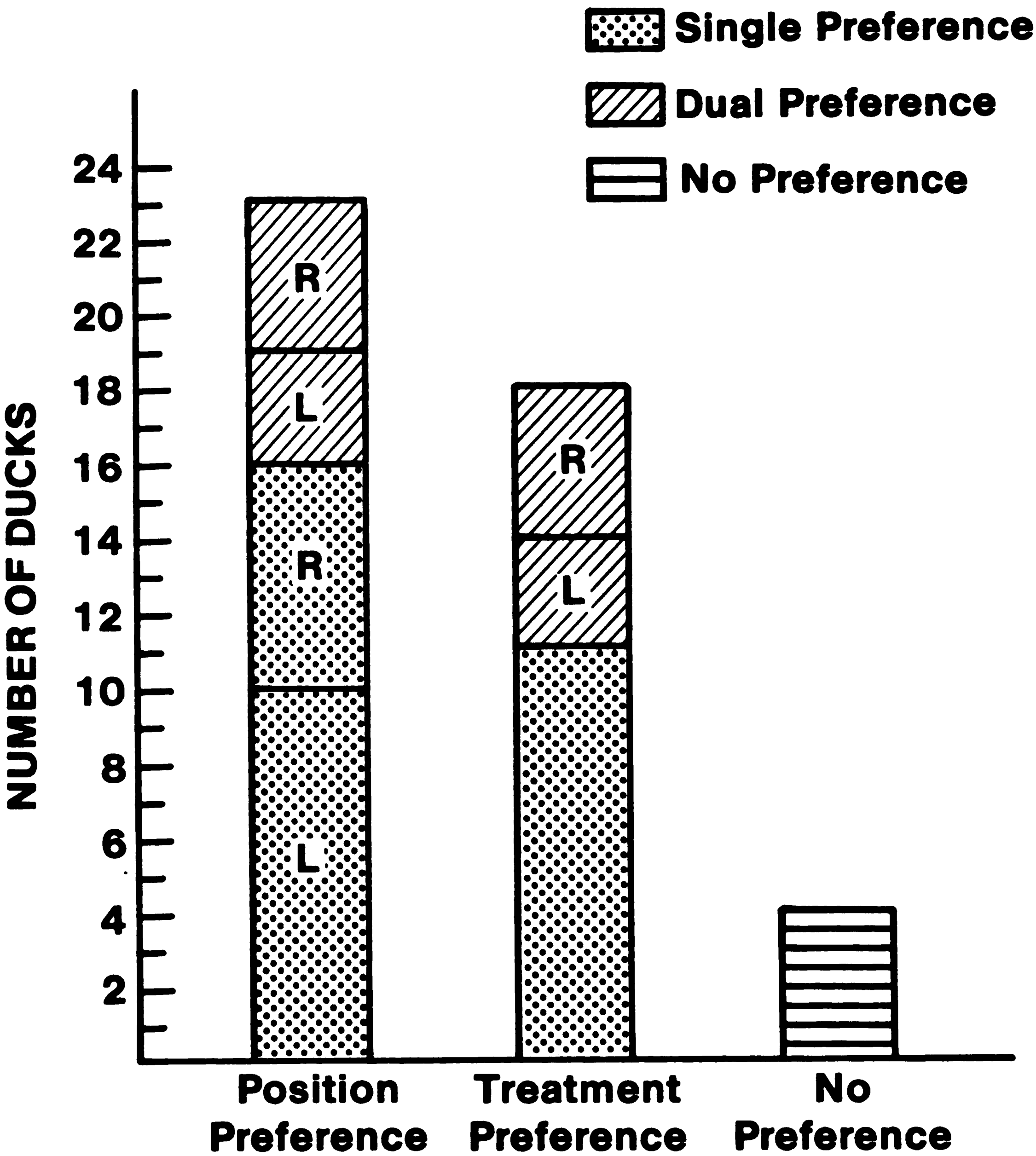

Single Preference
Dual Preference
No Preference
NUMBER OF DUCKS
24
22
20
18
16
14
12
10
8
6
4
2
R
L
R
L
R
L
Position Preference
Treatment Preference
No Preference

Figure 1.

preference (preference of the untreated or treated water supply) was recorded for 11 ducks. A dual position and treatment preference occurred in 7 ducks because random switching of the watering cups occassionally caused uneven distribution of treatments, so that it was possible to demonstrate both preferences. Four ducks showed no left or right waterer or treatment preference.

Water consumption from the treated and distilled water supplies are listed for each concentration of chemical in Table 2. Mallards drank an average of 353±5 gm of water per day during the treatment period. Mean daily consumption remained relatively constant even when a shift away from the treated water at 1000 ppm hydroquinone, or towards the treated water at 100 ppm copper sulfate occurred. Water consumption of ducks given simazine varied significantly from a mean daily consumption of 289±64 gm at 5 ppm to 454±80 gm at 50 ppm. Mean daily water consumption of ducks given simazine was not significatnly different from those given hydroquinone or copper sulfate. Although it was not statistically significant, ducks offered hydroquinone solutions appeared to have a greater consumption of distilled water per day (210±19 gm) than treated water (154±27 gm). The opposite was apparent for the copper sulfate treatment where ducks consumed more treated water per day (190±12 gm) than distilled water (151±4 gm). Consistent water consumption between treated (168±20 gm)

Table 2. Mean daily water consumption (gm) of mallards at three concentrations of hydroquinone, copper sulfate and simazine when offered treated and non-treated water simultaneously.

Treatment	Concentration (ppm)	Distilled water (gm)	Treated water (gm)
Hydroquinone	100	186±18 (3)[a]	160±9 (3)
	500	170±25 (3)	232±37 (3)
	1000	273±16 (3)	71±19 (3)[c]
Copper Sulfate	30	157±28 (3)	150±13 (3)[c]
	60	159±20 (2)	207±44 (2)
	100	137±13 (4)	214±14 (4)[b]
Simazine	5	142±26 (3)	147±20 (3)
	20	202±67 (2)	122±13 (2)[c]
	50	219±19 (4)	236±22 (4)

[a] $\bar{x} \pm$ S.E. (n)

[b] The two means in this row have a significant water main effect ($P \leq 0.05$).

[c] The two means in this row have a significant interaction ($P \leq 0.05$)

and distilled water (188 ± 14 gm) appeared to occur in the simazine treatment.

Preferences at individual treatment concentrations varied. No water preferences occurred for ducks at 100 or 500 ppm hydroquinone (Table 2). A significant duck-concentration interaction was apparent at 1000 ppm hydroquinone. Due to a significant interaction, no conclusion within the main effects can be drawn. At 30 ppm copper sulfate a significant interaction occurred and at 60 ppm ducks showed no preferences. Mallards preferred the treated water at 100 ppm copper sulfate. No preference was apparent at 5 and 50 ppm simazine; however, a significant interaction of main effects occurred at 20 ppm.

EXPERIMENT II

Chemical Studied

At 100 and 500 ppm hydroquinone, mallards did not avoid the treated water. Because of this nonavoidance response and the lack of toxicity data on this chemical a second experiment was conducted to determine if these unavoided concentrations of hydroquinone by adult birds would affect the growth of mallard ducklings.

Materials and Methods

Eggs from game farm mallards were incubated in a Petersime Model 4 incubator at 37.5°C and 70 to 80% humidity for approximately 24 days and then transferred to a David Bradley incubator maintained at 37°C and 90 to 95% humidity until hatching. The ducklings were web-punched for identification and sexed at 9 to 18 hours after hatching and then randomly assigned to a treatment group and transferred to a Petersime brooder unit with food and water *ad libitum* and continuous light. Ducklings ranging from 2 to 6 days of age were all offered 0, 100 or 500 ppm hydroquinone treated water for bathing and drinking. After 14 days of treatment, the ducklings were transferred to 204 by 70 by 28 cm compartments in a Petersime finishing battery where treatment continued for an additional 14 days. Behavioral observations were conducted periodically and body weights taken on days 0, 14 and 28 of treatment. Birds were sacrificed on day 28 and liver and kidney weights were measured. Two replications of the experiment were conducted. Comparisons of weight gains, liver weights and kidney weights were conducted with a Scheffe interval test with a significance level of ≤ 0.05. Liver and kidney weights were expressed as a percentage of the total body weight and transformed to arcsin $\sqrt{\%}$ for statistical analysis.

Results

Average pretreatment weights for the male ducklings equaled 72±6 gm while the females averaged 71±4 gm. After 28 days of treatment the final body weights ranged from 189 to 896 gm in the males and 493 to 904 gm in the female ducklings. Male ducklings given 500 ppm hydroquinone had significantly lower weight gains than males given 0 or 100 ppm after 28 days of treatment while females showed equal gains at all concentrations (Figure 2).

Posttreatment autopsies revealed enlarged livers (hepatomegaly) in ducklings given 500 ppm hydroquinone (Figure 3). Liver weights as a percent of the total body weight (transformed to arcsin $\sqrt{\%}$) averaged 3.8±0.1% for male

Figure 2. Change in body weight (gm) of male and female mallard ducklings after 28 days of exposure to drinking water treated with 0 (control), 100 and 500 ppm hydroquinone. Male duckling growth at 500 ppm was significantly different from control growth for both replications ($P \leq 0.05$).

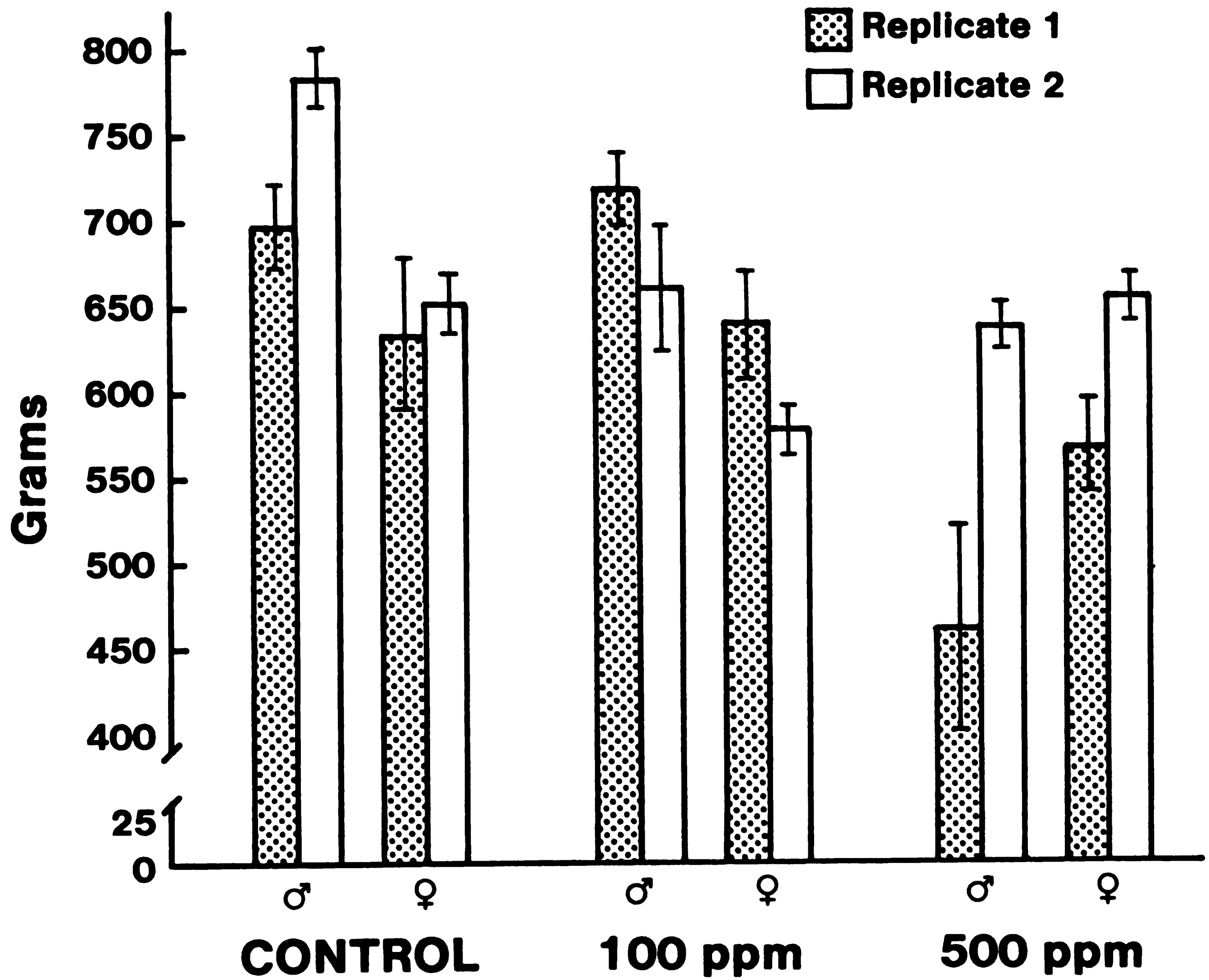

Replicate 1
Replicate 2
Grams
800
750
700
650
600
550
500
450
400
25
0
♂
♀
♂
♀
♂
♀
CONTROL
100 ppm
500 ppm

Figure 2.

Figure 3. Liver weight expressed as a percent of the total body weight (transformed to the arcsin $\sqrt{\%}$) of male and female mallard ducklings after 28 days of exposure to drinking water treated with 0 (control), 100 or 500 ppm hydroquinone. Liver weight percents for duckings of both sexes and replications treated with 500 ppm hydroquinone were significantly different from control percents ($P \leq 0.05$).

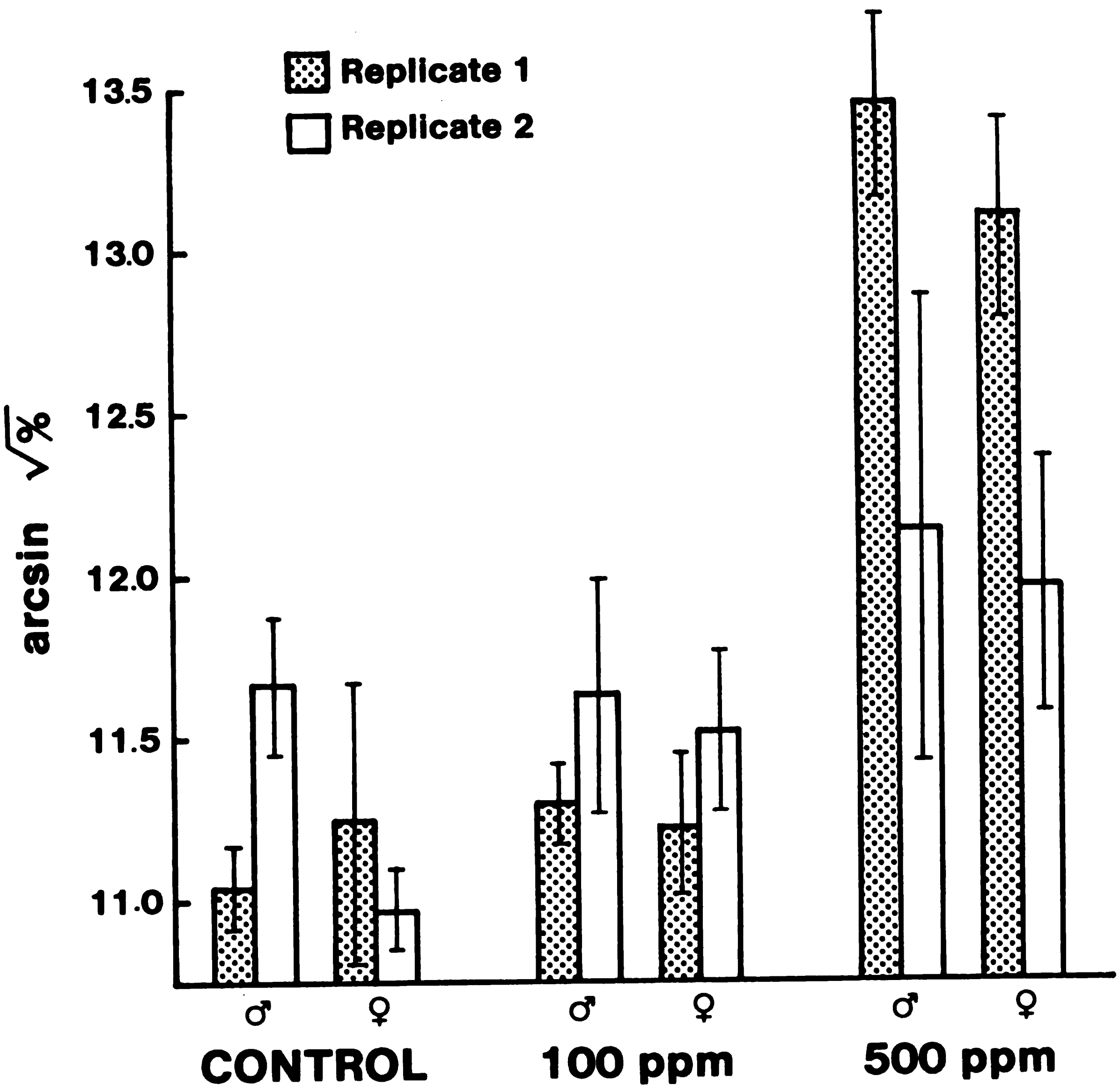

Replicate 1
Replicate 2
arcsin √%
13.5
13.0
12.5
12.0
11.5
11.0
♂
♀
♂
♀
♂
♀
CONTROL
100 ppm
500 ppm

Figure 3.

and 3.7±0.1% for female control ducklings. Both sexes had significantly greater percent liver weights ($P \leq 0.05$) after exposure to 500 ppm treatment.

Kidney weights, also analyzed as the percent of total body weight (transformed to arcsin $\sqrt{\%}$), were 0.64±0.02% for the male and 0.65±0.02% for the female control ducklings. Kidney weights were not significantly different at any treatment concentration (Figure 4).

Control and 100 ppm treated ducklings were attentive and curious throughout the study. Ducklings treated with 500 ppm hydroquinone however, exhibited hyperexcitability and excessive high-pitched vocalizations after day 14. By the final day of the treatment, some ducklings given 500 ppm showed weakness and immobility.

Figure 4. Kidney weight expressed as the percent of the total body weight (transformed to arcsin $\sqrt{\%}$) of male and female mallard ducklings after 28 days of exposure to drinking water treated with 0 (control), 100 or 500 ppm hydroquinone.

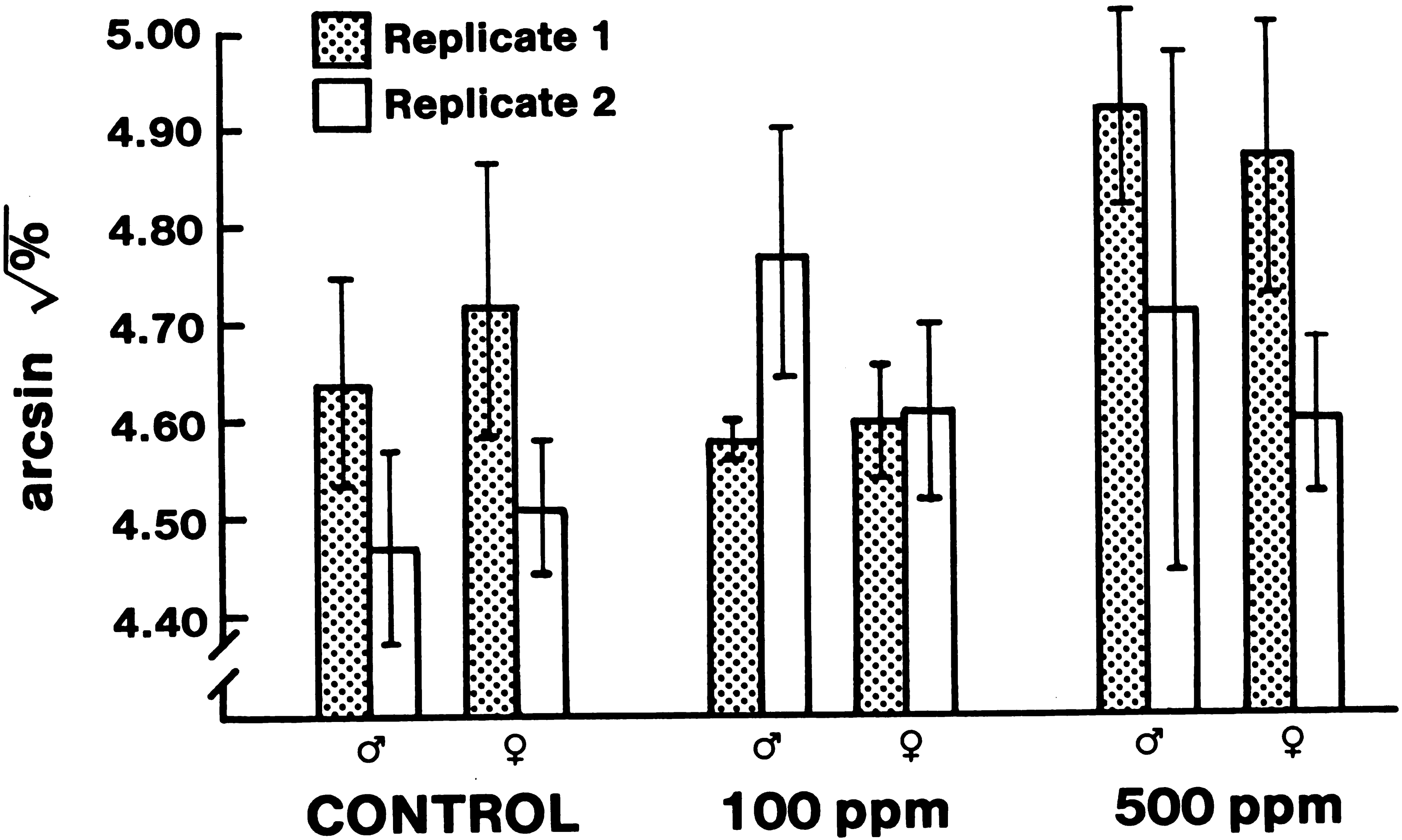

5.00
4.90
4.80
4.70
4.60
4.50
4.40
arcsin √%
Replicate 1
Replicate 2
♂
♀
CONTROL
100 ppm
500 ppm

Figure 4.

DISCUSSION

Many food preference studies have shown that birds can detect and avoid contaminated foodstuffs (Hill 1972, Bennett and Prince 1981, Ridsdale and Granett 1969). Although death due to toxic levels of contaminates in water systems has been observed in birds (Flickinger et al. 1980, Tucker and Crabtree 1970, Henderson and Winterfield 1974), only a few water preference studies have been conducted (Custer and Albers 1980, Lipicus et al. 1980). It has been noted that some waterbirds may avoid oil spills (Casement 1966, Bourne 1968); however, avoidance behavior of waterborne pollutants in natural systems is difficult to observe. In the present laboratory study, drinking preferences (i.e.: avoidance of treated water) of mallards could be observed as interruptions of prior drinking patterns.

Mallards developed a ritual in daily drinking when confined to a small cage. The ritualization of a drinking location was disrupted by some of the treatments. This disruption in position patterning was variable and included a shift towards and away from the treated water supply. When offered copper sulfate treated water at 100 ppm the mallards shifted their consumption to prefer the treated water supply. Hydroquinone treated water appeared to be avoided. Although treatment concentrations were additive and most shifts in position patterning occurred at the higher concentrations, total daily water intake remained constant.

Ducks given copper sulfate treated water were undergoing prebasic molt which may have influenced their response. Energy needs increase during molt and trace mineral requirements may rise. In the case of copper sulfate, an increased need of trace minerals may have resulted in a preference of a "metallic tasting" solution.

Although location seemed to be an important proximate cue used to establish a drinking pattern, cues to identify a water-borne contaminant may include vision, taste or smell. Taste, functioning as a discriminatory tool against toxins, is believed to be the method of detection in the present study. Visual stimuli may have been used in detection of hydroquinone, although the watering cups minimize sight contact of the drinking water.

At various concentrations of each chemical, a significant duck-concentration interaction occurred. This was partially due to individual preference among ducks. For example, at 30 ppm copper sulfate, one duck preferred the treated water while another preferred the nontreated water. Individuality of taste preferences within a species is reported by Kare and Rogers (1976) and adds to the plasticity of food habits of a species. Individual preferences and responses may play an important role in the impact environmental contamination has on a species.

Birds established use of a watering cup based on location and altered the patterning based on water-borne stimuli. Use of natural water areas could follow a similar pattern. Water use may be based on location and then modified by possible variations in water quality. A disruption of habitat utilization is a major deleterious effect of pollution.

Although the presence of hydroquinone at 100 and 500 ppm did not alter drinking patterns by adult drake mallards, ducklings showed negative responses at these concentrations. Liver size as a proportion of the total body weight increased in both sexes and growth rate declined for male ducklings only. There was a large variation in growth retardation of male ducklings at 500 ppm hydroquinone. Differences in the toxic response of males and females of a species to a chemical has been observed. Male Japanese quail (Coturnix c. japonica) fed dietary levels of p,p'-DDT over time tended to die earlier than female quail in the same experiment (Gish and Chura 1970). Breeding birds have the advantage of excreting toxins by egg-laying (Tucker and Haegele 1970) which may partially explain the sex selective differences found by Gish and Chura (1970).

Most sex differences to toxins are associated with factors dependent on the endocrine system such as the influence of sex hormones, and in mammals, pregnancy and lactation (Doull 1980). Ducklings in the present study were only 2 to 36 days of age and future studies on hydroquinone should be extended so that it can be determined if juvenile birds are more vulnerable to hydroquinone poisoning than adults.

Both field observation and laboratory preference studies must be conducted to determine the implications of waterway contamination on waterbirds. Results of the present study imply that waterbirds may be able to avoid polluted water systems even at non-toxic levels of contamination. Loss of wetlands due to drainage is already a serious problem, however a contributing loss due to pollution and the resulting avoidance by waterbirds should be considered. The opposite reaction of nonavoidance may result in the loss of a portion of the waterbird community.

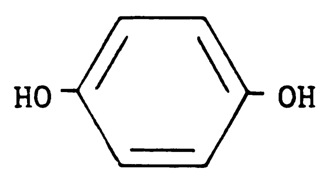
Future water preference studies need to consider individual preference behaviors. While this study observed avoidance and preference responses of mallards to contaminated drinking water, larger sample sizes may better describe the actual preference trends of a population. Measuring water intake in mallards is a difficult endeavor; however, the cups used were relatively accurate. Researchers conducting studies of this kind wishing to use waterbirds other than Anatidae should consider the waterer designed by Kendall and Scanlon (1980).

APPENDIX

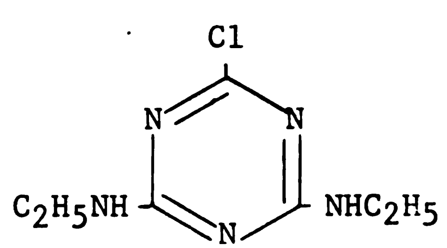
Appendix A

Structural Formulas for Hydroquinone and Simazine

Hydroquinone



Simazine



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