# RESIDUES OF ENVIRONMENTAL POLLUTANTS AND SHELL THINNING IN MERGANSER EGGS

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There is little information regarding the types and concentrations of environmental pollutants in mergansers. However, the reports that are available indicate that residues of certain toxic chemicals are high in eggs and tissues of Common (*Mergus merganser*), Red-breasted (*Mergus serrator*), and Hooded mergansers (*Lophodytes cucullatus*) from southern Canada, Michigan, and Wisconsin (Fimreite et al. 1971, Vermeer and Armstrong 1972, Faber and Hickey 1973, Vermeer et al. 1973, Fimreite 1974). Also, significant eggshell thinning has been detected in Common and Red-breasted mergansers from Wisconsin and Michigan (Faber and Hickey 1973).

Mergansers feed mostly on fishes and invertebrates (Munro and Clemens 1939, Timken and Anderson 1969, Bellrose 1976) and are more susceptible to chemical contamination than species feeding at lower trophic levels. This study was conducted (1) to determine the levels of environmental pollutants in merganser eggs, mainly those of Hooded Mergansers, as factors contributing to possible population declines and (2) to compare eggshell thickness with eggs of earlier collections. Hooded Merganser eggs were more readily available than those of Common or Red-breasted mergansers since Hooded Mergansers commonly use nest boxes on many federal and state refuges throughout their breeding range.

#### METHODS AND MATERIALS

Federal and state biologists assisted us in collecting clutches of merganser eggs in 1973 and 1975 (see Table 1 for collecting sites). Cooperators were sent insulated containers for shipment of eggs with instructions to collect only fresh whole clutches. So that hens would have time to renest, eggs were collected early in the nesting season and kept refrigerated until shipment to the Patuxent Wildlife Research Center, Laurel, Maryland. Most of the clutches were complete and only a few contained addled eggs or eggs with developing embryos.

Each egg was opened at its equator after determining its weight, length, breadth, and volume (by water displacement). One egg from each clutch was randomly selected for chemical analysis since eggs within a particular clutch usually contain similar residue levels (Klaas and Swineford 1976). The egg contents were stored frozen in chemically cleaned jars until analysis.

Eggshells were dried at room temperature for at least 30 days, then weighed and measured with the shell membranes left intact. Three thickness measurements were taken randomly around the equator using a Starrett Model 1010 M micrometer and a mean shell thickness was calculated for each egg. Similar procedures were used in measuring museum egg collections except that measurements were taken at the blow-hole of each egg. Mean clutch thickness values were calculated by averaging clutch means from each locality within a collecting region and not by averaging individual egg measurements (Klaas et al. 1974); this method gives an indication of average shell thickness by population as opposed to individual hens. In comparing clutch means, all shell measurements used were from fresh or early incubated eggs, therefore stage of incubation did not significantly bias the data. Historical collections of merganser eggs were measured at the American Museum of Natural History, Museum of Vertebrate Zoology at Berkeley, Philadelphia Academy of Sciences, and the Western Foundation of Vertebrate Zoology.

Contents of each egg were homogenized with a Virtis homogenizer. A 10 g aliquot was mixed with anhydrous sodium sulfate in a blender and extracted for 7 h with hexane in a Soxhlet apparatus. An aliquot of the extract was cleaned up by gel permeation chromatography or on a florisil column. Pesticides and polychlorinated biphenyls (PCB's) were separated into 3 fractions on a Silicar column and analyzed by gas chromatography. The limit of quantification was 0.1 ppm for pesticides and 0.5 ppm for PCB's on a wetweight basis. The analytical procedures have been described in detail by Cromartie et al. (1975). Residues in 10% of the samples were confirmed with a gas chromatograph/mass spectrometer. All residues were corrected for moisture loss as suggested by Stickel et al. (1973). Lipid content in eggs of Hooded, Red-breasted, and Common mergansers averaged 16%, 16%, and 14%, respectively. Residue arithmetic means and geometric means were very similar, therefore only arithmetic means were reported.

Egg contents were analyzed for total mercury at the Environmental Trace Substances Research Center, Columbia, Missouri. An aliquot of the homogenized sample was digested under reflux conditions with concentrated nitric acid. Stannous chloride was added to reduce the ionic mercury to elemental mercury which was measured photometrically on an atomic absorption spectrophotometer. The limit of quantification was 0.02 ppm on a wet-weight basis.

## RESULTS

Hooded Merganser eggs.-Residues of DDE, DDT, DDD, dieldrin, PCB's, and mercury in Hooded Merganser eggs are presented in Table 1. Residues varied greatly within and among localities. Of 96 eggs, DDE was found in 92, dieldrin in 22, and PCB's in 82. Eggs collected in 1973 from Necedah National Wildlife Refuge (NWR), Wisconsin had the highest mean of DDE; the highest mean of DDE for 1975 occurred in eggs from Iroquois NWR, N.Y. Sample sizes from these localities were small (2) however, and may not reflect overall contamination levels in the breeding populations. All collections from the Northeast (Maine, New Hampshire, New York, Vermont) had mean levels of DDE greater than 0.1 ppm. The highest mean level of dieldrin was in eggs from the Upper Mississippi NWR, Iowa. Usually dieldrin was detected in only 1 or 2 eggs from a locality, therefore mean levels are not indicative of all the breeding birds. The highest mean PCB level was found in eggs from New Hampshire; all eggs from this locality contained PCB's as did eggs from the other localities in the Northeast. Of the 90 Hooded Merganser eggs analyzed for mercury, 89 contained detectable residues. The highest mean level of mercury occurred in eggs from Big Lake NWR, Arkansas.

	Eccs
	MERCANSER
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TABLE 1	0F
	THICKNESS
	SHELL
	AND
	RESIDUES

				TROOPER ME	NUANSER EGU	•		
State vear		Mean clutch			Residues, pp	m wet weight		
(Location)	$N^2$	thickness (mm)	DDE	DDT	DDD	Dieldrin	PCB's <sup>3</sup>	Mercury
Arkansas—1975					-			
(Big Lake NWR)	9	$0.630 \pm 0.006$	$0.53 \pm 0.10$	$0.14 \pm 0.05$	$0.14 \pm 0.06$	$0.19 \pm 0.05$	$0.83 \pm 0.26$	$1.49 \pm 0.36$
Arkansas—1975				Ì	Ì	(0)		(0)
(White River NWR)	5	$0.621\pm0.002$	$1.12 \pm 0.33$	$0.27\pm0.12$	0.12	0.17	$0.80 \pm 0.09$	$0.48 \pm 0.06$
Idaho—1075		(55)	(2)	(3)	(1)	(1)	(3)	(2)
(Kootenai NWR)	61	$0.589 \pm 0.007$	$0.63 \pm 0.24$	$\mathrm{ND}^6$	ND	ND	$0.55 \pm 0.12$	$0.16\pm0.06$
Louro 1075		(13)	(2)				(2)	(2)
(IInner Mississinni NWP)	c	0.6444.0000	100	000				
(WMV) INTERSTSSIT	r	$0.504 \pm 0.006$	$0.84 \pm 0.24$ (3)	(1)	ΠN	$1.34 \pm 1.13$ (2)	$1.15 \pm 0.12$ (3)	$0.75 \pm 0.31$ (3)
Maine—1975								
(Central)	10	$0.583 \pm 0.008$	$1.45 \pm 0.36$	$0.21\pm0.09$	$0.18 \pm 0.06$	$0.21 \pm 0.07$	$3.50 \pm 1.28$	$0.97 \pm 0.16$
Michigan-1973			(01)	(+)	(7)	(6)	(10)	(10)
(Seney NWR)	9	$0.565 \pm 0.010$ (33)	$1.26 \pm 0.54$ (6)	$\begin{array}{c} 1.39 \\ (1) \end{array}$	ND	0.23 (1)	$1.59 \pm 0.37$ (6)	no analysis
Michigan-1975								
(Seney NWR)	6	$0.574 \pm 0.002$ (66)	$0.86 \pm 0.22$ (9)	$0.19 \pm 0.10$ (2)	ND	$0.37 \pm 0.15$ (4)	$3.03 \pm 1.08$	$0.53 \pm 0.09$
Minnesota1975								6
(Rice Lake NWR)	1	0.650 (2)	0.07 (1)	ND	ND	ND	1.59 (1)	0.25 (1)
Missouri1973								
(Mingo NWR)	10	$0.612 \pm 0.021$ (36)	$4.90 \pm 2.68$ (10)	13.90 (1)	$7.38 \pm 2.86$ (2)	0.37 (1)	$1.86 \pm 0.96$ (4)	$0.74\pm0.13$ (10)

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		E	ABLE 1 (con	tinued)				
					Residues, p	pm wet weight		
Stateyear (Location)	N²	Mean clutch thickness (mm)	DDE	DDT	DDD	Dieldrin	PCB's <sup>3</sup>	Mercury
Missouri—1975 (Mingo NWR)	2	$0.617 \pm 0.002$ (43)	$0.35 \pm 0.07$ (7)	ND	ND	0.11 (1)	$0.85 \pm 0.06$ (7)	$\begin{array}{c} 0.92 \pm 0.12 \\ (7) \end{array}$
New Hampshire—1975 (Central)	10	$0.546 \pm 0.004$ (105)	$1.84 \pm 0.50$ (10)	0.51 (1)	0.19 (1)	$0.15 \pm 0.07$ (2)	$4.91 \pm 1.56$ (10)	$1.11 \pm 0.23$ (9)
New York1975 (Iroquois NWR)	61	$0.589 \pm 0.006$ (14)	$3.24 \pm 1.94$ (2)	0.56 (1)	0.10 (1)	0.20 (1)	$\begin{array}{c} 2.37 \pm 0.82 \\ (2) \end{array}$	$1.44 \pm 0.30$ (2)
North Dakota—1975 (Clark Salyer NWR)	œ	$0.593 \pm 0.005$ (41)	$0.67 \pm 0.40$ (5)	ND	ND	0.14 (1)	$1.10 \pm 0.24$ (8)	$0.73 \pm 0.09$ (8)
Oregon-1975 (W. L. Finley NWR)	7	$0.604 \pm 0.012$ (12)	$0.34 \pm 0.13$ (2)	ND	ΟN	ND	$0.93 \pm 0.46$ (2)	$\begin{array}{c} 0.53 \pm 0.09 \\ (2) \end{array}$
Tennessee—1975 (Hatchie NWR)	10	$0.620 \pm 0.004$ (71)	$1.06 \pm 0.18$ (10)	$0.18 \pm 0.03$ (9)	ND	0.19 (1)	$\begin{array}{c} 0.90 \pm 0.09 \\ (9) \end{array}$	$0.94 \pm 0.18$ (10)
Vermont—1975 (Northwestern)	က	$0.598 \pm 0.008$ (24)	$1.54 \pm 0.21$ (2)	ND	UD	ND	$2.37 \pm 0.40$ (3)	$\begin{array}{c} 0.53 \pm 0.17 \ (3) \end{array}$
Wisconsin—1973 (Necedah NWR)	5	$0.584 \pm 0.011$ (6)	$13.20 \pm 9.77$ (2)	2.42 (1)	1.77 (1)	0.27 (1)	0.44 (1)	$0.56 \pm 0.21$ (2)
<sup>1</sup> Values are means $\pm$ standard e	rrors.							

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<sup>2</sup> N = total mean means a manufactory one egg per clutch was analyzed. <sup>3</sup> PCB's are quantified on the basis of Aroclor 1254. <sup>4</sup> Total no. of eggs in clutches that were measured. <sup>6</sup> No. of eggs having detectable residues. <sup>6</sup> ND = not detected.

Fi	ROM 31	REGIONS, 1975		
		Resid	lues, ppm wet we	ight <sup>1</sup>
Regional pool	N <sup>2</sup>	DDE	PCB's	Mercury
Northeast (Maine, New Hampshire, New York, Vermont)	25	$1.77 \pm 0.29^{a}$ (24) <sup>3</sup>	$3.84 \pm 0.08^{a}$ (25)	$1.01 \pm 0.12^{a}$ (24)
Midwest (Iowa, Michigan, North Dakota)	20	$0.79 \pm 0.16^{\text{b}}$ (18)	$\frac{1.97 \pm 0.52^{a}}{(20)}$	$0.64 \pm 0.07^{b}$ (20)
South-central (Arkansas, Missouri, Tennessee)	28	$0.78 \pm 0.10^{b}$ (28)	$0.86 \pm 0.04^{\text{b}}$ (21)	0.62 ± 0.12 <sup>b</sup> (28)

TABLE 2 RESIDUE COMPARISONS OF POOLED SAMPLES OF HOODED MERCANSER EGGS

<sup>1</sup> Values are means ± standard errors.

<sup>2</sup> N = total no. of samples in the pool. <sup>3</sup> No. of samples in the pool having detectable residues. <sup>ab</sup> Significant differences exist between means having different superscripts (P < 0.01, *t*-test).

In addition to the chemicals listed in Table 1, certain other toxicants were detected in some Hooded Merganser eggs at much lower levels. Heptachlor epoxide was found in 6 eggs, 1 each from Iowa and New Hampshire and 2 each from Maine and Michigan, but residues were low, ranging from 0.14 to 0.48 ppm. One egg each from Vermont and Michigan contained mirex at 0.08 and 0.18 ppm, and 4 of 10 eggs from Maine contained mirex, ranging from 0.15 to 0.66 ppm. Chlordane isomers were detected in 6 eggs, 2 from New Hampshire and 4 from Maine, ranging from 0.09 to 1.8 ppm. Toxaphene occurred in only 2 eggs, at 0.17 ppm in an egg from Seney NWR, Michigan and 0.10 ppm in an egg from Big Lake NWR, Arkansas. Hexachlorobenzene (HCB) was detected at 0.19 ppm in an egg from Seney NWR, Michigan.

We pooled residue data from localities within major regions if they were not statistically different (P > 0.05) from one another in order to compare DDE, PCB's, and mercury in Hooded Merganser eggs on a regional basis. Residues in eggs from Oregon and Idaho were not pooled because of very small sample sizes and mean differences. Means of pooled residues are shown in Table 2. DDE residues were significantly higher (P < 0.01, t-test) in eggs from the Northeast than in those from the Midwest or South-central states. However, these are relative comparisons based on specific localities and are not representative of whole areas. PCB's were significantly higher (P < 0.01) in the Northeast and Midwest samples than in those from the South-central region, probably resulting from heavy industrial use of PCB's in those regions. Mercury was significantly higher (P < 0.01) in eggs from the Northeast

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	Red-breasted Merganser (Door County, Wisconsin)	Common Merganser (Door County, Wisconsin)	Common Merganser (Seney NWR, Michigan)
N <sup>2</sup>	18	2	1
Mean shell thickness (mm)	$0.302\pm0.004$	$0.314 \pm 0.006$	0.346
	(178) <sup>3</sup>	(16)	(6)
DDE	$15.73 \pm 1.39 \ (18)^4$	$24.44 \pm 4.72$ (2)	9.85
DDT	$0.62 \pm 0.10$ (18)	0.70 (1)	ND
DDD	$0.40 \pm 0.04$ (17)	$0.34 \pm 0.08$ (2)	ND
Dieldrin	$1.00 \pm 0.11$ (18)	$0.64 \pm 0.10$ (2)	1.39
Heptachlor epoxide	$0.31 \pm 0.04$ (18)	$0.27 \pm 0.09$ (2)	0.17
Mirex	$0.42 \pm 0.15$ (8)	$\mathbf{ND}^{5}$	ND
Chlordane isomers	$0.57 \pm 0.06$ (18)	$0.82 \pm 0.32$ (2)	0.34
НСВ	$0.11 \pm 0.01$ (16)	ND	ND
Toxaphene	$0.26 \pm 0.04$ (3)	ND	ND
PCB's	$44.67 \pm 6.06$ (18)	$79.43 \pm 9.02$ (2)	24.19
Endrin	0.33 (1)	ND	ND
Mercury	$0.56 \pm 0.06$ (18)	$0.56 \pm 0.26$ (2)	0.52

# TABLE 3

Residues and Shell Thickness of Red-breasted and Common Mercanser Eggs, 1975<sup>1</sup>

<sup>1</sup> Values are means  $\pm$  standard errors. <sup>2</sup> N = total no. of clutches collected; one egg per clutch was analyzed. <sup>3</sup> Total no. of eggs in clutches that were measured. <sup>4</sup> No. of eggs having detectable residues. <sup>5</sup> ND = not detected.

than in those from the Midwest or South-central regions, although eggs from a locality in Arkansas had the highest overall mean of mercury (Table 1).

Red-breasted and Common merganser eggs .- In general, residues of DDE, dieldrin, and PCB's were higher in Red-breasted and Common merganser eggs, and other chemicals occurred more frequently, than in eggs of Hooded Mergansers (Table 3). A high of 29 ppm DDE was detected in a Common



Fig. 1. Relationship of PCB's in Hooded Merganser eggs and mean clutch thickness on a population basis. (Spearman's rank correlation, r = -0.63, P < 0.01)

Merganser egg from Door County, Wisconsin; a Red-breasted Merganser egg from the same locality had a high of 113 ppm PCB's. Residue levels in eggs of the 2 species were similar except that mirex, HCB, and endrin were not detected in Common Merganser eggs. Mercury residues were similar to those found in Black-crowned Night Heron (*Nycticorax nycticorax*) eggs from Lake St. Clair (Stendell et al. 1976).

Eggshell measurements and shell thickness changes.—Clutch thickness means by locality are shown in Table 1 for Hooded Mergansers, and in Table 3 for Red-breasted and Common mergansers. There was wide geographic variation in mean thicknesses among Hooded Merganser clutches (Table 1); clutch means ranged from a low of 0.546 mm in New Hampshire to a high of 0.630 mm in Arkansas (Minnesota mean excluded because of only 2 eggs in the sample). According to Klaas et al. (1974), variation in eggshell thickness among clutches (at least in some species) depends on many factors, including: differences related to clutch size and stage of incubation, genetic and physiological differences in environmental conditions between years.

There was a negative correlation (r = -0.28, Spearman's rank correlation,

#### TABLE 4

COMPARISONS OF EGGSHELL MEASUREMENTS FROM EARLY MUSEUM COLLECTIONS AND 1973. 1975 Collections

		Mean clutch thickness $\pm$ standard error, mm			
Species	Collection region	1880-1927	1973–1975	Percent change	
Hooded Merganser	Iowa, Michigan, Minnesota, North Dakota, Wisconsin	$0.628 \pm 0.025$ (6/55) <sup>1</sup>	$\begin{array}{c} 0.576 \pm 0.005 \\ (28/174) \end{array}$	-8.3	
Red-breasted Merganser	Michigan, Wisconsin, south Manitoba	$0.367 \pm 0.001$ (8/105)	$\begin{array}{c} 0.302 \pm 0.004 \ (18/178) \end{array}$	-17.7ª	
Common Merganser	Michigan, Wisconsin, south Manitoba	$0.426 \pm 0.011 \ (3/33)$	$\begin{array}{c} 0.326 \pm 0.015 \\ (3/22) \end{array}$	-23.5ª	

<sup>1</sup> Total number of clutches/total number of eggs within clutches. <sup>a</sup> Percent change highly significant (P < 0.001, analysis of variance).

Snedecor and Cochran 1967) between DDE residues and mean clutch thickness for each locality, but the relationship was not significant (P > 0.05). However, PCB's and mean clutch thickness also were negatively correlated (r = -0.63) on a locality basis and the relationship was highly significant (P < 0.01) (Fig. 1).

Regression analysis showed that a significant relationship (r = 0.61, P < 0.05) existed between DDE and PCB's, but when DDE and PCB's were combined and compared with mean clutch thickness by population, there was no significant (P > 0.05) relationship. It appears that PCB's were contributing more to the negative relationship between residues and mean clutch thickness than DDE. The results must be viewed with caution however, because of the wide variety of factors that may contribute to geographic variation in shell thickness of Hooded Merganser eggs. Controlled experimental studies are needed to clarify these findings. In order to test for possible eggshell thinning, we compared eggshell measurements from our collections with those of early museum collections (Table 4). Data from each major region were combined if the clutch means did not differ significantly (P >0.05) from one another. For Hooded Mergansers, we were able to obtain comparable data only from certain midwestern states, therefore comparisons with collections from the Northeast and South-central regions could not be made. Clutches of Hooded Merganser eggs were 8.3% thinner than earlier collections from the same general area (Table 4) however, the difference was not significant (P > 0.05).

Highly significant shell thinning (P < 0.001) was detected in the Redbreasted Merganser eggs. The clutch means were 17.7% thinner than those from early museum collections from the same general area (Table 4). Faber and Hickey (1973) found that Red-breasted Merganser eggs from Wisconsin in 1969 were 17.0% thinner than pre-1947 collections from the same area. Although their comparisons were made on an individual egg basis rather than on clutch means, the results were strikingly similar to ours.

Highly significant shell thinning (P < 0.001) also was detected in Common Merganser eggs. The 1975 collections were 23.5% thinner than early museum collections from the same region (Table 4); only 3 clutches were available from each time period for comparisons, but the results proved significant. Faber and Hickey (1973) also reported shell thinning in Common Merganser eggs from Michigan and Wisconsin; collections made in 1970 were 15.8% thinner than pre-1947 collections.

#### DISCUSSION

In general, residues of organochlorines in Hooded Merganser eggs were considered to be low. Geographical differences were detected however; residues of DDE, PCB's, and mercury were higher in the Northeast than in the other regions. It is doubtful that these relatively low levels of organochlorines could be responsible for overall population declines of Hooded Mergansers, but some hens with moderate to high levels of toxicants could experience poor reproductive success. Also, mercury averaged about 1 ppm in eggs from the Northeast and about 0.63 ppm at other localities; these levels may be sufficient to cause aberrant behavior in ducklings (Heinz 1975).

Most of the Red-breasted and Common merganser eggs contained potentially dangerous levels of DDE and possibly PCB's. In addition, mercury and a wide array of other toxic organochlorines were present in the eggs. Both species exhibited significant eggshell thinning. Mergansers are top predators, and consequently are highly subjected to contamination from their food sources. This is especially true for Red-breasted and Common mergansers, which feed almost exclusively on fishes of various types. Hooded Mergansers take fewer fish and more invertebrates than the other species; this may explain the lower residues in their eggs.

The effects cumulative concentrations of toxic chemicals in eggs might have on reproduction and survival of wild birds are unknown. A toxicant load of the magnitude found in Red-breasted and Common mergansers might cause reproductive failure or otherwise threaten the survival of merganser populations. Experimental studies with DDE have shown that reproductive impairment may be induced in Mallards (*Anas platyrhynchos*) and Black Ducks (*A. rubripes*) at residues similar to those found in some of the Redbreasted and Common mergansers (Longcore et al. 1971, Haegele and Hudson 1974). Also, in experimental studies with methylmercury, Heinz (1975) found that aberrant behavior of Mallard ducklings resulted when eggs accumulated 1 ppm or less of mercury. In our study, residues of mercury in Red-breasted and Common merganser eggs averaged 0.56 ppm and ranged up to 1.2 ppm. Field studies are needed to document reproductive success of mergansers in the Door County, Wisconsin area. Further, these data demonstrate the persistence and prevalence of DDT, DDE, and dieldrin in the environment, even though the use of technical DDT was suspended in December 1972 and the use of dieldrin was suspended in October 1974.

#### SUMMARY

Clutches of merganser eggs were collected in 1973 and 1975 to determine whether levels of organochlorines and mercury might be responsible for possible population declines and to compare eggshell measurements with those of early museum collections. One egg per clutch was selected randomly for chemical analysis. Overall, residues of DDE, PCB's, and mercury were low in Hooded Merganser eggs; locality means for DDE ranged from 0.07 to 13.2 ppm, PCB means ranged from 0.44 to 4.91 ppm, and mercury means ranged from 0.16 to 1.49 ppm on a wet-weight basis. Residues of DDE and PCB's appeared to be high in Red-breasted and Common merganser eggs. DDE averaged 15.7 ppm in Red-breasted Merganser eggs and PCB's averaged 44.6 ppm; Common Merganser eggs contained an overall mean of 19.5 ppm DDE and 61.0 ppm PCB's. Hooded Merganser eggs from the Midwest had thinned 8.3%, but the change was not significant. Highly significant shell thinning was detected in Red-breasted and Common merganser eggs; Red-breasted Merganser eggs were 17.7% thinner and those of Common Mergansers were 23.5% thinner than museum collections.

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