amounts of DNA shown in this paper will be important for biological and structural studies and that further experiments with smaller dies will permit infrared analysis of even smaller quantities.

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## Directional Differences in Pigeon Homing

The results of pigeon homing investigations made at the Max-Planck-Institut at Wilhelmshaven were the first to suggest a directional difference in orientation. The data from a number of releases showed a definite superiority of the homing results when the pigeons were taken south for release compared with the results when they were taken east. This was true for distances as short as 15 mi, but it was also true for 100 and more mi. Results from north and west releases were not available for a direct comparison.

Further work was done in the Carolinas (1). To collect data bearing more explicitly on the question, we made pigeon releases simultaneously from four points north, east, south, and west of the loft. Releases of single birds were made at each point of the "cross" release pattern at intervals of 10 min. Observers at the loft recorded the time of arrival of each bird. In the present report, we base the comparison of performance from the four directions of flight entirely on homing success.

A series of 12 cross releases was made with birds from two different lofts in the Durham region. In November 1954, pigeons from a loft located in the Duke Forest were flown twice at a distance of 16 mi and a third time at a distance of 53 to 60 mi. Birds from a second loft, which was located on the edge of Durham, were used in the period from February to April 1955 in a series of eight cross releases at  $17\frac{1}{4}$  mi and in a ninth release from 53 to 59 mi (2). In the 16to 17-mi flights, we selected release points that would provide a symmetrical cross pattern of release points and therefore could not choose places that were suitable for observing departure orientation. Forestry lookout towers were used as release points for the 53- to 60-mi flights; the cross pattern was not perfectly symmetrical. However, the distances for the flights from the north and from the south remained equal.

Within each series, the intervals between releases varied from 3 to 15 days; the same birds were used repeatedly, new ones being introduced to replace losses. On successive release days, the direction of displacement of individual birds was shifted to limit practice effects. In the series of releases at 171/4 mi, the whole groups were shifted, the sequence for the birds that were first displaced to the north being N, E, W, S, N, S, E, W; the others were rotated in step with these. For the other releases, new groups were formed-for example, birds that had last been sent north were assigned equally to groups that were to be taken E, S, and W. About half the birds were inexperienced in that they had never been removed forcibly from the loft area before they were used in the cross releases; the remainder had received a few previous homing releases from various directions. For their first cross release, the birds were always assigned to a group going in a different direction from that of their immediately preceding displacement.

Despite the 10-min release interval between birds, flight pairs or larger groups were formed on the way home in some cases. To meet the requirement of statistical independence in the data, we have considered only those birds that arrived singly and the fastest member of each group in the analysis of the results. The cross releases provided homing records for 558 of the shortdistance flights and for 117 of the 53to 60-mi flights. These were approximately equally distributed at each distance among the four directions. Figure 1 summarizes the homing performances for both distances separately. Birds displaced to the south yielded a relatively larger number of returns at 15 mi/hr or faster. Likewise, flights from the south showed a remarkably low number of losses. Birds displaced to the north, on the other hand, made the smallest number of quick returns and showed by far the largest number of losses. Chisquare tests of the data in Fig. 1 show significant departures from the distribution expected by random sampling (3). The winds, which averaged about 8 mi/ hr and were most often from the west, did not appreciably affect the results. Flights from the north were slightly favored over those from the south by the average wind direction.

The fact that directional differences

are found at only 16 to 17 mi strongly suggests that even at this short distance orientation is not primarily based on landmarks. Sheer landmark orientation or random searching should result in comparable homing performance from all directions. However, even with the practice afforded by eight flights from the 171/4-mi distance (twice from each point for each group), the north-south contrast in homing apparently was not erased (4).

There is no reasonable ground for doubting that a south-to-north superiority of homing exists in these birds as far as these two loft locations are concerned. It should be noted that the two Durham lofts are situated 2.6 mi apart, which makes it unlikely that individual features of the loft site are responsible for the observed effect. Since further work is





planned to test birds of the same and of different stocks at other home points, we must reserve judgment regarding the prevalence and consistency of the directional factor in homing until more results are available. Already, parallel data have been obtained at a loft in Mountville, S.C. (5) and in southern Germany; data from both points suggest that directional differences are a general phenomenon in pigeon homing. The combined data of these cross releases thus clearly confirm the earlier Wilhelmshaven findings of systematically unequal homing performances from different directions.

We are not able at this time to offer an explanation of the direction differences. However, it is conceivable that this discovery may provide a clue to the basis of the bird's orientation ability. Further study of the effect seems imperative.

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## **References and Notes**

- 1. These experiments were conducted under contract NR 160-244 between the Office of Naval Research, Department of the Navy, Washing-
- 2.
- Research, Department of the Navy, Washing-ton, and Duke University. We are indebted to the following for their as-sistance in the 53- to 59-mi release: M. H. Carson, T. H. Goldsmith, L. C. Graue, T. N. E. Greville, D. R. Griffin, H. B. Hitchcock, and G. V. T. Matthews. For the 16- to 17-mi flights,  $\chi^2 = 38.6$  (9 d.f.); P = < 0.0001. For the 53- to 60-mi flights, test-ing returns from each direction on the release day versus later and lost birds yields  $\chi^2 = 14.8$ (3 d.f.); P = 0.002. For both distances combined  $\chi^2 = 51.5$  (9 d.f.); P = < 0.000001. Comparing independent flights from N and S
- Comparing independent flights from N and S from a total of 38 birds that flew in all eight from a total of 38 birds that flew in all eight releases at 17¼ mi gives the following ratio of  $\geq 15$  mi/hr to < 15 mi/hr birds: (i) during the first four releases, 5/19 and 16/17 ( $\chi^2 = 4.57$ , 1 d.f.; P = 0.032); (ii) during the second four releases, 11/20 and 19/12 ( $\chi^2 = 4.13$ , 1 d.f.; P = 0.042). Thus, the only obvious effect of practice is a general increase in speed. We are indebted to John B. Cooley for pro-viding birds and assistance in these experiments.

29 August 1955

## **Formation Constants** for Cu(II)-Peat Complexes

A great deal of evidence, much of it indirect, points to the fact that soil organic matter forms relatively stable complexes with di- and trivalent metal ions. However, no quantitative information concerning the stability of such complexes is available. This is a preliminary report (1) on the determination of formation constants for metal ion-organic matter complexes; it deals entirely with the binding of Cu(II) by peat.

Table 1. Ionization	constants of	H-peat and	for
mation constants of	Cu(II)-peat	complexes.	

Cu(II) added (10 <sup>3</sup> mole/ lit)	KNO <sub>3</sub> (mole/lit)	pka	n	Kc (× 10-6)	В
2	0.01	5.5	2.2	80	2.5
2	0.1	4.8	2.2	8.0	2.5
2	1.0	4.3	2.2	1.6	2.5
0.6	1.0	4.3	2.2	1.0	
0.2	1.0	4.3	2.2	1.0	

Peat and other soil organic matter specimens possess acidic (proton-donating) groups thought to be carboxylic, phenolic, and enolic (2). Such groups are believed to be responsible for the cation exchange capacity, which generally lies between 2 and 3 milliequivalents per gram. The intrinsic ionization constant for the carboxylic groups appears to be about  $10^{-5}$  (3), and these are the only acidic groups thought to be ionized to an appreciable extent at pH of 7 and below.

The similarity of the acidic nature of peat to that of polyacrylic acid and the various cross-linked polymers whose Cu(II) complexes were studied by Gregor *et al.* (4, 5) suggested that a similar treatment might yield values for the formation constants of Cu-peat complexes.

The peat-Cu(II) reaction may be written in two ways, with P referring to the concentration of peat functional groups:

$$2\mathbf{P}^{-} + \mathbf{Cu}^{++} \overleftrightarrow{} \mathbf{Cu}\mathbf{P}_{2};$$

$$Kc = \frac{(\mathbf{Cu}\mathbf{P}_{2})}{(\mathbf{Cu}^{++})(\mathbf{P}^{-})^{2}} \qquad (1)$$

$$2HP + Cu^{++} \rightleftharpoons CuP_2 + 2H^+;$$
  
$$B = \frac{(CuP_2)(H^+)^2}{(Cu^{++})(HP)^2} \qquad (2)$$

For calculating the apparent formation constant Kc the condition is sought where  $CuP_2 = Cu^{++}$ —that is, where the degree of formation is 0.5 (6). Then  $Kc = 1/(P^{-})^{2}$ .

As is pointed out by Gregor et al. (4), since Kc is a constant for a reaction between a metal ion and charges on a colloidal particle, Kc should vary with the degree of neutralization and the ionic strength to the same extent as the acid ionization constant but in the opposite direction. On the other hand, B, which essentially is the product of Kc and the ionization constant ka, should be independent of ionic strength.

To evaluate Eqs. 1 and 2 for Cu(II)peat complexes, 0.2 g (0.46 milliequivalents of acidic groups) of acid-washed Florida peat was shaken for 48 hours with 50 ml of solutions containing 0.2, 0.1, 0.06, or 0.02 mmole of  $Cu(NO_3)_2$  and 0 to 0.35 milliequivalents of NaOH. The systems containing 0.1 mmole of Cu(II) were 0.01, 0.1 or 1N in KNO<sub>3</sub>; the systems containing the other amounts of Cu(II) were 1N in KNO<sub>3</sub>.

The pH's were measured with glass and calomel electrodes. Titration curves for the acid-washed peat and for the systems containing 0.02, 0.06, and 0.2mmole of Cu(II) are shown in Fig. 1. Strong binding of Cu(II) is indicated by the displacement of the curves.

The pH's of the partially neutralized peats at the three salt concentrations were plotted against log  $(1 - \alpha/\alpha)$ , where  $\alpha$  is the degree of neutralization calculated from the amount of base required to raise the pH to 7 in 1N KNO<sub>3</sub>. The points for each salt concentration were fitted to a straight line, leading to the values for pka (the negative logarithm of the acid ionization constant) and n listed in Table 1. From the derived equations relating the extent of ionization with pH and from the condition of electroneutrality. values for CuP2, P- and H+/HP were calculated. No corrections for activity coefficients were attempted.

To determine values for Kc and B,  $\overline{n}$ , the average number of acid groups bound for each Cu(II) ion in the system, was plotted against pP (the negative logarithm of the concentration of ionized peat) or log  $(H^+/HP)$ . The former vielded values of  $Kc(\log Kc = 2pP)$  at  $\overline{n} = 0.5$ ) that varied widely with salt concentration. The "corrected" constant Bwas independent of salt concentration in the range studied. Values for Kc and Bare listed in Table 1.

The Cu-peat systems were filtered, and Cu(II) was determined in the decolorized filtrates (darco carbon) with diethyldithiocarbamate. The mean of the formation constants (Kc) calculated from analytic Cu(II) data and the electroneutrality condition was  $3.2 \times 10^6$ , which is in reasonable agreement with the value deduced from the titration data.



Fig. 1. Neutralization curves of 0.0092N H-Peat in 1M KNO<sub>3</sub> (1) no Cu(II); (2) 0.0002M Cu(II); (3) 0.0012MCu(II); (4) 0.004M Cu(II).

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