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Preliminary study of PCBs in raccoons living on or near the Paducah Gaseous Diffusion Plant, Kentucky

January 15, 2016

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Introduction

The "Ecological Monitoring at the Paducah Gaseous Diffusion Plant: Historical Evaluation and Guidelines for Future Monitoring" report (Halbrook, et al. 2007) recommended the raccoon as a species for study at the Paducah Gaseous Diffusion Plant (PGDP). This species was selected to fill data gaps in ecological resources and provide resource managers with knowledge that will be valuable in making decisions and implementing specific actions to safeguard ecological resources and reduce human exposure (Figure 1). The current paper reports results of a preliminary evaluation to establish protocols for collection of tissues and initial screening of polychlorinated biphenyls (PCBs) in raccoons collected near the PGDP. These data are useful in developing future more comprehensive studies.

Methods

Cooperating trappers trapped 20 raccoons on or near the PGDP and 10 raccoons trapped from various locations in northwestern Kentucky (away from PGDP) during the fall and winter legal trapping season 2013 -14. Foothold and/or box traps were placed along streams and/or PGDP outfalls and checked daily while set. Captured raccoons were euthanized, skinned, and the carcass frozen prior to necropsy. During necropsy the sex and standard morphometric measurements were recorded, and liver, kidney, fat, and muscle tissues collected for potential contaminant analysis. Collected tissue were wrapped in aluminum foil, labeled and stored frozen until analysis. Skulls were collected, cleaned, and the lower left canine tooth removed and age determined by cementum analysis (Matson's Laboratory, Milltown, MT).

Sample preparation

During this preliminary study, only liver tissue was analyzed and evaluated. Liver tissue samples were thawed, freeze-dried for 48 hours, and well homogenized. Approximately 1 g of dried tissue was ground with diatomaceous earth. After spiking with surrogate standards (PCB-30, -65, and -204), the sample was subject to accelerated solvent extraction or ASE (Dionex ASE 350, Sunnyvale, CA, USA) with dichloromethae (DCM) at 100 °C and 1500 psi. After gravimetric determination of lipid content by using 10% of the extract, the remaining was purified by a Shimadzu Prominence Semi-Prep HPLC (Shimadzu America Inc., Columbia, MD) equipped with a Phenogel gel permeation chromatography (GPC) column (300 × 21.2 mm, 5µ, 100Å; Phenomenex, Inc., Torrance, CA) coupled to a Phenogel guard column (50 × 21.2 mm, 10µ, 100Å). The mobile solvent was 100% DCM and the flow rate was set at 4 mL/min. Target PCB compounds were collected in the fraction eluted from 16 to 35 minutes. The collected fraction was further cleaned and separated on a 2-g Isolute® silica solid phase extraction (SPE) column packed into a 6 mL polyesters SPE tube (SiliCycle Inc., Quebec City, Canada). The SPE

column was pre-washed with 10 mL hexane (HEX) to condition the silica gel sorbent. After the sample was loaded, the first fraction was eluted with 3 mL HEX and was discarded. The second fraction that contained target PHCZs was eluted with 6.5 mL 40:60 HEX:DCM, followed by 7 mL DCM. The latter fraction was concentrated to approximately 200 µL and transferred to an insert tube in a gas chromatography (GC) vial. Internal standard (decachlorodiphenyl ether or DCDE) was added prior to instrumental analysis.

Instrumental analysis

The separation and quantification of the target PCB congeners was performed on an Agilent 6890 GC (Agilent Technologies, Palo Alto, CA) coupled to a single quadrupole mass analyzer (Agilent 5973 MS) in electron impact (EI) ionization mode. The column used was a 30 m HP-5MS column (0.25 mm i.d., 0.25 µm, J&W Scientific, Agilent Tech.). The injector was operated in pulsed-splitless mode, held at 240 °C. Initial oven temperature was held at 100 °C for 1 min, increased to 130 °C at 20 °C/min, to 140 °C at 5 °C/min, and then ramp to 260 °C at 1.2 °C /min and held for 10 min. The quantification and confirmation of each target PCB congener was achieved via selected ion monitoring (SIM) for its molecular ions. Quantification was performed using calibration curves made from standard solutions at 4 – 5 concentration levels.

Statistical Analyses

As original data failed to meet the assumptions of parametric tests, they were log transformed before statistical analysis. Two-sample t-test and One-way Analysis of Variance (One-way ANOVA) were used to evaluate differences between data from raccoons collected near and away from the PGDP and among raccoons trapped along the North, East, South, and West boarders of the PGDP, respectively. A significance level of 0.05 was applied and all statistical tests were performed using OriginPro 9.

Results and Discussion

Of the 20 raccoons collected near the PGDP, 5, each, were collected along the North, East, South, and West edges of the plant (Figure 2). The age of all trapped raccoons ranged from 0 (first year raccoons) to 8 years old. The ages of the raccoons collected near the PGDP tended to be older (40% > age 2) than those collected away from the PGDP (10% > age 2) (Table 1). It is interesting that four of the raccoons trapped during the current study were 7 (one trapped away from and two at the PGDP) and 8 (trapped at the PGDP) years old while most raccoons in the wild usually live to age 4.

Considerable variation in liver ∑PCB concentrations among the raccoons collected near the PGDP reduced the probability that a statistical difference would be observed. Sum of PCBs were not significantly different (T-test, $p = 0.33$) between raccoons collected near

the PGDP (mean = 1014 ± 1266, range 114 – 5806 ng/g) and those collected away from the PGDP (mean = 543 ± 463, range 181 – 1750 ng/g). However, 35% of the raccoons collected near the PGDP (7 of 20) had ∑PCB concentrations that exceeded 1000 ng/g, compared to only 10% of those collected away from the PGDP (1 of 10). There also were no statistical differences ($F_{3,12}$ = 0.42, P = 0.74) between ∑PCB concentrations among the raccoons collected along the South (mean = 620 ± 830, range 114 – 2086 ng/g), West (mean = 1792 ± 2286, range 117 – 5806 ng/g), North (mean = 495 ± 234, range 329 – 906 ng/g), and East (mean = 1149 ± 858, range 252 – 2147 ng/g) borders of the PGDP. However, it is interesting to note that of the 7 raccoons collected near the PGDP with ∑PCB concentrations greater than 1000 ng/g, 6 were collected along drainages (outfalls) on the East and West sides of the plant.

There also was no correlation between age and ∑PCB concentrations (Figure 3). The oldest raccoon (8 years old) was trapped along the southern border of the PGDP and had the lowest ∑PCB concentrations (114 ng/g) of any raccoon trapped, including those trapped away from the PGDP (Table 1). The raccoon with the greatest ∑PCB liver concentration (5806 ng/g) was 1 year old and was trapped along the western border of the PGDP. This raccoon had more than twice the ∑PCB concentration of the raccoon with the next greatest ∑PCB concentration (2147 ng/g), which was also 1 year old, but trapped along the eastern border of the PGDP.

Summary and Recommendations

Although raccoons in the current study were trapped at specific locations, it is not possible with the current data to determine what locations they visited prior to capture. Although raccoon home ranges vary considerably depending on habitat and food resources, habitat and food availability near the PGDP suggests that home ranges would be relatively small. The abundance of raccoons near the plant also suggests that resources for the raccoon are readily available. This preliminary study does indicate that PCBs are accumulating in some raccoons located near the PGDP and may reflect increased bioavailability of PCBs at outfalls that drain surface water from the plant. The data also suggest that raccoons feeding along PGDP outfalls may accumulate greater concentrations of PCBs than those feeding along creeks and ditches that do not receive surface water from the plant. However, without knowing the specific drainages and frequency of visitation, one can only speculate about frequency and magnitude of exposure.

Because raccoons appear to be a good monitor of the bioavailability of PCBs in the environment at the PGDP, it would be advantageous to continue monitoring to provide additional more specific data. I suggest that raccoons be live captured near PGDP outfalls and fitted with telemetry collars and monitored for 6 months prior to the trapping season. Frequently locating raccoons with radio collars will allow determination of specific habitats being used, thus providing more specific data regarding habitat use and

bioaccumulation of PCBs. Resulting data would permit a better evaluation of potential exposure locations and assist managers in making decisions regarding future cleanup.

Literature Cited

Halbrook, R.S., H. H. Whiteman, and L. Roberts. 2007. Ecological Monitoring at the Paducah Gaseous Diffusion Plant: Historical Evaluation and Guidelines for Future Monitoring. Final Report to UK-Ky. Research Consortium for Energy and the Environment, Frankfort, KY

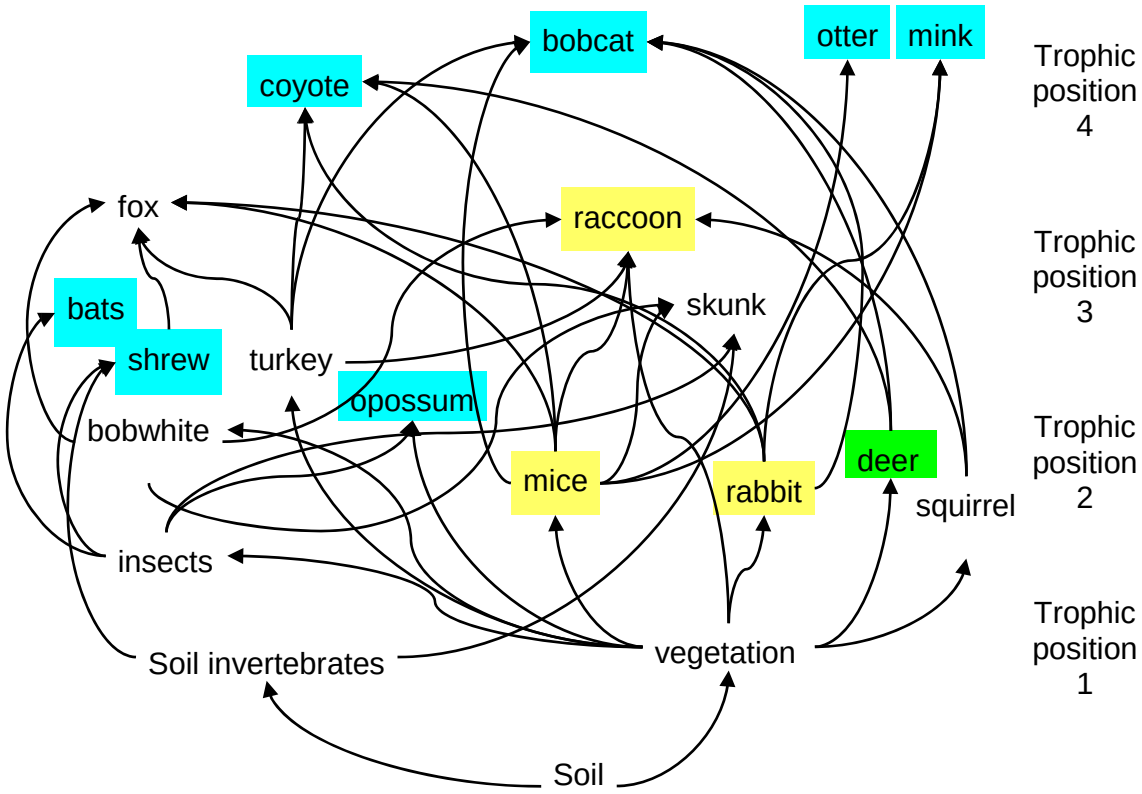
Appendix A: Tables and Figures

Table 1-- Raccoon age and liver PCB data. Color data correspond to South (red), West (green), North (blue), and East (yellow) borders of PGDP. White corresponds to data from reference raccoons.

Serial	ID	Age	Sum PCBs
1	KY001	1	981
2	KY002	7	393
3	KY003	1	474
4	KY004	1	384
5	KY005	2	1750
6	KY006	0	240
7	KY007	0	599
8	KY008	1	226
9	KY009	0	206
10	KY010	1	181
		Mean	543.4
		SD	462.74
11	P001	3	198
14	P004	8	114
15	P005	7	2086
27	P017	0	357
28	P018	0	344
		Mean	619.8
		SD	825.93
12	P002	3	1078
13	P003	4	117
26	P016	1	5806
29	P019	1	699
30	P020	2	1259
		Mean	1791.8
		SD	2286.17

16	P006	1	410
17	P007	2	906
18	P008	4	329
19	P009	7	456
20	P010	3	374
		Mean	495
		SD	234.45
21	P011	0	252
22	P012	2	366
23	P013	1	1107
24	P014	1	1875
25	P015	1	2147
		Mean	1149.4
		SD	857.69

Figure 1-- Terrestrial Mammalian Food Web and Trophic Position Model for the Paducah Gaseous Diffusion Plant, Paducah, Kentucky(1)



(1) Green boxes are species that have been monitored routinely, yellow boxes are species that have been periodically monitored, turquoise boxes are species that have been opportunistically monitored.

Figure 2 -- Raccoon capture locations and PCB histograms, PGDP, Kentucky.

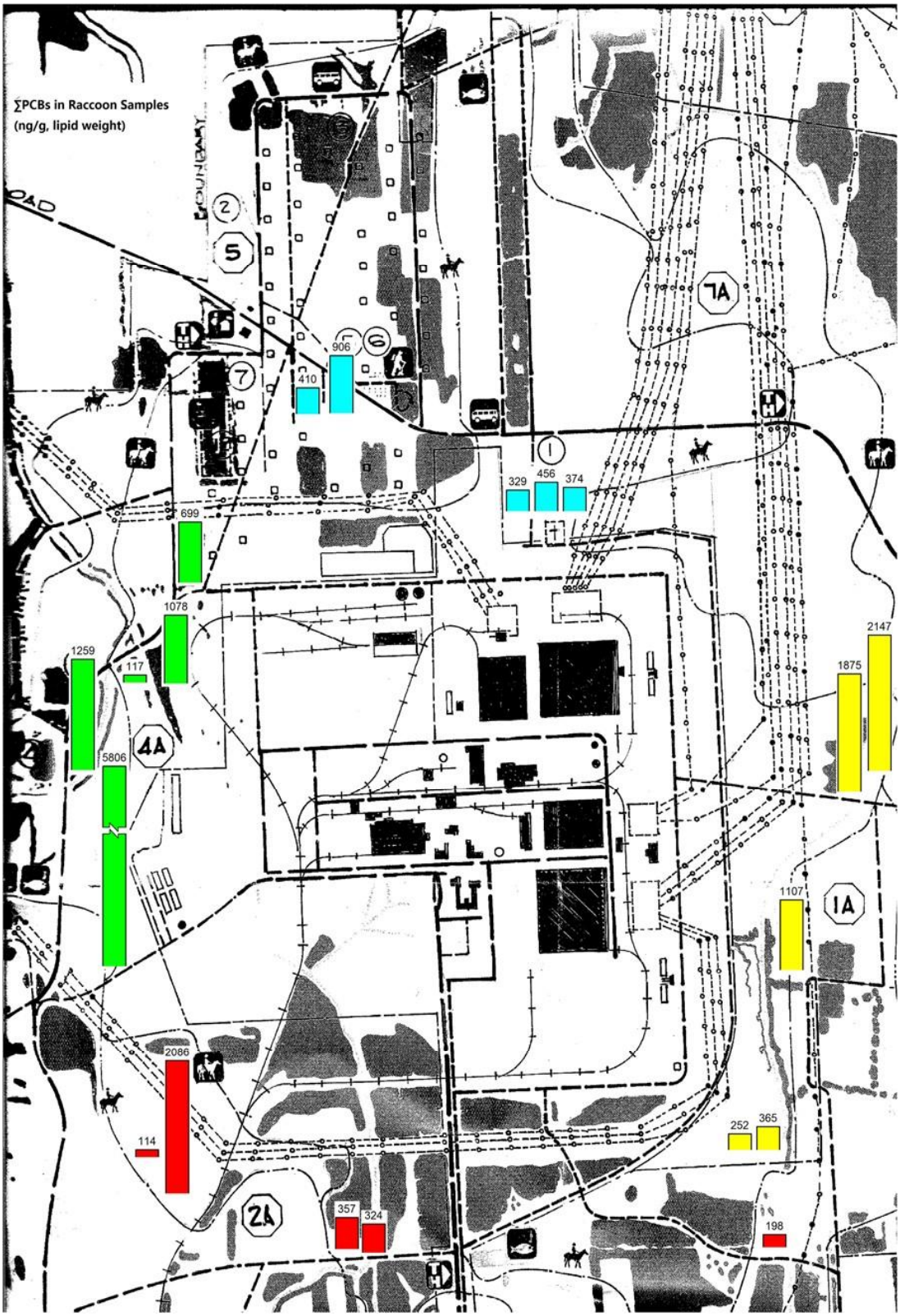
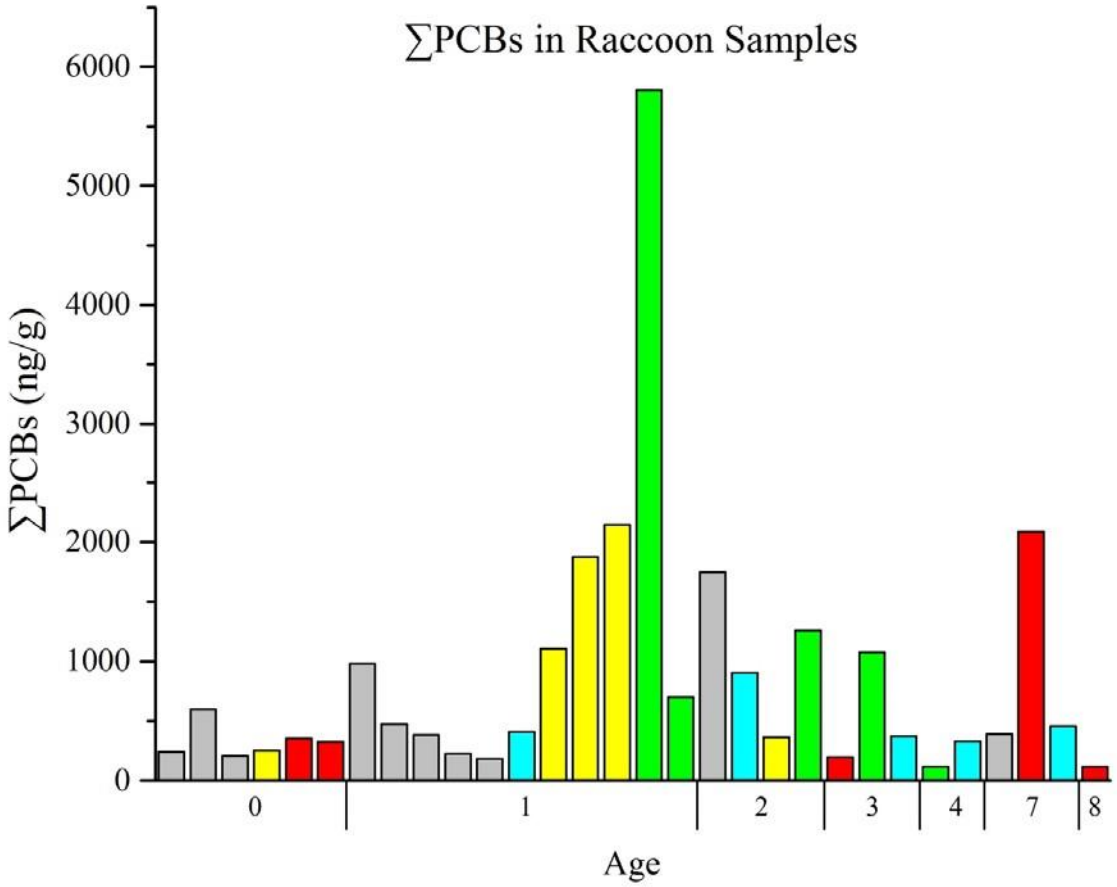


Figure 3 -- Age related ∑PCB concentrations measured in liver tissue of raccoons trapped at various locations in Northwest Kentucky (away from) and near the Paducah Gaseous Diffusion Plant, Paducah, Kentucky. (2)



(2) Raccoon ages are first year (age 0), 1 year old (1), 2 year old (2), 3 year old (3), 4 year old (4), 7 year old (7), and 8 year old (8). Gray color bars are raccoons trapped away from the PGDP, and blue, red, green, and yellow represent raccoons trapped along the North, South, West, and East borders of the PGDP, respectively.