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Atmospheric polycyclic aromatic hydrocarbon profiles and sources in pine needles and particulate matter in Dayton, Ohio, USA

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) were measured in pine needles (passive sampling) and on high volume particulate matter (PM) filters (active sampling) over a period of eight to ten months at two separate sites in the Dayton, Ohio, USA metropolitan area: Moraine and Yellow Springs.

Total PAH concentrations for PM ranged from 77.4 µg/g to 837 µg/g (dry wt.) at both sites with high molecular weight PAHs being the predominant form that tended to be higher in concentration during the colder months. Total PAH concentrations for pine needles varied by tree species and location. With an average concentration of 4187 ng/g, Austrian pine (*Pinus nigra*) needles in Moraine ranged from 2543 ng/g to 6111 ng/g (dry wt.) with the lowest and highest concentrations occurring in October and August, respectively.

The amount of phenanthrene was extremely high for August, 4200 ± 112, which could have resulted from the close proximity of the tree to the parking lot at a firehouse. White pine (*Pinus strobus*) needles in Yellow Springs had an average concentration of 384 ng/g and ranged from 127 ng/g to 589 ng/g (dry wt.) with September and November, respectively, having the lowest and highest PAH concentrations. The 2- and 3-ring PAHs were the predominant form in *P. nigra*, while the 4-ring PAHs predominated in *P. strobus*.

Total PAH concentrations in *P. nigra* were an order of magnitude greater than for *P. strobus*. A bivariate plot of BaA/(BaA þ Chry) versus Flt(Flt þ Pyr) allowed the PM and pine needle data to be included in the same source analysis and indicated sources of PM at both sites were biomass and/or coal combustion. This plot also suggested PAHs in Yellow Springs *P. strobus* originated from petroleum combustion sources, whereas PAHs in Moraine *P. nigra* originated from petroleum combustion with some sources more aged or remote.

References

Tomashuk, TA, Truong, TM, Madhavi, M, McGowin, AM. Atmospheric aromatic hydrocarbon profiles in pine needles and particulate matter and their temporal variations in Dayton, Ohio, USA, *Atmospheric Environment* (2012), 51, 196-202.

Yunker, MB, Macdonald, RW, Vingarzan, R, Mitchell, RH, Goyette, D, Sylvestre, S. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition, *Organic Geochemistry* (2002), 33, 489-515.

Acknowledgements

Images

Moraine sites:
Firehouse (A)
P. nigra (B)

Pinus nigra

Yellow Spring sites:
Government office (C)
P. strobus (D)

Pinus strobus

Methods

❖ Methodology for materials, sampling, filter extraction, pine needle preparation, and instrumental analysis are given in Tomashuk *et al.* 2012.

❖ An Anderson Instruments Model 1200 high-volume sampler (Anderson Instrument Company, Fultonville, NY) was previously installed atop the Moraine firehouse [39° 42' 52.23" N, 84° 13' 4.93" W], which was located about 500 m from an interstate highway on one side and about 100 m from a large train junction on the other side.

❖ In Yellow Springs, a Wedding and Associates Model 600 high-volume sampler (Wedding and Associates, Fort Collins, CO) was previously installed atop the Yellow Springs Government offices [39° 48' 30.07" N, 83° 53' 15.45" W]. It was situated about 200 m from a road with light vehicle traffic and to its east, State Highway 68.

❖ In Moraine, Ohio, an Austrian pine (*P. nigra*) was sampled near the firehouse [39° 42' 49.57" N, 84° 13' 1.82" W]. In Yellow Springs, a *P. nigra* could not be located near the PM10 sampler so a white pine (*P. strobus*) was selected 135 m from the active sampler [39° 48' 34.28" N, 83° 53' 15.25" W].

❖ Third-year needles were identified and selected by gaps between growing segments on *P. nigra*. Third-year needles were not identifiable on the *P. strobus* in Yellow Springs so second-year needles were sampled.

❖ The *P. nigra* was sampled in August, October, and December of 2009 and February of 2010. The *P. strobes* was sampled in September and November of 2009 and in January.

Results and Conclusions

❖ The particulate matter and pine needles collected different fractions of PAHs from the atmosphere. Most of the PAHs entrapped by the pine needles were 2-, 3-, and 4-ring PAHs compared to the particulate matter filters, which contained 4-, 5-, and 6-ring PAHs.

❖ Information inferred about the concentration of atmospheric contaminants in air quality testing could be misleading if analysis is limited to only particulate matter. There was also a tendency for PM to contain greater amounts of high molecular weight PAHs during colder months.

❖ The PAH profiles of the two different species of pine trees were very dissimilar. Exceptions to the seasonal trend are the *P. nigra* samples collected in August (2009), which had the highest measured PAH concentration during the warmest month due to a very high concentration of phenanthrene. Information extracted from pine needles proved to be more productive in assessing the level of PAHs related to traffic emissions (lower weight PAHs).

❖ However, relying solely on pine needle data would overlook the major presence of high molecular weight PAHs and significantly underestimate the contributions of combustion and industrial processes to the reduction in air quality of a particular region. In addition, it is still not clear how best to estimate concentrations of atmospheric PAHs from pine needle concentration measurements.

❖ This study is the first to combine data from both active and passive sampling in the same bivariant plot of BaA/(BaA þChry) versus Flt(FltþPyr) to identify the origin of PAH contamination demonstrating that PM and pine needle data complement each other. More importantly, the industrial and municipal activities in the area coincide with the conclusions drawn from the bivariant of PAH ratios.

Fig. 1. PAH patterns in percentages for aromatic ring number for each sample type at each site.

Fig. 2. Bivariate plot of PAH diagnostic ratios, IcdP/(IcdP + BghiP) *vs.* Flt/(Flt + Pyr). P is Petroleum; PC is Petroleum Combustion; C is Combustion; G/W/C C is Grass, Wood, and Coal Combustion. Threshold values and source designations are from Yunker and coworkers (2002).

Fig. 3. Bivariate plot of PAH diagnostic ratios, Ant/(Ant + Phen) *vs.* Flt/(Flt + Pyr). P is Petroleum; PC is Petroleum Combustion; C is Combustion; G/W/C C is Grass, Wood, and Coal Combustion. Threshold values and source designations are from Yunker and coworkers (2002).

Fig. 4. Bivariate plot of PAH diagnostic ratios, BaA/(BaA + Chry) *vs.* Flt/(Flt + Pyr). P is Petroleum; PC is Petroleum Combustion; C is Combustion; G/W/C C is Grass, Wood, and Coal Combustion. Threshold values and source designations are from Yunker and coworkers (2002).

Table 1

Concentrations of PAHs ($\mu g\,g^{-1}$, dry wt.) in particulate matter filters collected from Moraine, Ohio and Yellow Springs, Ohio from August 2009 to May 2010. ND is not detected.

PAH	Moraine particulate matter (PM_{10})					Yellow Springs particulate matter (PM_{10})				
	Aug ($\mu g\,g^{-1}$)	Oct ($\mu g\,g^{-1}$)	Dec ($\mu g\,g^{-1}$)	Feb ($\mu g\,g^{-1}$)	April ($\mu g\,g^{-1}$)	Sept. ($\mu g\,g^{-1}$)	Nov. ($\mu g\,g^{-1}$)	Jan. ($\mu g\,g^{-1}$)	Mar ($\mu g\,g^{-1}$)	May ($\mu g\,g^{-1}$)
Σ 2–3 ring PAH[a]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluoranthene (Flt)	32.1	29.9	50.6	29.7	67.1	31.1	23.3	40.9	72.6	59.4
Pyrene (Pyr)	29.3	20.7	33.1	27.5	57.1	26.5	16.3	38.5	66.1	52.3
Benz(a)anthracene (BaA)	54.2	24.2	45.3	44.1	76.8	19.8	18.9	62.8	129	75.4
Chrysene (Chry)	55.5	18.9	28.7	28.9	55.8	ND	13.4	36.0	62.7	50.3
Σ 4 ring PAH	171.1	93.7	157.7	130.2	256.8	77.4	71.9	178.2	330	237.4
Benz(b)fluoranthene (BbF)	ND	65.6	113	ND	ND	ND	ND	ND	ND	ND
Benz(a)pyrene (BaP)	ND	ND	ND	39.9	68.1	ND	ND	48.2	86.0	57.5
Benz(k)fluoranthene (BkF)	ND	58.8	124	47.1	66.4	ND	49.5	68.5	141	66.2
Indeno(1,2,3-c,d)pyrene (IcdP)	ND	59.5	124	58.4	89.9	ND	ND	82.5	169	88.3
Dibenzo(ah)anthracene (DahA)	ND	ND	ND	ND	72.5	ND	ND	ND	ND	73.0
Benzo(ghi)perylene (BghiP)	ND	59.7	123	40.3	78.2	ND	ND	54.9	111	75.1
Σ 5–6 ring PAH	ND	243.6	484	185.7	375.1	ND	49.5	254.1	507	360.1
ΣPAH	171	337	642	316	632	77.4	121	432	837	598
Average monthly temperature, K (°C)[b]	295 (22)	284 (11)	273 (0)	271 (−2)	287 (14)	291 (18)	281 (8)	270 (3)	279 (6)	289 (16)

[a] ND = Not detected; naphthalene (Naph), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Fluo), phenanthrene (Phen), anthracene (Ant) were not detected.
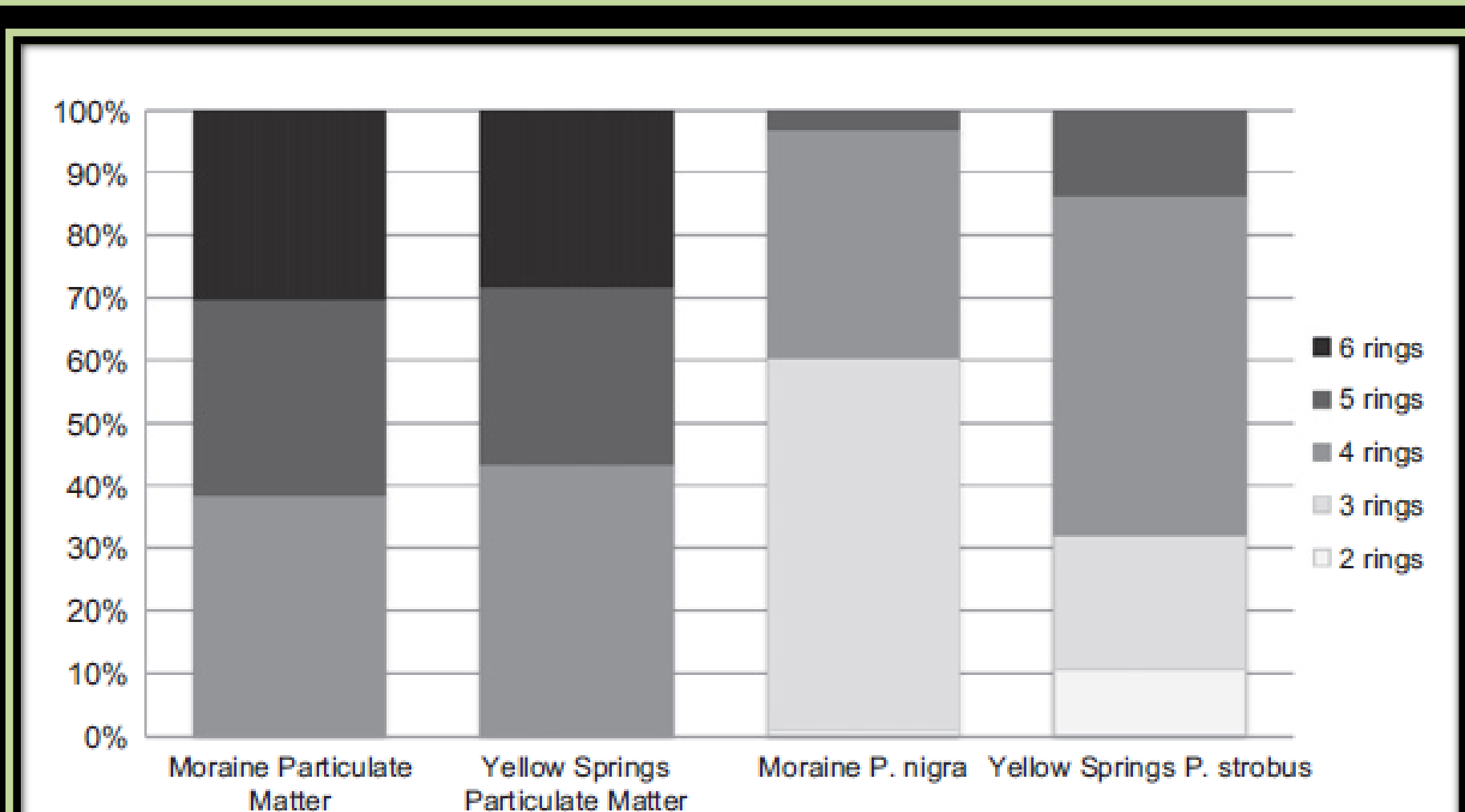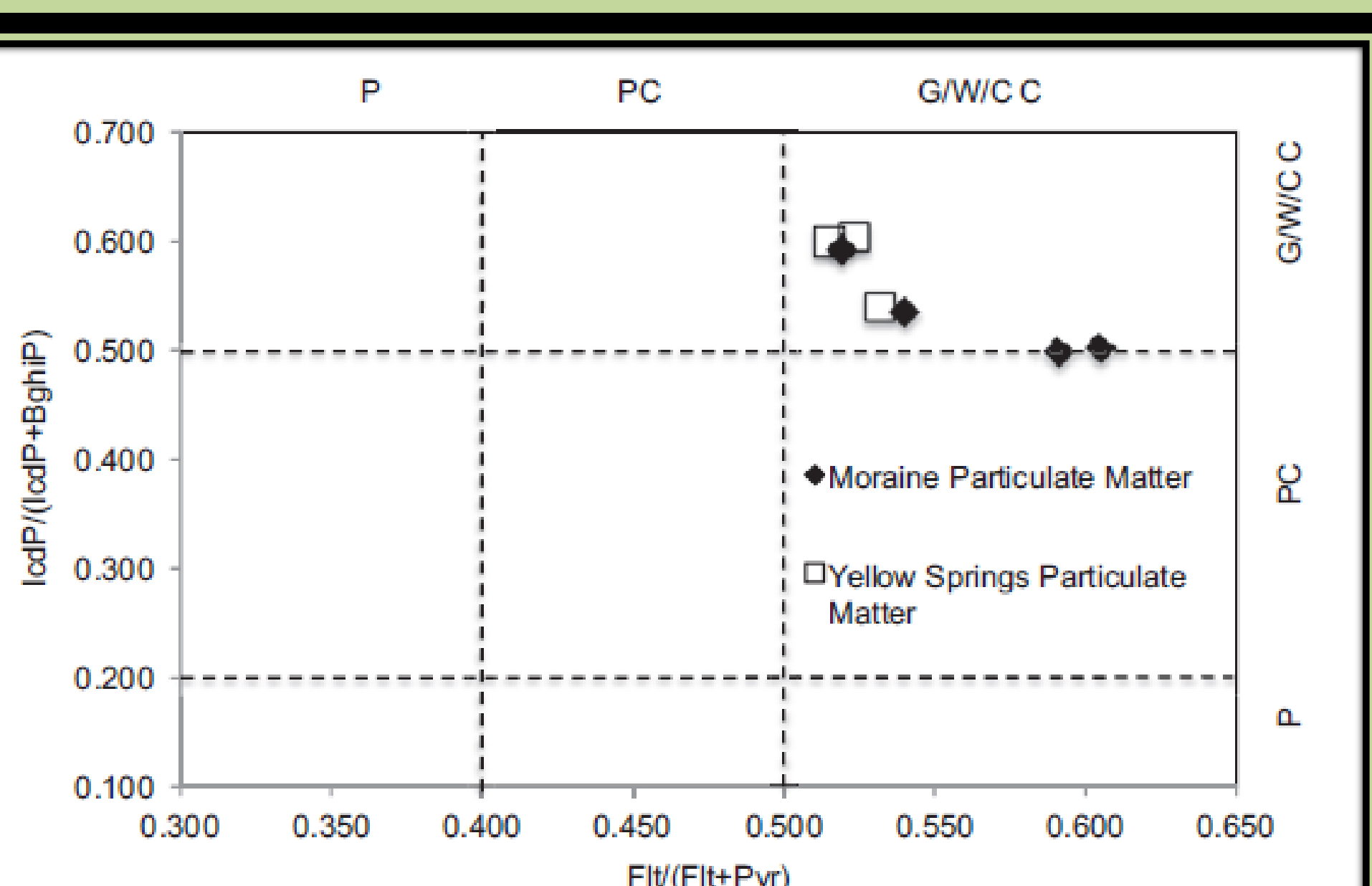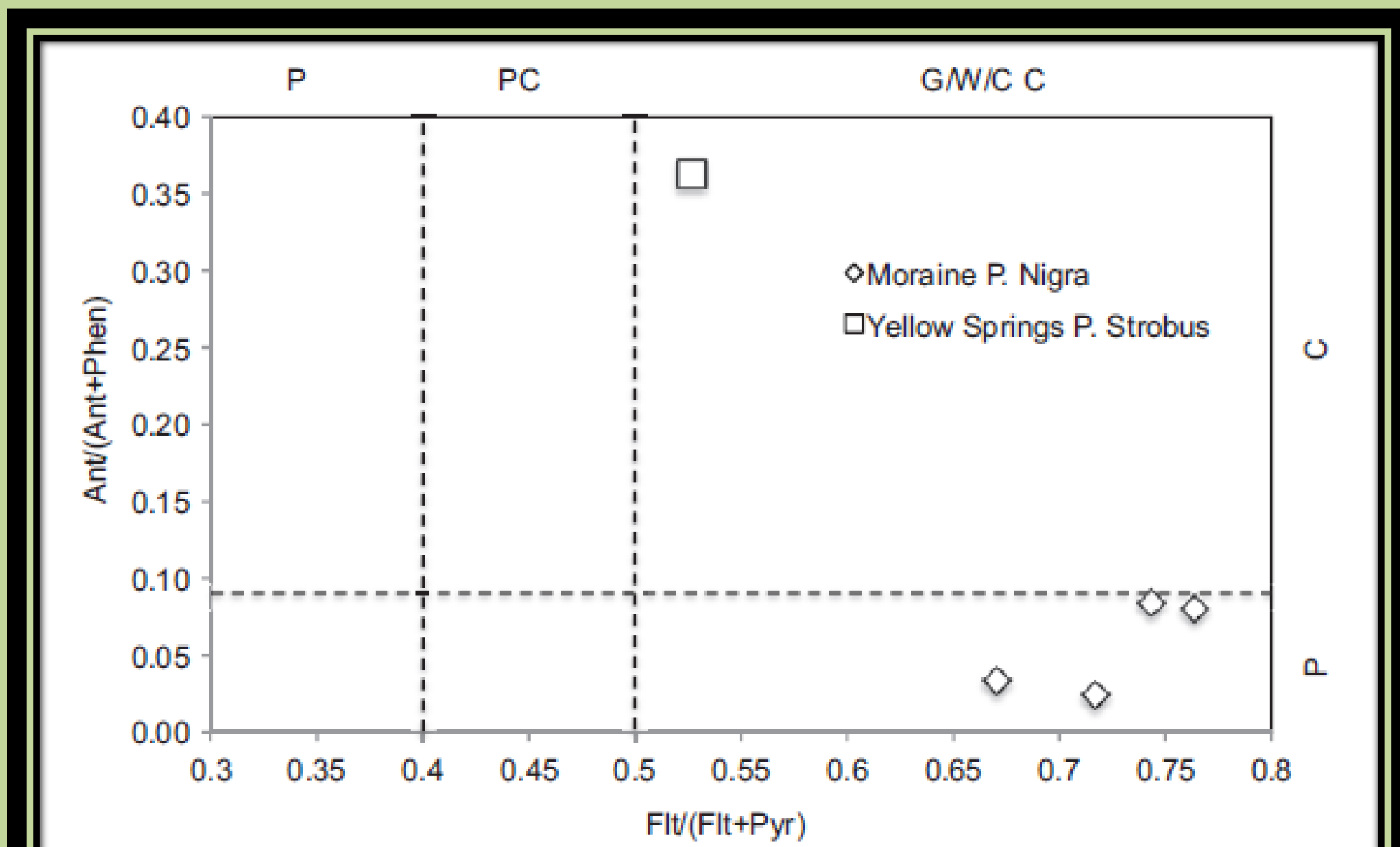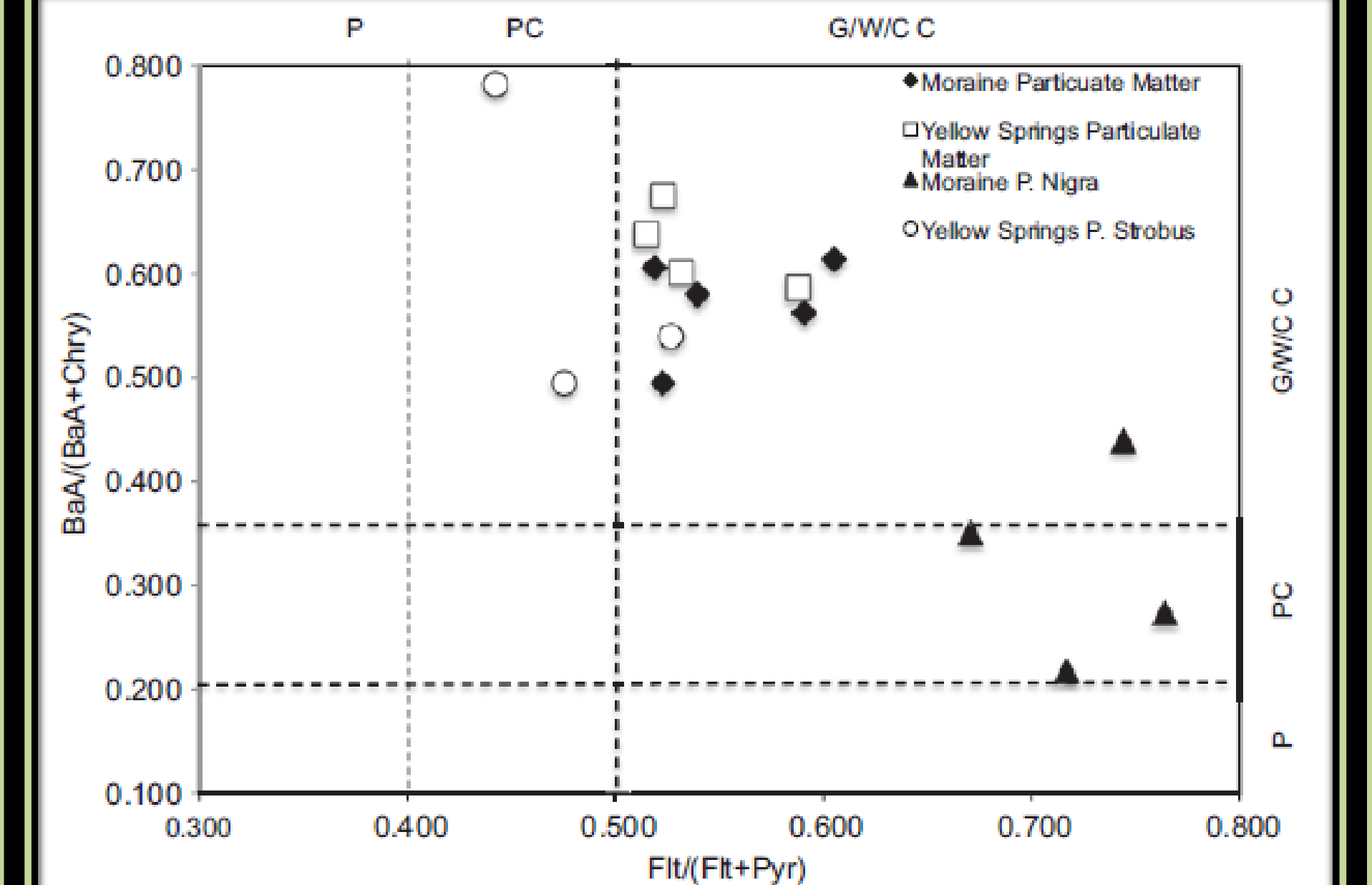[b] www.wunderground.com.

Table 2

Concentrations of PAHs ($ng\,g^{-1}$, dry wt.) in pine needles from a *Pinus nigra* in Moraine, Ohio and a *Pinus strobus* in Yellow Springs, Ohio sampled from August 2009 through March 2010. ND is not detected. Relative standard deviations are from triplicate analyses.

PAH[a]	Moraine (*Pinus nigra*)				Yellow Springs (*Pinus strobus*)			
	Aug ($ng\,g^{-1}$)	Oct ($ng\,g^{-1}$)	Dec ($ng\,g^{-1}$)	Feb ($ng\,g^{-1}$)	Sept ($ng\,g^{-1}$)	Nov ($ng\,g^{-1}$)	Jan ($ng\,g^{-1}$)	March ($ng\,g^{-1}$)
Naphthalene (Naph)	14.2 ± 2.3	22.4 ± 4.3	48.6 ± 7.1	55.5 ± 6.1	ND	34.9 ± 7.2	71.2 ± 24.5	58.6 ± 7.8
Acenaphthene (Ace)	ND[b]	27.8 ± 6.0	ND	ND	ND	15.2 ± 18.3	ND	ND
Fluorene (Fluo)	19.2 ± 5.9	116 ± 18	142 ± 9	175 ± 24	ND	94.8 ± 30.0	ND	ND
Phenanthrene (Phen)	4200 ± 112	1020 ± 185	1340 ± 72	2530 ± 549	60.3 ± 3.3	44.5 ± 6.6	78.7 ± 27.4	9.17 ± 0.06
Anthracene (Ant)	100 ± 6	88.4 ± 14.3	122 ± 31	88.6 ± 11.4	ND	25.4 ± 3.6	ND	ND
Σ 2–3 ring PAH	4333	1275	1653	2849	60.3	215	150	67.8
Fluoranthene (Flt)	1200 ± 47	857 ± 323	865 ± 259	984 ± 216	26.6 ± 1.61	28.8 ± 3.9	83.4 ± 18.4	17.1 ± 5.5
Pyrene (Pyr)	473 ± 7	264 ± 10	297 ± 90	483 ± 110	40.5 ± 7.20	25.8 ± 6.3	91.7 ± 30.8	21.5 ± 13.6
Benz(a)anthracene (BaA)	18.1 ± 2.2	26.0 ± 4.7	116 ± 1	88.3 ± 5.0	ND	58.2 ± 10.6	93.1 ± 18.5	154 ± 2
Chrysene (Chry)	64.8 ± 0.5	69.0 ± 11.9	148 ± 8	164 ± 32	ND	49.8 ± 8.6	95.5 ± 33.8	43.7 ± 5.4
Σ 4 ring PAH	1756	1216	1426	1719	67.1	163	364	236
Benz(b)fluoranthene (BbF)	ND	ND	107 ± 3	119 ± 14	ND	ND	ND	ND
Benz(a)pyrene (BaP)	ND	ND	114 ± 4	ND	ND	157 ± 79	ND	ND
Benzo(k)fluoranthene (BkF)	21.5 ± 2.7	51.5 ± 7.3	105 ± 10	ND	ND	53.9 ± 21.2	ND	ND
Σ 5–6 ring PAH	22	52	326	119	ND	211	ND	ND
ΣPAH	6111	2543	3405	4687	127	589	514	304
Average monthly temperature, K (°C)[c]	295 (22)	284 (11)	273 (0)	271 (−2)	291 (18)	281 (8)	270 (3)	279 (6)

[a] Acenaphthylene (Acy), indeno(1,2,3-c,d)pyrene (IcdP), dibenzo(ah)anthracene (DahA), andbenzo(ghi)perylene (BghiP) were not detected.
[b] ND = Not detected.
[c] www.wunderground.com