CORRELATION OF THE BLACKNESS INDEX OF HIGH VOLUME AIR SAMPLES WITH THE POLYCYCLIC HYDROCARBON CONCENTRATIONS IN URBAN AIR

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ABSTRACT

The blackness index of an air sample, measured by reflectance on an air sample filter, is an indication of the mean darkness of the particles collected on such a medium. As the presence of polycyclic hydrocarbons in air samples is associated with soot or carbon particles, it seemed reasonable to find out if a correlation between these two measurements could be established. The current availability of analytical methods of sufficient sensitivity allowed us to make accurate measurements of the two hydrocarbons. The polycyclic levels found were then compared with the measurements of particular matter and the blackness index to discover the best correlation. These correlations have been established for air samples from three different North American cities, and for different stations within the cities.

INTRODUCTION

The blackness index of an air sample, taken on a filter sheet and measured by reflectance, may be defined as 100 less the reflectometer reading. The instrument may be first set to 100 by means of a white surface of the unused filter material[1]. A standard curve may be prepared relating the blackness index and smoke concentration[1–3]. Using such a calibration curve, the observed blackness index will indicate the concentration of smoke for an unknown sample in some suitable units such as micrograms per square centimetre, which can be converted to micrograms per cubic metre. Although there is no well defined relation between particulate matter and the blackness index, such reflectance measurements have been used to measure air particulate loadings and from these to deduce polycyclic-in-air concentrations without weighing[4]. This disregards the fact that all airborne particulates are mixtures of light and dark particles in proportions which have to vary with the source, and which also differ in size. It is a common practice, in such measurements, to eliminate the larger particles in the sampling[2,3,5]. No attempt has been made to remove these particles in this work, since, according to Hemeon, 85 per cent by weight of the solids can be removed without any change in the optical density measurement[6].

The darkness of a sample being due to products of combustion, we thought that it would be interesting to find out if a relation could be established between the blackness index or the dark coloured fraction of the sample, and the polycyclic hydrocarbon concentration. Having deduced such a relation one could use this blackness index to indirectly measure the polycyclics in air samples. The time involved in measuring the blackness (a few seconds for a sample) is insignificant compared with the two days required for a complete determination of polycyclics in an air sample.

EXPERIMENTAL

The method for the measurement of benzo(a)pyrene (BaP) and benzo(k) fluoranthene (BkF) described by Dubois *et al.* is sensitive enough to permit the measurement of these two compounds in a daily sample by using only a small portion of the sheet[7]. Using the aforementioned technique, where eight samples can be analysed in one day by one person, BaP and BkF have been measured on approximately 250 samples taken on glass fibre sheet from three different stations in Ottawa (see *Figure 1*). At the same time,

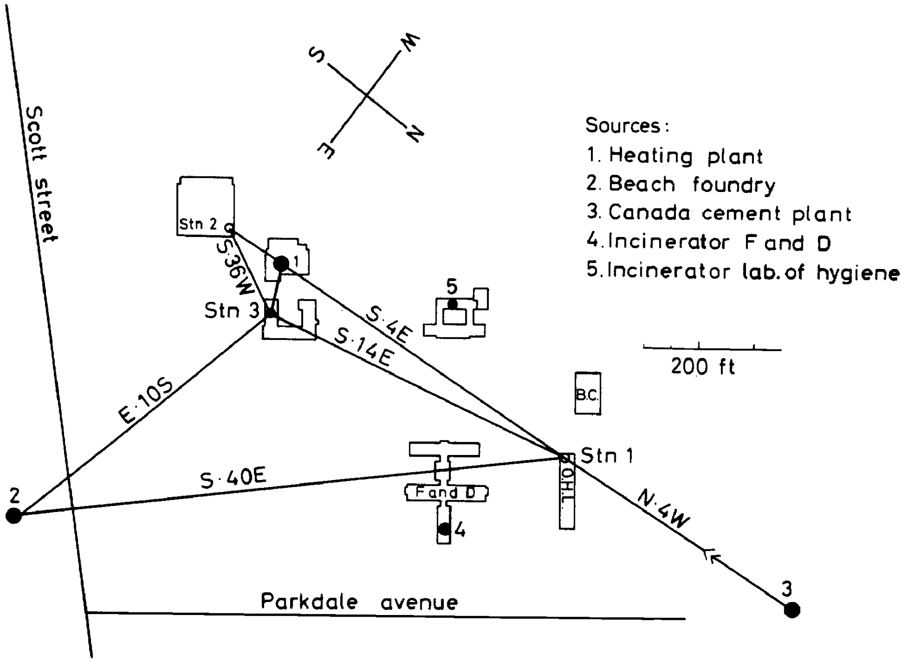

Figure 1. Map of Tunney's Pasture Area.

the blackness index was determined on each sheet with a Photovolt reflectance meter, model 610, using a blue glass filter transmitting in the 400–480 nm range. Two readings were made and the average taken. The particulates have been calculated from the actual weight of particulate matter obtained by weighing the sheet before and after sampling. *Tables 1*, *2* and *3* give the values obtained.

Table 1. Ottawa air samples—Station I

Sample number	*μg per sheet* BaP	*μg per sheet* BkF	*Milligrams per sheet Suspended particulates*	*Blackness index*	*Sample number*	*μg per sheet* BaP	*μg per sheet* BkF	*Milligrams per sheet Suspended particulates*	*Blackness index*
1	0·20	0·20	70	52·0	47	0·05	0·05	24	29·0
2	6·85	5·65	229	91·0	48	NM	NM	42	—
3	1·03	2·50	267	89·5	49	0·26	0·40	58	64·5
4	1·69	5·15	300	92·6	50	0·65	0·48	135	73·5
5	0·25	0·32	—	63·0	51	0·53	0·39	82	60·5
6	1·09	1·35	126	78·4	52	0·53	0·36	—	50·0
7	3·68	6·91	269	90·6	53	0·98	0·94	98	85·6
8	0·66	1·76	149	86·7	54	—	—	—	—
9	0·44	0·33	94	57·5	55	1·51	1·36	258	88·6
10	0·37	0·44	85	61·5	56	0·94	0·68	120	86·8
11	0·03	0·26	87	51·5	57	0·58	0·41	50	44·5
12	0·12	1·75	149	82·5	58	0·38	0·28	68	52·0
13	0·03	1·21	155	91·6	59	0·20	0·13	28	58·5
14	0·92	3·21	171	87·1	60	0·57	0·46	99	76·1
15	1·16	3·58	235	83·9	61	1·13	0·37	147	69·0
16	0·07	2·74	120	84·7	62	1·54	1·07	55	76·5
17	0·11	1·91	144	85·7	63	0·32	0·60	44	59·5
18	0·05	0·84	98	76·7	64	0·15	0·08	61	44·5
19	1·19	2·02	208	86·9	65	0·50	0·42	89	63·0
20	0·69	0·66	116	79·3	68	4·16	4·21	183	81·6
21	1·43	2·00	144	87·1	69	0·20	0·25	110	69·5
22	1·78	1·22	198	—	70	—	—	—	82·5
23	1·03	0·62	189	82·2	71	1·62	2·48	152	86·4
24	1·62	1·23	317	85·4	76	NM	NM	50	52·5
25	4·51	3·08	626	92·7	77	NM	NM	82	42·0
26	0·34	0·33	139	77·1	78	0·74	0·58	175	74·7
27	0·77	0·64	111	82·6	79	NM	NM	331	83·2
28	0·08	0·08	76	58·0	80	0·32	0·16	161	67·5
29	1·59	1·16	195	86·8	81	NM	NM	26	7·0
30	0·96	1·11	190	83·5	82	0·18	0·05	79	61·0
31	2·12	1·98	284	84·8	83	NM	NM	116	59·5
32	4·24	3·02	227	87·9	84	0·26	0·14	159	74·5
33	2·76	2·03	345	92·6	85	NM	NM	108	55·5
34	0·60	0·42	102	89·1	86	0·42	0·30	252	76·4
35	—	—	10	28·0	87	0·62	0·54	338	83·0
36	0·14	0·05	58	44·0	88	0·71	0·61	338	81·1
37	1·33	1·11	183	85·5	89	0·85	0·73	259	76·3
38	4·80	2·39	297	92·2	90	0·20	0·11	126	67·0
39	1·59	2·11	231	87·5	91	NM	NM	96	60·5
40	0·05	0·08	26	52·5	92	NM	NM	56	36·0
41	0·44	0·64	50	80·9	93	1·30	0·97	176	72·5
42	0·42	0·44	103	76·7	94	0·57	1·34	276	80·1
43	0·76	0·69	77	89·7	95	0·50	0·39	176	90·1
44	1·17	0·65	132	86·7	96	0·56	0·44	137	93·0
45	2·89	2·42	176	84·9	97	0·87	1·07	424	85·6
46	0·64	1·12	65	74·4	98	—	—	—	—
					99	0·15	0·06	178	71·0
					100	0·12	0·08	56	60·0
					101	NM	NM	68	55·0
					102	0·17	0·15	581	85·4

The results have been divided into classes, and frequency distribution curves were plotted[8]. The class intervals for particulate matter, blackness, BaP and BkF concentrations are respectively 100–150, 200–250, 300–350 etc., 94–92, 90–88, 86–84 etc., and 0·1, 0·3, 0·5–0·7, 0·9–1·1 etc. To these class intervals correspond the following class boundaries 95–91, 91–87, 87–83 etc. for blackness 75–175, 175–275 etc. for particulate matter 0–0·4, 0·4–0·8, 0·8–1·2 etc. for BaP and BkF. The curves are depicted in *Figure 2* to *5* inclusive. The same reverse J-shaped curve is obtained for all the variables. The frequency distribution curves for BaP and BkF concentrations are almost similar, suggesting an identical concentration of these two compounds in the samples analyzed. Most of the samples contain less than 300 milligrams per sheet of particulate matter. The mean values of all four measurements for each station are shown in *Table 4*.

To the class boundaries selected to obtain the frequency distribution curves of blackness index, the corresponding values for BaP or BkF or particulate matter were added and the mean values calculated. *Figure 6*

Table 2. Ottawa air samples—Station II

Sample number	*μg per sheet* BaP	BkF	*Milligrams per sheet Suspended particulates*	*Black-ness index*	*Sample number*	*μg per sheet* BaP	BkF	*Milligrams per sheet Suspended particulates*	*Black-ness index*
1	1·36	2·16	244	90·4	32	2·17	1·70	123	94·3
2	0·50	0·76	120	74·3	33	3·85	2·94	179	85·2
3	0·47	0·55	92	79·1	34	0·91	1·31	78	72·5
4	1·11	1·03	140	86·6	35	0·44	0·49	64	88·8
5	0·47	0·86	141	92·5	36	0·48	0·24	52	75·5
6	1·49	1·49	194	85·2	37	0·73	0·66	109	81·5
7	0·74	0·76	76	79·8	38	1·04	1·44	220	95·7
8	1·16	1·78	123	86·5	39	0·94	0·86	321	94·4
9	1·42	0·96	184	88·0	40	0·58	2·43	174	95·8
10	1·87	1·91	276	94·3	41	1·70	1·47	175	84·6
11	1·66	1·17	329	84·8	42	2·07	2·04	75	80·7
12	5·09	3·45	582	93·2	43	0·93	0·97	303	87·3
13	0·79	0·83	121	89·3	44	0·18	0·16	87	66·0
14	0·81	0·92	112	89·7	45	0·42	0·14	4	46·5
15	1·17	0·73	143	70·0	46	0·29	0·12	55	48·5
16	1·32	1·12	213	78·1	47	0·93	0·37	66	59·0
17	2·49	3·70	302	95·2	48	—	—	—	—
18	2·54	2·17	270	89·9	49	—	—	—	—
19	3·92	3·07	229	90·8	50	0·43	0·65	41	81·0
20	3·16	2·42	281	91·4	51	0·19	0·07	43	49·0
21	0·56	0·39	122	75·6	52	2·11	1·48	185	96·0
22	—	—	—	—	53	0·91	0·54	113	79·1
23	0·22	0·07	77	83·0	54	0·92	0·71	118	91·7
24	2·35	1·45	231	91·4	55	5·96	4·22	169	89·3
25	5·32	2·28	302	91·1	56	0·72	0·60	98	75·8
26	2·04	1·72	185	82·4	57	0·24	0·24	128	66·5
27	0·58	0·55	84	83·4	58	1·13	1·34	200	93·9
28	0·54	0·40	98	77·3	59	1·54	1·97	77	75·5
29	2·24	2·18	124	89·2	60	1·04	0·81	93	78·9
30	1·53	1·61	165	95·3	61	NM	NM	4	11·5
31	0·69	1·05	183	95·5	62	0·64	1·06	212	95·7

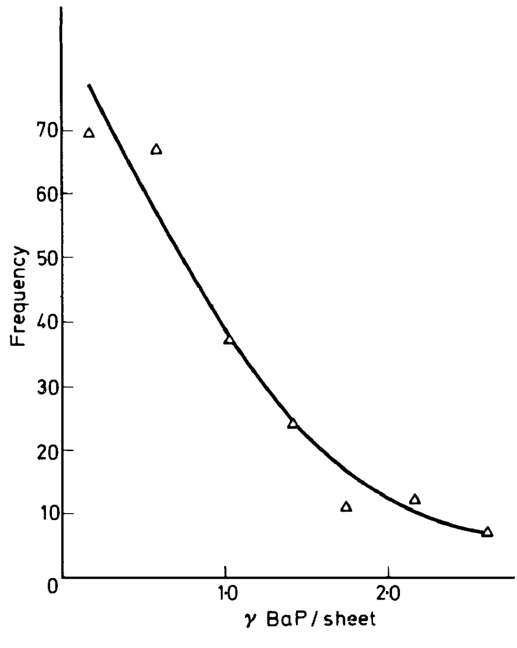

Figure 2. Micrograms of BaP per sheet versus frequency

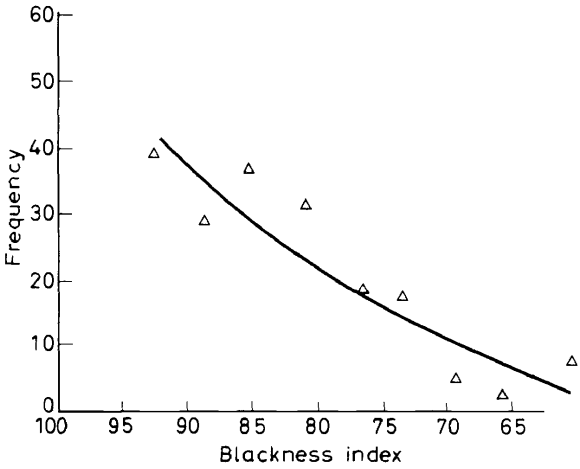

Figure 3. Blackness index versus frequency

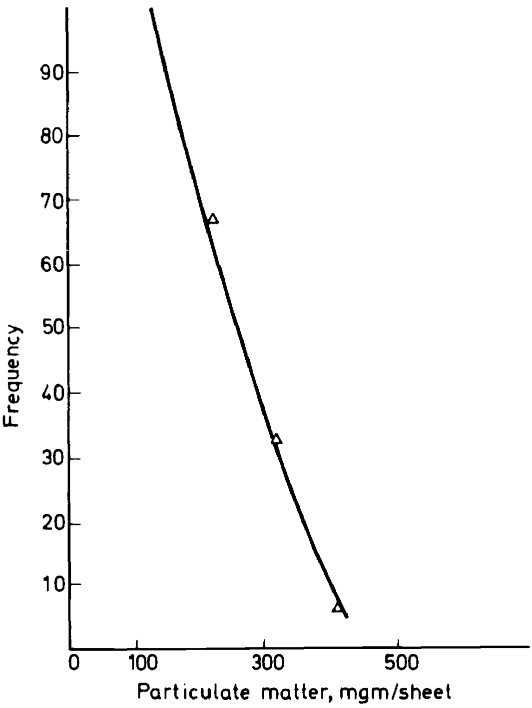

Figure 4. Total particulate matter versus frequency.

Table 3. Ottawa air samples—Station III

Sample number	*μg per sheet* BaP	BkF	*Milligrams per sheet Suspended particulates*	*Black-ness index*	*Sample number*	*μg per sheet* BaP	BkF	*Milligrams per sheet Suspended particulares*	*Black-ness index*
1	0·28	0·32	84	71·5	66	—	—	—	—
2	0·23	0·24	125	82·4	67	0·30	0·24	319	90·6
3	1·19	0·97	159	87·2	68	1·75	1·33	—	96·3
4	0·08	1·18	118	80·4	69	0·65	0·53	209	93·7
5	1·99	5·71	234	90·6	70	1·27	1·42	—	—
6	1·95	2·96	172	81·4	71	—	—	—	—
7	2·62	4·20	151	88·6	72	0·78	0·55	160	83·4
8	2·63	2·97	195	87·0	73	0·71	0·50	260	94·8
9	0·49	3·04	234	91·8	74	0·06	0·07	—	—
10	1·35	2·98	318	85·2	75	—	—	—	—
11	3·12	7·24	649	93·0	76	3·85	4·06	754	86·0
12	0·36	5·25	241	95·8	77	—	—	273	79·7
13	2·34	4·52	200	94·9	78	—	—	140	74·3
14	0·80	1·70	157	88·2	79	—	—	310	96·8
15	4·20	1·76	150	91·2	80	0·60	0·67	114	74·9
16	1·50	4·43	230	93·2	81	1·14	0·71	310	96·5
17	5·02	1·93	210	81·5	82	0·66	0·43	161	95·2
18	2·13	3·93	259	87·8	83	0·52	0·33	260	96·9
19	4·52	2·84	403	91·4	84	0·06	0·05	167	93·7
20	1·10	2·26	339	95·6	85	0·45	0·68	157	93·6
21	0·22	0·13	74	59·5	86	0·84	0·94	330	80·8
22	Traces		56	54·0	87	1·56	2·56	727	86·3
23	2·59	1·60	205	90·1	88	—	—	342	82·1
24	4·52	2·42	154	94·5	89	0·49	0·44	—	48·5
25	2·10	2·05	198	85·6	90	0·59	0·56	11	78·7
26	1·31	0·95	132	83·0	91	0·69	0·43	183	80·5
27	0·92	0·95	70	86·7	92	0·30	0·34	175	92·8
28	1·17	2·47	120	85·7	93	0·94	1·58	486	95·9
29	0·46	0·61	102	73·8	94	0·57	1·68	313	95·8
30	0·36	0·29	39	52·0	95	—	—	—	—
31	1·55	1·19	133	85·8	96	0·32	0·45	198	94·5
32	0·59	0·12	74	67·0	97	0·25	0·39	139	95·5
33	—	—	—	3·5	98	0·13	0·13	150	72·0
34	0·22	0·58	39	44·0	99	0·53	0·37	351	92·0
35	0·62	2·92	213	95·6	100	0·62	0·42	291	96·0
36	0·58	1·77	164	93·5	101	0·10	0·07	105	75·6
37	0·73	1·19	68	89·5	102	0·49	0·34	202	84·0
38	0·46	0·41	160	57·5	103	0·02	0·02	—	32·0
39	1·25	1·85	210	92·9	104	0·21	0·14	217	95·7
40	2·65	2·64	85	82·7	105	0·17	0·18	158	91·3
41	0·44	1·12	324	86·7	106	0·05	0·05	106	74·6
42	0·39	2·81	341	96·6	107	0·50	0·32	191	90·9
43	0·60	3·11	352	95·9	108	0·36	0·60	222	95·2
44	0·96	2·58	275	96·0	109	0·24	0·16	318	91·7
45	2·34	4·52	230	95·6	110	0·44	0·58	325	89·7
46	2·01	4·24	162	95·2	111	1·09	0·79	383	85·9
47	0·87	1·31	75	73·0	112	0·76	0·79	186	82·0
48	0·46	0·99	38	80·2	113	0·31	0·21	181	91·0
49	—	—	—	—	114	0·36	0·19	162	79·6
50	0·57	1·07	—	95·8	115	1·46	1·07	348	74·7
51	1·14	1·18	96	72·0	116	84·6	53·3	2014	91·9
52	0·20	1·50	227	94·6	117	0·43	0·28	174	94·2
53	0·50	2·75	182	93·3	118	—	—	96	88·9
54	3·16	7·81	194	85·3	119	0·08	0·07	116	81·8
55	1·44	2·65	146	95·3	120	0·12	0·09	236	82·8
56	0·79	5·95	392	96·2	121	NM	NM	384	79·3
57	1·34	3·85	113	95·5	122	0·05	0·04	282	75·8
62	1·68	1·21	174	91·2	123	0·15	0·11	1647	79·5
63	0·40	0·41	151	75·0	124	0·27	0·19	213	75·4
64	0·72	1·29	185	92·3	125	0·13	0·10	431	80·7
65	—	—	—	—	126	1·21	0·99	241	69·5

Table 4. Mean values for measurements at Stations I, II *and* III

	Station I	*Station* II	*Station* III	*All Stations*
BaP *γ/sheet*	0·94	1·41	1·02	1·07
BkF *γ/sheet*	1·09	1·26	1·55	1·49
Blackness index	72·8	81·3	85·3	79·4
Particulate Matter mg/*sheet*	154	149	209	195

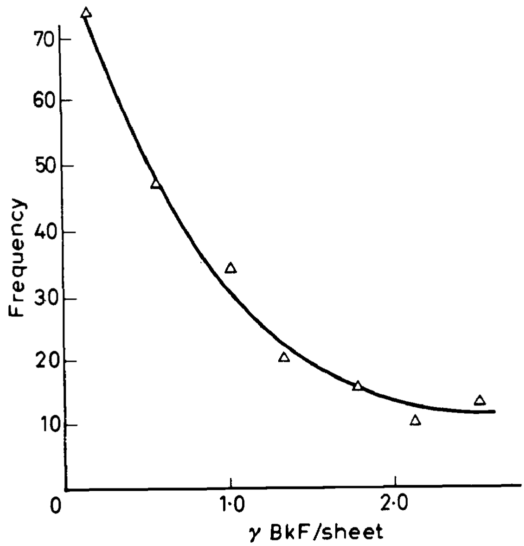

Figure 5. Micrograms of BkF per sheet versus frequency.

shows the relationship of blackness index and concentration of BaP or BkF for all the samples from the three stations. In general, for a given blackness, the concentrations of BaP and BkF are identical. The same curve could be used for the two compounds. However, at high indices, the BkF values seem to be higher than the BaP results. Although BaP is more interesting than BkF because of its higher carcinogenic activity, BkF results were used more generally instead of BaP, since BkF may be measured with greater precision and accuracy and it is not volatile. *Figure 7* shows the relation between the blackness index and BkF for each station. The curves being different from one station to the other, one could conclude that for a given station, a characteristic curve is obtained indicating different contamination sources.

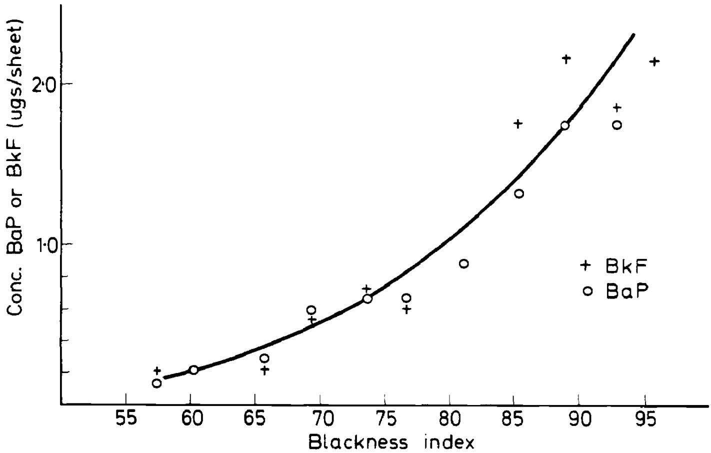

Figure 6. Blackness index versus total BaP and BkF per sheet.

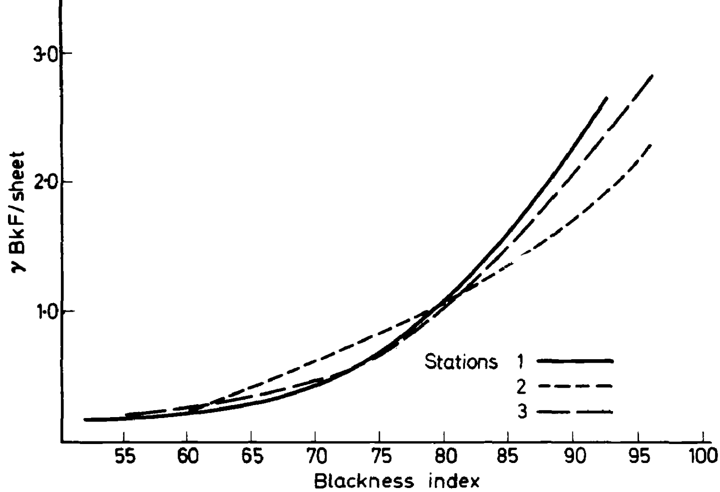

Figure 7. Blackness index versus total BkF per sheet for three stations.

On the other hand, Station I and Station III being almost similar, it is possible, as will be mentioned later, that they are the same and that the difference observed is due to a lack of accuracy in the measurement. By plotting the monthly values of Station III for blackness index and BkF, *Figure 8* is obtained. For a blackness index of 80, the concentration of BkF is

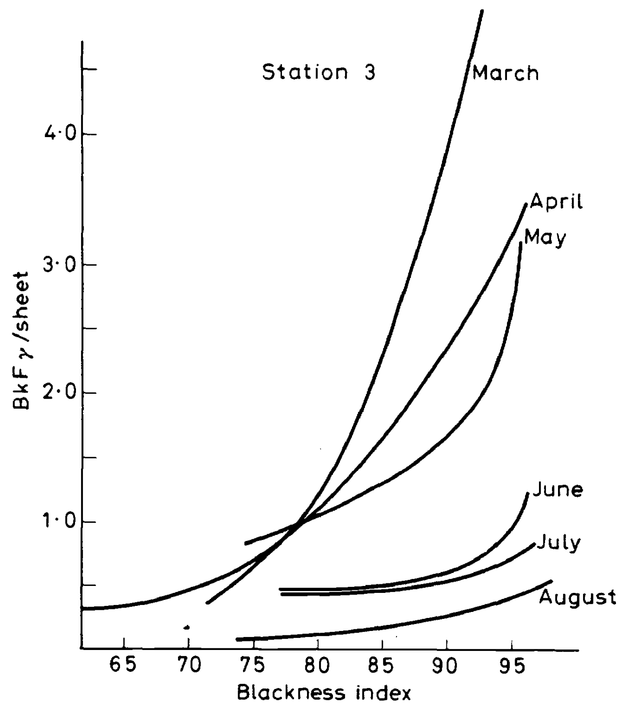

Figure 8. Blackness index versus total BkF per sheet for six months.

0·08 in August as compared to 1·25 in March and for an index of 85, 0·13 micrograms of BkF in August and 2·30 in March. It is then possible to obtain completely different curves from one month to the other. In general, the concentrations of BkF in March are 17 times higher than in August. For the months observed, the concentration of BkF is maximum in March and decreases to a minimum in August. Unfortunately no results are available for the other months. According to these curves, most of the polycyclics are generated in March, April and May. The blackness index obtained for these months is evidence of a completely different type of sample when compared to the blackness indices obtained in summer. The decrease in BkF concentration for a given blackness for Station III is observed from the mean monthly values calculated in *Table 5* and in *Figure 9*. The BkF concentration

Table 5. BaP in γ/sheet

	March	*April*	*May*	*June*	*July*	*August*
Station I	1·25	1·14	0·99	—	—	0·35
Station II	1·45	1·63	1·03	—	—	—
Station III	1·45	1·58	1·11	0·89	0·56	0·39
		BkF γ/sheet				
Station I	2·05	0·95	0·95	—	—	0·32
Station II	1·42	1·45	0·85	—	—	—
Station III	2·88	1·90	2·86	1·05	0·60	0·30
		Blackness index				
Station I	80	73·5	65	—	—	67·2
Station II	86.5	86·2	71·6	—	—	—
Station III	85·5	81·6	90·3	87·4	87·2	83·6
		Particulate Matter				
Station I	188	132	106	—	—	172
Station II	206	165	85	—	—	—
Station III	223	162	206	263	232	225

and the blackness index follow the same pattern. However, this trend is not so distinctly observed with the other two stations.

Another relation was also studied. The values for particulate matter per sheet were plotted in *Figure 10* against the concentration of BkF per sheet for each month of Station I and regression lines calculated. From March to August the slopes of the curves increase. For a given increase in particulate matter during Maıch a large increase in BkF is obtained, while in August, for the same increase in particulate matter, a smaller increase in BkF is observed. The slope of each curve could be a characteristic index of the pollution for a particular month. It is to be remembered that the curves do not go through the origin, the intercepts being the concentration of particulate matter in the samples which do not contain any polycyclics.

In *Figure 11* the values of particulate matter per square centimetre and blackness index are plotted. March and April show different curves for Station III. The standard curves for smoke measurement used by the Department of Scientific and Industrial Research, Warren Spring Laboratory, and at the Laboratoire d'Hygiène de la Ville de Paris, are also shown.

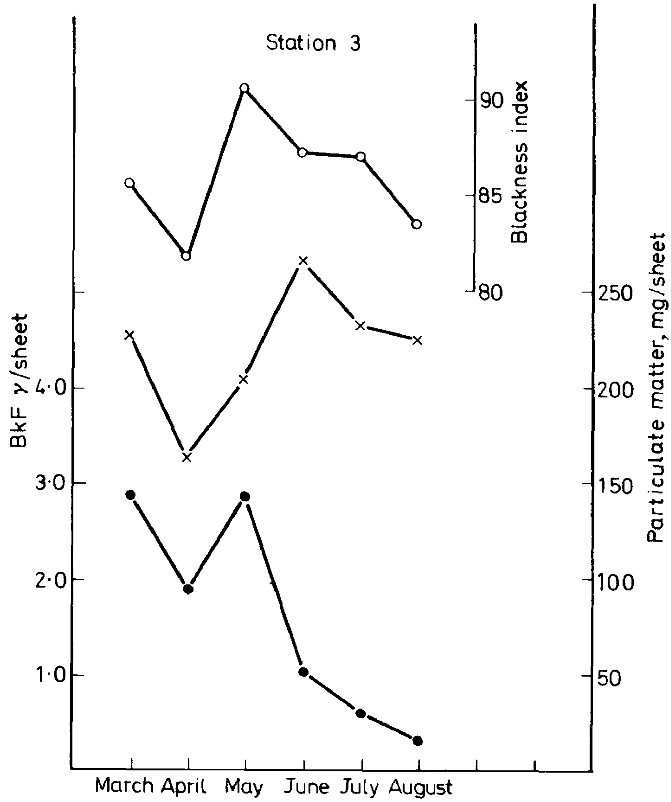

Figure 9. Relationship BkF and particulate matter for three stations.

The difference in the curves can be explained by the fact that the larger particles were not removed in our particular case. The concentration was calculated from actual weighing of the sample. On both the English and French curves the concentration of particulate matter per square centimetre is, in fact, the concentration of the dark material only.

CONCLUSIONS

One of the main problems encountered in the measurement of blackness indices on glass fibre sheets is the high values obtained. A large number of readings fall in the range 85 to 96. The precision and accuracy of these measurements are therefore lessened. However the following trends are observed in the particular case studied.

The relation between the blackness index and the concentration of BkF and consequently of polycyclics vary from one station to the other. Each curve is characteristic of a given station. However the variations are within comparable limits below an index of 85. An investigation on a larger number of stations and in different cities is in progress. Preliminary results on Rochester samples indicate that the curves are different from one city to the other although the difference from one station to the next or from one month to the next is more important in some cases.

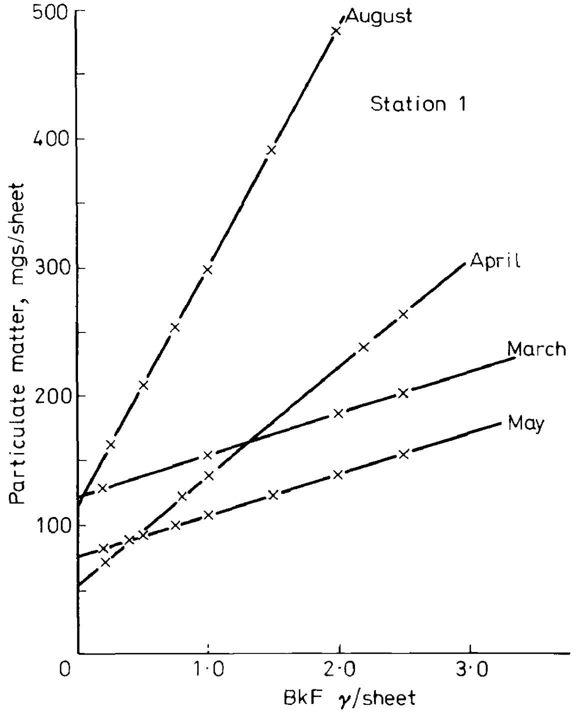

Figure 10. Total particulate matter versus total BkF for four months at Station I.

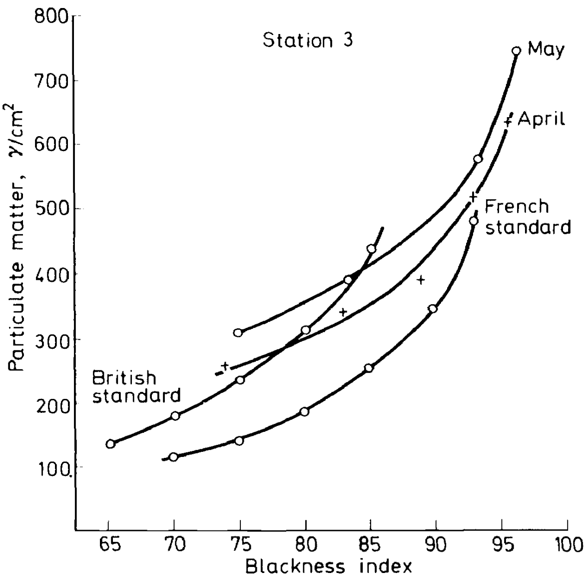

Figure 11. Particulate matter in area units versus blackness index at Station III.

The relationship between the blackness index and the concentration of BkF or polycyclics is different from one month to the next.

For a given blackness index, the concentration of BkF is lower in summer than in winter, and for a given amount of particulate matter, the concentration of BkF is also lower in summer. It then follows that the dark material is different, from summer to winter.

The blackness index seems to be a poor indicator of the polycyclic concentration in air samples and it would be unwise to use it to make such measurement unless a standard curve for a given city has been prepared.

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