Environment International, Vol. 18, pp. 153-162, 1992
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0160-4120/92 $5.00 +.00

THE SPECIATION PATTERN OF LEAD IN STREET DUSTS AND SOILS IN THE VICINITY OF TWO LONDON SCHOOLS

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EI 9012-212M (Received 4 December 1990; accepted 6 June 1991)

The chemical association pattern of lead in road dusts taken at locations near two schools in South East London and from soils located within the schools' grounds was investigated using a selective extractant speciation scheme. The results indicate that lead in road dusts is primarily associated with the carbonate and iron and manganese hydrous oxide fractions. In soils, this pattern is altered with lead levels in the carbonate fraction becoming reduced and percentage levels in the iron and manganese hydrous oxide and organic fractions becoming more important. Overall lead levels are variable; some tentative evidence suggests that these overall levels in road dusts may be affected by street-cleaning regimes. The results of the survey are assessed in terms of the potential hazard posed to children in the 0 to 6 y age range.

INTRODUCTION

In recent years, research conducted on the problems associated with lead contamination of the urban environment has focused on the dangers presented by urban dusts. Children, in particular, are considered to be at some risk from ingestion of lead in dust through hand-to-mouth activities (Duggan 1983; Hilburn 1979; Schwar et al. 1988). Several workers have demonstrated significant relationships between lead in dusts and blood and have identified significant transfer pathways (Bornschein et al. 1988; Sayre 1981). The U.S.E.P.A.'s uptake/biokinetic model, too, has been used to demonstrate the importance of dirt ingestion as a major contributor to blood lead levels in children (Hoffnagle 1988).

Even at low concentrations, lead may be responsible for nervous system disorders (Needleman 1979; Odenbro 1983). Recently, Ericson and Mishra (1990) reported on a pilot study which indicates that hyperactivity in school children may correspond with proximity to major highways and soil lead levels. Assessment of lead levels in soils and dusts in the child's immediate environment is thus an ongoing responsibility.

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Many previous studies in this area have measured total concentrations of trace metals in soils and dusts. It has become, however, increasingly common for metals in such matrices to be speciated. Such an exercise involves division of the metal of interest into fractions based upon its various chemical associations as determined by the sequential use of selective extractants (Gibson and Farmer 1986; Hamilton et al. 1984; Harrison et al. 1981; Harrison and Wilson 1983; Tessier et al. 1979). Such detailed work is considered to give greater depth of information concerning the mobility and bioavailability of trace metals in soils and dusts (Harrison et al. 1981; Fergusson and Kim 1991). As such, it ought to provide a more informed indication of the potential hazards associated with the given levels of a particular metal in a given soil (Davies 1981; 1983) or dust (Harrison et al. 1981) sample.

One of the more commonly used schemes is that devised by Tessier et al. (1979). Operationally, the metal content in the sample is divided up into five fractions: (a) soluble and exchangeable, (b) carbonate fraction, (c) associated with iron and manganese hydrous oxides, (d) associated with organic matter, and (e) residual. The order of bioavailability ranges from (a) the most bioavailable fraction to (e) the least available (Harrison et al. 1981; Clevenger 1990).

The purpose of this study was to assess the degree of environmental hazard posed to children attending two schools that are adjacent to a major road junction in South East London known as Fiveways Junction. A 12 h survey (0700 to 1900 h) indicated that some 46 850 vehicles may use the junction (London Borough of Greenwich, private communication). The major road passing through the junction is the A20, an important arterial road running into South East London from the suburbs and Kent.

EXPERIMENTAL

Site description

Fig. 1 is a schematic map showing the proximity of the two schools to the A20 and Five Ways Junction. On a typical working day, traffic will build up at this junction, causing at times long tail backs both on the main road and the side roads. In addition, the side streets experience high levels of on-street parking. At the time of sampling, the street-cleaning regime was as follows (London Borough of Greenwich, private

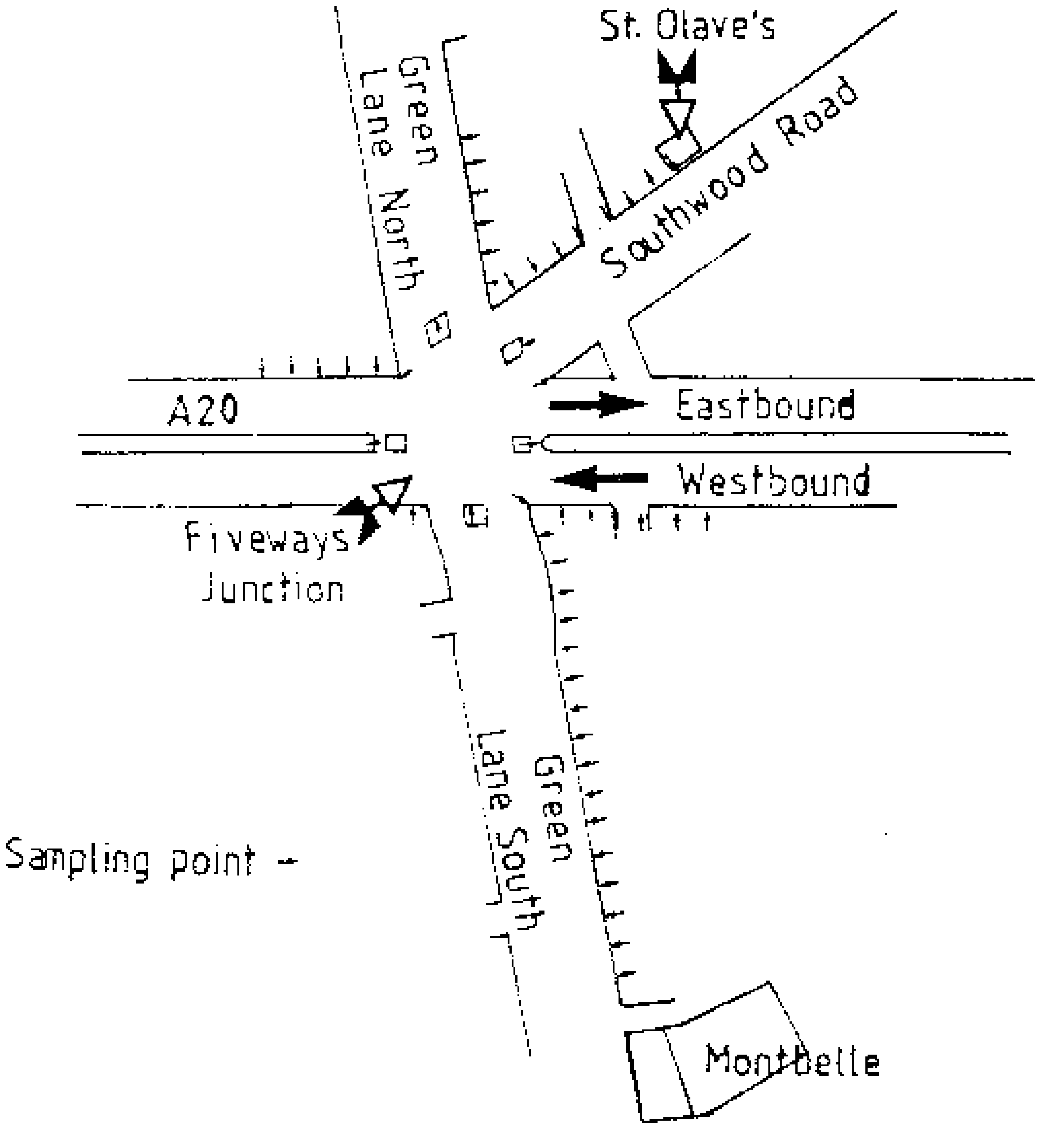


Fig. 1. Schematic map of Fiveways Junction.

communication): A20, once a week by street-cleaning truck; Green Lane, once a week by hand broom; and Southwood Road, twice a week by hand broom.

Sampling

All sampling was conducted in October 1989. Samples of road dusts were collected from the side roads and main road along transects measured from the cross roads at 20 m intervals. The dust samples were taken by careful sweeping of dust contents in gutters. Further samples were taken from the traffic light islands at the cross roads.

Soil samples were taken from the top 5 cm using an aluminum corer. Samples were taken from the playing fields in Montbelle School and flower beds in St. Olave's School. All samples were stored at -8 °C prior to analysis.

Sample treatment

Dust and soil samples were initially air dried. The samples were then passed through a 850 µm sieve to remove all large particles. This was followed by grinding in a mortar and pestle and subsequent passing through a 250 µm sieve. The samples were then dried at 37°C for 7 d. This was followed by the sequential extraction procedure outlined below.

Approximately 5 g of sample was accurately weighed out and treated as outlined in Table 1. At the end of each stage, the extract was separated from the residue by filtration through a Whatman No. 4 filter. The residue was then washed twice and subsequently used for the next stage of the sequential extraction scheme.

The supernatant was analysed for lead using Instrumentation Lab IL 351 flame atomic absorption spectrophotometer at a wavelength of 217 nm using background correction. Blanks were run to assure quality control. Laboratory dust samples were also collected to check for possible contamination of samples during processing. Only one sample gave a detectable lead reading and this was only of 8 µg g^{-1}.

Table 1. The sequential extraction scheme (Adapted from Gentry et al. 1987).

	Extraction Procedure	Fraction
1	1M $MgCl_2$, pH 7 for 1 hour	Exchangeable.
2	1M CH_3COONa pH 5 for 5 hours.	Bound to carbonate.
3	0.04M $NH_2OH.HCl$ pH 2. 25% CH_3COOH 5 hours at 96°C	Bound to iron and *manganese hydrous* oxides.
4	30% H_2O_2 / 0.02M HNO_3 pH 2. 5 hours at 85°C followed by CH_3COONH_4	Bound to organic matter.
5	HF / $HClO_4$	Residual.

However, due care was taken to protect the samples from laboratory dust contamination.

RESULTS AND DISCUSSION

Overall lead levels

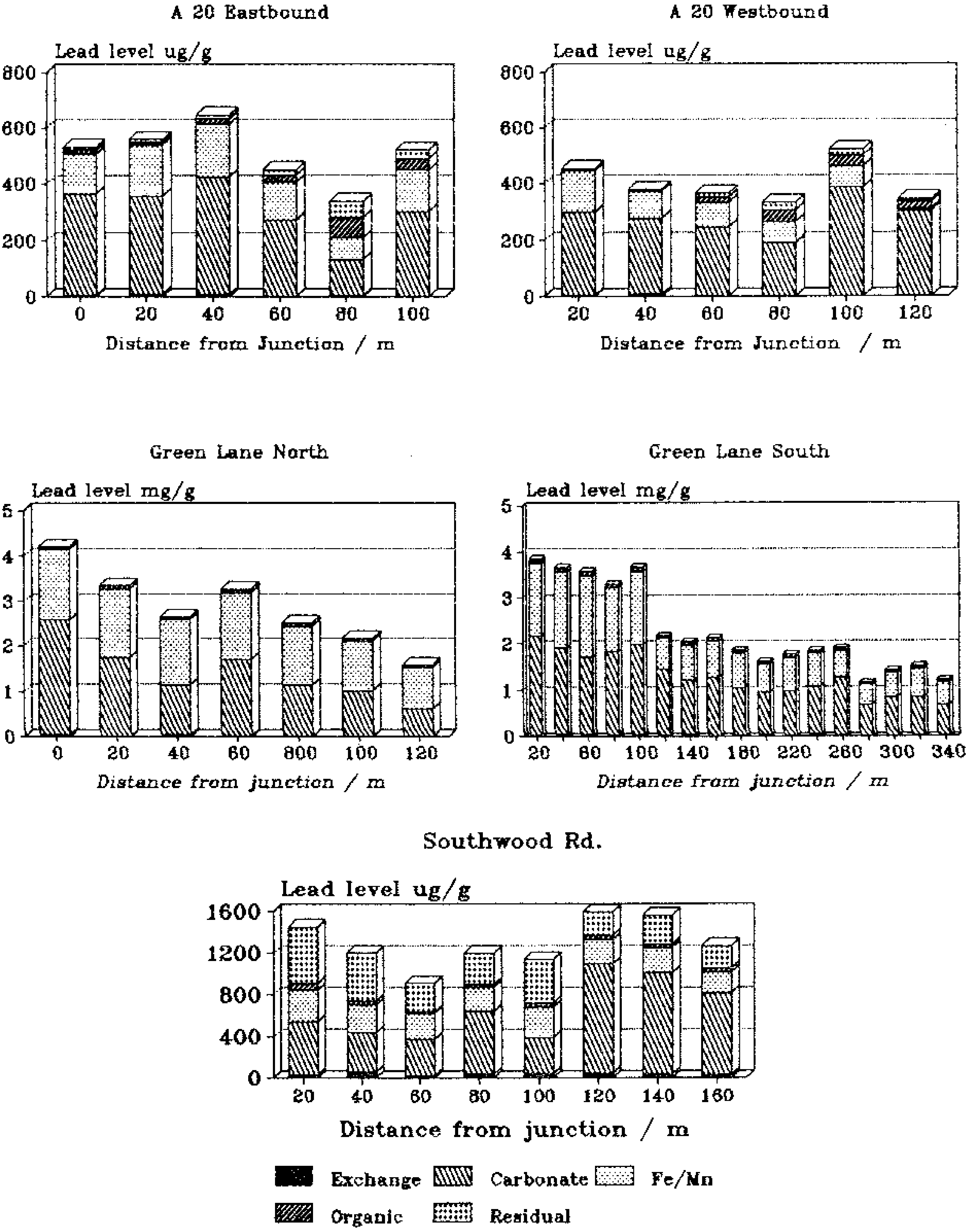
The overall lead levels are easily computed from a simple summation of the data obtained for each dust sample. Table 2 gives mean lead in dust levels for the roads surveyed. The results are somewhat surprising. The main road A20 may have been expected to have the highest results. Green Lane, which has fewer vehicles using it (London Borough of Greenwich, private communication), has lead levels which are some 10 times greater. There is no clearly established reason why the results should display such non-intui-

Table 2. Mean values for chemical associations of lead in soils and dusts. Lead levels are in µg g^{-1} of dry sample.

		Exchange	Carbonate	Fe-Mn	Organic	Residual	Total
A20 Eastbound Dust Samples	Mean	4.7	303.7	145.3	29.3	24.0	507.0
	SD	3.4	91.1	36.2	20.5	16.0	95.9
	%	0.9	59.9	28.7	5.8	4.7	100.0
A20 Westbound Dust Samples	Mean	2.3	282.0	80.3	20.3	14.3	399.3
	SD	2.9	60.2	40.5	16.5	7.7	66.6
	%	0.6	70.6	20.1	5.1	3.6	100.0
Southwood Road Dust Samples	Mean	35.0	625.8	252.5	34.8	341.6	1289.6
	SD	10.7	260.8	31.5	13.7	111.9	216.6
	%	2.7	48.5	19.6	2.7	26.5	100.0
Green Lane North Dust Samples	Mean	19.7	1394.3	1334.9	57.3	9.7	2815.9
	SD	14.1	591.7	227.1	11.1	4.2	804.8
	%	0.7	49.5	47.4	2.0	0.3	100.0
Green Lane South Dust Samples	Mean	22.5	1267.9	919.4	64.4	9.1	2283.4
	SD	11.9	529.4	493.4	19.7	4.1	1028.6
	%	1.0	55.5	40.3	2.8	0.4	100.0
Fiveways Junction Dust Samples	Mean	34.0	311.0	627.5	250.1	240.0	1462.6
	SD	16.0	104.0	286.6	92.3	111.3	524.0
	%	2.3	21.3	42.9	17.1	16.4	100.0
St. Olave's School Soil Samples	Mean	14.2	79.8	344.1	51.0	31.2	520.3
	SD	22.2	67.9	294.4	53.0	33.3	402.6
	%	2.7	15.3	66.1	9.8	6.0	100.0
Montbelle School Soil Samples	Mean	2.7	1.4	22.0	12.5	1.8	40.3
	SD	3.8	1.1	11.9	19.7	2.0	31.1
	%	6.7	3.4	54.5	31.1	4.4	100.0

tive behaviour. However, it is suspected that the street-cleaning regime may play a role. The gutters on the A20, which has no on-street parking are easily cleaned by street-cleaning vacuum machines. Southwood Road and Green Lane both have on-street parking, which makes gutter cleaning less efficient, a problem com-

Fig. 2. Speciation patterns obtained for road dust samples.



pounded by the use of a handbroom on these streets. This presumably gives rise to the greater build up of lead in dust levels. The fact that Southwood Road is swept twice a week and Green Lane North only once a week may also account for the significant difference (at the 99.0% confidence level) in overall levels between both streets. This is despite the fact that the 12 h traffic survey (London Borough of Greenwich private, communication) reported that some 8 400 vehicles used Green Lane (North) and 10 897 vehicles used Southwood Road.

Previous London-wide surveys (Schwar et al. 1988) of background metal in dust concentrations give mean lead in dust values of 660 µg g^{-1} for Greater London in 1982/83 and 1100 µg g^{-1} for Inner London. A survey in 1985 for Inner London (Schwar et al. 1988) gave a mean lead in dust level of 1050 µg g^{-1}. The side roads in this survey are considerably greater than these values. The spatial distribution of background levels of lead in dust throughout London are also reported (Schwar et al. 1988). The part of London we are interested in is shown as having background levels between 0 and 250 µg g^{-1}. The levels of lead in dust that we report are much higher than the background levels with the exception of those samples obtained from the A20. In the absence of any other major local source of lead emissions, the major roads are clearly responsible for the elevated lead in dust levels.

Sequential extraction

The results obtained from the sequential extraction experiments (Figs. 2 and 3) provide an interesting insight into the variability of lead associations in

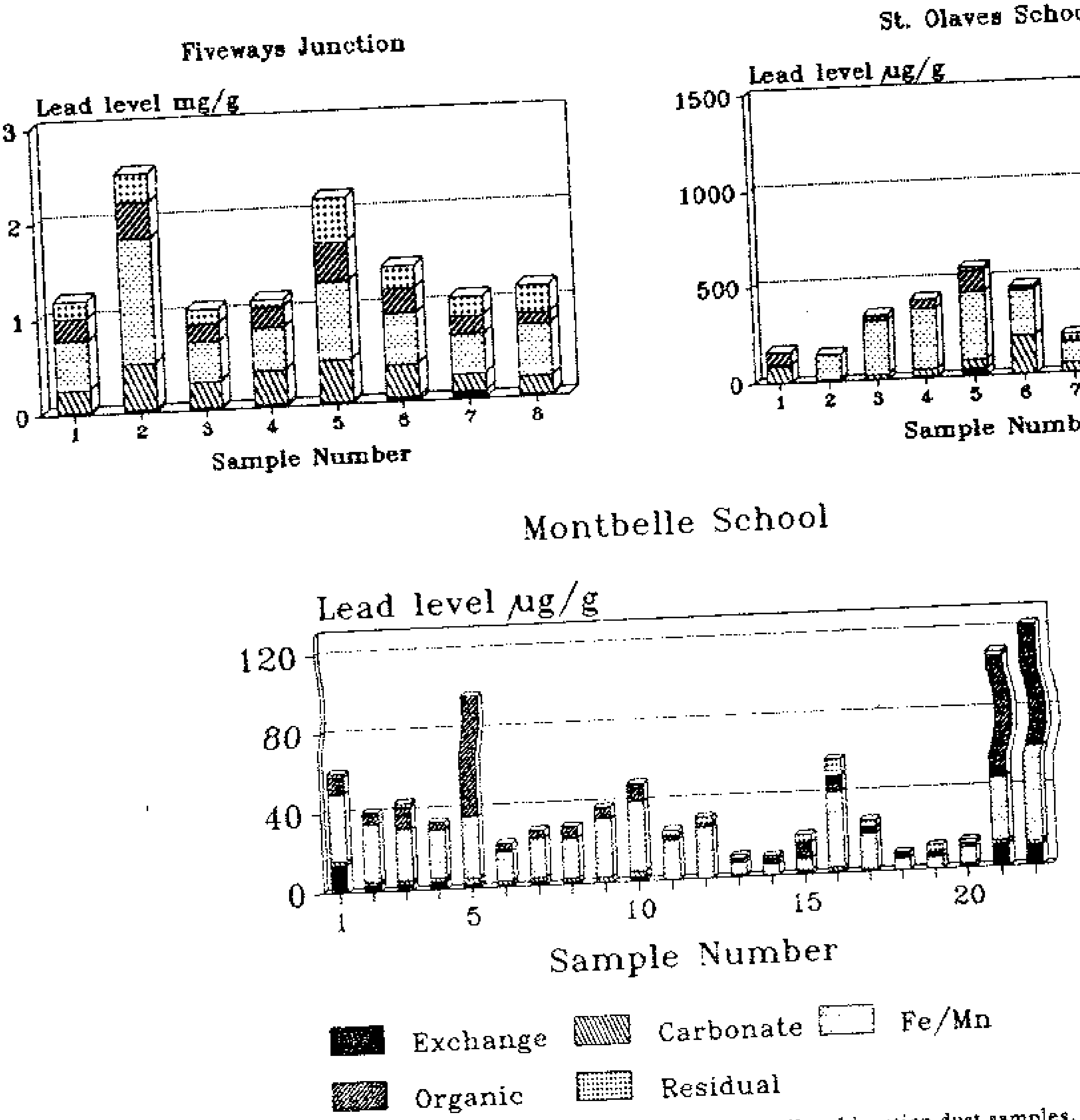


Fig. 3. Speciation patterns obtained for school soil and junction dust samples.

road dusts and soils in a small area. By and large, most of the lead is associated with the carbonate and iron/manganese hydrous oxide fractions. For the A20 and Green Lane, the total loadings in these fractions account for between 88 and 96% of the total lead found in the road dust samples. These results are broadly similar to those results obtained by Harrison and his co-workers (1981; 1983) Interestingly, this pattern of association is not repeated in Southwood Road where some 26.5% of the lead is found in the residual fraction. The reason for this is not obvious.

The samples taken from Fiveways Junction contain relatively sizeable proportions of lead associated with all fractions except the exchangeable fraction. The mean value showing that 17.1% of the lead is associated with the organic fraction may indicate soil input. This is reasonable considering that the central reservations of the A20, from where the Fiveways Junction samples were taken, do contain soils and vegetation.

The speciation patterns obtained for the soil samples are quite different. The carbonate fractions have become less important. This may be as a result of the acidic soil pH conditions. It would be expected that as the pH decreases the percentage of total lead associated with the carbonate fraction should also decrease (Xian and Shokohifard 1989). The mean pH of Montbelle soils is 5.8 (n = 19, sd = 0.28) and the carbonate fraction contains 3.4% of the total soil lead. The soil sampled at St. Olaves School has a pH of 6.7 (n = 10, sd = 0.33) and the carbonate fraction contains 15.3% of the total soil lead. It is clear that the iron/manganese hydrous oxide and organic fractions have become important repositories of lead burden in these soils. This in itself is a cause for some concern. Gibson and Farmer (1986) have already observed that despite reductions of levels of lead in petrol, the association of lead with the iron/manganese hydrous oxide fractions of soils gives rise to a pool of lead which, though relatively immobile, may create long term contamination problems. Lead associated with this fraction may act as a reservoir for replenishing the store of more easily mobilised lead as this latter fraction becomes depleted (Gibson and Farmer 1986).

Hazard assessment

An assessment of the hazard associated with the lead levels measured in the soil and dust samples collected within the vicinity of the two schools may be made in terms of the potential bioavailability of the materials ingested and in terms of potential con-

Table 3. Predicted blood lead contributions based upon total Pb levels. Assumptions: Dirt ingestion, 60 mg; Time outdoors, 2 h.

	Total Pb µg g-1	Ratio of indoor dust to outdoor dust	Contribution to Blood lead µg dL-1		
			0.5:1	1:1	1.5:1
A20 Eastbound Dust Samples	*507.0*		*1.98*	*3.65*	*5.32*
A20 Westbound Dust Samples	399.3		1.56	2.88	4.19
Southwood Road Dust Samples	1289.6		5.03	9.29	13.54
Green Lane North Dust Samples	2815.9		10.98	20.27	29.57
Green Lane South Dust Samples	2283.4		8.91	16.44	23.98
Fiveways Junction Dust Samples	1462.6		5.70	10.53	15.36

Table 4. Prediction of potential contributions made by school dusts to blood lead burdens. Assumptions: Time at school, 6 h, hence, 15 mg dirt ingestation. Indoor dirt levels = Outdoor dirt levels.

	Total Pb µg g-1	Contribution to blood lead level µg dL-1
Montbelle School Soil Samples	40.3	0.07
Green Lane South Dust Samples	2283.4	4.11
St. Olave's School Soil Samples	520.3	0.94
Southwood Road Dust Samples	1289.6	2.32

tributions to the blood lead burden of young children. For the latter assessment, it is possible to use aspects of the USEPA biokinetic/uptake model (Hoffnagle 1988) to estimate the potential contributions to blood lead levels from dust ingestion. The model is used since its predictions correlate well with actual data obtained for children in the 0 to 6 y age range. The model parameters are derived from data obtained for children aged 2 y, who are considered to be representative of children in this age range (Hoffnagle 1988). The model assumes that children ingest some 60 mg /d of dust and that some 30% of the lead ingested is absorbable. The amount of absorbable lead, expressed in µg, is multiplied by 0.4 to convert to µg of lead per dL of blood. For the hazard assessment, mean total lead levels (obtained by summation of all fractions) for each set of samples are used. It *is assumed that children in this age range spend* some 2 h outdoors. This is used to compute a time-averaged, lead-in-dust value. Since indoor dust lead levels have not been determined, some reasonable assumptions about their size must be made. Data obtained from Thornton et al. (1990) show that the ratio of the median levels of indoor to outdoor dust lead in London is approximately 1.3:1. In the absence of indoor dust data, Hoffnagle (1988) assumed that indoor and outdoor levels were equal. In Table 3, then, three sets of predictions have been made based upon assumed ratios of indoor to outdoor dust lead levels of 0.5:1, 1:1, and 1.5:1.

The predictions demonstrate that those streets with high dust lead levels and, consequently, potentially high indoor dust lead levels, could make a significant contribution to child blood lead levels. The scale of the contribution would be obviously attenuated by the temporal and spatial variations of the levels and by the scale of the contribution that such contaminated dusts make to the indoor environment.

The possible contributions made by street dusts and soils to the blood lead burdens of children whilst attending either of the schools may also be estimated. For this prediction, the child's day at school is considered to be 6 h long and the child is assumed to ingest 15 mg of dust. Indoor dust lead levels are assumed to be equal to either outdoor dust lead levels or to soil lead levels. For children between the ages of 4 to 6y attending Montbelle School, blood lead *contributions could range between* 0.07 to 4.11 µg dL^{-1}. For those at St. Olaves *(3 to 6 y), the range* could be between 0.94 to 2.32 µg dL^{-1}. This data is summarised in Table 4.

The hazard assessment, so far, has been based upon total lead levels. Yet the data obtained in this survey has also enabled the separation of lead into contributing fractions. It is a commonly held view that knowledge of physico-chemical associations is necessary for assessing environmental and health impacts (Tessier et al. 1979; Analytical Methods Committee 1985; Harrison et al. 1981; Clevenger 1990; Gentry et al. 1987; Gibson and Farmer 1986). Despite

Table 5. Prediction of % availability. Lead levels in μg g^{-1} of dry sample.

	Exchange	Carbonate	Overall Total	% Available
A20 Eastbound	4.7	303.7	507.0	60.8
A20 Westbound	2.3	282.0	399.3	71.2
Southwood Road	35.0	625.8	1289.6	51.2
Green Lane North	19.7	1394.3	2815.9	50.2
Green Lane South	22.5	1267.9	2283.4	56.5
Fiveways Junction	34.0	311.0	1462.4	23.6
St. Olaves soil data	14.2	79.8	520.3	18.1
Montbelle soil data	2.7	1.4	40.3	10.0

this, there appears to be little in the literature on the exact relationship between physico-chemical associations and contributions to blood lead burden.

Chaney et al. (1988) have reported that those materials which are readily soluble in weak acid solution were found, in acute rat feeding tests, to be highly bio-available. Though increasing bio-availability could also be achieved by decreasing the particle size, Tessier et al. (1979) have shown that at a pH of 5 all but the biggest carbonate particles are effectively dissolved in 5 h, using extraction procedure 2 in Table 1. The Analytical Methods Committee (1985) reported that the potential bio-availability of metals in foods may be assessed by the use of synthetic gastric juice (of pH 3.5) for 4 h. Given this pH value and time scale, it seems reasonable to suggest that the carbonate and exchangeable fractions will be released into such a solution. At low pH values, it is possible that some of the iron and managanese hydrous oxide fraction is partially attacked (Tessier et al. 1979). The severity of the conditions required to release this fraction, however, suggest that the scale of leaching in gastric solution should be small. It therefore seems likely that those dust samples which contain high amounts of lead in the exchangeable and carbonate fractions pose a greater risk than those samples with lesser amounts.

On the basis of this reasoning, Table 5 gives some indication of the proportions of lead that are possibly available in the acid conditions of the stomach. Soil lead and lead associated with samples obtained from the central traffic islands of the A20 appear to be less easily released under mild acid conditions than does lead associated with street dusts obtained from the gutters. This possibly indicates that lead in the former samples poses less of an environmental hazard. This is now under investigation in our laboratories.

CONCLUSIONS

From the results described, it would appear that lead in street dusts is primarily associated with the carbonate (the possibly more bio-available fraction) and the iron and manganese hydrous oxide fractions. However, this association pattern is variable and is altered when lead in soil speciation patterns are determined. There appear to be some reasons for believing that the street cleaning regimes may affect the overall levels of lead in gutter dusts. However, it is not at all clear if the cleaning regime has any effect upon the speciation pattern. The degree of hazard, in terms of possible blood lead contributions, posed to young children (between the ages of 0 to 6 y) living in and attending schools in the neighbourhood of these dust sample locations is varied, but may possibly amount to a substantial level in certain locations.

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