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An Environmental Survey Relating to Improvised and Emulsion/Gel Explosives

REFERENCE: Walker C, Cullum H, Hiley, R. An environmental survey relating to improvised and emulsion/gel explosives. J Forensic Sci 2001;46(2):254–267.

ABSTRACT: The detection and identification of traces of inorganic ions and sugars can play a major role in the forensic investigation of an explosives related incident. This survey investigated the background levels of these substances in the general environment. Six sampling locations were selected from around the mainland of the United Kingdom, representing urban and rural sites. Swab and vacuum samples were collected from different locations within each site including motor vehicles, private houses, hotels, the exterior of buildings, road surfaces, and street signs. Sampling was carried out in summer and winter to investigate changes in the levels of the target species due to seasonal factors such as road treatments or weather. The samples were extracted with water and analyzed for a range of inorganic anions, cations, and sugars using ion chromatography. Most of the target anions were found to be common to all locations. Chloride, sulphate, nitrate, and phosphate were found to be the most common and the most abundant. Chlorate was found at a low level in some external samples. Perchlorate and thiocyanate were not detected in any samples. There was a marked increase in the quantity of sodium and chloride detected in samples collected during the winter. Sodium and calcium were detected in most samples. Potassium and magnesium were detected in approximately half of the samples. Ammonium was less common but detected at significant levels in wall samples. Glucose, fructose, and sucrose were detected in the vacuum samples from the interior surfaces of houses, hotels, and cars.

KEYWORDS: forensic science, environmental survey, inorganic traces, sugars, improvised explosives, gel explosives, emulsion explosives

Following the detonation of an improvised explosive device, one of the major forensic tasks is to identify the type of explosive used within that device. Analysis of residues recovered from scenes where the criminal misuse of explosives is suspected frequently assists in the determination of the chemical components within the explosive material. The scene may be that of an explosion, where residues can be present on component parts of the exploded device, or a venue where it is suspected that explosive mixtures have been stored. When interpreting the significance of traces of such explosives residues, it may be necessary to consider the likely environmental background levels of the particular species. Explosives traces can be divided into two general categories: commercially produced organic high explosives, such as those from plastic explosives (Semtex-H, C4, and PE4 for example); and inorganic explosives ingredients which originate from proprietary gel or emulsion explosives (used in the blasting industry), or (illegally) decanted proprietary pyrotechnic articles, or from explosives improvised at home. It is widely known that low explosives can be produced in the home using commonly available substances such as perchlorates, chlorates, and nitrates mixed with various sugars or other fuels. Related residues can remain following the burning of these low explosive mixtures, i.e., chloride from a chlorate based mixture.

A survey of high explosives traces in the environment has been carried out by this laboratory (1). This further study was carried out to gather data on the levels of particular inorganic and sugars species relevant to improvised explosives mixtures, and gel/emulsion based explosives recovered from different sampling locations in areas around Great Britain in both summer and winter months.

Due to time constraints, identification of analytes of interest was carried out using ion chromatography only. It is the usual practice in forensic science to use two orthogonal techniques for confirmation of each particular species. The use of only one technique in this survey leads to a remote possibility that some responses were caused by interfering species and not by the ions to which they are ascribed. In any interpretation of forensic data this possibility must be borne in mind.

Sampling Locations and Samples Collected

Six sampling locations were selected from around the country in such a way as to cover both urban and rural sites. Climatic differences between the wetter western and drier eastern sides of the country were also taken into account. The sampling locations chosen were:

- urban sites: Coventry (Midlands), Enfield (London), Glasgow, and Manchester
- rural sites: Fort William (Scotland) and Lowestoft (East Anglia)

Samples were collected in both the summer and winter in order to take account of any changes in the levels of target analytes due to winter road treatments or weather conditions.

The following samples were taken at each location:

- inside and outside of motor vehicles
- inside domestic rooms in private houses
- inside hotel reception areas and rooms
- outside of buildings
- roads, pavements and street signs.

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Samples were also taken from a selection of used clothing obtained from charity shops. Samples from road signs, external walls, and road surfaces from two sites in each town were analyzed.

Table 1 shows the types and numbers of samples analyzed. Time constraints allowed the analysis of only 71 of summer samples for the presence of perchlorate and thiocyanate.

Materials, Preparation, and Procedures

Preparation of Sampling Materials

Preparation of all materials was carried out in a dedicated trace explosives laboratory which is regularly sampled to ensure the absence of conventional organic explosives traces. Although this sampling does not include screening for inorganic species and sugars, the laboratory is subject to a strict cleaning regime and is necessarily the cleanest laboratory at our facility.

Cotton wool swabs were prepared by washing with 18 MΩcm deionized water in a Buchner funnel, extracted in a soxhlet apparatus using acetone, then dried under vacuum. The dry swabs were heat sealed in batches of six inside nylon bags.

For convenience, swab sampling materials were assembled into kits. A batch of 115 kits was prepared, each comprised of a plastic pot with plastic lid containing the following:

4 pairs of gloves (bagged)
3 labelled glass vials (10.5 mL, snap top, bagged)
1 bag of swabs (6)
3 pairs of disposable artery forceps
1 sheet of glazed paper
1 piece of note paper
1 pen, and
1 bottle containing 18 MΩcm deionized water.

Each kit was labelled and sealed inside two nylon bags.

A4 cardboard templates, of the type normally used to mount transparencies, were sealed in polythene bags individually or in groups of two or three as required for each sampling location.

Vacuum sampling tubes were prepared by placing two filters inside a 5 mL plastic syringe barrel. The filters comprised one 13 mm diameter prefilter and one 13 mm 0.5 μm membrane filter. Each tube was capped with a rubber bung and sealed inside a self-seal polythene bag ready for use. PVC tubing for connecting the vacuum tubes to a vacuum pump was prepared in lengths of 1.5 to 2 m, each length being sealed inside a self-seal plastic bag.

Four of the prepared swabbing kits were chosen at random for quality assurance (QA) testing to determine any background levels of inorganic ions or sugar species. The swabs contained within each kit were used to sample each item in the kit.

Six A4 card frames were sampled on both sides using a separate swab for each side. Four vacuum tubes were also sampled for QA purposes by passing deionized water through each assembled tube.

All of the QA samples were analyzed by ion chromatography using the same conditions to be used for analysis of the survey samples. The samples were analyzed according to the conditions given in Table 2 and compared to standard solutions containing the following components:

- Anion standard—containing fluoride (1 mg/L), chloride (5 mg/L) and nitrite, bromide, chlorate, nitrate, phosphate and sulphate (all 10 mg/L).
- Cation standard—containing sodium (2 mg/L), ammonium, potassium, and magnesium (all at 5 mg/L) and calcium (10 mg/L).
- Sugar standard—containing glucose and fructose (both 50 mg/L) and sucrose (100 mg/L); and
- Perchlorate standard—containing chlorate and perchlorate at 10 mg/L.

Low levels of ions were detected, as shown in Table 3. Species not listed were not detected. No sugars or perchlorates were detected. Sodium detected is attributable to the use of soda glass vials.

TABLE 1—*Summary of sample type and number.*

Type of Sample	Sample Screened for Anions, Cations and Sugars		Number of Samples Screened for Percholrate and Thiocyanate
	Number of Summer Samples	Number of Winter Samples	
Clothing	25		12
Road signs	6	6	8
Roads	12	12	8
Walls	6	6	2
Houses	9	9	6
Hotels	9	9	7
Car swabs	30	30	19
Car vaccums	15	18	9

TABLE 2—*Ion chromatography conditions.*

	Anions	Perchlorate	Cations	Sugars
Apparatus	Dionex IC unit series 2010i	Dionex IC unit series 2010i	Dionex IC unit series 4000i	Dionex IC unit series 4000i
Pump	gradient pump	analytical pump	gradient pump	analytical pump
Flow rate	2 mL/min	1 mL/min	1 mL/min	1 mL/min
Detector	conductivity with ASRS in auto suppression mode	conductivity with AMMS and 5 mM sulphuric acid regenerant	conductivity with CSRS in auto suppression mode	pulsed amperometric applied to voltage: 200 mV range: 30 000 nA
Guard	AG9-SC (4 × 50 mm)	NG1 (4 × 50 mm)	CG12 (4 × 50 mm)	Carbopac PA1 (4 × 50 mm)
Column	IonPac AS9-SC (4 × 250 mm)	MPIC-NS1 (4 × 250 mm)	IonPac CS12 (4 × 250 mm)	Carbopac PA1 (4 × 250 mm)
Eluent	1.8 mM sodium carbonate and 1.7 mM sodium bicarbonate (in deionized water)	2 mM tetra-n-butylammonium hydroxide/1.5 mM sodium carbonate in 30:70 acetonitrile/water	20 mM methane sulphonic acid in deionized water	0.15 M sodium hydroxide

TABLE 3—*Average quantity of species found in QA samples.*

Sample	Quantity Recovered (μg/10 mL sample)							
	Fluoride	Chloride	Nitrate	Sulphate	Sodium	Potassium	Magnesium	Calcium
Gloves/forceps	0	3.3	0.6	4.2	21.6	0.6	0	2.4
Pot/lid/water bottle	1.0	2.8	0	3.4	27.6	0.2	0	0.2
Papers/pen	1.1	8.1	1.6	55.3	50.3	1.4	0.1	4.8
Water	1.4	0	0	0	17.2	0.8	0	9.7
A4 card frames	0	0.6	0	16.4	30.2	1.3	1.3	40.1
Vacuum tubes	0	0	0	5.5	10.8	0	0	0

The use of borosilicate vials which would have minimized this source of sodium in the samples was found to be prohibitively expensive. The presence of species on the A4 card frames was considered not to be a significant problem as the frames were only to be used as a guide to sampling area and only a very small area of each frame would come into direct contact with the swab or vacuum tube while sampling.

Sample Collection

Prior to the collection of samples, the sampler dressed in disposable oversuits, boots, and gloves. Samples were taken either by wiping the surface with a water-wetted cotton wool swab or by vacuuming. In the latter technique a vacuum pump is used to draw air through filters held in a plastic syringe barrel while this is passed lightly over the surface to be examined. The sampling area was standardized by using A4 size cardboard transparency frames as disposable sampling templates. A new template was used for each sample to avoid possible cross contamination. Two A4 areas per site were sampled giving a total sampling area of approximately 0.1 m^2 per sample. At each site the samplers' disposable paper suits and the glazed paper upon which the sampling materials were placed were swab-sampled as a "work surface/operator control". One wetted but unused swab was set aside as a materials control for each kit used, with the exception of vehicle sampling where one control was taken for every two kits used.

The external vehicle samples consisted of two swab samples collected from the doors and one swab sample each collected from the roof and bonnet. The internal vehicle samples were comprised of vacuum samples collected from the front seats, the rear seats, and the boot. The areas sampled from private houses were from the kitchen surfaces (swab) and a living room coffee table (swab) or similarly used surface. A vacuum sample was collected from the living room carpet. The hotel samples were collected from either the reception desk (swab) and waiting area, or from surfaces in a bedroom (swab). Again a vacuum sample was collected from a carpet. Samples from the outsides of buildings, roads, pavements, and signs were collected using swabs. The positions of the external samples were chosen in order to cover the location as fully as possible. In order to provide results from as wide a selection of locations as possible the vehicles sampled were unrelated to the private houses and neither were owned or occupied by employees of DERA.

Vacuum samples were collected from a selection of used clothing comprising equal numbers of men's and ladies' shirts and trousers. Again A4 templates were used to take a sample from the front of each garment. A sample was also collected from the pockets if present. These items were obtained from four charity shops local to this laboratory and sampled under Trace Laboratory conditions.

Sample Extraction and Analysis

All samples were placed in a freezer upon arrival at the laboratory and defrosted when required. The swabs were extracted using 5 mL of 18 MΩcm deionized water in the following manner. Each swab was agitated and compressed using the wide end of a clean Pasteur pipette (a new pipette being used for each sample). The solvent was decanted into a new vial, the pipette being used to compress the swab in order to drain as much solvent as possible from the sample. The extract was then made up to 10 mL using fresh 18 MΩcm deionized water prior to analysis by ion chromatography.

For quantitation purposes four point calibration graphs were prepared for each analytical system. One g/L stock solutions of each analyte were prepared and dilutions prepared to produce calibration solutions of the following concentrations:

- anions, cations, and perchlorate—10, 25, 35, and 50 mg/L
- sugars—10, 20, 50, and 100 mg/L

Calibration graphs were prepared at the beginning of each day. All the analyte calibration graphs were linear with the exception of ammonium which produced a curve.

Standard solutions were prepared for retention time comparison in each system, containing the species as listed above but all at concentrations of 10 mg/L. A maximum of five samples were analyzed between retention time standards. All samples were injected through disposable 0.2 μm filters. The retention time of each chromatographic peak produced by a sample was compared with that of the corresponding peak produced by the screening standard analyzed closest in time to that particular sample. The criterion for a positive peak identification was that the sample peak retention time lay within ± 2% of the standard. However, if the sample peak area is much greater than that of the standard then a shift in retention time is possible. Where this appeared to be the case the sample peak retention times were compared to those of the daily quantitation standards which had peak areas nearest to the area of the sample peak area. Once a peak had been identified, the corresponding concentration of the species was calculated using the appropriate calibration graph for that day. The total mass of the species in the full 10 mL sample was calculated.

Discussion

Figure 1 shows the recovery of four of the cations and four of the anions from clothing. No nitrite, bromide, chlorate, or phosphate was recovered from any of the clothing samples. Nitrate (1.3 μg) was recovered from only one clothing sample. Levels of sodium detected from the clothing were comparable to those in the corresponding controls (attributable to the glass vials) and thus no sig-

nificance could be attached to them. Figures 2 to 23 show the ranges of recoveries and the average recovery for individual species from summer and winter sampling of surfaces other than clothing.

Fluoride, shown in Figs. 2 and 3, was found in samples taken from each type of location (and in 62% of samples), the largest recovery being 110 μg recovered from two separate car vacuum samples. It should be noted that fluoride is the first component of the screening standard to be eluted (at approximately 1 min) and under the conditions used for these analyses elutes very close to the void dip (due to water). Quantitation of fluoride at the lower levels should therefore be regarded as less reliable than that for the other anions.

Chloride, shown in Figs. 4 to 6 (Fig. 6 omits the winter road samples) was found to be present in all types of sampling locations (in 85% of samples) and during both seasons. The levels tended to increase during the winter samples, especially on road surfaces, most likely caused by road salting.

Nitrite was only detected in one house carpet (3.9 μg) and six car swab samples (highest 39 μg, average of the six, 9.8 μg). Two of the car vacuum samples contained nitrite (4 μg and 5700 μg).

Bromide was detected only at low levels in road, carpets, car swab, and car vacuum samples (approximately 10% of these types of samples).

Chlorate was generally not detected, but 30 μg of chlorate was recovered from one car roof swab sample (during summer sampling) and 4 μg (in each) was detected in three further summer samples: from a road sign, a wall, and the swab sample of a car handle and from one winter road sample (also 4 μg).

Nitrate, shown in Figs. 7 and 8, was recovered from all types of sample locations (detected in 44% of samples). Vacuum samples from houses were found to contain nitrate, but nitrate was not detected in any of the swab samples taken from these houses.

Phosphate, shown in Figs. 9 and 10, was recovered from road samples (12%), house samples (33%), hotel samples (44%), and

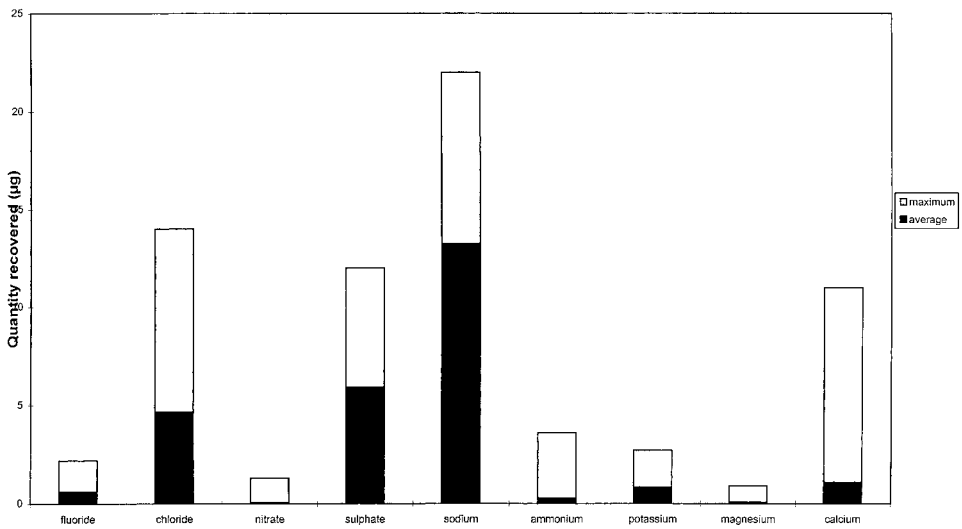

FIG. 1—*Distribution of species recovered from clothing.*

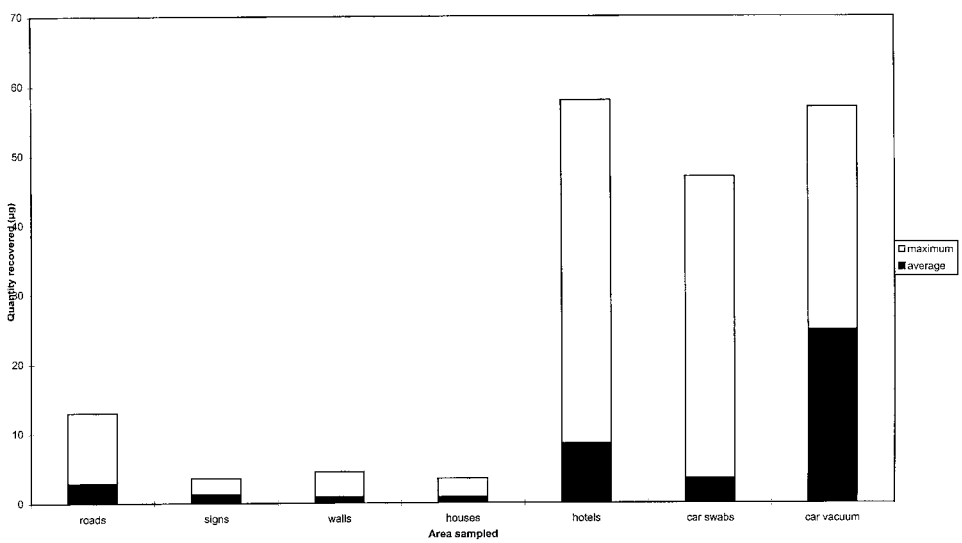

FIG. 2—*Fluoride levels—summer.*

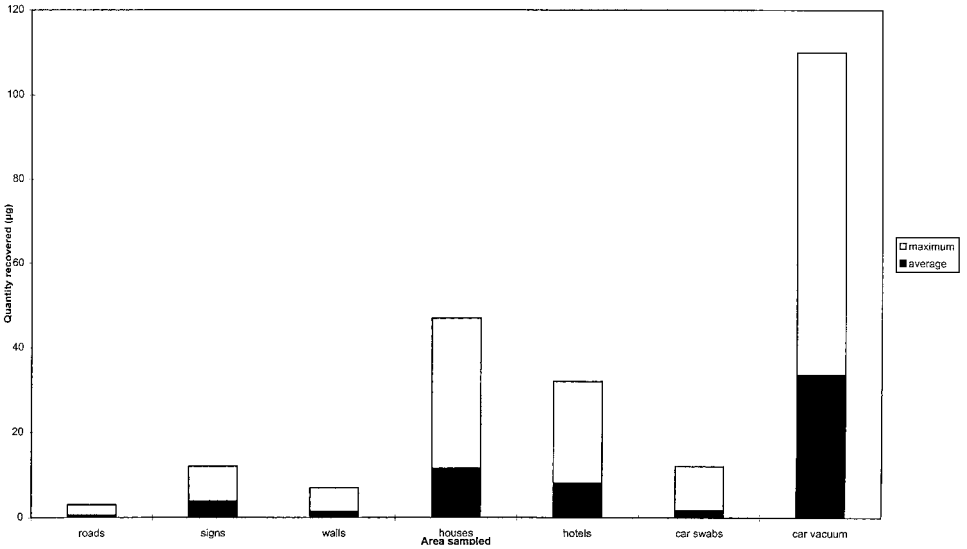

FIG. 3—*Fluoride levels—winter.*

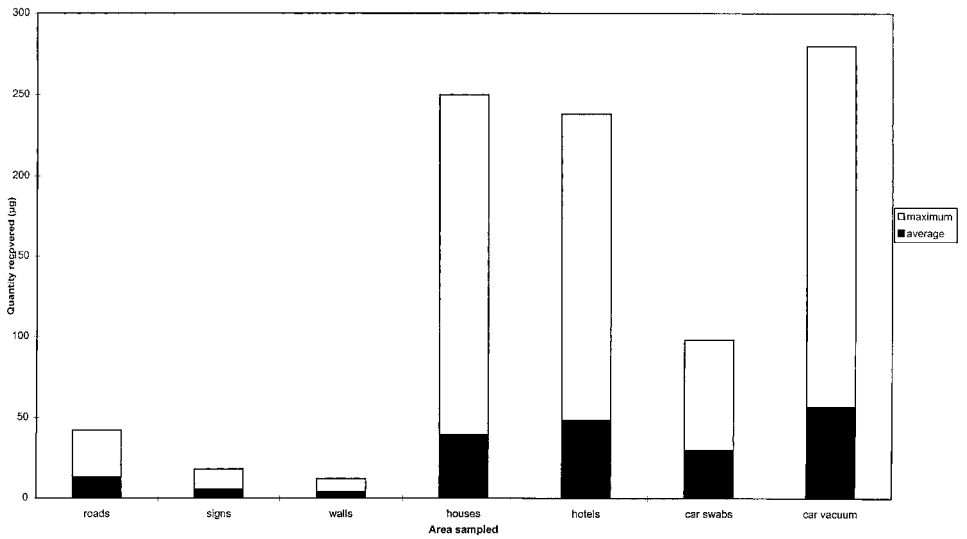

FIG. 4—*Chloride levels—summer.*

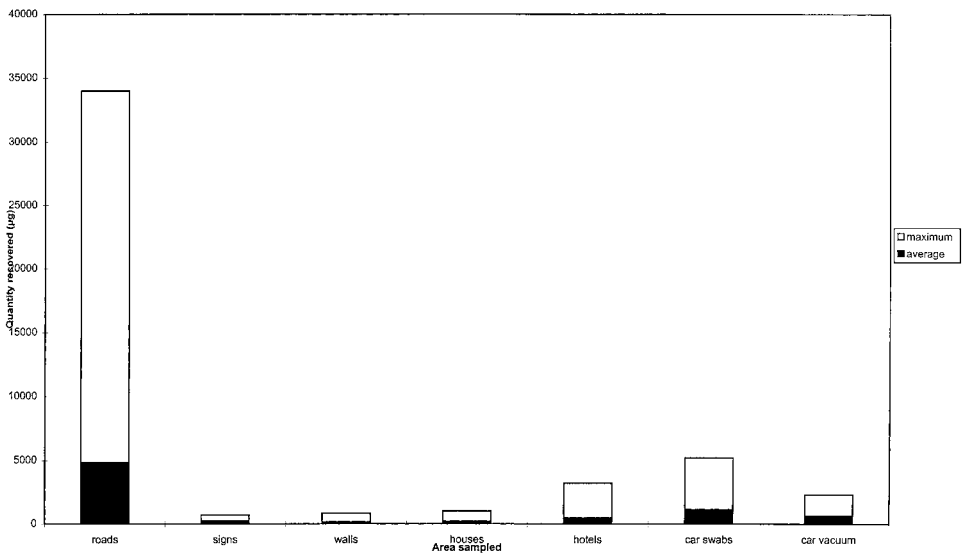

FIG. 5—*Chloride levels—winter.*

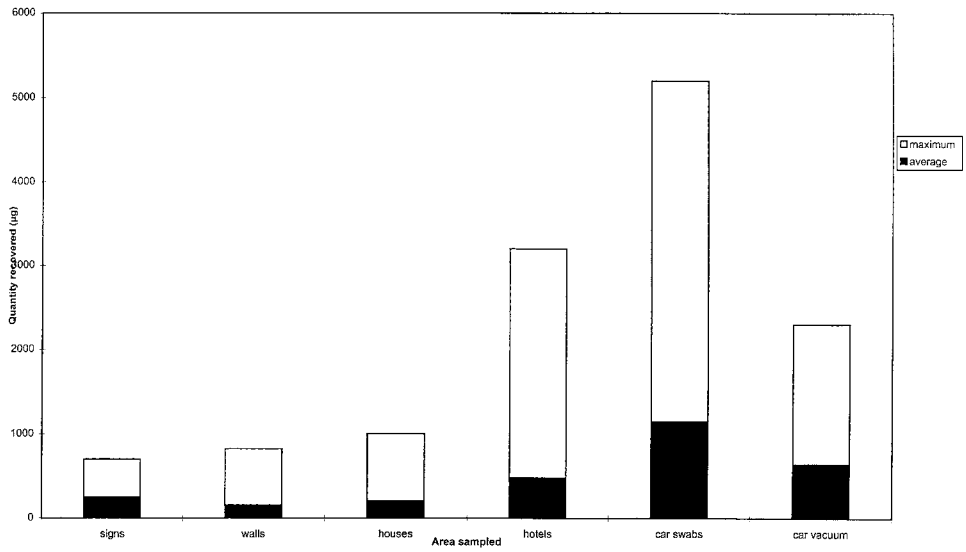

FIG. 6—*Chloride levels—winter—omitting roads.*

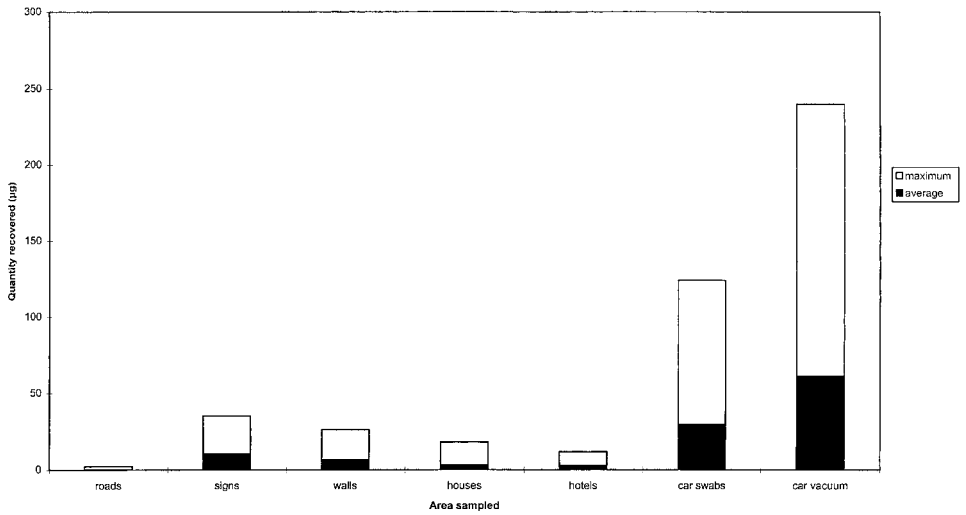

FIG. 7—*Nitrate levels—summer.*

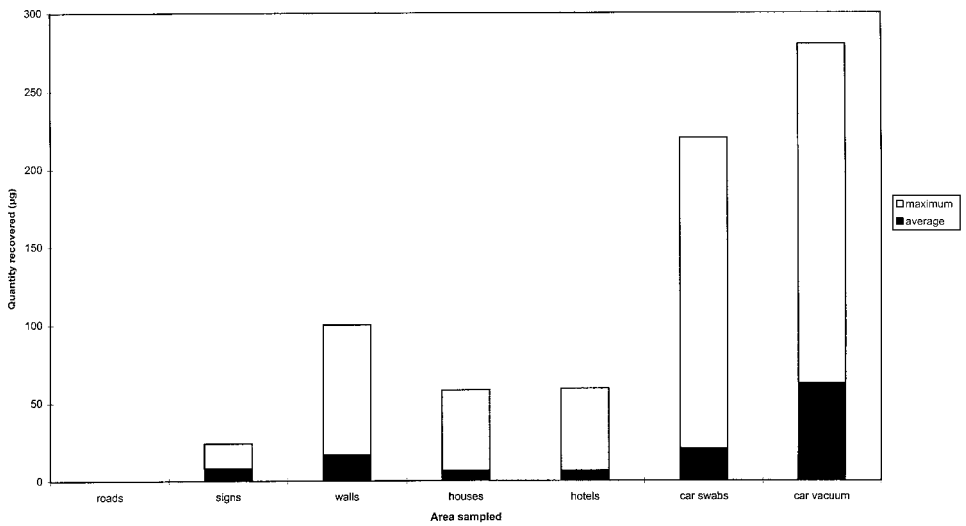

FIG. 8—*Nitrate levels—winter.*

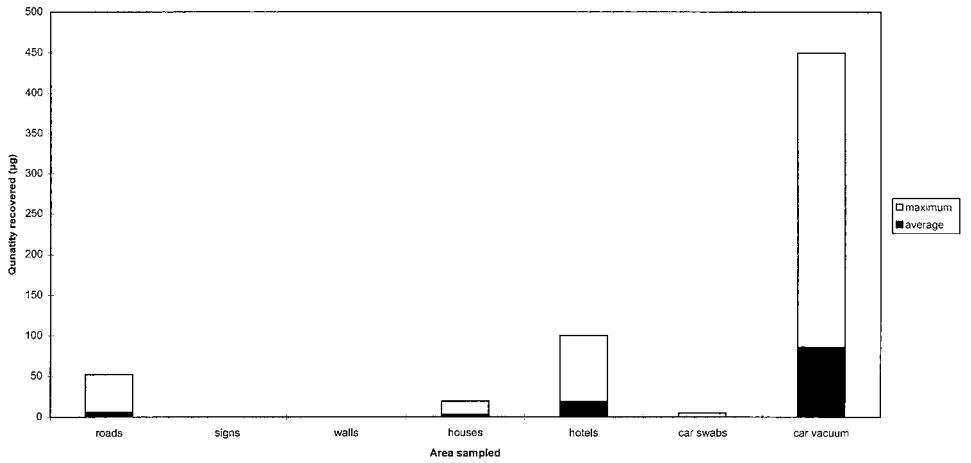

FIG. 9—*Phosphate levels—summer.*

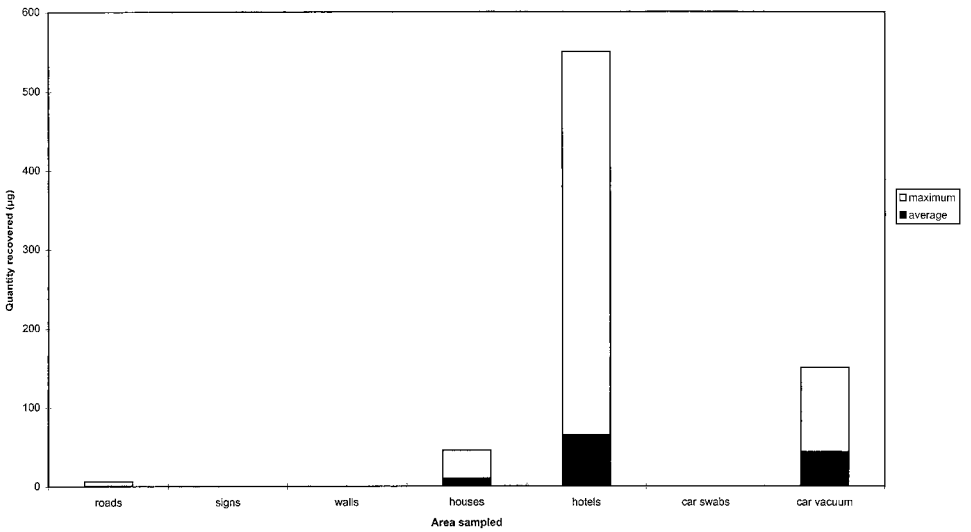

FIG. 10—*Phosphate levels—winter.*

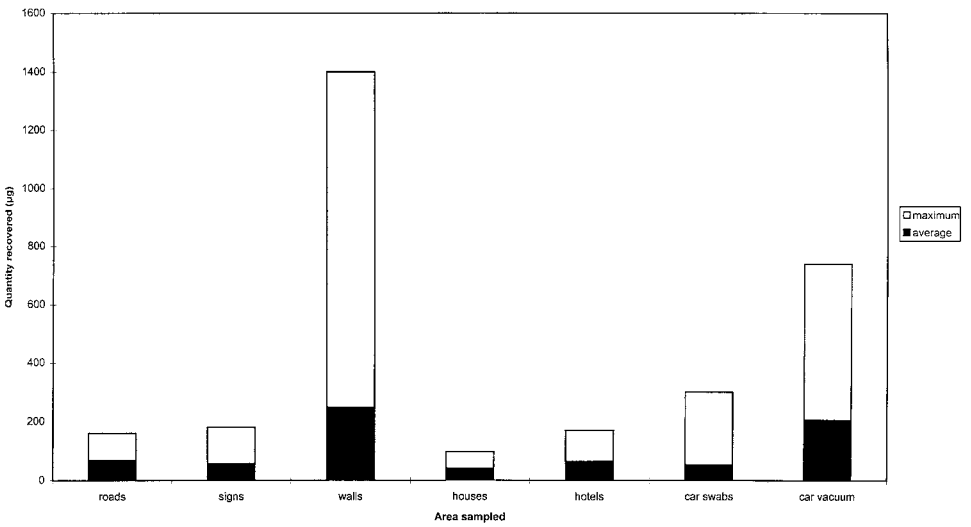

FIG. 11—*Sulphate levels—summer.*

car samples (2% of swab samples and 82% of vacuum samples). The carpet sample recoveries increased in the winter.

Sulphate, shown in Figs. 11 and 12, was found in all types of locations and in 95% of samples. The levels generally increased in the winter samples with levels of 7.9 mg recovered from a wall sample.

Sodium, shown in Figs. 13 to 15 (Fig. 15 omits winter road samples), was observed in all samples, but this was to be expected at a certain level as it is present in the sample vial glass. Roads, signs, and carpets all showed higher recoveries for sodium in the winter. Levels of 25 mg were recovered from road surfaces during the winter sampling (again probably due to road salt).

Ammonium, shown in Figs. 16 and 17, was recovered from all types of sampling locations (detected in 25% of samples).

Potassium, shown in Figs. 18 and 19 was detected in 49% of samples. Magnesium, shown in Figs. 20 and 21, was detected in 51% of samples. Calcium, shown in Figs. 22 and 23 was detected in 71% of samples. All three cations were detected in all types of sampling locations.

No perchlorate or thiocyanate was detected in any of the 71 samples analyzed.

Glucose (4 μg) and sucrose (16 μg) were recovered from one clothing item. Sugars were not detected on any other item of clothing.

Sugar species were not detected in samples from roads or walls. Glucose was recovered from one road sign only (8.6 μg East Anglia summer sampling).

Four house vacuum samples contained all three sugars at levels of between 48 μg and 850 μg. One house vacuum sample contained glucose and sucrose only and one swab sample contained only fructose.

Of the hotel samples, two vacuum samples contained all three sugars (44 μg to 610 μg), one swab sample contained all three sugars (13 μg to 350 μg) and five other hotel samples contained one or two of the sugar species.

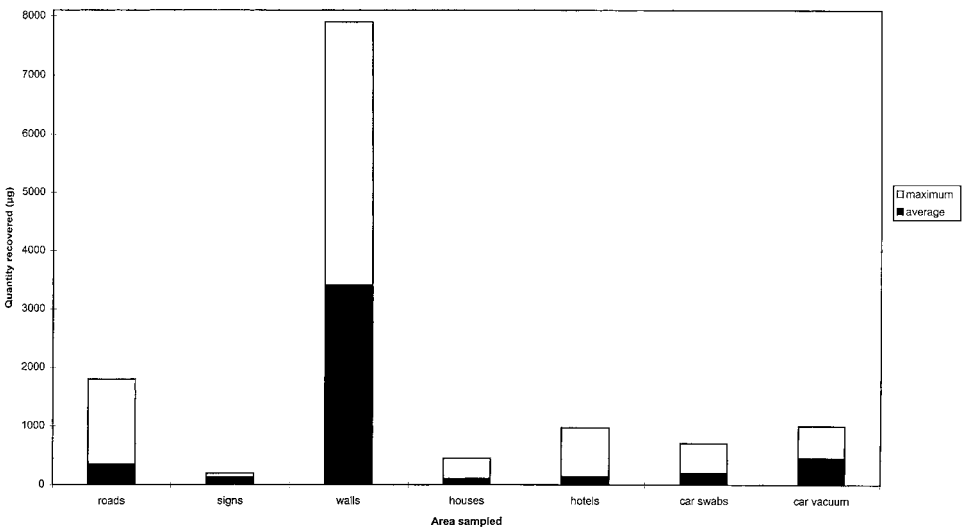

FIG. 12—*Sulphate levels—winter.*

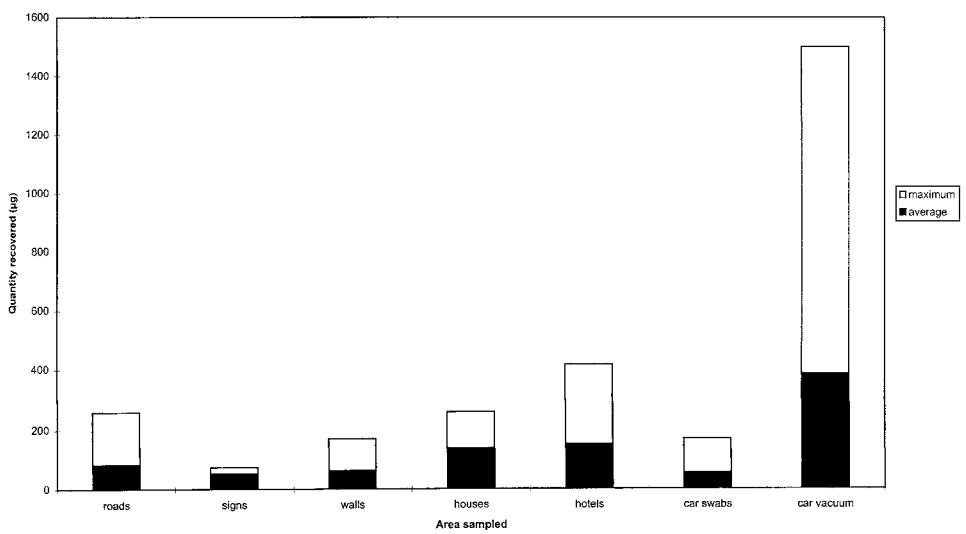

FIG. 13—*Sodium levels—summer.*

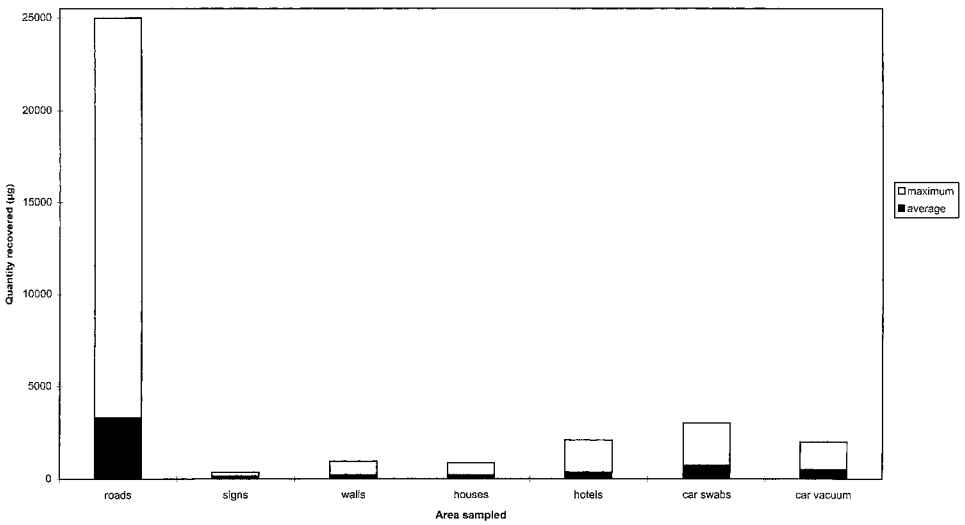

FIG. 14—*Sodium levels—winter.*

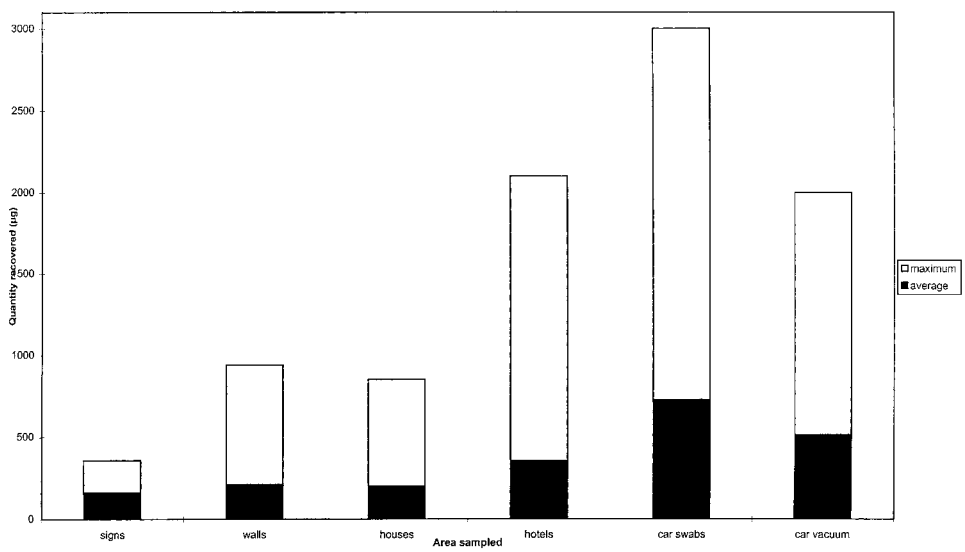

FIG. 15—*Sodium levels—winter—omitting roads.*

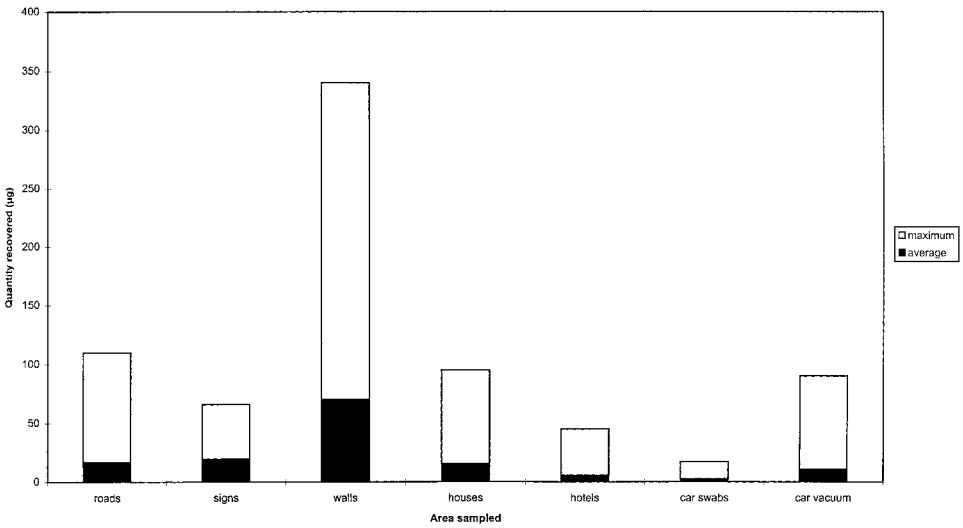

FIG. 16—*Ammonium levels—summer.*

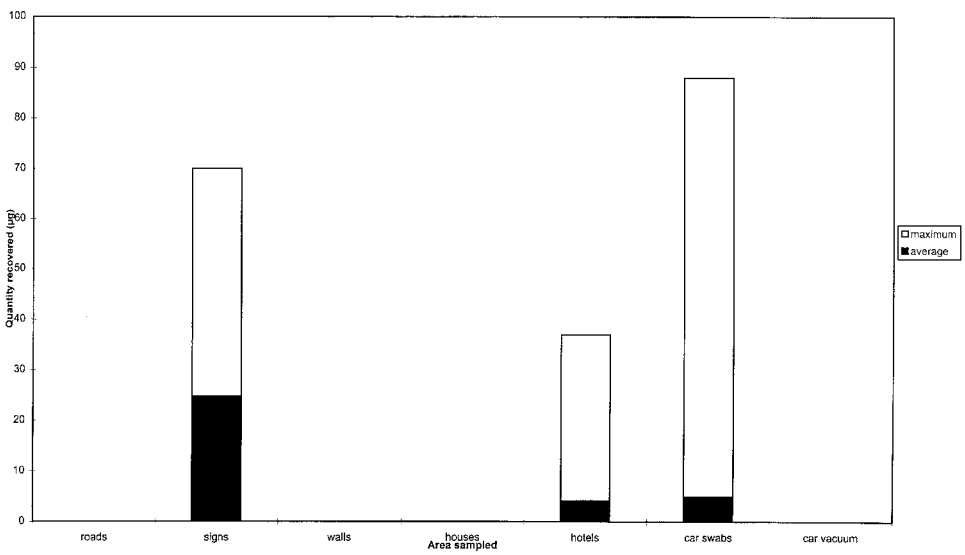

FIG. 17—*Ammonium levels—winter.*

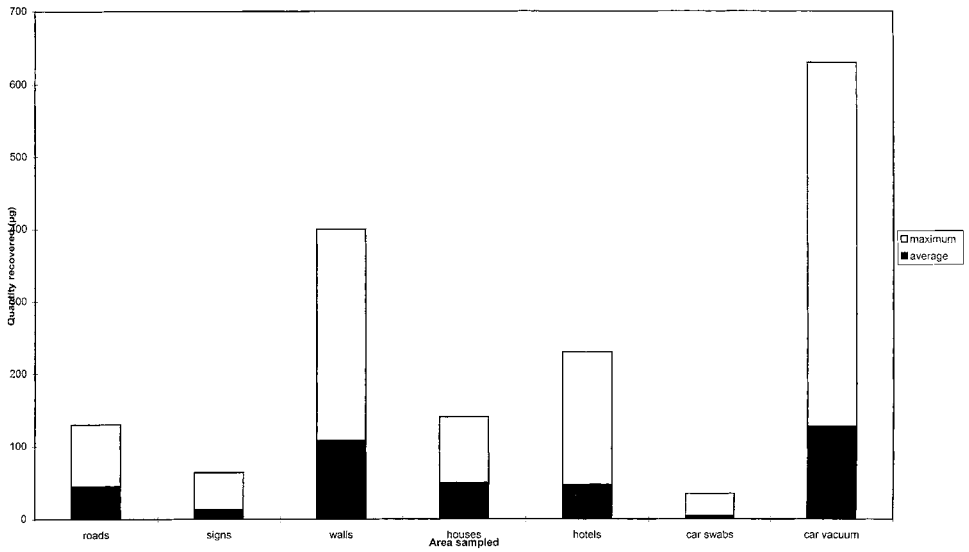

FIG. 19—*Potassium levels—summer.*

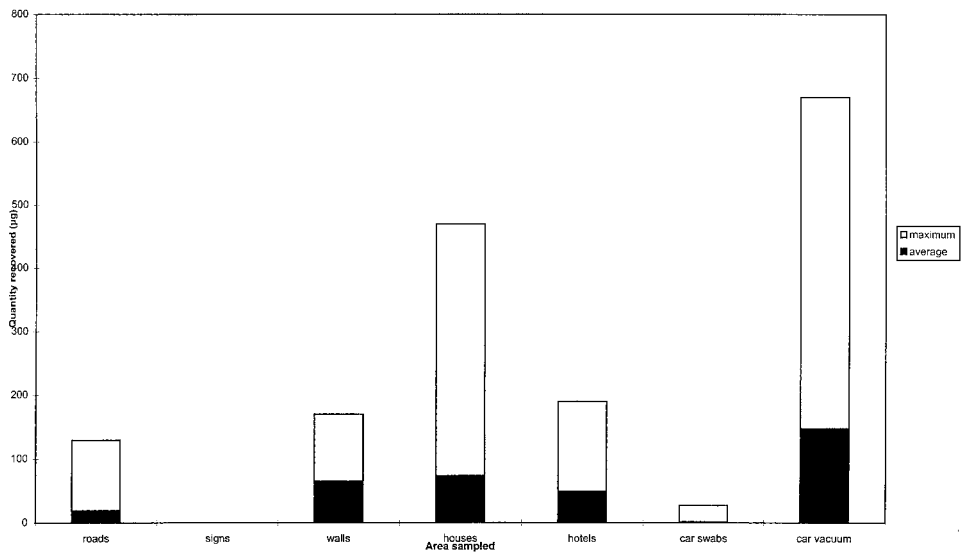

FIG. 19—*Potassium levels—winter.*

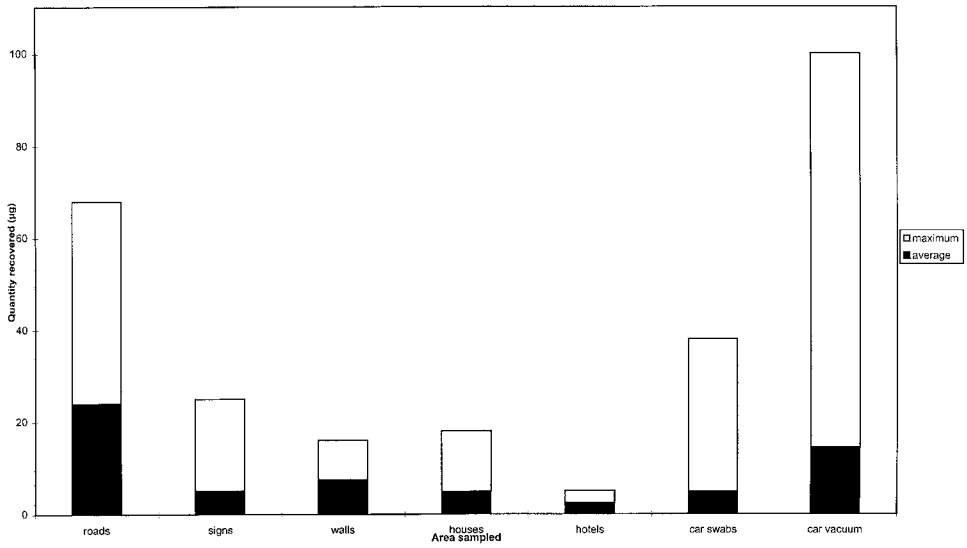

FIG. 20—*Magnesium levels—summer.*

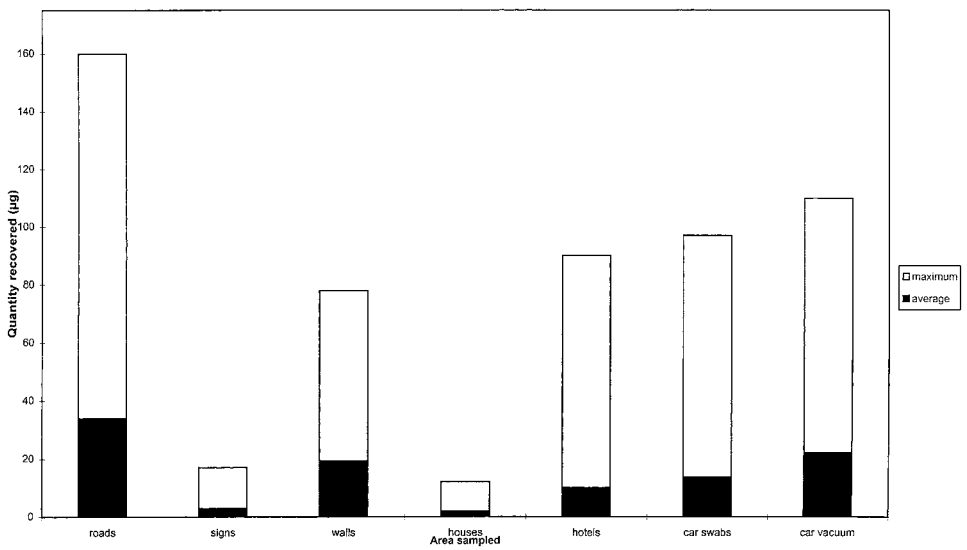

FIG. 21—*Magnesium levels—winter.*

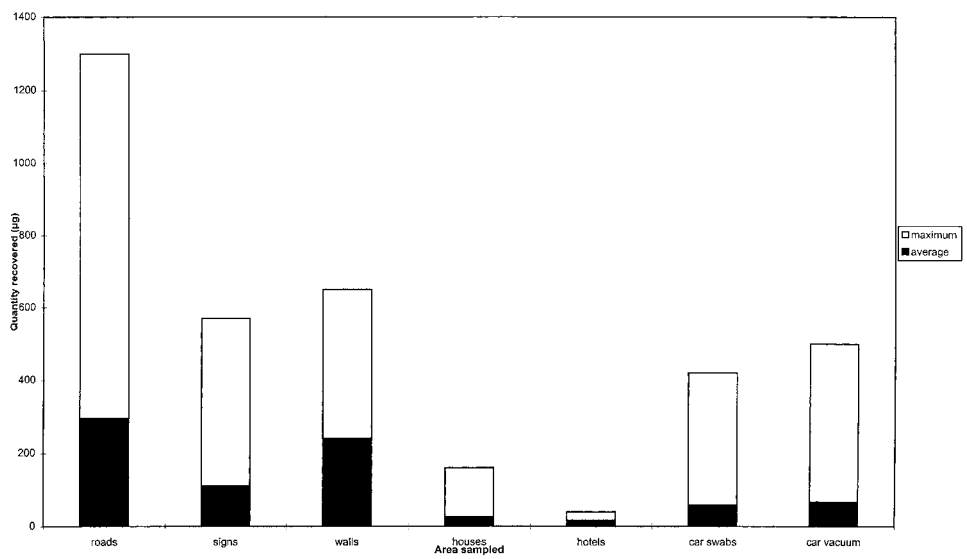

FIG. 22—*Calcium levels—summer.*

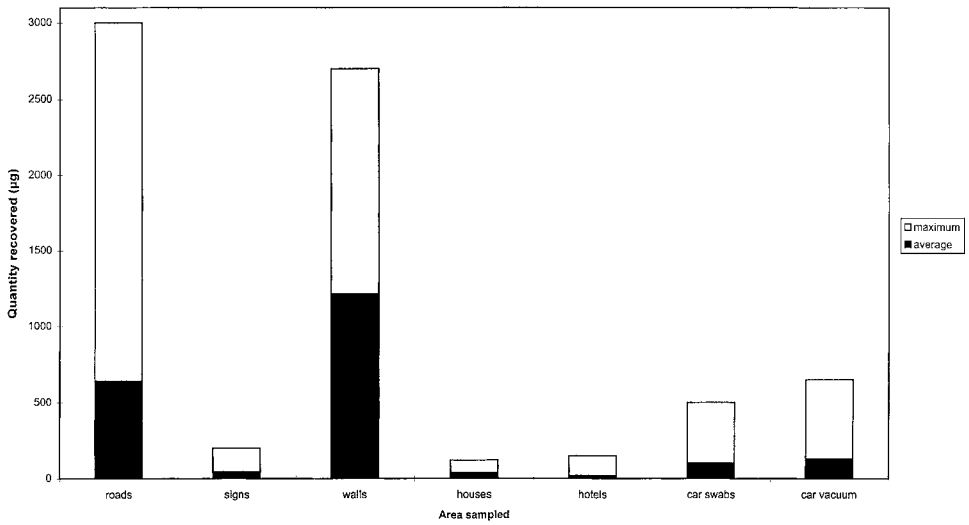

FIG. 23—*Calcium levels—winter.*

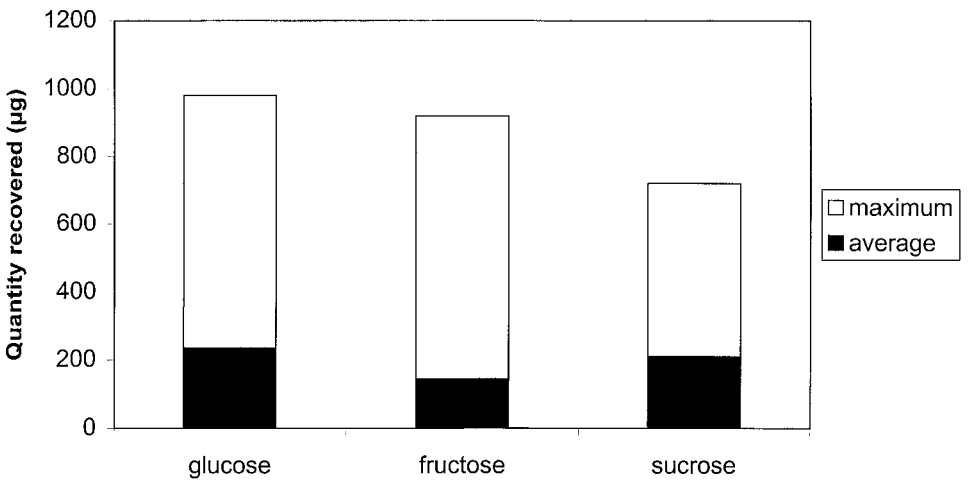

FIG. 24—*Sugar species—summer car vacuum samples.*

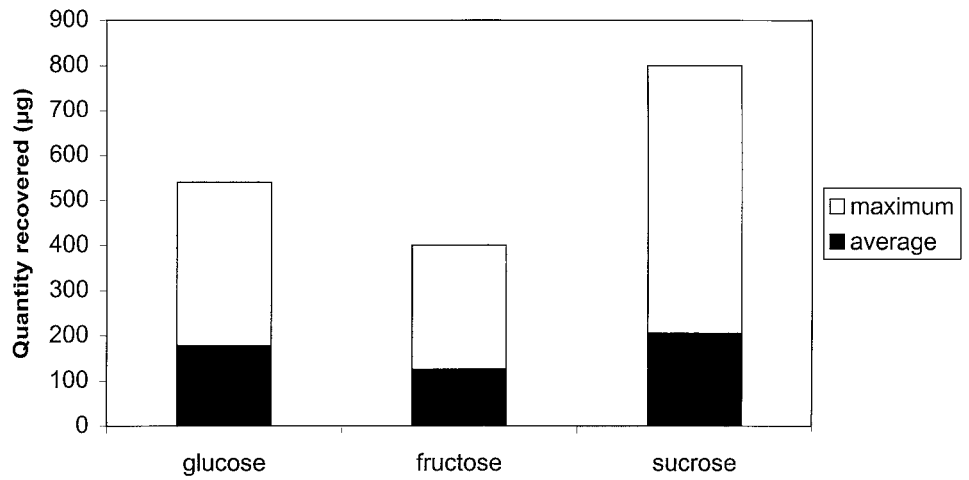

FIG. 25—*Sugar species—winter car vacuum samples.*

Five car swab samples contained all three sugars (33 μg to 970 μg) and two swab samples contained only glucose.

Recoveries of sugar species from the vacuum samples taken from the interiors of the cars are shown in Figs. 24 and 25.

Summary

Anions

Chloride and sulphate were found to be very common. Nitrate was also recovered from most types of sampling areas. Phosphate was identified in most samples. Fluoride, nitrite (except for one sample), bromide and chlorate were only detected at very low levels, when at all. The level of chloride recovered from road samples markedly increased in the winter samples.

Thiocyanate and perchlorate were not detected in any of the 71 samples, or appropriate controls, which were analyzed for these ions.

Cations

Sodium was found to be extremely common. Potassium and magnesium were recovered in approximately half of the samples. Calcium was recovered in 71% of samples. Ammonium was recovered in fewer samples, but was present in significant levels in wall samples. The level of sodium recovered from the road samples markedly increased in the winter samples.

Sugars

Sugars were detected in one house and hotel surface, but were present in most of the house, hotel, and car vacuum samples.

Acknowledgments

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References

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