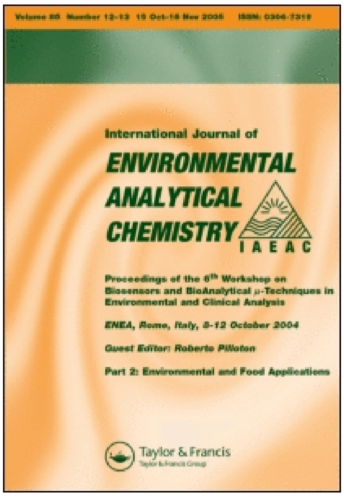

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An Assessment of Dust Analyses: With Particular Reference to Lead and Certain Other Metals

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AN ASSESSMENT OF DUST ANALYSES: WITH PARTICULAR REFERENCE TO LEAD AND CERTAIN OTHER METALS

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The last few years have shown an increase in the number of publications describing studies on dust as indicators of environmental pollution, especially by trace metals. The techniques of sampling and analysis used in these studies are reviewed, with particular attention to inconsistencies and differences which make data incomparable. The need for work on the development of standard methods is demonstrated. Only by the application of good quality control, reference materials and reliable techniques will an unsatisfactory situation be improved.

KEY WORDS: Dust, sampling, analysis, metals.

INTRODUCTION

As a first impression, the concept of analysing dusts may appear naive, but for many years investigators have used this medium as a convenient indicator of pollution levels. Dust analysis continues to be attractive to environmental scientists, influenced no doubt by its ubiquity and hence apparent ease of sampling. Dust is, indeed a common material throughout the environment, although the degree of accumulation and its composition depend on many variables, including weather conditions, building construction materials, traffic density and industrial activity.

The role of dust as a potential vehicle for the intake of trace metals by children, especially in their home environment, has prompted many studies on dust composition. Some of the many objectives of studies involving dusts are summarised in Table 1. Probably most investigations have concerned lead, with emphasis on industrial, traffic or paint sources. However, cadmium has also featured in such work, especially in relation to incineration of municipal waste, its major source in urban areas. Some studies have included a broad spectrum of metals.

Careful sampling and analysis of dust are fundamental to any of these investigations, but the inhomogeneous nature of dust presents many problems to the investigator. Unfortunately, different approaches to some of these problems make data from various studies not directly comparable.

In one of the earliest papers involving a large number of dust analyses,[16] several

Table 1 Typical objectives of studies involving environmental dusts

Objective	*Sample references*
Lead from motor vehicles: proximity of houses	1
significance to child health	2, 3, 4
Lead from external decoration	5, 6
Lead from scrap metal and car breaking yards	7
Lead around printworks	8
Lead around car exhaust replacement centres	9
Lead and cadmium around incinerators	10
Metals in city-wide surveillance	11, 12, 13, 14, 15, 16
Metals from past mineral workings	17
Contamination of highway catchments	18, 19
Contamination of household dusts	16, 17, 20, 21

important questions were raised and proposals made for investigation. The chemical form of the metals in dusts deserved particular attention as this would influence the development of standard methods of analysis. Until more was known of the nature of the samples, effects from variations of the matrix or chemical composition of metal could not be accounted for. Methods involving standard additions to test recoveries would prove nothing until it was known in what forms the analyte existed in the sample. A further suggestion was that correlation patterns for several metals may help identify the origins of metals from various sources. The need for standard methods was also stressed. Over a decade later Schwar *et al.*[11] noted that direct comparison of their results with those reported in other studies was complicated by the use of a variety of techniques for sample collection, preparation and analysis, as well as in the reporting of results. Thus, despite a relatively long history of the use of dusts in environmental studies, a number of important questions on sampling and analysis do not appear to have been fully addressed. With the present day approach to quality assurance aiming to ensure that data are reliable and comparable, the time to examine some of these problems is long overdue.

The Nature of Dust

In the context of air pollution there is no definition of dust in the legal provisions of the UK Clean Air Acts. "Grit" is defined in regulations[22] as "particles exceeding 76 μm in diameter," whereas "fume" is defined in the Clean Air Act, 1968, as "solid particulate matter smaller than dust." Hence a legal interpretation may be that dust is particulate matter smaller than 76 μm but with a lower limit of 1 μm. Such a size limitation may be applied by those involved in air pollution control, but more general environmental investigations tend to follow a definition such as that in the Shorter Oxford English Dictionary:

> "Earth or other solid matter so contaminated as to be easily raised and carried in a cloud by the wind; any substance pulverised; powder. Often extended to include ashes etc. from a house."

Some authors use the terms "dirt" or "sediment" as synonyms for dust, but all are referring to the general heterogeneous mixture of particulate matter deposited on surfaces. Clearly the sources contributing to deposited dust are legion, but Fergusson and Schroeder[21] suggest that approximately 60% of house dust is non-organic in nature, and this probably contains most of the lead. Of the inorganic material in house dust, 30–40% comes from soil, 25–30% from street dust and 1–2% from aerosol which has settled in the house.

Fergusson and Ryan[13] suggested that soil contributes more to larger than to smaller dust particles, and hence non-soil particles probably contribute more to smaller dust particles. As around 50% of dust occurs as large particles (963–213 μm) soil is a major component of street dust. This was so for all cities studies, although it was greater for some (75–90% for Halifax, Christchurch and Kingston) than others (60% in London and 57% in New York). More recently, Thornton[17] claimed that there is no reliable experimental method by which to quantify the soil component of house dust.

Define the Objectives

As demonstrated in Table 1, a variety of objectives have driven investigations involving dusts, but it is by no means certain that the design of the research programmes has been properly based on achieving these objectives. A clear precise definition of objectives makes the subsequent stages in an investigation capable of being designed efficiently, and ensures no wasted effort or wasted resources.

A sequential consideration of the factors involved in the design of a sampling programme may be adapted from recommendations for waters and associated materials[23] as follows:

Define objectives → select determinands and sampling positions
↓
select number of samples and time of sampling
↓
select accurate and convenient analytical methods
↓
select methods for collecting samples
↓
select methods for sample preservation

The aim of sampling is to collect samples whose quality represents the quality of the whole. To achieve this it is first necessary for the sample to truly represent the temporal and spatial variation of the quality of the whole, and this requires consideration of the sampling locations and the time and frequency of sampling. A second prerequisite is that the analyte(s) of interest have the same values as in the original. Hence it is essential to consider methods of sample collection, transportation and storage, with implications for representativeness again, as well as for avoiding contamination or analyte loss. Ultimately the results of analysis must be expressed and interpreted to relate to the objectives, as well as being comparable with other work. Elwood[24] commented that relevance of environmental measures to the actual exposure of subjects is probably one of the most difficult aspects of environmental research. While some compromise is usually necessary, some of the sampling procedures are utterly irrelevant. In particular, he cited that dust samples taken from a roadside gutter rather than from a pavement, or from under a carpet are of unlikely relevance to human exposure. He concluded that the need for rigour increases as a field is progressively explored. The now long established use of dusts as environmental measures suggests that rigour is now appropriate, and should start by clarifying the objectives and following a sequence such as that outlined previously. This sequence will be followed in reviewing much of the work on dusts.

Determinands

The study of the impact of motor vehicle emissions has been a major objective of many environmental dust studies, and consequently lead has been the common determinand owing to its presence as the antiknock additive. Lead from this source has been studied as a roadside pollutant, as a contaminant of exhaust replacement centres and in terms of the general urban burden. The use of lead as former pigments and drying agents in paints[25] makes it a potential contaminant from redecoration, and some studies have been concerned with such contamination in school playgrounds.[5] This source can also cause contamination in homes as can transport from the workplace on clothing.[16]

In view of the relative ease of extending analysis to other metals, several authors have included metals such as Cd, Cr, Cu, Ni, Fe, Zn and Mn, although not always with a particular objective in mind. Fergusson and Ryan[13] included 26 elements in their study.

The use of multiple element analyses may be useful in certain circumstances to trace the origins or pathways of trace metal pollutants. For example, Fergusson and Ryan[13] used the ratio of metal to aluminium concentration as an indicator of soil contribution to street dust. Enrichments with respect to crustal abundance occurred for most elements attributable to pollution (e.g. Br, Pb, Sb, Cd, Zn, Cu), and this was more marked in London and New York than in Halifax, Christchurch and Kingston. The use of tin as a tracer for lead from printworks[8] will be considered in more detail later.

Inorganic anions and organic species appear to have received little attention. Fergusson and Ryan[13] assessed "organics" merely by the weight loss of the sample after heating to 500 °C for 16 h. Extension of studies to examine organic substances such as pesticides in dusts, especially in internal samples, could offer interesting results in view of the potential health implications.

Sampling Positions

One of the earliest dust surveys[26] compared samples from urban and rural areas. Another study of similar date[16] was aimed at a city-wide survey of external and internal samples. External locations were classified according to road type, distance from industrial source or other characteristics according to a specified scheme. Some locations were repeatedly sampled on a seasonal basis while others were selected to give wide coverage. A later city-wide survey[11] included sampling at 2 × 2 km grid square intersections and subsequently on a 1 × 1 km grid.

As this programme was concerned with background levels, no samples were collected within 20 m of busy roads, 10 m of building facades or 100 m of factories. However, Archer and Barratt[16] had demonstrated that the impact of an industrial source could be identified within 400 m of the source. Clearly the height of discharge of dust will have an influence on the distance of contamination, and hence on the area for study or exclusion, depending on the objective. An elegant demonstration of dust sampling around a source was given by Hutton, Wadge and Milligan[10] in relation to Pb and Cd from a municipal incinerator. Samples were obtained at varying distances along radii at 15° intervals from 0–90° in the downwind area around the stack. Roadside sites were excluded from this sampling scheme. Unfortunately the report was marred by no description of the sampling procedure.

Where roadside contamination is of interest, the low level source suggests that shorter distances may be more significant than for elevated sources. For example, Archer and Barratt[16] noted the decline in Pb concentration in moving from the gutter to the pavement. Grottker[18] reported that 95.85% of street dust solids were found within 0.5 m of the kerb (gutter section) and that larger particles were more predominant in this gutter section than in the asphalt section. In contrast to this, Hamilton *et al.*[12] found that for heavily used roads, lead concentrations were uniformly distributed over all surfaces sampled. This they explained was due to the rapid speed of the vehicles resulting in the movement of many of the Pb-rich fine particles towards the side of the road, where "dilution" with soil-derived material gave an even distribution of Pb. At one site, however, these authors did find elevated levels of Zn and Cd in the gutter.

The uncertainty of spatial variations was a question raised by Archer and Barratt[16] and discussed by Duggan[27] who recognised that it was a problem difficult to contend with. No apparent reason could be found for differences in pavement samples spaced about 40 m apart, although samples collected on a 10 m grid pattern within playgrounds did not show significant differences. Fergusson and Ryan[13] reported that over a limited area, individual dust samples were reasonably representative of the area. For example, 10 samples collected 0.5 m apart and within a total distance of 5 m had a mean lead level of 3430 μg/g and a standard deviation of 270 μg/g. Data were also presented for Cr, Cu, Zn, and Cd to demonstrate reasonable uniformity and to justify characterising various cities by only two or three samples of dust. As these authors analysed a wide range of elements (26) and found that the concentration of the major elements (Al, Cu, K, Na, Ti) and several trace elements were similar, they suggested that this justified their approach. More work would seem to be needed in this area, for as stated by Hamilton *et al.*[12] it is an implicit assumption in all studies involving metals in dusts that representative samples have been taken. It is unfortunate that their own findings contradicted those reported elsewhere.

Table 2 Lead concentrations in urban dust samples

Sample type	*No. of samples*	*Lead concentration (mg/g)*	
		Median	*Range*
All roadside samples	1061	1200	160–50 000
Mixed residential/industrial area roadside gutter	161	950	300– 1 300
Residential road gutter	85	950	220– 4 300
Residential road pavement	180	700	200– 5 800
External surfaces other than roadside	455	1200	100– 6 700

Sample Replication

In the context of soil sampling, Allen *et al.*[28] noted that an investigator must allow for the inherent variability of soil samples. A high degree of spatial variability may exist over quite small areas and has been demonstrated by Ball and Williams.[29] Often the extent of this variation is unknown beforehand and hence sufficient samples must be taken to obtain a reliable measure of it. The absence of any indications of site variability can make it difficult to assess the significance of change such as seasonal variations which may be sampled by the data. Allen suggests that in practice 5–10 replicates should be regarded as a minimum. However, if it is desired to estimate site variability with the same precision as might be obtained under more uniform laboratory conditions, at least twenty samples might be required.

By comparison, the scientific rigour usually applied to soil studies is often not applied to dusts. Views on the numbers of samples required to produce meaningful results for dusts are as varied as the views on other aspects of dust sampling and analysis. Duggan[30] recommended that a considerable number of samples was necessary owing to the large spread of values expected. This broad spread was demonstrated by data in one of the largest of the early studies,[16] with typical ranges in a single city being reported as in Table 2.

In contrast, however, Fergusson and Ryan[13] compared pollution in six cities by taking two dust samples from each and three from a seventh. Each sample was obtained from an area not greater than 1 m^2. They noted the need for representative samples and commented that while few samples were taken, the "similar" concentrations for the major elements (e.g. Al, Cu, Na, K, Ti) and a number of trace elements suggested that the samples were reasonably representative. While this was true for some of the metals examined, close inspection reveals that some variations were wide by the standards of other studies. Thus, for example, lead levels ranged from 2008 to 4053 ppm in one city and 887 ppm to 1.07% in another. Few other studies have relied on such small sample populations. Duggan[27] explored in more detail the random variations over short distances. Repeated systematic sampling within school playgrounds (total area 5000 m^2) demonstrated wide ranges and standard deviations, but no significant difference between the three means on the three occasions. He concluded that despite sharp variations in concentrations over quite short distances, valid results could be obtained by taking

Table 3 Variations of concentrations within a confined area

	No. of samples	*Lead in dust* ($\mu g/g$)		
		Mean	*s.d.*	*Range*
Duggan[27]	*Samples over 5000 m*^{2}			
Set 1	44	760	750	110–4950
Set 2	44	730	440	110–1700
Set 3	25	700	360	280–1700
Fergusson et al.[31]	*Samples 0.5 m apart over a distance of 5 m*			
	10	3430	270	

a comparatively small number of large area samples, $5\,m^2$ being indicated. While this modified view on sample numbers lends some support to the approach taken by Fergusson and Ryan,[13] their sampling area of less than $1\,m^2$ is small. This is particularly notable since their approach of limited numbers of samples is based on their earlier studies,[31] again over a relatively small area. A comparison of these findings is presented in Table 3.

While there appears to be some doubt about the validity of using limited numbers of samples for wide-area and even city-wide studies, investigations of specific sources clearly require more samples over a limited area. Thus Hutton *et al.*[10] sampled at 15 points between 0.15 and 5 km along 15° radii between 0–90° in the downwind direction from an incinerator. Schwar and Alexander[5] collected 5–12 samples in a "corridor" close to the external face of school buildings, while Rundle and Duggan[6] collected 7–17 samples in each school playground. Over 600 samples (internal and external) collected over a long period of time within a 400 m radius of a major lead-using works were considered by Archer and Barratt.[16] The same report included a sequential collection of 50 samples within 0.5 km of the Motorway interchange in Birmingham.

The availability and cost of analytical facilities may determine the upper limit of the number of samples. One solution to the difficulty of analysing large numbers of samples involves bulking, in which individual samples are combined to give a composite mixture. This method may give a satisfactory mean value, but conceals any site variability. The validity of the mean is determined by the number of individuals making up the composite sample. Allen[28] cites that in variable soils even thirty individual samples may not be sufficient. Bulking procedures must be standardised by taking samples of equal volume from similar situations. Davies, Watt and Thornton[20] used composite samples comprising 25 subsamples from pavements and roads. The subsamples were collected over an unspecified area but outside individual houses under investigation. One form of bulking may be regarded as sampling dust by sweeping a relatively large area. This approach was advocated by Duggan[27] who indicated $5\,m^2$ as appropriate, whereas Schwar *et al.*[11] swept areas of 1–$5\,m^2$ to help overcome problems of localised spatial variation.

Table 4 Lead in dust concentrations within 0.5 km of a motorway interchange[16]

Date of sampling	*Lead concentration mg/kg*		
	Arithmetic mean	*Median*	*Range*
April 1974	1270	900	220–8650
July 1974	1040	700	160–3950
October 1974	990	800	180–4000
January 1975	1160	750	215–6120
April 1975	1068	850	200–7000
July 1975	1031	800	200–3000

The Significance of Time

With regard to soils, Allen[28] indicated that consideration should be given to the most suitable time for sampling. There was little evidence for diurnal variation but changes with season may occur. However most results, especially for cations, confirmed the work of Frankland *et al.*[32] and Ball and Williams[29] who found that spatial variability was likely to conceal any seasonal change. The same situation was suggested for dusts by one of the early studies[16] from which Table 4 is adapted. Fifty samples were collected from the same locations, so far as was practicable, at three monthly intervals.

The report noted atmospheric lead measurements in the area indicating higher values in winter than in summer, and while this was suggested by the dust data, insufficient evidence was available to confirm this owing to the wide range of results. There was an indication, however, that individual samples with high concentrations were more likely to be found in the late winter. A later study of seasonal variations in London[24] concluded that monthly average concentrations over the period August 1982 to March 1983 showed a gradual decrease over the period August to December followed by a slight increase in March. By comparison another study in London[27] concluded that there did not appear to be any seasonal or long term trends. Clearly, all of these investigators were concerned with the broad picture of lead from motor vehicle emissions. It would be interesting to review the effect following the phased reduction of lead in petrol and the increase in the use of unleaded petrol. Likewise it would be interesting to examine the influence of the removal of all newspaper printing from Fleet Street, London, since the study by Rundle and Duggan[6] in 1983 and 1984. Obviously any repeat studies should take care to use the same sampling and analytical protocols.

Certain temporal effects have been more clearly defined. Thus, while it is clearly easier to collect dusts on dry days as prescribed by some investigators,[11,20] Duggan[30] and Fergusson and Simmonds[15] both reported that rainfall caused marked reductions in lead values. In contrast Grottker[18] found metal concentrations higher after rain, although the small number of samples may make the observation invalid.

Schwar and Alexander[5] assessed the effect of playground cleaning on lead levels resulting particularly from old leaded paint. The average time for the mean lead in

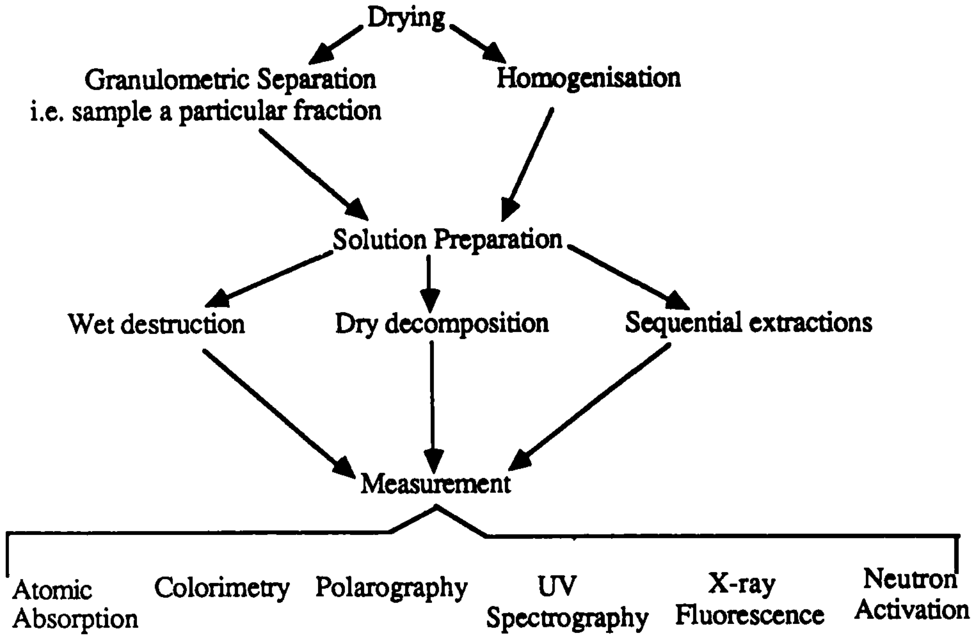

Figure 1 Possible steps in the analysis of dust for trace metals.

dust to decay to half its original value was 90–170 days, with variations according to the cleaning technique employed.

Grottker[18] found that heavy metal concentrations in street dust were higher after street cleaning than before. This fact was observed for Fe, Cd, Cr, Zn and Ni, but not for Pb and Cu. The effect was attributed to the more efficient removal of larger particles, but no explanation was given for the unexpected behaviour of Pb. Other than this study, the temporal effects on concentrations of metals other than lead do not appear to have been examined.

Selection of Analytical Methods

The options for sample analysis are varied and published descriptions of methods are sometimes full of detail and sometimes too brief to repeat. Some of these procedures are presented in the scheme in Figure 1. There are many possibilities in each step of the sequence, and several steps may be interchanged or associated. Of the many steps in the figure, the measurement is most easily considered first.

A general review of analytical methods used throughout the EEC[33] for principal pollutants demonstrated the dominance of atomic absorption methods for trace metals such as lead and cadmium, as Table 5 indicates.

This distribution of methods is generally found in reports on subsequent work on metals in dusts, with flame atomic absorption predominating for Pb, Cd, Zn, Ni and Cu. Polarography was used for 10% of samples in studies on lead by Day,

Table 5 Analytical methods used in member states of EEC[33]

Pollutant	*Atomic abs.*	*Colorimetry*	*Polarography*	*UV spect.*	*XRF*	*Neutron act.*
Pb	93%	0.5%	4%	2.5%	<0.1%	2.5%
Cd	88%	2.5%	6%	0.7%	—	—

Hart and Robinson,[26] who found agreement with atomic absorption analysis better than ±3%. The same two techniques, with polarography in the form of differential pulse anodic stripping voltammetry, were used by Hamilton *et al.*[19] Other techniques have included neutron activation for 24 metals[13] and inductively coupled plasma atomic emission spectroscopy.[2]

More variable than the choice of analytical method is the preparation for analysis and in particular the dissolution of the sample and the consideration of total or available metal.

Preparation of Solutions for Analysis

There is an extensive volume of literature on methods available for sample decomposition, which broadly divides into wet and dry techniques. In general terms, wet decomposition requires less equipment and there is less risk of volatilisation and retention losses than for dry methods. Unfortunately wet methods often require more reagents, more manipulations and hence present greater risks of contamination than dry decomposition. Dry methods require few reagents, little manipulation and bulky samples present little problem, although there is the volatilisation risk which is particularly relevant to metals such as cadmium and lead.

There are, of course, inevitable exceptions. Alkaline fusion as a dry method requires more reagent, whereas wet digestion in the pressurised or microwave mode requires little reagent, and such reagent is less contaminated. Such techniques do not appear to have found wide use in dust analyses. Reflecting on the relative merits of the options for sample destruction, it is perhaps no surprise that most investigators select wet methods. While it is hoped that reagent blanks and appropriate steps to control contamination and to purify reagents are included, it is unfortunate that the scant information on methods reported in many papers fail to mention these and other factors.

Table 6 illustrates a variety of techniques for sample destruction that have been used for dusts in the context of a total or single representative concentration of the metal content. It is clear from the table that a variety of methods for sample dissolution have been used to produce a total or representative concentration of metal in dust. At a first impression, this range of methods appears to make comparisons suspect.

It is clear from the table, that only one report describes dry decomposition, with dissolution of the residue in nitric acid.[16] Losses of metal (Pb) in the dry decomposition stage were avoided by maintaining the temperature below 550 °C. The dry method was attractive in view of the large numbers of samples being processed.

Table 6 Decomposition of dusts for trace metal determination

Reagent	*Time*	*Conditions*	*Metals*	*References*
$HNO_3/HClO_4$(9:1)	Overnight	—	Cd, Cu, Pb, Zn	12, 19
$HNO_3/HClO_4$(4:1)	24 h	50–190 °C	Pb	20
HNO_3/HCl	—	Boiling	Pb, Cd, Cr, Co, Cu	5, 6, 8, 34
HNO_3(2M)	30 min	—	Ni, Zn	26, 35
HNO_3(8M)	4 h	85 °C	Pb	36
HNO_3/H_2O(1:1)	—	—	Pb, Cd	7
HNO_3/H_2O(1:1)	—	—	Cd, Cu, Pb, Zn, Ni	9
HNO_3(4M)	30 min	—	Pb	13, 15, 21
HNO_3(25%)	15 min	Reflux after dry decomposition	Pb	16
CONC HNO_3	—	—	Cd, Pb	10
Hot aqua regia	—	—	Pb	4
$NH_2OH\cdot$(0.25M) in 25% CH_3COO_4)	Overnight	60 °C	Pb	3
$HF/HClO_4$(10:1)	—	200–230°C	Pb, Zn, Ni, Mn, Cu, Fe, Cr	15

Of the wet decomposition methods available, Fergusson and Ryan[13] found that acid extraction of samples (0.1–1 g) for 30 min in HNO_3 (4 M, 10 ml) recovered more than 90% of lead and cadmium, and over 80% copper. These estimates were made by comparison with tests on samples completely dissolved in $HF/HClO_4$, and agreed with previous work.[34] Farmer and Lyon[3] analysed soils and dusts using a single extraction procedure involving acetic acid and hydroxylamine hydrochloride. They found that for soils it was over 90% effective in recovering lead; the results were usually 5–10% less than those obtained when 8 M HNO_3 was used. Comparable studies on dusts were not quoted. The authors attributed the greater recoveries using HNO_3 to its ability to attack organic matter, which in other studies they carried out with H_2O_2. As less than 5% of dust and soil lead was recovered by H_2O_2, they concluded that only minor amounts of lead were associated with the organic phase, although subsequently[37] 14% was quoted. This latter figure is rather higher than that found by Fergusson and Ryan.[13] It must be remembered that a "good" recovery for soils is not necessarily indicative of the behaviour of dusts; the trace pollutant bound to the organic fraction of soils can be stripped off relatively easily. Many dusts may be silicaceous while others contain aluminates, the exact chemical species depending on the origin of the components. Thus wet digestion without HF is unlikely to be complete, and should not be expected to give the total metal content. While some studies have demonstrated comparability of wet digestion with and without HF, it cannot be assumed that all dusts will behave similarly. Clearly, the varying nature of dust samples from different sites may cause recoveries to differ from dust to dust, unless a reliable "total" decomposition method is used. This implies that all except the last method in Table 6 are subject to uncertainty.

In the absence of a standard method for extracting lead from dust, Jones and McDonald[38] compared the extraction efficiency of four methods used in city-wide surveys in Britain. The authors did note that the method reported for samples from London was insufficiently detailed and precise to enable replication. From the methods tested, however, it was concluded that the differences in the analytical methods may account for the different lead values found in the different cities. Considerable caution was therefore recommended when comparing data from different surveys, and it was concluded that the problem will persist until there is agreement on a standard method of extraction of lead from street dust. This view echoed that of Archer and Barratt[16] seven years previously, and even now the problem remains. As long as researchers refuse to use a total digestion procedure they cannot compare the results of analyses of different dusts.

The sample preparation methods considered so far are relatively simple and relatively rapid, although some procedures take up to 24h. The main problem is selecting a reagent that is effective in releasing the metal of interest in a form that represents the potential release in relation to the exposure of a subject in the environment. It may be argued that attempts to seek the "total" metal in the sample give the worst case of release into the environment. The methods considered so far, with the exception of HF digestion, should be called leaching methods. Virtually by definition, leaching methods give information on the way metals are bound in the matrix, and also by definition they do not give the total content.

Rather than carrying out a single stage solution preparation, it is possible to extract metals selectively according to the degree of bonding to the dust matrix. Five fractions are often considered as reflecting the strength of bonding to the matrix, and hence the environmental availability. A particularly detailed study of sequential extractions for the speciation of particulate trace metals in sediments was carried out by Tessier *et al.*[39] who adapted methods of soil analysis. The concept of partitioning the solid material into specific fractions proposes that these can be selectively extracted with appropriate reagents. The five fractions selected are summarised in Table 7.

One such extraction sequence for dusts is set out in the scheme in Figure 2, which represents the procedure reported by Fergusson and Ryan.[13] A similar scheme was used by Hamilton *et al.*[12] The exchangeable fraction represents the surface-bound material, which is readily subject to sorption and desorption. Next, the carbonate phase represents moderate availability, which term also describes the subsequent fraction known as the Fe-Mn oxide phase. Gibson and Farmer[37] further subdivided this latter phase according to the strength of adsorption to the Fe-Mn oxides.

Thus, they referred to an "easily reducible" fraction (residue shaken with 0.1 M $NH_2OH \cdot HCl/0.01\,M\,HNO_3$ (20ml, 30min at 20°C) followed by a moderately reducible fraction (residue shaken with 1 M $NH_2OH \cdot HCl/25\%\ CH_3COOH$ (20ml, 4h at 20°C). The general scheme continues with the organic fraction and concludes with the residual phase, which represents the environmentally immobile fraction.

For dusts from selected cities across the world, Fergusson and Ryan[13] found that Pb, Zn and Cd showed similar extraction patterns (except for exchangeable Cd), the patterns for Mn and Fe were similar, while the extraction patterns for Cu were unique. Typically 8.9–30.4% Cd was exchangeable while for the other metals

Table 7 Fractions for partitioning of trace metals[39]

1. *Exchangeable Fraction*

   Surface adsorption of trace metals. Changes in ionic composition (e.g. pH, Cl^-, etc.) are likely to influence sorption/desorption processes.

2. *Carbonate Fraction*

   Trace metals associated with sediment carbonates, and hence susceptible to pH changes.

3. *Fraction Bound to Iron and Manganese Oxides*

   Iron and manganese oxides are present as nodules, concretions, cement between particles or as a coating on particles. They are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions.

4. *Fraction Bound to Organic Matter*

   Trace metals may be bound to organic matter present as organisms, detritus, coatings on mineral particles etc. through complexations, peptization or bioaccumulation, etc. Under oxidising conditions the organic matter can be degraded, which releases the metals.

5. *Residual Fraction*

   Following removal of the previous four fractions, the residual solid may hold trace metals within the crystal structure. Normal environmental conditions will not release these metals.

the exchangeable component was relatively low (0–12.1%). Copper was present mainly in the organic fraction (32.6–74.3%) whereas the other metals were all present at less than 16.9% in this fraction. Lead and cadmium were about equally distributed between carbonate and Mn-Fe oxide bound forms, while Zn was bound mainly to the Mn-Fe oxides. The major difference between the cities was for organic bound copper which related to the greater organic content of the dust in the bigger cities.

Gibson and Farmer[37] reported broadly similar partitions for Pb, Zn, Cu and Cd across the phases with the exception of zinc which they found in the greatest proportion (26%) in the residual phase. However, they reported that a common feature of the four elements was a decline in the relative significance of the residual fraction with increasing concentration. This was not unexpected in contaminated environments with high input fluxes of metals from polluting sources. Leaching of samples with hydrochloric acid (0.07 M) to represent human stomach acidity indicated that an average 41% Pb, 44% Zn, 28% Cu and 47% Cd was released. The results suggested that Pb, Zn and Cd associated with the exchangeable, carbonate and easily reducible fractions were quantitatively released by the dilute hydrochloric acid, with some additional zinc being removed from the moderately reducible fraction.

Particulate Size—Granulometric Separation

The inhomogeneous nature of dust was highlighted as a problem in the Introduction, and this is of no greater importance than in the context of particle size. Fergusson and Ryan[13] examined nine particle size fractions in the range $33 \pm 8\,\mu m$ to $963 \pm 38\,\mu m$. They found that the amount of each element in each size fraction

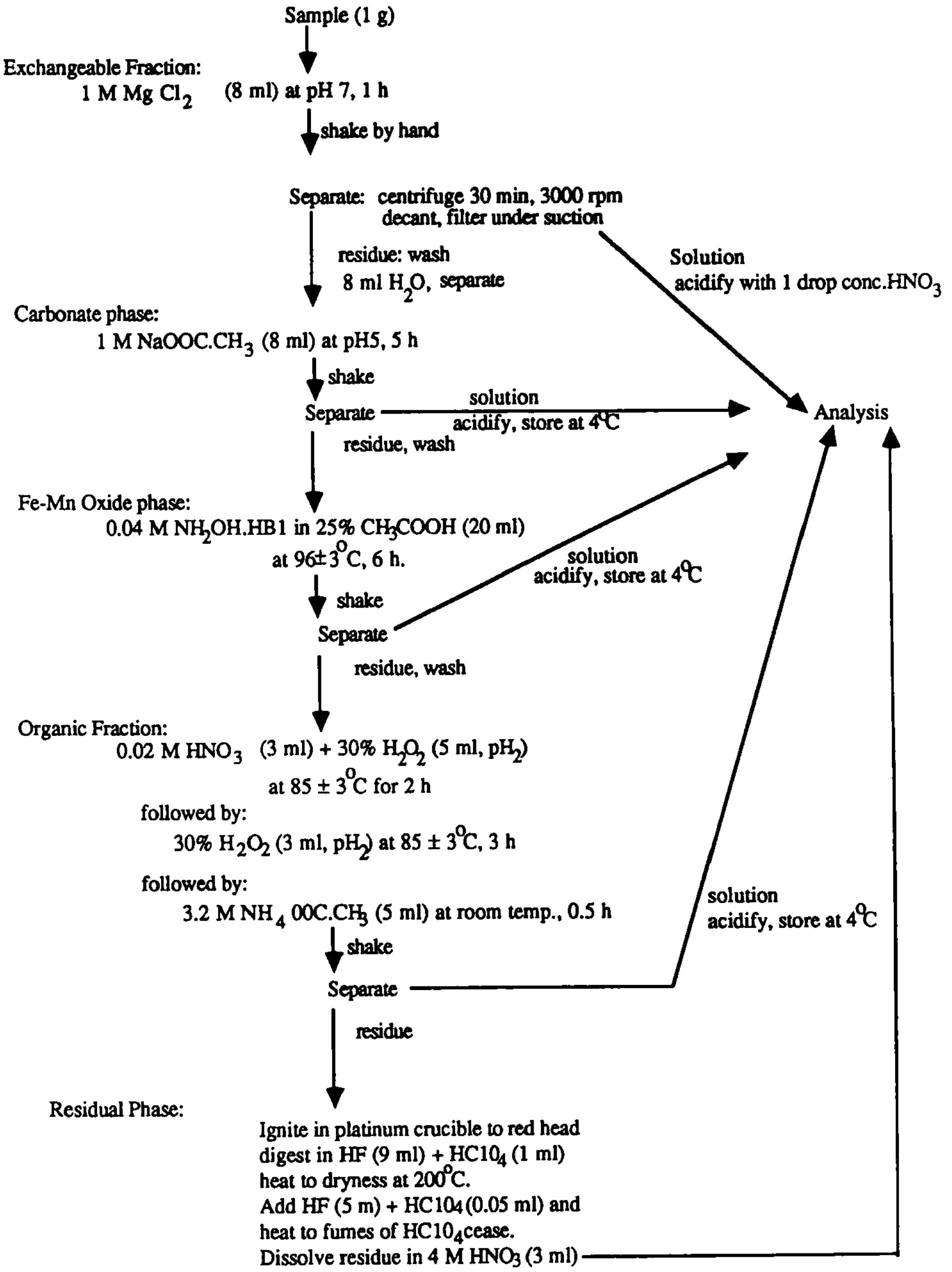

Figure 2 Sequential extraction scheme for dusts.

decreases with the particle size because of the decline in the amount of dust in the smaller size fractions. Typically, 38–51% of the amounts of all elements for all samples occurred in the coarse fraction defined as 213–963 μm. However, for most of the elements, their concentration increases with the decrease in particle size, although the extent to which this occurred may vary considerably from site to site.

The significance of the particle size effect in terms of environmental effects includes the greater contamination of storm water sediments through run-off flushing the finer particles into the drainage systems,[12] and the greater risk of contamination of children's fingers leading to a greater risk of elevated body burdens of lead.[26,40] From the analytical point of view, however, the problem is one of selecting a representative sample of the inhomogeneous mass.

For soils, Allen[28] suggested that the first step may be to reduce the sample bulk. Traditionally this has been done by mixing, heaping and quartering the air-dried sample. The two opposite quarters are mixed and the process repeated to give the required sample size. It is usual to pick out large stones before proceeding with this process. For dusts, it seems unlikely that bulk reduction will be necessary unless a large cumulative sample is obtained. However, even if not reduced in bulk, the sample must be brought to a relatively homogeneous state by thorough mixing before being treated further. Of the multitude of papers on dust analyses, only Solomon and Hartford[36] appear to refer to this problem.

The next problem concerns taking a specified size fraction for analysis or grinding the whole. Clearly if the latter route is chosen, care to avoid contamination of the sample, such as from cadmium in pigment of plastic grinding equipment, or to avoid differential loss of fine dust is essential. Hamilton *et al.*[12] stated that there was some evidence that grinding increases the measured metal level, presumably because there is a greater surface area exposed which makes metal extractions easier. This statement contradicts evidence presented by Jones and McDonald[38] which showed that ground samples gave lower values than sieved samples. However, both groups agree that grinding is inappropriate when dealing with environmental samples, as it is not the constituents of the core that are of interest. Despite this view, several groups have homogenised samples by grinding[5,10,26,35] while others have selected only the dust fractions below a certain particle size. Once again, the non-uniform approach makes it difficult to compare results, especially in view of the relationship between particle size and metal concentration. Thus, some groups have examined particle sizes below 250 μm,[15,21] some below 500 μm,[4,6,8,11] some below 1 mm,[20] some below 2 mm[7] while others have no specified size. It appears that the size is often selected merely because it relates to previous work in a city or within a group, but this does not facilitate wider comparison of data. This difficulty has been noted. In particular it was noted that Government sponsored research should have included initiation of studies on size relationships in order that advice could be given to researchers on standardisation of size fractions.[41]

Sample Collection

Recommendations of standard methods for the collection of dustfall[42] and for

Table 8 Comparison of brush and vacuum dust sampling techniques[16]

Technique	*Lead concentration* (mg/g^{-1})	
	Mean	*Range*
Vacuum	2700	1200–6300
Brush	3700	1300–11 000

collection of dust from flue gases[43,44] have been adopted and followed for many years, but no standard guidelines exist for deposited dust. Thus, as with many other aspects of dust analyses, the variety of methods used make it difficult to compare results and this problem is compounded by the failure of many to give details of procedures used in their work.

In general, sample collection methods may be grouped as brushing or vacuum methods. Brushing involves using a soft brush to sweep dust from hard surfaces directly into plastic containers or onto paper and thence into containers or plastic bags.[3,5,6,11]. Archer and Barratt[16] emphasised the need to avoid cross contamination from the brush. It is perhaps for this reason that some groups prefer the use of a spatula, which is also advantageous for damp samples.[16,37] Suction techniques were used by several groups,[20,21,36] often using adapted domestic vacuum cleaners with collection of material on cellulose filters in an appropriate holder. Fergusson and Schneider[21] gave one of the more detailed descriptions of sampling and suggest collection by suction (using a small diaphragm pump with vacuum of 27 kPa) from an area of 0.25 m^2 carpet on to glass fibre filters held at 6 mm above the carpet. While Davies *et al.*[20] also collected on filters, they and Thornton[17] also took samples from the dust bag of domestic cleaners. Hamilton *et al.*[12] observed that implicit in all of these studies was the assumption that representative samples have been taken. These workers used both vacuum and brush sampling techniques, but failed to show comparability. Only Archer and Barratt[16] did this in a matched set of brush and vacuum samples collected at each of 50 sites within a single office building. Their results were as set out in Table 8

The results suggested to these authors that suction collected small particles such as fibres which effectively diluted the lead concentration, but more significant was the conclusion that this was an important area for further work on sampling methodology. Fergusson and Schroeder[21] reinforced the view of a need for a standard sampling method, but this has yet to be done. It is particularly regrettable that part of a national survey of house dusts used techniques different from many others, and notably involved samples collected by both vacuum and brush techniques without confirming comparability.[20]

Sample Preservation

Fortunately problems associated with sample preservation are of lesser significance for dusts than for solutions, for example. Clearly the major factor is to avoid contamination of the sample after collection and to this end samples have been stored in containers such as polythene bags,[15,16] glassine envelopes[36] and plastic tubs.[6] As mentioned previously, only Solomon and Hartford[36] subsequently addressed the issue of stratification on storage, although subsamples were obtained from bulk samples in several studies.[6,8,20]

Where solutions or extracts from dust samples are stored, the possible losses of solutes to the vessel surfaces must be considered. As shown in Figure 2, acidification of the solutions has been used to avoid such losses.

The Presentation and Use of Data

Analyses of environmental samples may be carried out on the material as received, air dry or oven dry, but the final results are best reported on an oven dry basis. This is usually equivalent to drying to constant weight at 105 °C. Harrison,[34] Schwar *et al.*,[11] Fergusson and Ryan[13] and Hamilton *et al.*[12] dried samples at 105 °C, while others dried at temperatures ranging from 30 °C (air drying) to 80 °C. Solomon and Hartford[36] and Fergusson and Schroeder[21] equilibrated samples to constant temperature and humidity before weighing, while too many authors failed to mention whether samples were dried and on what basis their results were presented; their data are therefore of limited value to others working in the field.

Most workers have expressed total or extractable concentrations in units of $\mu g\,g^{-1}$ or similar derivatives, although some use ppm. Several[12,20,21,36] specify units of $\mu g\,m^{-2}$. As most studies involve many samples, the representative values may be quoted as arithmetic means (although in one case of two samples), as ranges, as geometric means or medians. The positive skewness of the frequency distributions of lead concentrations in dusts was demonstrated by Archer and Barratt,[16] with the log normal pattern characteristic of many pollution data being evident in the figures presented. Schwar *et al.*[11] showed similar frequency distributions for cadmium, copper, lead, zinc and iron, while Thornton[17] did likewise for cadmium and zinc. Schwar and Alexander[5] found a close fit to the log normal curve for mean values of lead in dust from schools within age categories, reflecting the patterns found for lead in paintwork on buildings.[45] It is clear from these observations that the use of median or geometric mean concentrations is a preferred representation of the "average" value of the metal concentration. It has been suggested[11] that the median concentration for dust samples from several sites varies with time by less than 30% for all metals. Thus, while individual results may vary widely, as ranges indicate, the median of a number of samples can provide a reliable picture of metal distributions. One comparison[5] of geometric and arithmetic means found that the average ratio of arithmetic to geometric mean was 1.5 for samples in a "corridor" adjacent to school buildings and 1.1 elsewhere in school playgrounds. There appears to be little significance in this ratio, however, because data from work by Schwar *et al.*[11] suggest a ratio of 1.79 while those from Archer and Barratt[16] indicate ratios varying from 1.36 to 4.95. The last cited reference suggests, however, that the ratio is consistently much greater close to buildings, and especially inside buildings. The same inference cannot be drawn from the data published by Davies, Watt and Thornton,[20] for while the ratios tended to be within a range from 1.3 to 2.3, sampling methods inside and outside buildings were different.

Measurements alone are of little value unless they are used in environmental management. Schwar *et al.*[5,11] noted the lack of nationally agreed reference levels for judging exposure to lead in dust, but noted the adoption by the Greater London Council of guideline concentrations for lead in dust of 500 μg/g as requiring investigation, and 5000 μg/g as requiring some control action. This latter figure had been used as the threshold indicating a need for further investigation in Birmingham many years previously.[16] In the latter case the figure had been adopted from the then statutory limit of lead in paint on children's toys, although this limit is now 2500 ppm.[46] The use of a standard implies specification of measurement and data presentation protocols, but such guidelines have not been developed as this review has repeatedly shown.

The breach of a guideline should prompt action, and in the case of dusts this may involve identifying a source of contamination. One technique that has been used for this is to measure the ratio of the lead isotopes ^{206}Pb: ^{207}Pb in environmental samples. Ault *et al.*[47] used isotopic tracer techniques to determine contamination in several environmental samples, and demonstrated the role of automotive lead as a roadside pollutant rather than lead released from coal combustion. Weaknesses of the method were discussed by Holtzman.[48] Likewise it has been advised[49] that extrapolating findings from Italy[50] to elsewhere should be treated with caution. A simpler approach is to compare the relationships of different trace metals in a sample. Fergusson and Ryan[13] used the metal to aluminium ratio to indicate the contribution soil made to street dust. They found that soil contributed more to larger particles and so non-soil particles probably contributed predominately to smaller dust particles. This observation may be a justification for size separation in sample pre-treatment. Jensen and Laxen[8] used tin as a tracer for lead from printworks. The composition of type metal alloy from the traditional printing process is 78% lead, 15% antimony and 8% tin and so the presence of tin provided a simple means of confirming the suspected printworks source of contamination. A graphical link between tin and lead was shown around the printworks, but not for samples from elsewhere; correlations were not given. The data showed that tin was a suitable tracer for printworks lead, and these authors suggested that antimony was analytically less suitable. Archer and Barratt[16] had suggested that correlation patterns between metals would have helped their study of contamination in homes, which they demonstrated as being caused in large part by transport of metals on clothing. In subsequent unpublished work by Barratt, this effect of transport of dust was clearly demonstrated through the correlations of lead and antimony from printworks. Typical data for the metal burdens in the dust on items of clothing are given in Table 9. These results clearly demonstrate not only the increased amounts of lead and antimony from dust on the clothing of personnel exposed to type metal, but also show the role of correlating the burdens of the two metals to confirm the source.

Thus, while vehicle mechanics show rather higher lead burdens in dust than the other control groups, the correlation with antimony is not significant. Multi-

Table 9 Lead and antimony burdens in the dust on garments of printworks personnel

	Metal burden (mg/garment)		*Correlation coefficient*
	Pb	*Sb*	
Control Groups:			
Drivers	0.26	—	—
Vehicle mechanics	0.85	0.08	0.41
Editorial staff	0.21	—	—
Advertising staff	0.17	0.07	−0.09
Exposed Groups:			
Linotype operators	5.47	0.58	0.97
Linotype mechanics	13.3	2.39	0.72
Melting room	19.6	4.1	0.97
Printing machine room	4.43	0.61	0.99
Management	0.36	0.10	0.98

element analyses therefore have a useful role in tracing sources of pollution of dusts.

In the absence of guidelines on concentration of metals in dusts other than that for lead mentioned previously, most workers have compared their results with those from other studies. It has been recognised by some workers that direct comparisons are complicated by the use of a variety of techniques for collection, preparation and analysis, as well as by the various ways of reporting of results. These points have been noted repeatedly through this review, and various authors have done likewise. Unfortunately they then proceed to compare their own and dissimilar data. An unfortunate example of this is the work of Davies, Watt and Thornton[20] who used different techniques within their own study and compared data with historical results using different methods. In their conclusion they noted reductions in the lead concentrations in dust apparently suggested by comparing their own data with those from an earlier study. In fact, bearing in mind the evidence of Jones and McDonald[38] on a comparison of analytical techniques, the differences in analytical method combined with the differences associated with particle size fractions studied could contribute significantly to the variations reported for the data. This example demonstrates the problems in comparing studies on trace metal concentrations in dusts. It is senseless comparing data unless the quality control of methods are demonstrated to be comparable.

Conclusions

A multitude of papers has been published containing reports on analyses of dusts for trace metal pollution, but few have acknowledged important questions about the validity of such work. Certainly, since some of the early papers on this topic, more is known about the chemical nature of dusts and the association of certain metals with components of the matrix. This information provides useful guidance on dissolution techniques, especially when "available" metal concentrations are sought. However, as long as leaching techniques alone are used, comparability of data will always be suspect.

Another major problem concerns lack of standardisation. Methods are often standard to a research group and so comparisons with data from other reports are often invalid. While several authors have identified the need for standardised guidelines on sampling techniques and on analytical procedures, few have addressed the problems in sufficient depth to produce guidelines. Dusts will always present a potential route of contamination by trace metals and organic substances and the need for future work in this area will not diminish. Only by the application of good quality control, reference materials and techniques allowing decomposition of the whole matrix will an extremely uncertain position be improved.

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