CADMIUM IN THE ENVIRONMENT AND HIGH RISK POPULATION GROUPS

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"CADMIUM IN THE ENVIRONMENT AND HIGH RISK POPULATION GROUPS"

SUMMARY

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Cadmium has been widely used in various industries for the past fifty years, with current world production standing at around 16,755 tonnes per year. Very little cadmium is ever recycled and the ultimate fate of all cadmium is the environment.

In view of reports that cadmium in the environment is increasing, this thesis aims to identify population groups 'at risk' of receiving dietary intakes of cadmium up to or above the current Food and Agricultural Organisation/World Health Organisation maximum tolerable intake of 70 ug/day. The study involves the investigation of one hundred households (260 individuals) who grow a large proportion of their vegetable diet in garden soils in the Borough of Walsall, part of an urban/industrial area in the United Kingdom. Measurements were made of the cadmium levels in atmospheric deposition, soil, house dust, diet and urine from the participants.

Atmospheric deposition of cadmium was found to be comparable with other urban/industrial areas in the European Community, with deposition rates as high as 209 g ha^{-1} yr^{-1}. The garden soils of the study households were found to contain up to 33 mg kg^{-1} total cadmium, eleven times the highest level usually found in agricultural soils. Dietary intakes of cadmium by the residents from food were calculated to be as high as 68 ug/day. It is suggested that with intakes from other sources, such as air, adventitious ingestion, smoking and occupational exposure, total intakes of cadmium may reach or exceed the FAO/WHO limit. Urinary excretion of cadmium amongst a non-smoking, non-occupationally exposed sub-group of the study population was found to be significantly higher than that of a similar urban population who did not rely on home-produced vegetables.

The results from this research indicate that present levels of cadmium in urban/industrial areas can increase dietary intakes and body burdens of cadmium. As cadmium serves no useful biological function and has been found to be highly toxic, it is recommended that policy measures to reduce human exposure on the European scale be considered.

KEY WORDS: CADMIUM, ENVIRONMENT, SOIL, VEGETABLES, TOXICITY.

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CHAPTER 1

INTRODUCTION

CHAPTER 1: INTRODUCTION

1.1 Discovery of Cadmium

1.2 Emergence of Cadmium as an Environmental Contaminant

1.3 Research Recommendations of the Commission of the European Communities and the UK Department of the Environment

1.4 Research Aims and Purpose of this Study

CHAPTER 1: INTRODUCTION

1.1 DISCOVERY OF CADMIUM

The name cadmium is thought to have originated in connection with a peculiar earth-like substance known as 'cadmia' found near the Black Sea and used in the manufacture of a bright yellow bronze in the First Century AD.[1,2]

It has been suggested that cadmium is probably the first metal ever to be used commercially which was not discovered in an ore of its own, for it was not until 1817 that the element was first recognised by F Strohmeier, a metallurgist, while investigating the yellow colour in a sample of zinc carbonate. Later, in 1818, Hermann obtained a yellow precipitate by passing hydrogen sulphide through an acid-zinc solution, a finding confirmed by several other workers, and Strohmeier's suggestion of the name 'cadmium' was accepted.[1,2]

The uses of cadmium, since its discovery by Strohmeier, developed slowly throughout the Nineteenth Century. Various inorganic compounds of cadmium were prepared and there was a small amount of use in low-melting alloys. By 1910 world production was only about 45,000 kg (45 tonnes) but by the end of the First World War cadmium electro-plating technology developed sufficiently to warrant its commercial use. By the mid

1920's cadmium became widely used as a protective coating in iron and steel, which led to a greatly increased demand for the metal. Today, the world demand for cadmium is in excess of 16,500 tonnes per annum.

1.2 EMERGENCE OF CADMIUM AS AN ENVIRONMENTAL CONTAMINANT

The earliest incident of cadmium poisoning was that reported by Sovet in 1858(1) caused by cadmium carbonate being used to polish sliver. The servants who were engaged for a day-and-a-half in polishing the silverware were affected by clouds of dust which were produced when the cadmium carbonate powder was brushed off after drying. The three servants involved showed similar symptoms of difficulty in respiration, vomiting and diarrhoea. Recovery was slow, with one servant who had been exposed the longest becoming very ill over the following days.[2]

Since this and other early reported incidents, cadmium has been recognised to be a highly toxic element and the need for safeguards in industrial operations in which workers are exposed to dusts and vapours containing cadmium or its compounds have been recognised. It is not until comparatively recent times, however, that concern has been expressed over the possible effects on human health of long-term exposure to low concentrations of cadmium. Indeed, the effects of long-term exposure to low levels of cadmium are still not fully understood.

The main reason for this is that many effects take up to 20 years to manifest themselves.

At present the European Community (EC) consumes between 5,500 and 6,000 tonnes of cadmium each year, which represents one-third of world production. Very little cadmium is ever recycled, with the demand being for dissipative uses. The ultimate fate of all cadmium is, therefore, the environment. Recently, and partly because of the outbreak of the Itai-itai disease in Japan in the late 1940's and the early 1950's, and because of the steadily increasing consumption and subsequent increase in the general environment of cadmium, concern has increased over the levels and possible harmful effects of the metal in the ambient environment. This concern has recently culminated in the Swedish Government imposing a ban on the production and importation of most cadmium-containing products.

1.3 RESEARCH RECOMMENDATIONS OF THE COMMISSION OF THE EUROPEAN COMMUNITIES AND THE UK DEPARTMENT OF THE ENVIRONMENT

The Commission of the European Communities (CEC) has recently commissioned two studies to evaluate the toxic effects of cadmium in the environment.[3,56] These studies have recommended that, firstly,

> 'Monitoring of the environment in Europe should be continued to better assess the overall exposure of the population and pinpoint groups at risk' (CEC 1979)[56]

secondly,

> 'With the use of sensitive biological parameters (eg B_2-Microglobulin in Urine ...) potentially high exposure groups in the general population should be investigated to find out whether critical human groups can already be found in Europe. The total exposure of the groups investigated should also be carefully evaluated' (CEC 1979)[56]

and, thirdly,

> 'Evaluations, supported by direct evidence should be made, so that population groups most at risk can be identified more precisely for risk assessment' (CEC 1981)[3]

These recommendations complement those of the UK Department of the Environment (DoE) who carried out a study of cadmium in the UK in 1980.[38] An additional recommendation made by the DoE, however, was that

> 'Levels of cadmium in food, beverages, water and air should be kept under surveillance, with special attention being paid to the pathways by which cadmium may reach man and to any changes which may influence these pathways'

1.4 RESEARCH AIMS AND PURPOSE OF THIS STUDY

To fulfil the requirements of the CEC and the UK DoE a broad research study is required, with an in-depth appraisal of sources, environmental flow and human exposure to cadmium in the EC.

In order to further these requirements, eight specific areas of study have been defined, namely:

1) To review by means of a literature search the trends in production and consumption of cadmium within the EC and to identify the major industrial uses of cadmium.

2) To identify the main emission sources of cadmium within the EC.

3) To highlight the effects on health of cadmium exposure.

4) To identify and study a potentially 'at risk' non-industrial population associated with high cadmium exposures.

5) To assess the factors contributing to high cadmium intakes amongst 'at risk' populations.

6) To investigate the actual levels of cadmium intake by the study population.

7) To evaluate the toxicological hazard of cadmium for the study population.

8) To suggest possible measures which might be taken to minimise exposure and uptake of cadmium by 'at risk' populations.

The study reported here is the culmination of three years' research into the eight areas of study defined above. Each of these are discussed in detail in the thesis, and where appropriate specific recommendations are made.

CHAPTER 2

PROPERTIES, PRODUCTION AND INDUSTRIAL USES OF CADMIUM AND ITS COMPOUNDS

CHAPTER 2: PROPERTIES, PRODUCTION AND INDUSTRIAL USES OF CADMIUM AND ITS COMPOUNDS

2.1 THE PHYSICAL AND CHEMICAL PROPERTIES OF CADMIUM
2.2 WORLD PRODUCTION AND CONSUMPTION
2.3 USES OF CADMIUM AND ITS COMPOUNDS
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    2.3.2 Pigments
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    2.3.4 Alloys and Solders
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    2.3.9 Catalysts
    2.3.10 Nuclear Reactors
    2.3.11 Cadmium Compounds
2.4 CONSUMPTION AND MARKET SHARES OF MAJOR CADMIUM USES IN THE EUROPEAN COMMUNITY
2.5 SUMMARY

CHAPTER 2: PROPERTIES, PRODUCTION AND INDUSTRIAL USES OF CADMIUM AND ITS COMPOUNDS

2.1 Physical and Chemical Properties of Cadmium

The element cadmium is number 48 in Mendeleev's Periodic Table and occurs in Group IIb along with zinc (Zn) and mercury (Hg) directly after the so-called transition elements. It occurs as eight stable isotopes of abundance: ^{106}Cd (1.22%); ^{108}Cd (0.88%); ^{110}Cd (12.39%); ^{111}Cd (12.75%); ^{112}Cd (24.07%); ^{113}Cd (12.26%); ^{114}Cd (28.86%); ^{116}Cd (7.58%); and two principal unstable isotopes: ^{109}Cd and ^{115}Cd which are frequently used for tracer work.[1,2]

Cadmium has a strong tendency to form soluble complexes with cyanide (CN) or amines (NH_2) as well as with Cl^-, OH^-, $SO^{2}_{4}{}^{-}$, $P_2O^{4}_{7}{}^{-}$ groups and humic acid derivatives. Cadmium also forms some very insoluble compounds, especially sulphide and phosphate. The sulphide is yellow in colour and is the form in which cadmium occurs naturally with other metal ores. For this reason cadmium sulphide (CdS) was one of the earliest yellow paint pigments used.[1,2]

The principal properties of cadmium (shown in Table 2.1) are that it is bluish or silvery white in colour, is relatively soft, ductile and malleable, and although it oxidises readily in a moist atmosphere it is resistant to rusting. It can be rolled into sheets and drawn into wire, and unlike many metals it does not pass through a series of brittle and ductile states on heating.[1]

Property	Cadmium (Cd)
Atomic number	48
Atomic weight	112.40
Melting point (°C)	320.9
Boiling point (°C)	765
Temp (°C) at 1 mm Hg (Vp)	394

TABLE 2.1: THE PHYSICAL PROPERTIES OF CADMIUM

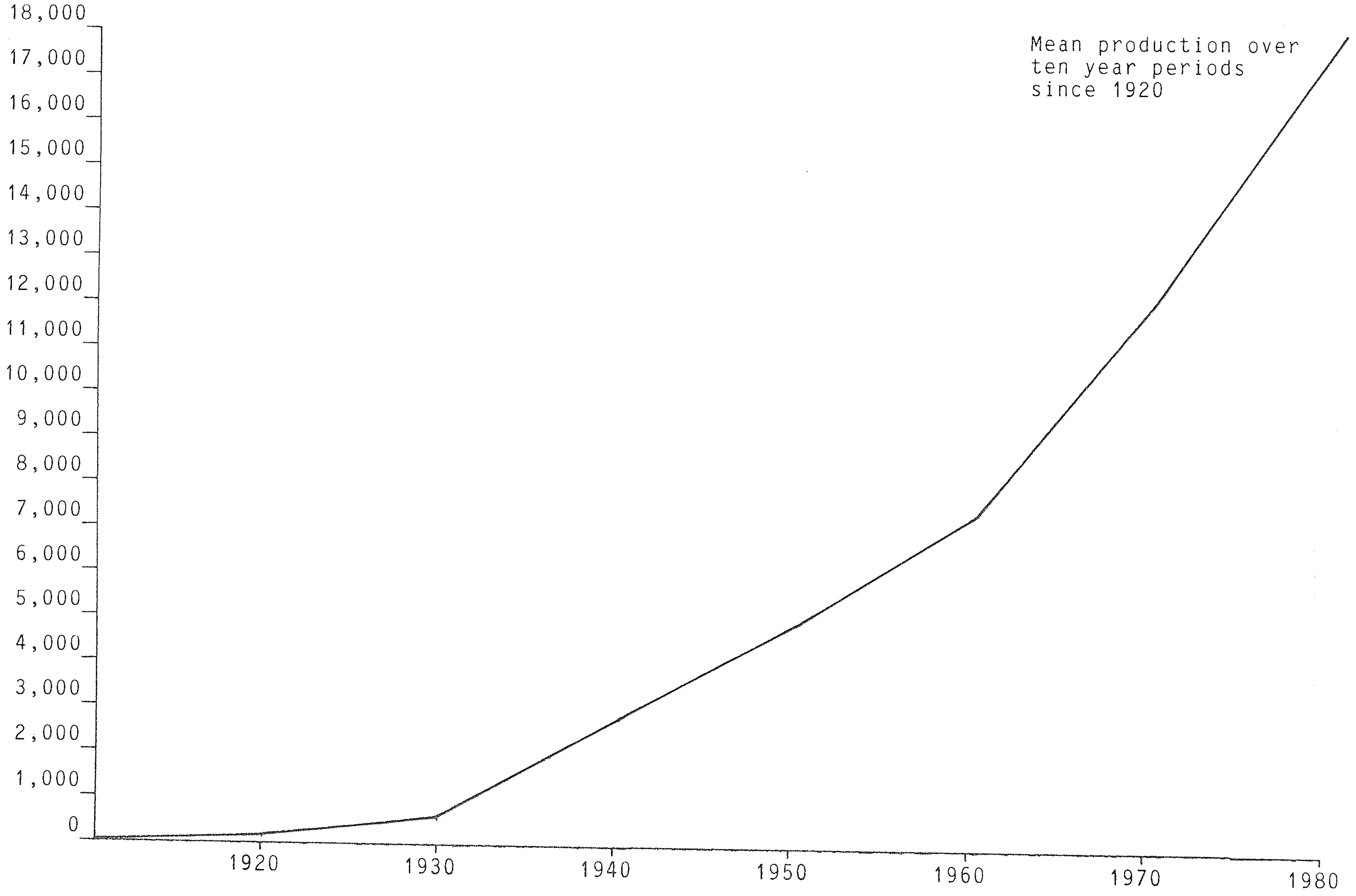
The low melting point of cadmium makes it especially valuable in low melting point alloys and solders. Its low boiling point and higher vapour pressure than Zn, Pb and Hg are critical factors in its separation in smelting and refining processes.[1,2,3,4] These properties, however, can result in losses to air when metals containing cadmium are heated and reduced, with the resultant volatilisation of cadmium to brown cadmium oxide (CdO) fume which is difficult to capture using current control technologies.[4,5]

2.2 World Production and Consumption

Production of refined cadmium has always been closely related to the production of zinc, since cadmium is derived from the smelting of primary zinc ore, usually at the ratio of three tonnes of cadmium per thousand tonnes of zinc. Production of cadmium began in the early 1900s and continued to increase throughout the industrialised nations of the world. (Figure 2.1 and Table 2.2)

The potential supply of cadmium in the early 1900s was much greater than the demand; consequently up until 1940 much of the available cadmium was either released to the environment, usually in effluent form, or retained as an impurity in the zinc metal, alloy or compound produced. In the early 1920s more applications were found for cadmium, with the result that there was a sufficient market to warrant small scale cadmium extraction and refining in the zinc industry. Consequently consumption of cadmium between 1930 and 1970 increased by an average of 6.9 per cent per annum throughout the world. During the 1960s, increased demand was limited, reaching the amount available in zinc ores. The 1970s saw an annual growth in cadmium consumption in the European Community of 10 per cent[3], although the world consumption is expected to increase by only 2 to 4 per cent per year up until the year 2000. Table 2.3 shows the amount of cadmium produced by each industrialised country; from this it

FIGURE 2.1: WORLD PRODUCTION OF REFINED CADMIUM SINCE 1920 (TONNES)



Period	Yearly mean (tonnes)
1910 - 1919	97.7
1920 - 1929	540
1930 - 1939	2,829
1940 - 1949	4,909
1950 - 1959	7,500
1960 - 1969	12,421
1968	14,973
1969	17,452
1970	16,526
1971	15,485
1972	16,888
1973	17,605
1974	17,456
1975	15,674
1976	16,933
1977	18,326
1978	17,153
1979	19,063
1980	18,012
1981	17,535
1982	16,755
TOTAL	538,805 tonnes

TABLE 2.2: WORLD PRODUCTION OF REFINED CADMIUM ESTIMATED (1910 - 1969) AND RECORDED (1968 - 1982)

(Source: Up to 1972 - US Bureau of Mines
From 1973 - American Bureau of Metal Statistics
From 1979 - Metal Statistics (UK).)

tonnes	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982
EC	2084	2803	3215	2983	3157	3700	3885	3379	4029	4604	4080	4865	4911	4317	3937
Germany, Fed Rep	342	792	1035	982	913	1221	1338	1017	1275	1335	1181	1266	1194	1192	1030
Belgium-Luxembourg	819	949	1095	947	1150	1100	1043	950	1196	1434	1139	1440	1527	1176	1001
France	545	523	528	579	572	606	644	455	532	790	689	792	792	664	580
Italy	250	422	426	350	416	397	505	411	439	448	378	527	568	489	475
Netherlands	128	117	131	125	106	62	75	271	397	302	402	416	455	518	497
United Kingdom	205	245	318	262	240	314	280	275	190	295	291	424	375	278	354
Europe[1]	2618	3382	3940	3731	3930	4268	4475	4029	4972	5746	5282	5996	6157	5621	5114
Japan	2195	2765	2541	2675	3029	3170	3027	2657	2500	2844	2531	2597	2174	1977	2021
Asia*	2236	2805	2575	2706	3064	3203	3087	2710	2539	2928	2699	2825	2638	2390	2472
Africa	487	544	533	426	454	397	399	370	356	339	265	343	289	280	441
United States[2,3,4]	4831	5736	4293	3597	3760	3477	2970	2056	2148	2188	1708	2058	1949	1871	1351
America**	6053	6978	5609	4697	5207	5323	4897	4008	4128	4704	4095	4497	4205	4137	3657
Australia	472	571	614	560	708	676	720	549	650	671	754	804	1012	1031	1010
USSR	2200	2250	2300	2400	2600	2800	2900	2950	2900	2900	3000	3000	2900	2800	2800
TOTAL WORLD[5]	14973	17542	16526	15485	16888	17605	17456	15674	16933	18326	17153	19063	18012	17535	16755

* Including Japan
** Including US

1 - Excluding Eastern Countries
2 - Including Secondary Cadmium
3 - Cadmium sponge used directly in the production of Cadmium Compounds
4 - Source: Until 1972 - US Bureau of Mines; From 1973 - American Bureau of Metal Statistics
5 - New reporting basis from 1974

TABLE 2.3: PRODUCTION OF REFINED CADMIUM (WORLDWIDE)

Source: Commission of the European Communities (1981)[3]

tonnes	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982
EC	3533	4591	4012	3888	4512	6743	7100	4470	6653	6408	6247	6825	6307	5545	5781
Germany, Fed Rep	1702	2298	1801	1788	1964	2183	2016	1139	2100	1892	1836	2048	1767	1326	1502
Belgium-Luxembourg	608	683	781	703	1086	1357	1682	1036	1735	1636	1464	1796	1689	1732	1652
France	874	1217	988	969	1018	1094	1454	825	958	1200	1085	1078	1182	912	1017
Italy	300	350	370	320	350	430	430	360	360	380	450	400	300	300	340
Netherlands	49	43	72	108	94	110	77	75	80	50	50	-	-	-	-
Denmark	24	23	24	17	8	6	-	3	6	8	8	-	-	-	-
United Kingdom	1439	1473	1313	1176	1354	1563	1441	1032	1414	1242	1354	1445	1311	1217	1212
Europe	5305	6361	5815	5571	6199	7157	7613	4987	7296	6981	6712	7395	6823	5972	6185
Japan	1504	2033	1495	1450	1886	1475	968	444	1181	771	1131	1275	1127	1206	1143
Asia*	1591	2101	1545	1558	2092	1660	1158	699	1377	1131	1321	1559	1452	1619	1736
Africa	10	10	10	10	10	12	12	10	12	12	13	12	12	15	15
United States	6054	6832	4110	4931	5727	5685	5488	3055	5381	4064	4545	4925	3922	4543	4127
America**	6175	6972	4227	5084	5892	5879	5749	3209	5617	4303	4695	5277	4273	5198	4787
Australia	188	237	220	210	206	202	165	138	178	140	113	280	270	160	150
USSR	1735	1767	1725	1800	1850	1950	2100	2200	2300	2400	2500	2500	2400	2200	2250
TOTAL WORLD	15974	18410	14599	15322	17474	18019	18015	12520	18051	16146	16784	18493	16600	16492	16473
TOTAL PRODUCTION-CONSUMPTION	-1000	-958	+1927	+163	-586	-414	-559	+3154	-1118	+2180	+369	+570	+1412	+1043	+282

* inc Japan ** inc US - indicates sales from stocks + indicates cadmium put into stocks

Total amount of cadmium stockpiled since 1968 = 6465 tonnes

TABLE 2.4: CONSUMPTION OF CADMIUM (WORLDWIDE)

Source: Until 1972 - US Bureau of Mines
From 1973-1978 - American Bureau of Metal Statistics
From 1978-1980 - Metal Statistics Monthly (UK)

is evident that Japan is, by far, the main producer (2,021 tonnes in 1982). The European Community (EC) member states produced 3,937 tonnes in 1982, making it the main producing industrial community in the world. Within the EC the Federal Republic of Germany is the main producer, with an annual production of 1,030 tonnes in 1982 and an average growth rate of 2 to 5 per cent in the previous decade. The UK is the smallest producer of cadmium in the European Community, with an output of only 354 tonnes in 1982.

The total world consumption of cadmium in 1982 was 16,473 tonnes, the main consumer being the United States using 4,127 tonnes. The EC, however, consumed 5,781 tonnes in 1982, making it the largest consuming industrial community in the world (Table 2.4). Within the EC, Belgium and Luxembourg are the largest consumers of cadmium (1,652 tonnes in 1982), followed by the Federal Republic of Germany (1,502 tonnes) and the United Kingdom (1,212 tonnes). The Federal Republic of Germany, Belgium and the United Kingdom between them accounted for about 75 per cent of the cadmium consumed in the European Community between 1978 and 1982, while the Community's share of world consumption has decreased from about 50 per cent in 1976 to 35 per cent in 1982, a fact indicating that consumption is rising in other western countries. Table 2.5 shows the per capita consumption of cadmium in the major western countries of the world. It is evident that

Country	Cadmium Consumption 1980 (a) (tonnes)	Population (b)	Area Miles^2 (b)	Per capita Industrial Consumption g/person/yr	Consumption per square mile (Kg)
Belgium	1,652	9,863,374	11,781	167.49	140.2258
Germany (FR)	1,502	61,546,000	96,011	24.41	15.644
UK	1,212	55,776,422	93,026	21.73	13.029
France	1,017	54,335,000	213,000	18.72	4.775
USA	4,127	226,545,805	3,536,855	18.22	1.167
Sweden	150	8,327,484	176,436	18.01	0.850
Brazil	179	119,098,922	3,289,440	1.50	0.054
Australia	150	15,276,100	2,968,000	9.82	0.051
Japan	1,143	118,390,000	142,812	9.65	8.003
Italy	340	56,500,000	131,000	6.02	2.595
Mexico	352	67,383,000	761,604	5.22	0.462
South Korea	170	39,000,000	38,500	4.36	4.416
Yugoslavia	90	22,420,000	98,725	4.01	0.912
Canada	79	24,343,181	3,851,809	3.25	0.021
India	216	683,880,051	1,261,816	0.32	0.171
Africa	15	401,000,000	11,683,000	0.04	0.001

(a) - Metal Statistics (UK) (b) - Whitaker's Almanac 1984

TABLE 2.5: INDUSTRIAL CONSUMPTION OF CADMIUM IN WESTERN COUNTRIES EXPRESSED AS GRAMS PER PERSON PER YEAR AND KG PER SQUARE MILE

FIGURE 2.2 : MAP OF EC MEMBER COUNTRIES SHOWING THE WORLDS FOUR LARGEST CADMIUM CONSUMING COUNTRIES ON A PER CAPITA BASIS'

(Figures shown in parenthesis indicate per capita consumption grams/year)

Belgium is by far the largest, consuming 167.4g/person/year, with the German Federal Republic and the UK in second and third place, utilising 24.4 and 21.7 grams per person per year respectively. All the top four consuming countries in the world, on a per capita basis, are in the European Community and in very close proximity (Figure 2.2).

2.3 USES OF CADMIUM AND ITS COMPOUNDS

2.3.1 Electroplating

Since cadmium was first introduced in the 1930s it has been used in preference to zinc plating of equal thickness because it has performed significantly better in corrosion tests using salt spray. Cadmium has also been used in preference to zinc because it gives a better appearance and there are fewer problems with staining or tarnishing. Cadmium plating has, therefore, had a more widespread reputation for better quality compared with zinc plating ever since its introduction.[6,8,14]

The reputation of cadmium as a plating metal is much less justified today than it was in the past. Salt spray testing has since proved to be a poor guide to performance in atmospheric conditions and is no guide at all to corrosion performance in industrial conditions where sulphur attack on cadmium plating is the more serious problem.[6,8,15]

Despite this, cadmium does have properties which confer advantages over zinc in certain types of electroplating.[6,8,15] The main advantages are shown below:

(i) It can be deposited easily and at high rates of application.

(ii) Only a thin coating is required to give a good standard of protection.

(iii) Cadmium's electrical resistance on plated contacts is low.

(iv) Intricately shaped objects can be uniformly plated.

(v) Cadmium has a high ductility, which enables plated articles to be shaped, stamped or formed.

(vi) When cadmium corrodes it does not cause bulky corrosion products.

(vii) The metallic lustre given by cadmium is retained for long periods.

(viii) Plated articles can easily be soldered.

(ix) Corrosion resistance to alkalis, sea water, soft water and tropical atmospheres is good.

(x) The physical strength of steel objects is not adversely affected with cadmium electrodeposits.

Cadmium plating is extensively used in the motor industry for plating nuts, bolts, screws, springs, fasteners, washers, rivets, carburettor parts, magnetoes, clutch throw-out parts and plungers, on disc brake assemblies, fuel and hydraulic systems, brake line connectors, hose fittings for radiators, for power steering and air conditioning systems and on springs used for doors and latches.[6] It is also used in the aerospace industry to prevent potential differences being set up between aluminium and steel in damp conditions, to prevent attack from alkalis, and to prevent galvanic corrosion of aluminium which is the main airframe material. It has subsequently been used in planes such as the Boeing 747 and the F111.[7,8,14] The electronic industry uses cadmium plating on chassis hardware, connectors, fasteners and other components. Electrical contacts are often plated with cadmium for corrosion resistance, ease of soldering and for maintenance of gap settings under high current conditions when arcing could occur. The textile industry employs cadmium plating to avoid fabric deterioration caused by corrosion products, to provide lubricity to weaving machinery operating in highly humid conditions and to avoid jamming of machinery by build-up of corrosion products.[6] Cadmium-plated components are also used in washing machines and other laundry equipment because of its good resistance to alkalis and detergents.[6,7,8] Uses in other industries are varied but include electroplating of marine equipment, household appliance parts, hardware, piano wires, telecommunications, industrial machinery such as metal cutting machine tools, locks and springs.[7,8,14]

Despite cadmium plating having many varied uses, there would appear to be little prospect of any increase in the use of cadmium as an electro-deposit because of changes in legislation and in the general climate of public opinion concerning the use of cadmium.[16]

2.3.2 Pigments

Although naturally-occurring cadmium sulphide, found as the bright yellow mineral greenockite, was used by artists as a yellow colouring more than 2,000 years ago, it was not until the nineteenth century that cadmium sulphide and cadmium sulphoselenides were synthesised to produce a range of yellow to red pigments for artists' colours. Since then, advances in the pigment industry have led to a much wider use especially since the development and formulation of cadmium lithopones.* [11,17,19]

The main disadvantage of cadmium pigments is that they can be toxic, although this is not as great a problem as with lead pigments because cadmium pigments tend to be extremely insoluble and stable under varying conditions.[11] Nevertheless, cadmium pigments are not permitted to be used with foodstuffs and the use in enamels for coating utensils is restricted in most EC member states.[11,17-21]

The main advantages of cadmium pigments, which subsequently warrant their widespread use, are their stability to sunlight and atmospheric conditions.[20]

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* A cadmium lithopone is a cadmium pigment diluted with a 'blanc fixe' - usually barium sulphate.

They do not 'bleed', they have good hiding power and colour intensity, and are insoluble in organic solvents - a factor most important since the pigment colour must not migrate in use or in disposal. Cadmium pigments are not resistant to even dilute acids, although they are resistant to hydrogen sulphide, detergents and alkalis.[11,20]

Cadmium red and yellow colours account for the largest part of demand, accounting for greater than 70 per cent of red and yellow pigment demand in the EC. Despite cadmium pigments being relatively more expensive, they are used in preference to other pigment types because of their heat stability (which is required for pigments used in plastics, coloured vulcanised rubber, or some epoxy resins which have to be moulded at high temperatures), for their resistance to hydrogen sulphide blackening (which is required in paints and artists' colours) and for their alkali resistance (which is required in some printing inks, cosmetics such as nail polishes and face powders, and some leather finishes).[6,11,18,20]

2.3.3 Polyvinylchloride (PVC) Stabilisers

PVC components degrade during processing, and on exposure to heat and to light due to the loss of hydrochloric acid (dehydrochlorination) which results in unsaturated links in the polymer, which in turn lead to increased absorption of ultra-violet light resulting in the hardening and embrittlement of the plastic. As free hydrochloric acid acts as a catalyst in the degradation process, once it has started the degradation accelerates.[12,24] To inhibit the degradation of PVC compounds a stabiliser is added during the manufacturing process. Liquid barium-cadmium stabiliser is the most common type used, although calcium, zinc, aluminium, lithium or strontium compounds are sometimes used. The cadmium is used mainly in the form of a stearate* or laurate[Ɨ] and is widely used as a general purpose stabiliser in transparent and flexible PVC.[22] The cadmium gives clarity to the transparent PVC and prevents ultra-violet degradation; the barium provides heat stability which is a necessary requirement during the manufacture of PVC.[12,22,23,24]

The main disadvantages of barium-cadmium stabilisers is that the cadmium compound is toxic and therefore cannot be used for food packaging. The use of cadmium-barium stabilisers in plastic drinking-water pipes and fittings has also recently been questioned.[12,22,23,33]

2.3.4 Cadmium Alloys and Solders

Although cadmium is a primary constituent in many alloys it is the copper-cadmium alloys which are the most important in the EC.[10]

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* Stearate: A salt or ester of stearic acid

Ɨ Laurate: A salt or ester of lauric acid

A typical copper-cadmium alloy can contain between 0.02 per cent and 1 per cent of cadmium by weight, and is used in preference to pure copper because the cadmium increases the tensile strength and increases its resistance to wear caused by sparking and abrasion, which occurs on overhead wires on electrical rail systems - one of its main uses. Although the conductivity of the alloy is slightly impaired by the presence of cadmium, the alloys have quite wide usage in telephone cables, power cables, electrode materials and electrical contacts.[6,10,25]

Apart from copper-cadmium alloys, cadmium is also added to some lead- and tin-based bearing alloys to harden the matrix and to increase the tensile strength, with the result that the bearing capacity of the alloy is significantly increased.[6,25]

Cadmium is also used in fusible alloys. These are alloys which are bright, silvery and non-tarnishing and can be repeatedly melted without appreciable loss. This is achieved because the metals used are stable at temperatures at, or around, the melting point of the alloy in which they are contained. The physical properties of the alloys do change, however, if the alloy is treated too high above its melting point.[10,25] The main uses of fusible alloys are in light engineering industry where, because of their controlled dimensional behaviour on solidification and their relatively low melting points, they are used for support of precision engineering products during shaping and turning.[10]

2.3.5 Batteries

Batteries are generally classified either as primary or as secondary. Primary batteries may be fully discharged only once because the active chemicals are used up during the reaction which produces the electrical energy. Once the primary battery is discharged completely, it is discarded. Secondary batteries, on the other hand, may be used repeatedly because the chemical reaction which produces electrical energy can be reversed to recharge the battery.[6,13,27]

Cadmium is one of the major active materials used in secondary alkaline batteries and accounts for approximately 30 per cent of cadmium used in the EC. There are three individual types of battery which use cadmium as the negative-active material; these are the nickel-cadmium, the silver-cadmium and the mercury-cadmium cells.[13] The first of these, the nickel-cadmium cell, is by far the most commercially important and has found a wide range of uses in both the domestic and industrial markets. The silver-cadmium and the mercury-cadmium cells are much more specialised and expensive and in terms of cadmium use in the EC are relatively insignificant.[6,27]

The main advantages of nickel-cadmium batteries over lead-acid batteries are that they have a much longer working life and do not deteriorate greatly when stored for long periods. They can, therefore, be used intermittently - for emergency lighting for instance. The Ni-Cd cell can stand up to rugged use such as overcharging or excessively rapid charging. They can be charged up to 500 times, unlike lead-alkali batteries which can be used only once.[26,27] The disadvantages of the Ni-Cd batteries is that they are more expensive and have low voltage capacity per unit cell, as well as a smaller capacity per unit of weight than the lead-acid cell. Ni-Cd batteries usually take much longer to charge than the lead-acid batteries, and the 'pocket-plate' Ni-Cd cells have poor performance when discharged at a high rate in low temperatures.[13] The fact that Ni-Cd batteries take a long time to recharge is the most important factor against their widespread use. If, however, a Ni-Cd cell is produced which can be recharged quickly the market for Ni-Cd batteries is likely to increase.[6,26-28]

2.3.6 Photocells and Solar Energy

Miniature photocells have been developed which use cadmium sulphide as their primary active element, and a number of European companies have recently been developing the cells for use in large scale solar collectors. Wet electro-chemical cells, which are driven by light, have also been developed recently. These photo-electrical chemical cells consist of an anode of cadmium sulphide or cadmium selenide, and a cathode of platinum in a sodium hydroxide or sodium sulphide electrolyte. It is not considered that the above uses of cadmium would increase the demand for cadmium in the EC to any extent. However, applications may broaden with further development, with subsequent increase in cadmium demand.[6,9,29-31]

2.3.7 Cadmium Phosphors

Cadmium sulphide, cadmium tungstate and cadmium borate, as well as several other cadmium compounds, possess fluorescent and phosphorescent properties which give them widespread use as visible indicators of certain invisible particles such as ultra-violet, X-ray and alpha particles, as well as cathode rays. The cadmium compounds used in these applications have the ability to directly convert the energy of these invisible particles into visible light. Consequently, they are used in television and radar cathode ray tubes, X-ray fluorescent screens, luminescent watches, phosphorescent tapes and markers, fluorescent lamps and various electronic devices.[6,9,30]

2.3.8 Fungicides and Anti-helminthics

Cadmium succinate, cadmium chloride and cadmium pentachlorophanate are all used as fungicides to protect cloth, wood and turf particularly on bowling greens and golf courses. At one time various cadmium compounds were used as sprays for beans, tomatoes and wheat but this practice is no longer carried out due to various restrictions on the use of toxic metals for these purposes.

2.3.9 Catalysts

Various organic acids of cadmium salts have been used satisfactorily as catalysts to form unsaturated primary alcohols and esters in the polymerisation of alkylene oxides, butacliene, diolefins, vinyl compounds and propylene; they are also used in the coagulation of polyvinyl chloride and the curing of organo-polysiloxanes.[6,9,32]

2.3.10 Nuclear Reactors

Due principally to the large thermal neutron cross-section of cadmium and its subsequent ability to act as a moderator, high purity cadmium is used as a shield against neutrons and for control rods to permit control of fission reactor rates.[6] However, within the EC only the Federal Republic of Germany uses cadmium in commercial nuclear reactors, the other member states preferring the use of boron control rods.[30,32]

2.3.11 Cadmium Compounds

The use of many cadmium compounds is very varied and a number are used in applications already mentioned. The principal uses and types of primary cadmium compounds are presented in Table 2.6.

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Aston University

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TABLE 2.6: THE MAIN CADMIUM COMPOUNDS AND THEIR USES

(Source: Roskill Information Services (1977)[6])

Cadmium has many varied and unique properties which have resulted in its widespread use in its primary form and in the form of various synthesised compounds and chemicals. Although a number of these uses have substitutes to varying degrees[4] many of them are reported to have such unique properties that their use alone is necessary for certain product users.[6,9] The use of cadmium in certain industrial sectors, particularly the battery, pigment and PVC stabiliser industries, is therefore likely to increase, whereas uses in solders and certain alloys is likely to decrease. Nevertheless, other uses for cadmium are constantly being found and the increasing demand seems likely to continue.[29-32]

2.4 CONSUMPTION AND MARKET SHARES OF MAJOR CADMIUM USES IN THE EUROPEAN COMMUNITY

Despite cadmium having five major, and a whole host of minor, applications detailed statistics on end-uses are published for only four countries - Germany (FR), Japan, the United Kingdom and the United States of America. Of these, the data for the first three countries is thought to be fairly accurate, being based on monthly compilations of actual tonnage used. The United States, however, bases estimates on a percentage breakdown rather than on reported consumption, and as such the figures are, at best, only an indication of actual consumption. The four countries which record statistics for the consumption of cadmium by end-use account for at least two-thirds of the world consumption and therefore give a fairly reliable guide to the quantities of cadmium used in various applications and changes in demand.[190,191] Figure 2.3 and Table 2.7 show the major consumption and market shares for the four countries which record the end-uses for cadmium.

Table 2.8 shows the major consumption and market shares of cadmium by end-use for the European Community calculated using the data in Table 2.7.[191] It is evident that over the past ten years the market share for plating has remained steady at around 33 per cent with a total consumption of 937 tonnes in the EC in 1982. The proportions of market share accounted for by pigments and stabilisers is around 11 per cent less than it was ten years ago for the four countries recording end-uses. Consumption of cadmium for pigments and stabilisers in the EC has, however, remained stable at around 47 per cent, with a total consumption of 1,339 tonnes in 1982. The market share of cadmium used in the production of batteries has increased from 15 per cent in 1970 to 29 per cent in 1982 for the four countries which record end-use. The EC demand for cadmium for batteries has increased by only 3 per cent in the same ten-year period, with a total consumption of 396 tonnes in 1982. The market share held by cadmium alloys in 1982 was 6 per cent, some 2 per cent less than in 1973, which is a reflection of the gradual decrease in the use of cadmium in alloys. In the EC, however, demand for

TABLE 2.7: MAJOR USES OF CADMIUM - COMBINED CONSUMPTION AND MARKET SHARES FOR THE UNITED STATES, GERMANY (FR), UNITED KINGDOM AND JAPAN (1973 - 1982)

(Source: Temple (1983)[191])

TABLE 2.8: MAJOR USES OF CADMIUM - COMBINED CONSUMPTION AND MARKET SHARES FOR THE EUROPEAN COMMUNITY (1973 - 1982)

(Source: Temple (1983)[191])

%

FIGURE 2.3: CONSUMPTION OF CADMIUM BY MAJOR END-USE EXPRESSED AS A PERCENTAGE OF THE COMBINED ANNUAL TOTAL AMOUNTS USED IN THE UNITED STATES, GERMANY (FR), UNITED KINGDOM AND JAPAN BETWEEN 1970 AND 1982

(Source: Temple (1983)[191])

cadmium for alloy manufacture has remained steady at around 3 per cent, with 81 tonnes being used in 1982.[190]

A major factor affecting the use of cadmium in the European Community over the past two to three years has been the Swedish Government's ban which prohibits the use or importation of cadmium-containing articles except those for military purposes. This has affected European producers who exported cadmium-containing goods to Sweden before the ban was imposed.[192] Denmark is also considering imposing a ban on the use and import of cadmium into that country, which may affect trends in usage over the next decade.[193,194] It is also thought that other countries in the EC are considering taking similar actions. Such a ban is within the terms of the Treaty of Rome and allowed under European law on free trade, provided the country's intention is to 'protect man and his environment'.[191]

2.5 SUMMARY

It is clear that cadmium has many qualities which have lead to its widespread application in a whole range of industries. As a result, the demand for cadmium has increased dramatically over the past 50 years. Europe is now the largest producing area and Japan the largest individual producing country. Europe also consumes most of the cadmium, although the United States is the largest individual consuming country. Of the five main uses for cadmium, plating has maintained the largest share of the market in the past ten years with batteries growing in importance. The demand for cadmium in pigments, stabilisers and alloys, however, has remained fairly stable although the use of cadmium in alloys is expected to decline.[190]

In the future, cadmium production will continue to depend essentially on the level of zinc production, while consumption is most likely to be affected by the level of industrial activity, which is forecast to rise.[190] The long-term future for cadmium consumption will, however, depend to a large extent on the type of controls and regulations introduced on health and environmental protection grounds.

CHAPTER 3

EMISSIONS OF CADMIUM TO THE ENVIRONMENT

CHAPTER 3: EMISSIONS OF CADMIUM TO THE ENVIRONMENT

3.1 Natural Sources of Cadmium
  3.1.1 Cadmium-bearing Minerals
  3.1.2 Weathering of Crustal Rock
  3.1.3 Volcanic Action, Windblown Dust, Forest Fires and Plant Exudates
3.2 Background Levels of Cadmium
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  3.4.6 Phosphate Fertilisers
  3.4.7 Cement Production
3.5 Summary

CHAPTER 3: EMISSIONS OF CADMIUM TO THE ENVIRONMENT

3.1 NATURAL SOURCES OF CADMIUM

3.1.1 Cadmium-bearing Minerals

Cadmium is a relatively rare element occurring throughout the lithosphere in varying concentrations invariably associated with the occurrence of zinc. The main cadmium-bearing minerals are shown in Table 3.1, but since these minerals never occur in concentrations to warrant their commercial extraction, and since metallic cadmium is never found in nature, all cadmium is prepared commercially as a by-product of the primary metal industries, and principally of the zinc industry.

Minerals of Cadmium	Formula	Structure	Occurrence
Greenockite	CdS	Hexagonal	Common
Xanthochroite	CdS	Amorphous	Rare
Hawleyite	CdS	Cubic	Rare
Octavite	$CdCo_3$	-	Rare
Cadmoselite	CdSe	Hexagonal	Rare
Monteponite	CdO	-	Rare
Soukavite	(Hg.Cd)S	Cubic	Rare

TABLE 3.1: MAIN CADMIUM-BEARING MINERALS

Zinc Sphalerite (ZnS) often contains between 0.1 - 1.0 per cent cadmium by weight, although concentrations up to 5 per cent have been known. The average cadmium content of zinc sulphide deposits range from 0.02 to 1.4 per cent, with a median content of about 0.3 per cent Cd. Fourteen other sulphides have been reported to contain more than 500 ppm cadmium, the most important being galena (PbS) and chalcopyrite ($Cu FeS_2$)[2,36].

3.1.2 Weathering of Crustal Rocks

As cadmium is a chemical element it is not destroyed by any chemical process, and quantities discharged into the environment will always remain. They may move from one sector or compartment of the environment to another; parts are then temporarily concentrated and immobilised, but they will always remain[3]. It is essential, therefore, that emissions resulting from natural, as well as anthropogenic, sources are considered. The weathering of crustal rocks and mineral deposits and the subsequent releases of cadmium to the environment can only be estimated because of the large number of variables present in such a calculation. Table 3.2 shows the concentration of cadmium in various igneous and sedimentary rocks analysed by Atomic Absorption Spectrophotometry after an acid digestion. It is evident that concentrations vary widely, depending on the nature and origin of the

Rock Classification	Rock Type	Cadmium Content PPM	
		Range	Average
Igneous	Rhyolitic	0.03-0.57	0.23
	Granitic	0.01-1.6	0.2
	Intermediate	0.017-0.32	-
	Basalts, diabases and Gabbros	0.01-1.00	0.13
	Peridotite	<0.001-0.029	0.03
	Durite	0.005-0.154	-
	Eclogites	0.03-1.6	0.1
	Alkalic rocks	0.04-0.90	0.25
	Syenitic rocks	-	0.13
Sedimentary	Limestones	-	0.10
	Sandstones	-	<0.03
	Shales	0.3-11.0	1.4
	org.C[a].<0.5%	<0.3-0,8	0.35
	org.C 0.5-1.0%	0.3-1.8	0.8
	org.C >1%	0.5-8.4	2.0
	Oceanic Sediments	0.04-1.88	0.5
	Lake Sediments	5-19	11
	Oceanic Mn Oxides	<3-21.2	8
	Phosphorites	<10-500	25
	Sea Water	-	0.1[b]
	Coal	0.2-30	0.5
	Coal Ash	-	0.1

a - Organic Content

b - Parts per Billion or Parts per Thousand Million

TABLE 3.2: CADMIUM CONTENT OF IGNEOUS AND SEDIMENTARY ROCKS

(Source: Fleischer (1974)[2] and Fulkerson (1973)[36]) rock. In general, however, igneous and metamorphic rocks contain less than 1 ppm, whereas sedimentary rocks show a higher cadmium content, this being concentrated in shale rich in organic matter which may have concentrations up to 11 ppm or more.

During weathering, cadmium sulphate and chloride salts are readily formed which are easily dissolved in acidic conditions such as those present in certain soils, ground waters and in acid rain. The subsequent fate of the dissolved cadmium depends not only on the Eh-pH conditions but also on the type of soil/country rock/water body in which the solution is in contact[2]. In general, however, the cadmium is precipitated fairly rapidly because it can be strongly absorbed onto solid materials whether suspended in the water body, deposited on the river bed or in a soil. For this reason, a large proportion of water-borne cadmium is eventually concentrated in river and lake muds usually bound to organic matter. It is due to these processes that sedimentary rocks contain higher levels of cadmium than igneous or metamorphic rocks.

3.1.3 Volcanic Action, Windblown Dust, Forest Fires and Plant Exudates

Volcanic action transports cadmium up from the lower crustal regions of the earth to the land surface and to the atmosphere[38]. Sub-marine volcanic activity will release cadmium directly into the sea and subsequently into the atmosphere from sea-spray.

Estimates of world-wide emissions of cadmium from volcanic action, windblown dust, forest fires, vegetation, seasalt sprays and natural rock degasification have been collated by Nriagu[39]. (Table 3.3)

TABLE 3.3: WORLDWIDE EMISSIONS OF CADMIUM FROM NATURAL SOURCES

(Source: Nriagu J O (1979)[39])

This author calculated that volcanic emissions accounted for 60 per cent of the cadmium emitted from natural sources compared with emissions of Nickel, Lead, Zinc and Copper of 15-25 per cent from the same source, and this reflects the abnormally high enrichment of cadmium in volcanic aerosols. Indeed Van Enk[40] has estimated the contribution of volcanic activity in the world to the average cadmium content of air in the European Economic Community to be 0.005 ng/m^3, considering a homogenous distribution.

Emissions from forest fires and seasalt sprays, on the other hand, represent only minor sources of cadmium in the global atmosphere, generally accounting for 10 per cent of the natural cadmium emissions.[39] Natural rock degassing has also been suggested as a significant source of airborne cadmium, but the contribution from this source is, as yet, unquantified.

Eroded soil particles account for approximately 6 per cent of natural cadmium emissions with plant exudates surprisingly accounting for approximately 22 per cent of natural cadmium emissions to the atmosphere.

3.2 BACKGROUND LEVELS OF CADMIUM

In order to assess the extent to which man's activities have increased the levels of cadmium in the environment it is necessary to establish the natural concentrations of cadmium in uncontaminated soils, natural waters and the atmosphere.

3.2.1 Soil

The available data indicates that the level of cadmium in uncontaminated soils ranges from 0.01 to several parts per million (ppm). In areas of mineralisation and close surface deposits, the cadmium level may reach 0.01 per cent (100 ppm). Vinogradov[41] who has analysed over 2,000 soil samples from a wide variety of soil types in the USSR has found cadmium concentration ranging from 0.01 to 0.7 ppm, with most values around 0.1 ppm. Vinogradov[41] has also itemised a number of generalisations regarding the concentration of cadmium in soil. He has suggested:

(i) The amount of cadmium in soils is highly dependent on the underlying rock. For granite, he reports an average of 0.1 ppm cadmium with a corresponding value for basic igneous rocks of 0.2 ppm.

(ii) The amount of cadmium in soils containing appreciable amounts of organic matter or humus is higher than in low-organic soils. Higher concentrations are also observed in soils with low permeability (clays) compared to loose-textured soil (sands, permeable podsols and laterites). This is due to the greater tendency for cadmium to be leached to the subsoil system in soils with loose texture and low absorbtivity.

(iii) Cadmium mobilisation is low in alkaline soils rich in limestone ($CaCo_3$) and high in acid soils with a pH <5.

Work by Lagerwerff[42] has indicated typical low, average and high concentrations of cadmium in soils of 0.11, 0.34 and 0.56 ppm respectively. Schroeder[43,44] on the other hand reports a cadmium content of 0.15 ppm for unfertilised soils, 0.8 ppm for tilled but unfertilised soil, and 3.38 ppm for phosphate fertilised soils.

As river and stream sediments trap a proportion of the cadmium which is eroded from surrounding rocks and soils, they provide useful indicators of localised natural cadmium levels. Extensive studies of river and stream sediments in England and Wales have been carried out for some twenty major and minor elements, including cadmium[45,46]. These studies have shown typical soil cadmium levels from <1.0 in the south east to >4.0 ppm in areas associated with sulphide mineralisation such as the south west, central England and Wales.

3.2.2 Fresh Water

Within the past 20 years there have been many studies of metals, including cadmium, in fresh waters in many European countries including the UK.[47,54] The occurrence in drinking water has been of special interest, since this directly affects man's intake. It has been concluded by the Department of the Environment[38] that the mean concentration of cadmium in uncontaminated surface waters in the UK is unlikely to exceed 0.001 to 0.002 ppm, and that even in urban areas 0.005 ppm is not normally exceeded. In mineralised regions, however, water can often be contaminated with cadmium, particularly in places where ores (especially Zinc) have been actively worked.

In addition to considering the total quantities of cadmium found in fresh water, it is essential to mention the different chemical and physical types of cadmium which may be present.[38] Cadmium can occur in a variety of inorganically bound forms, organically combined or physically absorbed onto particulates or colloidal matter. These various forms are likely to have differing effects on the toxicity and ease of removal from solution.

3.2.3 Air and Dusts

Individual volcanic incidents can release quite large quantities of cadmium to the atmosphere. These particulates can often be in the smaller particle size (<2 um in diameter) and are consequently suspended in the atmosphere for considerable periods, eventually becoming widely dispersed throughout the world. The Department of the Environment[38] has conducted a nationally co-ordinated programme of monitoring airborne cadmium at 20 urban sites across the country, which shows an annual mean concentration of cadmium in the atmosphere of 0.01345 ug/m^3.[55] (Table 3.4a). Given a mean natural atmospheric cadmium level of 0.01345 ug/m^3 (range 0.0009 - 0.026 ug/m^3) levels currently found in industrial areas can be compared with this.

Natural deposition of cadmium from air is shown in Table 3.4b. The deposition rate varies from region to region as a result of various meteorological, geological and geographical factors. It seems, however, that natural deposition of cadmium is in the range of 0.04 to 0.2 ug/m^2/month with a mean value of 0.1 ug/m^2/month.

TABLE 3.4a NATURAL LEVELS OF CADMIUM IN SOIL, WATER AND AIR

(Source: Inter Research Council Committee on Pollution Research (1973)[55])

Cadmium Deposition ($ug/m^2/month$)	Location
0.040	Residential areas, USA
0.1 - 0.06	Remote, Finland
0.2	UK, rural areas

TABLE 3.4b: NATURAL DEPOSITION OF CADMIUM FROM AIR

3.2.4 Summary

From the data presented in this section it is clear that cadmium is naturally present in soils, water and air and that there are no areas which are totally free of cadmium. This is an important consideration before examining anthropogenic emissions of cadmium and levels currently found in European urban/industrial areas.

3.3 INDUSTRIES DIRECTLY ASSOCIATED WITH CADMIUM

Direct atmospheric emissions to the environment from cadmium-using industries are estimated to be 5.2 per cent of the total annual amount of cadmium used industrially in any one country.[56] In the EC, this represents an emission of 300 tonnes of cadmium to the environment in 1983 and similar amounts in previous years.

Very little cadmium is ever recycled and consequently the ultimate fate of all cadmium incorporated in various products is to the environment. Indeed, it has been estimated that nearly one-third of the cadmium used each year reaches the environment within a few months, and that all cadmium ultimately reaches the environment.[56,57] A recent American study[58] and two European studies[5,57] have shown that the most significant sources of cadmium to the environment are from industries and human activities not directly associated with cadmium, the main sources being metallurgical processing (smelting operations), the incineration of metal-bearing refuse, and the combustion of fossil fuels. These sources are thought to contribute more than 90 per cent of the total cadmium emitted to the atmosphere, the burning of oil, tyres, PVC plastics and domestic waste also contributing.

Water pollution by cadmium is thought mainly to be a result of hydrometallurgy, mining, electroplating, landfill leachate and phosphate fertiliser processing. It is thought that elevated soil cadmium levels are a result of atmospheric fallout, phosphate fertiliser application and the addition of sewage sludge.[57]

Figure 3.2 summarises the principal sources of cadmium as a pollutant in an urban/industrial area. It is evident that the sources are mainly from industries and activities not directly associated with cadmium. Indeed, most of the potential sources of environmental contamination are as a result of the use and disposal of products from the cadmium-using industries, and from primary raw materials which contain trace amounts of cadmium, such as phosphate rock (fertiliser production) and fossil fuels. Generally, in the past, secondary sources of cadmium have to some extent been neglected in preference to studying primary sources of cadmium pollution. The following text, however, summarises all the human activities and industries which give rise to cadmium emissions, and assesses their relative significance in the European Community (EC).

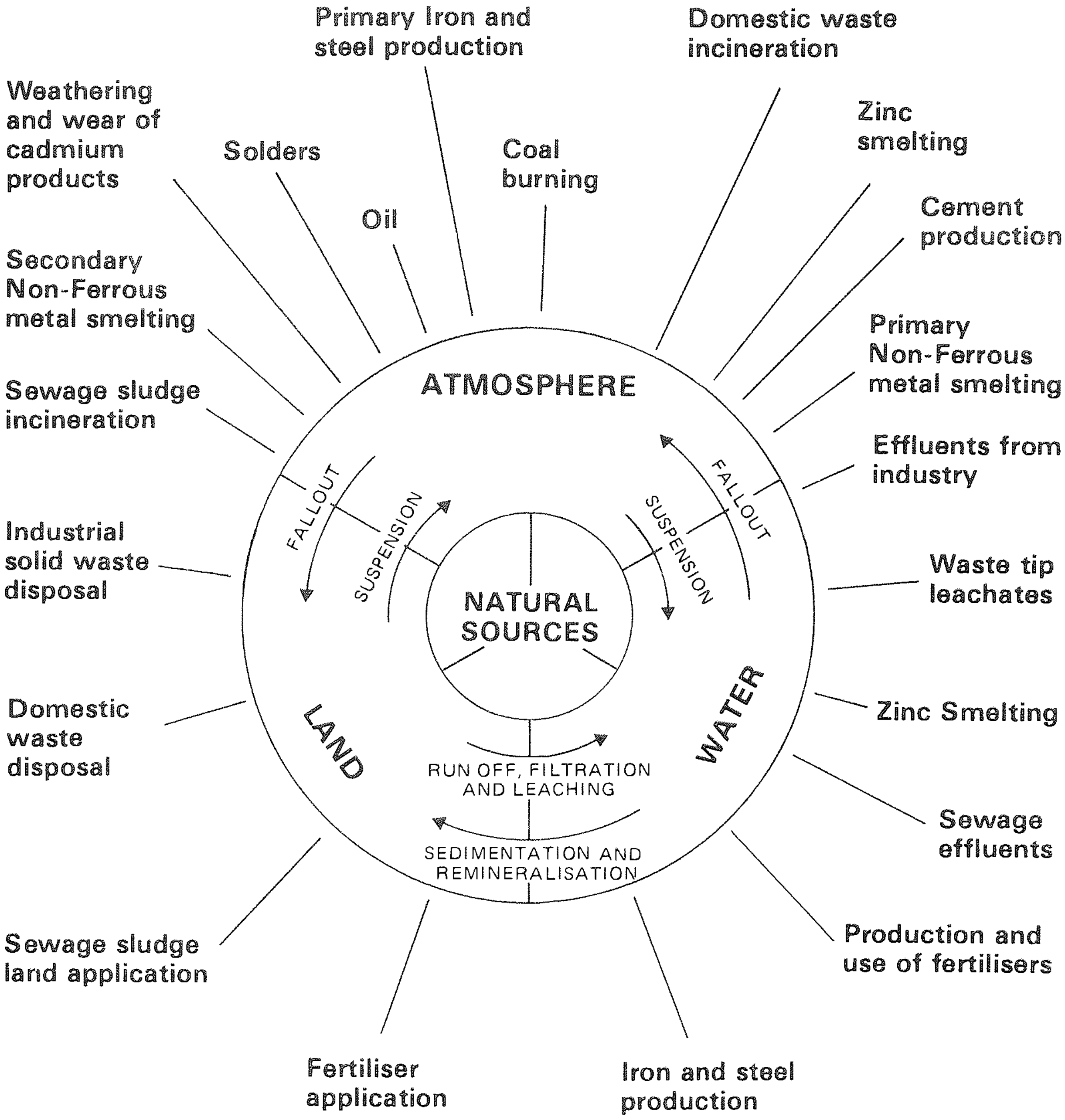

Figure 3.2 Principle sources of cadmium as a pollutant in an urban/industrial area

3.3.1 Production of Non-ferrous Metals

Cadmium containing minerals such as greenockite (CdS), cadmaselite (CdSe) and octavite ($CdCo_3$) never occur in concentrations to warrant their commercial extraction and, as referred to earlier, since metallic cadmium is never found in a natural form, all cadmium is prepared commercially as a by-product in the primary metal industries, and principally the zinc industry. Minor quantities arise from the smelting of lead and copper concentrates and from the treatment of secondary materials such as scrap. Cadmium is recovered with zinc, usually from polymetallic ores containing lead and copper to varying degrees. The cadmium, however, is generally held within the zinc sulphide mineral itself and is collected with the zinc. The cadmium content of the final zinc concentrate is usually around 0.5 per cent but may be as much as 1.5 per cent.

Initially, therefore, cadmium may be emitted to the environment from ore extraction and ore benefication practices before the concentrates reach the smelter. It is suggested that the Japanese Itai-itai problem was caused by such mining and ore benefication practices[60] and has also resulted in gross environmental contamination in other countries with similar practices.[59] Within the EC there are fifteen zinc-lead mines, nineteen zinc/cadmium refineries and three secondary cadmium refining plants (Figure 3.3). Production of primary concentrates by EC member states is relatively small and consequently over 60 per cent of concentrates are imported, chiefly from Australia, Peru and Canada.[61]

Zinc and cadmium are extracted from the concentrates by either pyrometallurgical or electrolytic processes and the cadmium is recovered and refined at various stages of the process. Both processes share a common initial step which involves the roasting of the ore concentrates to convert the natural zinc sulphide to zinc oxide. The next stage in the thermal refining process is the roasting of the concentrate at 700 to 1200°C under oxidising conditions in a sinter plant. This removes most of the sulphur and produces a 'blocky' sinter which is fed into the furnace as a charge.[9] As the cadmium contained in the concentrate is more volatile than zinc at the roasting temperatures, up to 70 per cent of the cadmium may be volatilised and collected as dust and fume. The collected material, which may contain up to 20 per cent cadmium and some lead, is leached with sulphuric acid, firstly to precipitate the lead as lead sulphate and then, in a second step, to precipitate cadmium as a metallic sponge by slowly adding zinc dust to the cadmium sulphate solution. The 'sponge' is subsequently dried and refined to a metal form.[9] The cadmium metal which remains in the

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Figure 3.3 Location of mines, smelters and refineries for zinc and cadmium production in the European Community

(Source: Hiscock (1978[61]))

sinter is later volatilised and condensed with the zinc to produce a zinc-cadmium alloy containing approximately 15 per cent cadmium. The alloy is subsequently redistilled under reducing conditions to produce pure zinc and pure cadmium which are cast into ingots. The cadmium is later re-melted and made into triangular cadmium sticks and cadmium balls before leaving the smelter.[9]

In the electrolytic process, the roasted desulphurised ore is leached with sulphuric acid to produce a zinc sulphate solution. Cadmium and other impurities such as lead are then precipitated into a sponge by the addition of zinc dust. The cadmium-rich sponge and the zinc sulphate solution are then processed separately in electrolytic cells.[9,57]

Emissions of cadmium from zinc refining in the EC have been reported in two recent studies.[57,62] These studies concluded that both electrolytic and thermal refining processes discharge cadmium-rich dusts into the atmosphere during the delivery and handling of zinc ores and concentrates. These emissions, however, consist of relatively large particles and tend to fallout close to the plant. Stack emissions from thermal facilities, on the other hand, tend to be greater in quantity due to the high temperatures involved in the smelting process and these will tend to remain airborne for greater periods due to their small particle size. Within the EC, of the nineteen primary zinc plants in operation only five are essentially thermal facilities, and emissions from these are shown in Table 3.5.

TABLE 3.5: THERMAL ZINC PLANTS IN THE EUROPEAN COMMUNITY: ZINC PRODUCTION AND ESTIMATED AIRBORNE CADMIUM EMISSIONS DURING 1979

(Source: Hutton M (1982)[57])

Liquid wastes containing cadmium are mainly derived from the use of gas-washing devices. In electrolytic facilities waste water can be recycled and metals electrolytically removed. However, waste waters from thermal plants tend to be a much larger problem as they are often discharged to adjacent water systems after undergoing primary settlement. It has been estimated that 50 tonnes of cadmium was released into waters in the EC from zinc production in 1979[57] and that this level of discharge has increased cadmium levels found in estuarine and coastal waters.[63]

The main solid waste produced by thermal facilities is smelter slag. This is reported to contain low levels of cadmium and seems not to present any disposal problems. Leach residues from electrolytic plants, however, can contain high levels of cadmium and must be disposed of with care. It has been estimated that 200 tonnes of cadmium enters landfills each year from zinc production, most of which consists of leach residue from the electrolytic plants. These leach residues are disposed of in landfills constructed with an impermeable under-layer and are thought not to present an environmental hazard, at least in the short term.[57]

Apart from zinc production, cadmium can be emitted during the primary and secondary production of copper and lead.[38] The primary production of copper from ores involves very similar operations to those for zinc and hence emission sources are similar. At present in the EC, primary production of copper is carried out in two member states, namely Belgium and the Federal Republic of Germany, which had a combined output of 159,700 tonnes in 1979. Much larger quantities of copper, however, are produced from refining copper blister* estimated to be 487,000 tonnes in 1979.[57] The temperatures used in copper refining are in excess of 1200°C and consequently any cadmium in the concentrate is volatilised. A recent US study[64] has estimated that 3 grams of cadmium per tonne of refined copper is emitted, which would mean an estimated atmospheric emission of 1.5 tonnes to the EC in 1979 from primary copper production.[57] Secondary production of copper from scrap is more widespread in EC member states. In 1976 secondary copper production totalled 1.13 million tonnes with an estimated atmospheric cadmium emission of 4.5 tonnes.[57,65] Total emissions of cadmium to the atmosphere from primary and secondary copper production in the EC is therefore calculated to be 6 tonnes per year, and the total discharge of cadmium to landfill sites from copper production is estimated to be around 15 tonnes per year.[57]

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* Copper blister is copper ore which has had excess sulphur removed, and fired at 1200°C to produce a 'blocky' copper-rich mass suitable as a furnace charge.

Production of lead in the EC in 1979 was suggested to be 1,252,000 tonnes[65], a third of which was derived from secondary materials, mainly discarded lead-acid batteries. A recent US study has estimated that 2.5 grams of cadmium per tonne of refined lead is emitted to the atmosphere, which would give an emission of 5 tonnes of cadmium per year in the EC.[66] Emissions of cadmium to water and landfill have additionally been estimated to be 20 tonnes and 40 tonnes respectively.[57]

3.3.2 Electroplating

Cadmium is normally applied by electro-deposition from cyanide or acid solutions in barrels or vats. Cadmium can also be applied by mechanical plating, vacuum deposition and metal spraying, but of these only mechanical plating is widely used commercially. Over 90 per cent of all cadmium coatings are produced by electroplating from an alkaline cyanide solution prepared from cadmium metal or oxide, cadmium or sodium cyanide and sodium hydroxide, together with various additional agents. A typical cadmium plating line is shown in Figure 3.4. Each of the processes in the plating line is a potential source of cadmium contamination in plant effluents.

The possible fate of cadmium in the electroplating industry of each member state of the EC is presented in Table 3.6. Losses have been estimated to occur at a rate of 10 per cent to aqueous wastes, during production of which 50 per cent is retained in sludge form and disposed of to landfill, and 50 per cent in water which is discharged to the foul sewer. Of the cadmium present on the finished product 60 per cent is landfilled and 40 per cent enters the scrap steel cycle.[57]

FIGURE 3.4: A TYPICAL CADMIUM PLATING LINE

(Source: Methods for Managing Cadmium Wastes in the Electroplating Industry
by K J Yost (1979)
Published by the Cadmium Council (USA)[67])

TABLE 3.6: FATE OF CADMIUM ASSOCIATED WITH ELECTROPLATING MANUFACTURE AND DISPOSAL IN THE EC (1975).

(Source: Hutton 1982[57])

3.3.3 Alloys

Very little data is available from which to quantify the emissions of cadmium to the environment from the manufacture and disposal of cadmium-containing alloys. A recent study, however, has suggested that losses of cadmium to landfill sites and water from alloy manufacture are relatively insignificant, and emissions to the atmosphere are probably less than 3 tonnes per year.[57]

3.3.4 Stabilisers

Cadmium-barium compounds in both liquid-solvent and powder form account for approximately 20 - 30 per cent of the total quantity of PVC stabilisers used today.[12] The powdered cadmium compounds are usually produced by a fusion process or a precipitation process, usually starting from cadmium metal or cadmium oxide as the raw material.

Losses to air occur in the production of stabilisers in powder form due to the drying, grinding and packing of the stabiliser. There are, however, hardly any losses to air in the manufacture of solvent-based products. Most of the dust lost is usually recovered by fine dust filters and mixed and sold with the stabilisers without any necessary treatment. Filter dust from the purification of exhaust air, which cannot be recycled, is normally disposed of at licensed waste disposal sites.

It has been estimated that 4 per cent of cadmium used in the production of barium-cadmium stabilisers is lost before the product leaves the manufacturer.[57] Within the EC, 722 tonnes of cadmium is used in stabiliser manufacture per year, 14 tonnes of which is emitted during manufacture. However, all 722 tonnes ultimately enters the waste disposal pathway, and should the waste be incinerated the cadmium will volatilise and be emitted to the atmosphere.

3.3.5 Pigments

It has been reported by pigment manufacturers that 0.75 per cent of total cadmium used is lost to water and air during production of cadmium pigments.[68] The EC member states, in 1979, had a combined usage of 1,322 tonnes of cadmium per year in pigment manufacture, which would yield an emission of 10 tonnes of cadmium to water and air. However, all 1,322 tonnes of cadmium used annually in pigment products ultimately enters the waste disposal pathway and is finally incinerated (and emitted to the atmosphere) or landfilled.

3.3.6 Nickel-Cadmium Batteries

Of the 900 tonnes of cadmium estimated to be used in Nickel-Cadmium Battery manufacture in 1979, 50 per cent was used for pocket plate cells and 50 per cent for sintered-plate or sealed cells. It has been estimated that 24 per cent (218 tonnes) of cadmium used in battery manufacture in the EC in 1979 was recycled, the remainder being discharged to landfill (22 tonnes), water (13.7 tonnes) and waste disposal (646 tonnes).[57,68] The emissions of cadmium to the environment from the manufacture of pigments, stabilisers and batteries is summarised in Table 3.7.

Use	Cadmium consumption (tonnes)	Compartmental Flow of Cadmium (t)			
		Landfill	Water pathway	Waste disposal	Recycle
Pigments	1315	-	26	1289	
Stabilisers	722	7	7	708	
Ni-Cd batteries	900	22	13.7	646	218

TABLE 3.7: FATE OF CADMIUM ASSOCIATED WITH THE MANUFACTURE AND DISPOSAL OF PIGMENTS, STABILISERS, AND NICKEL-CADMIUM BATTERIES IN THE EC (1975).

(Source: Hutton M (1982)[57])

(Consumption data for pigments and stabilisers refer to 1975; those for batteries are Hutton's estimate for 1980 assuming an annual increase of 5% from 1975.)

3.4 OTHER SOURCES OF CADMIUM TO THE ENVIRONMENT

3.4.1 Primary Iron and Steel Industries

Cadmium is present as a trace element in most metallic ores and also in certain fuels used in smelting and refining. The processes used in the iron and steel industry generate temperatures in excess of 1200°C which are needed to completely reduce the primary ore and scrap charge. As cadmium is volatilised at temperatures in excess of 700°C, much of the cadmium contained in the ore and scrap charge is converted to cadmium fume and fine particulates, which are difficult to capture with current control technologies.[4] Losses of cadmium to water will also occur, and a certain proportion of cadmium will remain in slags as well as in the iron and steel products.

A recent study in the UK has shown the environmental flow of cadmium through the iron and steel industry.[69] This study has shown that most of the cadmium emitted during the production of iron and steel is derived from scrap which contains a high proportion of cadmium-plated steel. The emissions of cadmium to air, solid waste and slags from each of the principle iron and steel production processes is given in Table 3.8.

Process	Emission Factor ($gCdt^{-1}$ material produced) Atmosphere	Solid Waste (flue dust)	Slag
Sinter Production	0.08	0	0
Iron Production	0	0.67	ND
Basic Oxygen Steelmaking	0.02	0.36	1.11
Electric Arc Steelmaking	0.40	3.65	0.29
Open-hearth Steelmaking	1.0	ND	ND

ND = No Data

TABLE 3.8: CADMIUM EMISSION FACTORS FOR THE EUROPEAN IRON AND STEEL INDUSTRIES

(Source: Prater (1981)[69] and Hutton (1981)[57])

In 1979 the EC member states produced 139 million tonnes of iron and steel, emitting a total of 383 tonnes of cadmium per year. Approximately 34 tonnes of cadmium was released to air, 229 tonnes as flue dust (which is disposed of to landfill) and 120 tonnes which was left in furnace slag. A further 70 tonnes of cadmium was also retained in the steel product.[57] The emissions of cadmium from iron and steel industries in each EC member state is presented in Table 3.9.

TABLE 3.9: ESTIMATED DISCHARGES (IN TONNES) OF CADMIUM FROM EC IRON AND STEEL INDUSTRIES IN 1979

(Source: Hutton M (1981)[57])

3.4.2 Foundry Industry

The Primary Iron and Steel industry estimated that most of the cadmium introduced into their industry came from steel scrap which contained pockets of cadmium in the form of plated and painted articles.[69] It was this which accounted for the high cadmium content of electric arc furnace fume and dust (317 ug/g^{-1}) because electric arc furnaces run predominantly on charges of scrap material.

The ferrous scrap, including galvanised and cadmium-plated material, which is recycled in the primary iron and steel industry is also used in the secondary iron and steel smelting industry, ie the foundry industry, as it is often referred to, but to a much greater extent and with less pollution control equipment, if any. Data on the actual level of cadmium in ferrous scrap are not readily available, but a level of 5.5 ug/g has been estimated for the UK.[38,69]

The UK foundry industry smelted 2.66 million tonnes of scrap charge in 1981[85] which would contain 14.6 tonnes of cadmium, assuming a concentration of 5.5 ug/g.* The foundry industry therefore produces 5.12 per cent of the UK's iron and steel. If it is assumed that scrap utilised in other EC member countries contains similar levels of cadmium (5.5 ug/g) and that 5.12 per cent of national iron production was produced by the foundry industry, then 102 tonnes of cadmium would have entered the EC foundry industry in 1979. Emissions of cadmium to the atmosphere can occur at seven stages in the foundry smelting process (Figure 3.5). If it is assumed that the atmospheric emission factor would be the same as for an open-hearth furnace (1g/Cd/tonne) then 18.5 tonnes of cadmium would be emitted to the atmosphere from the foundry industry in the EC. If 20 per cent of the

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* 100 units of scrap produces 60 units of casting. 40 per cent of scrap is therefore foreign matter.

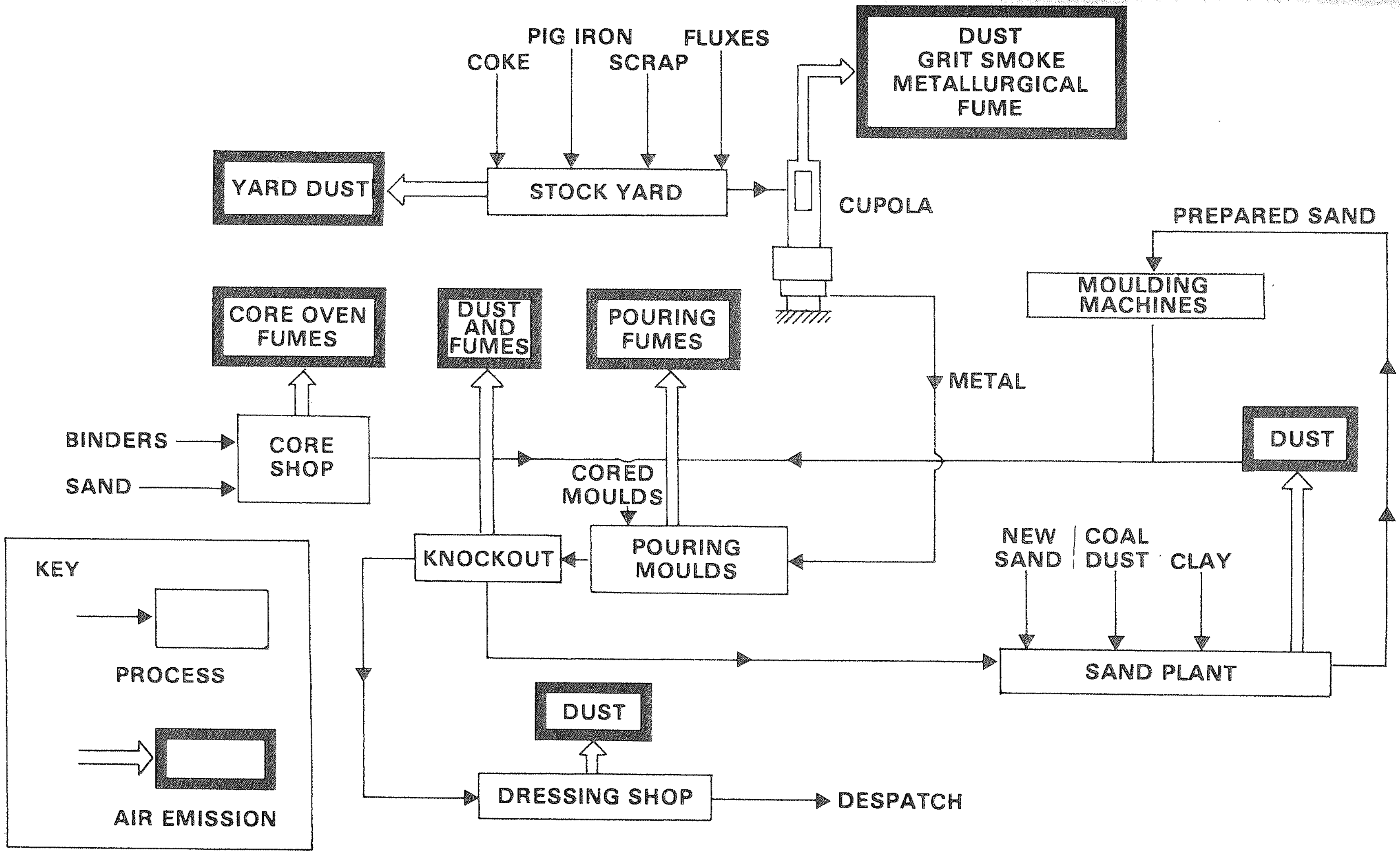

Figure 3.5 Diagram showing the main processes in a Cupola iron foundry, and the main sources of atmospheric Cadmium emissions

cadmium remains in the product as in the primary iron and steel industry, the discharge of cadmium to slag and the finished product would be 63.5 and 20 tonnes respectively. (Table 3.10)

3.4.3 Combustion of Fossil Fuels

Coal

All fossil fuels, including coal, contain cadmium to varying degrees. The emission of cadmium from the combustion of these fuels, however, is strongly dependent on the collection efficiency of the emission technology being used and the cadmium concentration in the fuel.

The cadmium concentration in a variety of British and West German coals has been reported in the literature to be in the range of 0.25 to 10 ppm, with a mean value of approximately 1 ppm.[2,70,71,72] In the EC at present, the largest coal consumer is the electricity generating industry and coke ovens, which accounted for 56 per cent and 29 per cent of coal consumption respectively in 1978.[57] On combustion in a power plant the cadmium contained in the coal is released at the firing temperatures, which may reach 1500°C, and is carried away with other metallic elements in the flue gases. A feature of cadmium, and other trace elements present in coal, is their tendency to concentrate on the finer particles of dust. Sometimes these can increase particle size by

Member State	Iron and Steel Production (tonnes x 10^6)	Secondary Scrap (tonnes x 10^6)	Cadmium Content (tonnes)	Discharge Medium (tonnes)		
				Air	Solid Waste and Slag	Product
Italy	50.3	2.573	14.2	2.6	8.8	2.8
Luxembourg	16.2	0.829	4.6	0.8	2.9	0.9
The Netherlands	13.2	0.675	3.7	0.7	2.3	0.7
United Kingdom	52.0	2.66	14.6	2.7	9.0	2.9
German FR	117.2	5.995	33.0	6.0	21.0	6.6
Belgium	35.7	1.826	10.0	1.8	6.2	2.0
France	76.5	3.913	21.5	3.9	13.3	4.3
Denmark	0.7	0.036	0.2	0.04	0.12	0.04
TOTAL			101.8	18.54	63.62	20.24

TABLE 3.10: ESTIMATED DISCHARGE OF CADMIUM (TONNES) FROM THE EC FOUNDRY INDUSTRY

one or two orders of magnitude because the finer ash particles attract a higher proportion of the more volatile elements as a function of their higher surface area to mass. These fine particles (< 1 um) are most likely to escape collection in the stack and become dispersed in the atmosphere.

An emission factor of 0.02 g of cadmium per tonne of coal calculated from published data[39,66] by Hutton[57] would mean an atmospheric emission of cadmium of just under 6 tonnes in the EC, using coal consumption figures for 1978. From Table 3.11, however, it is evident that the UK and the Federal Republic of Germany account for two-thirds of this emission.

TABLE 3.11: ESTIMATED DISCHARGES OF CADMIUM FROM COAL CONSUMPTION IN THE EC IN 1978

(Source: Hutton (1981)[57])

Oil

Data on crude oils by Israelyon[73] and by Porfinev[74] indicate ranges of cadmium content from 0.16 to 16 ppm. Other authors have found 0.42 - 0.53 ppm cadmium in heating oils, 0.07 - 0.10 ppm in diesel oils, and 0.20 - 0.26 ppm in motor oils[2] indicating that the trace metal content of oils is reduced on refining. A recent study has taken a mean value of 0.05 ug/g of cadmium in crude oil and proposed an emission estimate of 0.001 grams of cadmium per tonne consumed.[57] In 1978 the EC consumed 301 million tonnes of fuel oil which has been estimated to have given an atmospheric emission of 0.5 tonnes of cadmium, with a further 14.5 tonnes left in ashes which were disposed of to landfill sites.[57]

Gas

A recent UK study[38] has suggested cadmium has not been detected in natural gas, although Heinrichs[75] has found cadmium levels of 0.005ppm in natural gas - one hundred times less than heating oil. It would seem, therefore, that cadmium emissions from the combustion of natural gas is negligible.[5]

3.4.4 Refuse Disposal

The principal sources of cadmium in domestic refuse are cadmium-stabilised plastics, cadmium-pigmented articles, plated scrap, batteries, cadmium-soldered articles and cadmium alloys, as well as trace amounts in other waste fractions such as coal ash from domestic fires. Measurements of the amount of cadmium contained in domestic refuse ranges from 9-140 ug g^{-1} although a mean value of 15 ug g^{-1} is generally accepted.[12,57,78]

In 1977 the EC generated 97.7 million tonnes of waste with an estimated cadmium content of 1,465 tonnes (23 per cent of cadmium consumed in the EC in 1977). The UK and FR Germany are the two main contributors, together accounting for over half of this total. (Table 3.12). It has been calculated that 80 per cent of waste generated in the EC is landfill, which indicates that 1,152 tonnes of cadmium enters landfill sites.[57,78,79] The remaining 20 per cent of refuse, containing an estimated 313 tonnes of cadmium, is incinerated. The quantity of refuse incinerated by each EC member state is presented in Table 3.13.

A number of studies in the UK[77,80] have found high levels of cadmium associated with fly ash from waste incinerators, and a recent US study[76] has shown that up to 90 per cent of the cadmium present in domestic waste is volatilised and emitted to the atmosphere in the form of aerosols and fine particulates (< 1 um). Other studies have suggested that as little as 10 per cent of the cadmium is emitted, the other 90 per cent remaining in the ash. If it is assumed that 50 per cent of the cadmium present in refuse is volatilised and a further 10 per cent is captured in particulate control devices[76] then atmospheric emissions of cadmium in the EC from this source in 1977 would be 129 tonnes. The remaining cadmium, 32.3 tonnes, is captured in fly ash, and 161.5 tonnes in bottom ash which would be disposed of to landfill.

TABLE 3.12: QUANTITY OF REFUSE GENERATED IN THE EC IN 1977 AND ESTIMATED CADMIUM INPUTS FROM DIRECT LANDFILL

(Source: Hutton M (1981)[57])

The total of 193.8 tonnes of cadmium present in these ashes is thought to be a greater potential environmental hazard than the 1,152 tonnes estimated to be discharged directly to landfill in waste. This is due to the high solubility of cadmium in fly ash which will ultimately lead to leaching from landfill sites.[57,78]

TABLE 3.13: QUANTITY OF REFUSE INCINERATED IN THE EC IN 1977 AND ESTIMATED CADMIUM DISCHARGES

(Source: Hutton M (1981)[57])

3.4.5 Sewage Sludge Disposal

The precise origin of cadmium found in sewage has not been well established. In a UK study, however, the mean concentration of cadmium in sludges from sewage works receiving no industrial effluent was 7.5 mg kg^{-1} compared with 30 mg kg^{-1} (range 0-630 mg kg^{-1}) found in sludges containing industrial effluents.[5,38,82,82] This indicates that most of the cadmium contained in sewage sludges is a result of industrial discharges to foul sewers. Indeed, on the basis of unpublished monitoring data a UK Water Authority has suggested that only 20 per cent of cadmium is domestically derived, the remaining 80 per cent originating from industrial sources.[38]

Production of sewage sludge in the EC has been calculated to be 5.5 million tonnes (dry weight) in 1980. If it is assumed that the sludge has a mean cadmium content of 30 mg kg^{-1}, an estimated 165 tonnes of cadmium was present in sewage sludge generated in the EC in 1980.[57] Sewage sludge disposal practices vary between each member state of the EC although detailed information is available only from The Netherlands, The United Kingdom and The Federal Republic of Germany (Table 3.14). Using these figures a recent study has estimated that 75 per cent of sewage sludge generated in the EC is disposed of to land, 20 per cent to sea and 5 per cent is incinerated.[57]

TABLE 3.14: SEWAGE SLUDGE DISPOSAL PATTERNS FOR THREE MEMBER STATES OF THE EC

(Source: Hutton (1981)[57])

A recent study of atmospheric emissions of heavy metals from sewage sludge incinerators in the UK[38] has found that one-third of cadmium present in sewage sludge can be emitted as fine particulates and fume, the remaining two-thirds being disposed of with ashes to land. Using the sludge disposal patterns presented in Table 3.14 for all EC countries it has been calculated that 2.75 tonnes of cadmium is emitted to the atmosphere, 33 tonnes to water and 129.25 tonnes to land from this source.

3.4.6 Phosphate Fertilisers

Phosphate fertilisers are produced from one main raw material, a calcium/phosphate concretion commonly known as 'phosphate rock'. The phosphate rock, having resisted the leaching effects of water for centuries, is quite insoluble and, under most farming conditions, is of little value as a supplier of nutrient phosphate. To overcome this, the phosphate must be made into an 'available' form and the method used is treatment with a mineral acid, either sulphuric or nitric.[5,84] This technique converts the phosphate rock to useful phosphoric acid and waste calcium sulphate (gypsum).

The phosphate rocks used in the fertiliser industry differ widely in phosphate grade and in the nature and amount of impurities, although impurities such as cadmium are practically always present in small amounts. This is illustrated in Table 3.15 which shows the reported cadmium content of phosphate rock imported by EC member countries. As no cadmium is added during the phosphate fertiliser production process, the cadmium content of the waste gypsum and the phosphoric acid depends solely on the cadmium content of the raw material. The principal means of disposal of gypsum waste is dumping in coastal waters or landfill, although in the EC a proportion is recovered and used in the construction industries.[57]

Country of Origin	Cadmium Content $gCdt^{-1}$ P_2O_5
USA (Florida	35
Morocco	60
Senegal	225
Togo	160
Naura Island	239
USSR (Kola Peninsula)	0.8
Tunisia/Algeria	60
Israel/Jordan	35

TABLE 3.15: REPORTED CADMIUM CONTENTS OF PHOSPHATE ROCK IMPORTED BY EC MEMBER COUNTRIES ACCORDING TO COUNTRY OF ORIGIN

(Source: Hutton (1981)[57] and Feenstra (1981)[84])

In 1979 the EC imported 16.5 million tonnes of rock phosphate with an estimated total cadmium content of 408 tonnes. The estimated discharge of cadmium to land and water from fertiliser manufacture in the EC is 34 and 62 tonnes per year respectively, which amounts in total to 25 per cent of the cadmium present in the phosphate rock. The remaining 75 per cent (312 tonnes) is left in the phosphate fertiliser which is added to agricultural land throughout the EC.[5,84] (Table 3.16)

	Cadmium (tonnes/year)		
	Manufacture		Use
Country	Landfill	Water	Land
Italy	1.00	8.40	48.90
The Netherlands	1.30	18.00	6.80
United Kingdom	20.00	7.50	45.40
German FR	0.02	0.05	44.20
Belgium/Luxembourg	9.00	0.30	7.70
France	2.60	27.00	144.00
Denmark	-	0.50	6.90
Eire	-	-	8.30
TOTALS	33.92	61.75	312.20

TABLE 3.16: ESTIMATED DISCHARGES OF CADMIUM FROM THE MANUFACTURE OF PHOSPHATE FERTILISERS IN THE EC

(Source: Feenstra (1981)[84], DoE (1980)[38], Hutton (1981)[57])

3.4.7 Cement Production

Raw materials used in the production of cement are known to contain traces of cadmium. It has been estimated that the raw material required to produce 16 million tonnes of cement would contain around 44 tonnes of cadmium, equivalent to 2-3 ug g^{-1} in the raw material.[38] In 1980 the EC produced 135 million tonnes of cement, with a corresponding raw material cadmium content of 360 tonnes. Industrial sources have estimated that during the cement manufacturing process 2.3 per cent of the cadmium is emitted to the atmosphere in the form of dust and fume, 59.1 per cent is disposed of in solid waste and the remaining 61.6 per cent remains in the cement itself.[38] It is calculated, therefore, that the atmospheric emissions of cadmium in the EC in 1980 from the production of cement would be 8.2 tonnes and a discharge to landfill of 213 tonnes (Table 3.17).

3.5 SUMMARY

In the EC in 1982, 5,781 tonnes of primary cadmium metal were consumed together with an additional 953 tonnes in the form of raw materials such as fossil fuels and phosphate fertilisers. Estimated emissions of cadmium to the environment in the same year were 3,114 tonnes - 46.3 per cent of cadmium usage. Atmospheric emissions of cadmium accounted for 3.8 per cent of annual usage, land disposal for 38.4 per cent and water discharge 4.0 per cent. The remaining 53.7 per cent of cadmium used in 1982 is either unaccounted for* or contained in cadmium products which will contribute to discharges at a future date.

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* Estimated to be around 7 per cent (471 tonnes), which is probably emitted to the environment during the weathering, wear and loss of cadmium products while in use.

EC Member States	Cement Production 1980 (million tonnes)	Cadmium Content (tonnes)	Cadmium Emissions (tonnes/year)	
			Air	Land
German FR	34.60	95.15	2.16	56.22
Belgium	7.50	10.25	0.28	6.06
Luxembourg	0.30	0.83	0.02	0.49
Denmark	1.90	5.23	0.12	3.09
France	28.10	77.28	1.75	45.67
Ireland	1.90	5.23	0.12	3.09
Italy	41.90	115.23	2.62	68.09
Netherlands	3.70	10.18	0.23	6.02
United Kingdom	14.90	40.98	0.93	24.22
TOTALS	134.80	360.36	8.23	212.95

TABLE 3.17: ESTIMATED CADMIUM EMISSION TO THE EC FROM CEMENT PRODUCTION

Source	Environmental Sector (tonnes)		
	Air	Land	Water
Natural Sources	20	ND	ND
Non-ferrous Metal Production:			
Zinc and Cadmium	21	200	50
Copper	6	15	ND
Lead	5	40	20
Electroplating	ND	713	60
Cadmium Alloys	3	ND	ND
Stabilisers	ND	7	7
Pigments	ND	ND	26
Batteries	ND	22	13.7
Primary Iron and Steel Industry	34	349	ND
Foundry Industry	18.5	63.5	ND
Coal Combustion	5.8	282.5	ND
Oil Combustion	0.5	14.5	ND
Gas Combustion	ND	ND	ND
Refuse Disposal	129.2	193.8	ND
Sewage Sludge	2.75	129.3	33
Phosphate Fertilisers	ND	346	62
Cement Production	8.23	213	ND
TOTALS	253.98	2,588.6	271.7
Percentage of annual cadmium consumption:	3.8	38.4	4.0

ND = No data

TABLE 3.18: SUMMARY OF THE ESTIMATED ANNUAL CADMIUM INPUT TO THE EC ENVIRONMENT

CHAPTER 4

HUMAN EXPOSURE AND HEALTH EFFECTS OF CADMIUM

CHAPTER 4: HUMAN EXPOSURE AND HEALTH EFFECTS OF CADMIUM

4.1 Intake, Metabolism and Retention of Cadmium in the Human Body
    4.1.1 Intake
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4.3.11 Belgium: Liege

4.3.12 Belgium: Non-ferrous Smelting Area

4.1 INTAKE, METABOLISM AND RETENTION OF CADMIUM IN THE HUMAN BODY

4.1.1 Intake of Cadmium

The cadmium concentrations in the kidneys, liver and brain tissues of foetuses in their first, second and third trimesters have recently been reported.[86] This study has shown that cadmium may be found in very low concentrations in the tissues of the unborn.

The placenta provides an efficient barrier against the transfer of cadmium from the mother to the foetus during pregnancy.[60] When a child is born, however, it is immediately exposed to cadmium in air and food (milk) and since the rate of absorption in the human body is greater than the rate of excretion, accumulation of cadmium is unavoidable, increasing in the kidneys with age to a peak concentration of around 30 mg (range 20-50 mg) at 50 to 60 years of age. In the general population lower levels are found in the 60 to 80 year age range than the 40 to 60 year range, and a number of hypotheses have been put forward to explain why this should be so.

First , it has been suggested that the general population has been exposed to cadmium over only the past 50 years, since 70 per cent of the total world production of cadmium has occurred within the past 20 years. Secondly, people with high cadmium levels tend to have a greater mortality after 50 years of age and the current over 50 year old population is unrepresentative. Thirdly, there may be an increased loss of cadmium from the kidneys with age. Lastly, there is decreased cadmium intake in the older age group due to social habits.[56]

The first of these hypotheses seems the more plausible reason for a peak in cadmium levels in the general population between the ages of 50 and 60. This being the case, in future years this peak will disappear and be replaced by a steady trend in accumulation with age, assuming that the world consumption of cadmium does continue at or near its present level.

It is reported that absorption of cadmium through the skin is negligible[87] and that the two main routes of intake into the human body are firstly by inhalation, and secondly by gastro-intestinal absorption.

Inhalation

The amount of cadmium deposited in the lung compartment depends principally on the air concentration and on the particle size. However, it is reported that the deposition rate varies inversely with particle size, with the values of approximately 50 per cent for particles having a mean mass diameter of 0.1 μm (fume) and approximately 20 per cent for particles having a mean mass diameter of 2 microns.[56] Using data on 'Standard Lung Mode' and typical cadmium particle size distribution in air[88,89] it has been reported that approximately 20-30 per cent of the cadmium inhaled in the ambient air would be deposited in the pulmonary compartment.

The amount of cadmium absorbed from the pulmonary compartment, however, not only depends on the amount deposited and retained but also on the chemical form of the retained particles, which then ultimately determines the rate of solubilisation in the lung tissue fluids. Experimental data[88] suggest that 64 per cent of the cadmium deposited can be readily absorbed. If this figure is accepted it means that 13-19 per cent of the cadmium inhaled in ambient air is absorbed through lung tissue. It is worthy of note, however, that some of the particles deposited in the respiratory tract may be transferred to the gastrointestinal tract where a fraction may also be absorbed through the gut (see Figure 4.1).

If approximately 20-30 per cent of the cadmium inhaled from the ambient air is deposited in the pulmonary compartment, of which 64 per cent is readily absorbed, then assuming an average daily inhalation of 20 m^3 of air, the amount of cadmium deposited and taken up in

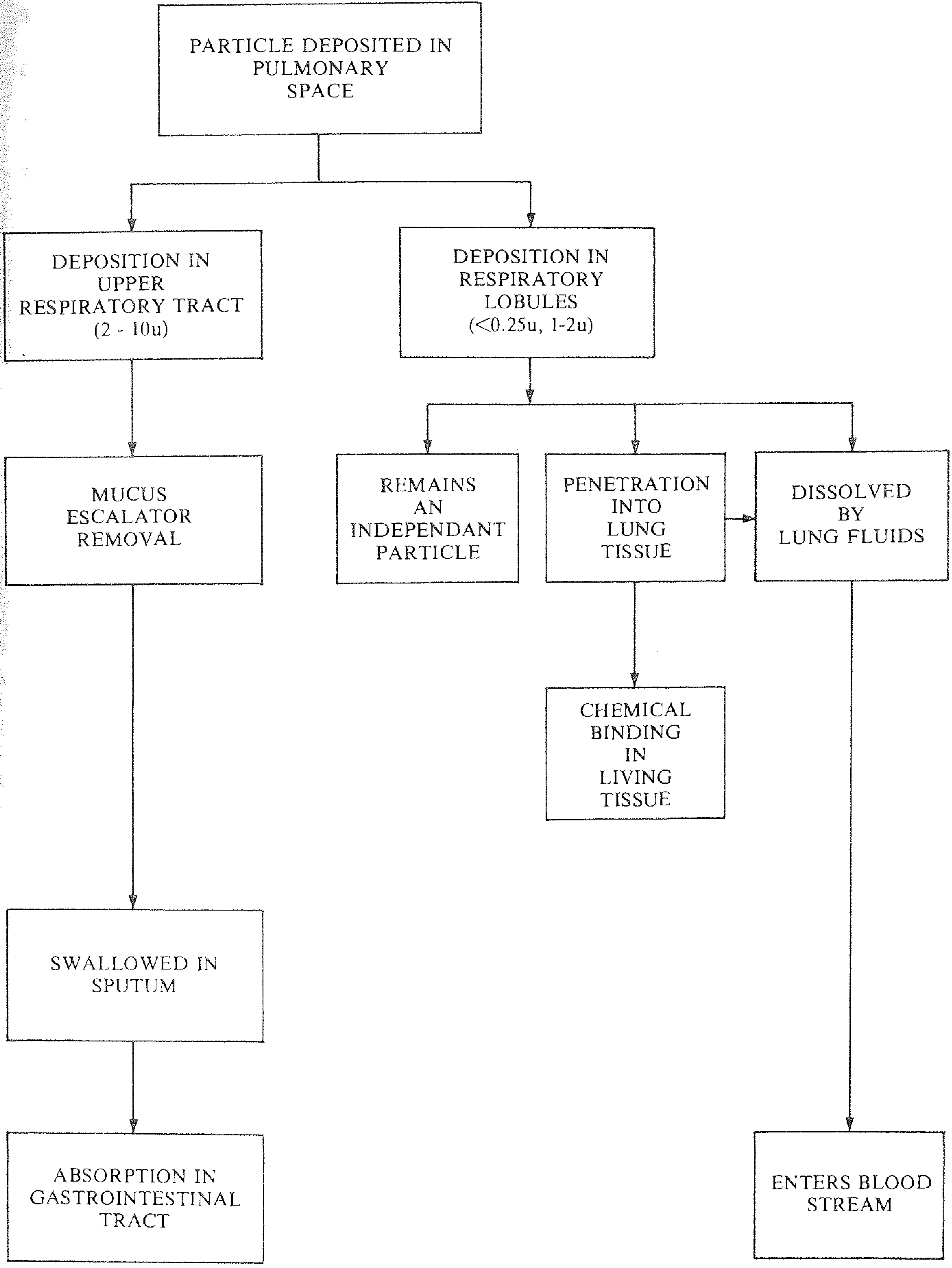

Figure 4.1 Fate of particles after deposition in the pulmonary space

the lower respiratory tract from rural, urban and industrial areas can be estimated (Table 4.1). For smokers, however, cadmium from cigarettes may represent a substantial contribution to body cadmium levels, and the amount may reach or exceed that from ambient air.[56] The US Environmental Protection Agency has estimated the cadmium absorption from cigarette smoking as follows:[90]

10 cigarettes per day corresponds to 0.70 ug/Cd/day
20 cigarettes per day corresponds to 1.41 ug/Cd/day
40 cigarettes per day corresponds to 2.82 ug/Cd/day
60 cigarettes per day corresponds to 4.22 ug/Cd/day

The reason for such a significant elevation in cadmium intakes is due to the small cadmium-enriched particles associated with cigarette smoke, which are around 0.3 um in size and which are vulnerable to absorption through lung tissue. The increase in total absorption via the pulmonary tract with the addition of smoking 40 cigarettes per day is shown in Table 4.2. It can be seen that for individuals who smoke more than 20 (unfiltered) cigarettes per day and who are not exposed to cadmium emission sources smoking is the largest single contributor to cadmium intake via the respiratory route.[56]

TABLE 4.1: CADMIUM DEPOSITION AND ABSORPTION FROM THE PULMONARY TRACT IN RURAL, URBAN AND INDUSTRIAL AREAS FOR NON-SMOKERS

(Source: CEC (1979)[56])

b - Assuming an absorption rate of 64%

TABLE 4.2: CADMIUM DEPOSITION AND ABSORPTION FROM THE PULMONARY TRACT IN RURAL, URBAN AND INDUSTRIAL AREAS FOR SMOKERS

(Source: CEC (1979)[56])

Gastro-intestinal Tract

Cadmium can enter the gastro - intestinal tract by consumption of food and drink, and by the swallowing of mucus containing particles of cadmium coughed-up or removed by cilia action from the respiratory tract. Cadmium contained in UK drinking water is reported to be below 5 µg/litre, with a typical value of 1.1 µg/litre (range 0.2-4.0 µg/litre). The intake of cadmium from water and water-based beverages has been reported to be an average 1-2 µg/day, although it is thought that consumption of other fluids, such as milk, could augment these figures.[38] In general, however, the total quantity of cadmium absorbed by the consumption of fluids is likely to be low compared with the amount derived from food.[56]

The concentration of cadmium in various foodstuffs has recently been reviewed in the UK[92] and values compiled from literary sources by others for the European Community.[3,56] These studies have shown that cadmium is present in trace amounts in all foodstuffs, ranging from 0.01 $\mu g\ g^{-1}$ for some soft fruits to 35 $\mu g\ g^{-1}$ for horse kidney and certain molluscs. People with different feeding habits, therefore, will take up quite different amounts of cadmium from their diet, especially those people who have a large intake of sea food.

A number of studies carried out in Europe[93-97] and the United States[98-103] have reported daily cadmium intakes of people in the general population to be between 10 and 88 ug, with a median of approximately 43 μg from food and 3 μg from water. A recent study in the UK, however, indicates daily cadmium intakes of only 15-30 ug for the general population.[102] It is clear from all the studies reviewed that the amount of cadmium entering the gastro-intestinal tract is much greater than that entering the lungs. However, the rate of cadmium absorption from the ingested material in the gut is reported to be much lower than that absorbed by pulmonary tissue. Experiments on five human volunteers using 'labelled' cadmium indicated that the oral absorption rate ranges between 4.7 and 7 per cent.[104] In animal studies, absorption rates between 0.5 and 12 per cent (mean 2 per cent) have been reported, variations depending on animal species and chemical form of the cadmium.[105,108] Age has also been shown to play a role in rate of gastro-intestinal absorption of cadmium in man and in mice.[109] If a gastro-intestinal absorption rate of 6 per cent is used in conjunction with the typical cadmium intakes presented above, then it can be assumed that between 0.24 and 5.04 (mean 2.58) μg of cadmium per day can be absorbed through the gut from food and a further 0.12-0.6 (mean 0.18) μg per day from water in a typical adult.[56]

4.1.2 Metabolism

The transport of cadmium in the human body, the organs affected by cadmium absorption, as well as the rate of cadmium excretion and accumulation are briefly reviewed.

The form in which cadmium is transported from the site of absorption, whether it be the gastro-intestinal tract or the pulmonary route, is relatively unknown, but it has been suggested that in blood cells as much as 60 per cent of the cadmium present is probably bound with metallothionein, a metal binding protein of low molecular weight,[110] the remainder of the blood cadmium being present in red cells.[111,112]

Immediately after absorption into the blood stream, either from the pulmonary or gastro-intestinal tract, it has been suggested that the protein-bound cadmium resides mainly in the plasma, but in the space of a few hours a redistribution in favour of the red cells occurs.[113] The cadmium is then transported around the body and is deposited particularly in the liver and kidneys with relatively large amounts also absorbed by the pancreas and spleen. Smaller amounts of cadmium are also stored in other tissue such as the bone marrow, testes and brain. Indeed, it seems that few, if any, tissues are totally exempt from cadmium absorption albeit in trace amounts. Work carried out by Sumino[114] has shown the total cadmium content (in milligrams) of various organs from 30 normal Japanese patients (average age 39) to be:

Kidney	12
Liver	8.5
Muscle	7.0
Skin	1.3
Bone	0.82
Blood	0.76
Lung	0.65
Digestive tract	0.75
Fat	0.45
Pancreas	0.27
Brain	0.16
Spleen	0.12
Heart	0.048

These results confirm findings of other studies which have shown that approximately 50 per cent of total body cadmium is found in the liver and kidneys[60,113-116] the kidneys being the major site of absorption (33 per cent of total body cadmium) and the target organ.

It is reported that metallothionein is not only involved in the transportation of cadmium within the body, but also absorption from the blood stream into the target organs.[56] Indeed, it has been suggested that the low molecular weight of metallothionein makes it possible for the protein to be filtered intact through the glomerular membranes of the kidney, and thereafter it is reabsorbed from the tubular fluid into the cells of the renal tubules. The metallothionein is then eventually broken down and the cadmium sequestered by the higher molecular weight proteins present in the kidney. This mechanism has been used to explain the selective accumulation of cadmium in the kidney cortex.[60] Confirmation of this has been strengthened by work showing that in mice injected with metallothionein-bound cadmium a more toxic effect to the kidney tubule was observed.[60,110,117]

The synthesis of metallothionein in the human body is thought to take place in the liver, kidney and intestine. The rate at which it is produced, however, is thought to be directly related to the amount of cadmium which is present and that toxicity from cadmium occurs when the level of metallothionein is insufficient to bind all of the cadmium.[118]

Recent studies have also shown that in animal experiments the absorption of cadmium increases when accompanied by a simultaneous low intake of calcium, zinc or iron.[119] A similar situation apparently also occurs in man, and since mild iron deficiency is common, especially among menstruating women, the findings may have importance for the evaluation of cadmium hazards in the general population.[120] High levels of zinc have also been found to reduce retention of cadmium in the kidney, as zinc is believed to successfully compete with cadmium for binding sites.[119]

4.1.3 Retention

As referred to earlier, the main source of cadmium intake is from food, the kidney is the target organ, and the rate of absorption of cadmium in the human body is greater than the rate of excretion. Subsequently, accumulation of cadmium is unavoidable in the exposed person and will increase in the kidneys with age.

A recent study has shown that the level of cadmium in wheat samples from 1972 were twice as high as those from 1916.[122] It seems likely that this increase may reflect increased industrial emissions and general environmental contamination from cadmium in the past fifty years or so. If this is the case, dietary intakes and kidney cadmium burdens of the general population today would tend to be greater than those in the nineteenth century.

A recent study has tested this hypothesis by collecting kidney samples from autopsies carried out during 1973 and 1974 on individuals who were non-smokers between the ages of 20 and 79 and who died a natural death. Kidney cortex samples were also collected from kidneys preserved in museums since the nineteenth century. The analyses have shown that the mean cadmium concentration of 42 kidney cortex samples from the former was 57.1 $\mu g\ g^{-1}$ dry weight with a 95 per cent tolerance interval of 14.6 to 224 $\mu g\ g^{-1}$. The corresponding values for the 30 nineteenth-century kidneys were 15.1 µg g^{-1} dry weight and 2.7 to 85.1. The differences between the two sets of data were found to be statistically significant (Figure 4.2). This study strongly suggests therefore that the mean cadmium burden in the current-day general population has increased during the twentieth century, most likely due to an increased consumption and dissipation of cadmium in the environment.

4.2 EFFECTS OF CADMIUM ON THE HUMAN BODY

4.2.1 Effects on the Kidney

As referred to in Section 4.1.2, metallothionein allows cadmium to be filtered through the glomerular membrane of the kidney and thereafter reabsorbed from tubular fluid into the cells of the renal tubules. When the metallothionein protein is eventually broken down, the cadmium is sequestered by higher molecular weight proteins present in the renal tubules and kidney cortex where it is bound. However, when the availability of 'binding' sites in the kidney cortex and tubules decreases and cadmium acculuIation reaches a critical level (200 µg of cadmium per gram of kidney tissue)[60] metallothionein-bound cadmium entering the kidney cannot be absorbed in the normal way and is consequently excreted via the urine. This occurrence, known as proteinuria (protein in the urine) is regarded as a symptom of kidney dysfunction. However, although

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20th CENTURY SAMPLES

WEIGHT IN KIDNEY CORTEX

Figure 4.2 Frequency distribution of cadmium concentrations in renal cortex from 19th century samples (estimated maximum values) and from 20th century samples. (Source: Elinder (1977)[121]) the number of binding sites in the kidney decreases, it is thought that one of the main causes of proteinuria in cases of cadmium poisoning is actual damage of the renal tubules (lesions), and restriction of normal function due to the presence of cadmium.[56] Although metallothionein is excreted in the urine when renal tubule lesions are present, other low molecular weight proteins such as B_2 - microglobulin, albumin, lysozyme, ribonucleose, retinol-binding protein and immunoglobulin chains are also present in urine in measurable quantities. The amount and type of these proteins has been suggested as possible indications of the extent of kidney damage. For example, if the glomerular is affected by the accumulated cadmium, an increased high molecular-weight protein clearance will take place in addition to the low molecular weight proteins caused by tubular lesions.[56,60,123]

4.2.2 Effects on the Lungs

Prolonged inhalation of air containing high levels of cadmium dust or fume is reported to produce pulmonary obstruction and possibly emphysema.[56,60] Other studies have shown that in tissues (kidney, lung and liver) of all persons who die from emphysema, chronic bronchitis and cancer of the lung, larger amounts of cadmium are found than in subjects who did not have these diseases.[36,56,115,124,125] However, it is not clear whether the cadmium came from cigarette smoke or some other source, and so it cannot be deduced that cadmium was solely, or indeed partly, responsible for the lung lesions.

Experiments carried out on rats have shown that of 20 rats exposed to 0.2 mg cadmium per m^3 in air for 66 days, seven died and of the surviving thirteen all had significant reductions in body weight, increase in lung weight, elevated concentrations of cadmium in lung and kidney (50 $\mu g\ g^{-1}$), emphysema associated with inflammatory changes in the lungs, as well as other detrimental physiological effects.[126] The levels to which these rats were exposed, however, are much greater than those found in the most polluted areas. Nevertheless, it has been suggested that continuous exposure (24 hours/day for 70 years) to 2 μg Cd/m^3 in air is probably close to the 'no effect' level for the lungs.[60] The World Health Organisation has set a tentative health based occupational exposure limit for long-term exposure to cadmium of 10 $\mu g/m^3$.[195] This level may be exceeded in some industrial areas, but it is unlikely that any localised population or group of individuals would be exposed long enough for irreversible lung damage to occur.[174] It can be concluded, therefore, that although the lung may provide an effective route for cadmium absorption, as noted earlier, it is unlikely that any damage occurs to exposed groups from air cadmium concentrations present in most industrial areas.

4.2.3 Effects on the Cardiovascular System

Much of the data in the literature implicate cadmium as a cause of hypertension in exposed animals. Schroeder[127] has shown that it is possible to induce hypertension in rats by long-term administration of cadmium (5 ug g^{-1}) in de-ionised water to which essential trace elements had been added. The dormant period before hypertension manifests itself is probably up to one year.[127-130] Other work has also shown that a statistically significant increase in blood pressure could be measured in rats fed on a diet containing only 0.56-0.63 ug g^{-1} cadmium by comparison with animals fed special diets containing 0.02 ug g^{-1} cadmium.[127-130] Work on rabbits injected with 2 ug g^{-1} cadmium acetate intraperitoneally at weekly intervals has shown that the presence of protein-bound cadmium ions in the blood vessels at concentrations of around 1.0 ug g^{-1} wet tissue, and in the kidneys at a much higher concentration, may have a role in the cause of cadmium hypertension.[131]

The basic mechanism by which cadmium can induce hypertension in animals is still highly speculative, but one suggestion is that the cadmium to zinc ratio in the kidney plays an important role.[127-129] On the basis of a great deal of work carried out on animals and the results of a clinical study indicating that patients with hypertension do excrete more cadmium than controls, it has been postulated that cadmium does contribute to the high prevalence of hypertension in the United States.[127-129,133] This existence of a causal relationship between cadmium and hypertension, however, has been questioned by other workers.[60]

Clinical and epidemiological work by many authors[130-132] however seems, on balance, to confirm that cadmium does play a role in the cause of hypertension.

4.2.4 Effects on the Liver

In the human body the liver is the second most active accumulator of cadmium. In the same way that cadmium affects the normal function of the kidney, it has also been shown to affect the liver.

One study[60] has found cirrhotic changes in rabbits injected with cadmium sulphate (0.65 ug g^{-1}, 6 days per week for 2 to 4 months). Other animal experiment studies have indicated that morphologically evident liver damage, as well as changes in the activity of certain enzymes in the liver, may occur with long-term moderate oral exposures.[134,135]

It is possible, therefore, that cadmium-induced effects on the liver may have been overlooked in the past and that much is unknown about the role of the liver in cadmium toxicity.[56,60]

4.2.5 Effects on the Bones

When storage sites in the kidney decrease, the liver accumulation of cadmium will become significant (as a percentage of that available in the body) and other binding sites are found by the metal in addition to the increased excretion in the urine. Although the liver will continue to store cadmium up to a level of 7,000 ug g^{-1} (compared to a kidney maximum level of 5,000 ug g^{-1})[136] in severe cases of cadmium poisoning the bones take up the metal with reported levels (in femur) reaching as high as 15,000 ug g^{-1}[136] with an associated osteomalacia(bone decalcification). However, it has been suggested that nutritional factors, in particular calcium and vitamin D deficiency, exacerbate the onset of bone decalcification in cadmium-poisoned individuals.[56,137,138]

Again, it has been reported that in animal experiments bone lesions were induced by giving cadmium orally (50 ug g^{-1}in water) along with a calcium-deficient diet.[139] Other studies have shown bone decalcification and cortical atrophy of bones in rats fed 10 ug g^{-1}cadmium in their diet.[140] In most animal experiments and human case studies a low calcium and/or low vitamin D diet (which affects calcium utilisation) was noted when bone decalcification was diagnosed. However, it is now recognised that cadmium can depress calcium absorption from the intestine, a fact indicating that even if calcium intake is satisfactory it may not be taken up by the body due to direct or indirect inhibition by cadmium.

4.2.6 Effects on the Formation of Blood Cells

It has been demonstrated that short term (8 day) administration of cadmium (10 ug g^{-1} or higher doses) to mice partially inhibits the absorption of iron through the gastro-intestinal tract.[139] As haemoglobin, the oxygen-carrying compound carried by the red blood cells, is composed essentially of the element iron its synthesis in the bone marrow is impaired when iron is deficient.

Animal experiments have shown that the administration of iron can prevent anaemia.[141] Whilst dose-response studies have shown that 10 ug g^{-1} cadmium in drinking water for one year does not cause anaemia in rats, but that 31 ug g^{-1} for one or two months is readily effective.[142,143] The occurrence of anaemia due to cadmium exposure has been found in occupationally-exposed individuals, but no data seem to be available on the occurrence of anaemia in population groups exposed to environmental cadmium contamination.

4.2.7 Effects on the Testes

Injection of a single dose of soluble cadmium salts (0.1-3 ug g^{-1} body weight) has been shown to give rise to a dramatic effect in the testicles of several species of experimental animals. Within a few hours of injection the organs have been found to undergo complete destruction, without any evident damage to other organs in the body.[60,110,144]

Although a vast literature on the various aspects of this effect of cadmium has been published, it is of limited value when judged in relation to environmental exposure to cadmium, as it has been shown that oral administration of cadmium does not appear to be effective in causing testicular damage, and that injection is the only harmful route.

4.2.8 Effects on the Female Reproductive Organs

Recent animal studies have shown that cadmium chloride injected subcutaneously at a rate of 0.18 ug g^{-1} body weight/day for 60 weeks adversely affects the blood vascular system of the uterus after the thirty-third week of exposure.[145] It was concluded from these experiments and from other studies reported in the literature that the vascular system of the uterus may be more sensitive to cadmium expsoure than the kidney.[145] However, the relevance of these findings to humans, and in particular the development of the foetus, requires much further research.

4.2.9 Carcinogenic Effects

Many animal studies have shown cadmium to be carcinogenic to a number of tissue types. However, the first report of a potential cancer risk of cadmium to man was reported in 1965.[146] This study noted a high incidence of cancer among workers who had been exposed to cadmium oxide (CdO). Of the 74 men studied, each having at least ten years exposure, eight died, including three from cancer of the prostate and three from other forms of cancer. In another study of 58 male workers in an alkaline battery plant it was found that fifteen had died, at least three deaths being attributed to cancer.[123]

Epidemiological studies designed to find possible associations between respiratory cancers and airborne elements, including cadmium, have not shown that cadmium levels present in urban air constitute a carcinogenic risk to the respiratory system.[147,148] The possible carcinogenic risk to other tissue types, however, has not been studied in environmentally exposed groups.

4.2.10 Mutagenic Effects

Within the literature there seems to be a great deal of conflicting evidence concerning the mutagenic properties of cadmium.[60,149-153] One study has reported that cadmium sulphide can induce chromosomal changes in cultured human cells,[153] whilst another study could not find any such effect with cadmium chloride.[149] Thus, speciation has been shown to be an important aspect. Similarly, there is evidence in the literature that cadmium binds to phosphates or the bases of ribonucleic acid (RNA), suggesting that cadmium may induce genetic alterations,[56,152] but generally attempts to induce heritable mutated genes have been unsuccessful.[60,154]

4.2.11 Teratogenic Effects

Cadmium has been reported to have a site specific teratogenic effect in certain animal species. For example, one study has shown that intravenously injected cadmium sulphate in hamsters can result in offspring with a high incidence of facial and other malformations, including imperfect cranium development, the brain lying outside the skull, and absence of eyes.[155] Other studies have shown that injection of more than 0.63 ug/g of cadmium chloride into mice can also bring about teratogenic effects.[156] Interestingly, some authors report that either zinc or sodium selenite will restrict the teratogenic effects of cadmium but the reason why is unclear.[157] Although a great deal of evidence exists in the literature on the teratogenic effects of cadmium and its compounds on a number of animal species, very little is known about the teratogenic effects of cadmium in humans. This is an area, therefore, worthy of further study.

4.2.12 Other Effects

Loss of the sense of smell (anosmia) has been reported to occur in workers industrially exposed to cadmium dust[146,158] but no data are available on the possible effect of environmental cadmium on any of the senses.

Similarly, it has been reported that cadmium injected during molar tooth development in the rat is strongly carie promoting, being particularly pronounced in females.[159] Research to determine the effect that environmental cadmium has on tooth development in human populations, however, has not been carried out.

It is clear that although much research still needs to be carried out to determine the dose response relationships of cadmium in humans, there is a growing body of evidence to suggest that cadmium is an extremely toxic element, even in relatively small doses.

4.3 ENVIRONMENTAL EXPOSURE STUDIES IN POLLUTED AREAS

Since cadmium was first discovered in 1817 and used industrially since the early 1900s, all reported cases of cadmium intoxication were due to occupational exposure. However, in 1960 health effects as a result of environmental cadmium pollution were recognised and documented in Japan where large scale cadmium contamination had been prevalent for a number of years. Recently, a number of other studies conducted in industrial areas of the United States and Europe have indicated possible health effects or elevated exposures due to environmental contamination from cadmium.

A pre-requisite to a review of these recent studies, however, is a brief account of the Japanese experience of environmental cadmium pollution and its health effects, for it is this data which originally gave rise to the concern, and much scientific research into sources, levels and effects of ambient environmental levels of cadmium found in industrial areas.

4.3.1 Japan: Toyama Prefecture

In 1946 Dr Hagino, a general practitioner returning from the Second World War, reopened a private clinic which had been in operation in Fuchu, Toyama Prefecture, since his grandfather's time. Shortly after rejoining his practice, Dr Hagino was visited by patients who were inhabitants of the lower stream of the Jinzu River. These patients were suffering from a painful disease which Dr Hagino called the 'Itai-itai byo' (meaning ouch-ouch disease).[161] The disease had occurred endemically in the area for a number of years previously, but its etiology was unknown. The disease mostly attacked farm women above middle age who had lived in the area for more than 30 years and who had borne several children. The symptoms displayed were similar to rheumatism, neuralgia, or neuritis. However, as the condition aggravated, gradually an unusual form of gait appears, ie wiggling the hips like a duck due to pain in the pelvic region.[136,161] As the disease progressed further, mild trauma gave rise to fractures in various parts of the skeleton. For instance, among the diseased subjects studied at autopsy by one author[136] one patient had 28 fractures of the ribs and 72 in the whole body. The disease also resulted in a marked decrease in body height and weight.

The symptoms mentioned above are the same as osteomalacia, a symptom of rickets often found in children and infants who have experienced vitamin D deficiency during bone ossification, usually occurring because of dietary deficiency as well as lack of exposure to ultra-violet light. As the symptoms found in Toyama Prefecture were similar to osteomalacia, treatment with cod liver oil was tried. This had no effect because, as it was later found, the type of osteomalacia indicative of the Itai-itai condition was either vitamin D resistant or renal osteomalacia, a condition almost indistinguishable from ordinary osteomalacia and requiring much larger concentrated doses of vitamin D. In the 1950s it was found that patients with Itai-itai disease exhibited symptoms of renal tubular damage characterised by proteinuria and glycosuria.

In 1957 Hagino presented a hypothesis that the Itai-itai disease could be related to the discharge of metals, particularly cadmium and zinc, from the Kamioka Mine 30 kilometres upstream of the Jinzu River, as the rice crops could not grow around the inlets to the paddy fields. It was not until the 1960s, however, that it was established that the renal damage shown by patients was caused by cadmium carried by the river. The contaminated water was not only drunk by the local population but the rice grown in the surrounding paddy fields took up cadmium from the soil, and the rice was the staple diet of these people. It is thought that the reason why only women above middle age, and especially those with many children, were affected was because women screened themselves from the sunlight while working, which resulted in a low natural formation of vitamin D by the skin. Their diet also contained low amounts of vitamin D and other fat-soluble vitamins, and in addition another important loss of bone minerals occurred in connection with pregnancy and lactation.[161] Thus, because of an upset calcium-phosphor us balance and a lack of vitamin D, these women were especially susceptible to disturbance of the kidney and osteomalacia.

An epidemiological study during the period 1962-1965 and a later, much larger study in 1967 showed that over 100 inhabitants showed clear, or suspected, bone symptoms with several hundred in the area having blood signs giving rise to suspicion of osteomalacia and requiring further observation.[60] It was also found that the distribution of the Itai-itai victims and the cadmium concentration in the soil of the endemic area revealed an evident co-variation. Epidemiological studies carried out elsewhere in Japan where cadmium had been used industrially for a long time revealed further cases of osteomalacia and an increased prevalence of proteinuria.

Cadmium pollution and adverse health effects like those found with Itai-itai disease have not been recorded anywhere since. However, since the Itai-itai episode, a great deal of research has been undertaken into the determination of low levels of cadmium in various environmental media. In particular, food intended for human consumption has been examined, as well as the health effects associated with levels of cadmium above those thought to be natural.

The Itai-itai disease, therefore, although unlikely ever to recur on its previous scale is instructive both to illustrate the toxic nature of cadmium and to emphasise the danger of environmental pollution by cadmium.

4.3.2 United Kingdom: Shipham

In 1977 a nationwide survey of metal concentrations in stream sediments in England and Wales revealed unusually high concentrations of cadmium around the village of Shipham in Somerset.[45] Preliminary analyses of soils and vegetation from the village also revealed high levels of cadmium, and subsequently a full-scale investigation was initiated by the Department of the Environment. The contamination was thought to have been derived from zinc mining activity which had taken place in the Shipham area until the end of the nineteenth century. Calamine ($ZnCo_3$), the zinc ore which occurred locally, was mined by means of a series of shallow pits which were left undisturbed until they were reclaimed for grazing pasture and residential development in the 1960s.

Soil analyses revealed average cadmium concentrations in individual properties to be 94 ug g^{-1} with levels in some vegetable plots reaching 520 ug g^{-1}. Vegetable samples taken from domestic gardens were found to contain elevated levels of cadmium. Kale, spinach, leeks, cabbage, lettuce and rhubarb were discovered to be particularly susceptible to high cadmium concentrations, with average levels being 1.23, 1.08, 0.69, 0.61, 0.69 and 0.41 ug g^{-1} wet weight respectively.[162,169,170]

Although the concentrations found in many of the vegetables were undesirably high they were not as great as might have been expected, given the large degree of contamination in the area. The reason for the relatively low levels found in the vegetables at Shipham was due to the nature of the cadmium in the soil, it being mainly bound to rock fragments and of low bio-availability.

Analyses of the Shipham soils showed that less than three per cent was extractable using standard techniques[162-163]. Dietary intakes of cadmium by Shipham residents was monitored during 1979 by asking 70 families to keep accurate records of food eaten during two 4-week periods in May and September. In addition, a further 65 individuals were asked to provide duplicates of their actual diets over a 1-week period. Results showed that most individuals drew most of their food from commercial sources[162] and consequently intakes of cadmium were found to be little different from the national average of 0.14 mg/week. Residents who tended to grow a proportion of their vegetable diet in Shipham soils did, however, have much larger estimated dietary intakes, with levels as high as 1.08 and 0.52 mg/week using the duplicate diet and diet diary techniques respectively.

The Joint FAO/WHO Expert Committee on Food Additives[164] have proposed a provisional tolerable weekly intake of cadmium of 0.45-0.5 mg/week per adult. Some of the Shipham residents were found to exceed this intake by 100 per cent. Average dietary intakes however were less than the FAO/WHO recommended limit, with values of 0.20 and 0.25 mg/week for the duplicate diet and diet diary techniques respectively. It is worthy of note that not all the households who took part in the dietary intake study grew all or part of their vegetable diet in Shipham soils, and that the average dietary intake reported is unrepresentative of the average cadmium intake for the group of vegetable growers in the village who, not surprisingly, tended to have the highest intakes.

During 1979 a pilot survey of Shipham residents revealed that 22 out of 31 residents had raised blood-cadmium levels, and some had clinical and biochemical findings (including hypertension and evidence of renal tubular damage) indicating toxic effects which could be attributed to the metal.[165] Two further studies found an association between the cadmium levels in soil and occurrence of hypertension in the Shipham residents[166] and small excesses of hypertensive, cerebro-vascular, and genito-urinary disease[167] which were not prevalent among a control group in the nearby village of North Petherton. The validity of these findings has been questioned because ofan unrepresentative sampling strategy adopted in both studies.[168]

Despite this, there is still doubt over the risks of cadmium exposure in Shipham[171-173] and residents have been warned to grass over any redundant soil, avoid eating locally-grown vegetables, particularly the leafy varieties which tend to take up larger amounts of cadmium, minimise cigarette smoking and lime all soils if vegetables are to be grown in them.

4.3.3 United Kingdom: London Borough of Islington

During 1976 a study was made of cadmium and lead levels around a small secondary metal recovery factory in an urban area as part of an environmental monitoring programme.[174] Results showed levels of cadmium in house dust collected near the factory to be in the range 12.3-387 ug g^{-1} with many readings in excess of 100 ug g^{-1}. The levels of cadmium in air were also found to be high.[174] Peak levels of cadmium were found to be 9.2 and 11.0 ug m^{-3} at widely-spaced sampling times. These are several times greater than those reported for typical urban situations (0.001-0.003 ug m^{-3}). Daily cadmium intakes were calculated from dust by adventitious ingestion (ie, pica), an activity normally associated with children. Assuming a maximum intake of 20 mg/24 hours[175] and the maximum cadmium concentrations found in house dusts (387 ug g^{-1}) it was calculated that 8 ug/24 hour could be ingested via this route, increasing a child's daily cadmium gastro-intestinal absorption by as much as 80 per cent above the norm.[174]

Estimates of the likely cadmium intake from air were also calculated. It was assumed that with a total respiratory air intake of 7,300 m^3/year[60] and a cadmium-in-air level of 11 ug/m^3 the intake would be approximately 220 ug Cd/24 hours or 80 mg/year. If a 40 per cent absorption at the respiratory surfaces was assumed[60] then the likely contribution to kidney cadmium burden may be as high as 40 ug g^{-1} wet weight in one year or 200 ug g^{-1} in five years. Although the authors[174] accepted that these tentative calculations of intakes were an extreme extrapolation of the measured data, it is illustrative of the potential severity of the contamination present and the potential health risk posed to local residents.

The cadmium emissions were derived from the melting of used metal scrap in order to reclaim lead. As cadmium was present in the scrap in the form of low melting alloys it was quickly volatilised in the gas-heated melting pots and exhausted to the outside air by means of ventilation fans. As the cadmium emissions from the factory constituted a health risk the factory management was given a period of seven days to cease emissions, either by stopping smelting or by technological means. The type of process being carried out in the factory is typical of a number of works in other industrial areas of Europe. It is not an unreasonable inference therefore that severe localised metallic pollution of this type is a widespread problem and becoming more so as cadmium is more widely used.[174]

4.3.4 United Kingdom: Chard, Somerset

In 1982 residents on a new housing estate in Chard, Somerset, complained to their local council that vegetables planted in their gardens either didn't grow or grew a little and then died. Soil and a few immature vegetable samples were collected and analysed for toxic metals. The results revealed a high level of contamination of both soil and vegetable samples, with copper, zinc, lead and cadmium. It was later discovered that the housing estate site had previously been used as a scrap yard for a period of over 50 years and, as a result, the ground became contaminated with toxic metals. The top two to three feet of soil was removed from the gardens of fifteen council houses and 11 flats on the estate and replaced with fresh top soil.

This occurrence of potential toxic levels of metal in these garden soils alerted the Environmental Health Department to the problem of siting housing developments on land previously used for industrial purposes. A subsequent review of recent housing developments in the Chard area, and in particular the previous use of the sites, revealed two other contaminated developments from which garden soil had to be removed to safeguard the health of the inhabitants.

It is now the policy of the local council to check the previous use of sites intended for residential development. It is suggested, however, that hundreds of other housing estates in the UK are built on similar contaminated sites which the Department of the Environment believe could put many residents at risk.[196,198] Consequently the Department of the Environment's Committee for the Redevelopment of Contaminated Land has sent guidance notes to all Environmental Health Departments in the UK with instructions to survey land which has been used for metal processing, before it is developed.[198,199] It is reported that many councils may still be ignoring this advice.[197]

4.3.5 Netherlands: Arnhem

In order to establish the major pathways for lead uptake by children aged 1-3 years living in close proximity to a secondary lead smelter, an epidemiological study was initiated in 1978 in the town of Arnhem (population 150,000).[176] A part of this epidemiological study was an investigation into the lead and cadmium pollution of soil and street dust in the vicinity of the smelter. Samples of soil and street dust were taken from residential areas at varying distances from the smelter. Cadmium levels up to 10.47 ug g^{-1} were found in garden soils (range 0.20-10.47, mean 1.60 ug g^{-1}) and levels of cadmium in street dust up to 16.17 ug g^{-1} (range 0.5-16.17, mean 3.81 ug g^{-1}). Cadmium contamination was found to decrease with distance from the lead smelter, and thus the suggestion was that the source of the contamination was atmospheric emissions from the smelter itself.

Dietary intakes of cadmium were not estimated and no vegetables or biological samples were analysed. Nevertheless, the potential for increased dietary intakes may be recognised from the high levels reported.[176]

4.3.6 United States: Missouri

In 1971 and 1972 a study was conducted in the lead-producing area of south-eastern Missouri to determine the uptake of metals by cattle grazing on nearby farms.[180] Cadmium and other metals were determined in blood and milk and the results showed increased body burden of cadmium, although no signs of toxicity were present. Levels of cadmium in the kidney cortex of one exposed cow reached 3.7 ug g^{-1} wet weight, which was 17 times greater than the corresponding value for the control. The study concluded that consumption of meat, particularly offal, and milk from the exposed cows would result in an elevated cadmium and lead intake.[180]

4.3.7 United States: Palmerton, Pasadena

A study carried out in 1973 around two zinc smelters in Palmerton, Pasadena revealed soils and vegetation to be highly contaminated with cadmium. Soils were found to contain up to 1,750 ug g^{-1} cadmium, with 90 per cent of the cadmium being located in the top 15 cm of the soil profile. Foliage from Depauperate trees within 2 km of the smelters were found to contain up to 70 ug g^{-1} cadmium on a dry weight basis. It was concluded that the high levels of cadmium in foliage was due to metal aerosols entering the leaves directly, probably through open stomata.[182] No reference was made in this study to the health of local residents but the levels reported would suggest a potential source of exposure to residents living in close proximity to the smelting complex.

4.3.8 United States: National Epidemiological Study

It was suggested in Section 4.2 that cadmium in small doses can produce hypertensive disease in rats, and that patients suffering from hypertension have increased cadmium levels in their renal tissue.[127-133] The existence of a correlation between the concentration of cadmium in urban air and cardiovascular disease has also recently been suggested.[148,189] One study used the average concentration of cadmium, lead, zinc, chromium, suspended particules, and Benzene-soluble organics in urban air of 28 cities in the United States, and data on death from a range of cardiovascular diseases. Rank correlation co-efficients of age-, sex- and race-standardised mortality ratios and the atmospheric pollutants mentioned above were then calculated. The results show a marked correlation of cadmium in air and death rates from hypertension and arteriosclerotic heart disease, with a co-efficient of correlation (r) of 0.76. This association could not be explained by the fact that large, industrialised cities tend to have both a high heart disease rate and heavily polluted air, since no correlation could be found with other indices of air pollution, such as total suspended solids.[189] These findings have also been confirmed in another study[148] which found that, of all the air pollutants examined as possible indications of heart disease mortality, cadmium proved to be the most highly correlated, followed by vanadium. It is suggested, therefore, that low doses of cadmium act not only as a hypertensive-promoting agent in laboratory experiments, but epidemiological data also correlate cadmium with heart disease mortality in urban areas.[148,189]

4.3.9 Poland: Silesia

During the late 1970s a group of scientists conducted a study of the Upper-Silesian Industrial Region in Poland to discover the degree of contamination in domestic gardens in the area.[183] The results of this work, which were reported only in August 1980, revealed heavy contamination of domestic garden soils. The main source of cadmium was from ferrous and non-ferrous smelting works in the area which had poor pollution control technology, if any. Levels of cadmium in vegetables were found to be 30-70 per cent higher than normal, with beetroot, carrot, parsley and celery containing the highest levels. Dietary intakes of cadmium and other heavy metals were not reported but the authors suggest that a higher incidence of cancer and other illnesses in the area could be attributed to the heavy metal pollution.[183,184]

4.3.10 Czechoslovakia: East Slovakia

In 1981 a study was initiated in the East Slovakia Industrial Region, Czechoslovakia, to evaluate the contamination of the environment in the major cities of Krompachy, Rudnony and East Slovakia, all of which have major steel works. Levels of cadmium in plant material, soil and dust fallout were monitored and compared with the findings from the control area of Hrabusica.[185]

Average levels of cadmium found in carrot, kohl-rabi, parsley, potato and 'grasses' were 0.27, 0.18, 0.14, 0.05 and 11.5 ug g^{-1} dry weight respectively. Average levels of cadmium in soil were 6.6 ug g^{-1} and levels of cadmium in dust fallout 2.2 kg/km^{-2} $year^{-1}$. The dietary intakes of cadmium by residents was not estimated but it was concluded by the author that the region suffers from cadmium pollution largely as a result of the smelting industries in the area.

4.3.11 Belgium: Liège

Belgium is the largest consumer of cadmium in the EC and cadmium pollution has been found in a number of industrial areas. A recent study reports that women who were 60 years of age or over and who had spent the majority of their life in the cadmium-polluted area of Liège constituted an exposed group, whilst women living in the two less polluted areas of Charleroi and Brussels acted as controls. All the women taking part in the study were residents of old folk's homes who had not been occupationally exposed to cadmium and who had no history of smoking. A questionnaire was used to gain the necessary information, particularly in respect of medical history and health status. All the women provided a urine sample which was then analysed for creatinine, proteinuria, aminoaciduria, B_2-microglobulin, albumin, cadmium and mercury. Blood samples were also collected and these were analysed for cadmium, lead, plasma creatinine and plasma zinc.[186]

The results show that the group of women from the Liège area had, on average, higher cadmium body burdens than the control groups, which was reflected by an increased excretion of cadmium in the urine. Analyses for B_2-microglobulin and albumin showed an increased prevalence of renal disturbance in the exposed group. The study concluded that environmental pollution by cadmium, such as that found in urban/industrial areas of Europe may exacerbate the age-related decline of renal function in population groups non-occupationally exposed to heavy metals.[186] These findings have, however, been questioned in the literature because it is suggested that there are too many gaps in the information to warrant such a conclusion.[187]

4.3.12 Belgium: Non-ferrous Smelting Area

During an initial survey in 1974, a follow-up survey in 1976 and a repeated surveillance between 1977 and 1978, a group of school children living near a non-ferrous metal smelting plant were studied for signs of ill-health due to environmental contamination by cadmium.[171,179] The cadmium content of blood, urine, water used for hand-rinsing, air, dust and soil from school playgrounds were compared with an urban and a rural control. The results showed an increased urinary excretion of cadmium in children living around the lead smelter, with a time-dependent trend in the renal accumulation of cadmium. It was suggested that the results indicate that the overall contamination of the environment by cadmium in Belgium is steadily increasing. The study found that both the pulmonary (inhalation) and gastro-intestinal (adventitious ingestion of dust) routes proved to be effective routes of exposure for the children near the lead smelter. The study concluded that the children had elevated cadmium intakes and that the long-term effects of such an exposure is in need of further investigation.[177]

CHAPTER 5

THEORETICAL FRAMEWORK, RESEARCH HYPOTHESIS AND EXPERIMENTAL DESIGN

CHAPTER 5: THEORETICAL FRAMEWORK, RESEARCH HYPOTHESIS AND EXPERIMENTAL DESIGN

5.1 Theoretical Framework and Research Hypothesis

5.2 Experimental Design

- 5.2.1 The West Midlands Metropolitan County
- 5.2.2 Background Levels of Toxic Metals in the West Midlands
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CHAPTER 5: THEORETICAL FRAMEWORK, RESEARCH HYPOTHESIS AND EXPERIMENTAL DESIGN

5.1 THEORETICAL FRAMEWORK AND RESEARCH HYPOTHESIS

Production and consumption of cadmium has increased considerably during the twentieth century with current world production standing at 16,755 tonnes per annum, and consumption in the EC around 6,185 tonnes per annum with an average annual increase over the past decade of 2 per cent. Only a minor proportion of this cadmium is ever recycled; thus, there is a real risk that the majority of cadmium will ultimately give rise to environmental contamination in one form or another. It has been estimated that around 90 per cent of global cadmium emissions are anthropogenic in origin and, that given the information available on current trends in use, releases are likely to increase still further.[3,57]

As cadmium is not destroyed when released into the environment it merely moves from one compartment to another. The rate of movement varies with subsequent accumulation in components such as soils and some biota. Accumulation in the environment can, therefore, be expected to rise as cadmium emissions continue to increase.

Figure 5.1 shows the inputs and environmental flow of cadmium in the European Community. It is evident that

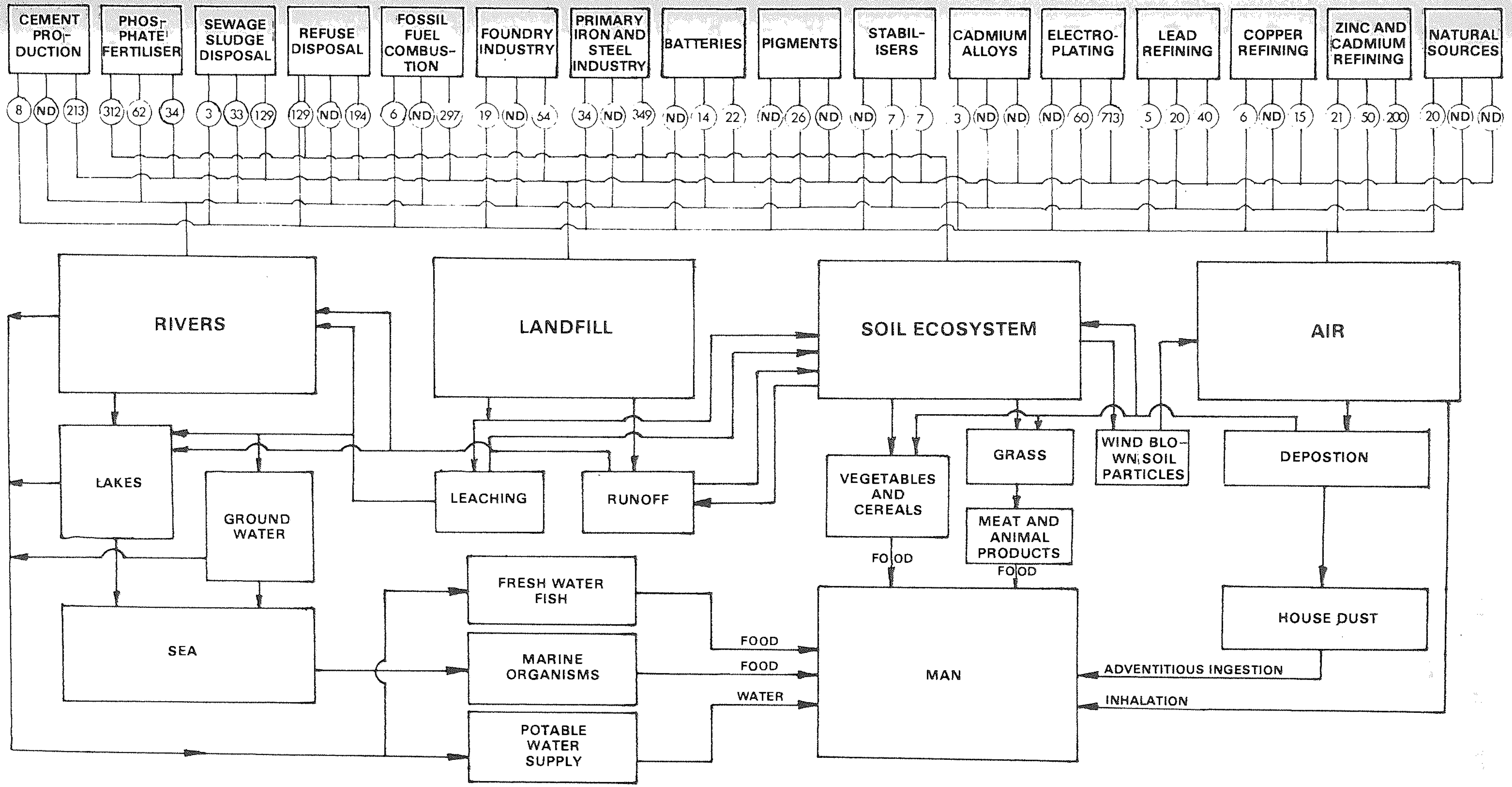


FIGURE 5·1. ANTHROPOGENIC EMISSIONS (TONNES/YEAR) AND ENVIRONMENTAL FLOW OF CADMIUM IN THE EUROPEAN COMMUNITY man is exposed to cadmium from many sources but most importantly from food. Analyses of uncontaminated biological materials have shown that cadmium is present in trace amounts in all foodstuffs. The lowest concentrations tend to be found in milk, meat, fish and fruit (0.001 - 0.01 ug Cd/g fresh weight) with the higher concentrations being found in vegetables and cereal crops (0.01 - 0.1 ug Cd/g fresh weight). Still higher concentrations, however, have been found in the liver and kidneys of adult animals and in certain sea foods, which may exceed 1 ug Cd/g fresh weight.[120]

Accumulations of cadmium in the environment, and in particular the soil ecosystem, can only serve to increase these levels further, and subsequently increase dietary intakes of cadmium. Indeed, a recent study has shown that the cadmium content of autumn wheat in Sweden has doubled during the period 1916 to 1972, and that a further increase of cadmium concentration in plant-based foods is predicted at a rate of 7 to 8 per cent over the next ten years.[3,122]

Estimated current average daily intakes of cadmium vary from country to country and generally appear to be correlated with the degree of industrialisation. For instance, dietary intakes of cadmium in Sweden are reported to be between 10 and 20 ug/day, whilst in the Federal Republic of Germany intakes are estimated to be of the order of 30 to 48 ug/day.[56]

When cadmium is absorbed into the body tissue very little is actually excreted, with the result that the level of cadmium in target organs, particularly the kidney and liver, will increase, reaching a peak later in life. At this time renal dysfunction may occur in those individuals who have been constantly exposed to elevated levels of cadmium.

In 1975 a Joint Food and Agricultural Organisation (FAO) and World Health Organisation (WHO) Expert Committee came to the conclusion that the critical level for cadmium in the renal cortex lies between 100 and 300 ug Cd g^{-1} wet weight, and 200 ug Cd g^{-1} wet weight should be regarded as the 'tentative critical level' above which renal damage could occur.[56] Subsequently a maximum tolerable weekly intake of 400-500 ug (70 ug/day) was proposed and this has since been widely accepted as the maximum tolerable intake above which health effects may be found. Recently, however, a study has shown that 5 per cent of the population may show kidney damage with intakes lower than 70 ug/day.[200]

Analyses of renal cortex specimens dating from the 1880s which had been preserved in museums have shown that the cadmium concentration in renal cortex at that time was considerably lower than that found in current-day kidney cortex specimens collected at post mortem.[113,121] It seems likely therefore that the increased usage and emissions of cadmium to the environment over the past

50 to 100 years has contaminated food, air and water, which in turn has increased average dietary intakes and body accumulations of cadmium in man.

From the evidence presented in the preceding chapter, it is evident that cadmium can have adverse physiological effects when accumulated by the human body. Research into the health effects of ambient environmental levels of cadmium, however, is in its infancy. Nevertheless, case studies have shown that cadmium can be toxic in concentrations present in polluted environments, and that people living in close proximity to secondary metal reprocessing plants are significantly more exposed to cadmium than other urban populations.

Kidney damage as a result of cadmium accumulation due to long-term exposure is characterised by the excretion of cadmium and low molecular weight proteins, including B_2-microglobulin, in the urine. These indices of cadmium-induced kidney damage have been studied in an elderly population living for a long period in a Belgian industrial area with high ambient levels of cadmium.[186] This study has shown an increased prevalence of clinical signs of kidney damage amongst the exposed group in comparison with two control groups.

The increase in exposure and dietary intakes amongst urban/industrial population groups, especially those growing a proportion of their vegetable diet in contaminated garden soils, is considered probable but intakes are thought to be below the World Health Organisation maximum tolerable intake of 70 ug/day. Nevertheless, the Commission of the European Communities has expressed the need to evaluate the numbers of persons at risk of exceeding the WHO limit and the geographical areas concerned.[3]

A number of studies, also reviewed in the preceding chapter, indicated that there are two distinct population groups who are likely to have increased intakes and body burdens of cadmium. Firstly, those living in typical urban/industrial areas, and secondly, those living close to primary and secondary metal refining operations. It is also evident that intakes can be increased still further by individuals who also grow a proportion of their vegetable diet in garden soils contaminated with cadmium.

The European Community is the largest cadmium-consuming industrial region in the world and contains the four largest consuming countries on a per capita basis, viz Belgium, Germany (FR), United Kingdom and France. Population groups exposed to high levels of cadmium are therefore more likely to be present in the EC than in any other industrial area of the western world.

It is suggested, therefore, that "people living in European urban/industrial areas contaminated with cadmium, and growing a large proportion of their vegetable diet in contaminated soils, are at greater risk of increasing their cadmium intakes up to, or above, the maximum tolerable intake recommended by the Joint FAO/WHO Expert Committee on Food Additives". It is also suggested that "a proportion of these high-risk population groups may tend to show increased clinical signs of renal impairment due to high cadmium intakes".

To further evaluate and test this central hypothesis a population group consuming vegetables grown in contaminated garden soils, and living in an urban/industrial area with high ambient environmental levels of cadmium, needs to be studied in detail.

5.2 EXPERIMENTAL DESIGN

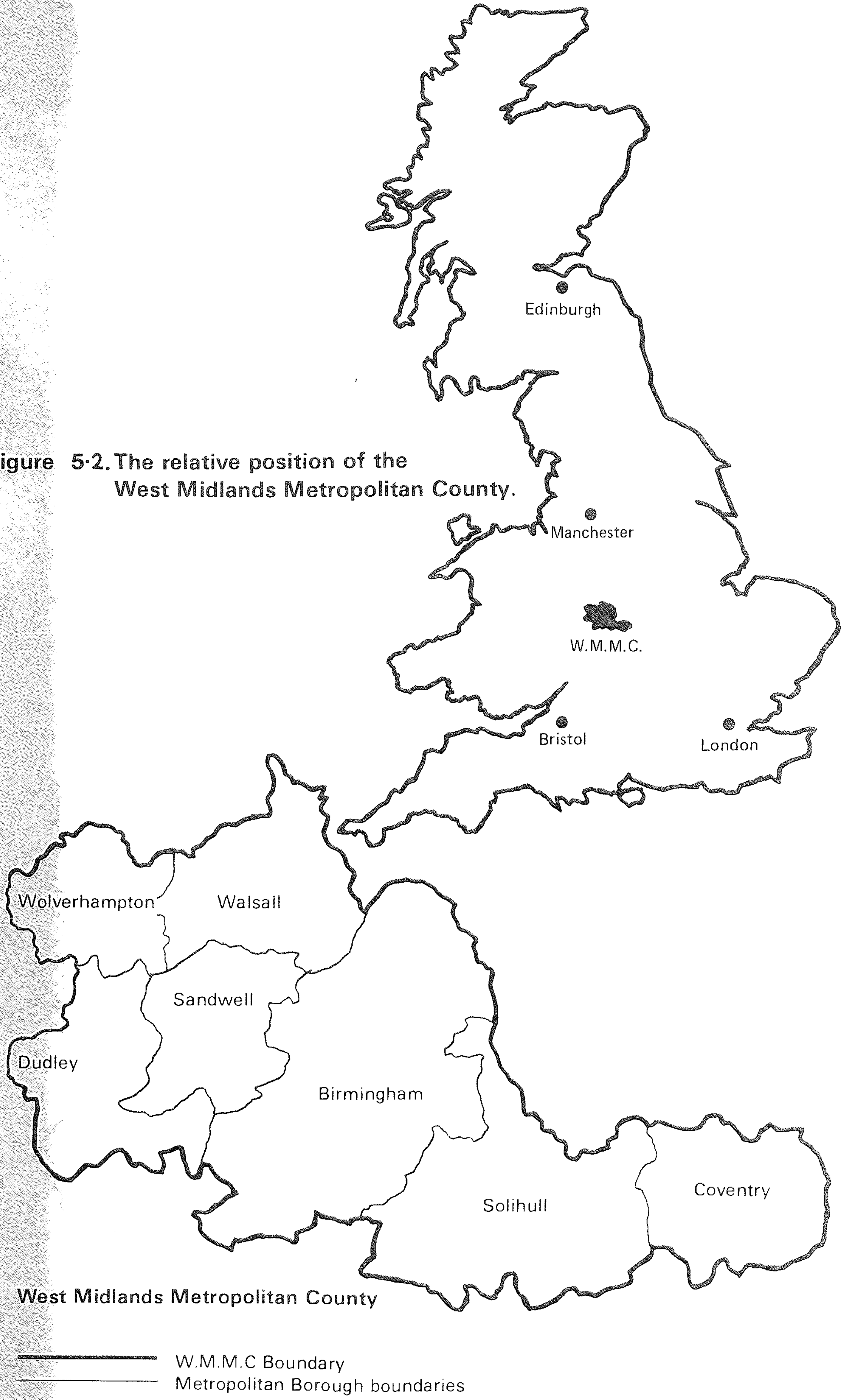
A primary task, and pre-requisite to the verification of the research hypothesis, is the identification of an urban/industrial area which has higher than background ambient environmental levels of cadmium, but typical of most urban/industrial areas in the European Community with regard to past and present industrial infrastructure and socio-economic status of its population. In the course of identifying a suitable study area within the EC, proximity of the research institute is a prime consideration although equally, due regard must also be given to the state of knowledge of an area and its environmental policies and problems.

5.2.1 The West Midlands Metropolitan County

The relative position of the West Midlands Metropolitan County in the UK is shown in Figure 5.2, together with its seven metropolitan boroughs. Up until the present economic recession the West Midlands had been variously described as Britain's most prosperous post-war provincial region, one of Europe's greatest industrial regions and the industrial heart of the nation, and its major city, Birmingham, as the most prosperous industrial city in Britain.[201,202]

The root of the region's rise to industrial supremacy in the period 1950 to 1976 can be traced to the 16th century, when the primary iron and steel industry established itself and later developed rapidly in the 18th and 19th centuries around the Middle Carboniferous mineral resources of ironstone, fire clay, coal and limestone, which outcrop between Stourbridge in the south west and Brownhills in the north west (Figure 5.3). When rapid industrial development took place in the 1830s over 2,000 puddling furnaces and nearly 200 blast furnaces were operating in the region, making Smethwick and West Bromwich important centres for the manufacture of iron and steel. Production of iron and steel declined in the latter 1800s and early 1900s due to the exhaustion of economically workable ironstone deposits, and by the early 1970s only three blast furnaces were in operation, situated within six miles of each other at Bilston, Wednesbury and Dudley, but these too closed in the early 1980s.

Figure 5·2. The relative position of the West Midlands Metropolitan County.



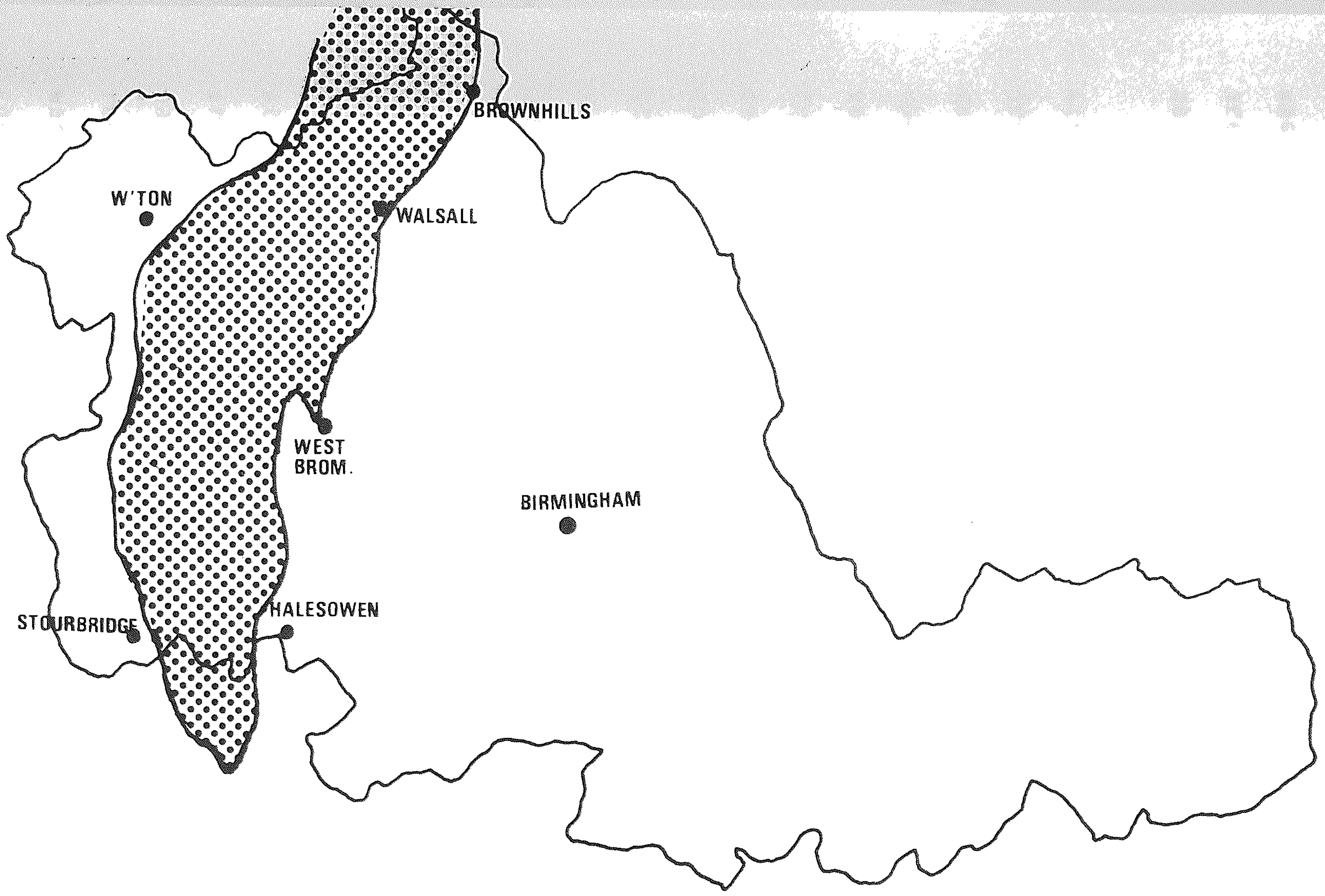


FIGURE 5·3. MAP OF WMMC SHOWING POSITION OF THE CARBONIFEROUS MIDDLE COAL MEASURES AND IRONSTONES.

Since the 1830s large quantities of waste materials have been generated which have been dumped around the old furnace sites on what was once farm land. These waste materials, containing high levels of toxic metals, are now present over much of the area which is now known as The Black Country.

Although the primary iron and steel industries have declined in the West Midlands, since the decline of the extractive industries, industrial development based upon secondary metal manufacture, particularly motor vehicle manufacture, has gradually increased with the raw metal being brought into the area in the form of ingots, and the use of locally derived scrap material. These secondary metal smelting foundries which are situated mainly in The Black Country area (Figure 5.4) are today thought to be the main source of emissions of toxic metals to the atmosphere in the West Midlands.[83,203]

5.2.2 Background Levels of Toxic Metals in the West Midlands

Atmospheric fallout of heavy metals emitted from the iron and steel industries over the past four centuries has inevitably led to elevated levels of metals in the region's soils, in addition to the contaminants in the waste materials deposited throughout the region. As cadmium has a long half life in soils it is considered that the cadmium emitted during the past century, and in particular over the past two decades, is still

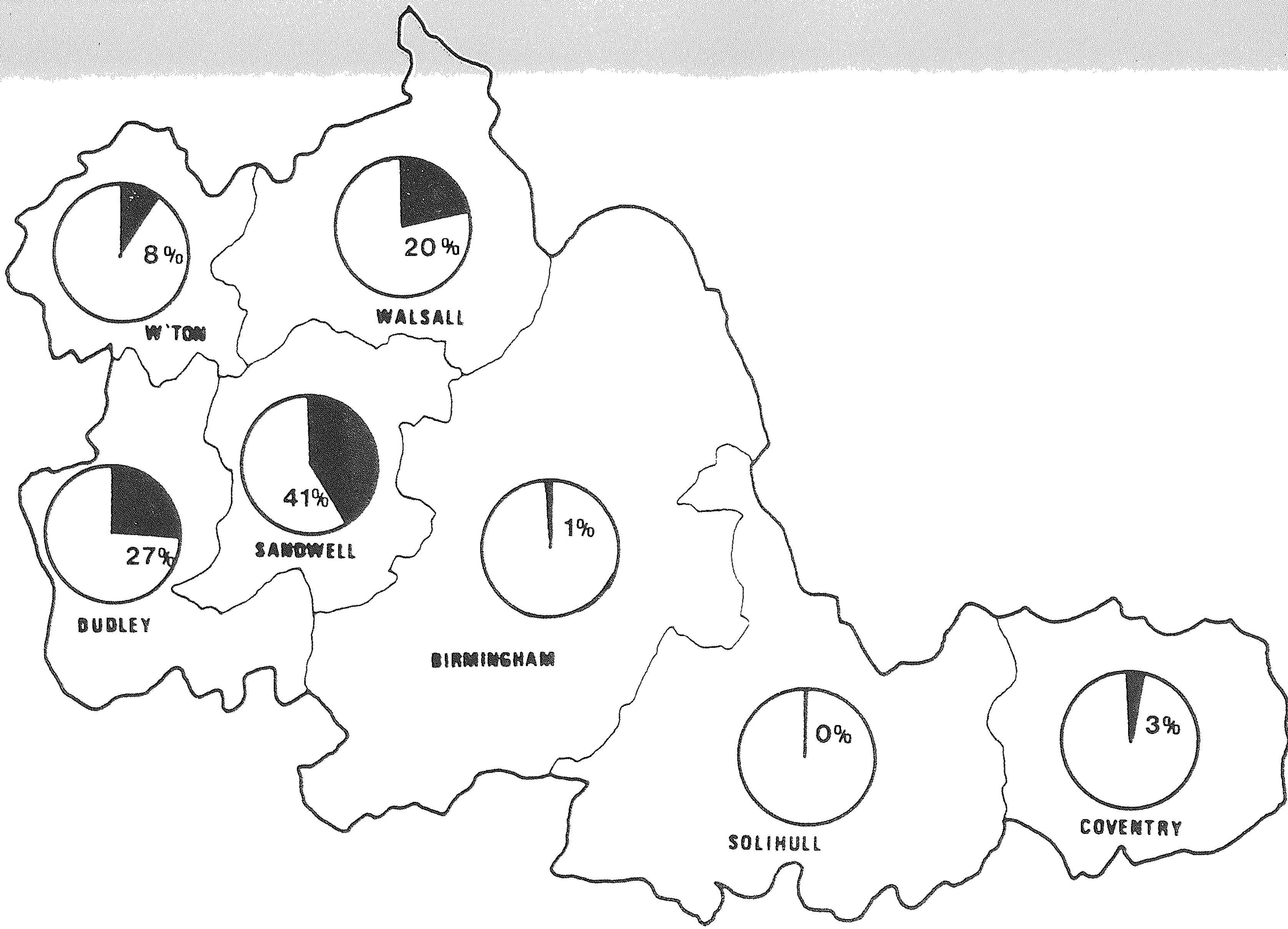


Fig. 5.4. Distribution of iron foundries in the West Midlands (% of county total).

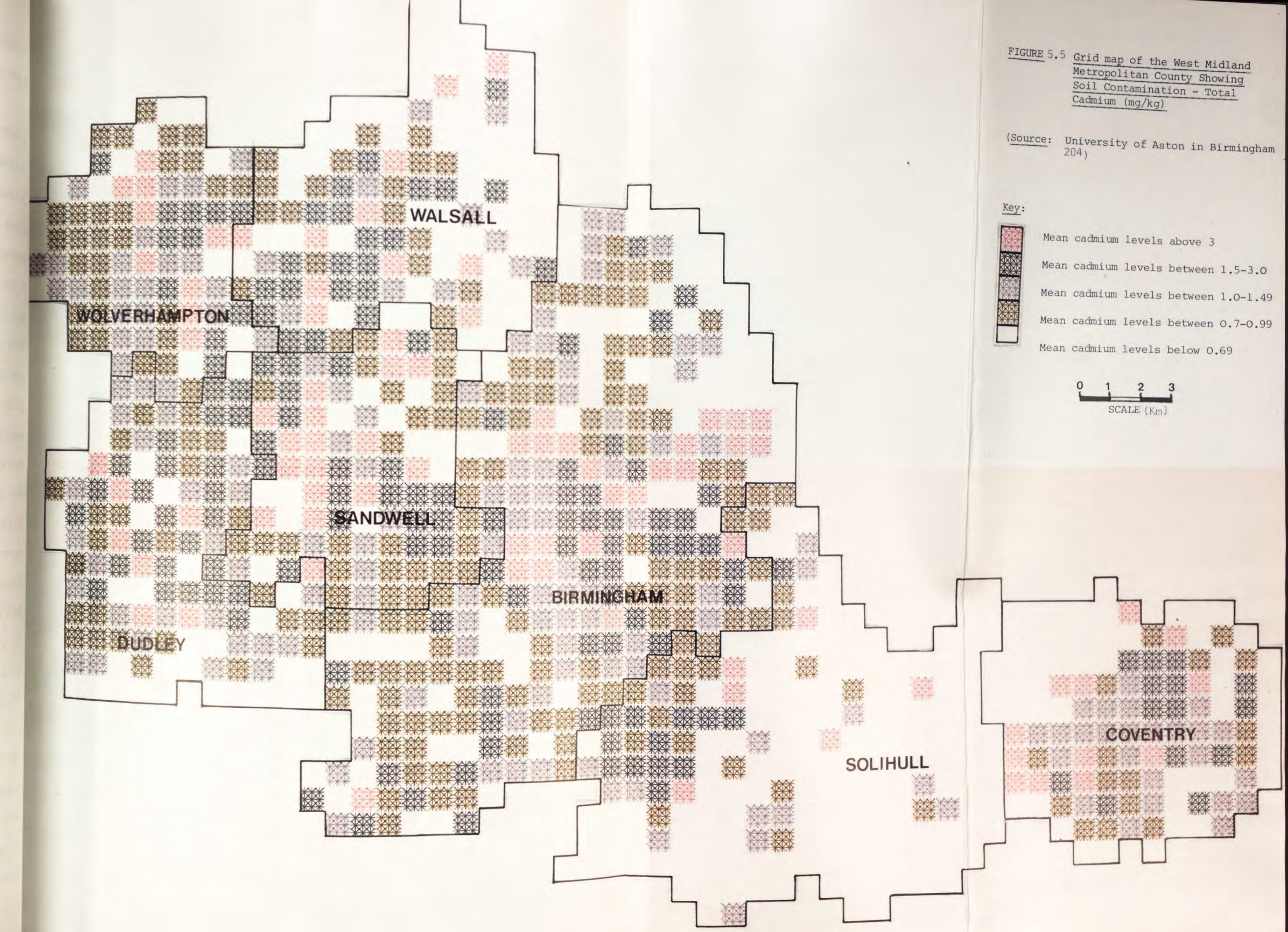
present in measurable quantities and is subsequently a source of human exposure.

In 1979 a study was initiated at the University of Aston in Birmingham for the UK Department of the Environment to identify contaminated sites in the West Midlands county.[205] This study was followed in 1980 by a more general study of the background levels of heavy metals in the county.[204] In this second study soil samples were collected at nine randomly selected points within forty 1-kilometre grid squares of the county. These nine samples were made up of a bulk of six sub samples which were collected within 30 metres of the main sampling point. The mean concentration of cadmium in each kilometre square was determined by calculating the mean cadmium level from all nine bulked samples collected. The forty kilometre squares sampled represented a wide range of land-use types in the county, and the results were used in conjunction with data on contaminated sites investigated in the area for the Department of the Environment to predict likely concentrations of metals in other kilometre squares of similar land-use types.

The results of these analyses, which were used to construct Figure 5.5, indicate that large areas in the West Midlands, particularly in The Black Country Boroughs of Walsall, Sandwell and Dudley, have soil cadmium concentrations above typical background levels.

FIGURE 5.5 Grid map of the West Midland Metropolitan County Showing Soil Contamination - Total Cadmium (mg/kg)

(Source: University of Aston in Birmingham 204)



The levels of total cadmium in the 360 soil samples collected showed a wide variation, but the pattern was clearly log normal with a 'tail' of higher values exceeding 3 mg kg^{-1} (Figures 5.6 and 5.7). The highest measured concentrations of cadmium from the 360 soil samples was 33 mg kg^{-1} found in an urbanised area, whilst at the lower end of the range the majority of soil samples had a total cadmium content between 0.3 and 1.5 mg kg^{-1}. Some 14 per cent of all soil samples had total levels in excess of 3 mg kg^{-1}, the upper limit in normal soils.[204]

From Figure 5.7 it is evident that there is a significant elevation of soil cadmium levels in urban/industrial areas. However, the range of total cadmium levels found in soil samples taken from the relatively unpolluted areas (agricultural and amenity land) exhibit broad similarities, with values ranging between 0.1 and 1.5 mg kg^{-1}. In residential areas cadmium levels ranged between 0.4 and 3.3 mg kg^{-1} with a cluster of results around the 1.0 mg kg^{-1} level.

This surveillance of background levels of heavy metals in the West Midlands serves as a valuable source of reference to identify areas of the county and conurbation which may have undesirably high background levels of cadmium in soil.

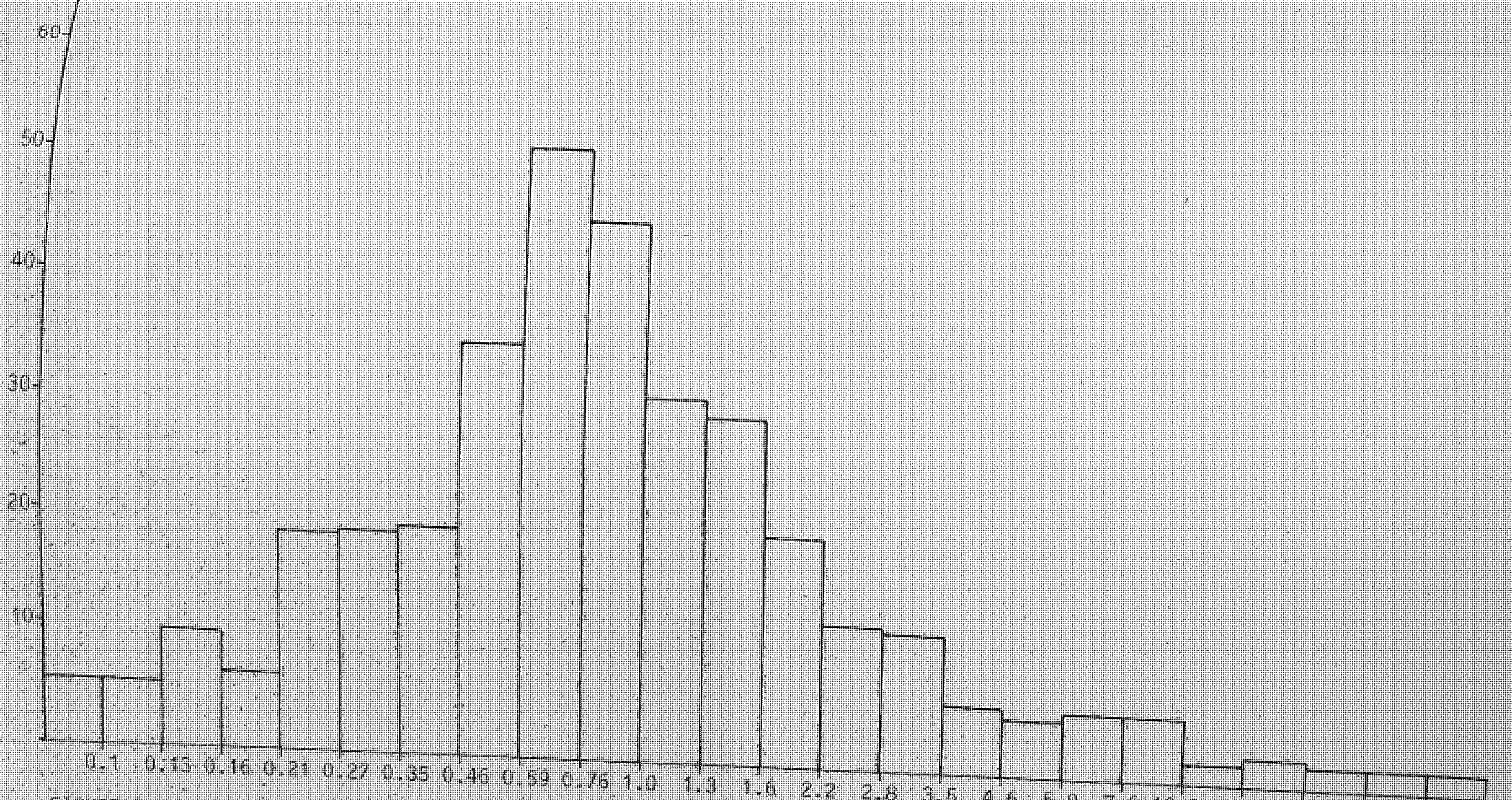


FIGURE 5.6: FREQUENCY DISTRIBUTION OF TOTAL CADMIUM (mg kg^{-1}) IN 360 SOIL SAMPLES COLLECTED THROUGHOUT THE WEST MIDLANDS COUNTY

(Source: University of Aston in Birmingham (1982)[204])

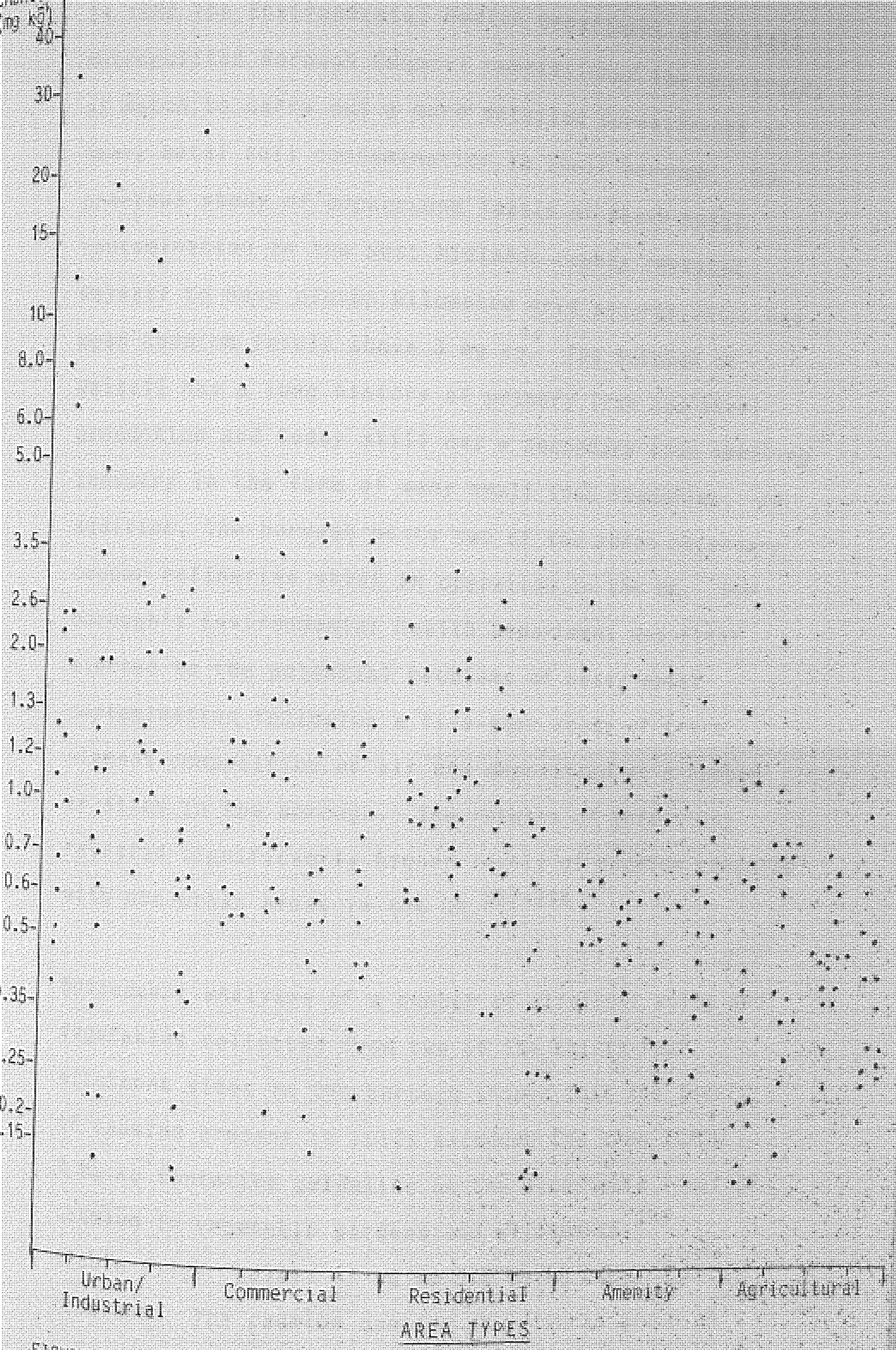


FIGURE 5.7: DISPERSION PLOT OF TOTAL CADMIUM (mg kg^{-1}) IN 360 SOIL SAMPLES COLLECTED THROUGHOUT THE WEST MIDLANDS COUNTY

(Source: University of Aston in Birmingham (1982)[204])

In 1982 the Environmental Health Department of Walsall Metropolitan Borough Council commissioned the University of Aston to carry out a more detailed surveillance of heavy metal soil contamination in their borough. The previous study of background levels of heavy metal contamination in the West Midlands county revealed Walsall to have eleven kilometre grid squares which had mean cadmium levels above 3 mg kg^{-1}. The Borough of Walsall has a long history of primary iron and steel production and today still has a secondary iron smelting industry in the form of many small iron foundries. In addition, the borough hosts two of the three secondary copper refineries still in operation in the UK. The borough's Environmental Health Department was first alerted to the potential problems of heavy metal contamination following a five-year study of trace element composition of air and deposition at a number of sites in the borough. The results of this study revealed significantly higher levels of cadmium compared with non-urban areas in the UK.[207-214]

Subsequent analyses of a number of allotment soils and vegetables collected from two of the thirty-four allotment sites in the borough showed that the levels of cadmium present in soils exceeded the then ICRCL 3 mg kg^{-1} tentative guideline on the acceptable level of cadmium in vegetable gardens and allotments.[199] (Table 5.1). Levels of up to 9.2 mg kg^{-1} cadmium in soil were recorded. The cadmium content of lettuces grown on these soils was found to be up to 7.5 ug g^{-1} dry weight compared with 0.2 ug g^{-1} dry weight for lettuce grown on uncontaminated soils.[215-218]

Walsall Environmental Health Department was therefore anxious to find out the full extent of soil contamination in the borough and subsequently a systematic surveillance was initiated by the University of Aston.[206]

TABLE 5.1

Vegetable gardens and allotments	Other gardens	Amenity land	Public open space
3	5	12	15

ICRCL TENTATIVE GUIDELINES ON THE ACCEPTABLE LEVELS OF CADMIUM IN SOILS FOR FOUR TYPES OF REDEVELOPMENT (mg kg^{-1} dry weight)

(Source: ICRCL (1980)[199])

Samples of soil were collected from sites within each of the 125 one-kilometre Ordnance Survey grid squares covering Walsall Borough. The number of sites chosen within each grid square depended on the relative significance of the soil contamination in that area. For instance, in areas where contamination was expected to be high and/or where redevelopment of land was likely in the near future, the sample density was higher than in areas where contamination and/or redevelopment was unlikely. Sampling sites, of which there were between 2 and 7, were located evenly throughout the grid square and soil was collected at 10 points on the ground within a radius of 30 metres of the sample site location. These 10 sub-samples were then bulked to give one single sample of soil representing the soil in a 30 metre zone of the sample point. In all, some 476 sites were sampled within the 125 grid squares of Walsall. An extended soil survey by the author in 1982 re-sampled soils from 126 worst contaminated sites in 18 grid squares of Walsall, followed by a further 70 samples from within 10 grid squares of the adjoining Borough of Sandwell. In total, 672 soil samples have been collected from 135 grid squares in Walsall and Sandwell. Average cadmium levels in each grid square were obtained in both surveys by averaging the sample measurements. Figure 5.8 shows the distribution of these average cadmium levels across the Borough of Walsall and the adjoining Borough of Sandwell.

The data on the levels of cadmium in the soil samples from both surveys was also analysed statistically to produce a figure termed the 'worst-case concentration' which is the soil metal concentration exceeded over 2½ per cent (1/40th) of the grid square area. This worst-case concentration was calculated using a statistical method based on the standard deviation of log-normalised soil metal concentrations.[206] (see Appendix A).

Contours were then constructed to isolate areas in which 2½ per cent of the soils would be equivalent to or exceed the value of that contour. Thus, the worst-case concentration contours indicate the peak concentrations that can be expected within any given area.[206] The worst-case concentration contours for cadmium in Walsall soils are presented in Figure 5.9, along with the contours for cadmium in North Sandwell.

In 1982 The Department of the Environment's Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) withdrew the tentative guidelines on the acceptable levels of cadmium in soil which were later replaced in 1983 by tentative 'Trigger concentrations' for cadmium in soil.[222] Under these new guidelines a site with a cadmium level below 3 mg kg^{-1} is considered uncontaminated, although a maximum permissible concentration for cadmium has not been set. The 3 mg kg^{-1} trigger concentration is suggested for land used for 'sensitive' purposes such as domestic gardens and allotments. However, a more lenient 15 mg kg^{-1} trigger concentration has been suggested for land used for less sensitive purposes such as public open space. It is interesting to note that these levels are the same as the tentative guidelines which were withdrawn in 1982.

From Figure 5.9 it is evident that the worst-case contamination levels exceed the 3 mg kg^{-1} DOE/ICRCL trigger concentration over almost all of the Borough, the only areas to fall below this guideline being The Barr Beacon and a zone stretching north-west from Aldridge through to the north of Shelfield. High cadmium levels were concentrated in the industrial areas of Walsall, with the main peak centred on the Bescot/ Pleck industrial areas, with subsidiary areas stretching north-east to cover the city centre and The Chuckery, and north-west towards North Darlaston. A peak was also found around the Kings Hill area, which then continued down into the Borough of Sandwell. The highest level of cadmium found was 81.4 mg kg^{-1} at a site adjacent to a housing estate in Bescot. Over much of these zones the worst-case concentration exceeded the ICRCL tentative most stringent trigger concentration for cadmium of 15 mg kg^{-1}, peaking at 35 mg kg^{-1} in Bescot. A second heavily contaminated zone centred on the Leamore Estate and here, too, levels exceed the 15 mg kg^{-1} ICRCL trigger concentration.[206]

Figure 5.10 shows the cumulative frequency distribution of worst-case concentrations of total soil cadmium levels across the Walsall area. From this figure it may be shown that 80 per cent of the land area is at risk of exceeding the most stringent 3 mg kg^{-1} ICRCL trigger concentration, and 11 per cent at risk of exceeding the more lenient 15 mg kg^{-1} trigger concentration.

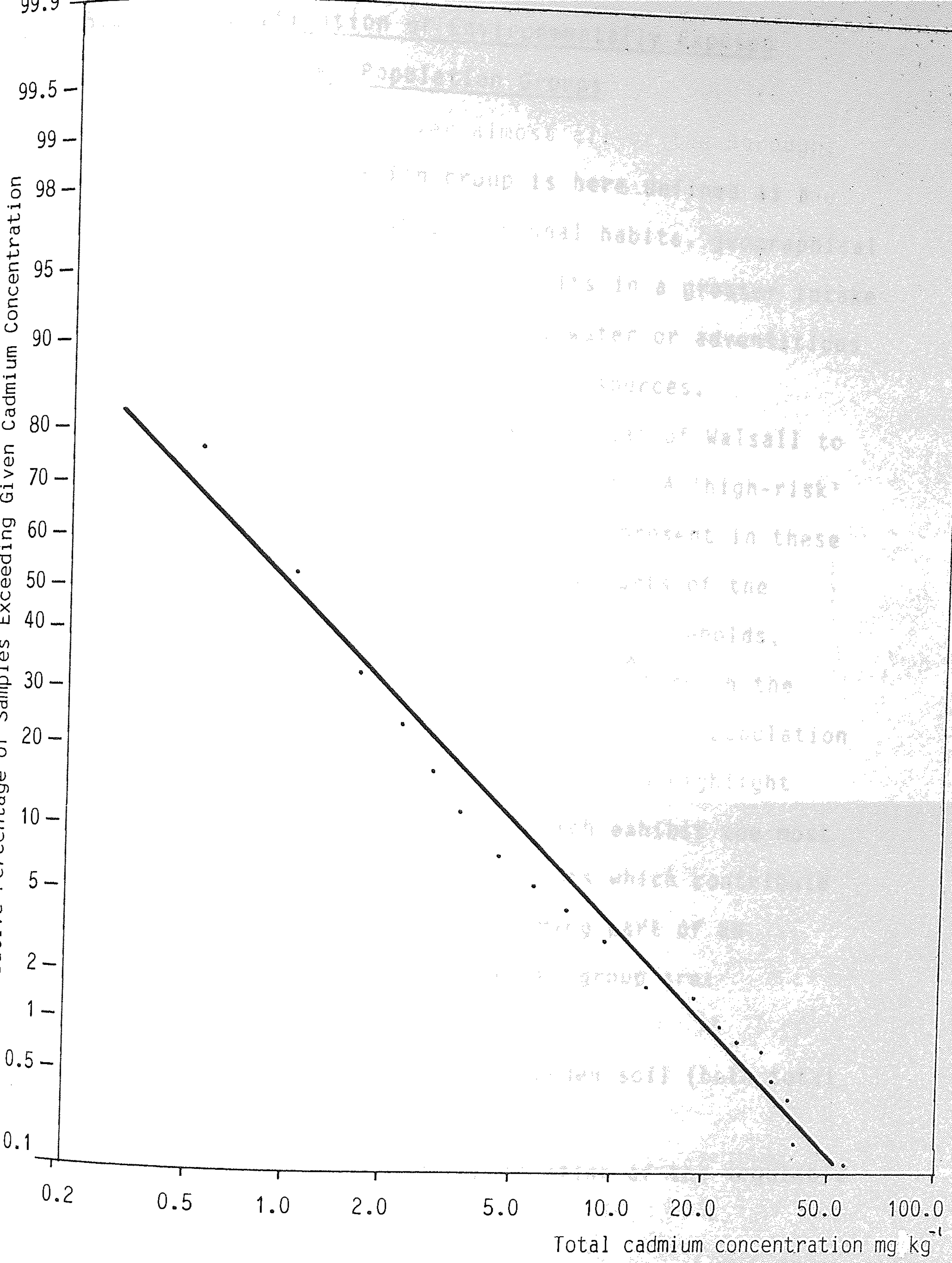


FIGURE 5.10: CUMULATIVE FREQUENCY DISTRIBUTION OF TOTAL CADMIUM IN WALSALL SOIL SAMPLES

5.2.3 Identification of Environmentally Exposed 'High-Risk' Population Groups

A 'high-risk' population group is here defined as a group of individuals whose personal habits, geographical location, diet or life style results in a greater intake of cadmium from either food, air, water or adventitious ingestion or from a number of these sources.
Figure 5.9 depicts the most likely areas of Walsall to have high background levels of cadmium. A 'high-risk' population group is more likely to be present in these areas of contamination than in other parts of the Borough. The high risk individuals or households, however, can be clearly identified only through the adoption of a selection strategy whereby the population of the contaminated areas are screened to highlight those individuals or households which exhibit the most 'risk factors'. The two main factors which contribute to a household or population becoming part of an environmentally exposed 'high risk' group are:

(i) high levels of cadmium in garden soil (both total and plant available), and
(ii) the growing of a large proportion of the vegetable diet in these soils.

These two factors can be termed '<u>Primary risk factors</u>'.

In addition, however, there are a number of other risk factors which include:

(i) a low soil pH
(ii) a reliance on garden vegetables for many years
(iii) a vegetarian diet, and
(iv) the deep freezing of garden vegetables for year-round consumption.

These factors, which only become 'risk factors' in the presence of one or more of the primary risk factors, can be termed '<u>Secondary risk factors</u>'.

Finally, there are two other factors which could contribute to a household becoming part of a high-risk group if present with Primary and Secondary risk factors:

(i) a high rate of cadmium deposition onto the garden
(ii) high levels of cadmium in house dust.

These can be termed '<u>Tertiary risk factors</u>'.

These three distinct categories of risk factor can be deliniated to form the basis of a selection strategy which can be used to highlight high risk population groups or households, for it is evident that individuals or households to which one or more of these risk factors apply could be in a high risk group. As Walsall has been identified as an urban/industrial area with high background levels of cadmium contamination, the central hypothesis of this thesis may be tested by the identification and study of the residents of Walsall to which one or more risk factors apply.

Clearly, these individuals constitute the most at risk sector of the population and if these individuals are not affected in any way by high intakes of cadmium from dietary and adventitious ingestion, then it is more than likely that other equally or less exposed persons in Walsall, or of similar urban/industrial areas in the EC, would not exhibit any adverse health effects from elevated cadmium intakes.

5.2.4 Optimal Sample Size

A pre-requisite to the calculation of optimal sample size is a consideration of what kind of households or individuals are to be investigated in the final study population. From the preceding section, it is clear that a population group which is exposed to the most risk factors, particularly the primary risk factors, is required.

In order to identify all high risk households in Walsall a survey of each household would be necessary. However, with the aid of the worst-case concentration mapping methodology it is possible to identify areas of the borough where high risk households are more likely to be found. Nevertheless, the number of households involved is still too great, and it is necessary to calculate the optimum number (n) of households to survey whilst retaining a high probability of inclusion of households with the most primary and secondary risk factors.

A formula for 'n' is reliant on some property, or properties, of the population which is to be sampled. In the case above we require information on the frequency distribution of the risk factors amongst the general population of Walsall, or amongst the population living in the most contaminated parts of the borough. The only information available on the occurrence of the risk factors amongst the general population is the distribution of soil cadmium levels. These data however do not represent the distribution of cadmium in garden soils which are used for vegetable cultivation. The worst-case concentration contours show areas in which 2.5 per cent of the soil cadmium levels are equivalent to or above a certain level. The vegetable gardens within any given contour, however, may only take up a small proportion of the land surface area. The worst-case concentration contours, therefore, can only indicate areas of the borough in which there is a high probability of elevated soil cadmium levels in gardens and the areas in which sampling would be best carried out. Furthermore, the optimisation of one risk factor (a high level of cadmium in soil) cannot ensure an optimisation of the other, quite independent, risk factors. Clearly, the value for 'n' must be appraised using the more finite considerations of the resources available for carrying out the sampling, in particular the constraints of time and labour.

On the basis of these calculations a final study population of one hundred households (including twenty controls) is considered the maximum possible. Should the number of control households be increased, which ideally should be the case, a smaller number of high risk households would be able to be studied. The twenty controls have been chosen, therefore, merely as a sufficient size of group of households which can be used as a source of reference, primarily to determine if the techniques adopted for assessing dietary intakes of cadmium yield normal intakes for households showing little or no 'risk factors'. Whether the total sample size of eighty high risk households is sufficiently representative of any high risk group, which may be present in the worst contaminated areas of the borough, can only be assessed after an initial survey has been carried out to determine the presence of 'high risk factors' amongst the population. The prime objective of the initial survey, therefore, is to collect such data, after which a re-appraisal of sample size can be made.[219-221]

CHAPTER 6

ANALYTICAL METHODS

CHAPTER 6: ANALYTICAL METHODS

6.1 Initial Survey

6.2 Garden Soils

- 6.2.1 Sampling of Soils
- 6.2.2 Preparation of Samples
- 6.2.3 Extraction of Total Cadmium
- 6.2.4 Extraction of Plant-available Cadmium
- 6.2.5 Cadmium Determination by Atomic Absorption Spectrophotometry
- 6.2.6 Determination of pH
- 6.2.7 Speciation of Cadmium in Soils

6.3 Atmospheric Deposition

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- 6.3.2 Analysis of Deposition

6.4 Household Dust

- 6.4.1 Vacuum Dust
- 6.4.2 Carpet Dust
- 6.4.3 Settled Dust

6.5 Garden Vegetables

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- 6.6.1 Diet Diary
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6.7 Urine Analysis

CHAPTER 6: ANALYTICAL METHODS

6.1 INITIAL SURVEY

The initial survey of Walsall households was carried out between 1 October and 20 December 1982 within the area enclosed by the 10 mg kg^{-1} worst-case concentration contour. The prime objective of the survey was the identification of those households or individuals to which the primary and secondary 'risk factors' apply. The area of Walsall enclosed by the 10 mg kg^{-1} worst-case concentration contour for cadmium stretches from Pelsall in the north of the borough to the Sandwell/Walsall border in the south, enclosing an area of approximately 35 square kilometres (see Figure 5.9). For the purpose of the survey the area was conveniently divided into eight sectors, the boundaries of which were determined by the presence of major roads, canals or green belts. In addition, a period of 1-2 weeks was spent in each sector identifying households which had vegetable gardens.

Those householders which were found to grow vegetables in their garden or in an allotment were asked if they would allow a soil sample to be taken. Those who agreed to this were also asked to supply the following information:

- number of persons residing in the house;
- number of years they had lived in the house;
- number of years vegetables had been grown by the occupier in the garden soil;
- whether the occupier had previously grown vegetables in other parts of Walsall;
- occupation and smoking history of householder(s);
- whether vegetables were deep frozen for year-round consumption;
- how much of vegetable diet is home grown.

In addition, householders were also asked what sort of vegetables they normally grew, whether they intended to grow vegetables the following season and, should any contamination be found in their garden soil, would they allow vegetable samples to be taken for analysis in the coming season.*

Whilst collecting the soil samples an assessment was made of the size of the garden area used for vegetable cultivation and whether the householder could actually grow the proportion of vegetable diet claimed, bearing in mind the age and number of residents consuming vegetables from the garden.

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* Copies of all correspondence and questionnaires are presented in Appendix B.

After all the sectors had been thoroughly surveyed it was estimated that around 70 per cent of the households were suitable for inclusion in the study on the basis of primary risk factors. However, a number of households which had large vegetable gardens could not have their soils samples and be considered for inclusion in the study because the occupier(s) were not at home during the day time. The trial sample, therefore, was biased towards those householders who were either unemployed or retired. Nevertheless, some 568 questionnaires were completed and the same number of soil samples taken.

Due to the large number of samples the questionnaires were sorted prior to any soil analyses to eliminate those householders which did not grow greater than 30 per cent of their vegetable diet in their gardens. The figure of 30 per cent was chosen because firstly it was considered unlikely that a householder who grew less than 30 per cent of vegetables in the garden would significantly increase dietary intake of cadmium, even if the soil was found to be contaminated, and secondly there were sufficient householders in the most contaminated areas of the borough who claimed to grow greater than 70 per cent of their vegetable diet and who were willing to take part in an extended survey should their garden soils be found to contain high levels of cadmium.

After the questionnaires had been sorted 195 respondents, 168 of whom grew greater than 70 per cent of their vegetable diet, had their soils analysed for total and plant-available cadmium, as well as pH. Householders of eighty of the most contaminated gardens who were also exposed to a number of secondary risk factors including high soil pH, were then selected for inclusion in the final study along with twenty households which had low soil cadmium levels, and which were situated on the rural fringe of Walsall. A schematic representation of the screening process adopted for identifying high risk households is shown in Figure 6.1.

6.2 GARDEN SOILS

6.2.1 Sampling of Soils

Soil samples were taken from the top 10 cm of the soil profile using stainless steel sampling equipment which was cleaned between each sample. The number of samples which were taken depended on the garden size, with a sample being taken from every one to two square metres of vegetable garden. In all cases a minimum of six soil samples were bulked to form one composite sample which represented the whole of the vegetable garden. Soil was not taken from any area of a garden which was not specifically used for vegetable cultivation. Two vegetable gardens of similar size from each of the

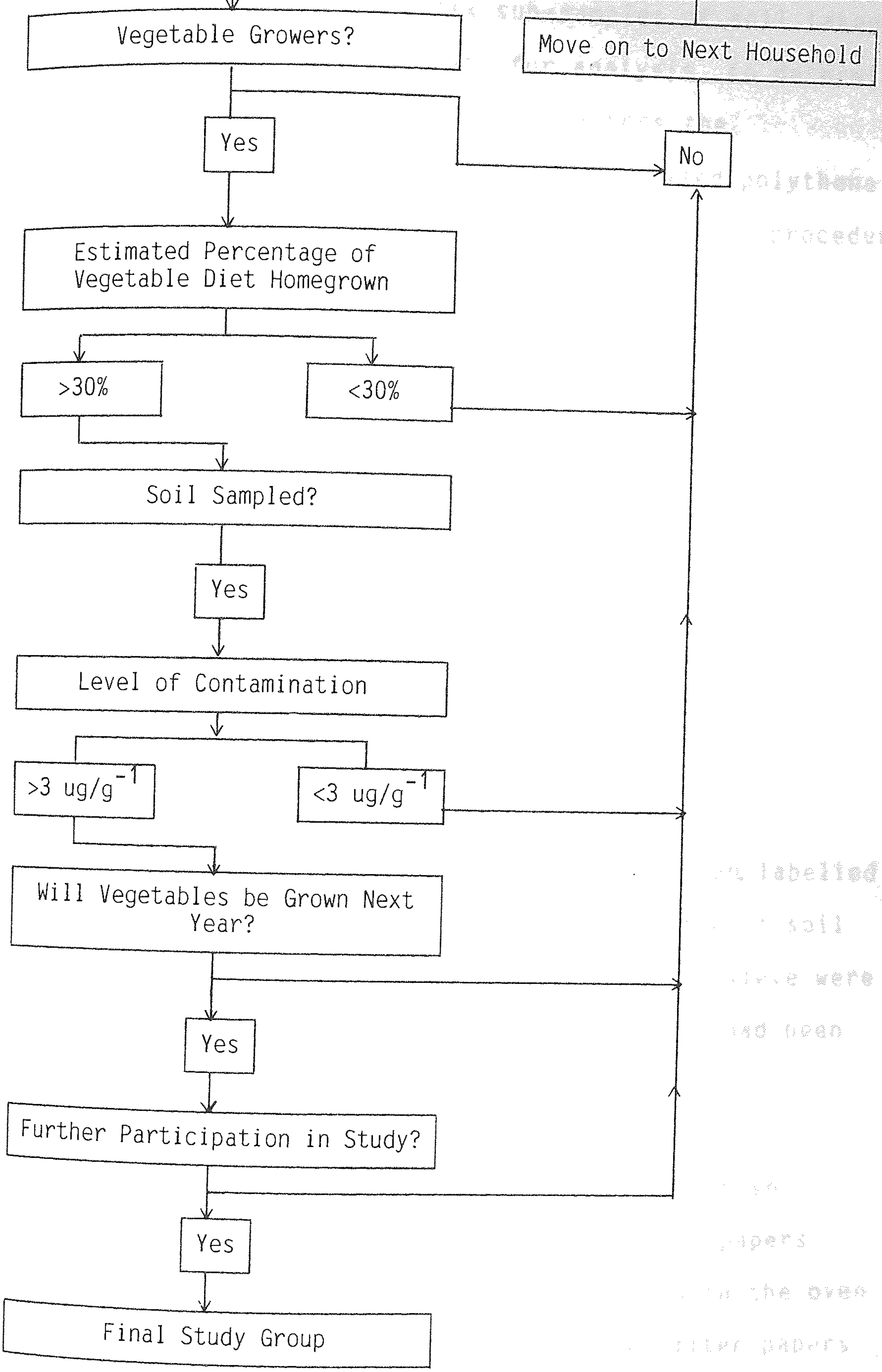

FIGURE 6.1: SCHEMATIC REPRESENTATION OF THE SCREENING PROCESS ADOPTED FOR IDENTIFYING 'HIGH-RISK' HOUSEHOLDS

eight survey sectors had six sub-samples of soil taken which were then kept separate for analysis, to determine the variability of cadmium levels across the garden. All samples were sealed in labelled polythene bags and returned to the laboratory. Sampling procedures and precautions recommended by the Ministry of Agriculture, Fisheries and Food were followed.[223]

6.2.2 Preparation of Samples

In the laboratory, soil samples were placed in aluminium foil trays and dried in an oven for 24 hours at 105°C. After drying, soil samples were removed from the oven and cooled in a desiccator. Each soil sample was then hand ground using a porcelain mortar and pestle to pass through a cleaned stainless steel sieve with a 2 mm mesh. The samples were then sealed into clean, labelled polythene bags. To avoid cross-contamination of soil samples at this stage the mortar, pestle and sieve were thoroughly cleaned and dried after each soil had been prepared.

As cross-contamination of soil samples could have occurred during drying, three ashless filter papers were placed in foil trays at various points in the oven when soil samples were being dried. The filter papers were removed and, together with three control filters, were analysed for cadmium. A comparison between 'exposed' and control filters indicated no cross-contamination or contamination from the oven itself.

6.2.3 Extraction of Total Cadmium

Duplicate 1 gram sub-samples of each ground soil were transferred to acid-washed 50 ml digestion flasks and 10 ml of Aristar grade concentrated nitric acid (HNO_3) were added to each flask and the contents thoroughly mixed. The digestion flasks were then positioned on an electric micro-distillation stand and left to cold digest for 24 hours. The digests were then gradually heated to approximately 50°C for 2-3 hours. The temperature of the digests was then increased to boiling point and heated until the organic matter had been digested.[224] The flasks were then removed from the heat and allowed to cool. After cooling, 2 ml of Aristar (70 per cent) perchloric acid ($HCLO_4$) was added to the digest in each flask. The contents were then heated until fumes of perchloric acid were emitted and the digest lightened in colour (2-4 hours). The residual digest solution was then allowed to cool before being filtered through Whatman No 41 ashless filter papers. The digest residue and flasks were rinsed with several aliquots of distilled water and the filtrate made up to a volume of 25 ml. Reagent blanks were prepared and run in the same manner as samples to take account of any cadmium introduced into the samples from the glassware or the chemicals.

6.2.4 Extraction of Plant-available Cadmium

Extraction of plant-available cadmium was made following guidelines recommended by the MAFF/ADAS.[225,226] The extractant consisted of 19 grams of Ethylenediamine tetra acetic acid Diammonium Salt (EDTA Diammonium Salt) in 1000 ml of glass distilled water. The pH was adjusted to 6.5 using nitric acid. Duplicate 1 gram sub-samples of ground soil were transferred to acid washed 50 ml Erlenmeyer flasks and 5 ml of 0.05M extractant added. The flasks were then thoroughly mixed on an orbital shaker at 250 rpm at room temperature for one hour. The flasks were then removed and the solution filtered through Whatman No 41 ashless filter papers. The residue was rinsed with several aliquots of distilled water and the filtrate made up to a volume of 10 ml. Reagent blanks were prepared and run in the same manner as samples to take account of any cadmium introduced into the samples from the glassware or chemicals.

6.2.5 Cadmium Determination by Atomic Absorption Spectrophotometry

The concentrations of cadmium in soil extractants was determined on a Perkin Elmer 560 double beam Atomic Absorption Spectrophotometer. Conventional flame absorption and single slot burner head with air-acetylene flame was used. Deuterium arc background correction was used throughout and the instrument was set up according to the manufacturer's recommendations. An absorption/concentration calibration curve was obtained by the use of duplicate standard solutions of 0.5, 1.0 and 2.0 ppm, made up from a commercially prepared (BDH Chemicals) stock standard solution of 1000 ppm cadmium as the nitrate. Fresh standard solutions were made up from stock on each day of analysis by dilution with 10 per cent nitric acid solution made up with glass distilled water.

A hollow cathode lamp was used as the radiation source and the 228.8 nm wavelength selected with a slit setting of 0.7 nm. Lamp alignment, burner angle, gas flow and nebulizer were adjusted to achieve maximum sensitivity of the instrument using the duplicate standards. The performance and calibration of the instrument was checked throughout by frequent atomisation of standards. This was carried out to correct for wavelength drift or lamp/burner misalignment.

6.2.6 Determination of pH

Soil pH was determined by transferring duplicate 10 gram sub-samples of ground soil into 100 ml acid washed Erlenmeyer flasks and diluting with 25 ml of glass distilled water. The pH was measured using a combined glass electrode and Calomel half cell probe with a Model 7020 pH meter supplied by Electronic Instruments Limited.

6.2.7 Speciation of Cadmium in Soils

After analysis had been carried out on the Walsall soils for total cadmium, six households which were found to have high levels of cadmium in their garden soils were visited to collect an additional soil sample. These samples were then analysed at Westfield College, University of London to determine the chemical speciation of cadmium in the soils. The analytical techniques used, based on Ion-Exchange Chromatography and Reverse-Phase High Pressure Liquid Chromatography (HPLC), were developed at the University of London and are reported in the literature.[227,228]

6.3 ATMOSPHERIC DEPOSITION

6.3.1 Installation of Gauges

Deposit gauges were constructed for the study from 60 mm diameter 500 ml capacity food grade plastic containers which were surrounded with steel pins on the rim to prevent contamination from birds settling on them (see Plate 6.1). The gauges were firmly attached to a 6 foot high wooden stake driven into the garden soil away from any possible interference factors such as walls, outbuildings, clothes lines etc. The positioning of the gauges on wooden stakes also prevented soil contamination from rain splash and other ground interferences (Figure 6.2). The gauges were left in the

PLATE 6.1: DEPOSIT GAUGE USED IN THE WALSALL STUDY

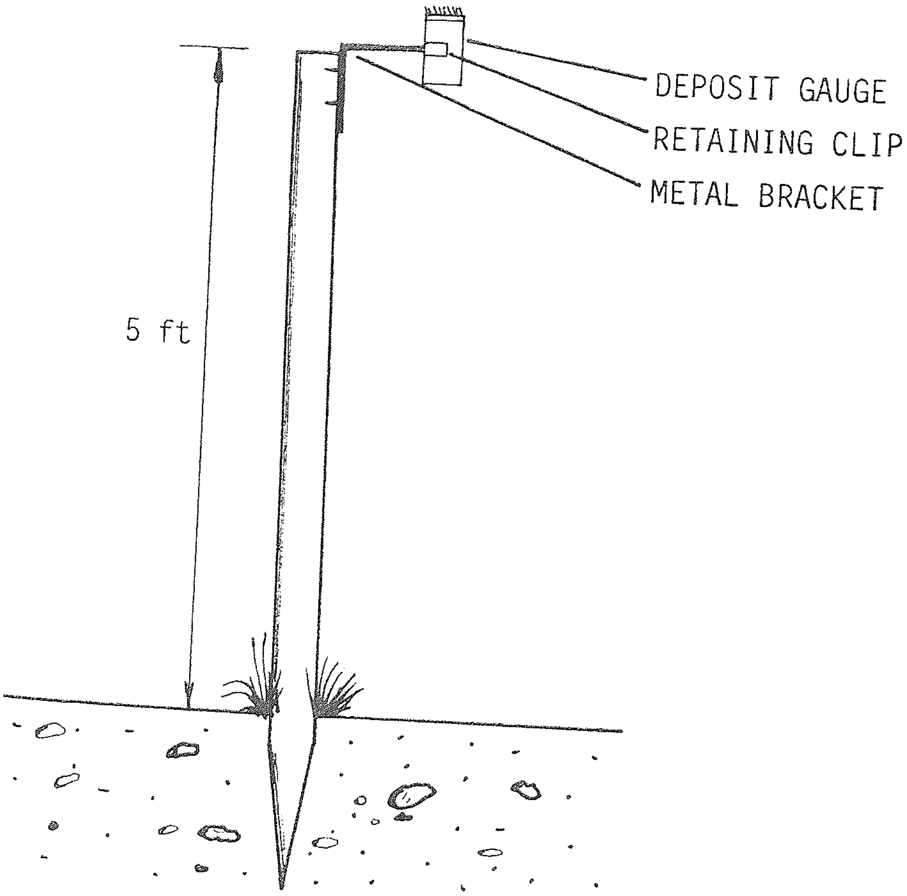

FIGURE 6.2: DIAGRAMATIC REPRESENTATION OF INSTALLED DEPOSIT GAUGE

gardens for a period of six months, June and November 1983 inclusive. Two 'control' gauges containing dilute nitric acid (10 per cent) and five steel pins were also left for this period in the laboratory, covered with a plastic lid. This was to determine if there was any contamination from the pigmented plastic container or from the pins.

6.3.2 Analysis of Deposition

When the gauges were collected and returned to the laboratory the contents of dust and rain water were transferred to acid washed 50 ml digestion flasks. The flasks were then positioned on an electric micro-distillation stand and heated to evaporate the water. The gauges were rinsed with glass distilled water and the inside wiped with a Whatman No 41 ashless filter paper which was then added to the digest flask with 10 ml of 'Aristar' nitric acid. The flasks were then treated in the same manner as for the total cadmium soil analysis described in paragraph 6.2.3.

Two 1 gram samples of steel pins, the same as those used to protect the tops of the gauges from birds, were digested in the same manner described above, along with reagent blanks, to take account of any cadmium which may have been introduced into the samples from these sources.

The cadmium content of the samples was determined using Atomic Absorption Spectrophotometry as described in paragraph 6.2.5. The absorbance readings from the calibration curve were adjusted to take account of the sample dilution, and the amount of cadmium present was calculated and expressed as deposition in grams per hectare per year (g ha^{-1} yr^{-1}) and milligrams per square metre per 30 days (mg m^2 30 days).

6.4 HOUSEHOLD DUST

A review of the methodological approach to household dust collection and analysis has been carried out by the author, and the techniques adopted for the Walsall study, and reported here, are based on this review.[229]

6.4.1 Vacuum Dust

Vacuum dust was collected by removing the homogenised material from the dust bag of the householder's vacuum cleaner and placing it in a labelled polythene bag which was then taken to the laboratory. The contents were then lightly sieved through a stainless steel 250 um sieve to remove all extraneous material such as carpet fibres and hair. The fine dust was then transferred into a small labelled polythene bag which was placed in a desiccator for storage. The sieve and all surfaces were rinsed with glass distilled water between each sample being prepared to avoid cross contamination.

Once all the dusts had been sieved, duplicate 1 gram sub-samples from each bag were transferred to 50 ml digest flasks. Subsequent digestion and analysis was carried out as described for soils in paragraph 6.2.3.

6.4.2 Carpet Dust

As vacuum cleaner dust collected from the householders' vacuums is not directly comparable because a different machine was used to collect each sample, a dust sample was collected from the carpet of the main living quarters of each household, usually the hall or living room. The carpet dust was collected from approximately two square metres of carpet using a technique devised by the author which made use of a vacuum cleaner which drew air, and carpet dust, through a specially constructed nozzle containing a 60 mm Soxhlet extraction thimble, which allowed the air to pass through but entrapped any dust particles or extraneous material (Figure 6.3 and Plate 6.2).

As the Soxhlet extraction thimbles were found to vary in weight, each one was weighed and placed into a labelled polythene bag, on which the weight was recorded. After the dust sample had been collected, the extraction thimble was cut open and any extraneous material removed. The thimble was then re-weighed to determine the weight of the dust sample.

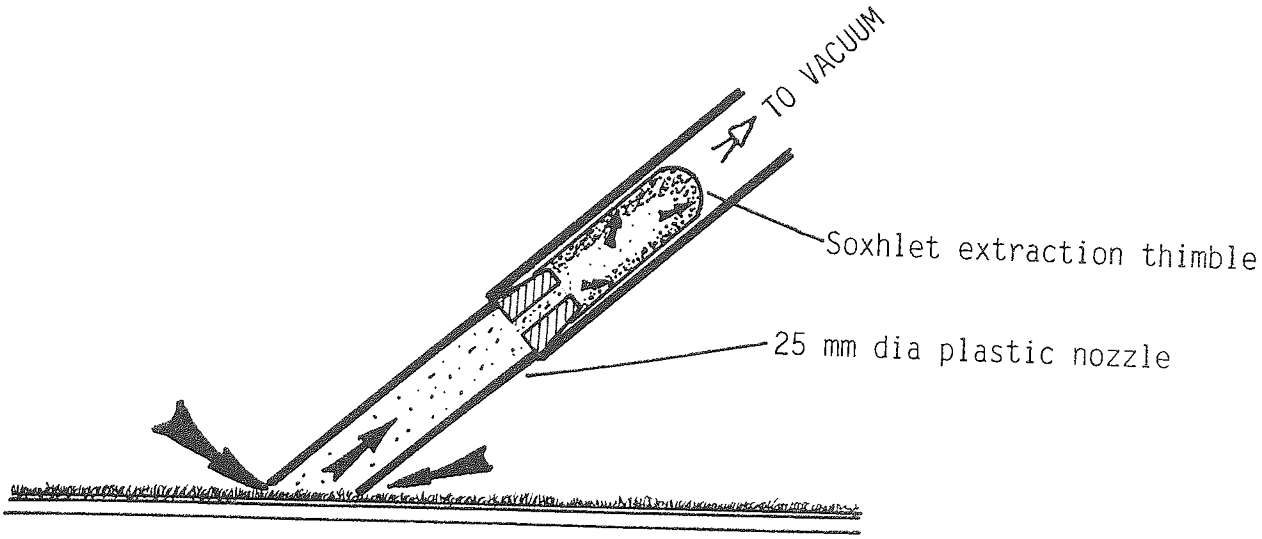

FIGURE 6.3: DIAGRAMATIC REPRESENTATION OF TECHNIQUE ADOPTED FOR THE COLLECTION OF CARPET DUST

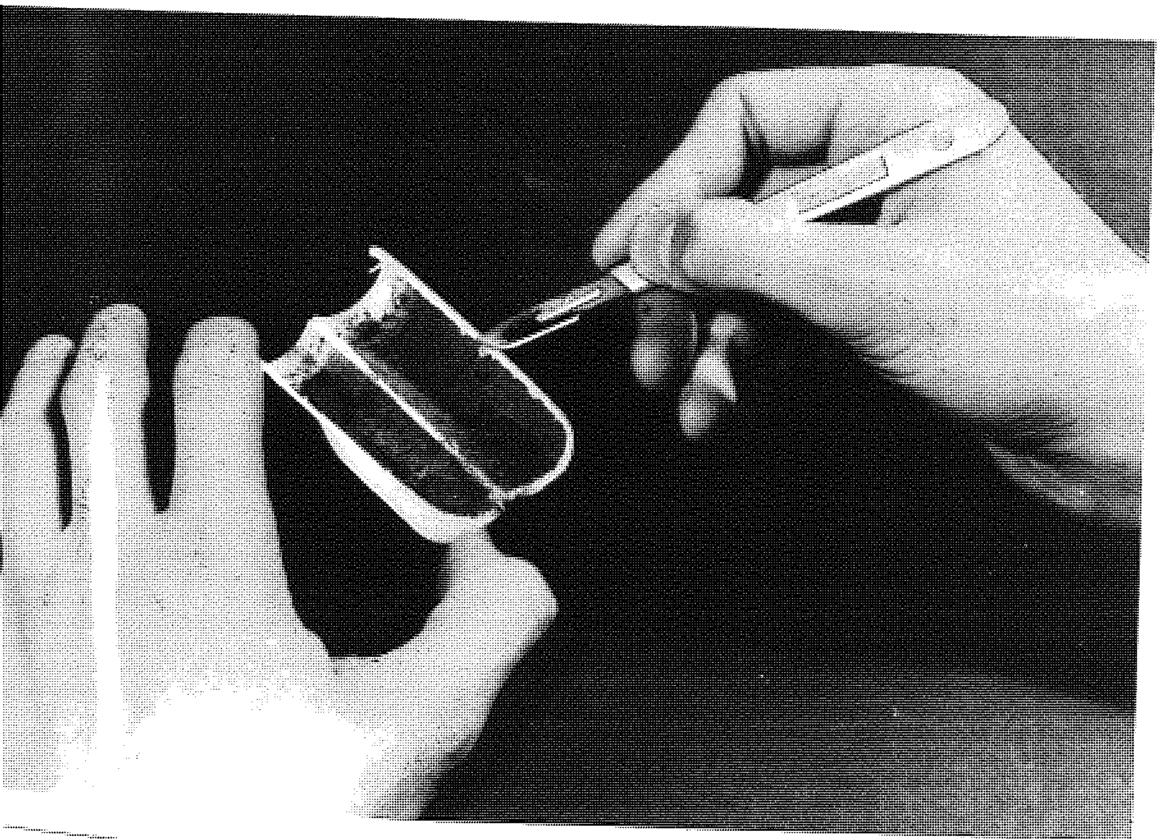

PLATE 6.2: SOXHLET EXTRACTION THIMBLE CONTAINING CARPET DUST SAMPLE

The dust and the thimble were then transferred to a 50 ml digest flask in which 20 ml of concentrated 'Aristar' nitric acid was added. The flasks were then positioned on a micro distillation stand and left to cold digest for 24 hours. The digests were then gradually heated to approximately 50°C for 4-6 hours. The temperature of the digests was then increased to boiling point and heated until the organic matter had been digested. The flasks were then removed from the heat and allowed to cool. After cooling, 4 ml of 'Aristar' (70 per cent) perchloric acid was added to the digest in each flask. The contents were then heated until perchloric acid fumes were emitted and the digest lightened (2-4 hours). The residual digest solution was then allowed to cool before being filtered through Whatman No 41 ashless filter papers. The digest residue and flasks were rinsed with several aliquots of distilled water and the filtrate made up to volume of 25 ml. Reagent blanks containing clean extraction thimbles were prepared and run in the same manner as samples to take account of any cadmium introduced into the samples from the glassware or the chemicals.

6.4.3 Settled Dust

Analyses of household floor dusts carried out elsewhere[230] has shown that the cadmium and minerological content are similar to that of surrounding garden soils. It is considered, however, that settled household dust has at some time been airborne and that the dust is of a different origin from the carpet dust.[229]

As no scientifically justified methodological approach to the collection and analysis of settled household dusts has been reported in the literature, a novel technique was developed for this study.[229] This technique was based on the principle of sucking the dust particles up from the household surface onto a filter paper which could then be digested whole. Laboratory trials with a prototype collector using 9 cm Whatman No 41 filters demonstrated a 93.47 per cent collection efficiency, which could be increased to 94.23 per cent if the filter paper was dampened with a fine spray before being fitted into the collector.[229] (Plates 6.3 and 6.4). Utilising this filter-suction technique, samples of settled house dust were collected from the Walsall households on surfaces which were more than 1.25 metres from the floor. Usually the tops of doors, pelmets or picture rails proved to be the most suitable collection surfaces. Dust was not collected from the kitchen areas because a high grease and oil content made collection difficult. Dust from the upstairs of households was also avoided because the high talc and skin content of this dust might well produce an unrepresentative sample.

Once the sample of settled house dust had been collected the filter paper was removed from the filter housing, folded carefully and placed into a labelled polythene bag. In the laboratory the folded filter paper was placed in an aluminium foil dish and dried in an oven

PLATE 6.3: COLLECTION OF SETTLED HOUSE DUST USING A NOVEL FILTER-SUCTION TECHNIQUE

PLATE 6.4: FILTER PAPER COATED WITH SETTLED HOUSE DUST SAMPLE

at 105°C for 24 hours. The filter paper containing the dust was then weighed and transferred to a 50 ml digestion flask and 10 ml of concentrated Aristar nitric acid (HNO_3) added. The flasks were then positioned on a micro distillation stand and left to cold digest for 24 hours. The digest procedure reported for soils in paragraph 6.2.3 was then followed.

The dry weight of the filter papers used to collect the settled dust samples was found to vary little so a subtraction of the mean filter paper weight from the weight of the dried dust-laden filter gave the weight of the dust sample collected in each case. Reagent blanks containing the same type of filter paper used to collect the settled dust samples were prepared and analysed in the same manner as the samples, to take account of any cadmium introduced during preparation.

The cadmium content of all dust samples and reagent blanks was determined using Atomic Absorption Spectrophotometry as described in paragraph 6.2.5. The amount of cadmium present was expressed as ug g^{-1} dust.

To take account of any sources of cadmium contamination from within a household, a questionnaire was completed whenever dust samples were taken. This questionnaire (presented in Appendix B) recorded the type of heating, the age of the house, presence of pets, distance from the road, road classification and whether the household had double glazing. These data, in addition to the data previously collected on number of residents and number of smokers in each household, were then individually correlated with the cadmium in dust level.

6.5 GARDEN VEGETABLES

6.5.1 Sampling of Vegetables

All 80 study households which had high soil cadmium levels, as well as 20 control households, were sent a letter in March 1983 requesting their further co-operation in the second stage of the research, which involved the sampling of garden vegetables (Appendix B). These households were then visited in April 1983 and the type of vegetables they intended to grow were noted, together with the approximate planting times. The participants were then re-visited at various times during the period May-December 1983 to collect vegetable samples as they matured.

Vegetable sampling techniques recommended by the Ministry of Agriculture, Fisheries and Food (MAFF)[223] were adopted throughout the study, not only for the sampling of vegetables for analysis but also the assessment of crop yield. However, as discretion had to be shown when taking vegetable samples from study gardens, the sample size varied depending not only on the type of vegetable but also on the amount of a particular vegetable type being grown. When more than one sub-sample of a vegetable type was required, samples were taken at randomly-selected points along a row. Table 6.1 summarises the general size of samples taken for each vegetable type.

When sampling a vegetable type, an average sized vegetable, or number of vegetables, was taken and placed into a labelled polythene bag. These samples were later weighed so that the crop yield on a weight basis could be estimated. In two cases, however, householders had recorded for previous years the amount of vegetables grown in their garden, on a weight and number basis. As the amount grown in their gardens from year to year did not vary greatly, the crop yield for the season of 1983 could be accurately predicted. These two gardens proved to be valuable yardsticks when the crop yield of other gardens had to be estimated by viewing the crops in the ground.

6.5.2 Sample Preparation

In the laboratory the vegetable samples were immediately washed in glass distilled water to remove debris and soil particles, and prepared as for ordinary culinary use by removing exterior leaves or peelings. The samples were then placed into disposable aluminium foil trays and weighed to determine fresh weight before being dried in an oven for 24 hours at 80°C.[215] After drying

VEGETABLE TYPE	SAMPLE SIZE
Beans	4-6 pods
Beetroot	1-2 (depending on size)
Broccoli	One whole sprig
Brussel Sprouts	6-10
Cabbage	One whole plant
Carrots	2-6 (depending on size)
Cauliflower	One whole plant
Celery	One whole plant
Courgettes	Two
Cucumber	One or ½ (depending on size)
Kale	2-4 plants (depending on size)
Leek	1-2 plants (depending on size)
Lettuce	1-4 plants (depending on size)
Marrow	One whole vegetable
Onion	1-2 sets (depending on size)
Parsnips	1-2 (depending on size)
Peas	6-10 pods
Potatoes	1-3 (depending on size)
Radish	6-10
Shallots	2-4 bulbs
Spinach	2-4 plants
Spring Onion	6-10
Swede	One whole vegetable
Tomato	1-2
Turnip	One whole vegetable

TABLE 6.1: SAMPLE-SIZE TAKEN FOR EACH VEGETABLE TYPE

the vegetable samples were removed from the oven and reweighed to determine dry weight. From these figures the moisture content was calculated. Each vegetable sample was then finely hand ground with a porcelain mortar and pestle. The samples were then transferred to clear, labelled sample bags which were then stored in a desiccator. All vegetable samples were dried and stored within 36 hours of being collected in the field, to avoid cross-contamination after each sample had been prepared.

6.5.3 Analysis of Vegetable Samples

A variety of techniques have been published in the literature on the destruction of organic matter prior to analysis for metallic impurities. Six methods reported in the literature, viz: wet digestion using Nitric/Perchloric acid ($HNO_3/HCLO_4$)[231], Nitric acid (HNO_3)[215], Nitric/Hydrochloric acid (HNO_3/HCl)[232], Sulphuric acid/Hydrogen Peroxide (H_2SO_4/H_2O_2)[233], and Nitric/Sulphuric acid (HNO_3/H_2SO_4)[234], as well as a dry ash/Hydrochloric acid (HCl) digest technique[234], were all arried out on two types of standard reference material and a sample of spring cabbage from a Walsall garden, and their relative efficiencies compared.

Six triplicate 1 gram oven dried sub-samples of the Walsall cabbage, Bowen's Kale* and US National Bureau

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* I am indebted to Dr H Bowen of the Department of Chemistry, University of Reading, for the supply of 100 grams of Standard Reference Kale.

of Standards (NBS) reference Bovine Liver (1577) were weighed and transferred to a 50 ml digestion flask and each of the six analytical techniques carried out on each series of triplicate samples. After filtering and making up to volume, cadmium determination was carried out using Flame Atomic Absorption Spectrophotometry as described in paragraph 6.2.5. The results of these analyses, presented in Table 6.2, show that the Nitric/Perchloric acid ($HNO_3/HCLO_4$) and the Nitric (HNO_3) digest techniques were the most sensitive for Bowen's Kale, although not so sensitive for NBS Bovine Liver. However, as a technique for the analysis of vegetable samples was sought it was considered that the most sensitive, and least dangerous of these techniques, Nitric acid (HNO_3) digestion, would be used for the analysis of vegetables collected from Walsall.

Duplicate 1 gram sub-samples of each Walsall vegetable sample were transferred to 50 ml digestion flasks and 10 ml of concentrated Aristar grade Nitric acid added. The samples were then placed on a micro distillation stand and left to cold digest for 24 hours before being gradually heated to approximately 50°C for 2-3 hours. The temperature of the digests was then increased to boiling point and heated until all the organic matter had been digested and the digest solution lightened. The flasks were then removed from the heat and allowed to cool. After cooling, the digest solution was filtered through a Whatman No 41 ashless filter paper

	BIOLOGICAL MATERIAL											
	BOWEN'S KALE (ug.g^{-1}Cd)				BOVINE LIVER (ug.g^{-1}Cd)				WALSALL CABBAGE (ug.g^{-1}Cd)			
REAGENT	SAMPLE 1	SAMPLE 2	SAMPLE 3	$\bar{x}$	SAMPLE 1	SAMPLE 2	SAMPLE 3	$\bar{x}$	SAMPLE 1	SAMPLE 2	SAMPLE 3	$\bar{x}$
$HNO_3/HCLO_4$	0.88	0.74	0.80	0.81	0.38	0.29	0.31	0.33	3.41	2.67	3.01	3.03
HNO_3	0.90	0.88	0.86	0.88	0.39	0.31	0.25	0.32	3.22	3.06	3.61	3.30
HCL	0.75	0.58	0.64	0.66	0.30	0.29	0.32	0.30	2.97	2.58	3.27	2.94
HNO_3/HCL	0.79	0.82	0.77	0.79	0.30	0.27	0.31	0.29	3.30	2.97	3.01	3.09
H_2SO_4/H_2O_2	0.51	0.46	0.22	0.40	ND	ND	ND	-	1.67	2.48	2.09	2.08
HNO_3/H_2SO_4	0.83	0.75	0.78	0.79	0.27	0.29	0.33	0.30	3.18	3.22	3.63	3.34

Published Cadmium Content of Standard Reference Materials: Bowen's Kale 0.874 ± 0.156 (0.718 - 1.03)
NBS Bovine Liver 0.27 ± 0.04 (0.23 - 0.31)

TABLE 6.2: COMPARATIVE EFFICIENCIES OF CADMIUM EXTRACTION FROM VARIOUS BIOLOGICAL MATERIALS USING SIX DIFFERENT PUBLISHED TECHNIQUES

and made up to 10 ml with glass distilled water. Reagent blanks were prepared and run in the same manner as samples to take account of any cadmium introduced into the samples from the glassware or the chemicals. Samples of Bowen's Standard Reference Kale were also run with each sample batch for reference purposes.

During 1983 the Ministry of Agriculture, Fisheries and Food (MAFF), Food Science Division, requested the author to take part in an Analytical Quality Assurance scheme, which entailed the analysis of a number of biological samples for lead and cadmium, for comparison with private and Governmental laboratories.[236,237] The Nitric acid digestion procedure described above was used on the submitted specimens. The results of these analyses, presented in Appendix C, show that the analytical procedures used produced results which were in an accepted range of values for each specimen.

6.5.4 Loss of Cadmium During Cooking

An experiment was carried out to determine the amount of cadmium which would be lost if the vegetable samples were cooked. Fresh samples of cabbage, swede, carrot, cauliflower, parsnip, marrow, beetroot, turnip, leek, brussel sprouts, runner beans, potato and dwarf beans were prepared for ordinary culinary use, as described in paragraph 6.5.2. Before the samples were oven dried, however, the vegetables were cut longitudinally into two halves and one half retained for cooking. This was carried out on six samples of each vegetable type except for marrow, dwarf beans and turnip, for which insufficient sample numbers were available. In total, 70 samples were prepared and cooked.

Each vegetable sample was placed in a 500 ml glass beaker and 300 ml of glass distilled water, containing 5 grams of NaCl per litre, was added. The samples were then cooked until tender before being drained and transferred to aluminium foil trays. The samples were then dried and ground in the same manner as the other vegetable samples described in paragraph 6.5.2.

6.5.5 Speciation of Leaf Surface Particles

In order to determine the presence and composition of environmentally derived particles on the surface of vegetables intended for human consumption, before and after their culinary preparation, two lettuce plants were collected from each of three study gardens situated within 500 metres of a secondary copper refinery in Walsall. After the outermost leaves of each lettuce had been removed and discarded, half of the inner leaves of each lettuce were thoroughly cleaned in glass distilled water and the remaining leaves left unwashed. The leaves of each lettuce were then placed into aluminium foil trays and dried at 80°C for 24 hours. Sub-samples of each leaf were then prepared using standard techniques for viewing under a Scanning Electron Microscope (SEM) and for characterisation of leaf surface particles by X-ray microanalysis.[238,239]

6.6 DIETARY INTAKES

6.6.1 Diet Diary

To determine the amount of home-grown vegetables which householders were consuming, and thus the amount of cadmium being taken in from this source, a number of households were requested to keep a record of the type and weight of vegetables they consumed. This survey was carried out over a period of 28 days during the month of September. Twenty households, including five from the control group, were selected according to the level of contamination in their garden soil and the proportion of vegetable diet claimed to be home-grown. The householders were then all given identical sets of kitchen scales (which had previously been calibrated for comparability and accuracy) and a diet diary (Appendix D).

Householders were then asked to keep a record over the period, of all vegetables and fruit (excluding tree fruit) consumed by the adult members of the household. Householders were not only requested to record the type of vegetable or fruit but also the weight of each after cooking and before serving, and to note whether it was home grown or produced elsewhere. If any vegetables were left over after a meal (and not saved for other meals) householders were requested to weigh the left-overs and deduct it from the original weight of the food before serving. If householders were away from home for any whole days they were requested to write 'Away' in the diary column for the day and continue the diary for an extra day. Hence, each household recorded the actual weight of vegetables consumed by the adult members of the household over a complete 28-day period. Using the data obtained from the analysis of garden vegetables a straightforward calculation was carried out to determine the dietary intake of cadmium from the vegetable part of their diet. With the use of published data on the intakes of cadmium from other food sources, a total dietary intake of cadmium was calculated for each adult on a weekly basis.

Hence:

Cadmium intake from Walsall-grown fruit and vegetables (mg week^{-1}) = Walsall-grown food consumption (kg person week^{-1}) x cadmium concentration in food crop (mg kg^{-1})

Total cadmium intake from diet = Intake from Walsall-grown fruit and vegetables + Intake from other fresh fruit and vegetables* + Intake from rest of diet

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* MAFF Annual Report of the National Food Survey Committee (1980) Household Food Consumption and Expenditure (HMSO)[241]

6.6.2 Standard Diet

Each year the Ministry of Agriculture, Fisheries and Food publish an annual report of the National Food Survey. This survey derives data from 7,695 private households throughout Great Britain and covers in detail the food brought into the home for human consumption. Each household is requested to keep a record over a period of seven days, with the survey work being carried out throughout the whole year to take account of seasonal variations.[241]

Amongst other interesting data, this survey produces figures* in ounces per week on the average national food consumption of individual food types. Using published data on the typical cadmium content of these food types[56,242] it is possible to calculate the dietary intake of cadmium for a typical UK adult.

Table 6.3 shows the amounts of each type of vegetable and fruit which a typical UK adult would consume in any given week, the reported cadmium content of these food types and the cadmium intake derived from fresh vegetables, frozen and tinned vegetables and fruit. It is evident that in a normal diet a typical UK adult would ingest approximately 0.18 mg of cadmium per week from vegetables and fruit, together with a reported 0.11 mg from other food sources such as meat and dairy produce.[240] This amounts to a weekly intake of approximately 0.29 mg Cd^{-1} per week, equivalent to around 42 ug day^{-1}.

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* These figures do not include meals eaten in restaurants, soft drinks, alcoholic drinks, sweets or chocolates.

Fruit and Vegetable Types	Vegetable Consumption Averaged over a 12-month period (grams person week^{-1})	Typical Mean Levels of Cadmium on a Wet Weight Basis (ug g^{-1})	Levels of Cadmium in Vegetable Intake (ug person week^{-1})	Sub-Totals
Cabbage, fresh	98.70	0.05	4.935	Fresh veg 117.52 ug
Brussel sprouts, fresh	40.54	0.03	1.2162	
Cauliflowers, fresh	72.01	0.02	1.4402	
Leafy salads, fresh	31.19	0.109	3.3997	
Peas, fresh	4.82	0.05	0.241	
Beans, fresh	7.66	0.047	0.36002	
Other fresh greens	2.84	0.02	0.568	
Potatoes, fresh	1103.10	0.08	88.248	
Carrots, fresh	91.85	0.09	8.2665	
Turnips & swedes, fresh	27.78	0.05	1.389	
Other root veg, fresh	16.16	0.04	0.6464	
Onions, shallots, leeks, fresh	88.45	0.04	3.538	
Cucumbers, fresh	27.22	<0.01	0.2722	
Mushrooms, fresh	17.01	0.02	0.3402	
Tomatoes, fresh	94.97	0.02	1.8994	
Misc veg, fresh	31.75	0.04	1.27	
Rhubarb, fresh	2.84	0.02	0.0568	
Canned Peas	66.91	0.07	4.6837	Other veg 54.666 ug
Canned Beans	116.80	0.04	4.672	
Canned veg (excluding potatoes and tomatoes)	34.59	0.09	3.1131	
Dried pulses	11.34	0.06	0.6804	
Air-dried veg	0.29	0.03	0.0087	
Vegetable juices (fl oz)	3.40	<0.01	0.034	
Chips (excl frozen)	30.62	0.08	2.4496	
Instant potato	2.27	0.08	0.1816	
Canned potato	3.69	0.08	0.2952	
Crisps	21.55	0.08	1.724	
Other veg products	9.07	0.04	0.3628	
Frozen peas	51.03	<0.02	0.96957	
Frozen beans	15.59	<0.04	0.60801	
Frozen chips	42.53	0.08	3.4024	
All frozen veg not elsewhere specified	29.20	<0.06	1.7228	
Oranges, fresh	86.18	0.01	0.8618	Fruit 9.189 ug
Other citrus fruit	54.15	0.01	0.5415	
Apples, fresh	184.84	0.015	2.7726	
Pears, fresh	32.04	0.015	0.36846	
Stone fruit, fresh	23.81	0.04	0.9524	
Grapes, fresh	16.16	0.01	0.1616	
Soft fruit other than grapes	15.03	0.01	0.1503	
Bananas, fresh	88.45	0.011	0.97295	
Tomatoes, canned/bottled	43.09	<0.01	0.4309	
Other fresh fruit	17.01	<0.01	0.1701	
Canned peaches, pears and pineapple	39.69	<0.01	0.3969	
Other canned and bottled fruit	34.02	<0.01	0.3402	
Fruit juices	112.83	<0.01	1.1283	
Other dried, frozen and canned fruit	37.14	0.01	0.3714	
TOTAL	2981.29			
Total contribution from vegetables and fruit =			181.3826 ug 0.1814 mg	
Contribution from other food sources			0.11 mg	
Total weekly dietary intake =			0.2914 mg 41.62 ug day^{-1}	

LE 6.3: CADMIUM INTAKE FROM VEGETABLES AND OTHER FOOD SOURCES FOR A TYPICAL UK ADULT

Should an individual grow vegetables in soil contaminated with cadmium, and consume the vegetables, the dietary intake of cadmium from the vegetable part of the diet would gradually increase as more contaminated vegetables are consumed. During the field work and sample preparation, reported in paragraphs 6.5.1 and 6.5.2 respectively, the amount and weight of each vegetable type grown by the Walsall residents was recorded, together with the estimated proportion of vegetable diet grown at home and the number of residents in the household. The dietary intake of cadmium can therefore be calculated for each Walsall householder if it is assumed that all the vegetables grown in the garden are consumed.

Hence:

Total cadmium intake from diet (ug person week) =

$$\frac{\sum \frac{xy}{n} + \sum a - a\left(\frac{p}{100}\right) + b}{52}$$

where:

x = amount of each vegetable type grown (grams/year)

y = cadmium concentration in the vegetable (ug g^{-1})

n = number of residents in the household

a = intake from other vegetables and fruit (ug Cd y^{-1})

b = intake from the rest of the diet (ug Cd y^{-1})

p = proportion of vegetable diet home grown (%)

This would then represent each householder's highest possible cadmium intake from home produced vegetables.

The figure can then be adjusted to take account of the cadmium which would be lost when the vegetables are cooked, and by a factor to take account of wastage.

This calculation was carried out for each Walsall householder in the study and the mean daily cadmium intake of the main study group compared with the intakes calculated for the control householders. In addition, the results obtained from the standard diet technique were compared with the results of the diet diary technique carried out on the same households. The results of these calculations are described in Chapter 7.

6.7 URINE SAMPLES

To determine the degree to which cadmium had been accumulated in the kidneys of exposed Walsall residents and to test for any signs of cadmium-induced kidney damage, a group of Walsall residents in the main study group were requested to provide urine specimens.

6.7.1 Collection of Samples

In all, 52 householders who grew vegetables in the most highly contaminated garden soils and who had no history of smoking, kidney disease or occupational exposure to cadmium were selected and requested to provide a single urine sample for analysis of cadmium, B_2-microglobulin, creatinine and pH. Samples were collected first thing in the morning directly into 50 ml labelled, plastic sample tubes. The samples were then taken straight to the laboratory for immediate analysis.

6.7.2 Cadmium in Urine (CdU)

Cadmium determination was carried out directly using Delves cup Atomic Absorption Spectrophotometry with a Perkin Elmer 560 Atomic Absorption Spectrophotometer set on the manufacturer's recommended conditions for cadmium analysis.[243] (See paragraph 6.2.5)

6.7.3 B_2-Microglobulin

Determination of B_2-Microglobulin was carried out by radio-immunoassay with the Phadebas B_2-micro test kit (Pharmacia Diagnostics AB, Uppsala, Sweden). The manufacturer's recommended procedure was followed throughout.[244]

6.7.4 Creatinine and pH

Creatinine was determined using standard colourimetric analysis as described elsewhere[245] and pH was measured directly using the technique described in paragraph 6.2.6.

6.7.5 Total Protein

Total protein was determined using a standard colourimetric assay technique.[243]

CHAPTER 7

RESULTS AND DISCUSSION

CHAPTER 7: RESULTS AND DISCUSSION

7.1 Initial Survey and Soil Analysis

- 7.1.1 Residential Development
- 7.1.2 Risk Factors Amongst the Population
- 7.1.3 Selection of Study Population

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- 7.3.2 Cadmium Content of Vegetables
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7.4 Household Dust

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7.6 Urine Analysis

- 7.6.1 Participating Residents
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- 7.6.5 Other Findings

CHAPTER 7: RESULTS AND DISCUSSION

7.1 INITIAL HOUSEHOLD SURVEY AND SOIL ANALYSIS

7.1.1 Residential Development

The initial survey revealed most of the areas with high background levels of soil cadmium to have residential development in the form of post-war council houses, with a large number of gardens being used for intensive vegetable cultivation. In addition, some 34 allotment sites were located within the borough which were being cultivated by local residents. In all, around two to three thousand households were considered for inclusion in the study and, of these, 568 had soils sampled because their gardens were being used for vegetable cultivation. When permission was asked of the householders to take a soil sample, a number of questions were posed to determine the length of residence, number of years vegetables had been grown and the proportion of vegetable diet which was home produced (see paragraph 6.1).

7.1.2 Risk Factors Amongst the Population

The information collected from the initial survey revealed a heavy dependence by many householders on home grown produce. It was also evident that, as the survey was carried out during normal working hours, a large number of unemployed and retired people were included. This is an important point, as it is the lower income groups such as the unemployed and retired who tend to rely on their gardens to provide a high proportion of their vegetable diet. In addition, as the sample was biased towards the older generation, which would have tended to have grown vegetables over many years, and to unemployed people, who would tend to spend much of their time gardening, the sample population comprised residents exposed to a greater number of risk factors than would have been obtained by a survey carried out outside working hours. On the basis of growing more than 70 per cent of their own vegetables, 193 households were chosen to have their soils analysed for total and plant-available cadmium, as well as pH. In addition, over 50 per cent of these households had freezers in which home grown produce was frozen for year-round consumption.

Figure 7.1 shows the distribution of total and plant-available cadmium levels in all 193 garden soils. It was found that 42 per cent of the garden soils had total cadmium concentrations above the ICRCL 3 mg kg^{-1} 'Trigger concentration' for land intended for vegetable gardens and allotments referred to in paragraph 5.2.2. The mean total cadmium concentration was 4.2 mg kg^{-1} but with levels as high as 23 and 33 mg kg^{-1} for plant-available and total cadmium levels respectively. Also, the levels of total and plant-available cadmium were found to be highly correlated ($r=0.9279$, $p=<0.001$).

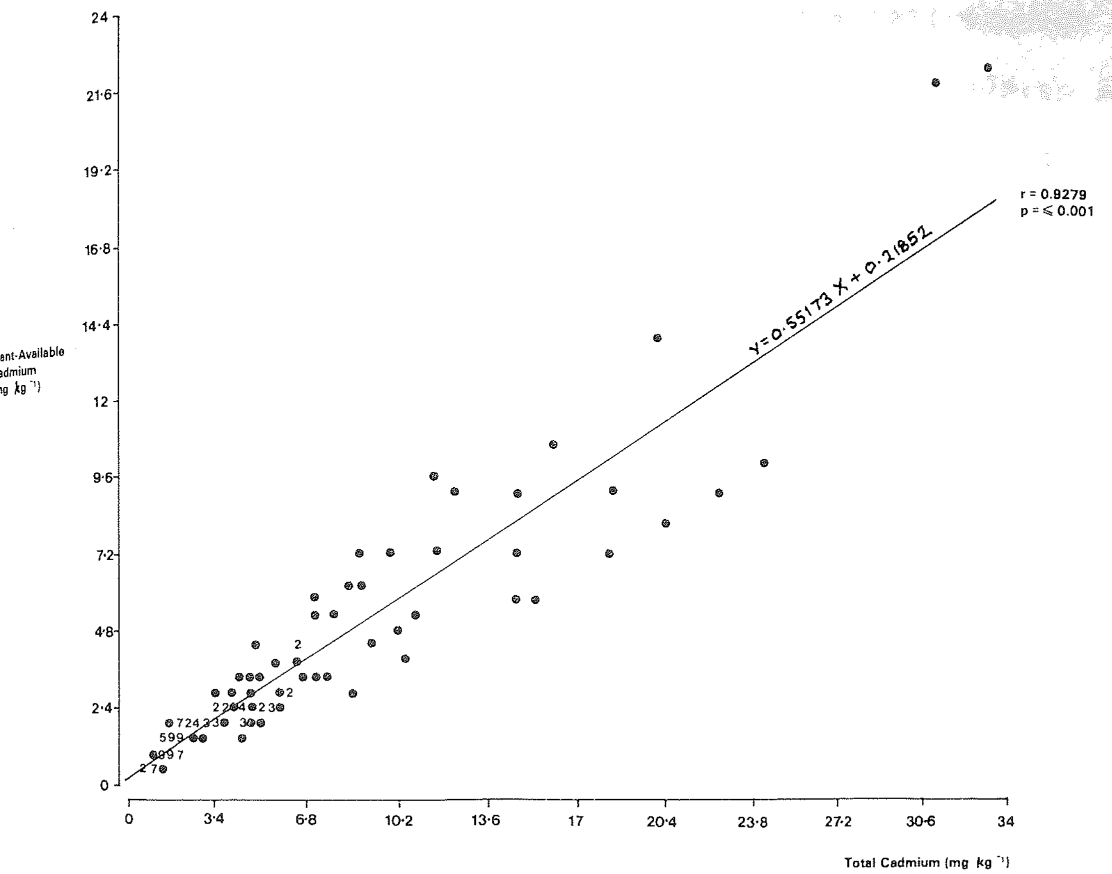

Figure 7.1 Plot of Total against Plant-Available cadmium levels in 193 Walsall garden soils. (Figures indicate the number of readings located at that point)

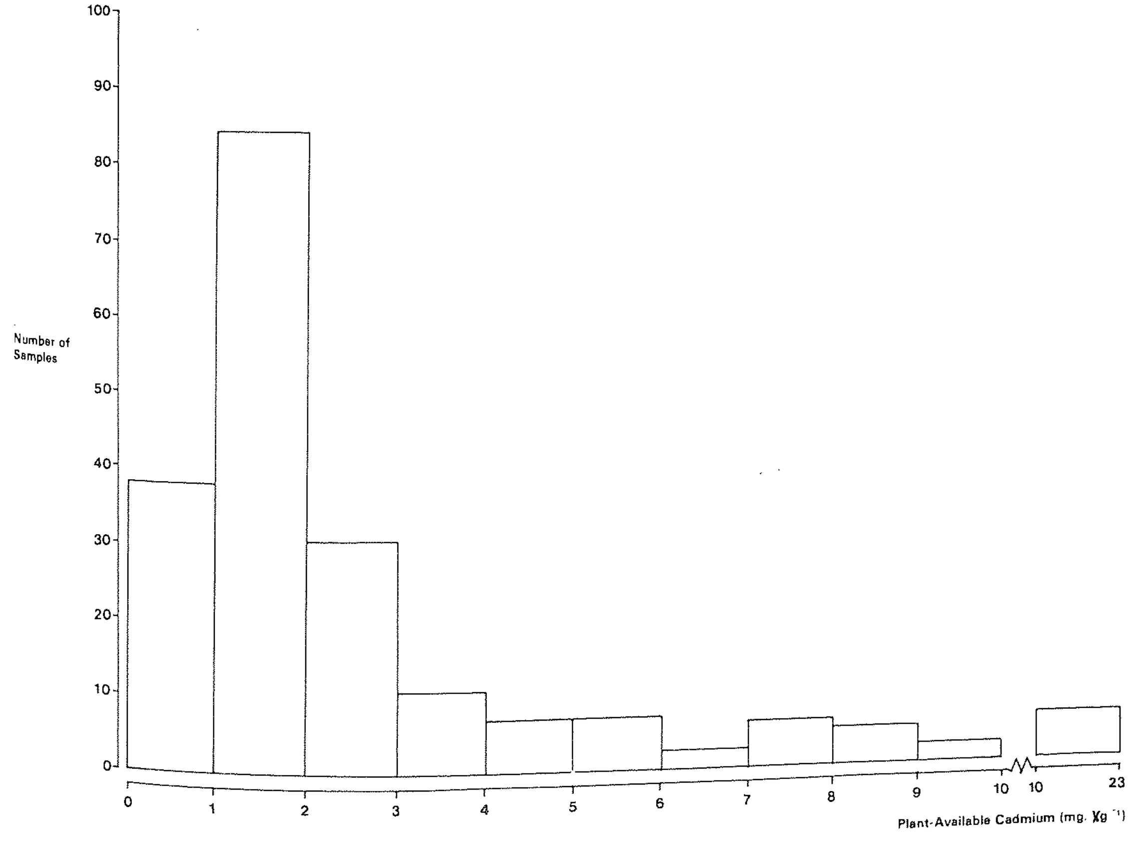

Figure 7.2 Frequency distribution of Plant-Available Cadmium in 193 garden soils.

Figure 7.2 shows the levels of plant-available cadmium to be log-normally distributed with a tail towards the higher levels. The distribution of total cadmium was also found to be log-normal, which is typical for soils in urban/industrial areas.

Figure 7.3 shows the relationship between plant-available cadmium and pH for the 193 Walsall soils. A significant correlation was noted between these two variables (r=0.2674, p=0.001). This could be due to the practice of spreading lime on the soil each year to counteract the effects of acid rain. Indeed, it can be seen from Figure 7.4 that the pH levels were normally distributed about a mean of 6.6 which is the ideal pH for vegetable cultivation. The cadmium in the soil may remain available when the acidity is reduced due to the chemical speciation and organic binding of the metal, which to an extent may be a result of its origin. In general, two-thirds of the cadmium in all Walsall soils was extractable using EDTA Diammonium Salt.

The frequency distribution of cadmium in the garden soils is similar to that reported earlier for the background levels of cadmium in the borough[206], whereas the pH levels have a somewhat more normalised distribution. This indicates that although the householders alter the pH levels of their garden soils, the cadmium content remains similar to those of background levels in the area.

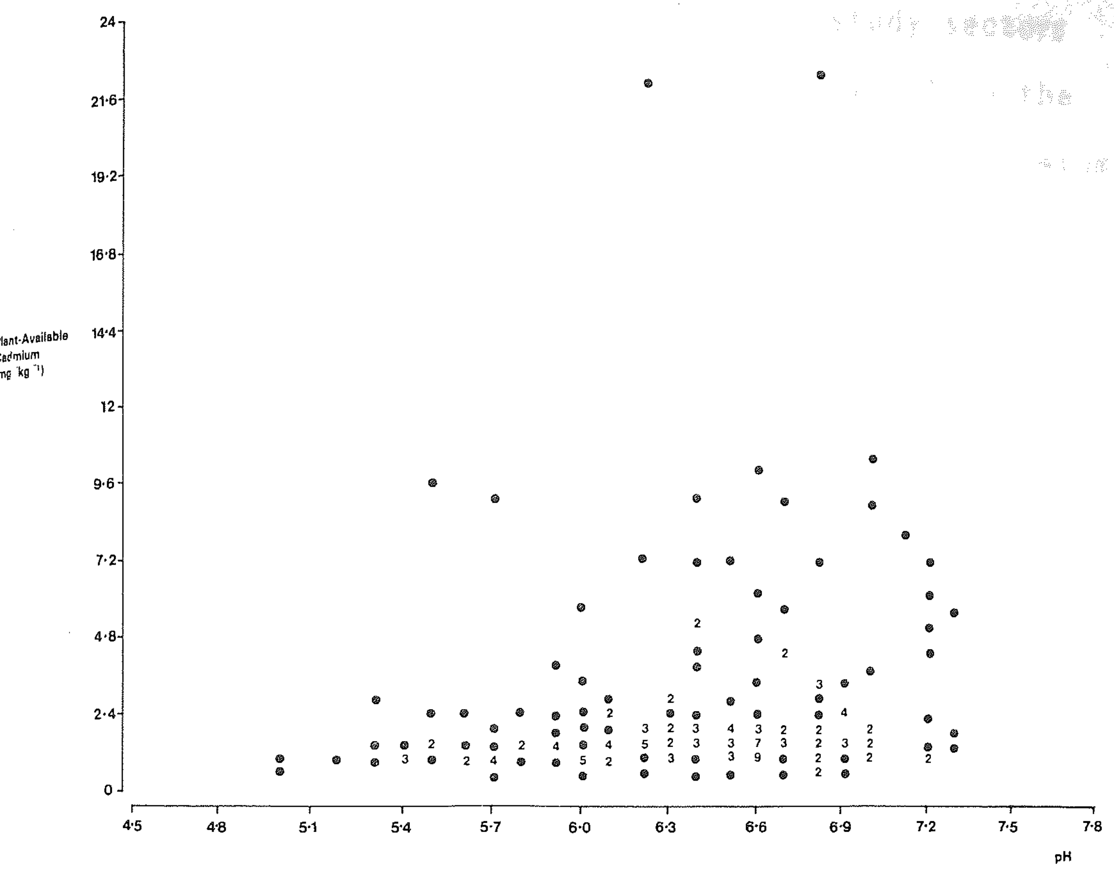

Figure 7.3 Plot of Plant-Available cadmium against pH for 193 Walsall garden soils. (Figures indicate the number of readings located at that point)

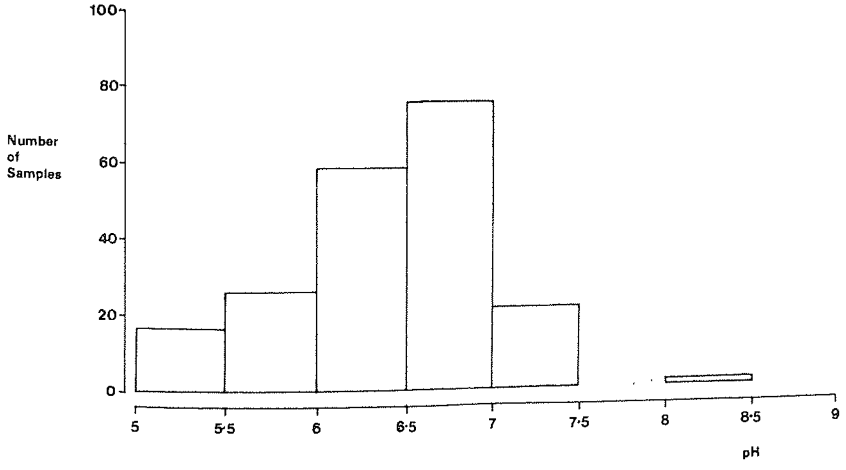

Figure 7.4 Frequency Distribution of pH levels in 193 Walsall garden soils.

Figure 7.5 shows the distribution of plant-available cadmium levels in each of the eight study sectors referred to earlier, starting with Pelsall in the north to Wednesbury in the south. The soil cadmium levels in the north of the borough are typical of normal background levels, whilst the soils in the Leamore, Primley Avenue and Pleck housing estates tend to be highly contaminated. These three estates were the areas identified earlier as having high background levels of cadmium, which demonstrates the usefulness of the worst-case mapping methodology in identifying areas in which high-risk populations are more likely to be found.

Figure 7.6 shows the distribution of plant-available cadmium levels in 193 Walsall soils against the number of years gardens had been used for vegetable cultivation. It is evident that the highest levels of cadmium are found in those gardens which have only recently been cultivated, whilst the gardens which have been cultivated for a long time (35 to 60 years) tend to have relatively low levels of cadmium. It is possible that when vegetables are grown in contaminated soils and removed for consumption the level of soil cadmium would gradually reduce over a long period, resulting in lower levels in those soils which have been cultivated for long periods. This assumes, however, that the rate of removal is greater than the rate

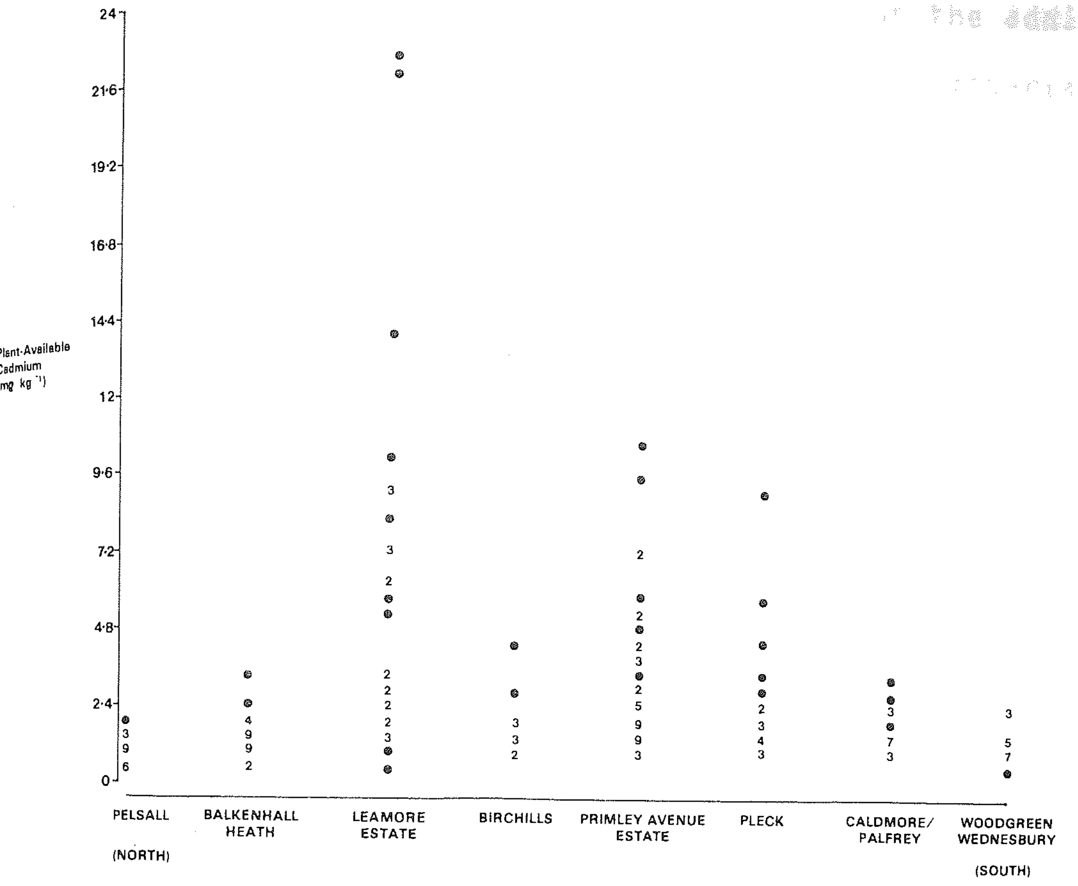

Figure 7.5 Levels of Plant-Available cadmium detected in garden soils in each of the eight study sectors.
(Figures indicate the number of readings located at that point)

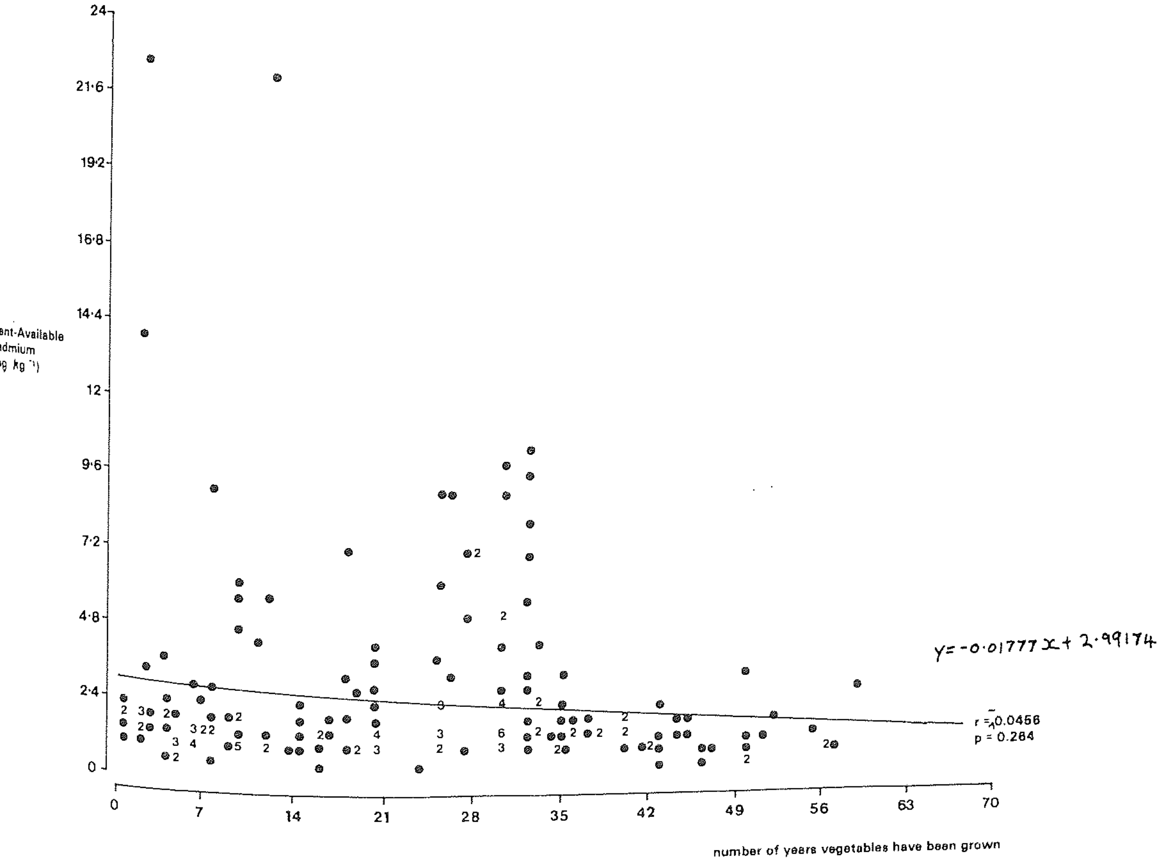

Figure 7.6 Plot of Plant-Available cadmium against the number of years vegetables have been grown in 193 Walsall garden soils.
(Figures indicate the number of readings located at that point)

at which cadmium is being added to the soil, whether in the form of atmospheric deposition or the addition of cadmium contaminated soil-conditioning material.

The correlation between plant-available cadmium and number of years vegetables had been grown was not significant (r=-0.0456, p=0.264) although the regression line shows a negative relationship between the two variables.

Figure 7.7 shows the distribution of total cadmium levels within seventeen garden vegetable plots referred to in paragraph 6.2.1. It is evident that the level of cadmium may vary considerably ($\bar{x}$=9.46, SD=3.06, range 5.88-13.5 μg.g^{-1}) or little at all ($\bar{x}$=0.89, SD=0.05, range 0.80-0.92 μg.g^{-1}) within a garden. A large variation in soil cadmium levels may prove important in some circumstances should vegetables which take up large amounts of cadmium (such as lettuce) be grown in the part of a garden with the highest soil cadmium concentration. The mean soil cadmium level, therefore, may not be a direct indicator of the level of cadmium which may be found in certain vegetable types.

Analyses carried out at the University of London on six soil samples collected from contaminated study gardens in Walsall showed similar levels of total and EDTA extractable cadmium to those detected by the author. Additional analyses to determine the level of cadmium in soil solution, the amount of cadmium extracted using Diethyltetrapenta acetic acid (DTPA) and 0.05M Calcium Chloride ($CaCl_2$), as well as the level of cadmium in cabbages grown in laboratory pot trials, showed that EDTA extractable and total soil cadmium are both poor indicators of the plant availability of cadmium in soil. Moreover, the results presented in Table 7.1 indicate that $CaCl_2$ and cadmium in soil solution are good indicators of bio-availability.

It is interesting to note that the garden soil with the lowest level of total and EDTA extractable cadmium (8.4 and 6.6 mg kg^{-1} respectively) had the highest level of cadmium in soil solution, and $CaCl_2$ extracted (117 ug l^{-1} and 3.5 mg kg^{-1} respectively). In addition, the cabbages grown in this soil in pot trials were found to contain the highest level of cadmium (11.0 ug g^{-1} dry weight).

These analyses and others carried out by the University of London have demonstrated that the form in which cadmium is found in contaminated soils directly affects the plant-availability of the metal. Furthermore, in general, the more cadmium in soil solution and $CaCl_2$ extract, the greater the plant-availability and potential human toxicity of the metal.

Soil Sample Site	Total Soil Cadmium $(mg\ kg^{-1})$	Cadmium Soil Solution $(ug\ l^{-1})$	Extractable Cadmium $(mg\ kg^{-1})$			Cadmium in Cabbage $(ug\ g^{-1}$ dry weight)
			EDTA	DTPA	$CaCl_2$ (0.05M)	
Leamore Estate	17.6	71	8.3	4.0	1.6	3.3
" "	15.4	79	8.8	4.8	1.1	4.1
" "	25.5	34	16.3	10.0	2.3	4.5
" "	27.3	84	14.4	7.0	0.5	2.7
Primley Ave Estate	8.4	117	6.6	4.0	3.5	11.0
Pleck/Bescot	14.6	58	8.5	5.0	1.7	3.4

TABLE 7.1: LEVELS OF CADMIUM EXTRACTED FROM SIX WALSALL GARDEN SOILS COMPARED WITH THE LEVEL OF CADMIUM IN CABBAGES GROWN IN LABORATORY POT TRIALS

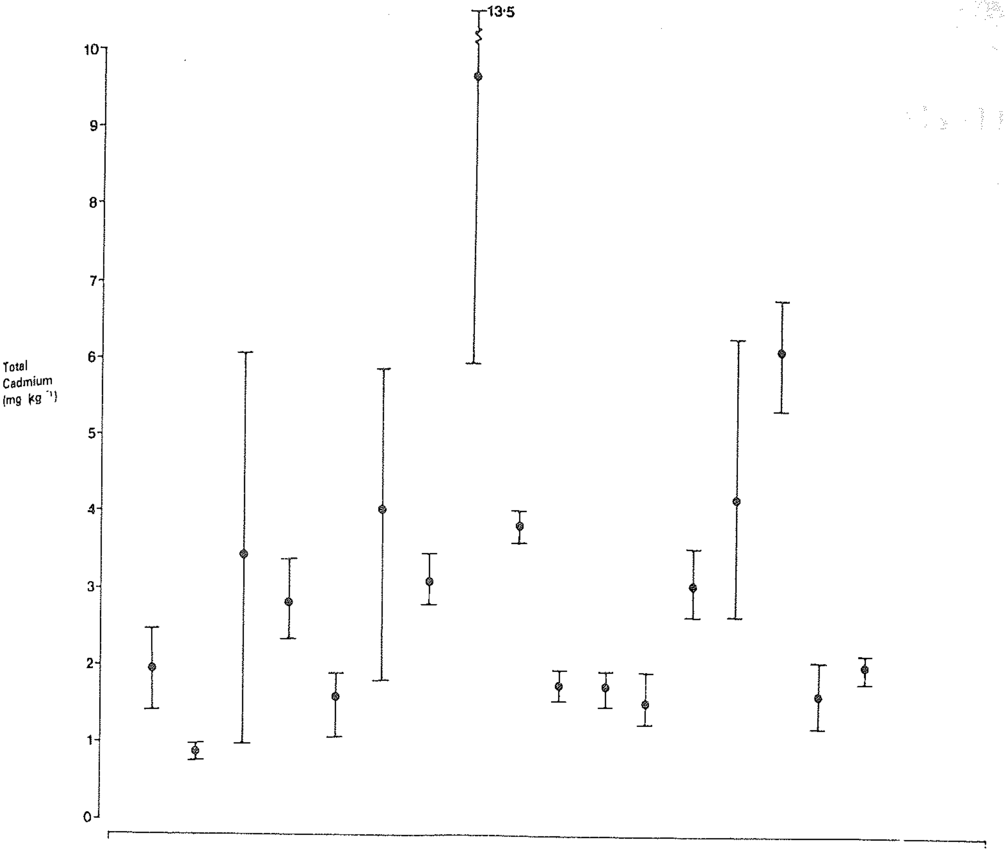

Figure 7.7 Distribution of cadmium levels in unbulked soil samples collected from 17 Walsall gardens.

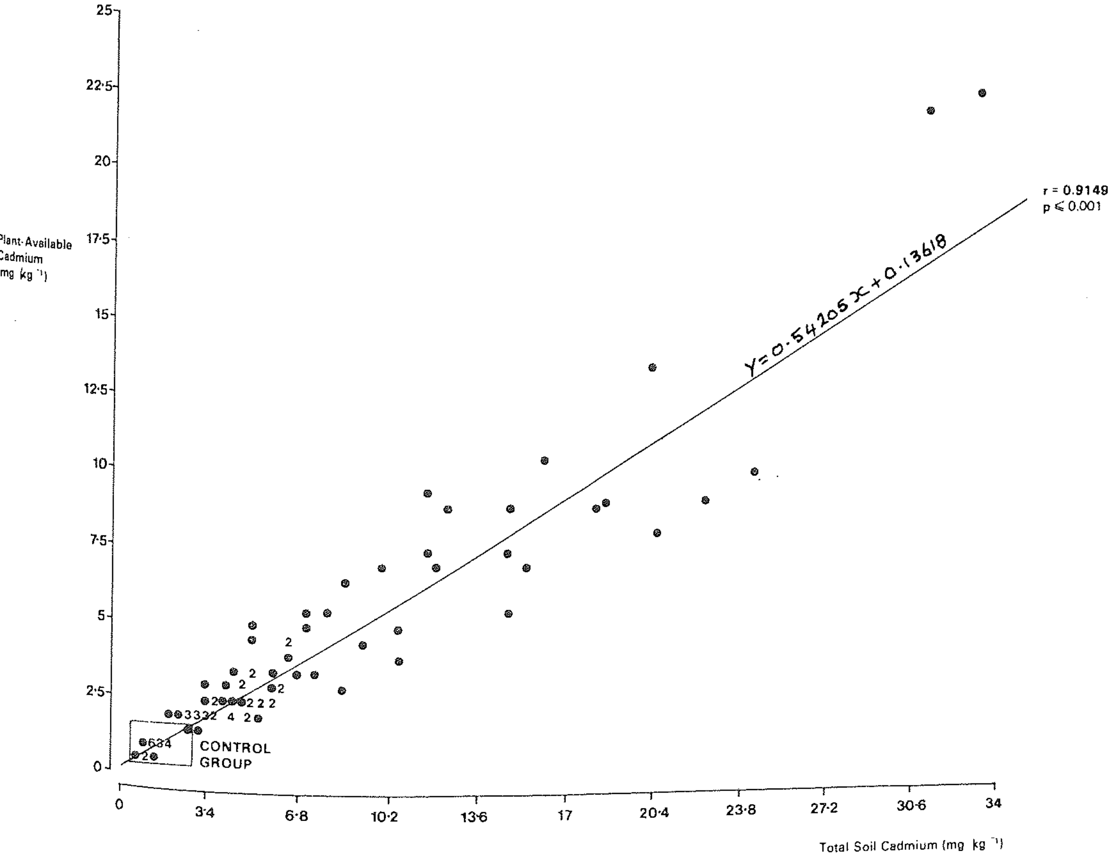

Figure 7.8 Plot of Plant-Available Cadmium against Total cadmium for 96 Walsall garden soils.

7.1.3 Selection of Study Population

Overall, the levels of cadmium found in Walsall garden soils show signs of contamination. It was stated in paragraph 5.2.4 that a maximum of 100 households could be studied due to restraints in time and of facilities. However, if twenty control households are selected from the low soil cadmium households in the north of the borough (Pelsall) and the 81 households which have soil cadmium levels greater than 3 mg kg^{-1} included, a study population of 101 households would be obtained. The control group would comprise residents growing a large proportion (>70 per cent) of their vegetable diet in uncontaminated soils (0.83-2.58 mg kg^{-1} total cadmium) and the main 'exposed' group comprising residents growing a large proportion of their vegetable diet in cadmium contaminated soils (3.0-33.05 mg kg^{-1} total cadmium). The two primary risk factors referred to earlier are, therefore, maximised in the exposed group.

During the first two months after the 101 households had been requested to take part in an extended study, five residents, including one from the control group, stated that they were not intending to grow vegetables in the summer of 1983. The final study group was, therefore, reduced to 96 households (including 19 controls) which represented 260 individual Walsall residents. Figure 7.8 shows the distribution of total and plant-available cadmium levels amongst the 96 households in the final study group.

7.2 ATMOSPHERIC DEPOSITION

Of the 96 deposition gauges installed, three were lost from gardens in the exposed group. Figure 7.9 shows the frequency distribution of cadmium deposition onto the 73 exposed households compared with the deposition onto control households. It is evident that the level of deposition in the exposed group is significantly greater than that of controls, with levels as high as 209.2 grams hectare^{-1} year^{-1} being recorded (range 2.7-209.2, mean 38.66 g ha^{-1} yr^{-1}). Levels of deposition in the control group, on the other hand, were much lower, with a highest recorded level of 59.9 grams hectare^{-1}year^{-1}(range 0.12-59.9, mean 19.36).

A recent study in the UK has shown that the typical rates of cadmium deposition in non-polluted areas are highly dependent on the level of rainfall, indicating that most cadmium is deposited in the form of wet deposition.[246] This study reported cadmium deposition rates of <100 g ha^{-1} yr^{-1} in Cumbria to <20 g ha^{-1} yr^{-1} in Chilton, Oxford. A study carried out in 77 cities in the United States, however, has shown typical deposition rates for residential, commercial and industrial areas to be 59, 61 and 70 g ha^{-1} yr^{-1} respectively.[247]

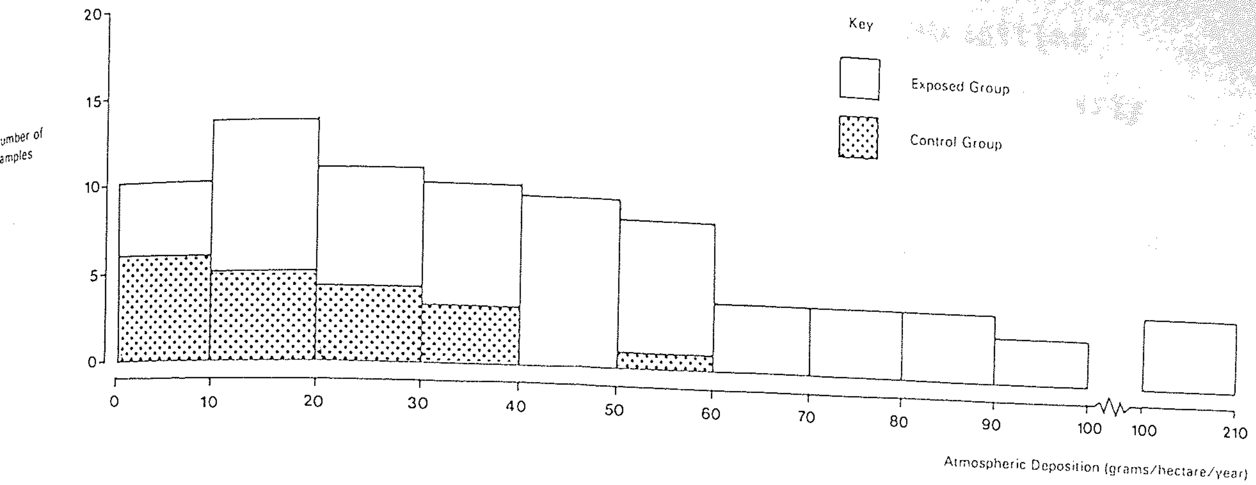

Figure 7.9 Frequency Distribution of Atmospheric Cadmium Deposition on 93 Walsall garden soils.

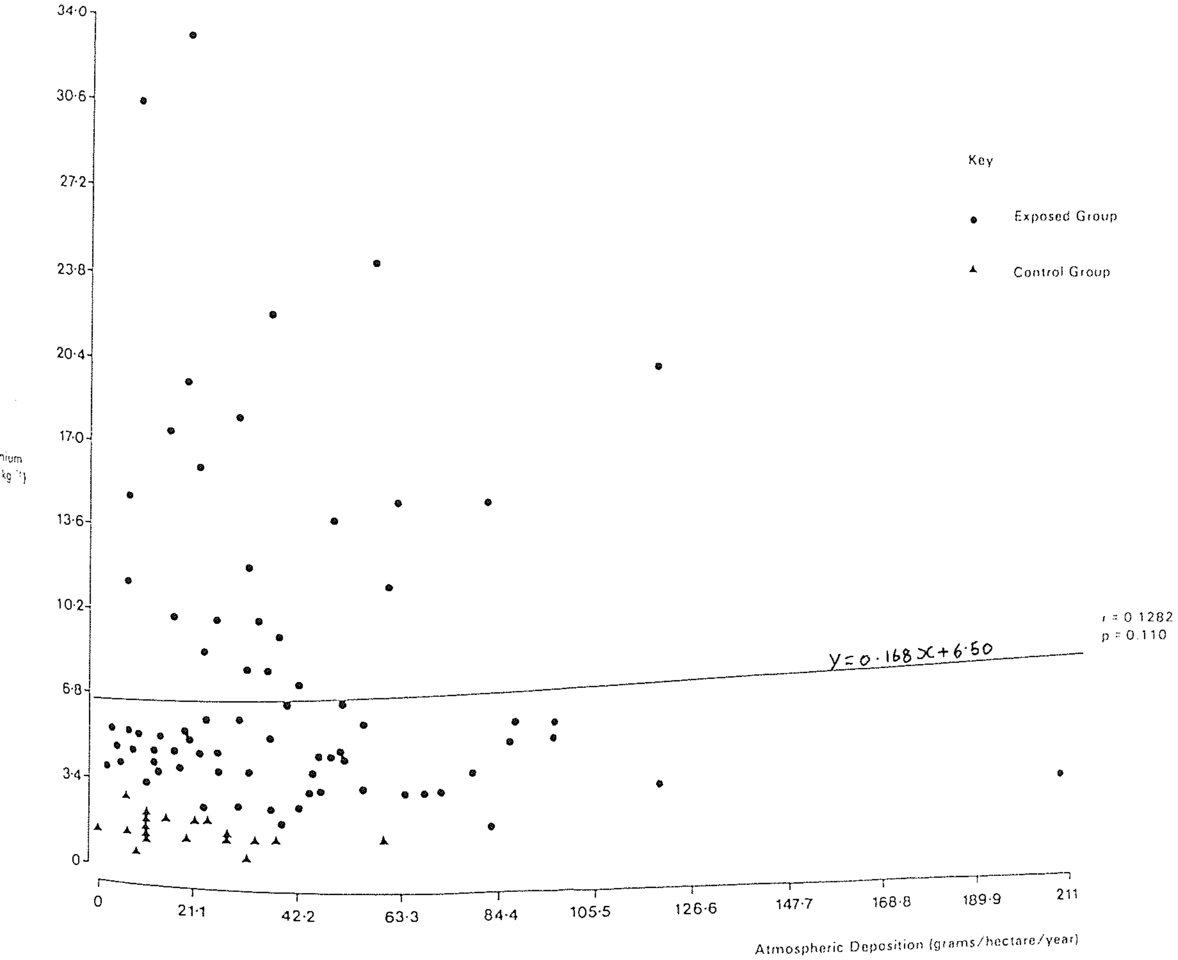

Figure 7.10 Plot of Total Soil Cadmium against Atmospheric Deposition of cadmium on 93 garden soils.

The deposition in Walsall was collected in the summer months and calculated to give an annual deposition rate, and as such would be much lower than the yearly rate determined by collecting wet and dry deposition throughout a 12-month period. Indeed, a study carried out in Walsall during 1980 found deposition rates of 100-175 g ha^{-1} yr^{-1} at two sites in close proximity to the exposed gardens being studied.[213] It is probable, therefore, that the rates of atmospheric deposition of cadmium reported for the 93 Walsall gardens are somewhat conservative figures, and the true annual deposition rates may be significantly higher. Nevertheless, it is evident that the overall rate of deposition onto garden soils in the exposed group is, on average, twice as high as that onto control households situated five miles to the north. It is also evident that the levels of deposition onto the exposed households is somewhat higher than the levels reported for industrial areas in the US.

Table 7.2 shows the total deposition of cadmium at various localities in the EC compared with Walsall. It is evident that the Walsall results are highly variable, with the highest deposition rate of 209.2 g ha^{-1} yr^{-1} being higher than any reported in the literature for other industrial areas of the EC. The deposition rates of the control group, however, are similar to those reported elsewhere for urban areas.

Area and Locality	Deposition Rate ($g\ ha^{-1}\ yr^{-1}$)	Comment
RURAL		
Norfolk, UK	2.6	-
Texel, The Netherlands	2.9	-
Belgium	19	Average of 19 Agricultural Sites
Denmark	3.0	Assumed Background Value
URBAN		
London, UK	24.7 - 29.6	Range of three Sites
Göttingen, FRG	3.9	-
INDUSTRIAL		
Liège, Belgium	82	-
Nordenham, FRG	135	Close to Zinc Smelter
Walsall, UK	150	<1 km from Cu Refinery
Walsall, UK (Rural/Residential)	0.12 - 59.9 (19.36)	'Control' Group
Walsall, UK (Urban/Industrial)	2.7 - 209.2 (38.66)	'Exposed' Group

TABLE 7.2: TOTAL ATMOSPHERIC DEPOSITION OF CADMIUM AT SELECTED LOCALITIES IN THE EC COMPARED WITH WALSALL

(Source: Adapted from Hutton (1981)[57])

Figure 7.10 shows the correlation between levels of total cadmium in each of the garden soils studied, and the level of deposition recorded during the summer of 1983 and expressed on an annual basis. The two variables are not correlated (r=0.1282) which would suggest that either the soil cadmium was not derived from atmospheric deposition, or that if the soil cadmium was derived from deposition this is no longer a major source. It is probably true to say that both of these may in part be true, for many of the known emission sources of cadmium in Walsall, such as primary and secondary steel production, have ceased or reduced the scale of operations. The cadmium in soil may be a legacy of the past when atmospheric deposition was much greater than at present. On the other hand, however, it is possible that some householders have added sewage sludge or other contaminated material to their gardens in the past. This was known to be the case for four households which had total soil cadmium levels of between 3 and 8 mg kg^{-1}. Lastly, it is possible that some houses were built on land which was contaminated by previous industrial activities. In five households where the garden soils were found to contain between 10 and 18 mg kg^{-1} total cadmium, it was known that they were built on land which had previously been used by a foundry.

It is difficult, without carrying out detailed cadmium speciation analyses and the use of multivariate analysis, to determine the precise origin of the cadmium contamination found in each individual garden soil, although it is likely that the cadmium in most soils has originated from a combination of atmospheric fallout, housing development on industrially contaminated land, and the addition of sewage sludge, foundry sand and other contaminated materials by owners or previous owners of the houses.

7.3 GARDEN VEGETABLES

7.3.1 Sampling of Vegetables

Due to heavy rainfall and late frosts during the spring of 1983, many of the early vegetables such as carrots, broad beans, and beetroot planted by Walsall households were lost and had to be either replanted or abandoned. The summer, however, provided good growing conditions and the vegetables grown later in the season generally did well, resulting in an abundant harvest for certain vegetable types such as cabbages, late carrots, swedes, leeks and onions, but relatively poor harvests for other vegetables such as runner beans, broad beans, beetroot, early carrots, potatoes and brussel sprouts.

In total, 920 vegetable samples were taken for analysis, which included 33 different vegetable varieties and four varieties of bush fruit. On average, each household grew between nine and ten vegetable types, with some householders growing as many as twenty-four.

7.3.2 Cadmium Content of Vegetables

Table 7.3 shows the cadmium content of vegetables from the control and exposed Walsall groups compared to the levels reported in the literature for vegetables grown in uncontaminated soils, and the levels reported for highly contaminated soils of Shipham, Somerset.

The 216 vegetable samples taken from the gardens of the Walsall control group tend to be slightly lower than the mean levels reported for vegetables grown in uncontaminated soils - generally being at the lower end of the range of values. This indicates, firstly, that no contamination was present in the soils of the control households and that, secondly, the analytical techniques used in the Walsall study produced typical levels for uncontaminated vegetable samples. The levels of cadmium in the 704 vegetable samples taken from the exposed Walsall group are much higher than those reported for the control group, and also higher than those reported in the literature for vegetables grown in uncontaminated soils.

Figure 7.8 shows the range of total and plant-available cadmium levels in the 77 garden soils of the exposed Walsall group compared to those of the control group. The levels of cadmium in the soils of the exposed group ranged from a little over background levels to high levels of contamination (3 - 33 mg kg^{-1}). It was

Vegetable Type	Uncontaminated Vegetables (ug g^{-1} wet weight)					Walsall (Control group) (ug g^{-1} wet weight)				Walsall (Exposed group) (ug g^{-1} wet weight)				Shipham (ug g^{-1} wet weight)			
	Mean	Lowest	Highest	Number of Samples	Ref	Mean	Lowest	Highest	Number of Samples	Mean	Lowest	Highest	Number of Samples	Mean	Lowest	Highest	Number of Samples
Beetroot	0.04	0.01	0.22	ND	56	0.026	0.004	0.064	13	0.117	0.011	0.339	39	0.14	0.04	0.38	29
Broad beans	0.047	0.019	0.075	ND	56	0.021	0.002	0.063	10	0.057	0.001	0.181	11	0.09	0.07	0.10	25
Broccoli	0.05	0.02	0.10	3	92	-	-	-	0	0.103	0.034	0.163	4	-	-	-	0
Brussel sprouts	0.03	0.01	0.11	16	92	0.027	0.003	0.051	13	0.067	0.013	0.273	40	0.17	0.02	0.79	46
Cabbage	0.05	0.15	0.15	23	92	0.015	0.004	0.042	15	0.073	0.001	0.441	58	0.61	0.02	3.56	75
Carrot	0.09	0.03	0.22	14	92	0.021	0.004	0.039	8	0.122	0.017	0.472	43	0.34	0.03	1.14	75
Cauliflower	0.02	-	-	ND	56	0.006	0.001	0.015	6	0.073	0.009	0.226	31	-	-	-	0
Celery	ND	-	-	-	-	-	-	-	0	0.160	0.076	0.234	4	-	-	-	0
Courgette	ND	-	-	-	-	0.003	-	-	1	-	-	-	0	0.02	0.01	0.04	13
Cucumber	<0.01	-	-	ND	56	-	-	-	0	0.02	0.01	0.028	4	-	-	-	0
Dwarf beans	ND	-	-	-	56	0.009	0.002	0.021	7	0.02	0.008	0.041	15	0.02	0.01	0.04	11
Kale	ND	-	-	-	-	-	-	-	0	0.774	-	-	1	0.28	0.08	1.06	18
Leek	0.04	0.02	0.09	4	92	0.039	0.016	0.091	7	0.162	0.043	0.386	28	0.38	0.06	1.77	52
Lettuce	0.109	0.02	0.198	ND	56	0.043	0.003	0.208	18	0.19	0.013	0.724	61	0.69	0.03	2.90	75
Marrow	ND	-	-	-	-	0.013	0.007	0.020	2	0.009	-	-	1	0.02	0.01	0.04	6
Onion	0.04	0.02	0.09	11	92	0.019	0.002	0.053	17	0.08	0.001	0.370	50	0.20	0.06	0.44	23
Parsnip	ND	-	-	-	-	0.022	0.002	0.051	8	0.239	0.034	0.850	24	0.29	0.12	0.82	41
Peas	<0.02	<0.01	0.09	6	92	0.016	0.001	0.046	8	0.047	0.002	0.126	21	0.06	0.02	0.18	24
Potato	0.08	0.01	0.17	19	92	0.015	0.002	0.038	17	0.102	0.002	0.444	53	0.13	0.125	0.15	62
Radish	ND	-	-	-	-	0.042	0.001	0.135	6	0.068	0.006	0.424	22	-	-	-	0
Runner beans	0.047	0.019	0.075	ND	56	0.014	0.001	0.040	19	0.059	0.002	0.312	58	0.03	0.003	0.30	59
Shallot	0.04	0.02	0.09	4	92	0.011	0.007	0.016	2	0.063	0.002	0.225	11	0.20	0.08	0.43	12
Spinach	<0.08	0.04	0.13	ND	56	0.061	-	-	1	0.641	-	-	1	1.08	0.20	1.74	21
Spring onion	0.04	0.02	0.09	ND	92	0.029	0.001	0.120	5	0.089	0.028	0.427	13	0.22	0.07	0.36	9
Swede	0.05	0.01	0.08	8	92	0.018	0.004	0.031	6	0.050	0.003	0.126	21	0.11	0.06	0.21	5
Tomato	0.02	0.01	0.08	10	92	0.018	0.004	0.088	7	0.074	0.002	0.211	25	0.06	0.02	0.12	11
Turnip	0.05	0.01	0.08	8	92	0.02	-	-	1	0.074	0.006	0.178	8	0.26	0.18	0.39	8
Blackberry	<0.01	-	-	ND	56	-	-	-	0	0.011	-	-	1	-	-	-	0
Gooseberry	<0.01	-	-	ND	56	0.007	-	-	1	-	-	-	0	0.03	0.01	0.09	16
Rhubarb	0.02	0.01	0.04	5	92	0.012	0.002	0.035	13	0.085	0.008	0.35	48	0.41	0.04	1.17	71
Egyptian onion	0.04	0.02	0.09	ND	92	0.008	0.006	0.011	2	-	-	-	0	-	-	-	0
Sweet corn	0.03	0.01	0.08	3	92	0.052	-	-	1	-	-	-	0	-	-	-	0
Chives	ND	-	-	-	-	0.02	0.017	0.023	2	0.128	0.071	0.235	4	-	-	-	0
Kohl rabi	0.04	0.01	0.22	ND	56	-	-	-	0	0.034	-	-	1	-	-	-	0
Squash	ND	-	-	-	-	-	-	-	0	0.031	-	-	1	-	-	-	0
Coriander	ND	-	-	-	-	-	-	-	0	0.470	-	-	1	-	-	-	0
Garlic	ND	-	-	-	-	-	-	-	0	0.050	-	-	1	-	-	-	0
TOTAL				>146					216				704				787

TABLE 7.3: CADMIUM CONTENT OF VEGETABLES GROWN IN WALSALL, AND FOR VEGETABLES GROWN IN UNCONTAMINATED AND HIGH CONTAMINATED SOILS

expected, therefore, that the levels of cadmium found in the vegetables of the exposed group would show a similar range. Table 7.3 does in fact show that the levels of cadmium found in vegetable samples collected from the less-contaminated soils in the Walsall exposed group to be similar or slightly higher than those levels reported for the control group.

The mean cadmium levels reported for each vegetable type in the exposed group, therefore, may give a false impression of the quite high levels which were found in vegetables sampled from the most highly contaminated soils. The highest levels of cadmium found in broad beans, dwarf beans, parsnips, potatoes, runner beans, spring onions and tomatoes of the Walsall exposed group were higher than the highest levels reported in the Shipham study. The mean level of total cadmium reported for vegetable garden soils in the Shipham study was 87 mg kg^{-1} (range 2-520 mg kg^{-1}) which is over ten times higher than the levels found in the garden soils of the Walsall exposed group. The high levels of cadmium found in the vegetables collected from the exposed Walsall households, therefore, may be a reflection of the chemical speciation of the cadmium in the Walsall soils, which in turn affects the bioavailability of the metal. In the Shipham study, much of the cadmium in the soils was found to be in particulate form bound to rock fragments and of geological origin. The cadmium in the Walsall soils, however, is derived from pollution sources and as a result is in soil solution or lightly bound to the surface of soil particles and anthropogenic material. The levels of cadmium in the vegetable samples collected from the contaminated Walsall soils suggest that the cadmium present in soils of urban/industrial areas is in a highly available form, and that vegetables grown in such soils can accumulate high levels of cadmium without any apparent adverse effects on the plants' physiology.

The Shipham study included the estimation of dietary intakes of cadmium by those residents who grew vegetables in local soils. The study found that the dietary intakes of cadmium by villages were often considerably higher than the national average, with the highest intakes being reported for villagers consuming large amounts of locally-grown produce. A proportion of residents showed an intake in excess of that considered tolerable by the FAO/WHO Joint Expert Committee on Food Additives. Although the results for individuals were not reported in the Shipham study, it would seem likely that the residents who exceeded the FAO/WHO recommended limit were those who grew a large proportion of their vegetable diet in local soils.
The households selected for the Walsall study are those which grow a large proportion of their vegetable diet in garden soils and, although the levels of cadmium reported for Shipham's vegetables were overall slightly

higher than those found in Walsall, it is likely that dietary intakes of cadmium by householders in the exposed Walsall group are higher than the national average and the control group, and that the dietary intakes of cadmium by the householders with the most highly contaminated soils in the exposed group may exceed the FAO/WHO recommended limit for dietary intakes of cadmium.

7.3.3 Loss of Cadmium During Vegetable Preparation

As reported earlier, all vegetable samples were cleaned and prepared for ordinary culinary use, and the levels reported in Table 7.3 are the cadmium content of prepared vegetables. However, the vegetables were not cooked as would normally be the case, so in order to determine the amount of cadmium which would be lost during cooking, 70 vegetable samples were divided into two halves, and one half cooked. Table 7.4 shows that the loss of cadmium seems to vary from one vegetable to another, although insufficient numbers of samples were analysed to determine a precise figure for each vegetable type. However, an overall mean figure for cadmium loss on cooking of 12.25 per cent has been calculated.

Of the 37 vegetable and fruit varieties analysed in the Walsall study, eleven do not require cooking and are generally eaten raw. In addition, it is probable that

Vegetable Type	Uncooked	Cooked	Loss:		
	ug g^{-1} dry weight		ug g^{-1}	%	$\bar{x}$
Cabbage	0.13	0.15	+0.02	+15.4)	10.34%
"	0.33	0.26	-0.07	21.2)	
"	0.57	0.55	-0.02	3.5)	
"	0.56	0.48	-0.08	14.3)	
"	0.23	0.18	-0.05	21.7)	
"	0.41	0.39	-0.02	4.9)	
"	0.27	0.21	-0.06	22.2)	
Swede	0.28	0.29	+0.01	+3.6)	15.68%
"	0.10	0.11	+0.01	+10.0)	
"	0.28	0.23	-0.05	17.9)	
"	0.32	0.29	-0.03	9.4)	
"	0.04	<0.01	-0.04	[>75])	
"	0.56	0.53	-0.03	5.4)	
Carrot	0.24	0.24	0.00	0)	5.8%
"	0.82	0.56	-0.26	31.7)	
"	0.70	0.68	-0.02	2.9)	
"	0.12	0.14	+0.02	+16.7)	
"	0.51	0.50	-0.01	1.9)	
"	1.33	1.13	-0.20	15.0)	
Cauliflower	<0.01	<0.01	0.00	0)	9.0%
"	0.27	0.21	-0.06	22.2)	
"	0.58	0.50	-0.08	13.8)	
"	0.92	0.86	-0.06	6.5)	
"	0.22	0.20	-0.02	9.1)	
"	1.25	1.22	-0.03	2.4)	
Parsnip	1.27	1.24	-0.03	2.4)	18.48%
"	0.94	0.37	-0.57	60.6)	
"	0.76	0.74	-0.02	2.6)	
"	0.42	0.34	-0.08	19.1)	
"	0.61	0.45	-0.16	26.2)	
"	<0.01	0.01	+0.01	NS)	
Marrow	0.28	0.21	-0.07	25.0)	12.5%
"	0.12	0.12	0.00	0)	
Beetroot	0.60	0.54	-0.06	10.0)	9.63%
"	0.28	0.25	-0.03	10.7)	
"	0.27	0.25	-0.02	7.4)	
"	0.23	0.25	+0.02	+8.7)	
"	0.62	0.53	-0.09	14.5)	
"	2.00	2.13	+0.13	+6.5)	
Turnip	1.17	0.87	-0.30	25.6)	35.93%
"	0.87	0.30	-0.57	65.5)	
"	0.18	0.15	-0.03	16.7)	
Leek	2.55	2.15	-0.40	15.7)	15.8
"	0.26	0.20	-0.06	23.1)	
"	0.17	0.11	-0.06	35.3)	
"	1.01	1.01	0.00	0)	
"	1.72	1.51	-0.21	12.2)	
"	1.44	1.38	-0.06	4.2)	
Brussel Sprout	0.04	<0.01	-0.04	75.0)	22.67%
" "	0.25	0.22	-0.03	12.0)	
" "	0.30	0.20	-0.10	33.3)	
" "	0.64	0.60	-0.04	6.3)	
" "	0.20	0.24	+0.04	+20.0)	
" "	0.17	0.12	-0.05	29.4)	
Runner Beans	0.78	0.68	-0.20	12.8)	9.63%
" "	0.47	0.30	-0.17	36.2)	
" "	0.29	0.27	-0.02	6.9)	
" "	0.11	0.13	+0.02	+18.2)	
" "	0.86	0.81	-0.05	5.8)	
" "	0.28	0.24	-0.04	14.3)	
Potato	0.57	0.57	0.00	0)	9.42%
"	0.55	0.44	-0.11	20.0)	
"	1.10	1.07	-0.03	2.7)	
"	0.46	0.40	-0.06	13.0)	
"	0.15	0.15	0.00	0)	
"	0.24	0.19	-0.05	20.8)	
Dwarf Beans	0.21	0.19	-0.02	9.5)	13.23%
" "	0.33	0.32	-0.01	3.0)	
" "	0.46	0.37	-0.09	19.6)	
" "	0.24	0.19	-0.05	20.8)	

TABLE 7.4: CADMIUM CONTENT OF COOKED AND UNCOOKED VEGETABLE SAMPLES

in certain cases the cadmium lost during vegetable cooking may still be consumed by a householder, particularly if the vegetables are cooked in a pressure cooker, or with meat, or the water used for boiling vegetables is used as a stock. Taking this into consideration it is suggested that between six and ten per cent of cadmium contained in the vegetable part of a diet may be lost during cooking. Any dietary intake calculated using the levels of cadmium in vegetables on a fresh weight basis, therefore, needs to be adjusted to take account of this loss.

7.3.4 Sources of Cadmium Contamination

The degree to which vegetables take up cadmium from the soil, the effect of pH, and the influence of atmospheric deposition on the level of cadmium in vegetables needs to be considered in order to identify the most important factors in the accumulation of cadmium in vegetables grown in urban/industrial areas.

Table 7.5 shows the Spearman rank correlation co-efficients and one-sided t-test of significance of plant-available cadmium, total cadmium, pH and atmospheric deposition against the level of cadmium detected in 20 vegetable types. It is evident that the level of cadmium in over 50 per cent of vegetable types is correlated with the level of plant-available cadmium in soil, and that the correlation is highly significant. It is also evident that for the same vegetable types, total cadmium is

		Beet-root	Broad Beans	Brussel Sprouts	Cabbage	Carrot	Cauli-flower	Dwarf Beans	Leek	Lettuce	Onion	Parsnip	Peas	Potato	Radish	Runner Beans	Shallot	Spring Onion	Swede	Tomato	Rhubarb
Available Cadmium, (mg kg^{-1})	r p	0.7297 (n=52) .001	0.4475 (n=21) .021	0.4491 (n=53) .001	0.6122 (n=73) .001	0.7602 (n=51) .001	0.6523 (n=37) .001	0.3427 (n=22) .059	0.6521 (n=35) .001	0.6418 (n=79) .001	0.6465 (n=67) .001	0.6921 (n=32) .001	0.3877 (n=29) .019	0.5702 (n=70) .001	0.4424 (n=28) .009	0.4533 (n=77) .001	0.5769 (n=13) .019	0.3891 (n=18) .055	0.4634 (n=27) .007	0.3884 (n=32) .014	0.5958 (n=61) .001
Total Cadmium, (mg kg^{-1})	r p	0.6965 (n=52) .001	0.5065 (n=21) .010	0.4531 (n=53) .001	0.5155 (n=73) .001	0.6915 (n=51) .001	0.6626 (n=37) .001	0.3623 (n=22) .048	0.6385 (n=35) .001	0.5748 (n=79) .001	0.6002 (n=67) .001	0.7647 (n=32) .001	0.2818 (n=29) .069	0.5032 (n=70) .001	0.4052 (n=28) .016	0.3640 (n=77) .001	0.3956 (n=13) .090	0.3602 (n=18) .071	0.5261 (n=27) .002	0.4223 (n=32) .008	0.5952 (n=61) .001
pH	r p	0.1113 (n=52) .216	-0.2031 (n=21) .189	0.0407 (n=53) .386	0.0836 (n=73) .241	0.1040 (n=51) .234	0.0807 (n=37) .318	0.0156 (n=22) .473	0.0148 (n=35) .466	-0.0773 (n=79) .249	0.1514 (n=67) .111	0.1519 (n=32) .203	0.3063 (n=29) .053	-0.1136 (n=70) .174	0.2999 (n=28) .061	-0.0869 (n=77) .226	0.1050 (n=13) .366	0.1133 (n=18) .327	0.1263 (n=27) .265	0.0705 (n=32) .351	0.1708 (n=61) .094
Atmos-pheric Depo-sition (grams/ hectare/ year)	r p	0.2407 (n=52) .043	-0.0247 (n=21) .458	0.1607 (n=53) .125	0.551 (n=72) .023	0.2552 (n=50) .037	0.0046 (n=35) .489	0.4242 (n=21) .028	0.0698 (n=34) .347	0.3437 (n=76) .001	0.3408 (n=65) .003	0.1096 (n=32) .275	0.1547 (n=29) .212	0.0444 (n=69) .358	0.1985 (n=28) .156	0.2468 (n=76) .016	0.3356 (n=13) .131	0.0526 (n=18) .418	0.0965 (n=27) .316	0.0750 (n=31) .344	0.1329 (n=59) .158

TABLE 7.5: MATRIX DIAGRAM OF NON-PARAMETRIC CORRELATION CO-EFFICIENTS (r) OF PLANT-AVAILABLE SOIL CADMIUM, TOTAL SOIL CADMIUM, pH AND CADMIUM IN ATMOSPHERIC DEPOSITION AGAINST THE CADMIUM CONTENT OF 20 VARIETIES OF VEGETABLE GROWN IN 96 WALSALL GARDEN SOILS

also correlated. For other vegetable types, however, no correlation was found with plant-available or total cadmium. This can be seen graphically in Figures 7.11 to 7.14 which show the scatter of observations and regression line for four calculated correlation co-efficients. It seems likely that the levels of cadmium in some vegetable types are not correlated with plant-available cadmium because the EDTA Diammonium Salt extraction technique recommended by ADAS/MAFF is not a reliable indicator of the cadmium which is plant-available. It is quite possible that the extraction techniques described in Section 7.1.2 would prove better indicators of plant availability.

To determine if atmospheric deposition has any effect on the level of cadmium in vegetables, particularly the 'leafy' or 'hairy' vegetable types such as cabbage, lettuce, dwarf beans and runner beans which can trap atmospherically deposited particles, lettuces were collected from three study gardens within 500 metres of a secondary copper refinery in Walsall. After the lettuces were prepared as described in paragraph 6.5.5 sub-samples of each leaf were viewed under a Scanning Electron Microscope (SEM) and the elemental speciation of the particles determined using X-ray micro-analysis.

The leaves which had not been washed during preparation were found to have a large number of particles on their surfaces, which were <20 um in diameter and found to contain high levels of copper, zinc, lead, nickel, cadmium, and silica (Plate 7.1). It was considered

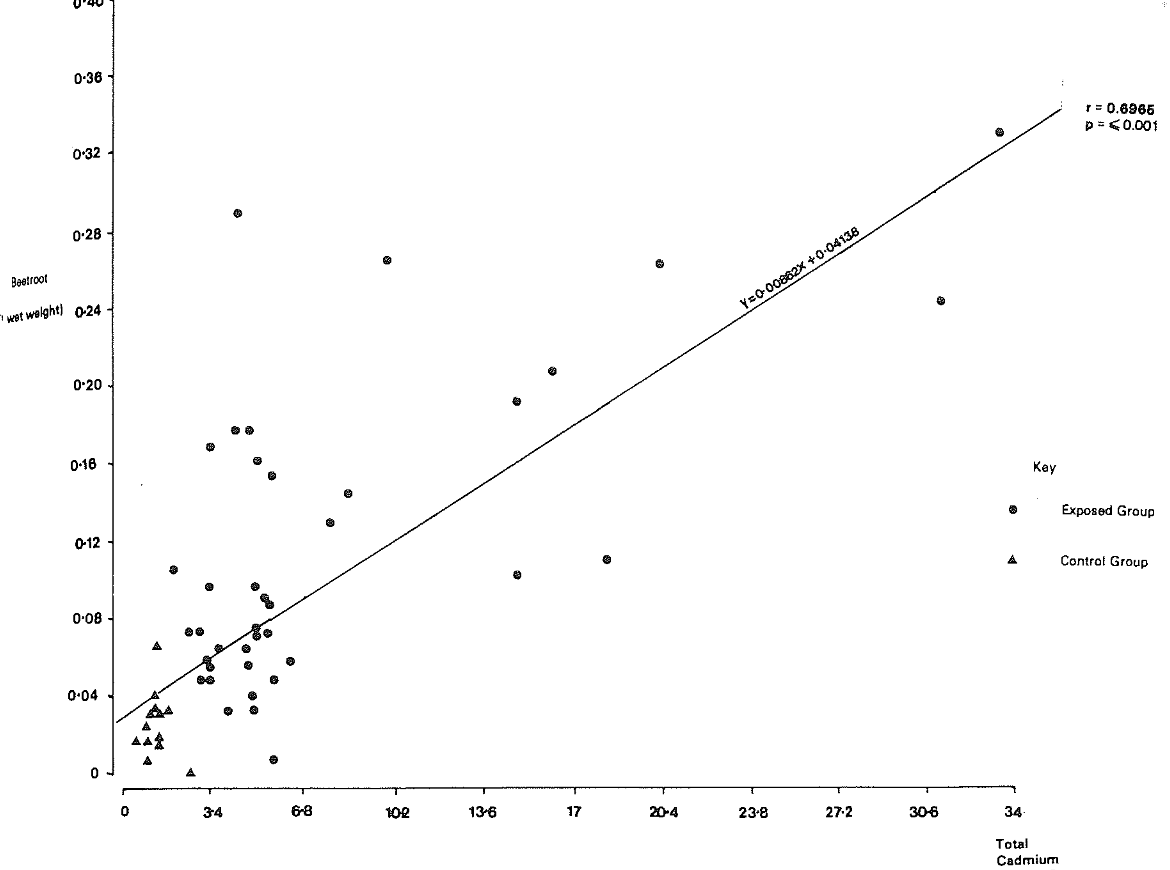

Figure 7.11 Plot of Total Soil cadmium against the cadmium content of Beetroot grown in 52 gardens.

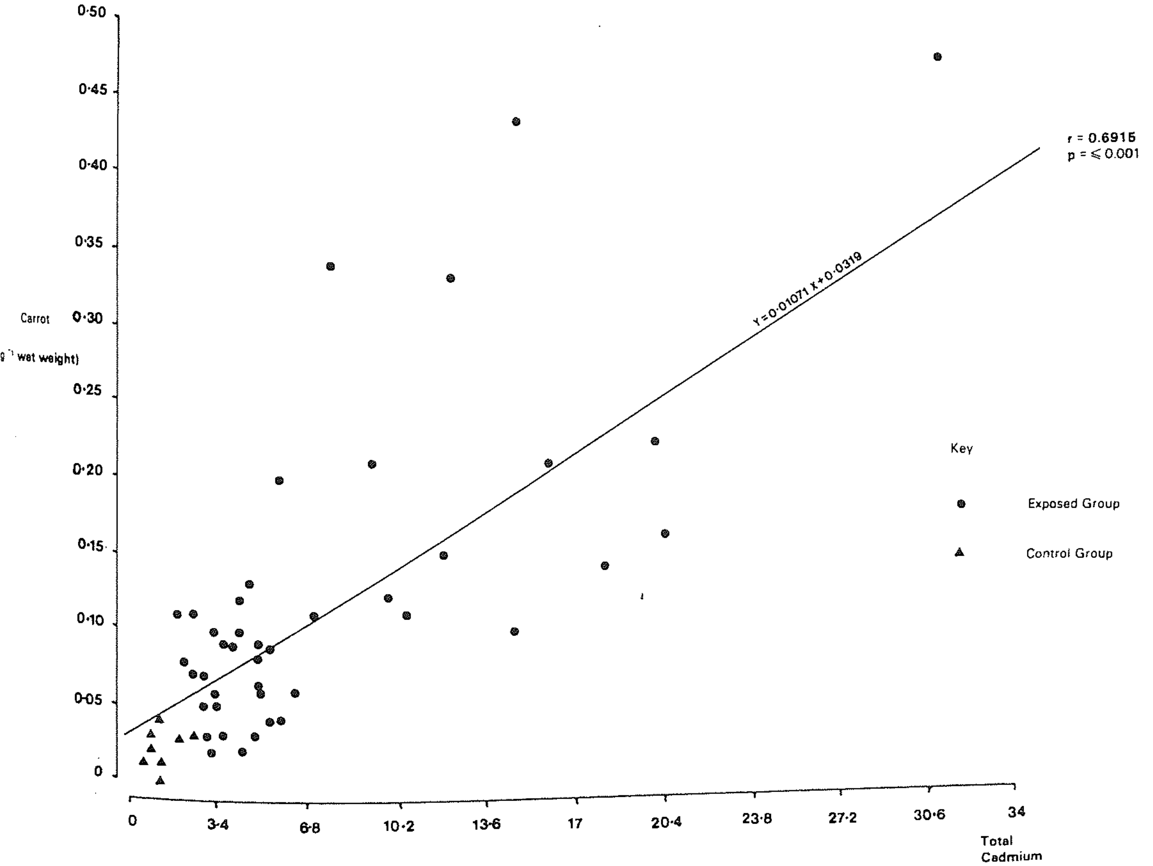

Figure 7.12 Plot of Total Soil cadmium against the cadmium content of Carrots grown in 51 gardens.

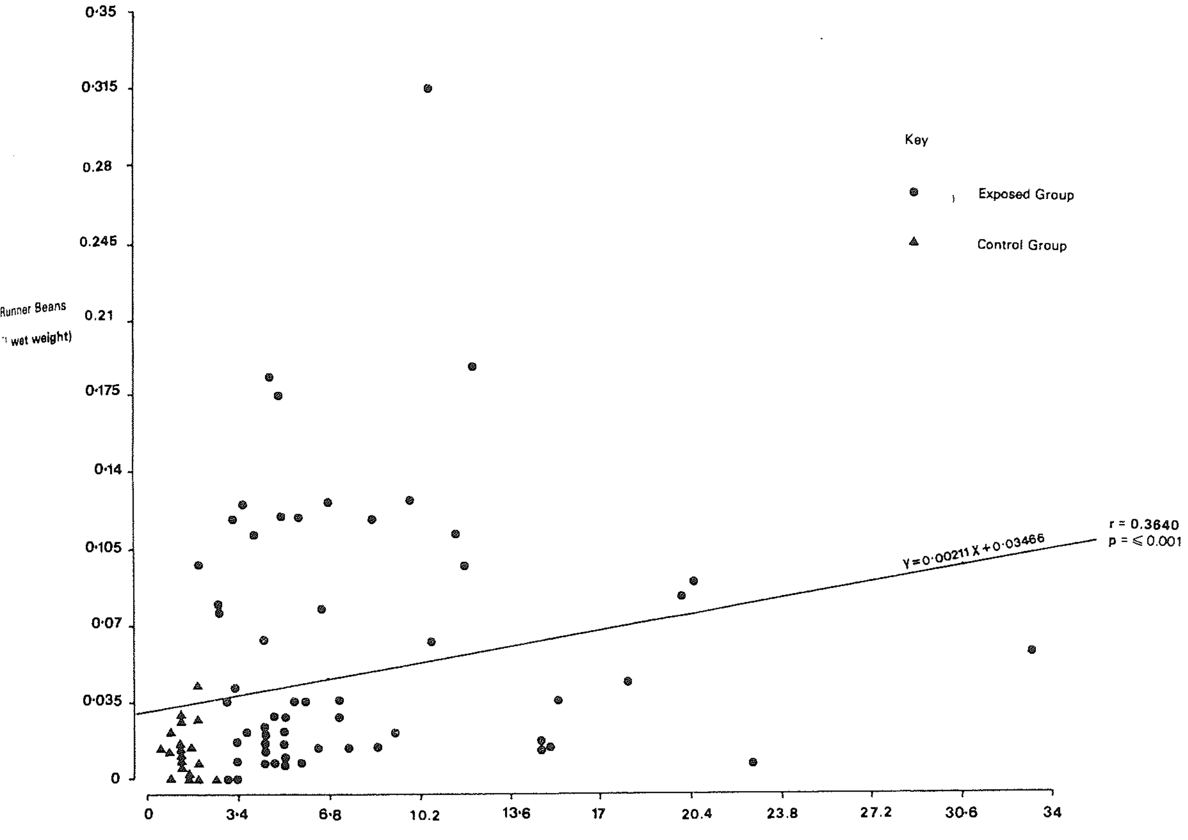

Figure 7.13 Plot of Total Soil cadmium against the cadmium content of Runner Beans grown in 77 gardens.

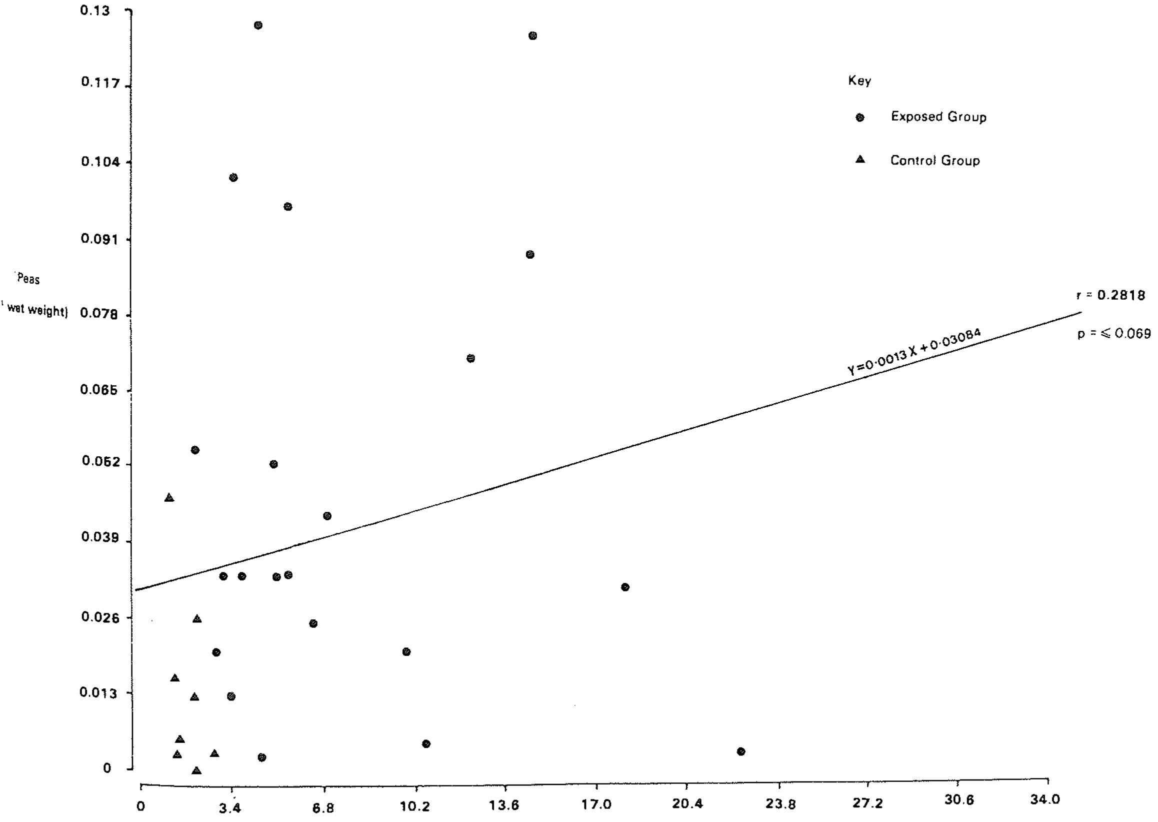

Figure 7.14 Plot of Total Soil cadmium against the cadmium content of Peas grown in 29 gardens.

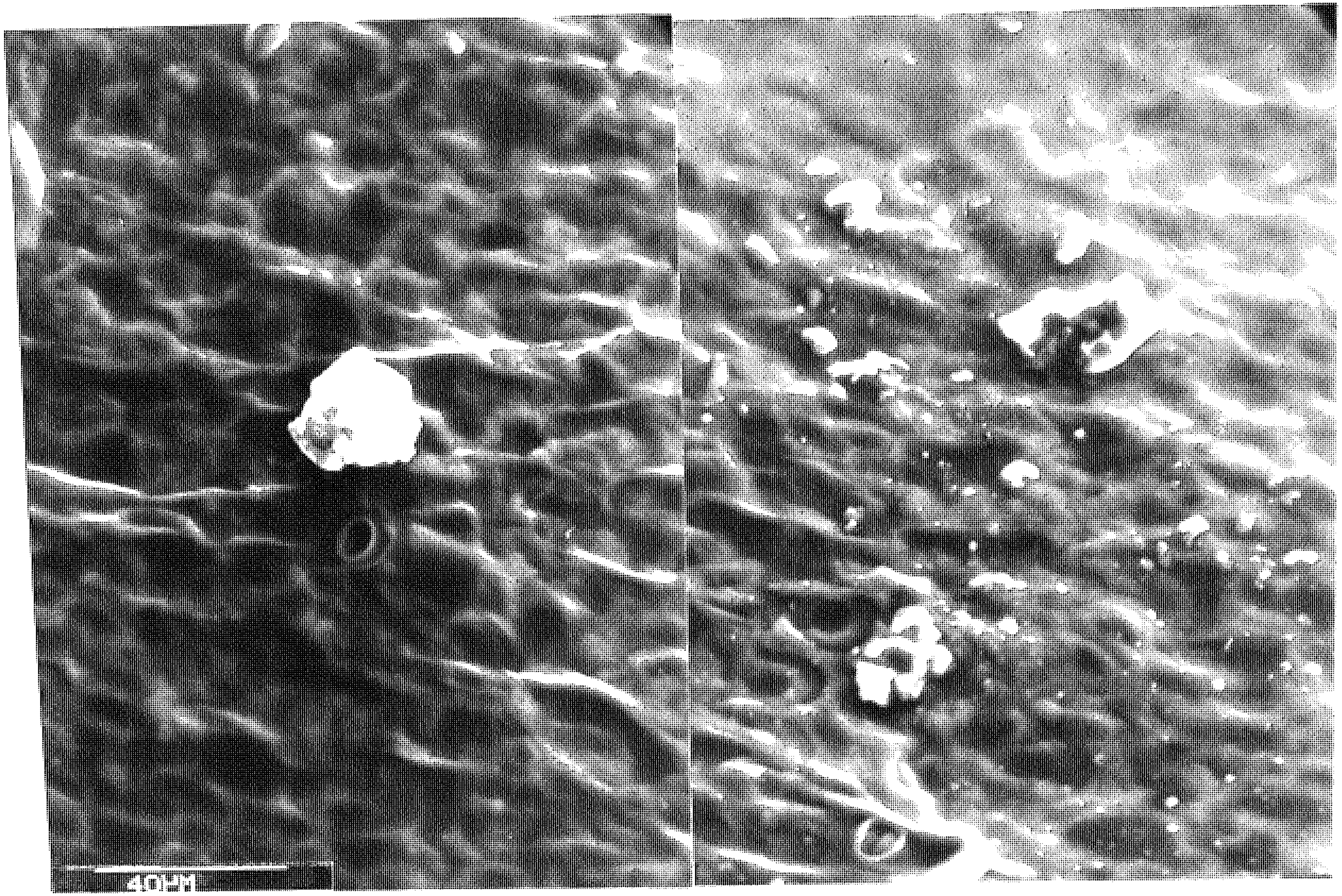

PLATE 7.1: SCANNING ELECTRON MICROSCOPE IMAGE OF THE SURFACE OF AN UNWASHED LETTUCE LEAF COLLECTED FROM WITHIN 500 m OF A SECONDARY COPPER REFINING PLANT

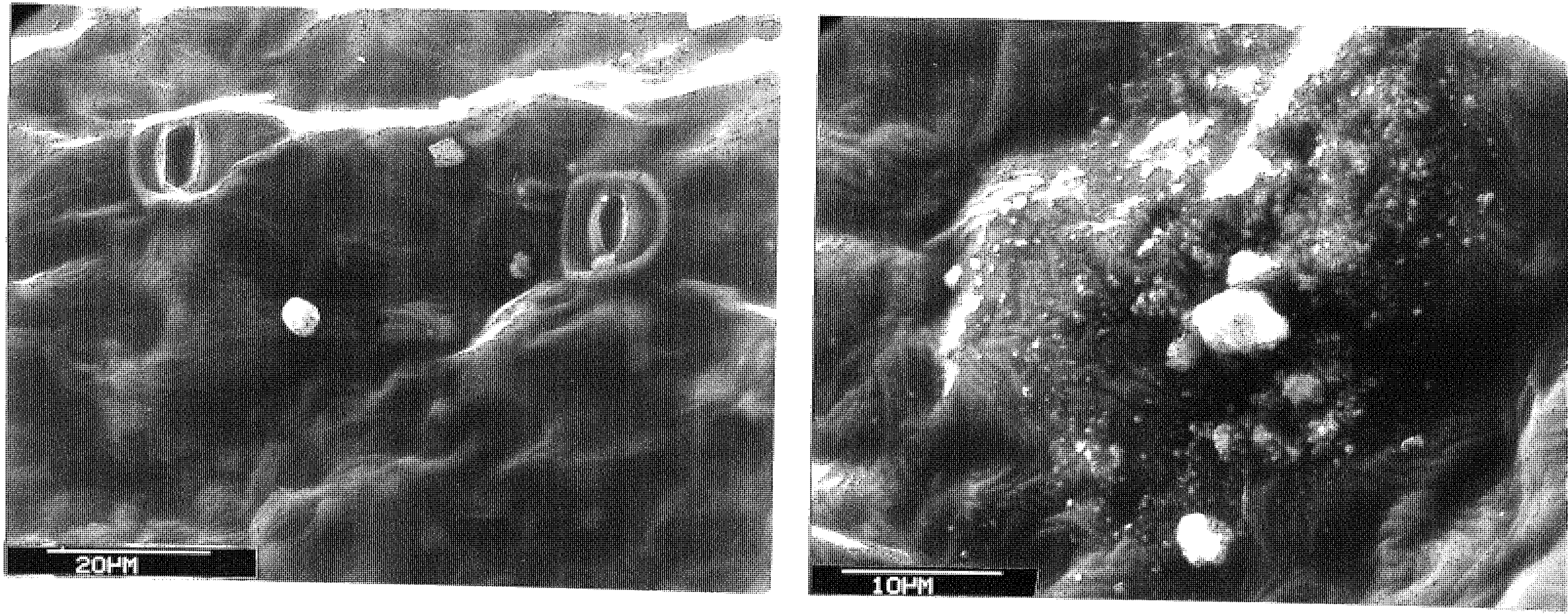

PLATE 7.2: SCANNING ELECTRON MICROSCOPE IMAGE OF A LETTUCE LEAF COLLECTED FROM WITHIN 500 m OF A SECONDARY COPPER REFINING PLANT AND AFTER WASHING WITH GLASS DISTILLED WATER

that the particles were made up of quartz (SiO_2) grains which were coated with heavy metals on their surfaces, which is typical of dust particles derived from thermal metal reprocessing plants. The leaves of the washed lettuce were found to have particles on their surfaces which were <5 um in diameter, but also contained high levels of copper, zinc, lead, nickel and cadmium (Plate 7.2). From the repeated analyses carried out on these lettuce samples it can be concluded that atmospheric deposition of particles may increase the cadmium content of certain vegetable types, and that washing does not remove the smaller particles which tend to have higher levels of metal on their surfaces per unit of particle weight. Atmospheric deposition of cadmium and other heavy metals onto vegetables intended for human consumption can therefore directly increase dietary intake.

Figures 7.15 to 7.18 show the plots of atmospheric deposition of cadmium against the cadmium content of cabbage, dwarf beans, lettuce and runner beans grown by Walsall householders. Although the regression lines are positively sloped no strong correlation was found between atmospheric deposition and the cadmium content of these vegetables. No correlation was found between atmospheric deposition and the level of cadmium in other vegetable types (Table 7.5). It is concluded, therefore, that although atmospheric deposition of cadmium may increase the cadmium content of certain vegetable types, soil is the most important source of

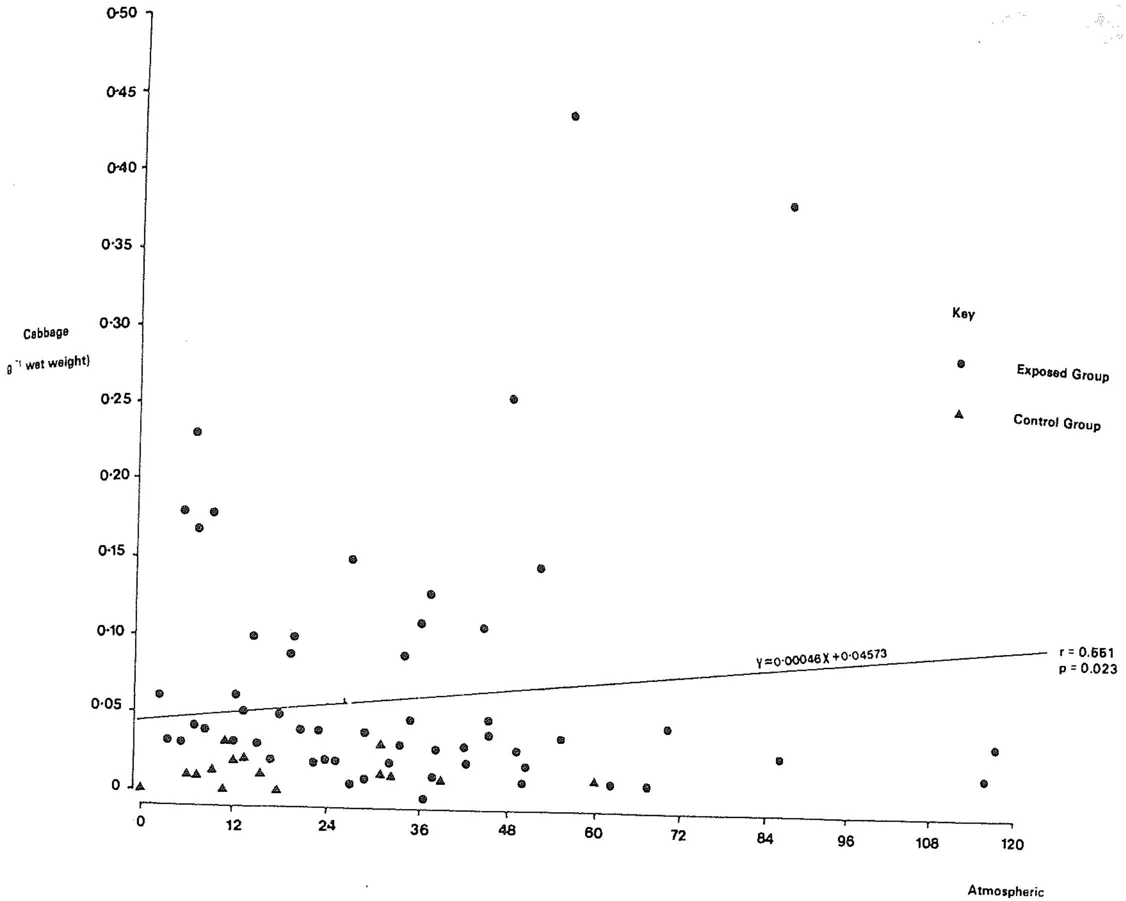

Figure 7.15 Plot of Atmospheric Deposition of cadmium against the cadmium content of Cabbages grown in 72 garden soils.

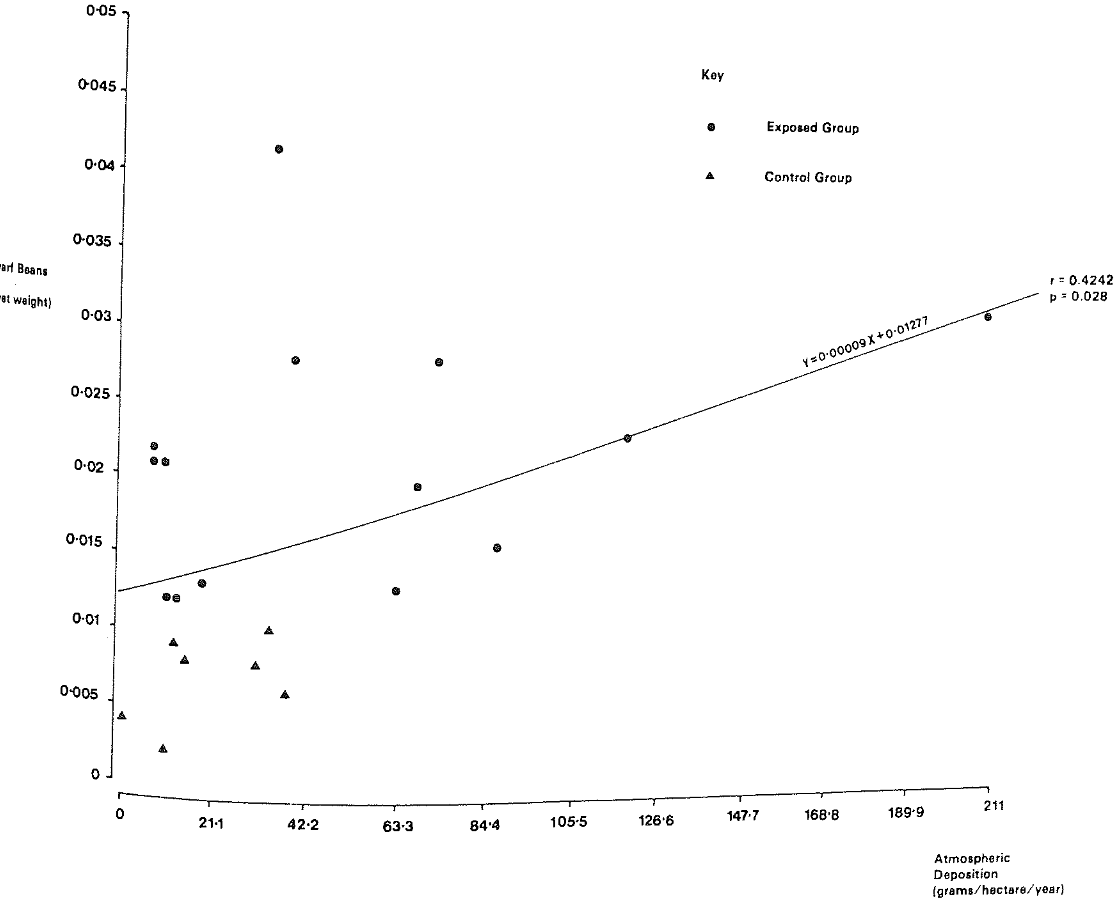

Figure 7.16 Plot of Atmospheric Deposition of cadmium against the cadmium content of Dwarf Beans grown in 21 garden soils.

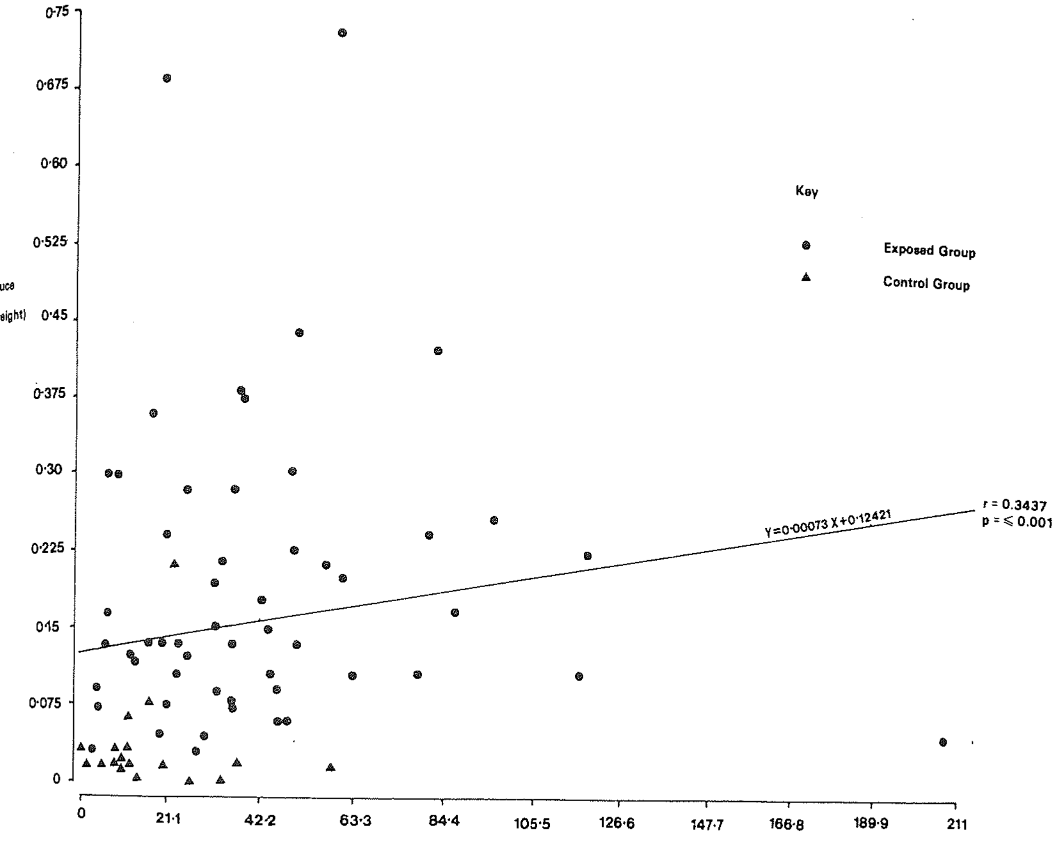

Figure 7.17 Plot of Atmospheric Deposition of cadmium against the cadmium content of Lettuce grown in 76 garden soils.

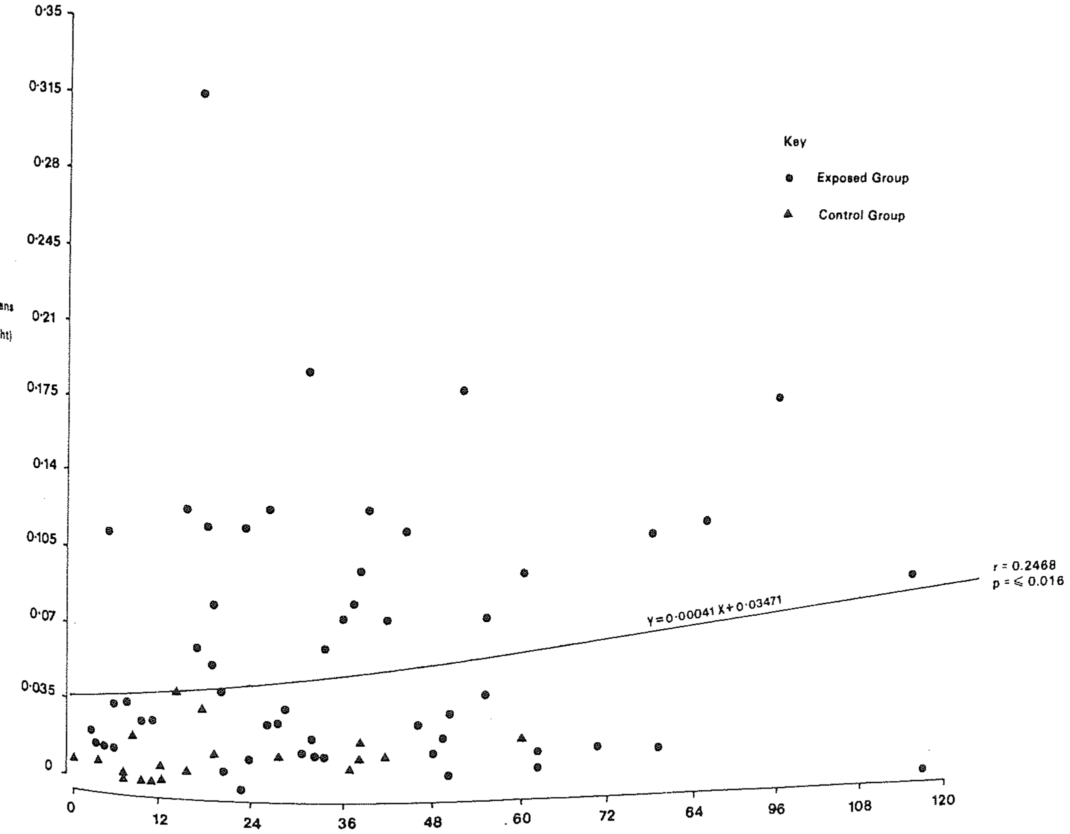

Figure 7.18 Plot of Atmospheric Deposition of cadmium against the cadmium content of Runner Beans grown in 76 garden soils.

cadmium uptake by vegetables, and that pH does not seem to influence uptake to any significant degree.

7.4 HOUSEHOLD DUST

7.4.1 Uptake of Cadmium from House Dust

A study of the routes of exposure and uptake of cadmium from house dust has been carried out by the author.[229] This study has identified the hand-to-mouth route as one of the most important mechanisms by which cadmium and other toxic metal-enriched dusts are ingested in exposed groups. The most at risk are children, especially those under four years old, who are prone to involuntary ingestion through finger and thumb sucking, mouthing objects and eating sticky sweets whilst at play. It is widely accepted that the amount of dust ingested is difficult to quantify and will vary considerably from child to child. However, studies[229,230] have shown that a child may ingest 20 mg of dust in any given day, assuming the fingers are sucked ten times. Should this dust contain 100 ug g^{-1} cadmium, a child may involuntarily ingest 2 ug of cadmium per day, equivalent to 10 ug per day for a typical adult.[229] Adventitious ingestion of house dust by adults is also very difficult to quantify, although it is generally considered that intakes are much lower than those for children.

7.4.2 Cadmium in Walsall House Dusts

The levels of cadmium found in house dusts collected from 96 study households (Table 7.6) show that, in general, the cadmium content of settled house dust is greater than vacuum dust, which in turn is greater than carpet dust. The relatively high levels of cadmium in settled dust are considered to be due to the small particle sizes which tend to contain higher levels of cadmium per unit weight. Table 7.7 shows the Spearman rank correlation co-efficients of cadmium in house dust against the levels of cadmium in atmospheric deposition and garden soil. It is evident that there is no correlation between these variables, indicating that there is no causal relationship and that atmospheric deposition and garden soils do not appear to make a significant contribution to the levels of cadmium in house dust. Table 7.8 shows the cadmium content of vacuum cleaner dust collected from the control and exposed study groups, compared to the cadmium content of dusts collected in a nationwide study of toxic metals in house dusts, and the cadmium content of dust collected in the Shipham study.[169,170,248]

A typical cadmium concentration of house dust in the United Kingdom is within a range of 1 to 20 ug g^{-1} but that concentrations as high as 450 ug g^{-1} may be found in isolated cases. The proximity of the households studied in the nationwide survey to known sources

		Settled Dust	Carpet Dust	Vacuum Dust
Control Group	$\bar{x}$ Range	21.7 (2.5 - 140.4)	3.7 (1.3 - 13.0)	8.7 (3.0 - 16.9)
Exposed Group	$\bar{x}$ Range	18.4 (3.0 - 105.3)	11.7 (0.6 - 311.9)	10.9 (1.0 - 34.3)

TABLE 7.6: CADMIUM LEVELS IN SAMPLES OF WALSALL HOUSE DUST (ug g^{-1})

		Settled Dust (ug g^{-1})	Carpet Dust (ug g^{-1})	Vacuum Dust (ug g^{-1})
Atmospheric Deposition (grams/hectare/year)	r p	0.2493 (n=92) .072	-0.1115 (n=93) .308	0.1642 (n=93) .130
Total Soil Cadmium (mg kg^{-1})	r p	-0.1060 (n=96) .398	-0.0353 (n=95) .033	-0.0909 (n=96) .334

TABLE 7.7: NON-PARAMETRIC CORRELATION CO-EFFICIENTS OF ATMOSPHERIC DEPOSITION AND TOTAL SOIL CADMIUM AGAINST THE LEVEL OF CADMIUM IN HOUSE DUST

	Cadmium in Vacuum Cleaner Dust ($ug\ g^{-1}$)		N of Samples
	mean	range	
Brighton	13.2	1 - 70	97
Bristol	10.8	2 - 68	100
Edinburgh	6.7	1 - 47	98
Liverpool	7.5	1 - 22	98
Hammersmith/Fulham	8.9	0 - 32	97
Newham	11.9	1 - 336	99
Newcastle-upon-Tyne	8.6	1 - 43	97
Portsmouth	16.5	1 - 450	98
Shrewsbury	10.6	1 - 64	96
Stoke-on-Trent	10.4	1 - 151	98
Shipham	26.7	1 - 373	281
Walsall (Control group)	8.7	3 - 16.9	19
Walsall (Exposed group)	10.9	1 - 34.3	77

TABLE 7.8: CADMIUM CONTENT OF HOUSEHOLD DUST COLLECTED FROM ELEVEN LOCATIONS IN THE UK, COMPARED WITH THE CADMIUM CONTENT OF DUST COLLECTED IN WALSALL

(Source of data other than for walsall: Culbard (1983)[248]) of cadmium emissions is unknown but the households were selected at random. The levels of cadmium found in the Shipham study show a similar trend, and were considered acceptable by the UK Department of the Environment.

Levels of cadmium in Walsall house dusts do not seem to be greater than any of the ten other towns studied in the UK and in certain cases are lower. However, a difference was detected between the level of cadmium in the control households of Walsall than the exposed group. It is considered, however, that this is of little importance due to the generally low levels detected.

The concentration of cadmium in settled house dusts was considerably higher than in vacuum and carpet dusts. However, as these dust samples were taken from high ledges and tops of doors they are unlikely to pose any hazard to residents.

Overall, therefore, it is considered that the levels of cadmium found in house dusts in Walsall are unlikely to pose any significant source of additional cadmium intake.

7.5 DIETARY INTAKES

7.5.1 Diet Diary

Of the twenty households requested to complete diet diaries, two declined to take part and subsequently only eighteen diaries were completed for the four-week period. The diet diary study represented a population of 46 individuals, 14 from the control group and 32 from the main study group.

Overall, the householders had no problems with the completion of the diet diaries. However, a major criticism of this type of technique is that the participants may forget to include certain food items or even whole meals. The results, therefore, may be underestimates of the true dietary intake of cadmium by the residents taking part.

Table 7.9 shows the characteristics of each of the Walsall households who completed diet diaries. It is evident that all grow a large proportion of their vegetable diet in their garden soils and that their soils contain high levels of cadmium. The dietary intakes of cadmium for the Walsall control households were very low, with a mean value of 0.15 mg week^{-1} (range 0.13 - 0.17). This is not surprising, due to the very low levels of cadmium detected in the soils and vegetables taken from the control gardens. The dietary intakes of cadmium in the Walsall exposed group, however, were much greater, with a mean value of 0.28 mg week^{-1} (range 0.14 - 0.37). The highest recorded dietary intake of 0.37 mg week^{-1} in the exposed group is equivalent to 52.9 ug day.

	House-hold	Household Population	% of Vegetables Home Grown	Soil Cadmium (mg kg^{-1})	Dietary Intake of Cadmium (mg week^{-1})
Control Group	1	3	90	1.68	0.15088
	2	2	100	1.00	0.17125
	3	4	90	1.18	0.1387
	4	3	90	1.53	0.13303
	5	2	90	1.25	0.16047
Exposed Group	6	2	100	10.0	0.37306
	7	2	90	12.33	0.26008
	8	2	100	14.68	0.36725
	9	4	90	19.95	0.25581
	10	3	90	11.63	0.32924
	11	2	90	33.05	0.31076
	12	2	70	8.4	0.17265
	13	2	90	16.15	0.34366
	14	3	90	7.58	0.13989
	15	2	90	10.5	0.31419
	16	1	100	9.34	0.22788
	17	3	100	7.83	0.33442
	18	4	80	11.85	0.1604

TABLE 7.9: CHARACTERISTICS OF THE 18 HOUSEHOLDS WHICH COMPLETED DIET DIARIES

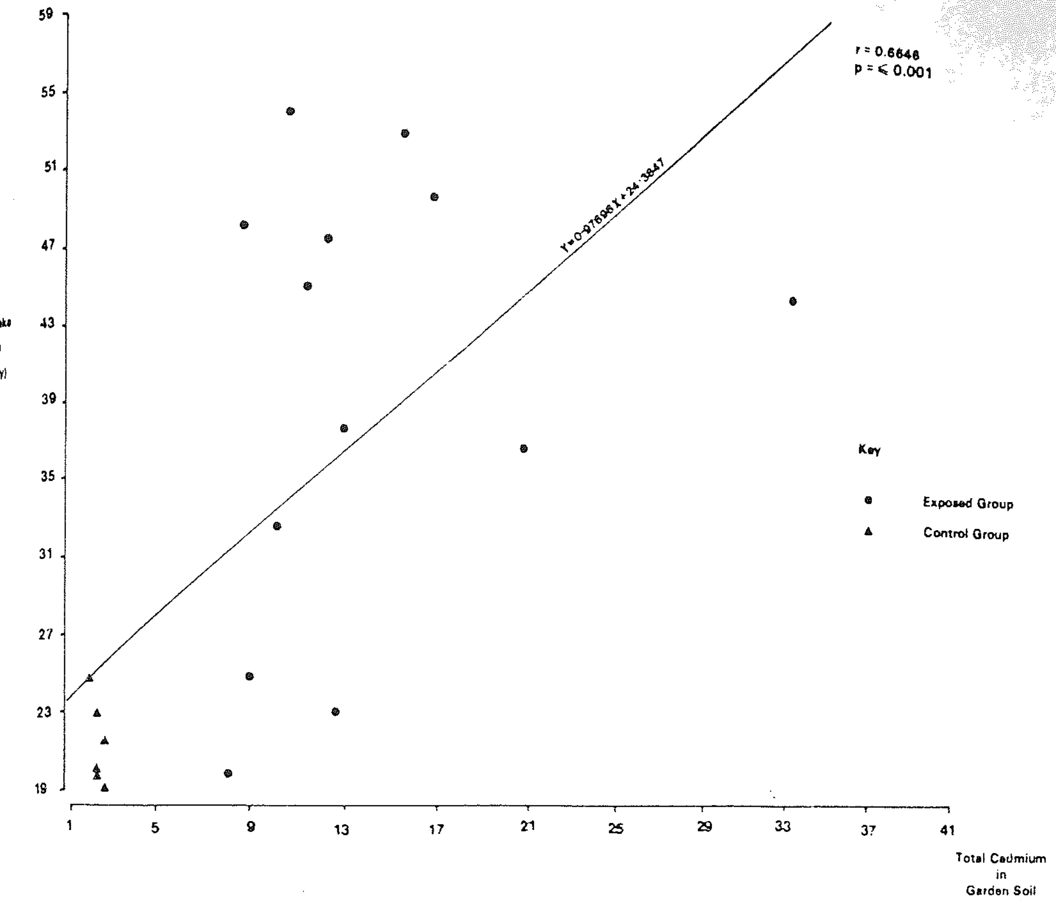

Figure 7.19 Plot of Total Cadmium in garden soil against dietary intake of cadmium calculated using the Diet Diary technique.

Figure 7.19 shows the scatter of dietary intakes of cadmium calculated using the diet diary technique against the level of total cadmium in garden soil. The dietary intakes are correlated with the level of soil cadmium, the correlation being highly significant using a one-sided t-test (r=0.6646, p=<0.001). This indicates that those householders with the higher levels of soil cadmium will have correspondingly higher dietary intakes. It is considered that the observations plotted in Figure 7.19 are not closely clustered in a linear pattern because not all the householders grew the same proportion of their vegetable diet in their garden soils, and subsequently will not have the same dietary intakes even if the vegetables were grown in soils with similar cadmium concentrations. Had the householders grown the same proportion of their vegetable diet in their gardens, the observations may have demonstrated a greater correlation. Nevertheless, these results do indicate that people growing vegetables in cadmium contaminated soils in urban/industrial areas can significantly increase their dietary intakes of this metal.

Table 7.10 shows the dietary intakes of cadmium for the Walsall control and exposed householders compared with the intakes reported for Shipham residents. It is evident that the mean dietary intake of cadmium for the exposed Walsall group (0.28 mg week^{-1}) is marginally higher than the mean dietary intake reported for Shipham residents (0.25 mg week^{-1}). The highest dietary intake of cadmium reported for a Shipham resident (0.52 mg week^{-1}) was found to be much greater than the maximum recorded intake in Walsall (0.37 mg week^{-1}). Nevertheless, it is evident that the Walsall exposed householders have elevated dietary intakes of cadmium which are nearly twice as high as those of the control householders.

7.5.2 Standard Diet Study

The aim of the standard diet technique was to provide estimates of the dietary intake of cadmium by all householders growing vegetables, assuming that all the vegetables grown are consumed by the residents of the household, and that the dietary intakes of cadmium from

	MEAN mg Cd week^{-1}	RANGE mg Cd week^{-1}
Intake from all fruit and vegetables consumed (Walsall control households)	0.04	0.02 - 0.06
Estimated total dietary intake	0.15	0.13 - 0.17
Intake from all fruit and vegetables consumed (Walsall contaminated households)	0.17	0.05 - 0.26
Estimated total dietary intake	0.28	0.14 - 0.37
Intake from home grown fruit and vegetables (Shipham residents)	0.10	ND
Estimated total dietary intake	0.25	0.13 - 0.52

TABLE 7.10: RESULTS OF DIET DIARY STUDY

AVERAGE CADMIUM INTAKES OF HOUSEHOLDERS GROWING VEGETABLES IN CONTAMINATED AND UNCONTAMINATED WALSALL GARDENS COMPARED WITH THE ESTIMATED INTAKES FOR SHIPHAM RESIDENTS sources other than vegetables remain the same as for a typical UK adult. Hence, the calculated dietary intake of cadmium using this technique would represent the maximum possible intake of the residents growing the amount of vegetables they did in the summer of 1983. Using the reported mean levels of cadmium in uncontaminated vegetables[56,92] and the published dietary intakes of vegetables and fruit by typical UK residents[241] the standard diet technique was used to calculate the dietary intake of cadmium for a typical UK adult. It was found that a UK adult would ingest approximately 0.29 mg of cadmium per week, equivalent to 42 ug day^{-1}. This is higher than the Department of the Environment's estimated dietary intake of cadmium for a typical UK adult of 0.14 mg $week^{-1}$ (range 0.09 - 0.18).

The Walsall control households which were investigated using the diet diary technique were found to have average dietary intakes of cadmium of 0.15 mg $week^{-1}$, which is consistent with the DoE estimate. However, the Walsall control households were found to grow vegetables with cadmium concentrations well below those levels reported for uncontaminated vegetables by the DoE[92] and the Commission of the European Communities.[56] In addition, as the diet diary technique is prone to giving an underestimate of the true dietary intake, the reported intakes of cadmium for typical UK residents may in fact be much greater than the official DoE published figure. Indeed, reported dietary intakes of cadmium for typical residents of other industrialised countries (Table 7.11) and calculated using standard diet, duplicate meal and fecal excretion techniques show that dietary intakes of cadmium for typical adults to be between 30 and 50 ug day. This would indicate that the official DoE dietary intake of 0.14 mg cadmium per week (20 ug day^{-1}) to be a very conservative estimate, and that 0.29 mg per week (42 ug day^{-1}) may be a much closer proximation to the actual dietary intake of cadmium by a typical UK adult.

As the standard diet technique was found to yield dietary intakes of cadmium for typical UK adults which were consistent with studies carried out elsewhere, this technique was used to calculate the maximum possible dietary intakes of cadmium by Walsall residents, assuming that 10 per cent of vegetables grown are lost through natural wastage.

The results of the standard diet calculations show that the householders in the control group had dietary intakes of cadmium which were less than those for typical UK adults. This was probably due to the low levels of cadmium found in the vegetables collected from these households. The mean cadmium intake of the control group was 0.204 mg week^{-1} (range 0.15 - 0.26 mg week^{-1}) which is equivalent to 29.2 ug day. The mean cadmium intake of the exposed Walsall group was 0.322 mg week^{-1} (range 0.202 - 0.533 mg week^{-1}) which is equivalent to

Country	Cadmium Intake (ug day^{-1})
Rumania	38 - 64
FR Germany (3 separate studies)	48
" "	30
" "	32.4
France	20 - 30
Czechoslovakia	60
USA (7 separate studies)	44.2
"	4 - 60
"	38 - 50
"	27 - 64
"	26 - 50
"	51.2
"	71.4

TABLE 7.11: PUBLISHED DIETARY INTAKES OF CADMIUM FOR TYPICAL RESIDENTS OF FIVE INDUSTRIAL COUNTRIES CALCULATED USING STANDARD DIET, DUPLICATE MEAL AND FECAL EXCRETION METHODS

(Source: Commission of the European Communities[56])

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46 ug day^{-1}. The mean cadmium intake of the Walsall exposed group is only slightly higher than the intake for a typical UK adult. However, figure 7.20 shows the frequency distribution of the dietary intakes of cadmium calculated for all 96 Walsall households using the standard diet technique. It is evident that a large number of exposed Walsall householders have dietary

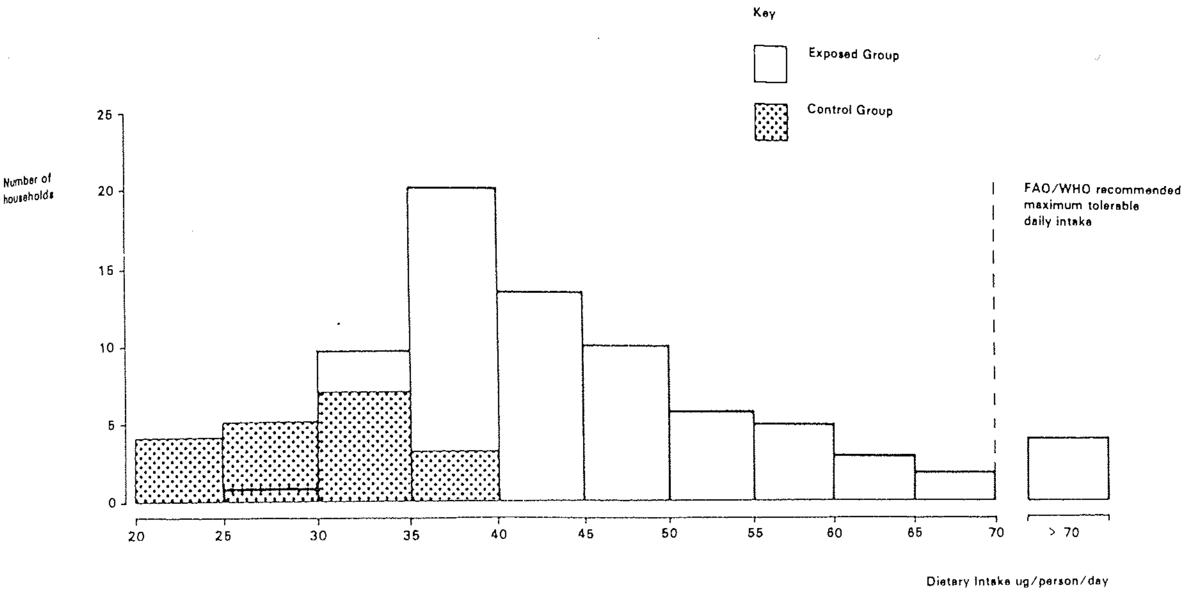

Figure 7.20 Frequency Distribution of dietary intakes of cadmium calculated using the Standard Diet technique for 96 Walsall households.

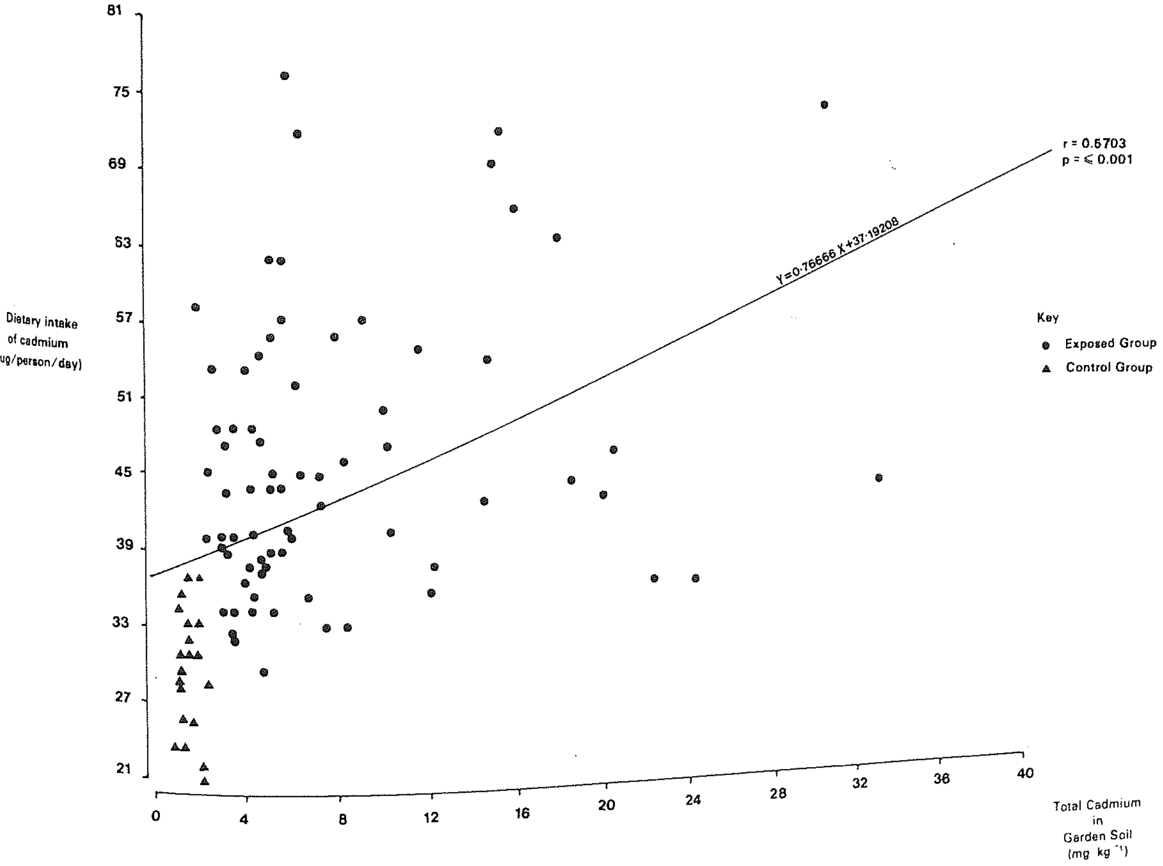

Figure 7.21 Plot of Total Cadmium in garden soil against dietary intake of cadmium calculated using the Standard Diet technique.

intakes of cadmium above the typical level for a UK adult, and that four households exceed the FAO/WHO maximum tolerable intake of cadmium.

Figure 7.21 shows the scatter of dietary intakes of cadmium calculated using the standard diet technique against the level of total cadmium in garden soil for the 96 Walsall households studied. It is evident that the householders with the lower soil cadmium levels (including control households) in general had the lowest cadmium intakes, whilst the householders with the higher soil cadmium levels tended to have the higher cadmium intakes.

The co-efficient of correlation (r=0.5703) and t-test of significance (p=<0.001) show that the total soil cadmium and dietary intakes are correlated, and that the relationship is significant. This would tend to confirm that those householders with the highest levels of soil cadmium are more likely to have elevated cadmium intakes than householders with low levels of soil cadmium but growing a similar proportion of their vegetable diet.

7.5.3 Comparison of the Diet Diary and Standard Diet Results

Figure 7.22 shows the scatter of dietary intakes of cadmium calculated using the standard diet technique

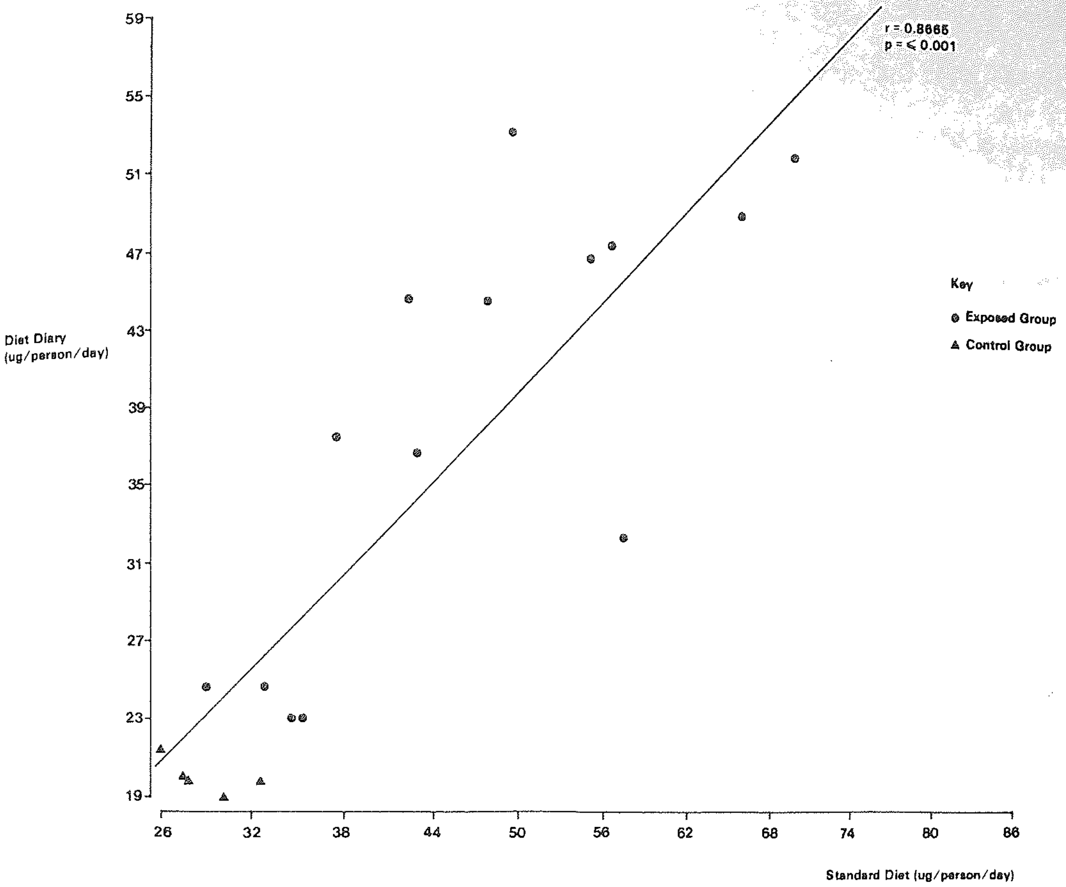

Figure 7.22 Comparison of calculated dietary intakes of cadmium for 19 households using the Diet Diary and Standard Diet techniques.

		Standard Diet	Total Soil Cadmium	Plant-available Cadmium
Diet Diary	r p	0.8665 (n=18) .001	0.6646 (n=18) .001	0.7142 (n=18) .001
Standard Diet	r p	******	0.5703 (n=93) .001	0.6636 (n=93) .001

TABLE 7.12: NON-PARAMETRIC CORRELATION CO-EFFICIENTS OF DIETARY INTAKES OF CADMIUM AGAINST THE LEVEL OF CADMIUM IN GARDEN SOIL

against the dietary intakes of cadmium calculated using the diet diary for the 19 Walsall households who took part in both studies. The results of both techniques are highly correlated with each other (r=0.8665, p=<0.001) indicating that those householders who were identified as having high cadmium intakes using the diet diary technique also showed high intakes using the standard diet technique. This suggests that the standard diet technique, when used in conjunction with a control population is a good indicator of the dietary intakes of cadmium by exposed populations.

Table 7.12 shows the Spearman rank correlation co-efficients and one sided t-tests of both dietary estimating techniques against the level of total and plant-available cadmium in the 96 Walsall study gardens. It can be seen that both techniques show correlations with the level of plant-available and total cadmium and, as such, both are useful techniques for estimating the dietary intake of cadmium by householders exposed to high levels of soil cadmium. The standard diet technique, however, is a much quicker and more reliable technique to use than the diet diary technique and can be carried out for large numbers of households. The author would argue, therefore, that it is the most suitable technique for estimating dietary intakes of cadmium for large numbers of people thought to be at risk.

Although the two dietary intake techniques are correlated it does not necessarily mean that both are accurate. As stated earlier, the diet diary technique can give underestimates of the dietary intakes due to the participants forgetting to include part of, or the whole of, a meal, or by inaccurate weighing of the food. In addition, if members of the household were away, or an extra serving was made, the participants may not record this. The standard diet technique, on the other hand, would, on the whole, give an over-estimate of the dietary intake of vegetables by the householders, since the maximum possible intake was calculated, less a 10 per cent wastage factor. The participants, therefore, may not ingest all the amount of cadmium stated.

It must also be borne in mind that the cadmium content of the vegetables was calculated on a fresh weight basis and as such, for both techniques, an allowance must be made for the cadmium which would be lost during cooking. A cadmium loss during cooking was estimated earlier (paragraph 7.3.3) to be between 6 and 10 per cent. If the mean of these two figures (8 per cent) is assumed, the intakes of cadmium can be reduced by this amount. The cadmium intake recorded using the standard diet technique (72.6 ug day^{-1}) would thus be 66.8 ug day^{-1}, just under the FAO/WHO maximum tolerable intake. As the diet diary results are considered underestimates of the true dietary intake of cadmium by the participants, it seems pointless reducing those figures to take account of cadmium loss during cooking.

At the commencement of the study the householders estimated the proportion of their vegetable diet grown in their garden or allotment. As an allowance was made for vegetables which were brought into the household to supplement the vegetables grown at home, those householders who claimed to grow more than they actually did were calculated to have lower dietary intakes of cadmium. For instance, if a householder claimed to grow 50 per cent of vegetable diet, half of the UK typical dietary intake of cadmium from vegetables would be added to the calculated intake from home grown vegetables. If, however, a householder claimed to grow 100 per cent of vegetable diet, but only in fact grew 50 per cent, no such allowance would be made, and the dietary intake would be calculated to be 3.9 ug day^{-1} less. Hence, the standard diet technique will yield an underestimated dietary intake of cadmium for householders who overestimated their vegetable production. The net effect of underestimating dietary intakes by the standard diet technique would be between 4 and 10 per cent.

The householders' dietary intakes of cadmium calculated using the standard diet technique have therefore been allowed 18 per cent for wastage and loss of cadmium during cooking, and if the underestimate of dietary intakes is not adjusted for, the householders would have been allowed in total between 22 and 28 per cent for loss of cadmium.

The dietary intakes calculated for the exposed households does not include the amount of cadmium which would be taken in from the air and adventitious sources. These sources of intake have been calculated by the Commission of the European Communities to be between 0.05 and 25 ug day^{-1} for a non-smoker and 3.05 and 28 ug day^{-1}* for a smoker living in an industrial area. The total dietary intakes of Walsall residents may, therefore, be much higher than the estimates produced in this section, especially amongst smokers.

Overall, however, it can be concluded that dietary intakes of cadmium by the exposed Walsall residents is twice as high as for the control residents, and that the main source of intake is contaminated home grown vegetables. Furthermore, the total intakes of cadmium by the most exposed householders may reach or exceed the FAO/WHO maximum tolerable intake of 70 ug cadmium per day.

7.6 URINE ANALYSIS

7.6.1 Participating Residents

A computer search of the data collected on the characteristics of all the 260 Walsall residents participating in the study was initiated to identify those householders who exhibited the most risk factors for a high intake of

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* Assuming a deposition of 3 ug day^{-1} from cigarettes at 40 cigarettes per day

cadmium and who had no history of smoking or occupational exposure to this metal. Hence, a selected group comprising individuals who had high soil cadmium levels, who had grown a large proportion of their vegetable diet for many years, and who tended to have higher estimated dietary intakes of cadmium was identified.

The search highlighted 52 suitable Walsall residents. Of these, 20 were males and 32 females. Each was contacted by letter to request their participation (Appendix B). When the residents were visited some days later all but 12 (3 males and 9 females) were willing to give a urine specimen for analysis. A sample population of 40 residents was therefore obtained.

The 40 residents were then instructed as to how the sample should be collected. At the same time a questionnaire was used to confirm that the residents were non-smokers and had not been occupationally exposed to cadmium in the past. The questionnaire was structured also to determine if the residents had, at any time, suffered from diabetes, kidney disease, hypertension or heart disease. The name and address of their General Practitioner was also noted.

Figure 7.23 shows the dietary intakes and total soil cadmium concentrations of the 40 householders who gave urine samples. The households are distributed throughout the study population as a whole, although those

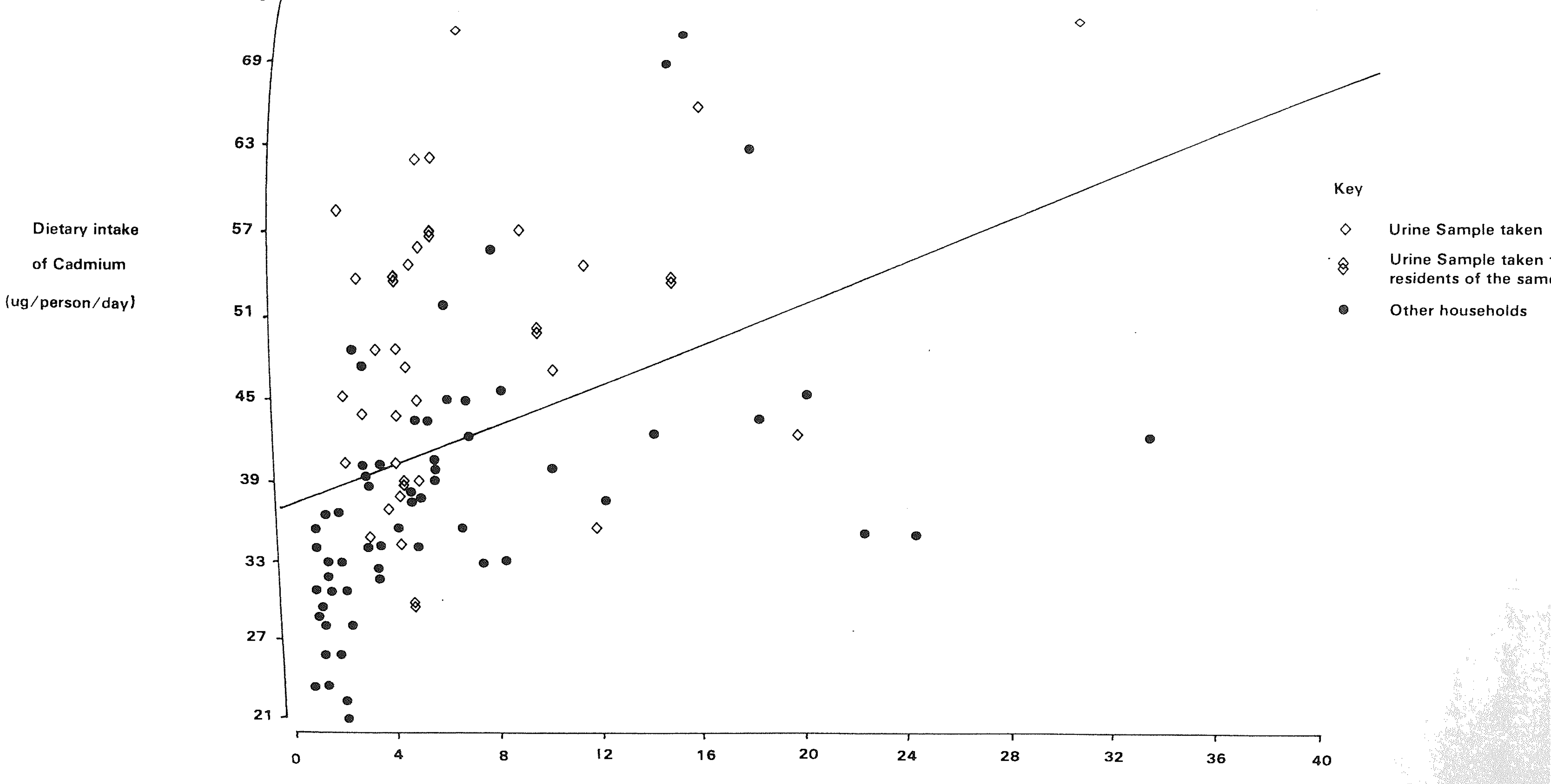

Figure 7·23 Plot of Total Cadmium in garden soil against dietary intake of cadmium showing the 40 householders from which urine samples were taken.

householders with the higher cadmium intakes tend to be well represented in the study group. Table 7.13 shows the other characteristics of the 40 residents providing urine samples.

Sex	Age	Length of Residence (years)	Length of Cultivation (years)	Amount of Vegetables Home Grown (%)	Total Soil Cadmium (mg kg^{-1})	Dietary Intake of Cadmium (ug day^{-1})
M	40	32	32	90	5.75	57.36
M	52	15	15	100	5.70	39.31
M	53	25	25	70	5.95	76.23
M	57	15	15	100	4.95	28.85
M	58	18	18	90 - 100	1.99	58.42
M	60	32	32	50	14.75	53.36
M	63	32	32	90	16.15	65.77
M	64	30	30	90 - 100	5.70	44.22
M	68	27	27	100	10.00	49.50
M	68	32	32	50	20.43	46.38
M	70	20	20	90 - 200	3.37	44.23
M	70	3+	3+	90 - 100	4.98	47.70
M	70	35	25	100	5.55	61.80
M	77	20	20	30 - 50	6.41	44.92
M	77	32	30	90	6.40	71.82
M	78	50	43	100	2.95	52.86
M	80	12	12	100	30.80	72.08
F	52	18	18	70 - 90	11.85	35.27
F	52	15	15	100	5.70	39.31
F	55	26	26	90 - 100	5.13	55.76
F	55	27	6	90 - 100	4.78	54.07
F	55	30	30	30 - 50	5.23	62.08
F	56	33	32	90 - 100	11.68	ND
F	56	15	15	100	4.95	28.85
F	57	30	30	90	5.35	34.31
F	58	4	4	90	4.93	37.30
F	59	32	32	50	14.75	53.36
F	60	32	10	90 - 100	10.50	47.53
F	66	31	7	100	3.50	39.73
F	69	28	28	90 - 100	11.63	54.73
F	69	27	27	100	10.00	49.50
F	70	35	35	70	3.88	52.84
F	70	44	44	50	4.35	43.28
F	72	25	25	70	4.95	38.38
F	74	32	32	90	5.75	57.36
F	76	40	40	100	3.55	48.86
F	78	50	43	100	2.95	52.86
F	79	52	52	100	3.65	31.38
F	81	33	33	100	9.34	57.18
F	81	59	59	100	6.04	39.68

TABLE 7.13: 'RISK FACTORS' AMONGST THE 40 WALSALL RESIDENTS WHO GAVE URINE SAMPLES

7.6.2 Cadmium in Urine

Levels of urinary cadmium amongst the non-smoking general population appear not to have been published for the United Kingdom. However, the level of cadmium in urine is known to increase with age, peaking at around 60 years of age. The mean levels of cadmium in urine of children are reported to be 0.21 ug g^{-1} of creatinine [60] and for adults between 0.25 and 0.62 ug g^{-1} creatinine.[249,250]

The cadmium content of urine collected in the Walsall study ranged from <0.45 to 3.39 ug g^{-1} of creatinine, with mean and median values of 1.11 and 1.3 ug g^{-1} respectively (Table 7.14). Figure 7.24 shows the donor age and cadmium content of urine specimens collected from 120 non-smoking residents of Stockholm, Sweden[250] compared to the cadmium content of the 40 Walsall urine specimens. It is evident that the Walsall urinary cadmium concentrations are significantly elevated above the levels normally found in typical adults of similar ages living in the urban area of Stockholm. Although the Swedish population may not be directly comparable with a population of the UK due to socio-economic differences, the difference in urinary cadmium content cannot be solely attributed to this. Moreover, it is considered that the elevated levels of urinary cadmium amongst the Walsall residents is a direct result of increased dietary intake of cadmium from contaminated home grown vegetables.

ITEM	n	MEDIAN	RANGE	MEAN
AGE (years)	39	66	40 - 87	65
pH	40	5.7	5.1 - 6.7	ND
CREATININE (g l^{-1})	40	0.84	0.26 - 3.87	0.90
B_2M (ug l^{-1})	38	93	<50 - 480	125.0
CADMIUM (ug l^{-1})	40	1.0	<0.5 - 3.0	1.03
B_2M/CREATININE (ug g^{-1})	38	112	<39 - 1000	1.03
CADMIUM/CREATININE (ug g^{-1})	40	1.11	<0.45 - 3.39	1.3

TABLE 7.14: MEAN, MEDIAN AND RANGE OF VALUES FOR ANALYSIS OF CADMIUM IN URINE SAMPLES FROM WALSALL RESIDENTS

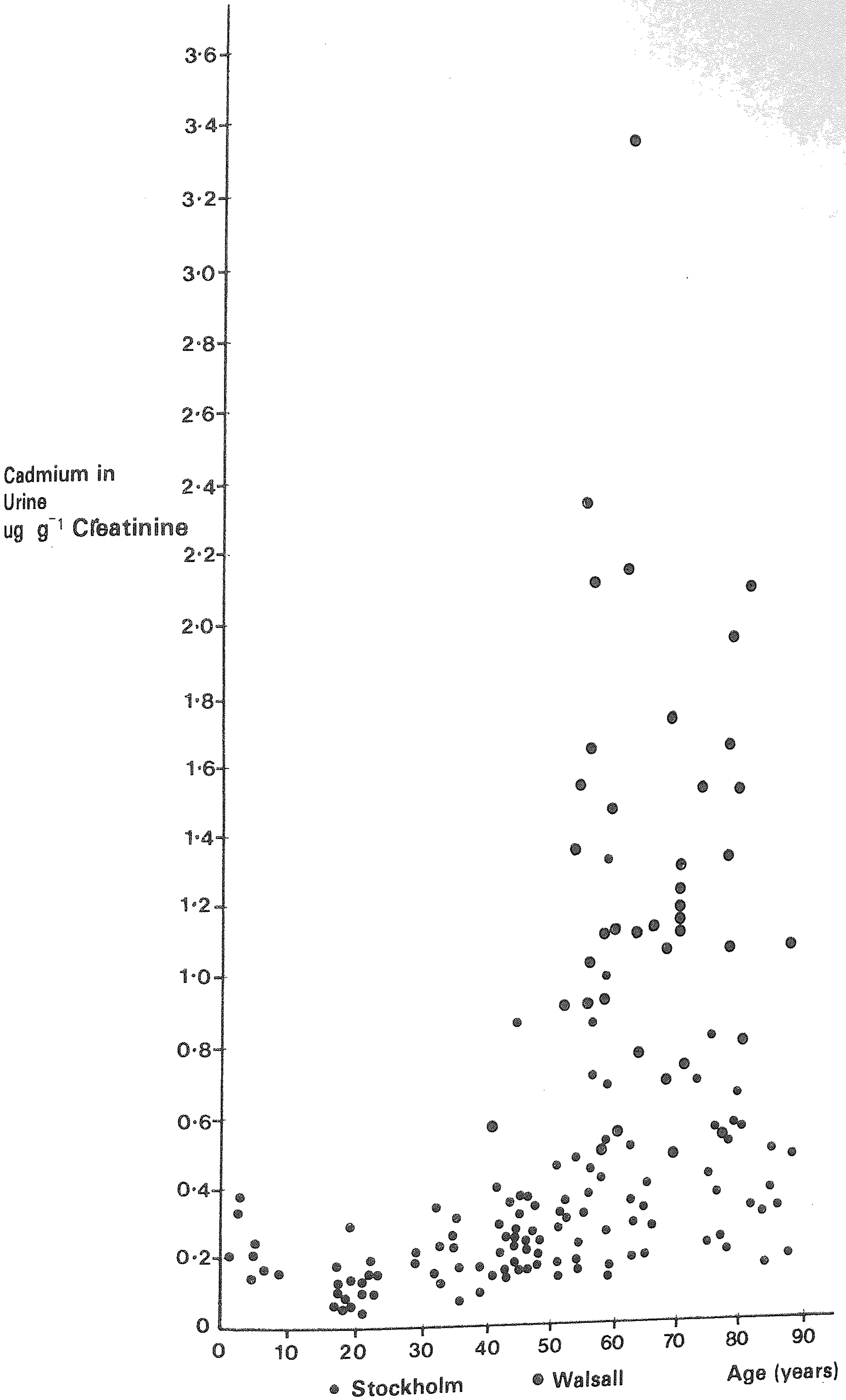

Figure 7.24 Urinary excretion of cadmium by 40 Walsall residents compared with 120 non-smoking residents of Stockholm, Sweden.

In 1980 the World Health Organisation recommended a 'Health Based Biological Limit' for cadmium in urine of occupationally exposed workers of 5 ug g^{-1} creatinine.[251]

The highest level of urinary cadmium detected in the environmentally exposed Walsall study group was 3.39 ug g^{-1} creatinine, which is well below the WHO recommended limit. However, it should be stressed that the Walsall study group were all non-smokers and that if a study group of smokers were selected from the same exposed Walsall study population this limit might be exceeded. In addition, an individual growing vegetables in contaminated soils in Walsall and being industrially exposed to cadmium may take up sufficient to exceed the WHO limit, and substantially increase body burdens.

7.6.3 B_2-Microglobulin

As reported earlier (paragraph 4.2.1) B_2-Microglobulin is a useful indicator of renal function. Should the levels of cadmium accumulated by Walsall residents be sufficient to cause renal tubular damage this would be apparent from an increased excretion of this protein.

Studies carried out elsewhere[252-254] have established that B_2-Microglobulin undergoes rapid degradation when the urinary pH is less than six and that this breakdown will occur in the bladder. Urine samples with pH levels less than this value are recommended to be discarded if

B_2-Microglobulin is intended to be measured.[200] The levels of pH in the Walsall samples had a median value of 5.7 (range 5.1 - 6.7) with 27 specimens (67.5 per cent) having a pH level below 6.0. Nevertheless, all the specimens were analysed and the effect of acid degradation of B_2-Microglobulin must be considered when interpreting the results.

Levels of B_2-Microglobulin in the general population are reported to be on average 76 ug g^{-1} creatinine.[255] The levels of B_2-Microglobulin in the urine specimens collected from the 40 Walsall residents (Table 7.12) had a mean value of 179.5 ug g^{-1} creatinine (range <39 - 1000 ug g^{-1} Cr) with one specimen having a level greater than the upper normal limit of 617 ug g^{-1} Cr.

The highest level of B_2-Microglobulin detected (1000 ug g^{-1} Cr) may be explained due to the low level of creatinine detected in this sample (0.48 g $litre^{-1}$) which may be too low for a proper assessment of B_2-Microglobulin excretion to be made. However, the level of B_2-Microglobulin (480 ug $litre^{-1}$) was the highest recorded amongst the Walsall residents. The pH of this specimen was also low (5.2) indicating that the level of B_2-Microglobulin may have been much higher prior to acid degradation.

The urine specimen which was found to contain the highest level of cadmium had a B_2-Microglobulin level of 85 ug g^{-1} Cr which is marginally above average for the general population but well within the range of normal values. As the levels of B_2-Microglobulin in the urine specimens collected from Walsall may have been affected by the low pH levels, it is difficult to form any firm conclusions. However, studies carried out by Tsuchiya[200] have indicated that at a mean urinary cadmium excretion of 1.35 ug g^{-1} Cr as was found for the Walsall population, 15 per cent of the population would have excessive B_2-Microglobulin levels (>520 ug g^{-1} Cr) rising to 20 per cent for a population with a mean urinary cadmium excretion of 2.2 ug g^{-1} Cr (Table 7.15).

	Percentage of the Population with Elevated B_2-Microglobulin Levels				
	10%	12.5%	15%	20%	50%
Urinary Cadmium (ug g^{-1} Cr)	0.5	0.93	1.35	2.2	40

TABLE 7.15: ESTIMATED PERCENTAGE OF THE POPULATION HAVING EXCESSIVE URINARY EXCRETION OF B_2-MICROGLOBULIN AT VARIOUS URINARY CADMIUM EXCRETION RATES

(Adapted from Tsuchiya (1983)[200])

This being the case, six of the urine samples should have shown high levels of B_2-Microglobulin. If a smoking 'general population' were selected, this figure may well have been reached.

Overall, it would seem that the levels of B_2-Microglobulin excretion amongst the 40 Walsall residents studied are typical of the general population, indicating no signs of renal tubular impairment due to the high levels of cadmium in home grown vegetables. However, the low pH levels may have caused a masking effect, resulting in lower levels of B_2-Microglobulin.

7.6.4 Correlation of B_2-Microglobulin and Cadmium in Urine with Risk Factors

Table 7.16 shows the non-parametric correlation coefficients of cadmium and B_2-Microglobulin in urine against cadmium intake, total soil cadmium, age, and number of years cultivation. It is evident that there is no correlation between any of these variables.

In view of the age structure of the sample population (range 40 - 87, median 66) the level of urinary cadmium was not correlated with age. A possible reason for this lack of correlation may be due to the peaking of cadmium excretion around the age of 60. The net effect of this would be the older residents (>65 - 80) excreting similar levels of urinary cadmium as the younger residents, with no apparent correlation between the two. Similarly, this may be the reason urinary cadmium was not correlated with dietary intake. If a larger population group were studied it is possible that a correlation would be noted between urinary cadmium and age, up to the age of 60 and an inverse correlation thereafter. This trend has been found in populations studied elsewhere.[250]

	Cadmium in Urine ug g^{-1} Cr	B_2-Microglobulin ug g^{-1} Cr
Cadmium Intake (ug. d^{-1})	r = 0.0499 p = 0.381	r = 0.0419 p = 0.403
Total Soil Cadmium (mg kg^{-1})	r = -0.1058 p = 0.258	r = -0.1452 p = 0.192
No of Years Cultivation	r = 0.0171 p = 0.458	r = 0.0675 p = 0.344
Age	r = -0.0062 p = 0.485	r = 0.2174 p = 0.095

TABLE 7.16: NON-PARAMETRIC CORRELATION CO-EFFICIENTS OF URINARY CADMIUM AND B_2-MICROGLOBULIN AGAINST DAILY CADMIUM INTAKE, TOTAL SOIL CADMIUM, AGE, AND NUMBER OF YEARS OF VEGETABLE CULTIVATION

7.6.5 Other Findings

As discussed earlier, cadmium has been found to play a role in the cause of hypertension, both in laboratory experiments and in epidemiological studies (para 4.2.3). If this is the case, a high prevalence of hypertension might be expected amongst the Walsall residents studied.

Although blood pressure was not recorded for the 40 Walsall residents by the author, eight of the 40 residents (20 per cent) who gave urine samples stated that they had been clinically diagnosed as hypertensive. Whether this is a high prevalence of hypertension amongst the study group, bearing in mind the age structure, is difficult to determine from the small sample size used for the urine analysis. Moreover, other residents of the study group may be hypertensive but not clinically diagnosed as such. The prevalence of hypertension, therefore, may be even greater. Further studies need to be carried out to determine if cadmium and hypertension have a causal relationship amongst the exposed Walsall residents.

CHAPTER 8

THE SIGNIFICANCE OF CADMIUM IN WALSALL AND IMPLICATIONS FOR POLICY

CHAPTER 8: THE SIGNIFICANCE OF CADMIUM IN WALSALL AND IMPLICATIONS FOR POLICY

8.1 CADMIUM IN WALSALL

8.2 URBAN/INDUSTRIAL AREAS IN THE EUROPEAN COMMUNITY

8.3 POLICY OPTIONS TAKEN BY THE CEC AND MEMBER STATES TO REDUCE CADMIUM IN THE ENVIRONMENT

8.4 CURRENT POLICY REQUIREMENTS OF THE EUROPEAN COMMUNITY

CHAPTER 8: THE SIGNIFICANCE OF CADMIUM IN WALSALL AND IMPLICATIONS FOR POLICY

8.1 CADMIUM IN WALSALL

It is evident from the preceding chapters that the levels of cadmium in much of the soil in the Borough of Walsall are elevated far above those accepted as normal. Furthermore, the cadmium contamination is not isolated to waste or derelict land, in that the garden soils of many households are contaminated. This study has shown that the levels of cadmium in garden soils can increase the dietary intake of cadmium of residents growing vegetables in these soils, and that in some cases the margin between dietary intakes and the maximum tolerable intake recommended by the FAO/WHO is severely eroded.

It is also suggested that with the additional intake of cadmium from urban air, smoking and occupational exposure, many residents may have acquired undesirably high body burdens of cadmium. The evidence therefore suggests that in the European Community as a whole the residents of urban/industrial areas who grow vegetables in garden soils may represent the most 'at risk' sectors of the population of increasing dietary intakes of cadmium up to or above the FAO/WHO maximum tolerable limit.

Recent studies carried out elsewhere have predicted a further increase in cadmium intakes of 30 per cent over the next 100 years for residents of the European Community.[57] If this increase were applied to the Walsall exposed group, some 20 per cent would have dietary intakes greater than the FAO/WHO limit.

8.2 URBAN/INDUSTRIAL AREAS IN THE EUROPEAN COMMUNITY

The background levels of cadmium in the West Midlands Metropolitan County presented in Figure 5.5 shows that the levels of cadmium found in the Borough of Walsall are typical of those found throughout the West Midlands area. Studies carried out by the author have shown that much of the cadmium present is as a result of a long history of metal manufacturing in the area, dating back to the 1800's. From this time, cadmium has been emitted to the environment but especially in the past fifty years.[5]

Figure 8.1 shows the principal urban/industrial areas amongst the nine major EC member states. It is evident that the West Midlands is just one of several large industrial areas in the European Community and it is highly likely that other industrial areas with histories of metal manufacturing will have similar elevated background levels of cadmium.

The presence of equally or greater at-risk population groups in other urban/industrial areas of the European Community therefore seems likely, and given that cadmium does not serve any essential biological function

Figure 8.1 Distribution of industrial areas amongst the nine major EC Member States (Source : CEC (1974) [263])

and is known to be highly toxic, urgent policies are required to reduce human exposure to this metal on the European scale.

8.3 POLICY OPTIONS TAKEN BY THE CEC AND MEMBER STATES TO REDUCE CADMIUM IN THE ENVIRONMENT

In February 1981 the Council of the European Communities proposed a directive concerning the limit values of discharges of cadmium into the aquatic environment, and environmental quality objectives (EQO's) for cadmium in the aquatic environment.[256] The purpose behind the proposal was to reduce cadmium discharges to fresh and sea water from industries using cadmium as a primary raw material as well as non-ferrous metal industries. This directive was accepted by EC member states and came into effect in January 1983.

Apart from reducing the cadmium content of surface waters used for potable water abstraction, which is already covered by other EC standards,[257] the directive will only reduce the dietary intakes of cadmium of those people who consume large quantities of estuarine and sea foods, which are know to accumulate high levels of cadmium. For the purpose of this study, therefore, this directive is of little relevance. The high level of cadmium in the urban/industrial environment is mainly derived from atmospheric emissions and direct contamination of land by industry and industrial wastes.

In March 1982 the Commission of the European Communities Environment and Consumer Protection Service produced a proposal for a Council directive on the use of sewage sludge containing heavy metals in agriculture.[258] Within this directive, restrictions were proposed on the total input of cadmium into agricultural soils over a period of 10 years. For cadmium, this was recommended to be on average <100 grams per hectare per year ($g\ ha^{-1}\ yr^{-1}$) whilst ensuring that a soil concentration did not exceed 3 $mg\ kg^{-1}$. A maximum cadmium content of sewage sludge intended for agricultural use was proposed as <40 $mg\ kg^{-1}$.

This directive, however, was intended for agricultural soils only and was not intended for use by Environmental Health Authorities who are in need of similar guidelines. The deposition of cadmium onto Walsall garden soils exceeded that recommended by the CEC for agricultural soils in a number of cases, and all the Walsall gardens had soil cadmium levels >3 $mg\ kg^{-1}$ even though the soils were, in essence, being used for agricultural purposes. This directive, which has now been accepted by EC member states, will protect most Europeans from increasing dietary intakes of cadmium except those who consume vegetables grown in urban/industrial areas.

Until this most recent directive on cadmium and the environment, no legislation has been adopted or proposed by the CEC to protect 'high risk' population groups.

However, certain EC member states aware of the potential problems of increasing levels of cadmium in the environment have taken positive steps to reduce human exposure.

In 1980, following a study of the environmental levels and uses of cadmium in Sweden, the Swedish Government imposed an effectively total ban on the production and importation of cadmium and cadmium-containing products (except those for military purposes). This action was taken on the grounds that cadmium has substitutes in all its major uses and that an effective ban would reduce the overall emissions of cadmium to the Swedish environment, thus reducing human exposure. The ban, which at first resulted in heavy criticism from the cadmium-using industries, was expected to reduce total emissions of cadmium to air from known point sources by 15 - 40 per cent, and reduce pollution of agricultural soils by 30 - 56 per cent.

In addition to restricting the importation and manufacture of cadmium-containing products, a maximum cadmium content of agricultural fertilisers was also proposed by the National Swedish Environmental Protection Board.[259,260] The effectiveness of the Swedish ban in reducing emissions of cadmium to the environment and reducing environmental levels is too early to assess, but studies are being carried out in Sweden to monitor such changes.

In 1980 the Danish Government completed a study of the production, uses and environmental levels of cadmium in Denmark. The working group which carried out the study recommended the Danish Government to 'restrict both the use and further spread of cadmium in the Danish environment, as far as it is administratively, technically and economically possible.' The working group considered that it would be realistic to reduce the total consumption of cadmium in Denmark by 43 - 44 tonnes/year over the next few years, equivalent to a drop of 57 per cent in current consumption.

To achieve these reductions, similar restrictions to the Swedish Government's were suggested by the working group but the Danish Government has suggested that it will first strive to reach a voluntary agreement with industry to reduce cadmium usage, and should this fail, impose a ban on the use of cadmium in auto-paints, surface treatments, plastic stabilisers and plastic pigments, together with the possible elimination of cadmium in phosphate fertilisers.

In 1980 the UK Department of the Environment Central Directorate on Environmental Pollution produced a report on the production, uses and environmental levels of cadmium in the UK.[38] Following the findings of this study, the UK Government set up two working parties with representatives from cadmium-using industries to examine the possibilities of reducing industrial uses of cadmium in the UK by a figure of 50 per cent.

The findings of the meetings held by the UK and Danish Governments with the cadmium industries have not been published although, to date, only the Swedish Government has imposed a ban on the use of cadmium-containing products. Nevertheless, both the Uk and Danish Governments recognise the need to reduce the total usage of cadmium rather than the emissions from industries which use cadmium as a raw material.

8.4 CURRENT POLICY REQUIREMENTS OF THE EUROPEAN COMMUNITY

National legislation and directives relating to the discharge of cadmium to the environment have so far been concerned with aqueous industrial wastes, sewage sludges and the setting of Environmental Quality Objectives (EQO's) for agricultural soils and water bodies.

Studies carried out by the author[5] and elsewhere[36,57] have all demonstrated that the main sources of cadmium emissions in urban/industrial areas are from industries not directly associated with the primary use of cadmium and are mainly from the disposal or recycling of cadmium-containing products. Reductions in the discharges of cadmium to the aqueous environment by manufacturers who use cadmium as a raw material will therefore not have any significant effect on the levels of cadmium found in urban/industrial areas where 'high risk' population groups have been identified.

Furthermore, in the light of studies which have shown that cadmium can be substituted in most of its major uses[4,36], directives are required which are primarily concerned with reductions in the industrial use of cadmium by member states and the setting of EQO's for urban/industrial areas. In addition, directives are required which are primarily concerned with setting acceptable levels of cadmium in all goods intended for human consumption, and the biological screening of populations for cadmium exposure throughout the EC.

The net effect of these directives would be first and foremost a reduction in the emissions of cadmium to the environment and a subsequent steady decline in environmental levels. As cadmium has a long half-life in soil ecosystems (up to 100 years)[56] the effect of reduced emissions will take time to be reflected in a reduction in ambient soil cadmium levels. The setting of acceptable limits of cadmium in foods intended for human consumption would assist in reducing high intakes of cadmium by residents consuming vegetables and other foods with elevated levels of cadmium.

The biological screening of populations throughout the EC would then be a means by which the levels of cadmium in human biological tissues, and hence intakes of cadmium, could be monitored.

CHAPTER 9

RECOMMENDATIONS FOR FURTHER RESEARCH

CHAPTER 9: RECOMMENDATIONS FOR FURTHER RESEARCH

From the studies reported in this thesis the following research recommendations have been made, which, if carried out, would provide essential information on the current and possible future trends in environmental levels and health effects of cadmium in the European Community, and indicate the most feasible policy options available for reducing exposures.

Other urban/industrial areas in the EC should be investigated to highlight other potentially 'at risk' population groups.

A data bank on the cadmium levels in body tissues and fluids of residents of the European Community, particularly those in urban/industrial areas, should be compiled.

The effects of zinc status on cadmium toxicity should be further investigated.

The role which cadmium has on the cause of hypertension amongst environmentally exposed groups should also be further investigated.

Further studies should be initiated to find additional less toxic substitutes for cadmium in industrial uses, particularly those which currently have few alternatives.

The feasibility of recycling cadmium in the European Community should be studied, and in particular the recycling of cadmium/nickel batteries.

Finally, the possibility of establishing a European environmental stockpile of cadmium should also be investigated further.

CHAPTER 10

CONCLUSIONS

CHAPTER 10: CONCLUSIONS

From the detailed investigations reported in this thesis a number of conclusions may be drawn.

It is evident that cadmium has many qualities which have led to its widespread application in a whole range of industries. As a result, the demand for cadmium has increased dramatically over the past fifty years and is currently increasing at two per cent per annum.

The European Community produces a quarter of the world's cadmium and consumes just over one-third - making it the world's largest producer and consumer. The four leading cadmium-consuming countries in the world on a per capita basis are in the EC and are situated in close proximity to one another.

The five main uses for cadmium are in plating, pigments, PVC stabilisers, batteries and alloys, accounting for ninety per cent of consumption by end use.

Only a minor proportion of cadmium is ever recycled, and thus, the majority of cadmium will ultimately give rise to environmental contamination in one form or another.

The main emission sources of cadmium in the European Community are from sewage sludge and domestic refuse disposal, the iron and steel industries, and from secondary non-ferrous metal refining. In all these cases cadmium is present as a contaminant or in discarded products containing the metal. The industries which use cadmium as a primary raw material are not directly responsible for increasing emissions of cadmium to the environment. The products they produce, however, are the ultimate source of environmental contamination.

It has been calculated that around forty-six per cent of cadmium used in the European Community is emitted to the environment in the same year as its use. This amounted to 3,114 tonnes in 1982, with similar amounts in previous years.

Cadmium is not destroyed when released into the environment and subsequently it moves from one compartment to another. The rate of movement varies with specific accumulation in components such as soils and some biota, including food intended for human consumption. With increasing use and emissions of cadmium, accumulation in the environment can only be expected to rise.

It has been shown that man is exposed to cadmium from many sources, but most importantly from food. Accumulations of cadmium in the environment, and in particular the soil ecosystem, can therefore only serve to increase man's dietary intake of cadmium.

Studies have shown that the placenta provides an efficient barrier against the transfer of cadmium from the mother to the foetus during gestation. A child is therefore born free of cadmium but is immediately exposed to the metal in air and food. Since the rate of absorption in the human body is greater than excretion, accumulation increases with age.

Cadmium is accumulated in the kidneys, which usually contain one-third of the body burden. The kidneys, therefore, are the target organ in the human body. In a normal life span a typical person does not accumulate sufficient cadmium to reach the critical level at which renal dysfunction is known to occur. For individuals exposed to high levels of cadmium in their diet, however, this critical level may be reached, resulting in renal impairment.

Cadmium has also been shown to be a factor in the cause of hypertension at low exposures, and to cause bone deformities and cancer of the prostrate at high rates of exposure. Animal experiments have also shown cadmium to have detrimental effects on the liver. Overall, the evidence shows cadmium to be an extremely toxic element, even in relatively small amounts.

Investigations reported in this thesis have shown that elevated background levels of cadmium exist in soils of the West Midlands Metropolitan County, an urban industrial area in the UK.

Detailed studies carried out in the Borough of Walsall, a part of the West Midlands County, have shown background levels of soil cadmium up to 81 mg kg^{-1}. Levels of cadmium in gardens used for vegetable cultivation have been found to be as high as 33 mg kg^{-1}. It is suggested that the West Midlands County is typical of many urban/industrial areas in the EC and that similar levels to those found in the West Midlands exist elsewhere.

As the main source of cadmium intake for man is food, population groups at risk of increasing their dietary intakes and body burdens of cadmium due to environmental contamination have been shown to be those people living in urban/industrial areas who grow a large proportion of their vegetable diet in their gardens.

The study of 260 Walsall residents has shown that intakes of cadmium by 'at risk' population groups may reach or exceed the maximum tolerable weekly intake recommended by the World Health Organisation. Urinary excretion of cadmium amongst a sub-group of the study population showed signs of elevation above those from the general population, although insufficient data was available to determine if kidney function was affected.

In the light of these findings and in view of the fact that cadmium can be substituted in most of its major uses by other metals, it is recommended that the CEC introduces directives primarily concerned with the reduction in industrial use of cadmium by member states, and produces Environmental Quality Objectives for cadmium in urban/industrial areas. In addition, recommended acceptable levels of cadmium in foodstuffs intended for human consumption should be introduced as a means by which member states can determine the significance of food cadmium levels in their respective countries.

In summary, therefore, the aims and purposes of this study set out in Chapter 1 have been achieved. In addition, the first part of the central hypothesis, ie 'that people living in European urban/industrial areas contaminated with cadmium and growing a large proportion of their vegetable diet in contaminated soils are at greater risk of increasing their cadmium intakes up to, or above, the maximum tolerable intake recommended by the Joint FAO/WHO Expert Committee on Food Additives' has been proved to be correct.

The second part of the hypothesis 'that a proportion of these high risk population groups may show increased clinical signs of renal impairment due to high cadmium intakes' has not been fully tested, and further, more detailed work is required before such a conclusion can be reached.

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APPENDIX A

CALCULATION OF WORST-CASE CONCENTRATION CONTOURS

APPENDIX A

The purpose of this Appendix is to describe the statistical procedure by which the worst-case concentrations were derived in the Walsall Study. The procedure described is similar to that carried out previously by the University of Aston.[206]

A.1 General Principles

Due to the high spatial variability in soil cadmium, and other toxic metals, not just amongst sub-samples at a site, but also between sites within a kilometre square, it is not of interest to know whether soil metal levels in an area are on average above a given guideline level, but whether any significant portion of an area exceeds a given guideline.

The ICRCL guidelines suggest that for land where redevelopment is proposed one per cent of the land must not exceed a given level of contamination (the level depending on the intended use). The principles of site assessment implied by this are that soil sampling and analysis should seek to determine not simply the average contamination level on an area of land, but the contamination level exceeded by the worst-contaminated one per cent of that land area. This is then the figure to be compared with the guidelines.

In the investigations carried out in Walsall by the University of Aston[206] and the author, the same principle of evaluation was applied, although rather more cautiously. A statistic was derived, termed 'the worst-case concentration', which describes the contamination level exceeded by the worst-contaminated 2½ per cent of the land within a radius of around 1 km of any given location.

A limit of 2½ per cent (1/40th) was used rather than one per cent because:

- it is easier to compute
- it is less sensitive to small pockets of extreme levels
- it results in lower concentrations, and is therefore a conservative rather than an 'alarmist' indicator of peak levels.

A.2 Statistical Procedure

Within a 'normal' (Gaussian) distribution of measurements in a study population, the measurement value exceeded by the top 2½ per cent of the population is to be found at a level equivalent to two standard deviations above the mean, represented by the formula

$$T(2.5) = \bar{x} + 2\sigma$$

where T(2.5) is the measurement exceeded by the top 2½ per cent of the population, $\bar{x}$ is the population mean, and σ is the standard deviation of the population.

The principle of the statistical approach adopted for mapping background levels of cadmium in the Walsall Study was, therefore, to take all the soil metal measurements within a 1 km radius of a given location, calculate the mean and standard deviation of this statistical sample, and calculate the worst-case concentration directly from the formula above.

In practice, this procedure was complicated by the fact that soil metal contamination occurs in the form of a log-normal rather than linear-normal population. It was necessary, therefore, to undertake a 'logarithmic transformation' of the data prior to conducting the statistical analysis.

The worst-case concentrations were calculated by taking four adjacent 1 km grid squares as a single population sample and applying the formula reported above to the logarithmic-transformed measurements. The results were then 'antilogged' to give the calculated worst-case concentration for those four squares, and the value was assigned to the central point. The procedure was then repeated for the next nearest intersection of four grid squares.

In this way, worst-case concentrations were calculated for every grid intersection. The data were then used as the basis for drawing contour maps of worst-case concentrations presented in Figure 5.9.

APPENDIX B

LETTERS TO WALSALL RESIDENTS AND QUESTIONNAIRES USED IN THE STUDY

Pages 331 to 335

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SURVEY OF GARDEN SOIL AND VEGETABLE CONTAMINATION

Name: .... Ref No: ☐☐

Address: ....

....

Telephone Number: .... (Days) .... (Evening)

Will participate in further study ☐ Yes ☐ No

Fallout Gauge Installed ☐

Carpet Dust Sample Taken ☐

Vacuum Dust Sample Taken ☐

'Settled' Dust Sample Taken ☐

Available Cadmium ug/g dry weight

Total Cadmium ug/g dry weight

Soil pH

Garden Plot Size

Employment History ....

....

....

....

....

Previous and Present Smoking Habits

....

....

....

....

VEGETABLES TO BE GROWN THIS SUMMER

Veg Type-Variety	Planting Time	Harvest Time	No Grown	Mean Wt	Sampled
1.					☐
2.					☐
3.					☐
4.					☐
5.					☐
6.					☐
7.					☐
8.					☐
9.					☐
10.					☐
11.					☐
12.					☐
13.					☐

Comments: ....

....

....

HOUSEHOLD DUST SURVEY

Name: .... Ref: ☐☐

Address: ....

....

I. Age of Property
(a). $>$100 years ☐
(b). 30-100 years ☐
(c). $<$ 30 years ☐
(d). Actual date ....

II. Form of heating.
(a). Coal fires ☐
(b). Gas fires ☐
(c). Central heating: Gas ☐ Oil ☐
(d). Electricity ☐

III. Pets. (Discount other than dogs or cats)
Yes ☐ No ☐ Dog ☐ Cat ☐
No. ☐ No. ☐

IV. Distance from road.
(a). $<$ 1m ☐
(b). 1-5m ☐
(c). 5-10m ☐
(d). $>$10m ☐

V. Road classification.
(a). Major arterial/ring road ☐
(b). Main road- heavy use ☐
(c). Main road- Light use ☐
(d). Minor road ☐
(e). Residential road ☐

IV. Double Glazing. Yes ☐ No ☐

CADMIUM IN WALSALL SOILS AND HOME GROWN VEGETABLES

CODE: ☐☐

Name: ....

Address: ....

....

....

SEX: M/F

AGE:

1 Have you smoked at any time in the past? YES/NO

If yes, please state when, for how long, and how many per day.

....

....

2 Have you ever worked in the foundry or any of the metal working industries? YES/NO

If yes, please state the type of industry and how long you worked

....

....

3 How long have you lived in the Walsall area? (Years) ....

4 How long have you consumed vegetables grown in the Walsall area? (Years) ....

5 Have you ever suffered from any of the following:

	Yes	No
Diabetes	☐	☐
Kidney Disease	☐	☐
Hypertension	☐	☐
Heart Disease	☐	☐

6 Please give name and address of your General Practitioner* (Doctor)

....

....

....

---

* Your General Practitioner will NOT be contacted for medical details. The results of the analyses however will be sent to your doctor.

APPENDIX C

RESULTS OF ANALYTICAL QUALITY ASSURANCE SCHEME

APPENDIX C

This Appendix summarises the results of the Ministry of Agriculture, Fisheries and Food Analytical Quality Assurance Scheme in which the author took part.

Six samples of finely ground organic matter were sent to the author for determination of cadmium content on a dry weight basis. The results '●' were then compared with the results obtained from other laboratories '*' throughout the UK, including the Laboratory of the Government Chemist.

The results presented in the following six figures demonstrate that, overall, the analytical technique used for determining the cadmium content of vegetables in the Walsall Study yields accurate results for the MAFF samples. In only one case was a result greater than the range of values considered satisfactory.

These results would seem to indicate that the analytical techniques used by the author in the Walsall Study are reliable, and that the levels of cadmium reported for Walsall vegetables are scientifically acceptable.

CADMIUM SAMPLE 1

Cadmium Content ug/g^{-1} Dry Weight	Number of Observations	
0.1000	0	
0.1400	0	
0.1800	0	
0.2200	2	**
0.2600	5	*****
0.3000	8	********
0.3400	1	*
0.3800	2	**
0.4200	4	****
0.4600	1	*
0.5000	0	
0.5400	0	
0.5800	0	
0.6200	0	
0.6600	0	
0.7000	0	
0.7400	0	
0.7800	0	
0.8200	0	
0.8600	0	
0.9000	1	*
0.9400	0	
0.9800	0	
1.0200	0	
1.0600	0	
1.1000	0	
1.1400	1	*
1.1800	0	
1.2200	1	*
1.2600	0	
1.3000	0	
1.3400	1	*
1.3800	0	
1.4200	0	
1.4600	1	*

CADMIUM SAMPLE 2

Cadmium Content ug/g^{-1} Dry Weight	Number of Observations	
0.1200	3	***
0.1600	10	**********
0.2000	4	****
0.2400	2	**
0.2800	1	*
0.3200	1	*
0.3600	0	
0.4000	1	*
0.4400	1	*
0.4800	0	
0.5200	0	
0.5600	0	
0.6000	1	*
0.6400	0	
0.6800	0	
0.7200	0	
0.7600	0	
1.1600	1	*
1.6200	1	*
1.8500	1	*

CADMIUM SAMPLE 3

Cadmium Content ug/g^{-1} Dry Weight	Number of Observations	
0.0150	8	********
0.0450	2	**
0.0750	2	**
0.1050	3	***
0.1350	2	**
0.1650	1	*
0.1950	0	
0.2250	0	
0.2550	0	
0.2850	1	*
0.3150	2	**
0.3450	1	*
0.3750	2	**
0.4050	0	
0.4350	0	
0.4650	0	
0.5900	1	*
1.0600	1	*
1.6000	1	*

CADMIUM SAMPLE 4

Cadmium Content ug/g^{-1} Dry Weight	Number of Observations	
0.100	0	
0.200	0	
0.300	1	*
0.400	2	**
0.500	2	**
0.600	1	*
0.700	3	***
0.800	4	****
0.900	8	********
1.000	1	*
1.100	1	*
1.200	0	
1.300	2	**
1.400	0	
1.500	0	
1.600	0	
1.700	0	
1.800	0	
2.020	1	*
2.240	1	*
3.530	1	*

CADMIUM SAMPLE 5

Cadmium Content ug/g^{-1} Dry Weight	Number of Observations	
0.050	0	
0.150	1	*
0.250	0	
0.350	1	*
0.450	4	****
0.550	9	[illegible]********
0.650	6	******
0.750	0	
0.850	2	**
0.950	0	
1.050	3	***
1.150	0	
1.250	0	
1.350	1	*
1.450	0	
1.550	0	
1.650	0	
1.750	0	
2.000	1	*

CADMIUM SAMPLE 6

Cadmium Content ug/g^{-1} Dry Weight	Number of Observations	
1.100	0	
1.600	0	
2.100	0	
2.600	1	*
3.100	1	*
3.600	0	
4.100	0	
4.600	1	*
5.100	1	*
5.600	0	
6.100	2	**
6.600	11	***********
7.100	6	******
7.600	2	**
8.100	0	
8.600	2	**
9.100	0	
9.600	0	
10.100	0	
10.600	1	*

APPENDIX D

DIET DIARY

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