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# Cadmium in the atmosphere

by C.R. Williams<sup>1</sup> and R.M. Harrison<sup>2</sup>

Department of Environmental Sciences, University of Lancaster, Lancaster LA1 4YQ (England)

Summary. Cadmium is present naturally in the air mainly as a result of volcanic emissions and release by vegetation. Anthropogenic sources, which overall give rise to emissions one order of magnitude greater than natural sources, are largely primary non-ferrous metals production and waste incineration. Measured concentrations of airborne cadmium are typically < 1 ng m<sup>-3</sup> at remote sites, 0.1-10 ng m<sup>-3</sup> at rural sites and 1-100 ng m<sup>-3</sup> at urban and industrial sites, dependent upon the nature and proximity of local sources. Particle sizes are generally < 2 μm, and often considerably smaller, consistent with an anthropogenic source and a long atmospheric lifetime. Cadmium deposition to the land occurs with fluxes varying from 0.05 ng cm<sup>-2</sup> month<sup>-1</sup> in Greenland to circa 1000 ng cm<sup>-2</sup> month<sup>-1</sup> in the vicinity of major industrial sources. The possible significance of a motor vehicular source of airborne cadmium is also reviewed.

## Introduction

The atmosphere plays an important role in the dispersal of cadmium within the environment. Despite the fact that the largest natural source of cadmium in air (volcanic emissions) as well as the major anthropogenic sources are very localized, their influence may

be seen at remote sites throughout the Northern Hemisphere. Thus within this article, the major sources will be reviewed, as well as the reported levels of cadmium measured in ambient air.

Sink processes for atmospheric cadmium are wet and dry deposition, which lead to cadmium enrichment of soil, vegetation and surface waters. The atmospheric source may provide an important cadmium input into these media, and consequently contributes to human exposure through food and drink, as well as more directly by the breathing of polluted air. Data on cadmium deposition fluxes are also reviewed to enable quantitative evaluation of this pathway in relation to cadmium enrichment of these media from other sources.

### I. Sources of atmospheric cadmium emissions

On a global scale, anthropogenic discharges of cadmium to atmosphere exceed natural sources by an order of magnitude; this is apparent in the global emission inventory for Cd which is given in table 1. Although the estimates used in this inventory are necessarily subject to considerable uncertainties, the values are of a similar magnitude to those reported by other workers; Galloway et al.  $^{25}$  state that the total emission rate from natural sources is  $0.29 \times 10^6$  kg year $^{-1}$ , whilst that from anthropogenic emissions is  $5.5 \times 10^6$  kg year $^{-1}$ .

From table 1, volcanic emissions represent about 60% of the Cd emitted from natural sources, reflecting the high enrichment of the metal in volcanogenic aerosols<sup>56</sup>. Vegetative exudates and windblown dust of crustal origin also form a significant proportion of the natural emission; for the former, it has been concluded<sup>3</sup> that the earth's vegetation-covered land mass contributes generally to the trace metal composition of the atmosphere.

Turning to the anthropogenic sources listed in table 1, non-ferrous metals production and use accounts for

Table 1. Worldwide annual atmospheric emissions of cadmium (source:  $Nriagu^{56}$ )

Source	Global production of particulate (× 10 <sup>9</sup> kg year <sup>-1</sup> )	emission rate	
Natural sources <sup>a</sup>			
Wind-blown dusts	500	0.1	
Forest fires	36	0.012	
Volcanogenic particles	10	0.52	
Vegetation	75	0.2	
Seasalt sprays	1000 ~	0.001	
Total		0.83	
Anthropogenic sources <sup>b</sup>			
Mining, non ferrous metals	16	0.002	
Primary non-ferrous metal			
production:		^	
Cd	0.0017	0.11	
Cu	7.9	1.6	
Pb	4.0	0.20	
Zn	5.6	2.8	
Secondary non-ferrous metal			
production	4.0	0.60	
Iron and steel production	1300	0.07	
Industrial applications	-	0.05	
Coal combustion	3100	0.06	
Oil (incl. gasoline) combustion	2800	0.003	
Wood combustion	640	0.2	
Waste incineration	1500	1.4	
Manufacture, phosphate	118	0.21	
fertilizers			
Total		7.3	

<sup>&</sup>lt;sup>a</sup> Based on 'most acceptable' production figures; <sup>b</sup> for the year 1975.

67% of the pollutant Cd released. For comparison, Faoro et al.<sup>20</sup> suggest that, in the U.S.A., 43% of the Cd emitted by stationary sources arises from smelters and metallurgical processing. The importance of these sources reflects the occurrence of Cd in polymetallic ores; of especial note in table 1 is the high emission from primary Zn production, where Cd metal is manufactured as a by-product<sup>37</sup>.

It appears that the incineration of wastes is a substantial source of airborne Cd on a global scale. Indeed, for the United States, this may be the principal emission source<sup>20</sup>. This reflects the dispersive end-uses to which Cd is put in plastic stabilizers and pigments. The average level of Cd in all plastics is about 37  $\mu$ g g<sup>-1</sup>, and the total Cd concentration in municipal waste is often taken as 12  $\mu$ g g<sup>-1</sup>, of which plastics contribute about 2  $\mu$ g g<sup>-1</sup> 14,73. Incineration can produce Cd concentrations of 319  $\mu$ g g<sup>-1</sup> in the particulate emitted by a residential incinerator<sup>66</sup>.

Of the remaining anthropogenic sources in table 1, it now appears that iron and steel production is a relatively minor emitter of Cd on a global scale. It had been suggested that iron blast furnaces account for major atmospheric Cd emissions<sup>70</sup>. However, Prater<sup>60</sup> has carried out a comprehensive analysis of the behavior of cadmium in the processes used by the UK steel industry, and has concluded that the atmospheric emission of Cd is slight (1.7 t annual total for the UK) when modern steel-making processes (basic oxygen and electric arc) are considered. Similarly, the cadmium emissions from combustion of coal appear to be relatively small. In the UK, where  $120 \times 10^6$  t of coal are burnt per annum, of which  $81 \times 10^6$  t are used for electricity generation, it has been estimated that an annual atmospheric discharge of 2.5 t Cd occurs<sup>14</sup>. For the German Federal Republic, it has been suggested that the  $140 \times 10^6$  t of brown coal burnt per annum for power production results in a Cd emission of 0.39 t<sup>35</sup>. However, the Cd emission figures from coal combustion may be subject to considerable errors, due to the wide range of Cd concentrations in coal (up to 10  $\mu$ g g<sup>-1</sup>, but very variable) and to the fact that domestic coal burning emissions have not been studied separately<sup>14</sup>.

In table 1, no figures are given for Cd emissions from mobile sources, although some authors have considered that emissions from motor vehicles may be significant. Cadmium is a component of tyre rubber, and tyre debris was ranked seventh in a list of 16 major sources of atmospheric Cd emissions in the United States<sup>23</sup>. Vehicle emissions will be considered in detail in section III (c).

# II. Particle size of emissions in relation to atmospheric transport and deposition

Cadmium exists in particulate form within the atmosphere. The dynamics of airborne particles depend upon the nature and locations of emission sources, as well as the mechanisms of removal of material following its entry to the atmosphere. When particles are very small, they may remain suspended in the air for prolonged periods of time. The resulting two-phase

system, or aerosol, has a stability which depends upon the particle size<sup>22</sup>.

Three particle size modes are observed in atmospheric aerosols. Firstly, the 'transient nuclei mode', of the order of 0.01 µm, is observed only when relatively fresh combustion aerosols are present<sup>71</sup>. Particles tend to remain in this size range for less than 1 h; they grow rapidly by coagulation or condensation to the 2nd, 'accumulation', mode having a size range from 0.1 to 1.0 µm. These fine particles may remain airborne for days; their gravitational settling velocity is very low<sup>5</sup>. They may be raised by updraughts and turbulence, and thereby be transported in the zonal circulation of the troposphere <sup>10</sup>. In contrast, particles of diameter greater than about 10 µm in the 3rd, 'mechanical aerosol', mode settle rapidly and have a short average lifetime in the atmosphere.

Sedimentation, impaction and Brownian diffusion comprise the mechanisms of dry deposition by which aerosols are transferred to the earth's surface; removal from the atmosphere occurs also by wet deposition via precipitation scavenging. For any element, a washout factor, W, and a dry deposition velocity, Vg, may be defined 11 as:

$$W = \frac{\text{concentration in rain } (\mu g \text{ kg}^{-1})}{\text{concentration in air } (\mu g \text{ kg}^{-1})}$$

$$Vg \text{ (cm sec}^{-1}\text{)} = \frac{\text{rate of dry deposition (} \mu g \text{ cm}^{-2} \text{ sec}^{-1}\text{)}}{\text{concentration in air (} \mu g \text{ cm}^{-3}\text{)}}$$

A high value of W is associated with greater dispersion in altitude and therefore a distant source, low W with a more local source. Vg is related to such factors as particle size, surface roughness and wind velocity; in the case of particle size, there is a flat minimum for Vg in the size range from 0.1 to 1.0  $\mu$ m<sup>11</sup>.

From the above discussion, it will be clear that the effect of Cd emissions depends critically upon the particle size; coarse particle emissions will tend to be deposited close to source and have a local influence only, whereas fine particle emissions may have a more widespread effect. In this regard, referring to table 1, much of the globally-emitted Cd consists predominantly of fine particles. Volcanogenic particles are mainly  $< 40 \mu m$  in diameter; their residence time in the atmosphere is lengthened by the injection height for the buoyant plume which has been recorded as 3.8 km for an Alaskan volcano<sup>38</sup>. Vegetation emits particles in the sub-micrometer size range<sup>3</sup>. The major anthropogenic emissions are associated mainly with high-temperature combustion processes. Flue dusts from the stacks of nonferrous smelters may consist of particles circa 0.1-0.2 µm in diameter, forming 'fused assemblages' 19. Lee and Duffield 45 have estimated that, in the U.S.A., 46.6% of the total particulate emitted by metallurgical processing and 67.3% of the particulate emitted by municipal waste incineration, is in the size range 0.1-2 µm. Heinrichs<sup>35</sup> has found that the Cd emitted by a coal-fired power station is not retained well by the electrostatic precipitators used for emission control. An explanation is that, during the combustion process, Cd is associated with particulate matter only to a limited extent: due to the volatility of elemental cadmium and its compounds, condensation of the metal may occur on fly ash, with preferential adsorption of Cd on the inefficiently collected submicrometer sized fly ash due to the large surface area presented by this particle size group.

Hence, most of the Cd which is emitted to atmosphere on a global scale is of such a particle size as to favor its transport over long distances in the atmosphere.

### III. The interpretation of environmental measurements

### a) Levels of cadmium in ambient air

Some measured concentrations of Cd in ambient air, and rates of Cd deposition from the atmosphere, are listed in tables 2 and 3 respectively. In general, these data show that levels of Cd in air are higher in urban areas than in rural areas. Heavily industrialized cities, and sites close to non-ferrous metal smelting and refining activities, show the highest levels.

When comparing the Cd concentrations listed in table 2, it should be noted that the range of values found at a particular site will depend, inter alia, upon the duration of sampling; for short-duration samples, the variability of results will tend to increase. Also, in table 3, most of the quoted deposition rates were obtained using deposit gauges or other 'artificial' collection surfaces. Generally, such devices will not match the aerodynamics and collection efficiency of a natural surface, and hence will provide only an approximate measure of the deposition rate of Cd on the land.

# b) Relating environmental measurements to stationary emission sources

In agreement with the discussion of particle sizes for emitted Cd (section II, above) it has been found that the metal exists at highest concentrations in the smallest particles collected from ambient air<sup>55</sup>. A technique which has been widely used to assess particle size distributions for airborne metals in that of fractionating airborne particles according to their aerodynamic diameters by means of a cascade impactor<sup>16,32,34,63</sup>. Using this method, a mass median aerodynamic diameter (MMAD) of 0.4 µm for airborne Cd in a rural environment, distant from industrial sources of the metal, has been reported<sup>34</sup>. Similar measurements at urban sites have shown MMAD values of 0.1-0.2 µm<sup>63</sup> and 0.9 µm<sup>34</sup>. At a site near a lead smelter, Dorn et al.<sup>16</sup> found that airborne Cd was associated mainly with particles of aerodynamic diameter smaller than 2 µm.

There is now a considerable amount of data which evidences the transport of airborne Cd over long distances in the atmosphere. The transport of atmospheric particulate pollutants from the European continent to the United Kingdom was noted by Lee et al.<sup>44</sup>. Thrane<sup>65</sup> has suggested that airborne Cd may be transferred from the U.K. to Scandinavia. Galloway et al.<sup>25</sup>, from analyses of lake sediment cores in the eastern United States, note that an increase in Cd de-

Table 2. Some measurements of airborne cadmium concentrations

Table 2. Some measurements o	i airborne cadmium co	ncentrations	
Site	[Cd] (ng m <sup>-3</sup> )	Sampling period/notes	Reference
Remote/rural			
North Atlantic	0.003 - 0.6		Duce et al. <sup>17</sup>
South Norway:	.1		
Birkenes	0.11–0.34	Monthly means (6 samples)	Thrane <sup>65</sup>
Vasser	0.21–0.96 J	I 1070 A 311073	0 9
Leiston, U.K.	1.7 < 4	June 1972–April 1973 Jan. 1971–Dec. 1971	Cawse <sup>9</sup> Cawse and Peirson <sup>10</sup>
Wraymires, U.K. Hazelrigg, U.K.	1.93		Cawse and Penson
Hazenigg, C.K.	0.1-8.2	Mean and range for 30 × 24-h samples	
	1.28	Mean and range for $56 \times 7$ -day samples	Harrison and Williams34
	0.1-4.7	Mean and range for 36 × 7-day samples	
Shap Summit,	0.1-0.5	Rural roadside site; 2 × 7-day samples	Harrison and Williams <sup>32</sup>
M6 Motorway, U.K.			16
Missouri, U.S.A.	3.7	16 days	Dorn et al. 16
Arizona, U.S.A.	2.0	Annual mean for 3 sites	Moyers et al. <sup>54</sup>
Urban/industrial			
Bombay, India	4-46	9 sites	Khandekar et al.41
Rio de Janeiro, Brazil	1.8-3.1	2 sites	Trindade et al <sup>66</sup>
Tel Aviv, Israel	40		Donagi et al. <sup>15</sup>
Tucson, Arizona, U.S.A.	2.4	Annual mean for 11 sites	Moyers et al <sup>54</sup>
Lancaster, U.K.	3.33	Urban roadside; mean and range for	
	0.3–14.8 ∫ 1.17	$30 \times 24$ -h samples	Harrison and Williams <sup>34</sup>
	0.1-3.3	Mean and range for $56 \times 7$ -day samples	
Glasgow, U.K.	13.6	13 months average at 14 sites	McDonald and Duncan <sup>50</sup>
20 sites in U.K.	4.4	April 1976-March 1977	McInnes 51
	3.4	April 1977–March 1978	McInnes <sup>52</sup>
Birmingham, U.K.	46	AugOct. 1973; 8 sites within 2 km	Turner <sup>67</sup>
		of non-ferrous metal factory	
Birmingham, U.K.	10–15	FebMay 1974; range of site means	Turner and Killick <sup>68</sup>
To describe siting in Delaisons	05 210	at 6 sites near battery factory	Ronneau and Desaedeleer <sup>62</sup>
Industrial cities in Belgium Missouri, U.S.A.	95–310 24.8	During pollution episodes when $[SO_2] \ge 30$ ppb 24 days; near Pb smelter	Dorn et al. 16
Cockle Creek, Australia	60	90 days; at point of maximum ground-level	Smith et al. <sup>64</sup>
Cookie Crook, Maditalia	00	Cd concentrations near Zn-Pb smelter	Officer of the
Avonmouth, U.K.	108	5 days; 0.7 km from Zn-Pb smelter, in prevailing	Williams <sup>72</sup>
<u> </u>		wind direction	

Table 3. Deposition rates for airborne cadmium

Site	Cd deposition rate (ng cm <sup>-2</sup> month <sup>-1</sup> )	Sampling period/notes	Reference
Remote/rural			
Greenland Ice Sheet	0.05	1 year	Davidson et al. <sup>13</sup>
Wraymires, U.K.	< 80 \		~ 0
Leiston, U.K	< 25 ∫	1973 annual mean	Cawse <sup>9</sup>
Hazelrigg, U.K	< 0.6–3.4	Range for $12 \times 1$ -month samples, $1978/79$	Harrison and Williams <sup>34</sup>
Chester, U.S.A	2–3	$3 \times 1$ -month samples, 1978	Feely and Larsen <sup>21</sup>
Ardennes, Belgium	11.4	2-monthly samples. Mean of 8 sites	Hallet et al. <sup>28</sup>
Urban/industrial			
New York City, 1.	3–37		
U.S.A. 2.	10–66 }	Ranges for 22 × 1-month samples, 1972–1974	Kleinmann et al. <sup>42</sup>
(3 locations) 3.	6-46 J		
Pasadena, U.S.A	3.9		Huntzicker et al.40
Liege, Belgium	780	Near zinc works	Duhameau and Noël <sup>18</sup>
Avonmouth, U.K.	3000	1 month. Near Zn-Pb smelter. 'Moss bag'	Parry et al. <sup>59</sup>
		deposit collectors	
Avonmouth, U.K.	113	1 month. 0.7 km from Zn-Pb smelter, in	Williams <sup>72</sup>
		prevailing wind direction	
Charleroi, Belgium	16.2	2-monthly samples, sub-urban site	Hallet et al. <sup>28</sup>

position rates began about 30 years ago: this indicates both an increase in anthropogenic emissions, and the importance of long-range atmospheric transport. Recently, Harrison and Williams<sup>34</sup> investigated airborne Cd at rural and urban sites in North-West England, in an area lacking any local industrial emissions of the metal. They found that, at all their environmental monitoring sites, airborne Cd was derived

primarily from distant sources in South-East England and continental Europe. This view was supported as follows: 1. For a given sampling period, the airborne Cd levels at the urban and the rural sites were very similar. 2. Airborne sulphate and nitrate, which are considered to be indicative of distant, rather than local, pollutant emissions<sup>30</sup> showed strong correlations with airborne Cd. 3. Meteorological analyses indicat-

ed that the highest Cd levels at all sites were associated with winds having a southerly component and with air masses having a continental origin.

At very long distances from emission sources, the impact of pollutant Cd appears not to be measurable: although analyses of Greenlandic ice indicate an increased deposition of Pb and Zn in snowfall between 1971-73 compared with pre-1900 deposition, and hence an enhanced pollutant input, no such increase is apparent for Cd<sup>36</sup>. At this remote location, deposition of cadmium occurs entirely by wet processes 13, as might be anticipated from the discussion in section II, above. From the analysis of snow layers deposited at the South Pole between 1929 and 1977, Boutron<sup>6</sup> found no change in the concentration of Cd (and all metals apart from Pb for which a local source was possible) over the past 50 years. He concluded that the influence of global atmospheric pollution is probably still negligible in the remote areas of the Southern Hemisphere.

By investigating the associations between Cd and other components of airborne particulate, an indication may be gained of likely sources of pollution, although the results of such analyses alone tend not to be specific. For example, Moyers et al.<sup>54</sup> have used correlation analysis to investigate the relations between the chemical components of the atmosphere at Tucson, Arizona, U.S.A. In urban air, Cd was not apparently related with any other chemical component; in rural air, Cd, Cu, Pb and Zn showed a significant correlation both with each other and with  $SO_4^{2-}$  and  $NO_3^{-}$ . It was suggested that this could indicate similarities in particle size distribution (transport and residence time phenomena), identical sources, or a chemical association between cadmium and sulphate ions. From a statistical analysis of these same data using pattern recognition and factor analysis, Gaarenstroom et al.24 suggested that airborne Cd might be associated with distant and/or diffuse sources, small particles, and combustion sources. In the U.K., McInnes<sup>53</sup> has found that strong inter-site correlations exist for airborne pollutant metals in urban atmospheres, indicating diffuse rather than localized emission sources.

Hallet et al.<sup>28</sup> measured deposition fluxes for a wide range of airborne metals in and around the industrial town of Charleroi in Belgium and in the rural Ardennes region. Cadmium, together with inter alia Pb and Zn displayed a rather diffuse behavior relative to many other metals, which were deposited primarily close to the urban or industrial sources. This was attributed to the diffuseness of their emitters (e.g. incineration plants for Cd).

A quantity sometimes used in assessing the source of a metal in the atmosphere is the enrichment factor, *E*, relative to a crustally-derived species such as aluminium<sup>54</sup>, scandium<sup>10</sup> or iron<sup>50</sup>. Thus, for Cd,

 $E = \frac{\text{airborne concentration of Cd}}{\frac{\text{airborne concentration of Al}}{\text{crustal concentration of Al}}}$ 

Whilst airborne metals whose source is predominantly crustal have enrichment factors close to unity, the value of E for Cd is typically >>100 at urban and rural sites, suggesting the anthropogenic origin of the airborne metal<sup>34,50,54</sup>. However, it should be noted that volcanic emissions and sea spray may provide material which is enriched in certain elements to the same degree as industrial emissions<sup>13</sup>.

One aspect of airborne cadmium, upon which it appears that there is little information, is that of the atmospheric chemistry of the metal. This contrasts with the chemistry of airborne lead emitted from motor vehicles, which has been investigated by Biggins and Harrison<sup>4</sup>. By means of X-ray powder diffraction spectrometry, CdO has been positively identified in the emissions from a zinc refinery<sup>72</sup>. Also, from the thermal stability criteria for sulphates, it has been postulated that the predominant cadmium compound emitted from the sintering of zinc-lead ores may be CdSO<sub>4</sub><sup>33,72</sup>. Where ambient air samples are concerned, it is likely that the levels of cadmium will invariably be too low for this type of compound-specific analysis to be considered. However, in a study of metal solubility in a sample of airborne particulate from an urban site, Lum et al. 48 state that all the cadmium present in the sample was extractable by 1 M MgCl<sub>2</sub> at pH 7, indicating that the cadmium was present in air as a soluble compound.

Where specific known emission sources are concerned, ambient air data generally support the relative importance of sources which was expounded in section I, above. Thus, at an otherwise rural site, Lindberg<sup>46</sup> states that the concentration of Cd in rainfall is not elevated by local coal-fired power plant emissions, indicating that these emissions are not a significant source of airborne Cd. Conversely, the incineration of wastes does appear to have a significant effect upon levels of Cd in ambient air: Trindade et al.66 state that the concentrations of airborne Cd in Rio de Janeiro declined after the incineration of garbage had been prohibited. In the case of primary nonferrous metallurgical operations, a well-documented example of the nature of Cd emissions is provided by the primary zinc-lead smelting works at Avonmouth, U.K. Here, emissions are made to atmosphere via stacks which are 50-60 m high<sup>61</sup>; emission control is mainly by wet gas-cleaning methods. Studies of airborne Cd deposition to land in the vicinity of this smelter indicate that dispersion and deposition are dominated by the prevailing wind direction<sup>8,47,59</sup>; at a distance of 15 km downwind from the smelter, deposition rates<sup>8</sup> for Cd exceed background levels by a factor of a least 158. This suggests that a substantial portion of emitted Cd is associated with fine particles. Parry et al.<sup>59</sup> have found that blowage of coarse, metal-rich dusts may occur from, for example, smelting waste tips. However, it appears that in the case of an operating smelter, fine particle emissions from the stacks of the smelter comprise the major percentage of the total emissions, with blowage of coarse dusts being of very limited significance<sup>72</sup>.

# c) Cadmium from motor vehicles

It is well established that motor vehicles contribute to the Cd deposited in the environment close to highways. Enhanced levels of Cd have been found in roadside soils and vegetation <sup>12,27,43,49</sup>. Cd concentrations in street dusts are higher than the values typical of local soils<sup>29</sup>. Ward et al.<sup>69</sup> note a significant correlation between the traffic flow on a highway and the Cd concentrations in surface soil from a 1-m-wide central strip between carriageways. The heaviest deposition of Cd occurs close to the road; at a site with 48,000 vehicles day<sup>-1</sup>, Lagerwerff and Specht<sup>43</sup> have found that the level of Cd in surface soil falls from 0.94 µg g<sup>-1</sup> at a distance of 8 m from the road to 0.24 µg g<sup>-1</sup> at 32 m.

The most obvious source of this cadmium is as an impurity in technical-grade zinc compounds; zinc dithiophosphate is present as an antioxidant in lubricating oil, and zinc oxide or zinc-diethyl or -dimethyl carbamate is used in the vulcanisation of tyre rubber<sup>43</sup>. Hence there are potential sources of airborne Cd both from exhaust emissions and from tyre wear; both of these sources are evidenced from physico-chemical analyses of deposited dust from an urban roadway<sup>39</sup>. However, the major contribution to deposited Cd appears to be from tyre wear<sup>12</sup>. Cadmium exists in American tyres<sup>43</sup> at concentrations between 20 and 90 μg g<sup>-1</sup>, but at much lower levels, circa 0.14 μg g<sup>-1</sup> in Australian tyre rubber<sup>12</sup>. In the U.K., the level may be 5-6  $\mu$ g g<sup>-1</sup> <sup>14</sup>. In the case of vehicle exhausts, the concentration of Cd in emitted particulate<sup>57</sup> is between 1.3 and 3.8  $\mu$ g g<sup>-1</sup>.

It has been suggested that these vehicular Cd emissions might contribute substantially to levels of the metal in urban air. For example, Harrison et al.<sup>31</sup> note variations in the deposition of Cd from the atmosphere over London, in the absence of any local industrial emissions. In Bombay, the highest levels of airborne Cd are observed at sites having a high density of motor traffic<sup>41</sup>. Ondov et al.<sup>58</sup> have found that the Cd level in the air inside a road tunnel is 77 ng m<sup>-3</sup>, which is seven times the concentration outside the tunnel. In this lastmentioned example, however, it is likely that the re-suspension of deposited dust due to turbulence would be greater than for a non-enclosed highway.

Contrary findings, namely that motor vehicles do not contribute substantially to Cd in ambient air, have been reported recently by Harrison and Williams<sup>34</sup>. From a lengthy programme of air sampling conducted simultaneously at rural sites and at a site immediately alongside a heavily-trafficked urban roadway, it was concluded that the influence of local vehicular sources of Cd was very slight: the advection of polluted air masses was the dominant source of airborne Cd at all sites. Overall, then, it seems that vehicular sources of airborne Cd are of very limited significance, even near to roads. Large particles up to 30 µm in diameter dominate the mass of tyre wear<sup>7</sup>. These Cd-containing particles would be deposited close to source, and their contribution to air pollution would be slight. It should, of course, be borne in mind that the magnitude of the vehicular source will depend critically upon the Cd content of tyres and motor oil.

#### IV. Further research needs

Cadmium has received less attention than some other airborne metals, most notably lead. There is, therefore, a case for considerable further measurement of ambient airborne concentrations, their spatial and temporal variation, and of deposition fluxes.

Separate measurements of wet and dry deposition of cadmium are lacking, and the use of more realistic dry deposition collectors is desirable though experimentally difficult, so as to obtain a better measure of deposition to natural surfaces. This point is highly relevant to the important question of the relative contribution of direct deposition and of soil uptake to the ultimate cadmium content of growing crop plants. Fuller studies of cadmium deposition are also necessary to aid budget studies for cadmium in lakes (where atmospheric deposition can be a substantial input) and for studies of cadmium cycling in ecosystems.

Virtually no information is available on the atmospheric chemistry of cadmium. Since the chemical form of cadmium affects the respiratory absorption efficiency, and will also influence the environmental mobility in terrestrial and aquatic systems, data in this area are crucial to a fuller comprehension of the environmental pathways of the metal.

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# Biological indicators of cadmium exposure and toxicity

by Z. A. Shaikh\* and L. M. Smith

Department of Pharmacology and Toxicology, University of Rhode Island, Kingston (Rhode Island 02881, USA)

Summary. The increasing environmental and occupational exposure of populations to cadmium creates the need for biological indicators of cadmium exposure and toxicity. The advantages and disadvantages of monitoring blood cadmium, urinary, fecal, hair, and tissue cadmium, serum creatinine,  $\beta_2$ -microglobulin,  $\alpha_1$ -antitrypsin and other proteins, and urinary amino acids, enzymes, total proteins, glucose,  $\beta_2$ -microglobulin, retinol-binding protein, lysozyme, and metallothionein are discussed. It is concluded that urinary cadmium, metallothionein and  $\beta_2$ -microglubulin may be used together to assess cadmium exposure and toxicity.

### Introduction

Cadmium is a heavy metal of increasing prevalence in our environment, due to its industrial production and usage and its emissions from fossil fuel combustion. Specific populations exposed to high levels of cadmium have been studied intensively in order to determine not only the mechanisms of cadmium toxicity, but also biological indicators which can be used to prevent its toxic manifestations by giving an estimate of body burden.

There now exists a great awareness of cadmium's potential health hazard and measures have been taken to reduce the exposure both in the environment and in industry. However, the continuous life-long accumulation of cadmium in the body creates the need for a monitor of body burden and not recent exposure. Also, the severe and possibly irreversible renal tubular dysfunction caused by cadmium necessitates the development of a therapeutic index which is sensitive enough to detect cadmium body burden before irreparable damage is done. Therefore, a search is needed to discover the most sensitive parameters which accurately reflect body burden and also exhibit a measurable change after cadmium exposure.

Many schools of thought exist concerning which parameter would be the best indicator of exposure and of toxicity. A review of the advantages and disadvantages of each one suggested will aid in the development of a rational approach for monitoring cadmium toxicity in susceptible populations. Some of the more commonly used parameters are listed in the table.

### Blood cadmium

There is general agreement that although blood cadmium levels do increase with exposure, this increase mainly reflects recent exposure rather than body burden of the metal. Lauwerys et al.<sup>26</sup> showed that blood cadmium correlated with recent exposure in occupationally exposed workers. Also, it was found that blood cadmium reflected recent exposure after an equilibrium was reached at 4 months<sup>28</sup>. Bernard et al.<sup>5</sup> found a similar relationship in rats, in which blood cadmium reached an equilibrium at 3 months, after which it reflected recent exposure. In agreement with this data, blood cadmium was found to be a good indicator of acute exposure to cadmium<sup>3</sup>. Contrary to this evidence, however, Elinder et al.<sup>14</sup> found a signifi-