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IMPACTO

AMBIENTAL

DE METALES

PESADOS

EN CHILE

19 Y 20 DE ABRIL DE 1994

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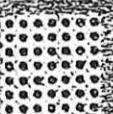
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GEOQUÍMICA DE METALES PESADOS EN CHILE

Heavy metal geochemistry in Chile

SERGIO GONZÁLEZ MARTINEAUX[1]

C O N T E N I D O

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INTRODUCCIÓN

Desde hace tiempo, se conoce el riesgo que, para la salud humana[1] y la sanidad ambiental, involucran las descargas antrópicas de elementos metálicos al ambiente. Por tratarse, en su mayoría, de elementos de densidad superior en 5 o 6 veces la del agua (Davies, 1981), se les ha llamado metales pesados, que ha pasado a constituir un nombre impactante para uno de los procesos contaminantes de mayor riesgo ambiental, aunque no involucra a todos los elementos posibles de presentarse en estas descargas, como cinc y molibdeno.

También, se ha usado el término elemento traza, que agrupa los elementos presentes en la corteza terrestre en contenidos < 0,1% (Cuadro 1), los que pueden verse fácilmente incrementados por aportes antrópicos e inducir efectos negativos en quienes habitan y/o se nutren del ambiente afectado. Otro término usado es el de micronutriente, que reúne los elementos esenciales y excluye los no esenciales, justamente los más tóxicos; en todo caso, la creciente exquisitez de las técnicas analíticas, está permitiendo detectar la esencialidad de elementos cuyos roles fisiológicos no habían podido ser experimentalmente comprobados.

No existe un término ideal, que represente todos los posibles elementos contaminantes. Sólo a modo de ejemplo, considérese lo difícil de clasificar al hierro o al manganeso, metales pesados y macroelementos de la corteza terrestre pero micronutrientes para plantas y animales. O bien, al aluminio, metal no pesado que es a la vez, macroelemento de la corteza terrestre y no esencial, además de muy tóxico en ambientes ácidos.

La riqueza geoquímica del norte del país, sustenta una minería de alto nivel, lo que se traduce en una alta

Cuadro 1. Contenidos naturales ($mg\ kg^{-1}$) de elementos en suelos y rocas (Adriano, 1992; Bridges, 1991[1]; Berrow y Burridge, 1977; Davies, 1981, 1984)

Elemento	Rango en suelos	Promedio rocas
Arsénico	0,1 - 40	
Boro	2,0 - 100	
Cadmio	0,01 - 1	0,2
Cinc	10,0 - 300	70
Cobalto	1,0 - 40	25
Cobre	2,0 - 100	55
Cromo	5,0 - 1000	100
Estaño	<1,0 - 10	2
Estroncio	50,0 - 1000	
Flúor	30,0 - 300	
Hierro	$1 \cdot 10^3 - 2 \cdot 10^6$	$6 \cdot 10^4$
Litio	5,0 - 200	
Mercurio	<0,01 - 0,5	0,08
Manganeso	100,0 - 4000	950
Molibdeno	0,2 - 5	1,5
Níquel	5,0 - 500	75
Oro		0,05
Plata	0,01 - 5	0,07
Plomo	2,0 - 200	13
Selenio	0,1 - 2	

[1] Bridges, Bridges. Swansea College, U.K. Comunicación personal

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[1] Recuérdese los episodios que condujeron a la tipificación de las enfermedades de Itai-Itai y Minamata, por intoxicación de cadmio y mercurio, respectivamente

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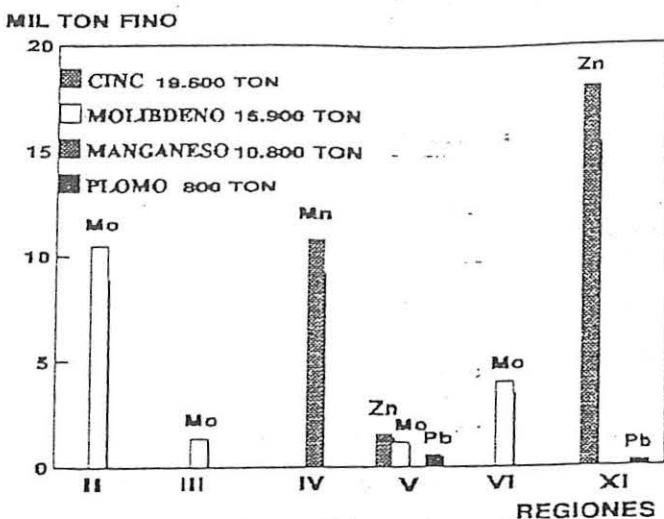
FIGURA 2. PRODUCCION REGIONAL DE OTROS METALES (INE, 1987)

- el poder modificador del paisaje, reflejado por la producción de relaves, que al año equivale a más de 30 veces el cerro Santa Lucía, en Santiago. La expansión que ha experimentado la minería del cobre, durante los últimos quince años, señala que el país está obligado a disponer -en forma más segura e inocua- volúmenes crecientes de relaves que, por lo demás, no son las únicas materias residuales voluminosas.
....

En forma sucinta, el impacto ambiental de los relaves tiene relación con, al menos, las siguientes cuatro áreas de impacto ambiental:

- profunda transformación física y funcional del escenario ambiental, al ser apilados en los llamados tranques de relaves, y donde necesariamente terminan alterando el paisaje y modificando la dinámica hídrica,

- alto riesgo de avalanchas, por derrumbe de tranques durante sismos de alta magnitud; aunque, luego de abandonado el tranque, la superficie de los relaves termina secándose, internamente preserva suficiente humedad como mantener la capacidad de amplificar las ondas sísmicas,

- potencial contaminante de aguas dulces, mediante las descargas de aguas claras -normalmente, con alta carga residual química y de elementos disueltos- o por percolación hacia napas profundas, y

potencial fuente de material particulado a la atmósfera, desde tranques abandonados, si se emplazan en sitios ventosos.
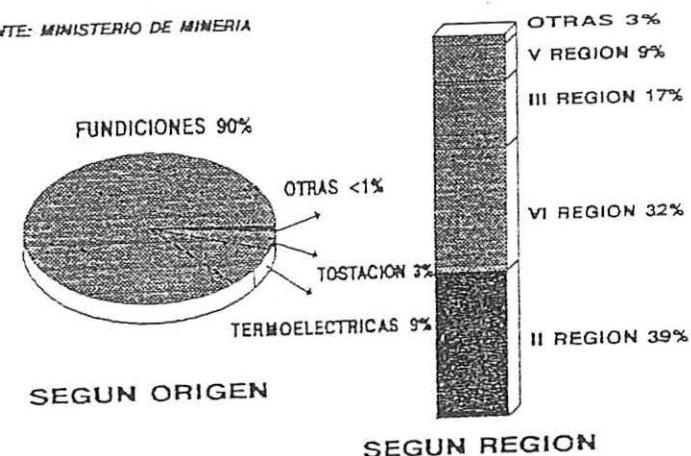

FIGURA 3. EMISION DE AZUFRE A LA ATMOSFERA, % DEL TOTAL EMITIDO (1.043 MIL TON EN 1989)

En Chile, las fundiciones de cobre han generado importantes procesos de contaminación atmosférica, gracias a emisiones fumígenas no controladas hasta 1992, año de dictación del D.S. 182, del Ministerio de Minería. El principal componente de estas descargas, es el anhídrido sulfuroso (SO_2), gas irritante y cáustico que, bajo ciertas condiciones atmosféricas, genera un aerosol ácido y causa la lluvia ácida. Sin el desarrollo de país industrializado, pero gracias a las emisiones desde las fundiciones, Chile es un productor importante de SO_2 (Figura 3).

Un componente poco considerado de estas descargas, es la masa de material particulado, que se emite asociado a los gases y que es rico en metales. Un elemento, que se presenta con frecuencia en estas partículas, es el arsénico, cancerígeno pulmonar, al ser inhalado, o gástrico, al ser ingerido (Figura 4). Este componente de las descargas fumígenas tiende a ser mal evaluado, quizás debido a que no induce evidencias inmediatas de daño. Sin embargo, debido a la larga residencia de los metales en los suelos, la contaminación metálica es un proceso de un pronunciado impacto ambiental de largo plazo.

GEOQUÍMICA REGIONAL

El conocimiento de la riqueza natural de metales pesados en Chile, es

de empresas asociadas a cultivos industriales, como remolacha azucarera[1], tabaco (Rodríguez y Suárez, 1987) y maravilla, y de antecedentes encontrados en la literatura (MISR-SAC, 1985; Pendias y Kabata-Pendias, 1985), permiten establecer que el contenido de cobre, en algunos sitios, cae en el nivel tóxico para algunos cultivos.

Plomo. El perfil de plomo en suelos (Figura 12) permite deducir que el rango de oscilación de los promedios de plomo por ecosistema, es bajo, presentando el promedio máximo un valor de 1,8 veces el mínimo. Si bien hay una reducción de los promedios hacia el sur, este descenso es más bien difuso y de baja magnitud. No se detectó una relación entre

FIGURA 12. PERFIL DE PLOMO TOTAL EN SUELOS DE CHILE: ESTRATA SUPERFICIAL (0-20 cm)

riqueza en plomo de los suelos y existencia de yacimientos plúmbicos; si éste fuera el caso, los mayores contenidos deberían provenir de los suelos de la XI Región. Los valores máximos, por unidad, se alejan fuertemente de los respectivos promedios, excepto en los valles Maipo-Mapocho, Tinguiririca y VIII Región.

En cuánto al origen, es indudable que los contenidos totales de plomo son debidos mayoritariamente a causas naturales, con excepción del sector de Puchuncaví y Nos, donde los altos contenidos de plomo se asocian a altos contenidos de cobre, siendo ambos de origen industrial. En el valle del Maipo, los contenidos máximos alcanzados en el área vecina a las industrias de Nos, son de origen antrópico pero, por su escasa representación geográfica, no alcanzan a influir significativamente sobre el promedio del valle.

Cinc. El perfil de cinc total en los suelos (Figura 13) indica que la curva de los valores promedios presenta una situación menos variable que la del cobre, aunque algo más que la del plomo, a lo largo del transecto reconocido; la amplitud del rango de variación de los promedios fue de 3,5 veces. Sin embargo, no es evidente que

haya asociación entre estos tres perfiles.

Se estima que la presencia de cinc de la estrata superficial de los suelos es de origen natural, resultando de los aportes de los materiales parentales de los suelos, por una parte, y la intensidad de los factores de formación de suelos, especialmente la pluviosidad, por la otra. La influencia de las lluvias queda en evidencia por la tendencia a que los menores promedios se ubiquen hacia el sur del país.

FIGURA 13. PERFIL DE CINC TOTAL EN SUELOS DE CHILE: ESTRATA SUPERFICIAL (0-20 cm)

El valle del Huasco (III Región) y el sector de Puchuncaví (V Región) son excepciones, ya que poseen valores similares a los del sur. En estas unidades, puesto que el factor climático no favorece el lavado de bases, los contenidos de cinc en suelos están reflejando la pobreza en cinc de los materiales parentales. En cuanto a Puchuncaví, se detectó un incremento del cinc, en paralelo al cobre, plomo, cadmio y arsénico (González e Ite, 1992), lo que identifica un origen industrial común.

Cadmio. En general, el contenido total de cadmio cayó bajo el límite de detección de la técnica analítica empleada (alrededor de 1 mg kg^{-1}, para espectrofotometría de absorción atómica, con atomización de llama). De ello, se exceptúan un sector del valle Catemu y otro de Puchuncaví, vecinos a fundiciones de cobre en la V Región (Cuadro 3); es indudable que el enriquecimiento cúprico de estos suelos ha sido acompañado por notables aumentos del contenido total de cadmio. Este aumento involucra un alto riesgo para la salud humana, por su fuerte carácter tóxico y por la facilidad en que entra a ser transferido dentro de las cadenas tróficas, a pesar de algunos antecedentes que apuntan hacia su esencialidad para plantas (Regius-Mocsenyi et al., 1985).

Arsénico. Existen escasos antecedentes de arsénico en los suelos del país. Es una situación que debería superarse, ya que se trata de un elemento con fuerte impacto sobre la salud humana, no por su poder fitotóxico sino que por su capacidad de ser libremente absorbido por las plantas y así, transferido en las cadenas tróficas. Se cuenta con alguna información sobre altos contenidos en suelos de los valles de Azapa y Lluta (I Región) (por estudios desarrollados por académicos de la Universidad de Tarapacá), la que parece deberse al riego prolongado con aguas arsenicales, y en la estrata superficial de suelos aledaños a la zona industrial de
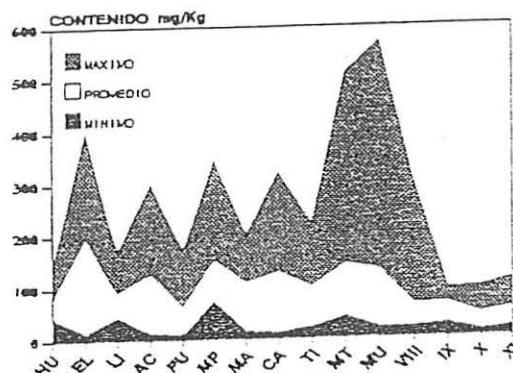
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PRESENCIA DE METALES PESADOS EN ÁREAS URBANAS DE CHILE

Heavy metal in urban areas of Chile

M. MARGARITA PRÉNDEZ B.[1]

CONTENIDO

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CONCENTRACIONES DE METALES PESADOS EN SANTIAGO

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INTRODUCCIÓN

En la actualidad, no cabe la menor duda de que el cuidado del ambiente no sólo significa la conservación y preservación de especies sobre el planeta, sino la salvación misma de él y de los seres vivos que lo habitan. A nivel nacional, la temática ha ganado adherentes rápidamente y los científicos debemos responder a esta situación, en una forma organizada, efectiva y eficiente.

El problema acuciante de la contaminación de algunas áreas en el país, debe ser atacado con prontitud, pero además se debe realizar acciones que consideren los riesgos potenciales a mediano y largo plazo, de modo que se impida una vuelta atrás al cabo de pocos años.

Los metales pesados, la mayoría de los cuales son adicionados al ambiente por acciones no naturales, pueden constituirse en contaminantes que generen graves problemas en el corto, mediano y largo plazo. Por lo tanto, deben ser cuidadosamente cuantificados y estudiados en su comportamiento una vez que han ingresado al ambiente.

Las áreas urbanas, en tanto que centros con altas cifras de población, están sujetas a una potencial contaminación de sus suelos, aguas y aire, derivada tanto de la actividad natural de los seres humanos, como de las actividades industriales y de servicios que complementan la vida urbana.

En este trabajo, el foco de atención se centra en los metales pesados presentes en el aire o detectados en otros medios, pero sin duda transportados hasta ellos a través del aire. En especial, se entregarán resultados obtenidos en la ciudad de Santiago, fundamentalmente debido a la escasez de información existente para otras ciudades del país.

ANTECEDENTES GENERALES

Para el estudio de los elementos traza, en especial metales pesados, es necesario entender primeramente algunos conceptos básicos sobre el substrato en el cual se encuentran dichos elementos en el aire. En líneas generales, en el aire se pueden distinguir dos grandes tipos de contaminantes: los gases, cualquiera sea su naturaleza química (orgánica o inorgánica) y el material particulado suspendido, denominado también aerosoles atmosféricos o simplemente, partículas. Este trabajo se refiere específicamente al segundo tipo de contaminantes, en el cual se detecta la presencia en el aire de los metales pesados.

Relación tamaño del aerosol-impacto sobre la salud

Los aerosoles atmosféricos se presentan en una amplia gama de tamaños, forma y composición química. Con respecto al tamaño y para nuestros efectos, los aerosoles atmosféricos presentan diámetros que se sitúan entre los 45 y los 0,01 μm. Para el establecimiento de las normas, esto es, de las concentraciones máximas que pueden estar presentes en el aire, sin causar daño a la salud humana, interesan

sólo las concentraciones totales de los aerosoles de tamaños < 45 μm y < 10 μm. Estos últimos se denominan, también, la "fracción inhalable" del aerosol, o sea, aquella capaz de penetrar en el aparato respiratorio.

Es importante enfatizar que dichas normas son determinadas considerando la salud humana y se denominan normas primarias. Cuando se trata de la protección del ambiente (suelos, aguas, plantas, etc.), los valores de las normas son bastante menores, esto es mucho más exigentes, y en Chile no existen; se trata de las normas secundarias.

Figura 1. Esquema del aparato respiratorio, indicando cualitativamente la penetración del aerosol, según tamaño y porcentaje de respirabilidad para aerosoles < 10 μm

Desde el punto de vista de la salud humana y debido a la estructura del aparato respiratorio, es muy importante el conocimiento de las concentraciones del aerosol en sus distintos tamaños bajo los 10 μm y sus correspondientes composiciones químicas. Esto resulta del hecho de que esos aerosoles pueden penetrar hasta diferentes niveles del aparato respiratorio, alcanzando mayor profundidad en la medida que presentan menores diámetros.

La Figura 1 muestra cualitativa y cuantitativamente la situación anterior (Préndez et al., 1991). Se aprecia que, estrictamente, las partículas < 45 μm y hasta 10 μm, carecen de interés desde el punto de vista salud. Pero, en la medida que sus diámetros disminuyen bajo los 10 μm, su penetración al organismo es cada vez mayor. El aerosol de 10 μm, prácticamente, no se retiene en el aparato respiratorio, pues es rápidamente reexpelido hacia afuera de él. Los porcentajes de retención de las partículas aumentan a medida que, por su aún menor tamaño, ellas son capaces de alcanzar las zonas no ciliadas del aparato respiratorio, esto es, los pulmones y los alvéolos pulmonares, situación que ocurre ya para partículas de diámetro < 3 μm.

A estas profundidades del aparato respiratorio, la remoción de las partículas es muy difícil, de modo que ellas pueden permanecer dentro de los pulmones por largo tiempo. Este hecho es particularmente importante cuando se agrega al tamaño de la partícula, su composición química y con ello, su potencial toxicidad.

Relación tamaño del aerosol-origen y fuentes de emisión

El tamaño del aerosol también está relacionado a su origen y sus fuentes de emisión. Un método que permite la separación entre los elementos de origen natural y los antropogénicos está dado por el cálculo del llamado factor de enriquecimiento (FE), que se obtiene haciendo una cierta razón entre las concentraciones de los elementos en estudio, de forma relativa a un elemento tomado como referencia.

FIGURA 2. FEg PARA Mg, Mn, Ni, Cu, Zn, Cd y Pb, EN AEROSOLES DE DISTINTOS LUGARES DE SANTIAGO

Prendez y Ortiz, 1989

FEg= factores de enriquecimiento promedio geométrico

Dicho valor suele situarse en el rango entre 1 y 10 aproximadamente, para los elementos de origen natural. Valores superiores indican que los elementos se encuentran enriquecidos en el aire por los respectivos aportes desde una fuente de origen antrópico.

La Figura 2 ejemplifica la utilización de este criterio (Préndez y Ortiz., 1989). En ella, se ha representado el FE promedio geométrico (FEg) para diferentes metales pesados cuantificados en el aire, en diferentes sitios de la ciudad de Santiago. El manganeso y el magnesio (no metal pesado, pero sí elemento traza), tienen un factor de enriquecimiento < 10 y por ende son de origen natural.

El hierro ha sido elegido como elemento de referencia, pues previamente se ha demostrado su origen natural en Santiago (Préndez et al., 1984). Los restantes elementos (niquel, cobre, cinc, plomo y cadmio) presentan FEg > 10 y, en consecuencia, tienen un origen antrópico. Esta conclusión es válida para cualquier zona de la ciudad de Santiago.

Respecto del cobre, es fundamental indicar que, cuando el cálculo de los FE se hace respecto del contenido de cobre de los suelos chilenos y no en función de los promedios internacionales atribuidos a la corteza terrestre, como es la situación generalmente empleada en la literatura, la asignación de su origen cambia de antrópico a natural. Será de esta forma que se le deberá considerar normalmente, en la ciudad de Santiago.

La conclusión anterior es de especial trascendencia cuando se pretende asignar el origen del cobre presente en el aire o a través de él en el suelo, emitido desde una fuente puntual determinada. Por otra parte, esto entrega mayores
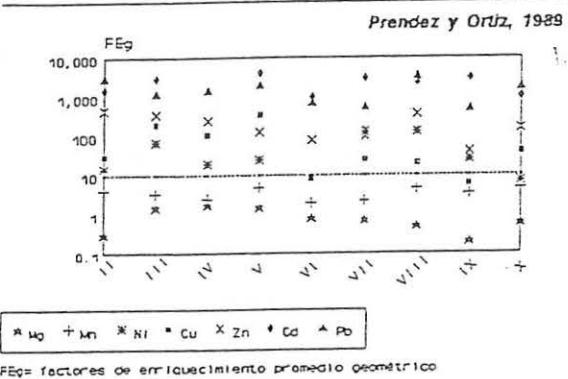
fundamentos a la posición de que los problemas ambientales sólo pueden resolverse realmente si se conocen adecuadamente el ambiente y sus condiciones naturales, o sea las líneas de base.

FIGURA 3. CONCENTRACIONES PROMEDIO DE NI, Cu, Pb, Mn, Zn y Fe, EN AEROSOLES ATMOSFERICOS DE SANTIAGO

PRENDEZ Y ORTIZ, 1982

EN FUNCION DEL DIAMETRO DE LA PARTICULA

Por otra parte, las concentraciones de los elementos cambian en una forma que relaciona sus fuentes de emisión y sus diámetros, tal como se ve en la Figura 3 (Préndez y Ortiz, 1982), donde ECD corresponde al diámetro de corte efectivo, que es una forma de expresar el diámetro de las partículas, teniendo en consideración su forma. Se observa que los elementos antropogénicos aumentan sus concentraciones hacia las partículas de menor diámetro. Casos típicos son plomo y niquel.

En cambio, las concentraciones de los elementos naturales aumentan hacia los diámetros mayores. Aquí los casos típicos son hierro y manganeso. Cobre y cinc tienen comportamientos atípicos. El cinc, generalmente emitido en los procesos de incineración, se presenta en diámetros más bien grandes ("fly ash").

De este modo, se cumple también en Santiago, la aseveración comúnmente aceptada de que los aerosoles más pequeños, de 1 a 2 μm o menos, provienen en general de fuentes antrópicas o derivadas de las actividades humanas vinculadas a procesos que ocurren a elevadas temperaturas. La excepción es el fly ash. En cambio, los de mayor tamaño, mayores de 2 μm, tienen un origen natural.

NORMAS

Un problema grave que se suscita para poder evaluar el impacto de los metales pesados contenidos en los aerosoles, es la falta de normativa que oriente al respecto de las concentraciones máximas permitidas, compatibles con la salud de las personas (normas primarias) y con la salvaguarda del ambiente (normas secundarias).

Algunos países tienen reglamentados los contenidos máximos de ciertos metales en el aire, como norma primaria. Sin embargo, no se encuentran normados todos los elementos potencialmente tóxicos y además sus valores no están explícitamente vinculados a la fracción respirable.
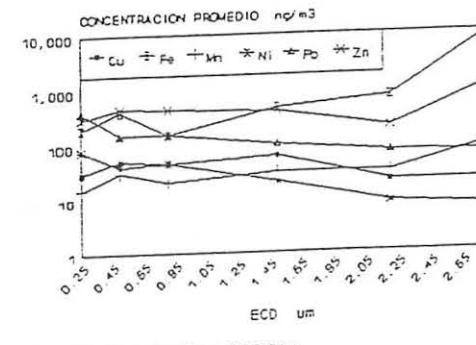
El Cuadro 1 muestra los valores de la norma para plomo, cadmio y vanadio en aerosoles < 45 μm, en algunos países del hemisferio norte. Una característica de las normas es que deben explicitar, además de las concentraciones máximas, los tiempos de exposición. Así, la reglamentación para plomo por ejemplo, corresponde al valor de 1,5 μg m^{-3}, permitido como media aritmética para 3 meses.

En Chile, recién el 18 de abril de 1994, se estableció la norma primaria para arsénico, la cual fue derogada a los pocos días. Para apreciar la magnitud de los valores establecidos en las normas, se pueden comparar por ejemplo, con la concentración de plomo y cadmio encontrados en los aerosoles de la Antártica chilena (Cuadro 2) y que corresponden a los de una atmósfera limpia. Se observa que la norma de plomo, por ejemplo, admite valores 50 a 200 veces superiores al del aire puro. En el caso de cadmio, el rango es entre 3000 y 5000 veces superior.

Cuadro 1. Normas primarias para algunos metales pesados, en el aire (μg m^{-3})

Elem.	Conc.	Ciudad, País
Pb	1,5	Ciudad de México, Caracas, USA
	0,7	ex URSS
Cd	50	USA
	30	ex URSS
V	50 a 1000	USA
	100	ex URSS

CONCENTRACIONES DE METALES PESADOS EN AREAS URBANAS

Es usual estimar que las concentraciones de los elementos traza en el aire, están vinculadas a la acción antropogénica y por lo tanto, son mayores en las ciudades que en las áreas rurales y mayores también en las cercanías de fuentes emisoras puntuales.

En el Cuadro 3, se dan los valores encontrados para tres ciudades latinoamericanas, haciendo la comparación en función de la fracción del aerosol considerada. Se observa

Cuadro 2. Rango de concentraciones de metales pesados en la península antártica (ng m^{-3}) (Préndez et al., 1993b)

Elem.	Fracción aerosol	
	< 45 μm	< 3 μm
Pb	0,017- 0,030	0,0043- 0,136
Cd	0,0 -<0,009	0,0 -<0,002

que las concentraciones de diferentes metales pesados, encontradas en la fracción de alta respirabilidad en Santiago y en Sao Paulo son muy similares, pese a que las emisiones en Sao Paulo son del orden de 4 veces mayores a las de Santiago (Préndez, 1994).

Por su parte, la comparación del aerosol total entre Santiago y Caracas muestra valores claramente mayores para nuestra ciudad, a pesar de tener emisiones que son aproximadamente tres veces menores (Préndez, 1994). Particularmente

notables resultan las mayores concentraciones de cinc, cobre y cromo en Santiago.

La comparación con otras ciudades chilenas es difícil, fundamentalmente porque hay muy pocos estudios para ellas. Hacen excepción las ciudades de Antofagasta y Chillán, donde se han cuantificados algunos metales pesados en la fracción del aerosol < 15 μm[1] y las ciudades de Arica (Hrepic et al., 1983) y Rancagua (Alvarez, 1981), para las cuales existe información para la fracción <45 μm. Los resultados se presenta en el Cuadro 4.

Los estudios efectuados en Arica, con respecto a los metales pesados presentes en la fracción <45 μm, indican que, de

Cuadro 3. Concentración de metales pesados (ng m^{-3}) en ciudades latinoamericanas

Elem.	Sao Paulo < 4 μm 1984[2]	Santiago < 3 μm 1983[2]	Caracas < 45 μm 1978-1980	Santiago < 45 μm 1976-1983[2]
Pb	1041	1245	<< 20[3]	1211
Cd		11		10
V	340		760[4]	
Hg				6
Mn	129	90	129[3]	115
Zn	1109	596	690[4]	1105
Cu	74	63	60[4]	370
Fe	2099	1468	1880[3]	4102
Cr	260		< 5[4]	75
Ni	19	33	< 80[4]	35
Ti	151			276

[1] Orsini y Boveres, 1980; [2] Información de la autora; [3] Sanhueza et al., 1979; [4] Sanhueza y Lissi, 1980

acuerdo al Cuadro 4, en general, las concentraciones no son muy elevadas. Por otra parte, se ha demostrado que cobre, níquel, cinc, plomo y cromo tienen un origen antrópico (Hrepic et al., 1984).

A la situación general, hacen excepción dos casos puntuales, uno referido a las concentraciones de plomo en el aire, proveniente de suelo contaminado en las cercanías de una antigua vía férrea de transporte de mineral y la otra, relativa a la presencia de níquel y plomo y a cinc, emitidos en procesos diferentes por una misma industria de tostación de minerales y arrastrados por los vientos sobre un sector de la ciudad (Hrepic y Quintana, 1990).

Las concentraciones de arsénico en el aire de Rancagua, son varias veces superiores a las detectadas en Santiago, como se deduce al comparar los valores dados en el Cuadro 4, con los valores citados más adelante.

CONCENTRACIONES DE METALES PESADOS EN SANTIAGO

Santiago es la ciudad de Chile que presenta las mayores concentraciones

[1] J.R. Morales. Comunicación personal

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THE HEAVY ELEMENTS

Chemistry, Environmental Impact and Health Effects

by

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CHAPTER 7

THE HEAVY ELEMENTS IN THE ATMOSPHERE

In this chapter we will survey the heavy elements in the atmosphere, including the properties of aerosols, and the chemistry of the heavy elements in the air. In addition we will review the levels of the elements in the air, and efforts to determine their sources.

THE ATMOSPHERE

Composition

The earth's atmosphere consists of four principal zones the troposphere, the stratosphere, the mesosphere and the thermosphere. The zones are separated by regions of temperature inversion, called the tropopause, the stratopause and the mesopause respectively. The relationship between the height of the zones above the earth and the temperature changes are shown in Fig 7.1. The principal species in each sphere are also listed. We will be concerned in this chapter with the troposphere, the sphere closest to the earth. The composition of which near sea level, is given in Table 7.1 [91]. Around 50% of the material in the troposphere occurs up to 5 km and 90% up to 12 km. The majority of the heavy element species are in the particulate matter or aerosol. However, because of the volatility of mercury, and of some heavy element compounds, they may also occur in the vapour state.

Meteorology of the Troposphere

The movement of the air around the world is dominated by two processes, air currents giving vertical movement and winds giving horizontal movement.

Vertical movement The stability of the air determines its vertical movement. If a parcel of air in the atmosphere rises it will expand as the pressure of the surrounding air drops. If the expansion is adiabatic, i.e. if there is no transfer of
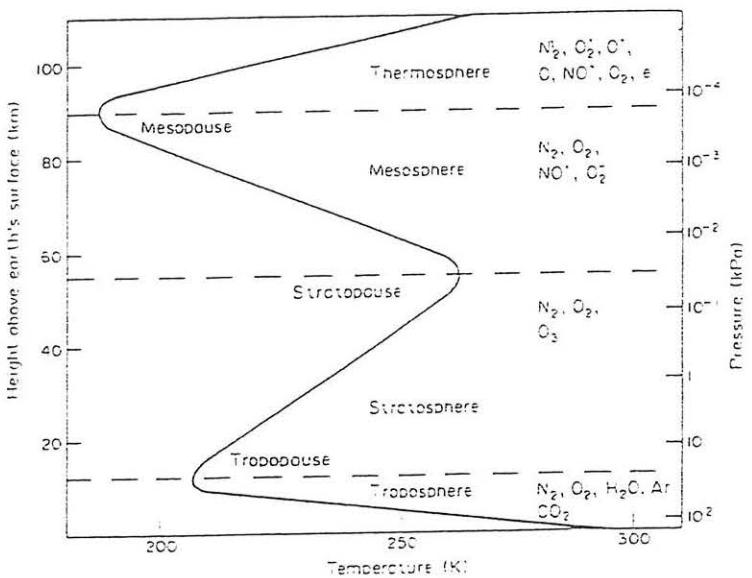
Fig. 7.1 Structure of the earth's atmosphere.

TABLE 7.1 The Composition of the Atmosphere Near Sea level

Component	Level (ppm)	Component	Level (ppm)
Major		Trace	
Dinitrogen, N_2	780,840	Neon, Ne	18.18
Dioxygen, O_2	209,460	Helium, He	5.24
		Methane, CH_4	1.4
		Krypton, Kr	1.14
		Dihydrogen, H_2	0.5
		Nitrous oxide, N_2O	0.25
Minor		Carbon monoxide, CO	0.08
Argon, Ar	9340	Ozone, O_3	0.025
Carbon dioxide, CO_2	325	Ammonia, NH_3	6×10^{-3}
Water vapour, H_2O	variable	Nitrogen dioxide, N_2O	4×10^{-3}
		Sulphur dioxide, SO_2	2×10^{-4}

heat between the parcel of air and its surroundings, the gas temperature will fall. When the temperature drop, called the adiabatic lapse rate, is greater than the temperature change of the surrounding air the parcel of air will begin to decend. Such a situation is called stable. Therefore for a parcel of gas (p), using the ideal gas law,

$$P_p V_p = nRT_p$$

and replacing n/V_p by d the density of the air we get,

$$P_p = d_p R T_p.$$

Similarly for the surrounding air (a),

$$P_a = d_a R T_a.$$

Since the two pressures P_p and P_a will be the same, we have,

$$d_p = d_a \frac{T_a}{T_p}.$$

Initially the two temperatures will be the same, but as the parcel of air rises and its temperature falls, $T_p < T_a$, and therefore $d_p > d_a$ and the gas will decend, a stable situation. However, if $T_p > T_a$ then $d_p < d_a$ and the gas will continue to rise, an unstable situation, which allows for the vertical dispersion of material emitted into the atmosphere. When the temperature of the surrounding air increases with height a particularly stable situation results, called a temperature inversion.

Atmospheric temperature inversion Normally in the troposphere the temperature falls with increase in altitude, but the reverse, a temperature inversion can also occur. A subsidence inversion happens when the hot air, produced around the equator, rises until it reaches the tropopause. As the air rises it will expand, cool and lose its moisture in the humid tropics. The cooled air then moves towards the poles until around latitude 30°N or S when it begins to decend. The resulting increase in pressure raises the air temperature and cooler air is trapped below (Fig. 7.2). Seasonal variation causes the subsidence to move north or south with the zone of greatest heating.

A radiative inversion can occur on clear cold nights, when the earth's surface cools rapidly, radiating heat into the atmosphere. The air near the ground cools compared with the air higher up (Fig.7.3a). The following day the surface air is warmed giving a limited mixing area above which sits warm air trapping in the low level material (Fig. 7.3b). During the day as the air warms up the inversion is likely to disappear (Fig. 7.3c).

Cold air from the ocean, being heavier than warm air on the land, can slip under the the warm air. This air produces a sea breeze, but when the movement is slow a frontal inversion occurs on the land near to the coast (Fig 7.4).

A fourth temperature inversion called an advective inversion occurs when the sides of a valley cools at night and the adjacent cooled, and more dense air, falls into the valley. Warmer air may flow across the top of the valley trapping the cold air (Fig. 7.5).
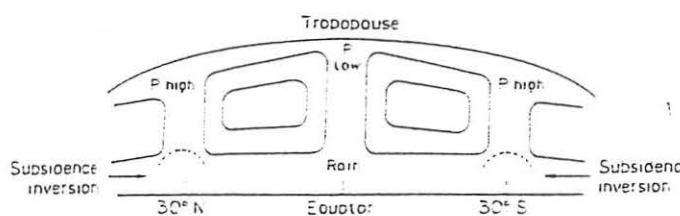
Fig. 7.2 The formation of a subsidence inversion.
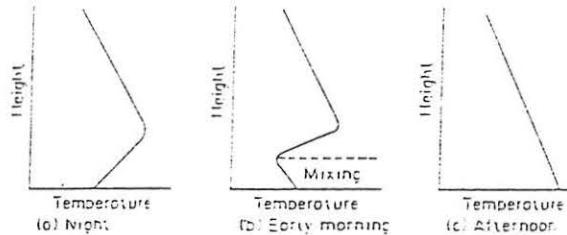
Fig. 7.3 Development of an inversion after a clear cold night.
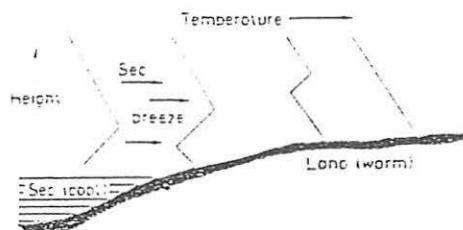
Fig. 7.4 Development of an inversion on land close to the sea.
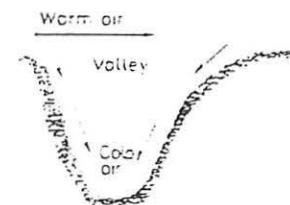
Fig. 7.5 Formation of an inversion in a valley.

Winds Wind, which is the horizontal movement of air, varies from light to very strong. It promotes the dilution and dispersal of air pollutants. The horizontal movement arises from the interplay of three factors; a pressure gradient (the air moving from high to low pressure), the Coriolis deflection and friction with the earth's surface. The coriolis deflection (Fig. 7.6) arises from the influence of the spin of the earth on the surrounding air. As a parcel of air moves north (in the northern hemisphere) its velocity is greater than at any point north of it, due to
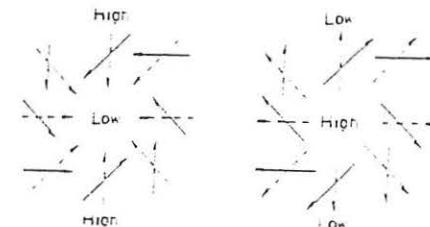
Fig. 7.6 Deflection of the wind by the Coriolis effect (the broken arrows indicate the direction of the wind if the earth did not rotate).

the fact that a point on the equator has a greater velocity than any other points on the earth's surface. Therefore to an observer the parcel of air appears to be deflected to the east (in the northern hemisphere). The result is that the wind moves along rather than across the isobars (lines of constant pressure) with some deviation because of the effect of friction. Wind strength is influenced by terrain, such as buildings in cities, and air turbulence is due to eddies, i.e. packets of air moving randomly, but with a circular motion.

Emission behavior An emission plume behaves in a variety of ways depending on the vertical temperature gradient, and the presence or absence of temperature inversions. Some behaviors are illustrated in Figs. 7.7a-f. The dashed lines represent the adiabatic lapse rate and the full lines the vertical temperature gradient of the air. Fastest dispersal of the emission occurs through looping (Fig. 7.7a), followed by coning (Fig.7.7b). In the last four examples (Fig. 7.7c-f) the emission is entrapped in inversions, the worst being fumigation (Fig. 7.7e).

The climate in cities The climate within cities can be different to surrounding rural areas, and is influenced by the terrain, i.e. buildings, high energy consumption and subsequent loss to the atmosphere, and reflecting surfaces. Some of the differences are highlighted in Table 7.2 [60]. The reduced wind speed, loss of heat to the atmosphere at night from surfaces, which are good heat conductors, provide the conditions that trap pollutants. In addition cities become heat islands and air circulates within them which helps to keep the material within the city. The build up of material within a city can be estimated using a box model. In a steady state, with good mixing, the concentration of material in a city's atmosphere is given by;

$$C(mass/vol.) = \frac{Emission\ rate(E)(mass/time)}{Air\ flow\ rate\ (vol./time)}.$$

The air flow rate into a box of width l and mixing height h and a wind speed v is vlh, hence;

$$C = \frac{E}{vlh}.$$
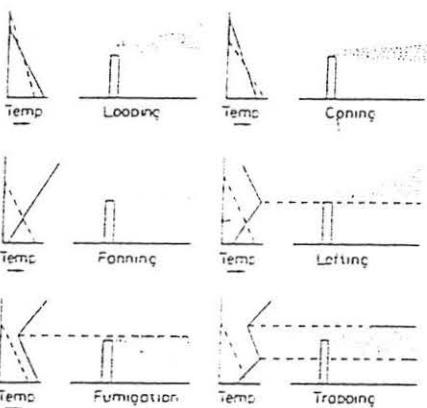
Fig. 7.7 Behaviour of emissions from smoke stacks in relation to air temperature (the full line is the temperature gradient, and the broken line the adiabatic lapse rate).

TABLE 7.2 Climate Differences Between Urban and Rural Areas

Element	Comparison with rural areas
Temperature	0.5–1.0 °C higher
Relative humidity	6% lower
Dust particles	10 times more
Cloudiness	5–10% more
Radiation	15–20% less
Wind speed	20–30% lower
Calm	5–20% more
Precipitation	5–10% more

Source of data; Landsberg, 1962 [60].

The build up of an emission in a box will increase when v and h are low. For a city with l = 30 km, h = 200 m and v = 8000 m h^{-1} and E = 50 × 10^6 mg h^{-1} of particulate matter.

$$C = \frac{50 \times 10^6 \, (mg\,h^{-1})}{8 \times 10^3 \, (m\,h^{-1}) \times 3 \times 10^4 \, (m) \times 2 \times 10^2 \, (m)}$$

$C \approx 1.0$ mg m^{-3}.

If the wind speed is halved the concentration would double, demonstrating the importance of wind.

Atmospheric Particulate Material (Aerosols)

Particle size The size of atmospheric particles range from molecular species to material that settles out rapidly, i.e. from 10^{-9} to 10^{-4} m (0.001 to 100 μm) in diameter [85]. The particles, whose size varies with the source, are either dispersed into the air, or formed from condensation of species already present in the atmosphere. The diameter of atmospheric particles has been defined in different ways, and it is not always clear what definition is used in some publications. The aerodynamic diameter, is the diameter of a spherical particle with unit density, but with the same properties of the real particle. It is similar to the Stokes' diameter, which is the diameter of a sphere with the same falling velocity and density as the real particle. The mass size factor describes the variation in mass with the size of the particles, and the mass median diameter, MMD (or mass median equivalent diameter, MMED) is the diameter below which 50% of the total mass of the particles, or the total mass of an element occurs [77].

The shape of aerosols range from spherical to quite irregular. The range of particle sizes for various aerosols are listed in Fig. 7.8 [6,16,85,94,102], the majority of particles lie within 0.01-100 μm. Particles with diameters in the range 0.38-0.76 μm have comparable dimensions to the wavelength of visible radiation, and will therefore affect its transmission producing haze.

The distribution of the sizes of aerosols is log-normal [29, 70], skewed at the higher end of the size range. Within this distribution most of the mass of aerosols is in the 0.01-10 μm range [106] with a mean around 1 μm [20]. However, the plot of mass distribution versus size, for a chemical element, is of the form;

$$\left(\frac{\Delta C}{C_T}\right) / \Delta \log d_i \text{ versus } dp_{\mu m}.$$

It is often bimodal with peaks at <1 and >5 μm; where ΔC is the airborne mass concentration of metal M, C_T is total airborne mass concentration, $dp_{\mu m}$ is the particle size and $\Delta \log d_i$ is the difference $dp_{max} - dp_{min}$, [21]. Other studies have found that the particle size distribution has two or three modes, around ~0.02 μm, ~0.4 μm and ~10 μm in mass or size distributions [89]. The Aitken nuclei range mode is characteristic of the freshly formed aerosol, the accumulation range mode is characteristic of the degree of aging and the coarse particle mode is characteristic of the amount of windblown dust, sea spray or mechanically produced dust such as fly ash [105].

Coagulation and sedimentation The small sized particules (i.e. <0.1 μm) in the atmosphere can combine into larger particles by coagulation, the movement and contact being controlled mainly by Brownian motion. If each contact produces coagulation the reduction in the number of particles is given by;

$$n = \frac{n_0}{1 + k n_0 t},$$

Size μm	0.0001	0.001	0.01	0.1	1	10	100	1000	10000

Fig. 7.8 The sizes of atmospheric particles. Source of data; Paulhamus, 1972 [85].

where n = final concentration, n_c = initial concentration, t = time and k is a constant 10^{-10} to 10^{-6} cm^3 s^{-1}. For particles < 0.01 μm the decrease is 50% in a hour, and for < 0.05 μm the decrease is 50% in a day [29].

The larger particles in the atmosphere fallout rapidly, and in still air the settling or sedimentation velocity is given by Stoke's law;

$$v_d = \frac{2(\rho - \rho_0)g}{9\eta}\left(\frac{d}{2}\right)^2,$$

where v_d = velocity, $\rho - \rho_0$ = density difference between the air and particle, η = viscosity of the air, g = gravitational acceleration constant, and d = diameter of the particle [106]. The velocity will range from 9×10^{-5} to 1.3×10^{-1} cm s^{-1} for particles of diameter 0.1 to 20 μm.

PARTICULATE MATTER AND THE HEAVY ELEMENTS

The Size of Heavy Element Particles

Particles <2 μm generally come from anthropogenic sources, whereas when they are above 2 μm the main source is wind blown and re-entrained dust [78]. For a number of cities, where anthropogenic sources dominate, the aerosol sizes mainly span 0.12-0.7 μm, of which 20-25% lies at the lower end of the range [78]. For example the elements Sb, As, Pb, coming from man made sources, are mostly associated with the smaller sized fraction of the aerosol, i.e. <1.1 μm [80,83]. Particles containing cadmium have been identified in the size range 0.6-10 μm with a mean diameter of 2.2 μm [77,83]. A range of MMD's 0.28-5.5 μm have also been reported for cadmium containing particles [21]. A good proportion of these particles are respirable [77]. Around 50-90% of the cadmium in fly ash aerosol is <5 μm size [98].

Lead The size of lead particles have been extensively studied, because of concern over automobile lead emissions. Three particle types are emitted by cars, the primary exhaust particles (0.01-0.1 μm), chain aggregates, mostly diesel smoke (0.3-1 μm), and large material (>1 μm) [14]. The MMD's of lead containing particles are reported to be approximately 0.25-0.3 μm [15,16,66], but for aerosol near to motorways, the MMD is around 0.02-0.05 μm [14,65,66]. A plot of lead concentration against particle size displays two concentration minima, around the 1.1-2.0, and 2.0-3.3 μm sizes, and the concentration of lead is higher in the smaller particles, i.e. <1.1 μm [98].

The size of particles from motor vehicles decreases with distance from the road, up to 10% of the particles are coarse within 3.7 m from the road, and around 50% of the particles are greater than 6.5 μm, 600 m away [16,78]. Lead containing particles are bigger in urban areas compared with rural areas or along motorways, [15,65]. For example around 30% of the particles in the urban situation are <0.5 μm, whereas along a motorway the proportion is 67% [15,65,66]. The lead containing particles are probably larger in urban areas because of the association between the aerosol and general urban aerosol [65].

Residence Times

The lifetime of aerosols in the air, which contain heavy elements, is a function of the particle size. The smallest particles, 0.001-0.08 μm, have a lifetime of <1 hour, because of coagulation into bigger particles, whereas in the accumulation range, 0.08-1.0 μm, the life time is 4-40 days, and the large particles >1.0 μm have a life time of minutes to days [6,39,77,78,102,105].

Because of the volatility of mercury it is recycled through the environment, including the atmosphere, which increases its residence time over land from 7 to 315 days. The oceanic residence time is about 14 days, because in this case, there is less recycling of the element [71].

Transport of Aerosols

Because of the long residence times, transport of particulate material in the atmosphere can extend over long distances e.g. 100 to 1000 km. In ice cores of the Arctic and Antarctic, pre-1940 lead levels are ≤ 0.08 ng kg^{-1}, whereas those found for 1965 are 0.15-0.42 ng kg^{-1}, a 2 to 5 fold increase, attributed to transport of lead from industrial areas [106]. The relationship between the aerosol levels of trace elements and their concentration in snow is expressed by;

$$C_i = kC_{s'}$$

where C_i is the concentration in the air, k is a transfer constant, and C_s is the concentration in the snow. Another expression is;

$$C_i = ke_n\eta/L,$$

where e_s is the mass fraction of aerosol used in condensation nucleation, η is a factor linked to evaporation below the cloud, and L is the liquid water content of the cloud. Taking h close to 1 and $0.1 \leq e_s \leq 1$, $1 \leq L \leq 3$ g m^{-3}, the estimated value of k is 1.0 to 6.0 g m^{-3} which is close to experimental values [7].

A model for the transport of mercury which includes a number of recycling pathways is [71];
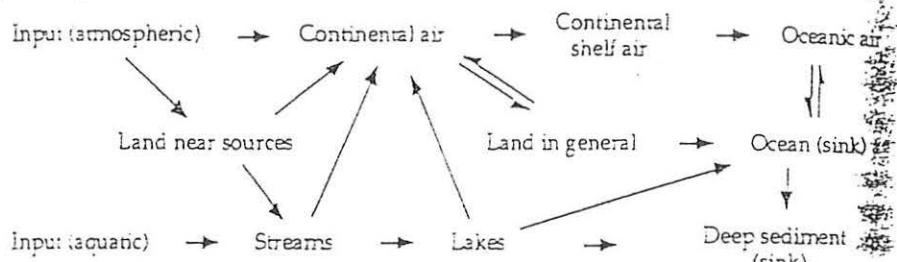
To a lesser extent the same processes will occur for selenium and arsenic. Cadmium has been observed in air, which has not originated from local sources [40].

HEAVY ELEMENT EMISSIONS AND FLUXES

Heavy element emissions into the atmosphere, globally or locally, are either natural or anthropogenic. Heavy element atmospheric fluxes are expressed as emissions or fluxes into the atmosphere or as fluxes from the atmosphere to the earth. The flux depends on the amount of aerosol and the concentration of the element in the aerosol. Natural fluxes of total particulate matter are estimated to be around 1000 Tg y^{-1} or 7.1 x 10^{12} g m^{-2} s^{-1}. The sources are desert material, grasslands, forests, oceans and point sources such as volcanoes, and forest fires.

The urban flux is estimated to be 100 Tg y^{-1} or 7.1 x 10^{11} g m^{-2} s^{-1}. On the basis of these fluxes the concentrations of total particulate matter are; troposphere 1-10 μg m^{-3}, over deserts 1-1000 μg m^{-3}, over steppes and grasslands 10-100 μg m^{-3}, over forests 10-500 μg m^{-3}, over marshlands 10-100 μg m^{-3}, over oceans 1-50 μg m^{-3}, and urban 1-1000 μg m^{-3} [39]. A separate estimate suggests higher levels i.e. the natural flux of particulates in the air as 773-2200 Tg y^{-1} and 185-415 Tg y^{-1} for man made aerosol [70].

Some estimates of natural emissions of the heavy elements into the air are listed in Table 7.3 [55, 61, 84] in units of ng kg^{-1} (or pg g^{-1}) of dust emitted. The highest concentrations occur in the volcanic emissions, however, compared with the amount of windblown material the total contribution of volcanic emissions is less. Around 60-85% of the total natural emissions of lead (18.6 x 10^6 kg y^{-1} [78] or 29.5 x 10^{6}kg y^{-1} [88]) come from the windblown material, 5-10% from emissions from vegetation and the rest from sea-spray, volcanic emissions, forest fires and meteoritic material [78, 88]. The natural emissions of cadmium to the atmosphere are estimated to be (in 10^6 kg y^{-1}); windblown dust 0.1, forest fires 0.012, volcanic emissions 0.52, vegetation emissions 0.2 and sea spray 0.4, a total of 1.232 x 10^6 kg y^{-1} [88]. For mercury the natural degassing of the element is estimated to be 0.02-0.03 μg m^{-2} h^{-1}, whereas around mineralized areas the emissions are as high as 1.7 μg m^{-2} h^{-1} [63]. Global natural emissions of mercury vapour are estimated as 6 x 10^6 kg y^{-1} and anthropogenic as 2 x 10^6 kg y^{-1} [62].

Global estimates of anthropogenic emissions from a variety of sources and emissions from coal and oil combustion are listed in Table 7.4, in 10^6 g y^{-1} [4,62,69,71,82,83,88,101,107]. The data suggests that oil is a significant source of mercury, and coal is a significant source of selenium.

The emissions of lead to the atmosphere, from smelting and refining processes, have decreased from 5% in Roman times to 0.5% today. However, over the last 50-60 years the use of tetraalkyllead in petrol has increased emissions 3 to 4 fold. More than 1/2 of the lead produced today gets into the air in some form or other, around 60-68% from tetraalkyllead and 28% from metal production [28,95]. Emissions vary considerably with location, for example in New Zealand they are estimated to be 1.33 x 10^6 kg y^{-1}, over US cities it is 1.2-

TABLE 7.3 Natural Inputs of Heavy Elements into the Atmosphere (ng kg^{-1} of dust)

Element	Volcanic	Windblown	Forest fires	Vegetation	Sea spray
As	300-800	0.5-2.0	0.5-4.4	3.5	0.1-0.6
Cd	30-800	0.002-1.7	0.03-2	2.7-36	0.001-0.003
Pb	100-9600	0.4-70	1.1-78	21-280	0.001-0.09
Se	10-1700	0.6			
Sb	30				

Sources of data; references 55,61,78,84.

TABLE 7.4 Global emissions of Heavy Elements and the Contribution from the Combustion of Coal and Oil (10^5 g y^{-1})

Element	Total	Coal	% of total	Oil	% of total
As	23.6	0.7	3.0	0.002	0.008
Se	1.1	0.42	38.2	0.03	3.3
Cd	7.3	-	-	0.002	0.03
Hg	2.4	0.0017	0.07	1.6	66.7
Pb	449	3.5	0.8	0.05	0.01
Bi	-	0.75	-	-	-

Sources of data; references 4,62,69,71,82,83,88,101,107.

2.0×10^4 ng cm^{-2} y^{-1}, remote rural 2.5×10^3 ng cm^{-2} y^{-1}, remote mountain 4×10^2 ng cm^{-2}y^{-1}, and over the oceans the flux is 7×10^{-2} to 50 ng cm^{-2} y^{-1} [95]. At a site in Antarctica the lead concentration in the snow is ~4 pg g^{-1} and the deposition in snow is ~3 g cm^{-2}y^{-1}, which gives a flux of 12 pg cm^{-2} y^{-1}, for both dry and wet deposition. Extrapolation to the whole of the Antarctic, with a snow accumulation of 17 g H$_2$O cm^{-2} y^{-1} the total lead flux is ~70 pg cm^{-2} y^{-1}, approximately 9 tons y^{-1}. In the South Pacific easterly the lead flux is ~2 ng cm^{-2} y^{-1}, hence the flux ratio Antarctica/Sth Pacific ~1/30. Similar ratios occur for other land masses and ocean environments, for Greenland/Nth Pacific ~1/22 and Greenland/Nth Atlantic ~1/34 [8].

The principal source of anthropogenic lead emissions is the combustion of tetraalkyllead, but as more countries reduce the amount of lead used this source will decrease. The quantity of lead consumed by a car engine is a function of the concentration of lead in the petrol, rate of petrol consumption, the size, efficiency and running speed of the engine, and the engine load. The proportion of lead exhausted depends on the age, temperature and physical state of exhaust system, and the manner in which car is operated. The amounts exhausted can range from 20-300% with an average around 75% [15]. Therefore, for 1000 cars h^{-1}, a petrol lead concentration of 0.49 g l^{-1}, fuel consumption of 0.24 l km^{-1}, and for a 75% emission of lead, the source strength is 10 μg s^{-1} m^{-1} [14]. In Los Angeles, for a lead in petrol concentration of 0.56 g l^{-1}, and a 75% emission factor, the total emissions added up to 17.9 t d^{-1}, (0.3 from evaporation, 16.7 as aerosol and 0.9 as organic vapour). The material dispersed by the wind was 5.6 t d^{-1} (5.3 aerosol, 0.3 organic vapour), whereas 11.5 t d^{-1} deposited on the ground, (9.5 nearby and 2.0 further away) [54].

Other aerosol lead sources are, workroom exhausts, e.g. where soldering is carried out, natural weathering and burning of paint, incineration of plastics and the recycling of lead batteries [16].

ATMOSPHERIC LEVELS OF THE HEAVY ELEMENTS

The levels of the heavy elements in the atmosphere are diverse over the earth's surface, depending on the particular environment and prevailing conditions. There are difficulties in comparing results from different studies, because of the factors that can influence the actual level measured. Details of the sampling time, the period over which the mean level was determined, and the year when the work was done are necessary for making any comparisons. The data given in Table 7.5, are for air lead levels for a number of environments, where some of the above details are available, and comparisons can be made.

Levels of Heavy Elements in Urban Aerosol

Much urban aerosol is generated from polluting sources within the urban area. There is a wealth of data on air lead levels, and typical urban air lead levels lie in the range 0.5-2 μg m^{-3}, but approach 10 μg m^{-3} in heavy traffic areas (Table 7.5) [6,17,37,38,42,78,80,81,88,93,95]. The levels closely relate to the combustion of petrol lead, this being the main lead source (~90%) in urban areas. For example in Belgium on traffic free days the air lead levels in urban areas were around 0.6 μg m^{-3} compared with the usual 5 μg m^{-3}. Other environments where alkyllead sources are clearly implicated are in tunnels with air lead concentrations in the range 20-100 μg m^{-3}, close to traffic, (8-40 μg m^{-3}) and close to highways (5-20 μg m^{-3}) [17,78,79,80]. An approximate order of air lead levels in different urban settings are: central business area > heavy density residential > shopping commercial > heavy industrial > central park areas > medium density residential > light traffic residential > open fields. Air lead levels also relate to population densities as shown by the following mean data for USA cities [78]; < 0.1 million people, 1.47 μg m^{-3}; 1-2 million people, ~2.0 μg m^{-3}; and >3 million people, >3 μg m^{-3}.

Other aerosol heavy metal levels have not been as well studied as for lead, cadmium being the next most investigated. Some data for arsenic, cadmium, mercury, indium, antimony and selenium are listed in Table 7.6. The concentrations are generally, 2 to 3 orders of magnitude, less than for lead.

Levels of Heavy Elements in Rural Aerosol

The levels of the heavy elements are significantly less in rural areas, because of the dilution of the urban materials as they are transported away. The heavy element concentrations in rural air in Belgium, given in Table 7.7, were measured at times of low pollution. The background levels were estimated by comparing the measured values with those of sulphur, using the equation,

$$[E] = a [S] + b,$$

where [E] and [S] are the concentrations of the metal and sulphur respectively, at low pollution times, a is the E/S ratio from the correlation coefficient calc-

TABLE 7.5 Some Selected Levels of Lead in the Atmosphere

City	Location	Years	Sampling interval	Level μg m⁻³	Comments
Osaka	Main streets	1955-56	30 min	10.2	
Los Angeles	Freeway	1963-64		8.2-18.3	Mean daily range
Warwick	City centre	1965-66	weekly	2.80-4.46	Monthly means
Palo Alto	Freeway	1966	5 min	1-19	Range during day
Los Angeles	Downtown	1966-75	24 h	5.1, 2.8	Ann. mean 1971 & 76
San Diego	Mission Val.	1969	weekly	2.16-4.61	Quartely means
New York	45th. St.	1969	2 h	9.3	Two hourly means
London, UK	Fleet street	1972-73	24 h	3.3	Daily means
London, UK	Fleet street	1972-73	daytime	6.0	Daytime only
Melbourne	City centre	1974-75	hourly	1.4-3.9	Means 2-7 h
Birmingham	Various	1975	weekly	0.5-1.40	Not exposed to cars
Brisbane	Freeway	1975	24 h	5.17	Mean
London, UK	M4	1978	daytime	8.9	2 m from berm
London, UK	M40	1978	daytime	3.3	2 m from berm
Sydney	Urban	1979	2.5-5 h	2.44	Daytime mean
Los Angeles	Lennox	1979	24 h	0.62-3.91	Monthly means
Christchurch	Urban	1981	2 h	3.3	Daily mean

Source of data; Simmonds et al. 1983 [93].

ulation, and b is the estimated background level. In the rural areas the levels are high compared with remote places, indicating some pollution material was present [86].

On a mass basis the concentration of lead in particles in cities is around 1-10%, which drops to 0.1-1% in rural areas, and still further, to < 0.1%, in remote areas. The fall is due to dilution of the aerosol with other dusts [78]. The air lead levels in northern hemisphere rural areas lie in the range 0.05-0.2 μg m⁻³, whereas in the southern hemisphere the levels are around 0.02 μg m⁻³ [79]. The difference reflects the greater anthropogenic inputs in the north.

Levels of aerosol cadmium in rural areas are generally <1 ng m⁻³ [30,38,77], and the air levels of mercury are reported as; continental air, 20 ng m⁻³, continental shelf air 2.9 ng m⁻³ and oceanic air 0.7 ng m⁻³ [71]. Similar levels of atmospheric arsenic, antimony and selenium are reported in rural areas, i.e. 1.4-3.8 ng m⁻³, 2.4 ng m⁻³ and 1.1-2.6 ng m⁻³ respectively [38].

Levels of the Heavy Elements in Remote Areas

Rural and remote areas merge into each other, and the aerosol levels of some of the heavy elements are given in Table 7.8. The concentration ranges vary considerably, but depend on the closeness of the area to urban, industrial or high emission natural sources.

TABLE 7.6 Levels of Arsenic, Cadmium, Mercury, Indium, Antimony and Selenium in Urban Aerosol

Element	Location	Concentration ng m⁻³	Year Reported	Reference
As	Washington DC	3.2	1986	38
	Portland Or.	5.0	1986	38
	UK cities	6.4	1979	88
	Swansea	15	1974	88
	Toronto	2-20, mean 15	1976	80
	Toronto freeway	2-43, mean 10	1976	80
Cd	Hobart	1-9, mean 3	1977	6
	Urban	2-15, 1-50	1980	77
	UK cities	2.8	1979	88
	Urban	2-370	1974	30
	Bronx, NY	6-22	1974	30
	Cincinnati	80	1974	30
	Chicago	19	1974	30
	Polish towns	2-51	1974	30
	Ann Arbor	100-300	1971	42
	Washington DC	2.5	1986	38
Hg	Long Is USA	2.9	1985	95
	New Zealand	1.15 mean	1985	95
	Toronto	16	1976	80
	Toronto expressway	19	1976	80
	Urban	2-30	1982	62
	Large cities	5-50	1974,75	62
In	Swansea	<0.7	1974	88
Sb	UK cities	7.3	1979	88
	Swansea	2.9	1974	88
	Toronto	0.9-36, mean 8	1976	80
	Toronto expressway	1.6-24, mean 6	1976	80
	Washington DC	2.1	1986	38
	Boston	0.55-40, 0-58, 8.1	1976	53
Bi	L. Michigan	≤0.05-3, mean 6	1971	41
Se	Swansea	2.7	1974	88
	Boston	0.19-9.1, 0-3.8, 1.23	1976	53
	Washington DC	2.4	1986	38
	Portland Or.	3.0	1986	38

Other reference 13.

Lead Lead levels decrease with height into the troposphere, but are reported to increase again in the stratosphere [78]. Remote continental and oceanic levels in the northern hemisphere are reported as 0.5-1.5 ng m⁻³ and 0.2-6.0 ng m⁻³ respectively, in the southern hemisphere the levels are 0.5-5.0 ng m⁻³ and <10 ng m⁻³ respectively, the latter results are from limited data [79]. Lead levels in the Arctic region have been observed to vary with the season, and over different

TABLE 7.7 Levels of the Heavy Elements in Rural Belgium

Element	Average ng m^{-3}	Range ng m^{-3}	Estimated background ng m^{-3}
As	2.3	0.39-5.1	0.7
Se	0.62	0.18-1.21	0.17
Cd	0.78	0.29-1.9	0.37
Sb	1.7	0.42-3.0	1.05
Hg	1.2	0.07-4.1	
Pb	125	54-230	93

Source of data; Priest et al., 1981 [86].

TABLE 7.8 Levels of Heavy Elements in Remote Areas (pg m^{-3})

Metal	Remote (range)	UK Lake	Jungfrau District	Antartica Sum.	Antartica Wint.	Enewetok Dry	Enewetok Wet	Green-land
As	8.4-2300	1990	158	17	8.4			42
Cd	2.5-720	830	332	<200	49	4.6	2.5	15
Hg	600-3400	39	20					
In	0.054-78	22	7	0.19	0.054			
Pb	46-97,000	31,540	2988			130	96	490
Sb	0.45-930	655	133	2.1	0.45	5.2	2.4	
Se	6.3-1400	672	28	6.9	6.3	150	110	

Sources of data; references 6,7,10,13,18,19,22,26,38,62,77,78,88,95,98.

sites the range is 1.7-3.84 ng m^{-3}, with higher levels occurring in the winter months 3.49-6.38 ng m^{-3} [3,50].

At Enewetok in the North Pacific(11°N, 162°E) atmospheric lead levels are 90-260 pg m^{-3}. The lead rich particles are smaller in size than the silicate dust particles, and there is no temporal association between the two particles. This suggests that the lead derives from a source different from the silicate dust, and is probably a continental source [95]. The lead and other heavy elements display a seasonal change (Table 7.8) which is related to the amount of precipitation, the concentrations being less in the wet season [26].

At Te Paki (Nth tip of New Zealand) the rainfall contained 17 pg g^{-1} of lead and was associated with the air flow from the Indian Ocean. In the mid Tasman Sea, however, a level of 490 pg g^{-1} was associated with the air flow from Australia, which fell to 41 pg g^{-1} when the flow swung further south [95]. In remote areas of Tasmania levels of 1-160 ng m^{-3} have been reported [6]. Air lead concentrations in the Himalayas of 110-160 ng m^{-3} are enriched 20 fold, and may arise from open fires [23].

Other elements Over the South Polar regions the concentrations of the elements As, Se, Sb, Cd and In are in the <1 to few pg m^{-3} range [67]. The levels of cadmium

in remote areas are around 3-620 pg m^{-3}, but in areas of high natural sources, such as Mt. Etna, levels in the volcanic plume of 92 ng m^{-3}, and above a hot vent of 30,000 ng m^{-3} have been recorded [77]. Around natural mercury deposits, concentrations of the element in the air are around 30-1600 ng m^{-3}, and at geothermal areas concentrations of 10-40,000 ng m^{-3} are reported [63]. In Norway background levels of some heavy elements (measured at two sites during 1974) were as follows: Hg 20-30,15-31 ng m^{-3}, Cd 20-31, 3-29 ng m^{-3} and Pb 23-31, 3-29 ng m^{-3}. Most of the mercury comes from natural sources, whereas some of the lead and cadmium is anthropogenic. There was a direct relationship between the concentration of Cd and Pb and the wind direction, with the concentrations increasing when the flow was from pollution sources [98]. In remote areas the range of mean concentrations of mercury in aerosols is 0.015-0.4 ng m^{-3}. The total atmospheric levels of mercury fall rapidly with height, suggesting the flux comes from the soil [69]

Industrial Levels of the Heavy Elements

Concentrations of the heavy elements around industrial areas, such as smelters, can reach very high values and, unlike other areas it is not possible to give typical levels. Cadmium levels of around 500, 200, and 160-320 ng m^{-3}, have been reported around Japanese smelters at distances 100, 400 and 500 m away respectively. Around Swedish smelters weekly means of cadmium aerosol levels were 600, 300 ng m^{-3}, at distances 100, 500 m away. A maximum value of 54,000 ng m^{-3} has also been recorded [30].

Levels of mercury around chlor-alkali cell waste ponds were, 18, 64 and 90 ng m^{-3} at temperatures around 6°C, and 991 ng m^{-3} at 29°C. Approximately 2 km away the level had dropped to 3-9 ng m^{-3}. A similar fall off in concentrations was observed at different distances from a coal fired power station as shown by the data in Table 7.9 [63].

A study of the lead levels around a smelter in El Paso (during 1969-1971) indicated that at the smelter's boundary, and downwind, the air lead concen-

TABLE 7.9 Levels of Mercury Associated with a Coal Fired Power Station

Source	Hg vapour in air, ng m-3	Hg aerosol ng m-3	Total particles µg m-3	Hg in solid µg g^{-1}	µg/g particle µg/g coal
Coal				0.28	1
Ash				0.0037	0.01
Plume					
0.25 km	1700	150	3460	43	150
7 km	1000	30	740	40	140
22 km	200	2	95	20	70
Background	12	0.1	17	6	-

Sources of data; Lindberg, 1987 [62] and 1986 [63].

tration was 15-269 µg m^{-3} (annual mean = 92 µg m^{-3}) and this had fallen to background levels 4-5 km away. Later, in1972-1973, the annual mean had fallen to 43 µg m^{-3} after some changes had been made. The concentration of lead was highest in the particles < 1 µm, and 42% of the lead at 250 m from the smelter was < 2 µm. At the smelter the 10 monthly mean for the particulate matter was 204 mg m^{-2} month^{-1} [59].

VARIATIONS IN ATMOSPHERIC LEVELS OF THE HEAVY ELEMENTS

One of the central problems in comparing the concentrations of the heavy elements in the air, determined in different studies, is the variety of factors that influence the levels. Some of the factors can be controlled by the experimenter e.g. position of the sampler, whereas some are outside the control of the experiment e.g. the weather.

Factors Influencing Heavy Element Levels

Some of the factors that have a bearing on the measured level of a heavy element are: height of sampler above ground, distance from the source, distance from buildings, type of sampler, wind speed, wind direction, air temperature, air stability, season, topography, vertical spread of the plume, and in the case of lead arising from petrol; traffic density, date of sampling, amount of lead in the petrol, driving mode, traffic turbulance, bouyancy of the exhaust gases, petrol consumption, age and condition of the car [1,14,15,66].

Models for estimating atmospheric levels take into consideration some of the above factors. One model for the atmospheric concentration of lead is [27];

$$\text{Concentration} = \frac{\text{emission rate}}{\text{mean wind speed} \times \text{vertical mixing height}}$$

Another model, relating to traffic as the source of lead, is [93];

$$\text{Aerosol lead levels} = K\left(\frac{VE}{TSH}\right)D,$$

where K is a constant, V is traffic volume, E is the lead emitted, T is the temperature, S the wind speed, H the mixing height, and D the wind direction factor. It is not possible to produce a satisfactory quantitative model that encompasses all factors.

Seasonal or climatic effects Seasonal variations in heavy metal aerosol concentrations occur, but differ with site, e.g. in New York levels were highest during the fall and spring, whereas in Los Angeles (see Table 7.10) and Boston the highest levels were in the winter. Seasonal variations maybe due to variations in source intensity, climatic variations, scavenging efficiency of precipitation, and temperature inversions [16, 78]. The seasonal pattern of air lead levels in Denver during Jan 72-June 75, was peaks in the summer, with a gradual decrease in levels over the years. The seasonal pattern was related to the lead

TABLE 7.10 Atmospheric Lead Levels in Los Angles (µg m^{-3})

Place		Season		Diurnal	
Downtown	3.0	Summer	1.9	11pm-3am	1.0
Outlying	2.0	Fall	2.8	3am-7am	1.1
		Winter	3.1	7am-11am	1.2
		Spring	2.1	11am-3pm	0.7
				3pm-7pm	0.8
				7pm-11pm	1.1

Source of data; NAS, 1972 [16].

in the petrol, which was at a higher concentration in the summer, and the over all decrease to the introduction of catalysts to cars, which could not use leaded petrol. However, at six sites the plot of monthly mean air lead levels was at a maximum in the winter, when the input from petrol sales were at a minimum. This was due to the mixing heights being lower in the winter (800-1000 m) compared with the summer (2600 m). The dispersion factor, hv, where h is the mixing height, and v the speed of the wind, correlated well with the concentration of air lead (p < 0.001) [27].

Wind speed is a significant factor in determining the atmospheric levels of the heavy elements, whereas air temperature is relatively less important. These factors, and traffic density, are compared with the levels of aerosol lead in Fig 7.9. The dramatic effect of increase in wind velocity on the air lead concentrations is clear from the diagram [93]. However, low concentrations because of the wind, does not mean that the element is not being emitted from the source, but rather it is more rapidly dispersed and diluted [93]. Cadmium levels, on the other hand, 0.0024 µg m^{-3} (urban) and 0.0020 µg m^{-3} (rural), are reported to be less influenced by these factors [72].
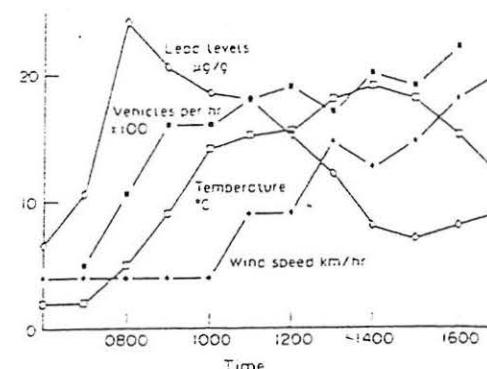

Fig. 7.9 Variation of lead levels with number of vehicles, wind speed, and temperature. Source of data; Simmonds et al., 1983 [93].

Seasonal affects have also been reported for arsenic antimony and cadmium with higher levels in the winter. This is probably due to extra emissions in associated with combustion for heating and production of power [77,88]. However, the reverse seasonal situaton has also been observed, and this may relate to different dispersal modes in the summer and winter [77].

Diurnal variations Diurnal variations correlate with traffic density for lead (Table 7.10, Fig 7.9), and concentrations are also low in the weekends [16,78,93]. In urban and rural areas cadmium levels show diurnal and day to day variations. The reason is due to the variation in source emissions, wind and local ventilation characteristics.

Sampling factors A number of sampling factors influence the observed levels of the heavy elements. Levels of lead in streets vary with height above the ground, e.g. 10.4 μg m^{-3} at 0.3 m, 8.3 μg m^{-3} at 1.5 m and 5.1 μg m^{-3} at 9.2 m [78]. The length of sampling time has a marked effect on what is observed. Short intervals may pick up peak or low emission times that would be missed using longer sampling times [6]. Other factors are; the direction of the wind with respect to the sampler, the distance from the source, the porosity of the filter, and the relation of the sampler to vertical or inclined surfaces that modify air movement [78,93].

The influence of the automobile The concentration of lead in air relates to traffic density and mode of operation. More lead is emitted along highways than in city driving, approximately 20% is emitted in suburban driving, and 200% at full throttle when accelerating to 60 mph. From an analysis of exhaust dust it appears that about 21-28% of the petrol lead is retained in the exhaust system [78, 93, 51]. Both the physical and chemical characteristics of the particulate matter is affected by fuel consumption, engine wear, nature of the engine oil, the exhaust system and air/fuel ratio [78].

In West Germany petrol lead was reduced from 0.6 to 0.4 g l^{-1} in 1972 and then to 0.15 in 1976. The reduction in the lead content by 60% (1976) produced a reduction in air lead by 55-60% in streets carring heavy traffic. For example in Frankfurt the mean air lead was 2.56 μg m^{-3} before reduction in the petrol lead, and 1.04 μg m^{-3} after. However, in streets with lower traffic levels the reduction in air lead was less, around 30%. This may be because of an additional source of lead, but could also be due to the nature of the exponential fall off in lead levels with distance from the source. In the Ruhr area the drop in air lead was only 20%, whereas in the lead mining area, Stolberg, the reduction of lead in petrol had no effect on the air lead levels [56].

THE DEPOSITION OF HEAVY ELEMENT AEROSOLS

Aerosols eventually deposit on the earth, either as a dry deposit or as wet deposit (in rain or snow). The data in Table 7.11 indicates the magnitude of

TABLE 7.11 Wet Deposition for Some Heavy Elements (μg l^{-1})

Element	Marine	Rural	Urban
As	5.8	0.005-4 (0.286)*	0.019
Cd	0.48-2.3 (0.7)*	0.08-46 (0.5)	0.004-0.639 (0.008)
Hg	0.002-3.8 (0.745)	0.005-2.2 (0.09)	0.011-0.428 (0.079)
Pb	5.4-147 (44)	0.59-64 (12)	0.02-0.41 (0.09)
Sb	-	-	0.034

* Values in parenthesis are mean levels. Sources of data; Buat-Mènard and Duce, 1987 [10], Galloway et al., 1982 [33].

deposition levels (in μg l^{-1}) in rain found in different environments.

Deposition Levels

Most information available is on lead, and some data are given in Table 7.12. The deposition is expressed in mg m^{-2} y^{-1}, or μg l^{-1} (for wet deposition), though a number of other units have been used. The deposition levels of lead range from < 5 mg m^{-2} y^{-1} in remote areas, to 25-300 mg m^{-2} y^{-1} in urban areas, and much higher close to lead based industries, and roads busy with traffic. For deposition of cadmium, the bulk precipitate (wet and dry) has a mean concentration of the metal in the wet material of $0.6-37$ μg l^{-1}, with most concentrations around 1-2 μg l^{-1}. In the case of dustfall (dry deposition), concentrations of 13 and 200-1000 μg g^{-1} have been reported [77].

A number of factors influence the level of deposition in any area, such as the locality i.e. remote, rural, urban or industrial. Wet precipitation depends on the existence of rain or snow, the amount, its duration and intensity. The concentration of lead in precipitation decreases with increasing intensity of the precipitation. The rates of deposition of cadmium containing aerosol have increased over the years. This relates to increasing population density, local variations and is a function of land use [77].

Deposition Models

Different models for both wet and dry deposition have been developed. For wet deposition the flux rate is given by,

$$Flux = WRA\left(\frac{C}{\rho}\right),$$

where W is the washout coefficient, R the annual rainfall (m), A the area (m^2), C is the metal concentration in air, and r is the density of the air = 1200 g m^{-3} [78]. Wet deposition is intermittent and the washout factor or scavenging ratio W is given by [10];

$$W = \frac{C_R \cdot \rho}{C_A},$$

where C_R is the concentration of the element in the rain μg kg^{-1}, ρ the density of air, and C_A the concentration of the element in the air, μg m^{-3}. The washout factor

TABLE 7.12 Levels of Deposited Lead Aerosol

Location	Deposition level	Reference
Northern hemisphere	0.8 mg m^{-2} y^{-1}	78
Southern hemisphere	0.4 mg m^{-2} y^{-1}	78
Remote	< 5 mg m^{-2} y^{-1}	78
France, mountains (wet)	9 µg l^{-1}	92
Remote terrestial		
winter snow	0.5 mg m^{-2} y^{-1}	28
summer snow & rain	0.4 mg m^{-2} y^{-1}	28
dry	2.0 mg m^{-2} y^{-1}	28
Remote	0.01-4 mg m^{-2} y^{-1}	17
Rural areas	5-20 mg m^{-2} y^{-1}	78
France, rural (wet)	16 µg l^{-1}	92
Rural	6-34 mg m^{-2} y^{-1}	17
Polluted areas	> 20 mg m^{-2} y^{-1}	78
Paris traffic (wet)	43 µg l^{-1}	92
Urban areas	10-30 mg m^{-2} y^{-1}	28
Urban	25-300 mg m^{-2} y^{-1}	17
France, industrial (wet)	5052 µg l^{-1}	92
Near lead sources	600-6000 mg m^{-2} y^{-1}	17
Near motorway, 0 to 33 m	13.4-0.5 mg m^{-2} d^{-1}	66
	7.1-1.6 mg m^{-2} d^{-1}	66

tends to be greatest for the larger particles [10,89], particularly over land masses, but over remote marine areas (e.g at Enewetok) there appears to be no relationship [10]. The efficiency of the washout of aerosols is given by;

$$\text{Efficiency} = \frac{[M]_{(\text{in unit volume of rain)}}}{[M]_{(\text{in corresponding volume of cloud)}}},$$

where M is the element [10,100].

The velocity of dry deposition (V$_c$) in rural and remote areas is < 1.0 cm s^{-1} (mean is 0.3 cm s^{-1}), but the velocity depends on the particle diameter and wind speed. The flux rate (F) (mg m^{-2} y^{-1}) for dry deposition is given by;

$$V_c(\text{cm s}^{-1}) = \frac{-F(\text{downward flux) mg m}^{-2}\text{ y}^{-1}}{C(\text{airborne conc.) mg m}^{-3}},$$

where C is the metal concentration in the air [10,20,78,89]. In polar regions V$_c$ = 0.5 cm s^{-1}, and over the oceans 0.8 cm s^{-1}. The removal of large particles take place by sedimentation, i.e. gravitational settling, and small particles by diffusional transport and inertial impaction and interception [89]. The model is not adequate if a small fraction of the airborne mass is responsible for the bulk of the deposition. The deposition velocity is a function of the aerosol aerodynamic diameter (the diameter of spherical particles of unit density which behaves like the particle) the wind speed and surface conditions e.g. the roughness. The

deposition velocity of cadmium varies by a factor of 20 because of different size distributions [20].

Dry Versus Wet Deposition

The ratio of dry to wet deposition is controlled by the amount of precipitation, and the dry fraction can vary from 0.2-0.6, or 0.2-0.9, of the total deposition [9,22,33,77,89]. It appears that wet deposition for trace elements is as important, or more so, than dry deposition.

Moss for Detecting Aerosol Fallout

Atmospheric deposition has been measured using the levels of the trace elements accumulated in moss, such as *sphagnum*. For reliable results the site needs to be treeless, ombrotropic (wet and rainy), contain hummocks with as little shrub cover as possible. The deposition rate is given by;

$$R = (CP) - L + U,$$

where R = deposition in mg m^{-2} y^{-1}, C = metal concentration in mg kg^{-1}, P = biomass production in kg m^{-2} y^{-1}, L = leaching of element from the moss, and U = uptake of the element from older organic material. In Europe the annual rate of metal accumulation in *sphagnum* mosses is 2.1-63 mg m^{-2} y^{-1} [35]. The reproducibility of the method for Pb (59.3 µg g^{-1} d^{-1}), and cadmium (2563 ng g^{-1} d^{-1}), is demonstrated by the coefficients of variation of 16.7% and 16.3% respectively. By using a network of bags it is possible to build up contour diagrams of equal concentrations of the elements in any area [64,96].

Fallout From Automobiles

Numerous studies have been carried out on the deposition of lead around roadways from automobiles. The following data (in mg m^{-2} d^{-1}) clearly shows a fall off in the deposited lead with distance from the road.

Central reserve	2	8	18	33 meters
13.40	5.20	2.91	1.00	0.52
7.05	7.36	5.58	2.82	1.61

A deposition rate of >3.3 mg m^{-2} d^{-1} is considered excessive for residential areas. This is not normally encountered at more than 15 m from the road [66]. Approximately 10% of the lead emitted from a car at cruise speeds is deposited within 100 m of the road, when there is no intercepting surfaces. The fall in atmospheric lead concentrations with distance from the road is in part due to deposition and in part due to the upward movement of the plume. The large particles deposit close to the road (> 90% within 1.5 m when the size >5 µm) [15].

HEAVY ELEMENT SPECIES AND REACTIONS IN THE ATMOSPHERE

The identification of the chemical forms of the trace elements in aerosols is a difficult problem, because, for most methods available for solids, relatively high concentrations of the species are required. The instrumental methods employed are the scanning electron microscope, electron microprobe and XRD. The first two methods are only useful for particles >0.5 μm, though the transmission electron microscope can be used on particles down to 0.1 μm. In the case of XRD only crystalline materials are observed and each species needs to be >5% in concentration [46].

Lead Species

Automobile lead Most work has been done on lead species, because of the high levels of lead in the particulate matter. The list of lead compounds reported in aerosols from a variety of sources is given in Table 7.13 [78]. The actual lead compounds in a particular aerosol will depend on other constituents in the atmosphere, and the age of the aerosol. The primary material from the exhausts of motor cars is mainly $PbClBr$ (when both CH_2Cl_2 and CH_2Br_2 are used in the petrol). However, PbO, $Pb(OH)X$ ($X = Cl$, Br), and some $PbSO_4$, $Pb_3(PO_4)_2$, $PbO \cdot PbSO_4$ and Pb may also occur in the larger particles, whereas in the smaller particles α and $\beta NH_4Cl \cdot 2PbClBr$, $2NH_4Cl \cdot PbClBr$ are found. When phosphorus is present in petrol the compound $Pb_5(PO_4)_3(Cl,Br)$ may form. [5,43,46,47,51,78]. Some organolead compounds, such as R_4Pb and R_3PbCl are also emitted. A

TABLE 7.13 Lead Species in Aerosols

Source	Lead species in aerosols
Automotive	$PbCl_2$, $PbBr_2$, $PbClBr$, $Pb(OH)Cl$, $PbCl_2 \cdot PbClBr$, $PbO \cdot PbBr_2$, $PbO \cdot PbClBr$, $PbO \cdot PbCl_2$, PbO, $PbSO_4$, $PbO \cdot PbSO_4$, PbP_2O_7, $Pb_3(PO_4)_2$, $Pb_3(PO_4)_2 \cdot PbClBr$, $Pb_5(PO_4)_3(Cl,Br)$, $Pb_4O(PO_4)_2$, $2NH_4Cl \cdot PbClBr$, $\alpha NH_4Cl \cdot 2PbClBr$, $PbCO_3$, $(NH_4)_2ClBr \cdot 2PbClBr$, $\beta NH_4Cl \cdot 2PbClBr$, $PbO \cdot PbCO_3$, $(PbO)_2 \cdot PbCO_3$
Mining activities	PbS, $PbCO_3$, $PbSO_4$, $Pb_5(PO_4)_3Cl$, $PbS \cdot Bi_2S_3$, PbO, Pb-silicates
Base metal smelting and refining	Pb, PbO, $PbCO_3$, $PbSO_4$, $PbO \cdot PbSO_4$, $(PbO)_2 \cdot PbCO_3$, Pb in metal oxides, Pb-silicates, PbS
Coal-fired power stations	PbO, $Pb(NO_3)_2$, $PbSO_4$, $PbO \cdot PbSO_4$, surface sorbed material $PbCl_2$, PbS, Pb
Cement manufacture	$PbCO_3$, $Pb_5(PO_4)_3Cl$
Fertilizer production	$PbCO_3$, PbO, $Pb_5(PO_4)_3Cl$
Ferroalloys	Pb, Pb-alloy particles
Lead products	Including lead arsenate, antimonate, chromate, cyanamide, iodide, fluorosilicate, molybdate, nitrate, selenide, silicates, titanate, vanadate

Sources of data; Harrison, 1986 [43], Nriagu, 1978 [78], Pacyna, 1987 [83].

study of the main crystalline lead compound in the primary lead aerosol was found to be the solid solution $PbBr_{1.4}Cl_{0.6}$, based on the unit cell dimensions [93]. From the speciation results given in Table 7.14, it is clear, that the proportion of halogen containing compounds decrease with time and distance, while there is a corresponding increase in the oxy-compounds. There is a close similarity between the lead species in the aerosol collected directly from the exhaust, and collected near the road, also there is a similarity between aged aerosol and aerosol collected some distance from the roadside (Table 7.14) [57]. The principal components in aged vehicle aerosol are oxy-lead species, $PbCO_3$, $(PbO)_2 \cdot PbCO_3$, $PbSO_4 \cdot (NH_4)_2SO_4$ and PbO and $PbSO_4$ (a total of about 80%) [43,78,97].

Smelter lead The lead species from smelters are similar to aged automobile aerosol (cf. Table 7.13) [78,83]. Particulate materials from smelters contain PbS (from the primary ore), $PbSO_4$, and $PbO \cdot PbSO_4$ (both from the sintering of the PbS ore) in the stack and in the ambient and internal atmospheres. Lead oxide comes from oxidation of Pb during smelting, and the metal from reduction of compounds added to sawdust [43]. The lead species, in the stack emissions from a primary lead / zinc smelter, identified using XRD, differ in form depending on the position of the samples in the stack. For different positions the species were; (a) $PbSO_4$, $PbO \cdot PbSO_4$, (b) PbS, (c) PbO, Pb, and (d) CdO. Outside the smelter the aerosol lead species varied with the size, as follows; PbS, $PbSO_4$ in >7 μm particles, PbS, $PbSO_4$ in 3.3-7 μm particles, and $PbSO_4$ in 2-3.3 μm particles [45].

Reactions of lead species In a study [43,47] of the chemistry of $PbClBr$ the following chemical processes were identified;

$$PbClBr \xrightarrow{hv \text{ (natural)}} \text{ no reaction,}$$

$$PbClBr + SO_2 \rightarrow \text{ negligible reaction,}$$

$$PbClBr + NH_3 + H_2O \rightarrow Pb(OH)Br + \text{ other products,} \atop \text{slow reaction}$$

$$2PbClBr + 2(NH_4)_2SO_4 \rightarrow PbSO_4 \cdot (NH_4)_2SO_4 + (NH_4)_2BrCl \cdot PbClBr, \atop \text{main product}$$
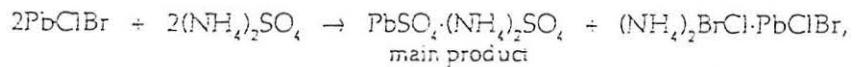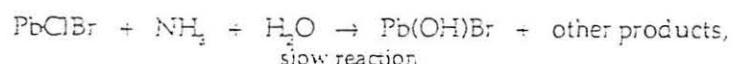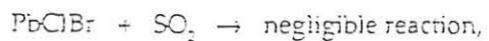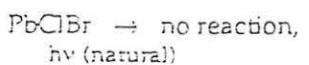
The last reaction, proceeds in moist air, and is the principal one because ammonium sulphate is a major component in aerosols. In addition the reactions;

$$PbClBr + H_2SO_4 \rightarrow PbSO_4 + HCl + HBr$$

$$6PbClBr + 2NH_4HSO_4 \rightarrow 2PbSO_4 + \alpha NH_4Cl \cdot 2PbClBr + NH_4Br \cdot 2PbClBr + HCl + HBr$$
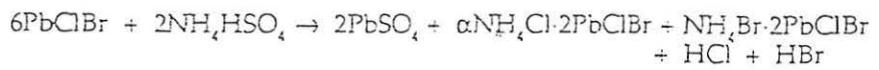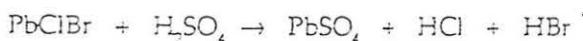
TABLE 7.14 Lead Compounds in Automobile Exhaust Material

|	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Exhaust gas														
0 h	10.4	5.5	32.0	7.7	2.2	5.2	1.1	31.4	1.2	-	2.2	1.0	-	0.1
18 h	8.3	0.5	12.0	7.2	0.1	5.6	0.1	1.6	13.8	-	21.2	29.6	0.1	-
Near a busy road														
Near	11.2	4.0	4.4	4.0	2.0	2.8	0.7	2.0	15.6	0.2	12.0	37.9	1.0	2.2
400 y	10.5	0.7	0.6	8.8	1.1	5.6	0.3	0.6	14.6	0.3	25.0	21.3	4.6	6.0
Rural	5.4	0.1	1.6	4.0	-	1.5	-	1.0	30.2	-	20.5	27.5	5.0	3.2

Where 1 = $PbCl_2$, 2 = $PbBr_2$, 3 = $PbClBr$, 4 = $Pb(OH)Cl$, 5 = $Pb(OH)Br$, 6 = $(PbO)_2 \cdot PbCl_2$,
7 = $(PbO)_2 \cdot PbBr_2$, 8 = $(PbO)_2 \cdot PbClBr$, 9 = $PbCO_3$, 10 = $Pb_3(PO_4)_2$, 11 = PbO_2, 12 = $(PbO)_2 \cdot PbCO_3$,
13 = $PbO \cdot PbSO_4$, 14 = $PbSO_4$. h = hours, y = yards. Source of data: Servant, 1986 [92].

occur whereby bromine is lost from the aerosol [43,47,93]. The lead halides in the atmosphere are said (in contrast with above) to be photochemically decomposed liberating free dichlorine and dibromine [0519]. The lead halides (e.g. PbClBr), react with acid sulphates and nitrates also forming the dihalogens and HX. Many of these reactions reduce the Br/Pb ratio in the aerosol [44]. When heated in air to 250° C the PbClBr compound showed no change, but at 400° C PbO and Pb_2O_4 were formed [93].

Tetraalkyllead compounds react in the atmosphere with ozone and the radcals ·O and ·OH, and are photoreactive [24,43].

e.g. $(CH_3)_3PbCH_3 + \cdot OH \rightarrow (CH_3)_3PbCH_2 + H_2O.$
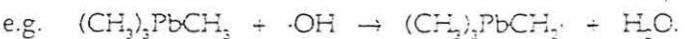
The Pb-C bond can be broken [43], producing other members of the organolead species, as well as inorganic lead.

$$2R_3PbX \rightarrow R_2PbX_2 + R_4Pb,$$

$$2R_2PbX_2 \rightarrow R_3PbX + RX + PbX_2.$$
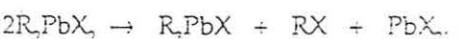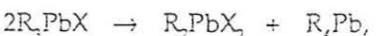
Species for Other Elements

Much less is known about the species of the other heavy elements in aerosols, mainly because of their low concentration, making it difficult to identify the compounds. The cadmium species in aerosols are probably Cd, CdS, CdO, $Cd(OH)_2$ and mixed oxides with copper and zinc [77,83]. From smelters there is evidence that the oxide CdO occurs in the stack, and CdO, Cd and $Cd(OH)_2$ have been identified in the internal atmosphere [43,55]. Cadmium dichloride may also form during the incineration of refuse [83].

Mercury in the vapour state, which may be >90% of the total atmospheric mercury, is most likely to be Hg, $HgCl_2$, CH_3HgCl, $(CH_3)_2Hg$ and other

organomercury compounds. Elemental mercury may account for 50% of the volatile species [43,71,83].

The major chemical species for arsenic are As, As_2O_3, As_2S_3 and organoarsenic compounds from combustion and metallurgical processes. Also, because of the possibility of chlorides in refuse, incineration could produce volatile $AsCl_3$ [83].

Solubility of Aerosols

The solubility of the heavy elements in aerosols in water, such as in precipitation, will influence the reactivity of the elemets in the air. The solubility of lead aerosols is reported as being around 50-90% in water, whereas for deposited dust it is <1% [78,92]. Lead species are relatively soluble in wet samples, but are less so (<10%) in dry samples [34]. Cadmium aerosols are relatively soluble in water and acids, so that as much as 30 to 95% of the metal will be in solution in precipitation. Cadmium is reported to be more concentrated on the surface of particles produced by combustion. The ratio of surface to bulk levels of cadmium in aerosols is ~30, and this may be why its solubility is high [77]. In general, particulate cadmium is more soluble than particulate lead [34], and both their solubilities increase with decrease in particle size [88].

SOURCES OF THE HEAVY ELEMENTS IN AEROSOLS

A number of ways have been developed to determine the source of the elements in aerosols. The methods fall into three main categories, (a) calculation of enrichment factors and relating these to sources, (b) direct measurement, such as historical changes, and (c) determination of the composition of source receptors and the relation of these to the sources by use of techniques such as a chemical element balance.

Enrichment Factors

Relative enrichment of the elements The calculation of enrichment factors (EF) for some heavy elements in aerosols produced the order Se > Pb > Sb > Cd for the elements with the EF > 1. The factors are calculated with reference to elements, such as Al, Ce, Fe, Si and Ta [13]. Another measure is the mobilization factor (MF), which is the ratio of emissions from human and natural sources. The order in this case is Pb > Sb > Cd > As, Se > Hg. A study of historical samples gives the orders Pb >> As > Cd > Se and Sb > Pb > Cd. A summary of these results, for low, moderate and high enrichments, is given below indicating a good level of consistency [33,61,88].

Factor	Low	Mod.	High	No data
Mobilization	Hg	As, Se	Cd, Pb, Sb, Se	Te, Tl
Enrichment			Cd, Pb, Sb, Se	Te, Tl, Hg, As
Historical		Se	Cd, Pb, Sb, As	Te, Tl, Hg

Another measure is the 'human activity' factor (similar to the mobilization factor) which is the ratio of the concentrations of a particular element in urban to remote areas, or rural to remote areas. The order is Pb (489, 128) > As (305, 15) > Cd (88, 66) > Hg (9.4, 1.1). The values for mercury are low because of inefficient collection in wet deposition, and there are insufficient data for Sb, Se, Te, and Tl [33].

In remote areas the order of enrichment factors, calculated with respect to aluminium, are Se > Cd > Pb > Sb > As, (EF's range 3500-49) [18,104,107]. The volatile elements appear to be under-estimated. The enrichment can not be entirely accounted for by crustal dust, sea spray and meteoritic dust. However, volcanic dust appears to be significant. In the Antartica the enrichment of As and Se (and Sb, In) increased in 1975, a few weeks after the eruption of Mt. Ngauruhoe in New Zealand [18]. The selenium and antimony levels in the air at Heimaey (Iceland) were elevated after the 1973 volcanic eruption. Both elements were enriched in the aerosol, lava ash, and fumerole deposits, and for two aerosol samples, the enrichments, relative to crustal aluminium, were Se 6200 and 21,600, and Sb 97 and 115. These factors are similar to what was found at Kilauea 1400-36,000, 17000, Sth pole 18,000, 1300, and Nth Atlantic 10,000, 2300 for Se and Sb respectively. This suggests that volcanoes may be a significant source of both metals [67,73]. In the Nth. Atlantic aerosol the enrichment factors for Cd 730, Pb 2200, Sb 2300 and Se 10,000 (GM) are greater than expected from crustal weathering and from the oceans. It is suggested, however, that the enrichment has a natural origin, and arises from the volatility of the elements and their compounds. This is based on the similarity of the enrichments in the Nth. Atlantic with those at the Sth Pole, as it was suggested that not all of the material from the north would get to the south, because of losses by precipitation [25]. However, it is not so much the amount that is transported that is important, but the concentration, and this could well increase with movement from the north to the south, because of the increase in the proportion of small particles during transport.

The EF's in urban air, such as in Toronto, are as follows: As 260, Hg < 6300, Sb 1300 and Pb 2500 [80]. The heavy metal enrichment factors in dry deposition, suspended particles and rainwater, generally increase in the orders portrayed by the data in Table 7.15 [38,107]. Greater enrichment occurs in the wet deposition, which may be because the finer particles tend to be removed by rain and these generally have the higher concentration of the heavy elements. Around a chemical factory using antimony, its EF is elevated compared with other elements: Sb 20,000, As 200, Se 4000, Hg 500, Cd 400, Pb 2000 and Bi 200 [75].

The estimated EF's for some heavy elements measured in the air at Enewetok in the North Pacific, with respect to crustal Al, and to Na (in sea water) are given in Table 7.16. The factors for selenium and lead have also been estimated with respect to the size of the particles, and the results are listed in Table 7.17. Lead is enriched relative to the crust and seawater but in the dry season in the size range 1.5-3.0 μm the EF tend towards the crustal level,

TABLE 7.15 Enrichment Factors in Different Portions of Urban Aerosols

Element	Dry Deposition	Suspended Particle	Rainwater*
In	3.4	16	10
As	24	100	800
Sb	380	580	970
Se	170	1400	4700

* also contains fine particles. Source; Gordon, 1986 [38].

TABLE 7.16 The Enrichment Factors for some Heavy Elements at Enewetok

Elements	Dry season	Wet season	All
Se	3700 (8300)*	48,000 (8000)	23,000 (8200)
Cd	75 (71,000)	180 (10,000)	130 (41,000)
Sb	29 (39)	180 (27)	93 (34)
Pb	11 (23,000)	110 (30,000)	40 (26,000)

* EF's in parenthesis are with respect to sodium (seawater)
Source of data; Duce et al., 1983 [26].

TABLE 7.17 Enrichment Factors for Se and Pb with Respect to the Size of the Aerosol

| Element | Sizes | | | | | |
	7.4	3.0	1.5	0.95	0.49	<0.49 μm
Se (D)*	1900*	2400	2800	7900	4700	4600
	640ᴷ	5500	15000	30000	55000	130000
Se (W)**	32,000	32,000	57,000	75,000	66,000	37,000
	870	5600	32,000	48,000	99,000	18,0000
Pb (D)	23	4.9	4.6	15	40	-
	5500	10,000	28,000	14,0000	56,0000	-
Pb (W)	360	35	70	210	810	-
	6600	17,000	64,000	22,0000	19,00000	-

* dry season, ** wet season, ' EF with respect to Al, ᴷ EF with respect to Na. Source of data; Duce et al., 1983 [26].

indicating that some factor is masking the anthropogenic inputs. Selenium is very enriched, especially in the size range 1-3 μm. The size distribution is bimodal suggesting multiple sources [26], and it is very likely that volcanic activity is contributing to the high enrichment factors.

Enrichment of lead Enrichment factors are high for lead in remote places e.g. 130-3500 in polar and oceanic regions. They are generally lower over the oceans compared with land. The factors are around an order of magnitude greater than enrichments attributable to soil (~1), fuel combustion (~9) and volcanic sources (~60-100). Relative to titanium the EF of lead in Greenland aerosol (1979-1981) was 122-1330, and bromine was also highly enriched, 2000-7000, [48,49] suggesting that the high enrichments are from lead bromide emissions from cars. Approximately 10 times more lead has been found in precipitation compared with what was measured in the air. This may be because the small particles which are lead rich, are missed in air sampling, i.e. they would go through the filter, whereas precipitation removes a greater proportion of the small particles. Levels of lead in snow have increased 300 times over 300 years, and concentrations today, are around 50 times more than would be expected from air lead levels, suggesting an efficient removal of the lead particles by the snow [76,90].

Another indicator for lead sources is the bromine to lead concentration ratio. The [bromine]/[lead] ratio may be used because of the addition of CH_2X_2 ($X = Cl$, Br) to petrol to scavenge the lead. Ratios are often <0.386 (the value expected from petrol lead) because of loss of volatile bromine compounds, loss of bromine by reaction in the atmosphere, other sources of lead, some lead emitted as organolead, aged particles containing re-entrained dust, over compensation for marine bromine, loss during storage and analytical errors, especially bromine loss during XRD analysis [44]. The bromine loss can be as much as 53%, with a mean of 36% [68]. On the other hand, the ratio may be high, because of the lead retained in the exhaust system relative to bromine, evaporation of ethylenedibromide, analytical errors, inadequate correction for other sources of bromine including agriculture, industrial and coal burning sources. Near industrial sources of lead the ratio can be less than 0.1 [44]. The [Br]/[Pb] ratio 200 m from a lead smelter at El Paso was 0.016, which rose to 0.385, 5-6 km away, the ratio expected for automobile lead [59]. In another example, sampling for lead and bromine two hour intervals revealed a concentration profile which was the same for each element, suggesting a common source, and probably the automobile [103]. Seasonal variations in the lead levels in the Arctic, with a peak around late Jan and Feb suggests an anthropogenic source, which was confirmed by the bromine levels having a similar seasonal profile [3]. A similar association is found for Greenland aerosol (1979-1981) [48,49].

Direct Measurement

Frequently direct measurement of the levels of the heavy elements in aerosols enables identification of the source of the heavy element. For example seasonal changes in levels point to a source as discussed above for lead [3,48,49]. Some of the air lead in New Zealand comes from Australia, and this is seen from the relatively high level of lead in the Tasman Sea (490 pg g^{-1}), when the air flow came from Australia [95].

Historical changes in emissions help in identifying sources of the heavy elements. A decrease in lead emissions from smelting has occurred over recent years even though the amount of lead smelted has increased. This has, however, been offset by petrol lead emissions. The data in Table 7.18, for estimated aerosol lead emissions and the lead levels in air and snow, show the relationship between the quantites of lead smelted and emitted and the environmental levels. The last two columns of the table may be compared directly, if it is assumed that the lead in the snow contains a constant proportion of the aerosol lead. It appears that the increase in the environmental lead since 1933 has been mainly due to petrol lead emissions [74]. Virtually all present day lead that is in excess over natural in the Arctic and Antarctic is due to anthropogenic sources, as shown from historical trends in concentrations, mass inventories and measurement of lead in volcanic plumes [76].

A sampling time of two hours allows for the resolution of changes in sources over time. For example, in a study it was found that on certain days the lead and bromine concentration profiles differed from each other, whereas the profiles for the elements Pb, Hg, Sb, As, In and Se were similar. This indicated a source of lead different from automobiles. The results were also found to relate to the direction from which the wind blew [103].

A comparison of the levels of lead in air, rain and rocks, has provided the suggestion that some part of the metal in the air has come from volatilization from the earth's surface [36]. Lead isotopes may also be used to identify the lead source because ^{210}Pb only forms in the air from ^{222}Rn. The isotope ^{222}Rn emanates from the earth and in the atmosphere decays to give ^{210}Pb (^{222}Rn ($t_{1/2} = 3.8$ d) $\rightarrow$ ^{210}Pb ($t_{1/2} = 22$ y)). The lead has a mean lifetime in the air of 5 days, not long enough for much of the lead isotope to have decayed to ^{210}Po. Therefore the activity of ^{210}Pb in aerosols is a guide to its source. At Enewetok a relationship exists between the ^{210}Pb activity and the aluminium concentration in the dust flux from Asia, indicating the same source [99].

TABLE 7.18 Historical Trend in Lead Emissions and Environmental Lead

Date	Pb smelted 10^4/y	% in aerosol	Pb aerosol from smelting 10^3/y	R Pb burned 10^5/y	% in aerosol	Pb aerosol from R.Pb 10^3/y	Total Pb aerosol 10^3/y	Pb pg g^{-1} in snow
1753	1	2	2	-	-	-	2	0.01
1815	2	2	4	-	-	-	4	0.03
1933	16	0.5	8	0.1	40	4	10	0.07
1966	31	0.06	2	3	40	100	100	0.2

Source of data; Murozumi et al., 1969 [74].

Source Receptor Models

The third method of locating the source of the heavy elements in an aerosol sample is comparing the elemental composition of the source and receptor. Some of the methods used are, pairwise comparisons, chemical element balances, cluster analysis, dendograms, principal component and factor analysis [11,57,58,75,84,87]. The methods of factor analysis and chemical element balances are the most commonly used, and are based on multi-element analytical results on aerosols and sources. The results reported here are just for the heavy elements, and mainly lead, but normally many other elements are considered in the analyses.

Factor analysis results By the use of factor analysis, the main sources of lead in Greenland aerosol were estimated to be combustion, engine exhaust, and to a lesser extent metal sources [48,49]. From a factor analysis of Boston aerosol it was found the main sources of selenium in urban areas were: oil > soil > road dust; and in suburban areas: soil > road dust. For antimony in urban areas the main sources were: refuse > soil = road dust, and in suburban areas: road dust > refuse > soil. There is reasonable agreement between the predicted and observed levels of the elements as shown by the data in Table 7.19 [2,53].

Chemical element balance results In determining the source of trace elements in aerosols, the chemical mass balance method assumes that the unique trace element content of a source can be used as a tracer for the presence of that source in the aerosol. The equation is:

$$x_{ij} = \Sigma \alpha_{ik} a_{ik} m_{kj}$$

where x_{ij} = concentration of ith element in the jth aerosol sample, α_{ik} = coefficient of fractionation (due to settling) between source and receptor (often neglected, or taken as 1, i.e. no fractionation, which is unlikely to be correct), a_{ik} = concentration of ith element in the kth source, and m_{kj} = fraction of particles from the kth source in the jth aerosol. If there are more sources than elements analysed, or if sources can not be identified on the basis of their chemical composition then the number may be reduced using principal component analysis [11,52,58].

The sources of lead in the fine aerosol collected in Houston Texas, were 8% from a tetraethyllead plant, 29% from a steel mill and 60% from mobile sources, such as cars [11]. In a different study in a different environment, the lead sources in aerosol at E. Helena are estimated to be: road and soil dust 18.5%, blast furnace 26%, fugative emissions 35.3%, copper kiln, 0.6%, ZnO materials 9.4%, slag pouring, 2% and motor vehicles 3.8% [52]. In the case of Los Angeles aerosol the sources considered were sea salt, soil and dust, auto exhaust, fuel oil, fly ash, portland cement and tyre dust. The lead in the aerosol was 3.3% by mass, and came from auto exhaust [31]. For the fine particle emissions 83% of lead was said to arise from car exhausts, and 9% from re-suspended road dust [12].

TABLE 7.19 Sources of Selenium and Antimony in Boston Aerosol (ng m⁻³)

Element	Soil	Oil combust.	Refuse inciner.	Marine	Motor vehicle	Road dust	Predicted	Observed
Suburban								
Se	0.5	0	0.02	0	0.09	0.4	1.1	1.3
Sb	0.4	0.2	1.6	0	0.3	2.6	5.1	6.3
Urban								
Se	0.3	0.6	0.08	0	0	0.2	1.1	1.2
Sb	2.6	0.7	4.7	1.7	1.1	2.6	13	15

Source of data, Alpert and Hopke, 1980 [2].

The aerosol in Washington DC was investigated using the method of chemical element balance. The range of levels of some elements in the aerosol were (in ng m⁻³): Pb 82-5800, Se 1.6-10.1, As 0.82-14.7, Cd 0.81-7.0, Sb 1.75-26. The sources investigated were soil, marine, coal, oil, refuse, motor vehicles and the results are listed in Table 7.20. These indicate that the main sources are; Cd and Sb from refuse, As and Se from coal, and Pb from motor vehicles. There are limitations in the method, as Se, Cd and Sb are not completely accounted for, as

TABLE 7.20 Sources of the Heavy Elements in Aerosol from Washington DC (ng m⁻³)

Metal	Soil	Marine	Coal Comb.	Oil	Refuse Inciner.	Motor Vehicles	Predicted	Observed
Pb	0.23	<0.001	2.9	0.86	81	1300	1380	1400
As	0.09	<0.001	4.4	0.061	0.24	-	4.8	5.7
Se	0.001	<0.001	1.1	0.076	0.037	-	1.2	3.5
Cd	0.002	<0.001	0.19	0.006	1.5	-	1.7	3.5
Sb	0.012	<0.001	0.18	0.015	2.1	-	2.3	9.7

Source of data; Kowalczyk et al., 1978 [57].

TABLE 7.21 Sources of the Heavy Elements in Aerosols*

M	Soil	Limestone	Coal Comb.	Oil	Refuse Inciner.	Motor vehicle	Marine	Predicted	Obs.
As	0.061	0.002	3.1	0.028	0.10	-	0.0001	3.32	3.25
Se	0.0009	0.0002	0.78	0.035	0.016	0.035	0.0001	0.87	2.5
Cd	0.0011	0.0001	0.13	0.0028	0.064	1.03	<0.0001	1.80	2.4
In	0.7	0.1	2.3	<0.1	2.4	-	0.4	5.9	20
Sb	0.0081	0.0004	0.13	0.007	0.89	0.60	<0.0001	1.6	2.1
Ba	7.1	0.02	4.7	2.0	0.30	6.4	0.0006	21	19
Pb	0.15	0.019	2.1	0.39	34	428	<0.0001	465	440

* Concentrations ng m⁻³, except for indium pg m⁻³. Source; Kowalczyk et al., 1982 [58].

seen by comparing the last two columns of the table. It is possible, that because of the volatility of these elements, some fraction of them had been missed. Other factors that may influence the results are; that cement was not used as a source, there is a wide varibility in the trace element composition of oils, it is assumed that all the particles leaving the source reach the receptor, and it is possible that some fractionation of the elements that derive from soil had taken place [57,107]. The results of another analysis are given in Table 7.21. Again the predicted and observed levels of selenium are not in agreement [57,58,138]. The contribution of the sources to all sampling sites (i.e. average of each site) is for urban sites, in $\mu g\ m^{-3}$, soil 16.2, limestone 1.8, coal 4.3, oil 0.39, refuse 0.65, motor vehicles 4.8, marine 0.69 (total 28.9), and for rural sites soil 10.7, limestone 1.6, coal 2.5, oil 0.19, refuse 0.42, motor vehicles 2.7, marine 0.54 (total 18.6) [58]. From another study it was estimated that the aerosol arises from car emissions, 20%, from fuel and fly ash, 1-2%, and from soil and road dust 20-50%. Most cadmium comes from stationary sources and industrial processes [12].

Pattern recognition and construction of dendograms have been used to identify sources of lead and cadmium in desert aerosol. It appears that they have not come from the soil, but from some long range source such as combustion and transport emissions [32].

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