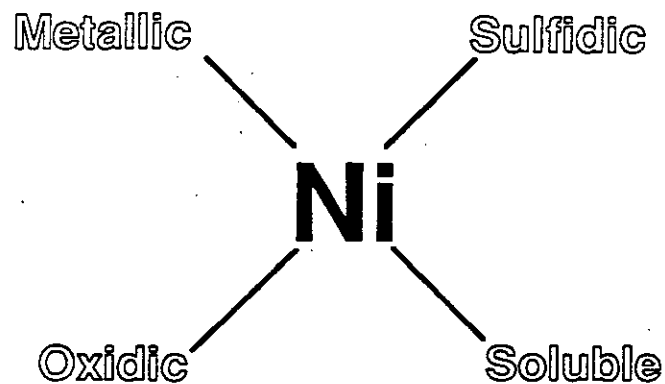


INITIAL STATEMENT OF REASONS FOR RULEMAKING

**PROPOSED IDENTIFICATION
OF NICKEL
AS A TOXIC AIR CONTAMINANT**



TECHNICAL SUPPORT DOCUMENT

Part A

State of California
Air Resources Board

June 1991

INITIAL STATEMENT OF REASONS FOR RULEMAKING

TECHNICAL SUPPORT DOCUMENT

PART A

PUBLIC EXPOSURE TO, SOURCES OF, AND ATMOSPHERIC FATE OF NICKEL
IN CALIFORNIA

REPORT TO THE AIR RESOURCES BOARD ON NICKEL

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June 1991

(This report has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflects the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.)

Public Exposure to, Sources of, and Atmospheric Fate of Nickel in
California

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INTRODUCTION

The purpose of this report is to evaluate the exposure to nickel in California. Throughout this document, if not otherwise indicated, the word "nickel" refers to metallic nickel and inorganic compounds of nickel, and the words "nickel compounds" refer to inorganic compounds of nickel. The report examines the status of nickel with respect to estimated population exposure, ambient and indoor concentrations, uses, sources, emissions, chemical properties, and atmospheric persistence. This information, together with the health assessment report (Part B), will be used to decide whether metallic nickel and inorganic compounds of nickel should be identified as toxic air contaminants.

Nickel is present in many forms including soluble and insoluble compounds. Human epidemiology has shown that nickel sulfate and combinations of nickel oxides are carcinogens in humans. Several nickel compounds are genotoxic or carcinogenic in animals.

Nickel concentrations are monitored at the ARB's 20-station toxic air contaminant network sites. Analysis of samples taken for 1985-1986 show approximately 20 million people (about 70 percent of California's population) were exposed to an average ambient concentration of 7.3 ng/m³ nickel.

Tobacco smoke is the main source of indoor exposure to nickel although wood smoke and suspended soil particles are other sources of indoor exposure. Although nickel is present in mainstream smoke, sidestream smoke is the significant source of indoor exposure to nickel. The ARB has research underway to investigate the exact contribution of tobacco smoking to indoor air nickel concentrations.

The major source of ambient nickel emissions in California is fossil fuel combustion. Minor sources include: asbestos mining and milling, secondary smelting, municipal refuse and sewage sludge incineration, electroplating, and cement manufacturing. These minor sources could contribute to higher near source exposures to nickel. The total nickel emissions from stationary sources are estimated to be 18 to 353 tons per year; mobile sources are estimated to contribute approximately 5.4 to 7.2 tons per year of nickel.

Atmospheric nickel emissions originate from natural (16-36 percent) and anthropogenic sources (64-84 percent). Natural sources of nickel are windblown dusts and volcanic eruption. No information is currently available about the chemical transformations of nickel and its compounds in the atmosphere.

II. PRODUCTION, USES, AND EMISSIONS

A. PRODUCTION

Nickel is a commercially important metal because of its resistance to corrosion in air and aqueous environments (U.S. EPA, 1984).

In 1986, the U.S. imported 140,000 tons of nickel and exported 3,000 tons. Figure II-1 shows that the production, use, import and export of nickel fluctuated from 1976 through 1984 and appeared to decline from 1984 through 1986. Total domestic production was 42,300 tons (U.S. DOI, 1987). The use of nickel was calculated from the sum of reported primary and secondary nickel consumption given in the Mineral Commodity Summaries.

The production of nickel in the United States is referred to as either primary or secondary depending on the source of the raw material (U.S. EPA, 1984), as described below.

1. Primary

Primary nickel is produced by the mining and smelting of nickel ores, the refining of foreign matte, or the recovery of nickel as a co-product of copper refining. Matte can be defined as an impure metallic sulfide product obtained from the smelting of sulfides of metal ores such as copper, nickel, and lead (U.S. EPA, 1984). The last mine and smelter of domestic nickel ore in the United States, Hanna Mining and Nickel Smelting Company, closed its facility near Riddle, Oregon in May 1986 (U.S. DOI, 1987). According to INCO Ltd, the Hanna's facilities in Oregon was reopened in 1989. The smelter is currently processing ore that was stockpiled prior to closure in 1986.

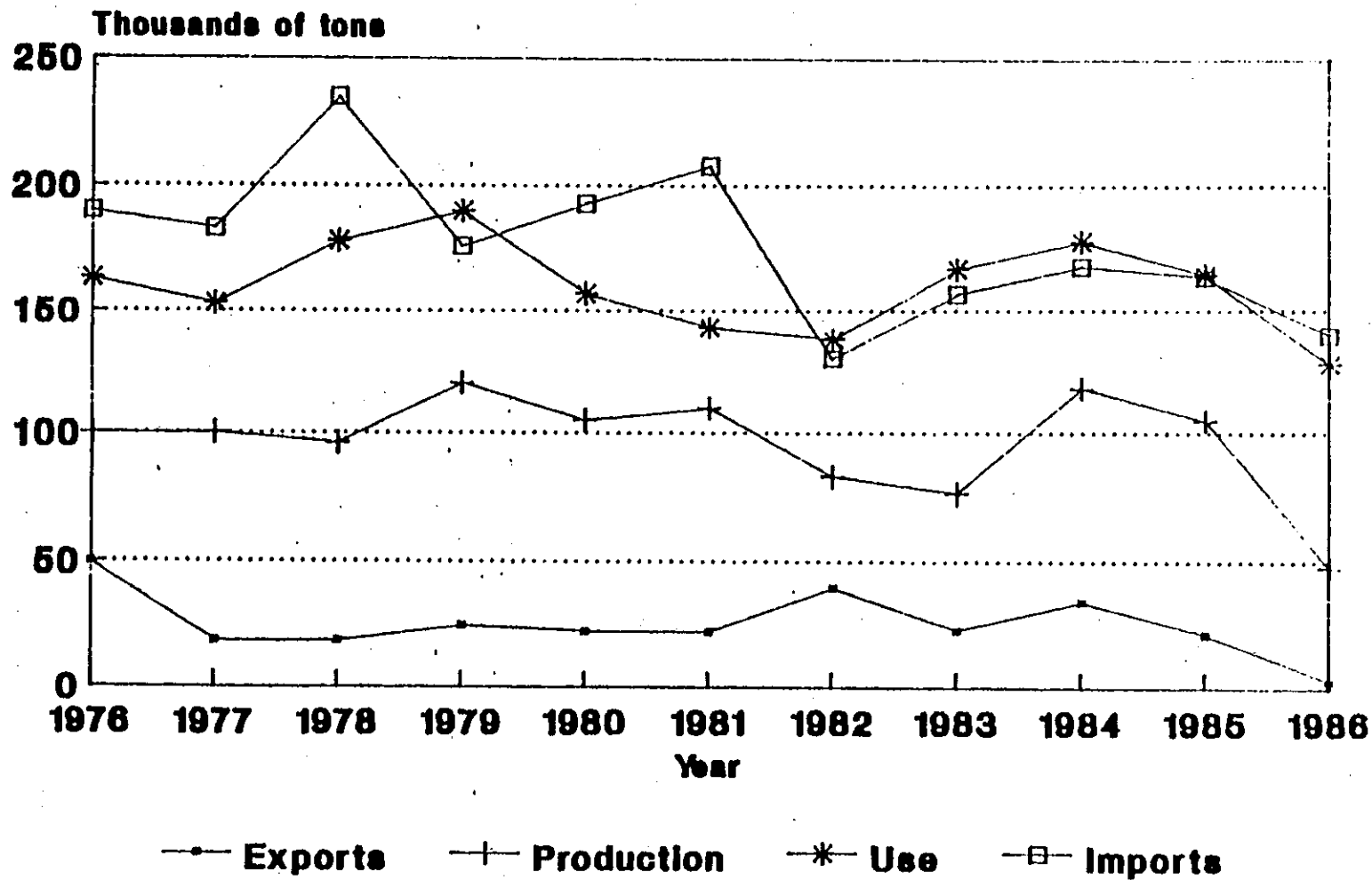
Primary nickel is produced domestically by AMAX Nickel Division of AMAX, Inc. at its nickel-copper refinery at Port Nickel, Louisiana (U.S. DOI, 1985). The feed material for this refinery is an imported matte containing nickel, copper, and cobalt. According to INCO Ltd, AMAX closed its Louisiana nickel operations in the last quarter of 1985 and a small section of this refinery has been reopened to recover nickel from spent petroleum catalysts. Ore processing and matte refining sources produced 3,100 tons of nickel in 1986 (U.S. DOI, 1987). There are no primary nickel producers in California.

2. Secondary

Secondary nickel is produced by the secondary recovery and refining of nickel-containing scrap metal such as stainless steels, low alloy steels, nickel-base alloys, aluminum alloys and copper-base alloys.

In the U.S. more nickel is produced from secondary recovery than from primary nickel production as an example, 39,200 tons of nickel were produced from secondary recovery operations in 1986 (U.S. DOI, 1987).

Figure II-1 **U.S. PRODUCTION, IMPORTS, EXPORTS,
and USE OF NICKEL**



-A3-

Several secondary aluminum and copper recovery facilities operate in California; however, tests have not been conducted to determine if these facilities produce nickel as a by-product.

B. USES

More than 90 percent of all nickel is used in its metallic form, principally as nickel-alloys (U.S. DOI, 1985). There are several nickel alloy systems of major commercial importance: pure nickel, nickel-copper, nickel-chromium, nickel-iron, nickel-molybdenum, nickel-chromium-molybdenum and others.

The national use of nickel in 1986 is shown in Figure II-2. As shown, 25 percent was used in the transportation industry, 15 percent in the chemical industry, 9 percent in electrical equipment, 9 percent in the construction industry, 9 percent in fabricated metal products, 8 percent in the petroleum industry, 7 percent in household appliances, 7 percent in machinery, and 11 percent in miscellaneous processes (U.S. DOI, 1987).

Nickel-based superalloys are used for aircraft parts such as jet engines, gas turbines, and turbosuperchargers. The nickel-base superalloys can contain up to a dozen different alloying elements and most of them were developed for a particular severe service condition such as high strength at elevated temperature. Nickel-containing stainless and alloy steels are used in aircraft frames and for many electroplated parts of aircraft. Nickel is primarily used in motor vehicles to electroplate vehicle trim on bumpers and wheelcovers. In ships and boats, nickel alloys, copper-nickel alloys, and bronzes are applied on parts exposed to saltwater such as the hulls, propellers, propeller shafts, and pumps (U.S. DOI, 1985).

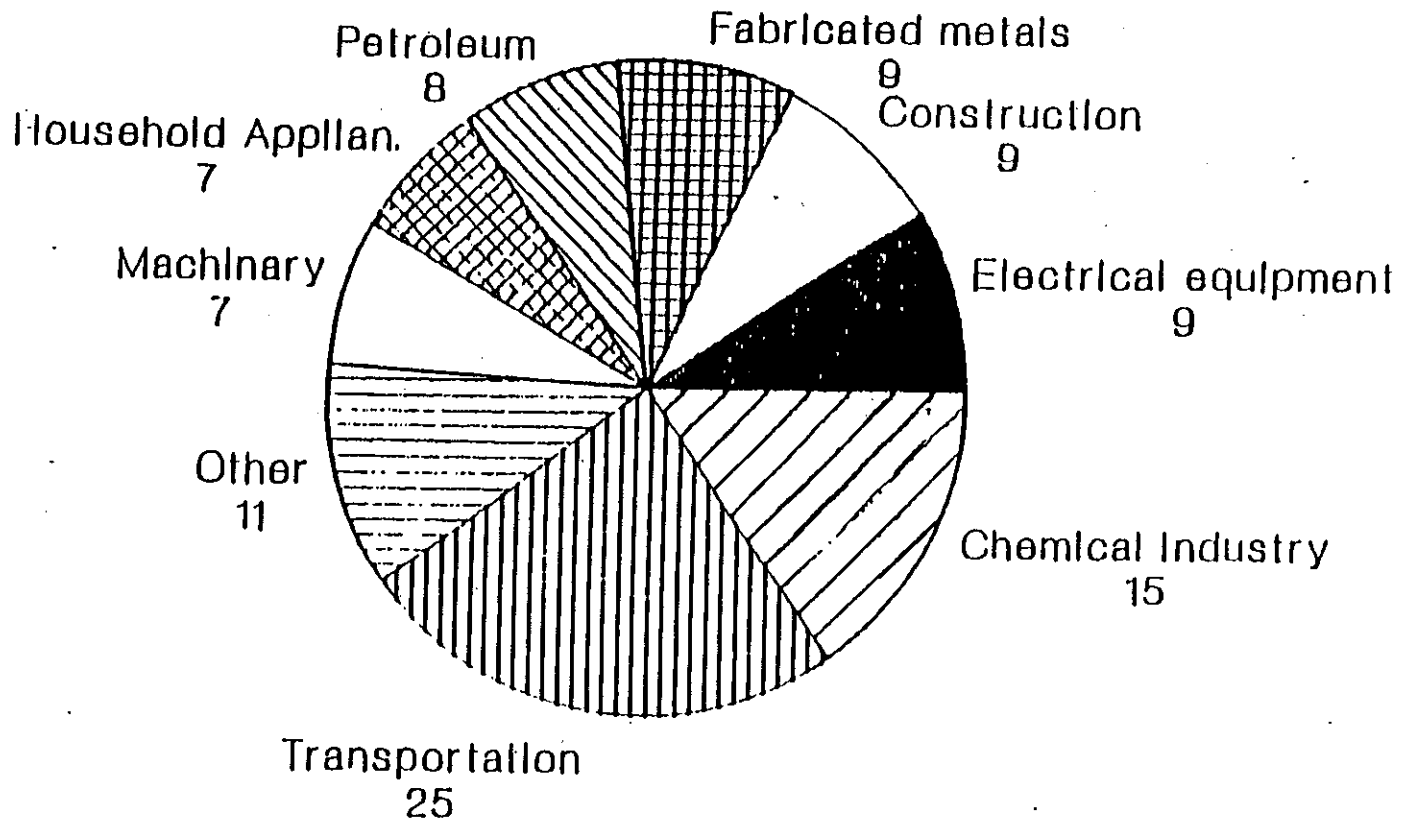
Both the chemical and petroleum industries use nickel-based alloys on parts for corrosion resistance in caustic solution (U.S. DOI, 1985a). Nickel chemicals are used as catalysts in the hydrogenation of fats and oils and in the production of some ceramics, plastic additives, organic dyes, and pigments (Kirk-Othmer Encyclopedia of Chemical Technology, 1980).

Nickel is used in various types of electrical equipment, machinery, and supplies. The majority is used in power plant turbines, heat exchangers, condensers, stack scrubbers, and nuclear power applications (U.S. DOI, 1985). Nickel is also used in nickel-containing transistors, glass-to-metal seals, batteries, and fuel cells. The construction industry utilizes nickel-containing stainless, wrought and cast steels for structural applications because of their high strength-to-weight ratios (U.S. EPA, 1984).

Figure II-2

USE OF NICKEL IN THE U.S.A. IN 1986

per cent



-A5-

Source: Mineral Commodity Summaries

Nickel provides strength and corrosion resistance in the stainless steels, alloy steels, and nickel-based alloys employed in fabricating metal products such as kitchen utensils, cutlery, hand tools, sheet-metal boilers, and ductwork. Stainless steel and electroplated food processing equipment contain nickel and nickel-copper alloys (U.S. DOI, 1985).

C. TRENDS IN NICKEL USE

Reflecting a predicted annual growth rate of 2.6 percent between 1983 and 2000, total domestic demand for nickel in the year 2000 is expected to be about 350,000 tons. This forecast was based on the correlation of nickel demand with economic indicators (U.S. DOI, 1985).

Barring the widespread use of nickel substitutes, the demand for nickel in most use-categories is expected to increase. The use of nickel in aircraft is expected to grow because it allows higher engine operating temperatures which increase turbine engine efficiency. Nickel use is also expected to increase in the chemical, petroleum, electronic, machinery manufacturing, and construction industries. Furthermore, greater utilization of nickel-cadmium, nickel-zinc, and nickel-iron alkali batteries is predicted (U.S. DOI, 1985). The use of nickel in motor vehicles may increase if electric vehicles become popular.

Besides imported nickel, the Bureau of Mines expects secondary nickel, primarily stainless steel scrap, to be the most important future supply of nickel.

Presently, there are no primary nickel producers in California, however, Hanna Mining Company holds 5,000 acres of Red Mountain in San Bernardino County which could possibly be developed for nickel mining (U.S. DOI, 1985). In addition, Ni-Cal has considered the possibility of extracting nickel from laterite deposits at Gasquet Mountain in Del Norte county (INCO, 1990).

D. EMISSIONS

Stationary sources emit approximately 18 to 353 tons of nickel per year and mobile approximately 5.4 to 7.2 tons of nickel per year in California. Majority of nickel is emitted through the combustion of fuels containing nickel as a trace contaminant (residual oil, coal etc.). Other sources of nickel are: nickel alloy manufacturing, petroleum processing, iron and steel foundries, secondary smelting processes, electroplating, municipal sewage sludge incineration, cement manufacturing, asbestos mining/milling, and cooling towers.

Table II-1 on page A7 summarizes the emissions data for both stationary and mobile sources of nickel in California.

The discussion on nickel emissions from different sources is important for many reasons and one of them relates to the effect of particle size on the respiratory system. Sources emit particles of various sizes. The

Table II-1

Estimated Total Nickel Emissions in California

STATIONARY SOURCES

	<u>Nickel Species*</u>	<u>Emissions</u> (tons/year)	<u>Inventory</u> Year
Fuel Combustion			
Coal (w/o cem.prod.)	Nickel Sulfate	0.39	1986
Coke	Not available	4.4	1985
Diesel Oil	Nickel Sulfate	Not available	
Distillate Oil	"	1.7	1984
Residual Oil	"	8.8 - 344	1984
Waste Oil	"	0.38	1983
Jet Fuel	"	Not available	
Gasoline	"	"	
Cement Production (incl.coal combustion)	Nickel Sulfate	0.03 - 0.22	1985
Asbestos Mining & Milling	Nickel Magnesium Silicate	0.004	1987
Municipal Waste Sludge Incineration	Oxidic Nickel	0.055	1984
Iron & Steel Foundries	Oxidic Nickel	Not available	
Ferrous & Non-Ferrous Metal Production	Complex Oxides of Nickel	"	
Secondary Metals Recovery			
Aluminum	Complex Oxides of Nickel	"	
Copper	"	"	
Lead	"	"	
Zinc	"	"	
Electroplating	Not available	(1.4)**	1985
Cooling Towers	Nickel Ion (2+)	Not available	
Resource Recovery	Nickel Metal	Neg.	1987
Coal Gasification	Not available	Not available	
Petroleum Processing	Nickel Metal & Nickel Carbonyl***	"	1984

MOBILE SOURCES

Gasoline-Powered			
Catalyst	Not available	3.2	1984
Non-Catalyst	Not available	1.6	1984
Diesel-Powered			
Heavy-Duty Trucks	Not available	0.59	1984
Other Vehicles	Not available	0.06 - 1.8	1984

* The most likely form of nickel expected to occur in emissions.

** Estimated emissions are from preliminary South Coast (SCAQMD, 1985) data: actual emissions may be lower.

*** Based on EPA (U.S. EPA, 1984); emissions in California unknown.

nickel concentration is inversely proportional to the particle size i.e. the smaller the particle size the greater the nickel concentration. Also, the smaller the particle the deeper penetration into the respiratory tract. In Chapter IV these relationships are discussed in more detail.

1. Stationary Sources:

a. Fuel Combustion

Nickel is a trace contaminant of fuels and is inadvertently emitted to the atmosphere when fuels are burned. The level of nickel emissions from fuel combustion depends primarily on: 1) the amount of nickel originally present in the fuels, 2) the types of boilers or engines burning the fuels, 3) the internal parameters of the boilers and engines such as temperature and pressure, etc. and 4) the partition between fly ash and bottom ash.

(1) Coal Combustion

Several analyses of fly ash from coal combustion show that nickel is emitted predominantly as nickel sulfate and, to a lesser extent, as complex nickel oxides (Radian, 1985).

Nickel is emitted from the cement production processes as well as from the combustion of coal. The cement industry is the largest coal user in California. In 1986, the California cement industry used approximately 1.2 million tons of coal. For the years 1990 and 2000, it is estimated that this industry will use approximately 1.5 million and 1.7 million tons of coal, respectively (see Appendix IV). Nickel emissions from coal combustion are included in the cement production estimate because it is not currently possible to distinguish emissions from cement production from those of coal combustion.

Other California coal users such as sugar manufacturers and coal-fired cogeneration facilities burned approximately 372,000 tons of coal in 1985. As a result of this coal combustion, we calculated that 0.1 tons of nickel were emitted by using the nickel emission factor for a coal-fired industrial boiler controlled by an electrostatic precipitator¹ (see Appendix IV).

In addition to the facilities that have been identified in the Emission Data System, as of February 1990, 12 coal-fired power

1. A device that removes particles from a gas stream (smoke) by electrically charging them so that they adhere to metal plates inside the precipitator.

cogeneration plants have been permitted in California representing about 502 Mw of electric power. Five of these facilities are commercially operating, the other facilities are in various stages of development (Fletcher, 1990). Assuming a heat content of 12,000 BTU/lb of coal and a 30 percent efficiency of heat input, when all 12 plants are operating they will use approximately 2.1 million tons of coal per year. Assuming that the nickel emission factor is 3.2×10^{-7} ton of nickel/ton of coal (Appendix IV), nickel emissions from these cogeneration plants are estimated to be 0.67 tons/year. The five operating cogeneration plants are representing about 199 Mw of electric power. The estimated nickel emissions from those plants are 0.27 ton/year.

Nickel emissions from coal combustion are expected to increase in the future as the number of cogeneration facilities grow.

(2) Coke Combustion

Nickel is present in petroleum coke as a trace contaminant. Based on limited data, nickel emissions from coke combustion in California were estimated to be 4.4 tons in 1985 (see Appendix IV). Data are not available on the different chemical species of nickel emitted from coke combustion.

(3) Oil Combustion

Fuel oil combustion involving distillate, residual, and waste oils is responsible for approximately 10.5 to 345 tons of nickel emissions to the atmosphere per year (see Appendix IV). The species of airborne nickel that result from oil combustion are predominantly nickel sulfate and, to a lesser extent, nickel oxide as well as complex oxides of nickel and other metals (Radian, 1985). Utility boilers used in residual oil combustion account for 3.1 to 112 tons of the nickel emissions while oil and gas production activities account for approximately 2.2 to 88 tons. The remaining nickel emissions from fuel oil combustion are from sources such as refineries, chemical manufacturers, sugar manufacturers, and food processing facilities.

Because nickel and sulfur contents in fuel oils are related, low sulfur oils tend to have low nickel concentration and vice versa. Therefore, the nickel concentration in fuel oils varies with sulfur content. According to the district rules, liquid fuels burned in the South Coast Air Basin cannot exceed a maximum of 0.25 percent sulfur while fuels burned in the Bay Area Air Basin can contain as much as 0.50 percent sulfur. However, these oils are relatively low in nickel concentration compared to as high as 3.5 percent sulfur oils. Thus, nickel emissions from utility boilers are expected to be low because most of the power plants in California are located either in the South Coast or in the Bay Area air basin.

Data from 1984 indicate that 17 percent of the total residual oil burned in California was used by utilities to produce electricity and heat (ARB, 1987b). The use of residual fuel oil by California utilities declined from 124 million barrels in 1977 to 3.6 million barrels in 1984 (California Energy Commission (CEC), 1984; and CEC, 1985). There was a slight increase in residual oil burned by utilities in 1985 (4.5 million barrels) and 1986 (5.3 million barrels) (CEC, 1986a; and CEC, 1987). More recent information from the California Energy Commission shows that California utilities used approximately 134 million gallons of residual oil in 1987 and 526 million gallons in 1988 (about 3.9 fold increase) (CEC, 1988; and CEC 1989).

The California Energy Commission forecasts that the amount of residual oil used by the utility industry will increase 250 percent from 1986 to 1997 (CEC, 1987; and CEC, 1986b) and then drop to the 1984 level of 3.6 million barrels by 2005. The use of residual oil in the industrial, commercial and transportation sectors is predicted to remain about the same through the year 2005 (CEC, 1986b). Due to the passage of the California Clean Air Act in 1990, the South Coast Air Quality Management District (SCAQMD) has proposed to restrict the use of residual oil in its jurisdictions. If the proposal is implemented, the use of residual oil in California may decrease sooner than 1997 as forecasted by the CEC.

b. Asbestos Mining and Milling

Chrysotile, the type of asbestos used commercially, contains from 1.5 to 1.8 mg of nickel per gram (Streib, 1978). Based on the average concentration of nickel in chrysotile and the estimated chrysotile emissions from asbestos mining and milling operations in 1987, such operations were responsible for approximately 0.004 tons of atmospheric nickel in that year (see Appendix IV). It is thought that the nickel emitted from asbestos mining and milling is in the form of nickel magnesium silicate (Radian, 1985).

c. Municipal Sewage Sludge Incineration

Nickel emissions from municipal sewage sludge incinerators depend primarily on the nickel content of the sludge which varies by location. For example, the nickel content of the sludge may be high if nickel electroplators are located in the region. The data on nickel, from municipal sewage sludge in 16 American cities vary from region to region; the nickel concentration of dry sludge in Los Angeles was analyzed to be 402 ppmw (part per million by weight) while it was 223 ppmw in San Francisco (Furr et al., 1976). Thus, there is no typical sludge.

Based on a survey conducted by the ARB in 1987, there were nine municipal sewage sludge incinerators in the State; one shut down its operation before 1987 and one incinerated sludge only for testing

purposes. The seven facilities in operation incinerated approximately 17,200 tons of dry sludge in 1987 (ARB, 1987a).

For lack of specific information from individual incinerators in California, the staff used data obtained from source tests (Bennett and Knapp, 1982; and Cross, et al., 1970) conducted at five different municipal sewage sludge incinerators located outside the state. The staff used these source test data and the amount of sludge incinerated to estimate that municipal sewage sludge incinerators in California emitted approximately 110 lbs of nickel in 1987 (see Appendix IV).

d. Electroplating

Potential sources of nickel emissions from the nickel electroplating process include: 1) the handling of nickel compounds in preparing the plating bath, 2) the process of nickel plating, and 3) the grinding, polishing, and cutting operations on the finished products (Radian, 1985).

Nickel sulfate, nickel chloride, and nickel sulfamate are the compounds most often used in nickel plating baths, however, different nickel compounds are used depending on the purpose of the plating operation (Durney, 1984). During the plating process, electric energy decomposes water in the bath into hydrogen and oxygen gases.

These gases form bubbles which rise to the surface and escape to the atmosphere. There are enough hydrogen and oxygen gas bubbles formed during plating to cause entrainment of small nickel-containing drops of electrolytic solution. The less efficient the plating process, the more gas bubbles formed and nickel emitted.

The South Coast Air Quality Management District (SCAQMD), reported 1.4 tons of nickel emitted to the atmosphere from electroplating operations in 1984 (SCAQMD, 1985). The emissions may be significantly lower than the SCAQMD survey estimated (Personal Communications with Industry Representatives, 1991). The emissions data being submitted under the AB 2588 program will provide more accurate estimates by the end of 1992. These emissions may be declining based on industry study which showed a recent nationwide decline in nickel electroplating. There is insufficient data to estimate statewide nickel emissions from electroplating operations.

Although not part of the electroplating process, metallic nickel particulates are emitted when the final products of nickel plating are cut, ground, or polished. However, emissions data are not available for any of these operations.

e. Coal Gasification

Even though a number of coal gasification programs have been, or are being, considered by the utility industry, only one plant in

Southern California is currently known to gasify coal. This plant used 108 thousand tons of coal from June 1984 through January 1985 (Wolk et.al, 1985). Nickel emissions from this plant are not available.

2. Mobile Sources

Several researchers have identified nickel in the vehicular exhaust of gasoline-powered and diesel-powered vehicles (Pierson and Brachaczek, 1983; U.S. EPA, 1980; Gabele et al., 1982; and Hare and Baines, 1979). In 1984, an estimated 5.4 to 7.2 tons of nickel were emitted by on-road California vehicles based on the number of on-road vehicles miles traveled and the amount of nickel emitted per mile (see Appendix IV). There is insufficient data to determine the chemical species of nickel in vehicular exhaust.

The primary source of nickel in motor vehicles is the combustion of nickel-containing fossil fuels. Canadian diesel gasolines contain an average of 0.05 ppmw nickel. Regular, premium, and low-lead Canadian gasolines contain 0.02 ppmw, 0.09 ppmw, and 0.10 ppmw nickel respectively (Barrie, 1981). Unpublished data from the analysis of a small number of samples indicate that the nickel levels of U.S. gasolines are similar to those of Canadian gasolines. There are no data concerning the amount of nickel emitted in the exhaust from aircrafts and off-road vehicles and engines. In addition to the combustion of nickel-containing fuels, engine abrasion may contribute nickel to vehicular exhaust.

3. Indoor Sources (Also see Section III. C.2.)

a. Indoor Smoke

Indoor smoke, particularly that originating from tobacco smoking, is the major source of nickel in indoor air. Indoor smoke also originates from the combustion of home-heating fuels (especially coal and oil), cooking fuels, and wood.

Tobacco smoking is considered to be the major source of indoor nickel (for detailed discussion see Section III, pg. A23). Although further testing is necessary to determine the exact contribution tobacco smoking makes to indoor air concentrations of nickel it is known that a single cigarette contains 1-3 ug of nickel and that a portion of that nickel becomes entrained during smoking.

The amount of indoor air nickel from the burning of home heating and cooking fuels in California has not been determined. The species of nickel emitted from the combustion of fossil fuels is predominately nickel sulfate which is water soluble. The remaining insoluble nickel in the fly ash is mostly nickel oxide (U.S. EPA 1986).

Smoke from wood burning can be emitted directly into the living space from stoves and fireplaces. Wood smoke from chimneys may penetrate indoors from natural or forced ventilation. Sexton et al. (1984) examined several communities for the effects of residential wood combustion on outdoor and indoor levels of particulate matter in indoor aerosols. They reported that the fine particulate fraction of the indoor aerosol contained 1 to 6 ng/m³ of nickel, and the coarse fraction contained 1 to 3 ng/m³ of nickel. Thus, the nickel contributed to indoor air from wood smoke ranges from 2 to 9 ng/m³. Other sources of indoor nickel emissions include house dust and the use of consumer products containing nickel.

b. In-Vehicle Source of Nickel

The major source of nickel in the air inside a motor vehicle is emissions resulting from fuel combustion. A study was conducted by the South Coast Air Quality Management District to sample in-vehicle concentrations of 14 toxic air pollutants including nickel. The samples were collected within two periods corresponding to a summer (May 1987 to October 1987) and a winter period (November 1987 to March 1988). The vehicle characteristics, driving habits, and vehicle ventilation were analyzed and summarized. Results showed that an average in-vehicle concentration for nickel is 9.0 ng/m³ ± 6.0 ng/m³ (Shikiya et al., 1989).

4. Natural Sources

From 16 percent (Grandjean, 1984) to 36 percent (Nriagu, 1980) of atmospheric nickel is contributed by natural sources such as nickel-containing windblown dusts and volcanic eruptions. The major characteristic of particles from natural sources is their size (greater than 10 um). These soils which contain nickel as an inorganic crystalline mineral, free ion, or chelated metal complex may reach indoor air through natural or mechanical air ventilation (Nriagu, 1980). The concentrations of nickel in decomposed igneous and sedimentary rocks range from 5 to 500 ppm (ug/gm) (U.S. EPA, 1986) while the nickel concentrations in soil derived from serpentine rocks may be as high as 6,000 ppm. Serpentine is found in many locations throughout California. Up to 24,000 ppm nickel is found in soils near nickel smelters and metal refineries. Geologic disturbances such as mining, quarrying, roadbuilding excavating in nickel-rich soils and rock can result in air emissions of nickel.

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III. EXPOSURE TO NICKEL

A. AMBIENT AIR MONITORING FOR NICKEL IN CALIFORNIA

Ambient nickel concentrations for this analysis were obtained from the 20-station toxic air contaminant network monitoring sites and are based on individual samples collected over a 24-hour period on Teflon filters from January 1985 through February 1987. The locations of the monitoring sites where nickel samples were collected in the six air basins are shown in Figure III-1. Samples from the eleven Northern California (Concord, Fremont, Richmond, San Francisco, San Jose, Bakersfield, Fresno, Merced, Modesto, Stockton, and Citrus Heights) and nine Southern California (El Monte, Los Angeles, No. Long Beach, Riverside, Upland, Santa Barbara, Simi Valley, Chula Vista, and El Cajon) sites were analyzed for nickel using X-ray fluorescence spectroscopy.

The limit of detection (LOD) for this analytical method is 1 ng/m^3 . Less than one percent of the samples collected during the 1985-1987 time period were below the LOD. The total number of samples per site for the January 1985 through February 1987 period ranged from 29 to 176. On the average, four samples per month were collected at the Northern California sites and three samples per month were collected at the Southern California sites.

Ambient nickel data from a consecutive 12-month period (November 1985 through October 1986) were selected for population exposure estimates. The amount of data available for each site is summarized in Table III-1.

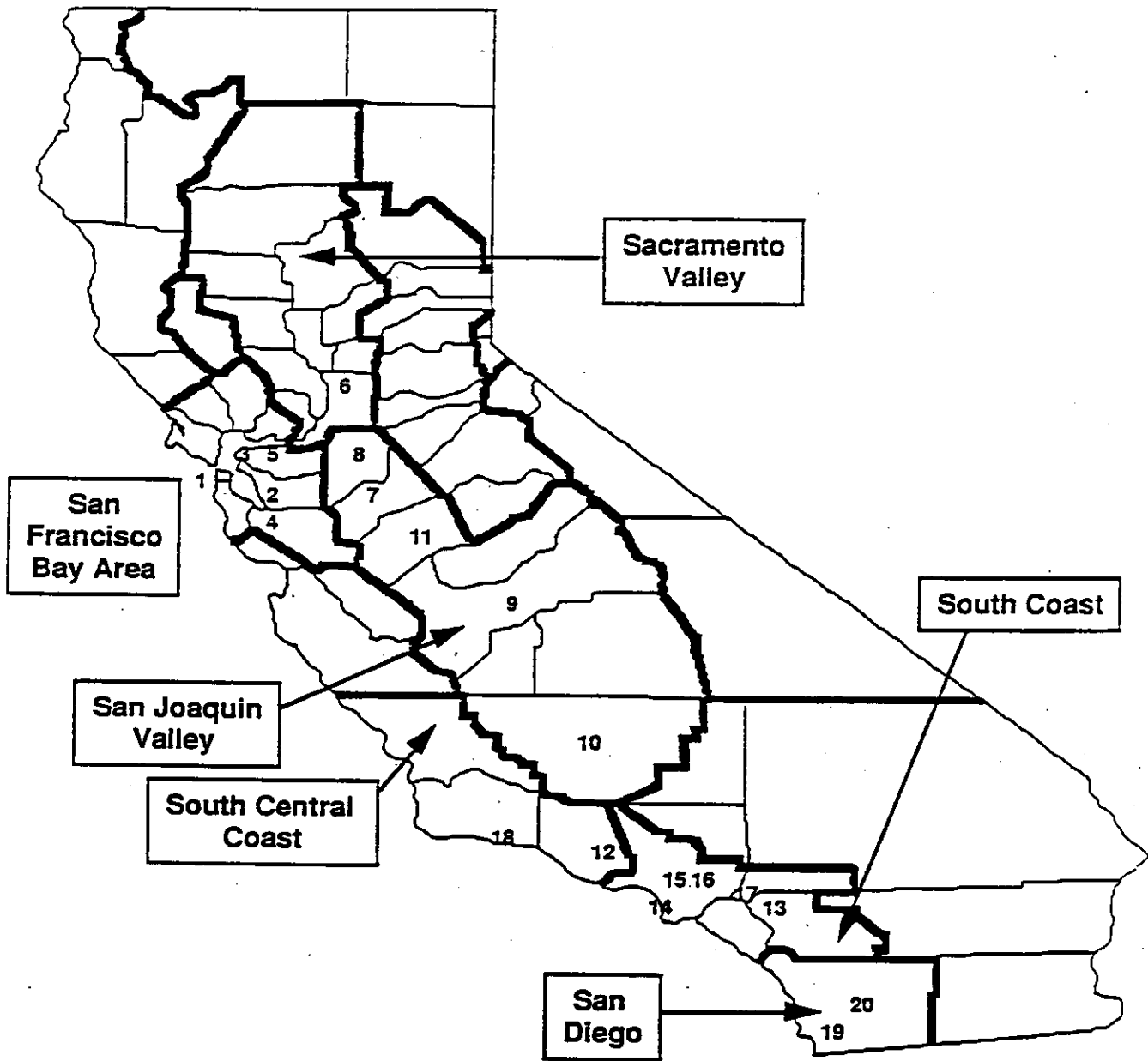
Data was missing from the monitoring stations at Stockton, Merced, and Fremont for five, two, and one month(s) respectively. An average of five samples per month were collected at the Northern California sites and two samples per month were collected at the Southern California sites.

B. AMBIENT CONCENTRATIONS OF NICKEL IN CALIFORNIA

The ambient nickel concentrations from November 1985 through October 1986 range from below the LOD of 1 ng/m^3 to a high of 77 ng/m^3 recorded at Bakersfield. The absolute range of concentrations sampled at each site during the study period is summarized in Table III-2.

Figure III-1

ARB Toxics Network Monitoring Sites



-
- | | | | |
|------------------|-------------------|-----------------|-------------------|
| 1. San Francisco | 6. Citrus Heights | 11. Merced | 16. El Monte |
| 2. Fremont | 7. Modesto | 12. Simi Valley | 17. Upland |
| 3. Richmond | 8. Stockton | 13. Riverside | 18. Santa Barbara |
| 4. San Jose | 9. Fresno | 14. Long Beach | 19. Chula Vista |
| 5. Concord | 10. Bakersfield | 15. Los Angeles | 20. El Cajon |

TABLE III-I

SUMMARY OF NICKEL DATA AVAILABLE FROM EACH MONITORING SITE
1985 THROUGH 1987

AIR BASIN Site Location	1985 JFMAMJJASOND	1986 JFMAMJJASOND	1987 JF	TOTAL SAMPLES
SOUTHERN CALIFORNIA SITES				
SOUTH COAST AIR BASIN:				
El Monte	●●●●●●●●●●	●●●●●●●●●●	● o	176
Los Angeles	o●●●●●●●●●	●●●●●●●●●●	● o	57
No. Long Beach	o●●●●●●●●●	●●●●●●●●●●	● ●	62
Riverside	o●●●●●●●●●	●●●●●●●●●●	● o	60
Upland	o●●●●●●●●●	●●●●●●●●●●	● ●	62
SOUTH CENTRAL COAST AIR BASIN:				
Santa Barbara	o●●●●●●●●●	●●●●●●●●●●	o o	50
Simi Valley	●●●●●●●●●●	●●●●●●●●●●	o o	64
SAN DIEGO COAST AIR BASIN:				
Chula Vista	●●●●●●●●●●	●●●●●●●●●●	● ●	58
El Cajon	o●●●●●●●●●	●●●●●●●●●●	o o	49
NORTHERN CALIFORNIA SITES				
SAN FRANCISCO BAY AREA AIR BASIN:				
Concord	o●●●●●●●●●	●●●●●●●●●●	o o	80
Fremont	o●●●●●●●●●	o●●●●●●●●●	o o	70
Richmond	o●●●●●●●●●	●●●●●●●●●●	o o	79
San Francisco	o●●●●●●●●●	●●●●●●●●●●	o o	67
San Jose	o●●●●●●●●●	●●●●●●●●●●	o o	77
SAN JOAQUIN VALLEY AIR BASIN:				
Bakersfield	o●●●●●●●●●	●●●●●●●●●●	o o	82
Fresno	o●●●●●●●●●	●●●●●●●●●●	o o	59
Merced	o●●●●●●●●●	o●●●●●●●●●	o o	46
Modesto	o●●●●●●●●●	●●●●●●●●●●	o o	81
Stockton	o●●●●●●●●●	o●●●●●●●●●	o o	29
SACRAMENTO VALLEY AIR BASIN:				
Citrus Heights	o●●●●●●●●●	●●●●●●●●●●	o o	84

● A solid dot indicates at least one sample was collected per month.

Table III-2
 SUMMARY OF NICKEL DATA FROM
 NOVEMBER 1985 THROUGH OCTOBER 1986
 (units are nanograms per cubic meter)

AIR BASIN Site location	Minimum Conc.	Maximum Conc.	Mean Conc.	Standard Deviat.	Estimate Conc.<LOD

S O U T H E R N C A L I F O R N I A S I T E S					
SOUTH COAST AIR BASIN:					
El Monte	1.0	19.0	10.3	4.3	0.9
Los Angeles	1.0	18.0	8.0	4.7	0.8
No.Long Beach	1.0	18.0	9.1	4.5	0.9
Riverside	<1.0	16.0	5.4	3.9	0.7
Upland	<1.0	9.0	4.7	2.5	0.8
BASIN SUMMARY:	<1.0	19.0	7.5	4.0	0.8
SOUTH CENTRAL COAST AIR BASIN:					
Santa Barbara	2.0	9.0	4.6	1.8	0.9
Simi Valley	<1.0	16.0	4.8	3.3	0.8
BASIN SUMMARY:	<1.0	16.0	4.7	2.6	0.8
SAN DIEGO AIR BASIN:					
Chula Vista	1.0	16.0	4.9	3.5	0.8
El Cajon	1.0	8.0	3.7	1.9	0.8
BASIN SUMMARY:	1.0	16.0	4.3	2.7	0.8
N O R T H E R N C A L I F O R N I A S I T E S					
SAN FRANCISCO BAY AREA AIR BASIN:					
Concord	1.0	9.0	3.2	1.6	0.9
Fremont	<1.0	11.0	3.0	1.9	0.8
Richmond	1.0	12.0	4.3	2.1	0.9
San Francisco	1.0	19.0	5.1	3.6	0.8
San Jose	3.0	25.0	10.4	5.0	0.9
BASIN SUMMARY:	<1.0	25.0	5.2	2.8	0.9
SAN JOAQUIN VALLEY AIR BASIN:					
Bakersfield	2.0	77.0	23.1	18.3	0.9
Fresno	2.0	14.0	5.5	2.6	0.9
Merced	1.0	19.0	6.3	5.3	0.7
Modesto	<1.0	19.0	4.6	3.6	0.8
Stockton	3.0	45.0	15.4	10.3	0.9
BASIN SUMMARY:	<1.0	77.0	11.0	8.0	0.9
SACRAMENTO VALLEY AIR BASIN:					
Citrus Heights	1.0	6.0	2.8	1.4	0.8

* Gleit's method was used to estimate the concentration of samples below the limit of quantitation.

** The limit of detection (LOD) of the method is 1.0 nanogram per cubic meter.

Minimum, maximum and mean concentrations, the standard deviations, and the estimated values for samples below the LOD (using Gleit's method) are reported for each site. Mean nickel concentrations were calculated as the average of all site-specific values.

The site-specific mean nickel concentrations ranged from 2.8 ng/m³ at Citrys Heights to 23.1 ng/m³ at Bakersfield. The highest basin mean 11.0 ng/m³ was found in the San Joaquin Valley Air Basin due to the Bakersfield and Stockton sites with mean concentrations of 23.1 ng/m³ and 15.4 ng/m³ respectively.

Site-specific standard deviations for the nickel data ranged from 40 to 85 percent of the estimated mean concentration. These large standard deviations indicate a high degree of variability in the data. The possible reasons for variability include seasonal variations, meteorology, etc.

Gleit's method estimates for the concentrations below the LOD by setting them equal to the "below-LOD mean" (the mean of that part of the normal distribution which is below the LOD). The simulations reported in Gleit's paper show that this method is more accurate than other methods presented in this paper. A detailed description of the method used to estimate the concentration of data below the LOD is provided in Appendix IV. Gleit's method was employed on the logarithms of concentrations to calculate the estimated values for samples with concentrations below the LOD and are listed in Table III-2.

Table III-2 shows that the estimated values for samples below the LOD range from 0.7 to 0.9 ng/m³ for the November 1985 through October 1986 time period.

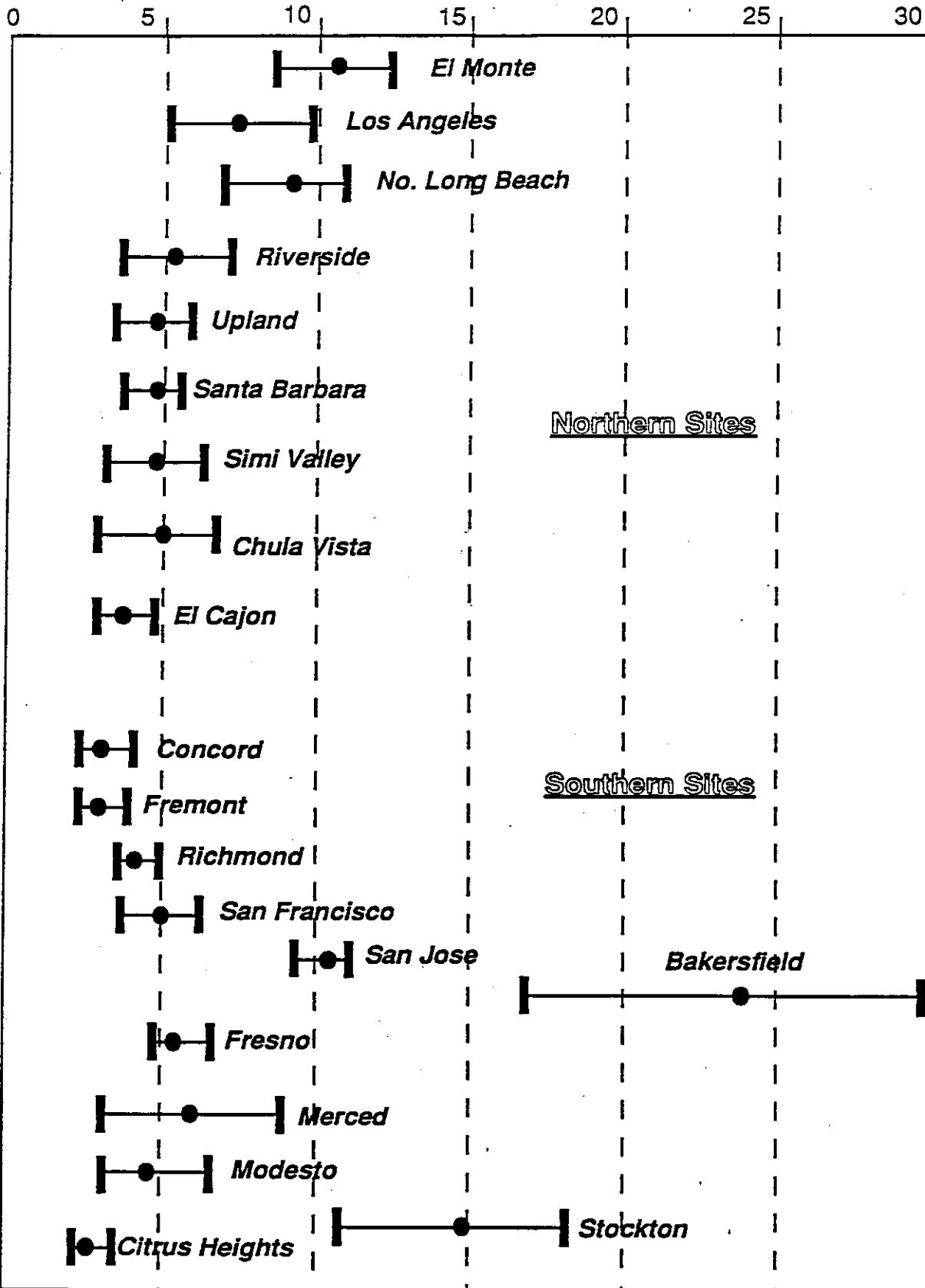
To evaluate whether nickel concentrations have changed, ARB staff compared 1986 data with 1987 data and 1988 data. The data for 1988 was the last year for which data were available. The results showed no statistically significant changes between the mean nickel concentrations for 1986 and those of 1987 and 1988.

The site-specific ranges of the ambient nickel concentrations for the individual sites were plotted in Figure III-2. The upper and lower bound concentrations about the mean were also plotted in order to characterize variability in the mean annual exposure estimates on a site-by-site basis.

As shown in Figure III-2 Bakersfield and Stockton demonstrated the highest concentrations.

Figure III-2

Statewide Mean Nickel Concentrations
Upper and Lower Bounds Intervals
from November 1985 through October 1986
Concentrations in ng/m³



C. POPULATION EXPOSURE IN CALIFORNIA

1. Ambient Exposure

Mean population-weighted exposure estimates were calculated using data from November 1985 through October 1986. Exposures for the South Coast Air Basin and the San Francisco Bay Area Air Basin were estimated by calculating three estimates of exposure, the site-specific mean annual nickel concentrations, and the upper and lower Bootstrap confidence interval bounds about the exposure means (see Appendix VIII for description of technique). These parameters are given in Table III-3 and are plotted in Figure III-2.

We assumed that all the people in those areas were exposed to the single mean value estimated for that air basin. Population estimates used in the exposure analysis represent 1985 census data. The results of the exposure analysis, which are discussed below, are summarized in Table III-4.

The overall statewide nickel exposure, weighted by population is estimated to be 7.3 ng/m^3 . A total of approximately 20.3 million people are estimated to reside in the study areas, representing approximately 70 percent of the state's population. Basin-specific, population weighted mean concentrations vary from a minimum 2.8 ng/m^3 for 889,800 people in the Sacramento Valley Air Basin to 11.0 ng/m^3 for nearly 2 million people in the San Joaquin Valley Air Basin.

Figure III-3 shows the number of people in a total population of 20.3 million exposed to average estimated mean nickel concentrations ranging from 2.5 to 11.5 ng/m^3 .

The distribution reveals that over 50 percent of the people in the study area are exposed to $3.6.0 \text{ ng/m}^3$ total nickel with over six million people exposed to 8.5 ng/m^3 total nickel. A minimum of 20.3 million people in the study area are exposed to concentrations of, at least 2.5 ng/m^3 total nickel while nine percent are exposed to 11.5 ng/m^3 total nickel.

2. Indoor Exposure

Section 39660.5(d) of the Health and Safety Code states "the state board shall identify the relative contribution to total exposure to the contaminant from indoor concentrations, taking into account both ambient and indoor air environments." At this time we are unable to estimate the precise indoor contribution of nickel to total exposure, but based on available data, California's population is exposed to some level of airborne nickel in indoor as well as outdoor environments. Available information regarding exposure to nickel in enclosed spaces is summarized below and discussed more fully in Appendix II.

A recent time-activity pattern study shows that Californians, on the average, spend about 87 percent of their time indoors. Consequently, the presence of indoor sources of nickel may result in a significant exposure.

Table III-3
 SUMMARY OF MEAN NICKEL CONCENTRATIONS AND
 UPPER AND LOWER BOUND INTERVALS
 FROM NOVEMBER 1985 THROUGH OCTOBER 1986
 (units are nanograms per cubic meter)

AIR BASIN Site Location	Lower Bound Interval	Mean Concentration	Upper Bound Interval
SOUTH COAST AIR BASIN (SoCAB):			
El Monte	8.5	10.3	12.0
Los Angeles	5.2	7.6	9.7
No. Long Beach	7.1	9.1	10.7
Riverside	3.2	5.2	6.8
Upland	3.5	4.8	5.9
SOUTH CENTRAL COAST AIR BASIN (SCCAB):			
Santa Barbara	3.9	4.7	5.3
Simi Valley	3.2	4.7	6.1
SAN DIEGO AIR BASIN (SDAB):			
Chula Vista	3.1	5.0	6.6
El Cajon	2.9	3.8	4.5
SAN FRANCISCO BAY AREA AIR BASIN (SFBAAB):			
Concord	2.6	3.1	3.6
Fremont	2.4	3.0	3.7
Richmond	3.8	4.2	4.6
San Francisco	3.9	5.0	6.1
San Jose	9.5	10.4	10.9
SAN JOAQUIN VALLEY AIR BASIN (SJVAB):			
Bakersfield	16.9	23.7	31.0
Fresno	4.6	5.5	6.4
Merced	3.1	5.8	8.4
Modesto	3.1	4.6	6.3
Stockton	10.9	14.7	17.9
SACRAMENTO VALLEY AIR BASIN (SVAB):			
Citrus Heights	2.3	2.8	3.3

* Means are calculated as the mean of monthly means.

Table III-4

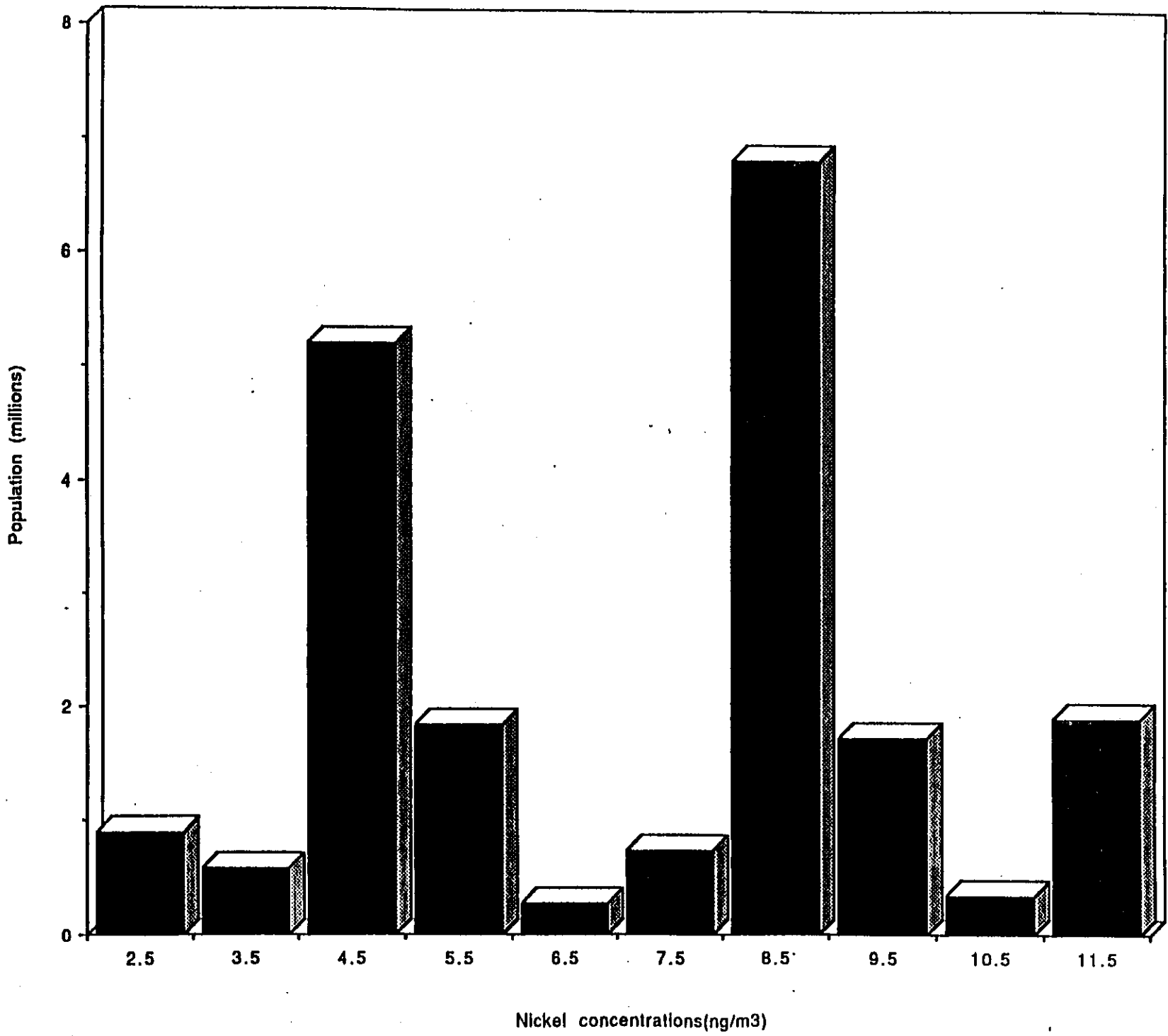
SUMMARY of NICKEL POPULATION-WEIGHTED EXPOSURE
 ESTIMATES: NOVEMBER 1985 THROUGH OCTOBER 1986
 (units are nanograms per cubic meter)

Air Basin Site Location	Mean Estimate	Population Represented
<u>SOUTHERN CALIFORNIA SITES</u>		
Population-Weighted Exposure for South Coast Air Basin	8.2	10,092,133
Population-Weighted Exposure for South Central Coast Air Basin	4.7	925,822
Population-Weighted Exposure for San Diego Air Basin	4.3	2,135,872
<u>NORTHERN CALIFORNIA SITES</u>		
Population-Weighted Exposure for San Francisco Bay Area Air Basin	5.5	4,394,374
Population-Weighted Exposure for San Joaquin Valley Air Basin	11.0	1,901,243
Population-Weighted Exposure for Sacramento Valley Air Basin*	2.8	889,806
<u>OVERALL POPULATION-WEIGHTED EXPOSURE</u>	7.3	20,339,250

* Exposure estimates are for Sacramento County residents only.

Figure III-3

ESTIMATED MEAN AMBIENT ANNUAL OUTDOOR NICKEL EXPOSURE
BASED ON NOVEMBER 1985 THROUGH OCTOBER 1986 DATA



available data, California's population is exposed to some level of airborne nickel in indoor as well as outdoor environments. Available information regarding exposure to nickel in enclosed spaces is summarized below and discussed more fully in Appendix II.

A recent time-activity pattern study shows that Californians, on the average, spend about 87 percent of their time indoors. Consequently, the presence of indoor sources of nickel may result in a significant exposure. There are three main sources of indoor exposure to nickel: 1) tobacco smoke, 2) fuel combustion (wood and fossil fuels), and 3) street and soil dusts. The estimated daily doses of nickel from different environmental media are presented in Table III-5. The derivations of the dose estimates are presented in Appendix II.

The primary source of indoor nickel is thought to be tobacco smoke. Currently, there are insufficient data related to the amount of nickel contributed to indoor air by tobacco smoke to permit accurate exposure estimates for indoor environments where smoking occurs. It is known that during the combustion of tobacco, a small portion of metals, including nickel, vaporize and are entrained in micro-fragments of ash (IARC, 1985). A single cigarette contains from 1 to 3 ug of nickel. While the burning of a whole non-filter cigarette results in the release of 20 to 80 ng of nickel in the particulate phase of the mainstream (MS) smoke, it results in 13 to 30 times as much nickel in sidestream (SS) smoke (NRC, 1986). Hoffmann and Wynder (1986) list the release of total nickel as 20 to 3,000 ng per cigarette with a ratio of SS to MS of 13 - 30 to one. In addition, the SS particles are an order of magnitude smaller than those of MS smoke: 0.01 to 0.8 um for SS versus 0.1 to 1.0 um for MS (NRC, 1986). The SS particles inhaled by the passive smoker will, therefore, reach the deep lung and be absorbed to a greater extent than those in the mainstream smoke.

Another indoor source of nickel is wood burning. Smoke from wood burning can be emitted directly into the living space from stoves and fireplaces, or wood smoke from chimneys may penetrate indoors from natural or forced ventilation. A study of the organic and elemental content of wintertime aerosol from residential woodburning (Sexton, *et al.*, 1984) determined that the fine particulate fraction of the aerosol indoors contributed 1 to 6 ng/m³ of nickel, and the coarse fraction contributed 1 to 3 ng/m³ of nickel. Thus, residential woodburning may contribute a total of 2 to 9 ng/m³ of nickel to indoor air. Finally, street and soil dusts contribute 32-64 ng over a 24 hour exposure.

In indoor environments where no indoor sources of nickel are present, outdoor sources would make the greatest contribution to the total exposure, although the indoor exposure could still be significant because people spend most of their time indoors and some nickel from the outdoors would enter the building at a rate dependent on the air exchange rate.

For a discussion of in-vehicle media see pg. A13.

Table III-5

ESTIMATED PRESENTED DAILY DOSES OF NICKEL THROUGH DIFFERENT MEDIA*

<u>Media</u>	<u>24-Hour Exposure</u>	<u>Other Exposure</u>	<u>References</u>
<u>INDOOR AIR**</u>			
Homes with smokers		20 - 3,000 ng released per cigarette***	Szadkowski, <u>et al.</u> , 1969; Grandjean, 1984; Hoffman & Wynder, 1986
Wood Combustion	40 - 180 ng	25 - 112 ng (15 hr. exp.)	Sexton, <u>et al.</u> , 1984
In-Vehicle	180 ng	13 ng (1.67 hr. exp.)	Shikiya, <u>et al.</u> , 1989
Soil and dust	32 - 64 ng	20 - 40 ng (15 hr. exp.)	Grandjean, 1984 Bennett, 1981
<u>CUTANEOUS</u>	Negligible		
<u>IATROGENIC</u>			
Dental alloys		4200 ng/cm ²	Moffa, 1982
Prostheses		0.27 ng/cm ²	Marek & Treharne, 1982
Dialysis		100,000 ng/treatment	Sunderman, 1983
I.V. Solutions		35,000 ng/treatment	Sunderman, 1983
<u>FOOD AND BEVERAGE</u>	62,000-165,000 ng		Pennington & Jones, 1987; NRC, 1975
Beer and Wine		30,000 ng/l	Ellen, <u>et al.</u> , 1978
Milk		100,000 ng/l	Clemente, <u>et al.</u> , 1980
<u>DRINKING WATER</u> (Surface water)	20,000 ng		NRC, 1975; U.S. EPA, 1986; Cronin, <u>et al.</u> , 1980

* Note that estimated doses across media are not directly comparable, since the degree of absorption and effect on the body vary depending on the route of intake.

** Assumes an individual inhales 20 m³ air per day and drinks two liters of water per day.

*** Insufficient data at present time to calculate presented dose.

3. Other Routes of Exposure

Inhalation is not the only route of exposure to nickel. Other routes of exposure are: skin, iatrogenic (leaching of nickel from implanted medical devices), and ingestion of food and water.

a. Skin Exposure

Skin (cutaneous) exposure to nickel from stainless steel utensils, and nickel-plated materials such as coins, jewelry, clothing fasteners, suspenders, handles, and car doors is common. Additional cutaneous exposure to nickel occurs via contact with soaps, fats and oils that are manufactured by hydrogenation using nickel catalysts. However, the amount of nickel absorbed cutaneously is not known. Cutaneous absorption appears negligible relative to total intake.

Nickel hypersensitivity may cause dermatitis, pulmonary asthma, conjunctivitis, and inflammatory reactions around nickel-containing implants and prostheses (Sunderman, 1987). Hypersensitivity to nickel is a common cause of allergic contact dermatitis. Positive dermal patch tests for nickel occur in 8-11 percent of women and 0.2-2 percent of men. Many people become sensitized to nickel when their ears are pierced with nickel plated needles and when nickel plated earrings are inserted (Fisher, 1987; Iwatsuki et al., 1987).

b. Iatrogenic Exposure

It is estimated that nickel-containing materials used in dentistry contribute 4.2 ug of nickel to saliva per square centimeter of alloy surface each day.

Nickel leaching may occur from slow corrosion of the alloys exposed to body fluids. Various nickel-containing alloys, such as stainless steel (10-14 percent nickel) or cobalt alloy (up to 2.5 percent nickel), are implanted for joint prostheses, plates, screws for fractured bones, surgical clips and sutures. The wire probes leading to the heart muscles from nickel-cadmium battery pacemakers may contain 35 percent nickel (Samitz & Katz, 1975). Nickel is present in the framework of early prosthetic heart valves implanted in rheumatic heart patients (Lyell, et al., 1978).

Leaching of nickel may contaminate intravenous fluids. Sunderman (1983) suggested a maximal permissible amount of nickel in I.V. fluids of 35 ug per day for a 70-kg adult. The limit was set at 35 ug per day because it was recently found that a 10-fold higher dose (350 ug/day) caused problems in the heart muscles of dogs.

c. Food Ingestion

Plant roots absorb nickel from the soil. As a result, cultivated crops and natural vegetation generally have concentrations of nickel between 0.05 ppm and 5 ppm. Sunderman et al. (1989) confirmed the findings of Solomons et al. (1982) that "certain dietary constituents (e.g. ascorbic acid) and beverages (e.g. milk, coffee, tea, orange juice) reduced the bio-availability of orally administered nickel in humans...." It is estimated that 1 to 10 percent of dietary nickel is absorbed. In a study by Christensen and Langesson (1981) adult human volunteers ingested 5.6 mg of nickel in the sulfate form. Over three days cumulative urinary excretion of nickel was 176 ug. This demonstrated that at least 3 percent of gastrointestinal absorption is excreted by the kidney into the urine. Gastrointestinal absorption of nickel is surprisingly high compared to other toxic elements.

It is difficult to determine the average amount of ingested nickel because of variability in diets. However, several studies estimated the average dietary nickel intake by adults to be approximately 62 to 500 ug/day (NRC, 1975; Myron et al., 1978; Bennett, 1981; Pennington and Jones, 1987; Sunderman, 1987;).

Diets rich in oatmeal, cocoa, chocolate, leafy vegetables, nuts, and soya products may produce a dietary intake as high as 900 ug/day (Nielsen and Flyvholm, 1984). Vegetables such as peas, beans, lentils, lettuce, spinach and cabbage contain in excess of 1 ug of nickel per gram of vegetable. The nickel content of edible parts of crops grown on soil contaminated by nickel smelter fallout ranged from 15 to 400 ppm.

Food processing may add nickel to the levels naturally occurring in food stuffs. The nickel catalyzed hydrogenation of fats and oils may also add to the nickel content. Nickel may enter the diet when leaching occurs while cooking foods using stainless steel kitchen utensils. Stainless steel saucepans and pots used to boil water containing 4 percent acetic acid three times for 30 minutes each time, released an average of 49 ug of nickel per liter. An electric kettle released 36 mg/l nickel when water alone was used for the boiling test and released 137 mg/l when 4 percent acetic acid solution was used (Rasmussen, 1983).

d. Water Ingestion

Although water ingestion is usually considered a secondary source of nickel when compared to food ingestion, there is growing evidence that more nickel is absorbed from drinking water than from food and beverages. It appears that food interferes with the absorption of divalent nickel from the alimentary tract. Solomons et al. (1982) studied the effects of certain foods and beverages on gastrointestinal absorption of nickel. After post-prandial ingestion of 5 mg of nickel sulfate hexa-hydrate there was no significant elevation of plasma nickel. However, sustained elevation of plasma nickel occurred when the same dose was given to fasting subjects.

Surface water sources such as lakes and rivers provide a portion of California's drinking water for California. Nickel in surface water across the U.S. ranges from 5 to 1000 ug/l (STORET, 1984). Water flowing through mineralized areas (serpentine) may have elevated levels of nickel. The average level of nickel in California surface water may be high relative to other areas of the United States due to the abundance of nickel-containing serpentine-rock soils in the state. In addition, mining, agricultural, and industrial discharges may result in localized water supplies with elevated nickel concentrations. Nickel may also be transferred to the water from pipes and fixtures containing nickel. Measurements have shown that 18 to 900 ug of nickel may leach from faucets filled with 15 ml of deionized water (Grandjean, 1984).

Los Angeles drinking water was reported to contain 4.8 ug/l; San Diego water contained 7.8 ug/l of nickel (U.S. EPA, 1980). The mean nickel concentration in drinking water in the U.S. is 4.8 ug/l as calculated from a survey of 969 water supplies covering eight metropolitan areas (NRC, 1975; U.S. EPA, 1986). However, in view of the STORET data for California surface waters mentioned above, the average concentration of nickel in California drinking water is estimated to be about 10 ug/l.

e. Deposition Exposure

The population can also be exposed to nickel from emission sources through deposition. When nickel enters the atmosphere it may remain suspended and available for transport or it can be removed by wet or dry deposition. The size of the particle influences the type of deposition from the atmosphere: fine particulates and gases become incorporated into raindrops, larger particles are more subject to gravitational settling near the emission source.

Nickel from emission sources deposit in soil, water, and deposits on or is taken up into vegetation. Subsequent exposure to nickel from these media through ingestion or skin-absorption can contribute to the individual's overall dose of atmospheric nickel. However, at this time we do not have enough information to estimate the contribution of deposition to total nickel exposure.

4. Exposure Near Emission Sources

Stationary facilities with nickel emissions are capable of creating high localized ambient concentrations ("hot spots") of nickel. A source of such localized emissions are crude oil fired external combustion units. To assess the potential impact of localized "hot spot" nickel emissions, the ARB looked at nickel emissions information for crude oil fired steam generator units in the Oildale-Bakersfield area. Information is available for 1985 nickel emissions from 672 steam generator units, which were firing with crude oil. We do not have an estimate of how many units are currently firing with crude oil in this area. Therefore, we have assumed that all units burned only oil and that this oil contained 60 mg of nickel per kilogram.

We do know that the amount of BTUs from oil fired units has decreased between 1985 and 1988 by 45 percent. These fuel trends are due to stricter emission requirements for steam generating units, the availability of natural gas, and the replacement of external combustion steam generating units with natural gas fired cogeneration units.

For the purposes of modeling a potential "hot spot" exposure, the ARB used the 1985 data in conjunction with meteorological data to estimate the potential impact on the nearby Oildale-Bakersfield area. Because of the lowered use of crude oil in steam generator units, we would expect the current exposure to nickel emissions to be less than that estimated by this analysis. However, the analysis is useful in demonstrating the worst case of "hot spot" exposure conditions.

ARB modeled the units using the Industrial Source Complex Short Term (ISCST) pollutant dispersion model. The 672 individual external combustion sources were modeled as 177 point sources since many of the external combustion units are served by the same SO₂ scrubber and thus have the same stack parameters and location. The meteorological data used were the most recent five years of acceptable meteorology available for Bakersfield i.e. 1960-1964.

Table III-6 shows the potential population exposure distribution estimated from the gridded annual average concentrations.

Table III-6

1985 Estimated Population Exposed to Nickel Emissions From Oil Fired Combustion in Central Kern County

Annual Exposure (ng/m ³)	Population Exposed
9 - < 25	8,159
25 - < 50	129,992
50 - <100	92,985
100 - <150	61,138
150 - <200	16,307
200 - <250	8,975
250 - <400	2,935

For determination of the gridded annual average nickel concentrations, a 51 km by 51 km grid with approximately 320,000 people was selected. The maximum annual average nickel concentrations at a gridded 1 km receptor was 386 ng/m³.

The concentrations presented in the Table III-6 would not represent the total ambient air exposure of the people living in the vicinity of the modeled sources. The predicted concentrations are those which would exist if the modeled facilities were the only nickel emission source affecting the nearby population. In reality, there are other emission sources, large and small, located in the basin which contribute to the total nickel concentration that the modeled population is exposed to. Results of the modeling study demonstrate that several hundreds of thousands of people could be exposed to nickel at concentrations higher than annual average concentrations monitored in the SJVAB (11.0 ng/m³).

Also the study population may be exposed not only to nickel from these "hot spots" but to additional nickel from the ambient "background" concentration. Again, although we do not have an estimate of how many oil fired units are currently operating in the Bakersfield area, we do know that the amount of BTUs from oil fired units has decreased from 1985 to 1988. Therefore, we would expect that current exposure to nickel will be less than that predicted by the modeling study discussed above.

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IV. PROPERTIES AND PERSISTENCE IN THE ATMOSPHERE

A. PHYSICAL AND CHEMICAL PROPERTIES

Nickel is a silvery white, malleable metal that is highly resistant to atmospheric and aqueous corrosion. Additional attributes that make nickel a particularly useful metal are that it: 1) retains a high polish, 2) is highly ductile, and 3) has good thermal and electrical conductivity. The same procedures used in steel manufacturing may be easily applied to fabricating nickel products. Moreover, nickel is ferromagnetic at ambient temperatures and becomes paramagnetic when heated above the Curie point (353°C).²

Nickel (atomic number 28 and atomic weight 58.71) is more resistant to corrosion than iron and cobalt. Metallic nickel has a density of about 8.9 g/cm^3 , a melting point of 1726°K (1453°C), and a boiling point of about 3005°K (2732°C) (Nriagu, 1980).

Nickel can be found in several valence states including (-I), (0), (I), (II), (III) and (IV). The most prevalent nickel compounds are nickel (II) species (U.S.EPA, 1984).

The physical and chemical properties of nickel are summarized in Table IV-1.

B. FORMATION AND ATMOSPHERIC FATE

The nickel associated with atmospheric pollutants is almost always detected in particulate matter. Nickel is continuously transferred among environmental compartments (air, water, soil) by natural chemical and physical processes such as weathering, erosion, runoff, precipitation, stream and river flow, and leaching.

Atmospheric nickel-containing particulate matter is subject to dispersion and transport by winds, and is transferred from the atmosphere to soil or water by wet or dry deposition, impaction, or gravitational settling. Acid rain has a marked tendency to mobilize nickel from soil and to increase nickel concentrations in ground water since most nickel compounds are relatively soluble at pH values less than 6.5.

2. One unique property possessed only by iron, cobalt and nickel among the common elements is ferromagnetism (in a magnetic field the metal ions are oriented in the direction of the field and the same material becomes magnetized). Paramagnetism is when a substance such as nickel forms an induced magnetic field which is in the same direction but stronger than the magnetic field which induced it.

Table IV -1
 PHYSICAL PROPERTIES OF NICKEL AND NICKEL COMPOUNDS

Name	Formula	Formula Weight	Color, Crystalline Form	Density	Melting Point (°C)	Boiling Point (°C)	Solubility in 100 parts water
Nickel	Ni	58.71	silver, face-centered cubic	8.90	1455	2920	insoluble; soluble in dilute HNO ₃
Nickel acetate tetrahydrate	Ni(C ₂ H ₃ O ₂) ₂ · 4H ₂ O	248.86	green pyramidal	1.744	--	--	16; soluble in alcohol
Nickel ortho-arsenate	Ni ₃ (AsO ₄) ₂	453.97	yellow-green powder	4.982	--	--	insoluble
Nickel bromate hexahydrate	Ni(BrO ₃) ₂ · 6H ₂ O	422.62	green monoclinic	2.60	--	--	28 (20°C)
Nickel bromide trihydrate	NiBr ₂ · 3H ₂ O	272.57	yellow-green deliquescent needles	--	loses H ₂ O 200	--	very soluble
Nickel carbonate	NiCO ₃	118.72	light green rhombic	--	--	--	0.009 (25°C)
Nickel carbonate hydroxide	NiCO ₃ · 2Ni(OH) ₂	304.17	green cubic	2.6	--	--	insoluble
Nickel chloride	NiCl ₂	129.62	yellow deliquescent	3.55	1030	sublimes at 970	60.8 (20°C)
Nickel chloride hexahydrate	NiCl ₂ · 6H ₂ O	237.70	green monoclinic	--	--	--	111 (20°C)
Nickel fluoride	NiF ₂	96.71	yellow-green tetragonal	4.72	1450	1740	2.56 (20°C)
Nickel hydroxide (hydrate)	Ni(OH) ₂ · H ₂ O	110.74	green powder	--	decomposes 230	--	solubility 0.0013 (20°C)
Nickel nitrate hexahydrate	Ni(NO ₃) ₂ · 6H ₂ O	290.81	green monoclinic deliquescent	2.05	56.7	136.7	150 (20°C)
Nickel oxide	NiO	74.71	green cubic	7.45	2090	--	insoluble; soluble in acid
Nickel phosphate octahydrate	Ni ₃ (PO ₄) ₂ · 8H ₂ O	510.20	light green powder	--	decomposes 600	--	insoluble; soluble in acid
Nickel sulfate hexahydrate	NiSO ₄ · 6H ₂ O	262.86	α blue-green tetragonal β green monoclinic	2.07 --	53.3 (forms β) loses water at 280	-- --	40.1 (20°C) 44.1 (20°C)
Nickel subsulfide	Ni ₃ S ₂	240.26	light yellow cubic	5.82	790	--	insoluble; soluble in HNO ₃

Dash indicates data not available.

Source: Antonsen (1980) and Dean (1979).

Although the ultimate sink for nickel is the ocean, some nickel in ocean water is released to the atmosphere in sea spray aerosols which burst and release minute nickel-containing particles. The global cycle of nickel is depicted in Figure IV-1.

Nickel is introduced in the atmosphere by both natural and anthropogenic sources. Estimates of the portion attributed to either source category are based on emission rates which vary according to the nickel concentration in the materials being dispersed (Nriagu, 1979). Total nickel emissions (73,000 ton/yr) are composed of 26,000 ton/yr from natural sources and 47,000 ton/yr from anthropogenic sources as indicated in Figure IV-2.

Wind erosion and volcanic activity contribute 40 to 50 percent of the atmospheric nickel from natural sources (Nriagu, 1980). Other natural sources include forest fires, sea salt spray, and meteoric dust (Schmidt and Andren, 1980). Within a given geographical area, the nickel contributed to the atmosphere by natural sources varies with local meteorological conditions, soil type, and physical factors. About 80 percent of anthropogenic nickel emissions are contributed by fossil fuel combustion and the production of nonferrous metals. The atmospheric portion of the global nickel cycle is presented in Figure IV-2.

There are a number of properties of particles which are important to their role in atmospheric processes. These include, in addition to their concentration, mass, size, chemical composition, and aerodynamic and optical properties (Finlayson and Pitts, 1986). The major factor governing the atmospheric behavior of natural and anthropogenic emissions of environmentally important metals such as nickel is particle size. It is important because small particles (less than 1 μm in diameter) most effectively enter the deep regions of the lung and then into the bloodstream. Particles less than 1 μm deposit predominantly in the alveolar regions of the lung where the absorption efficiency for most trace elements is 50 to 80 percent (Natusch et al., 1974).

It is generally accepted that elements associated with particles less than 1 μm tend to result from combustion and other high temperature sources, while large particles (greater than 10 μm) are likely to arise from wind action on soils, deposited dusts and fugitive emissions from dust-producing operations. Anthropogenic nickel (as well as several other toxic metals) is usually associated with the fine (diameter <2.5 μm), respirable particulate in the ambient air. These fine particles tend to persist in the atmosphere where they can be transported over long distances until they deposit in water and soil. The measurements of nickel content in fly ash released from coal-fired power plants showed that the nickel is concentrated in the smallest respirable particles and are most likely to reach deep into the lungs (NAS., 1975).

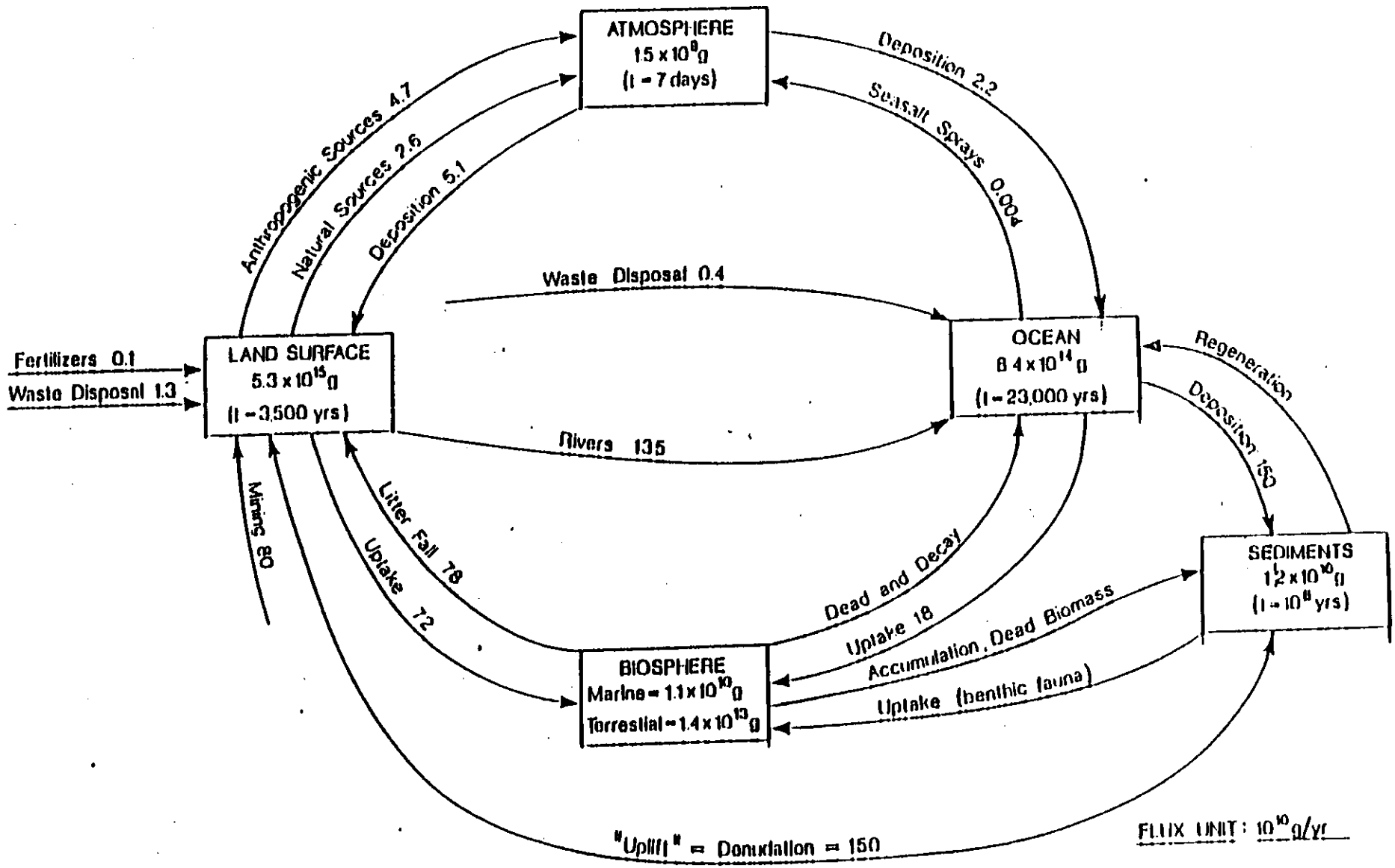


Figure IV-1. The global cycle of nickel on a 1-year frame.

Source: Nriagu 1980

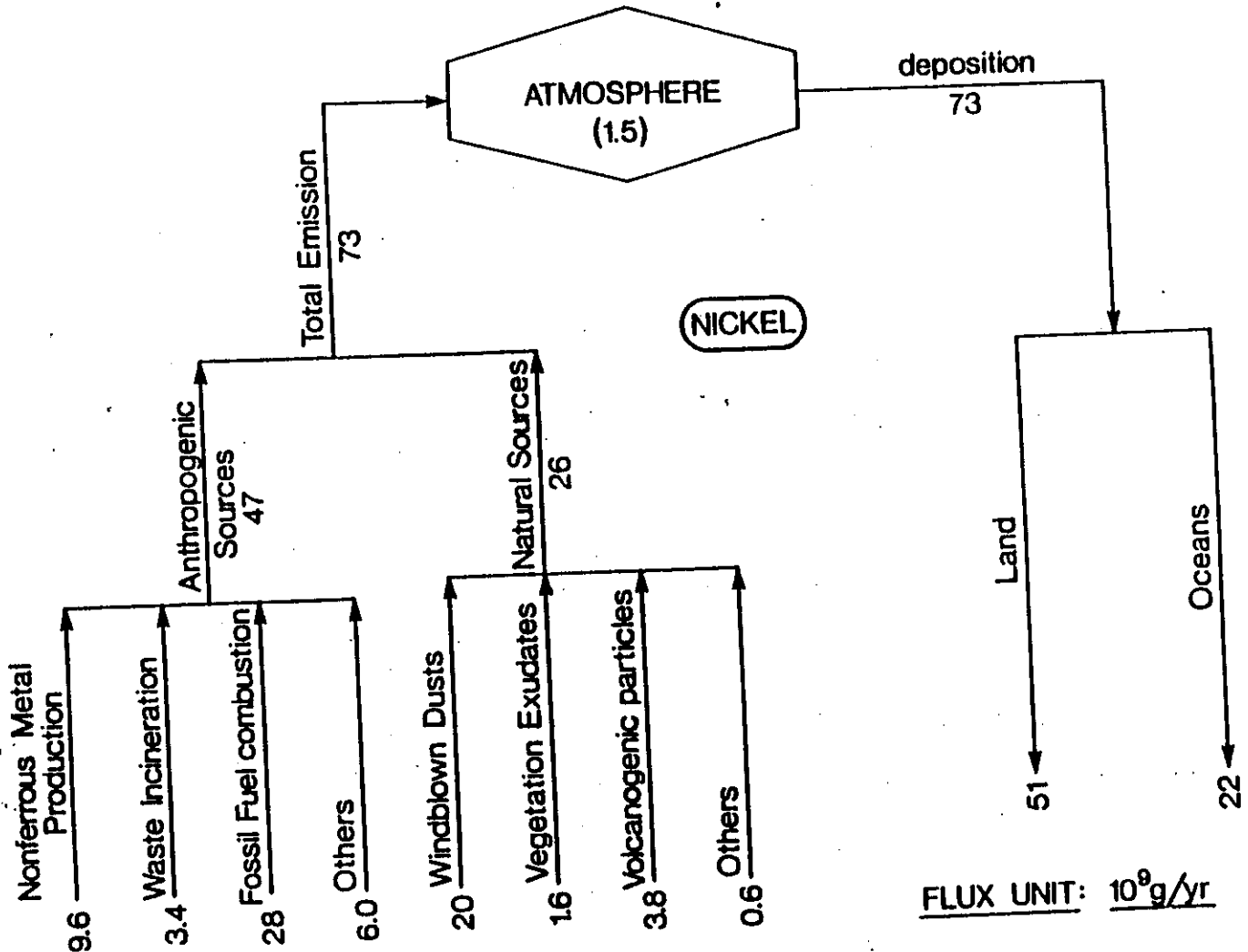


Figure IV-2. Atmospheric portion of the global nickel cycle.

Source: Nriagu, 1980.

1. Chemical Forms

The most toxic form of nickel in air is nickel carbonyl $[\text{Ni}(\text{CO})_4]$ which is the most acutely toxic nickel compound. The lung is the target organ in nickel carbonyl poisoning in humans and animals (U.S. EPA, 1986) and a detailed discussion on the health effects of nickel carbonyl is presented in Part B.

Nickel carbonyl is a volatile liquid at room temperature, boiling at 43°C and decomposing at 60°C (Schroeder, 1970). Nickel carbonyl is widely used as a catalyst in the petroleum, plastics, and rubber industry; as a vehicle for depositing thin films or coatings of nickel in the electronic industry; and as an intermediate process for refining nickel matte in the nickel industry (NAS, 1975). Nickel carbonyl is insoluble in water and relatively unstable in ambient air (half-life of about 100 seconds) (U.S. EPA, 1986). While the EPA (U.S. EPA, 1984) has cited that nickel carbonyl may be emitted by petroleum processing, we do not currently have emissions estimates for California.

Forms of nickel other than nickel carbonyl are utilized industrially to some extent and may find their way to the atmosphere. Nickel compounds used in the electroplating industry include nickel carbonate hydroxide, nickel chloride, nickel cyanide, nickel nitrate and nickel sulfate. Nickel is also applied in the process of pigmentation in the forms of nickel carbonate hydroxide, nickel nitrate, nickel sulfate, nickel diethylglyoxime, nickel oxide, and nickel phosphate which may be released to the atmosphere (Schmidt, et al., 1980).

It is now well established that many trace elements including nickel are mobilized in association with airborne particles derived from high-temperature combustion sources such as fossil-fueled power plants, metallurgical smelters and blast furnaces, municipal incinerators, and automobiles (Science, 1991). The atmospheric lifetime of nickel in the ambient air is approximately seven days.

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APPENDIX I

TOTAL NICKEL SAMPLING AND ANALYSIS METHOD

AIR RESOURCES BOARD
PROCEDURE FOR THE SAMPLING AND ANALYSIS
OF
ATMOSPHERIC TOTAL CHROMIUM, LEAD, MANGANESE AND NICKEL
METHOD 105

Haagen-Smit Laboratory Division
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Procedure for the Sampling and Analysis
of
Atmospheric Total Chromium, Lead, Manganese and Nickel
Method 105

1. Introduction

1.1 This procedure describes a method of sampling and analyzing atmospheric concentrations of total chromium (Cr), lead (Pb), manganese (Mn) and nickel (Ni).

1.2 With a sample volume of 24 cubic meters, the lower detectable limit for Cr, Mn, and Ni is about 1 ng/M^3 , while the lower detectable limit for Pb is about 5 ng/M^3 .

2. Method

2.1 A low-volume sampler is used to collect ambient suspended particulates containing total chromium, lead, manganese and nickel in air parcels.

2.2 A measured volume of air passes through a Teflon filter where particulates are collected.

2.3 The procedure and apparatus for low-volume sampling is described in Appendix C, "Procedure for Lo-Volume Sampling."

2.4 The Teflon filter is removed from the sampler and returned to the laboratory for elemental measurement by X-ray fluorescence (XRF) analysis.

3. Apparatus

3.1 The XRF analyzer consists of the following:

3.1.1 A sample holder which contains an X-ray tube, detector, preamplifier and liquid nitrogen trap.

3.1.2 Amplifier

3.1.3 Multichannel analyzer

3.1.4 Buffer unit

3.1.5 Calculator with printer

3.1.6 The buffer unit and calculator can be replaced by a computer.

3.1.7 A separate unit houses the X-ray tube power supply and control.

Principles of Operation

- 4.1 Fluorescent X-rays are produced by irradiation of the sample with a beam of X-rays from an X-ray tube.
- 4.2 Fluorescent X-rays are detected when they pass into a solid-state detector. The detector is made of lithium-drifted silicon and must be maintained at a very low temperature.
- 4.3 Each X-ray knocks a pulse of electrons free as it passes through the detector. The number of free electrons in the pulse is proportional to the energy of the parent X-ray.
- 4.4 Each pulse of electrons is converted into a small voltage which is proportional to the number of electrons in the pulse. The voltage of each pulse is amplified, digitized and sent to a multi channel analyzer.
- 4.5 The multichannel analyzer sorts the pulses from the amplifier into channels according to the voltage of the pulse. The analyser may be used to process the resultant spectrum in a number of ways.
- 4.6 The buffer stores pulses from the analyser and feeds them into the computer at an acceptable rate.
- 4.7 The computer program subtracts the background of raw spectrum, removes contributions from secondary X-rays, calculates net atmospheric concentrations and sends them to the printer.

5. Procedure

- 5.1 The sample is placed in the X-ray sample holder where a molybdenum X-ray tube irradiates the sample.
- 5.2 The sample chamber is evacuated to less than 500 microns.
- 5.3 The x-ray voltage and tube current are gradually raised to 35 KeV and about 0.2 ma., respectively. The tube current is chosen so that the total X-ray flux into the detector is 4000 to 6000 cps.
- 5.4 An X-ray spectrum is acquired in the pulse height analyser for 600 sec.
- 5.5 After a scan is completed, the X-ray pulses are converted into elemental concentrations and the results are typed out automatically on the printer.

6.

Calculations

- 6.1 Elemental concentrations are obtained assuming a proportionality between net counts and concentration; the proportionality constant is obtained from calibration standards which are stored in the computer.
- 6.2 The standards are thin films obtained from Inmatter Company or dried solutions on filters obtained from Columbia Scientific Industries.
- 6.3 Fluorescent count rates from these standards are proportional to elemental concentrations of Cr, Pb, Mn and Ni expressed in micrograms per cm^2 .

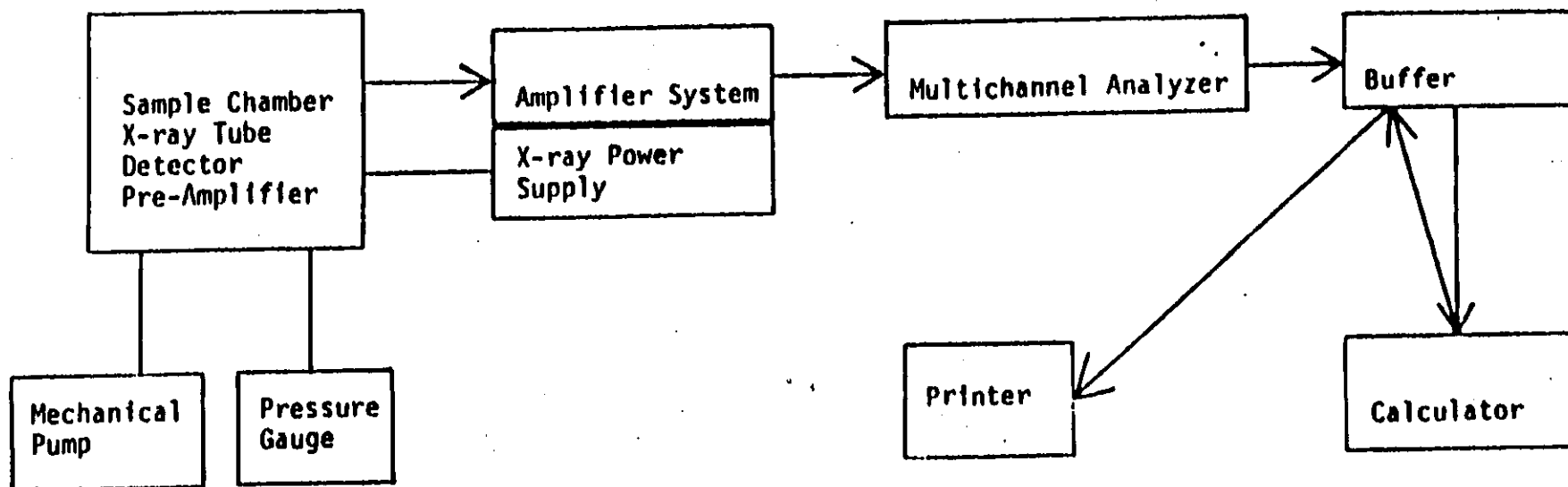
7.

Quality Control

- 7.1 Quality control for the X-ray fluorescence analysis is primarily the monitoring of a fluorescent peak from an elemental standard.
- 7.2 Calibrations are performed every 12 months for the toxic elements Cr, Pb, Mn, and Ni. The result of each calibration is a span factor which is stored in the XRF computer. Elemental calibrations should be within 10% of the last calibrations.
- 7.3 The XRF calibrations are checked several times daily using an elemental standard which is left in the XRF sample holder. The X-ray output must be constant to within ± 3 percent. If the count rate is stable the samples in the sample holder (1 to 8 samples) are analyzed. If the count rate is not within the prescribed limits, the system is checked for the source of the deviation.
- 7.4 Approximately 5 percent of the ambient air samples are reanalyzed. All elemental concentrations must be reproduced within $\pm 10\%$ or ± 2 nanograms per M^3 , whichever is larger.
- 7.5 Interlaboratory analyses of selected samples are performed on a non-routine basis. The laboratories involved since 1982 include U. C. Davis, the South Coast Air Quality Management District, and the Inorganic Analysis Section of the Haagen-Smit Laboratory. The analytical methods included Atomic Absorption Spectrometry, Proton Induced X-ray Emission, and Wavelength Dispersive XRF. All interlaboratory analyses for lead agreed with the Energy Dispersive XRF to within $\pm 10\%$.

Figure 3.2

Block Diagram of Instrumentation



XRF L.O.D.'s

The minimum detectable signal is commonly defined in XRF analysis (and elsewhere) as three times the uncertainty in the background signal N , or $3\sqrt{N}$. The limit of detection (L.O.D.) is proportional to the minimum detectable signal:

$$\text{L.O.D.} = \frac{3\sqrt{N} \cdot A}{C \cdot T \cdot V} \quad (1)$$

In equation (1), A is the area of the aerosol deposit on the filter, C is the elemental calibration constant, T is the scan-time, and V is the sampled volume of air. Also, the calibration constant C is very nearly proportional to the X-ray tube current. The tube current is varied in order to maintain the total X-ray flux into the detector within a certain range. The detector efficiency and spectral resolution depend to a small extent on the X-ray flux. We note here that variations in the sample volume are minor and do not affect the L.O.D. much.

The background signal N is also found to be nearly proportional to the X-ray tube current, as is C . Therefore the L.O.D., by equation (1), is nearly proportional to the inverse of the square-root of the X-ray tube current.

At a tube current of 0.2 ma., the background signal was measured for chromium, manganese, nickel and lead. It and the calibration constant C were almost the same for Cr, Mn, and Ni. This happens because their X-rays fall within a narrow energy region. An L.O.D. of 1.0 ng/M³ for these elements was found at a tube current of 0.2 ma. For lead, C was lower by a factor of three, but N was about the same. Therefore, the L.O.D. for lead was 3 ng/M³ at 0.2 ma.

The tube currents fall within the range of 0.08 to 0.4 ma. for nearly all samples encountered so far from the ARB toxics network. Smaller tube currents correspond to more heavily loaded filters, which scatter and fluoresce more X-rays into the detector. The above range of tube currents gives a range in the L.O.D. for Cr, Mn, and Ni of 0.7 to 1.6 ng/M³, and 2.1 to 4.7 ng/M³ for the L.O.D. of Pb.

These L.O.D.'s, predicted from equation (1), were checked by iterated runs of network samples with measured lead and chromium levels near the predicted L.O.D.'s. First, a sample containing about 1 ng/M³ of total chromium was analyzed thirty times at a tube current of 0.24 ma. The mean was 1.2 ng/M³ with a standard error of the estimate (σ) of 0.55 ng/M³. Twenty of these analyses (67%) were within 1σ of the mean; 28 (93%) were within 2σ , and 100% were within 3σ . Therefore, the chromium analysis seems meaningful at the predicted L.O.D. of about 1 ng/M³.

Similar results were obtained for a sample containing lead at a mean level of 4.9 ng/M³ and a σ of 2.2 ng/M³. Twenty-two analyses (73%) were within 1σ , 28 (93%) were within 2σ , and 100% were within 3σ .

A third sample gave a mean lead concentration of 22.8 ng/M³ with a σ of 1.4 ng/M³. Sixteen analyses (53%) were within 1σ of the mean; 29 (96%) were within 2σ , and 100% were within 3σ .

METHOD OF ANALYSIS

TOTAL AMBIENT NICKEL

I. REAGENTS

Nitric Acid EM Suprapur Nitric Acid (65%)
EM Science Cat. No. 441-2, Lot No. 9061

Perchloric Acid 'Baker Analyzed' Perchloric Acid, (69-
72%), J.T. Baker Inc, Cat. No, 9652-02. Lot
No. B47820

Hydrofluoric Acid 'Baker Analyzed' Hydrofluoric Acid, (48-
51%), J.T. Baker Inc. Cat. No. C1131.

Distilled Deionized Water
Distilled water which has been deionized
using a Millipore Milli-Q deionization
system.

II. SAMPLES

Ten samples of air particulates collected on Whatman PM₁₀ quartz filters were supplied by Bill Davis, ARB, along with both cut and uncut unused filters to be used as blanks. The samples consisted of 0.1944 to 0.2500 (19.44 to 25.00%) of an 8" x 10" filter.

III. DIGESTION

The procedure developed by Dr. Vladimir J. Zatka for INCO Limited was followed. Dr. Zatka was consulted regarding details of the procedure.

The samples were digested in Nalgene Type HP heatable plastic beakers (100 mL Teflon beakers with a graphite base, Nalge Cat. No. 1550-100) with Teflon beaker covers (Nalge Cat. No. 1550).

As eight beakers were available, the ten samples were split into two batches of five each for digestion. A reagent blank, a filter blank, and a spiked blank filter sample were included in each batch. All the samples were treated uniformly in each batch.

Initially, the beakers were cleaned following the recommendation of the Nalge Company. First, 1 N hydrochloric acid was placed in the beakers and they were soaked for more than eight hours. Secondly, the beakers

were rinsed with deionized distilled (D.D.I.) water and filled with 1 N nitric acid and they were soaked for another eight hour period. After this soak, the beakers were again rinsed with D.D.I. water. After a trial run with an unused filter, the results were erratic. Dr. Zarka suggested using aqua regia. Following Dr. Zarka's suggestion the beakers were refluxed for one hour with aqua regia, cooled and rinsed with D.D.I. water. This process was repeated two times and satisfactory results were obtained.

The filter samples were carefully folded so that the surface on which the particulate matter was collected was on the inside of the folded filter and the folded filters were placed into the Teflon beakers. Five milliliters of hydrofluoric acid were added to each beaker to dissolve the quartz filters. Once the filters were dissolved, five milliliters of each, nitric acid and perchloric acid were added. The beakers were covered and gradually heated to 210-240°C on a hot plate. The beaker covers were then adjusted, if necessary, to allow some venting of acid fumes.

When evolution of the heavy perchloric acid fumes had substantially diminished and the samples were approaching dryness they were inspected for completeness of digestion, as indicated by the color of the residue and the appearance of the interior walls of the beakers. Nitric acid and perchloric acid were added in 1 mL aliquots and heated as above. This was repeated until digestion was complete for the entire batch.

The walls of the beakers and the beaker covers were rinsed with D.D.I. water several times, and the beakers were heated as above each time to near-dryness to eliminate residual HF and HClO₄, as much as possible.

When the digestion was complete, the samples were taken to dryness at 210 - 240°C. The residue was dissolved in 1 mL of 8N nitric acid while the beakers were still warm, then quantitatively transferred to a 10 mL volumetric flask and made to volume with D.D.I. water.

IV ANALYSIS

Minor modifications of the analytical method used by ARB South were found to be necessary, probably due to the difference in instrumentation. A Perkin-/Elmer model 603 Atomic Adsorption Spectrophotometer with a model HGA 400 graphite furnace was used.

The Perkin-Elmer model AS-40 autosampler was programmed to inject 20 µL of sample and 5 µL of Mg(NO₃)₂ matrix

modifier containing 0.05 mg $Mg(NO_3)_2$ into the graphite furnace.

Pyro-coated tubes with L'vov platforms were used.

Peak area of absorbance at 232.0 nm integrated over 7 seconds was recorded.

Quantitation was based on standard curves constructed using a SPEX Industries nickel standard diluted to concentrations of 0.010, 0.020, 0.030, 0.050 $\mu g/mL$ nickel in 0.08 N HNO_3 .

A generally negative drift in response during analysis was not eliminated, but the effect was minimized by analyzing a limited number of samples between each standard curve.

The graphite furnace was programmed as follows:

Stop No.	Temperature (°C)	Program
1	110	Ramp = 20 sec. Hold = 15 sec.
2	1500	Ramp = 20 sec. Hold = 25 sec
3	2650	Ramp = 0 sec. Hold = 6 sec. Stop Flow = 6 sec.
4	2700	Ramp = 1 sec. Hold = 4 sec.
5	20	Ramp = 5 sec. Hold = 30 sec.

APPENDIX II
EXPOSURE TO NICKEL FROM INDOOR AIR
AND OTHER MEDIA

Dr. L.Saloum

EXPOSURE TO NICKEL FROM INDOOR AIR AND OTHER MEDIA

I. BACKGROUND

Health and Safety Code Section 39660.5 directs the Board to assess exposures to toxic air contaminants in indoor as well as outdoor environments and to identify the relative contribution of indoor exposure to the total air exposure. Indoor air exposure assessment has become increasingly important as an integral part of risk assessment because:

1. Californians on the average spend 87 percent of their time indoors (Wiley et al., 1990); and
2. personal and indoor air monitoring data indicate that some pollutant concentrations are regularly higher indoors than outdoors.

Indoor air exposure data can therefore provide a realistic estimate of personal exposure through the air environment. Improved exposure estimates permit more accurate public health risk estimates to be developed.

While the main objective of this report is to estimate exposure through indoor air, estimates of exposure through other media are also presented. The inclusion of these estimates will provide a useful perspective of the overall exposures to toxic air contaminants through environmental media. The need for total exposure assessment and some of the issues and concepts involved in developing total exposure estimates are discussed in Appendix A.

II. INDOOR AIR EXPOSURE TO NICKEL

Nriagu (1980), Bennett (1981), Bencko (1983), Grandjean (1984), and Sunderman (1986) have all reviewed environmental sources of and human exposure to nickel. While nickel is the 24th element in order of abundance in the earth's crust, and while nickel compounds are relatively soluble and widely distributed in the environment, the only major source of indoor air contamination by nickel is smoke from indoor combustion. Indoor smoke may originate from combustion of tobacco or from combustion of fuels, especially coal and oil, as a source of heat. Nickel from combustion of fossil fuels is predominately nickel sulfate, which is water soluble. Insoluble fly ash usually contains nickel oxide (U.S. EPA, 1986). There is a small amount of indoor air contamination from windblown soils and volcanic emissions, and from consumer products containing nickel.

Wallace et al. (1984) identified nickel on filters in a U.S. EPA initiated indoor air monitoring program in 1982 in five indoor locations. This was a pilot study that identified the presence of certain substances indoors. The total mass of nickel collected was not quantified.

A. NICKEL FROM FUEL COMBUSTION

Smoke from wood burning can be emitted directly into the living space from stoves and fireplaces, or wood smoke from chimneys may penetrate

indoors from natural or forced ventilation. Sexton, et al. (1984) determined the organic and elemental content of wintertime aerosol in many communities to examine the effects of residential wood combustion on outdoor, indoor, and personal exposures to particulate matter. They report that the fine particulate fraction of the aerosol indoors contributed 1 to 6 ng/m³ of nickel, and the coarse fraction contributed 1 to 3 ng/m³ of nickel.

B. NICKEL FROM CIGARETTE SMOKING

Indoor concentrations of total suspended particles and respirable particulates often exceed outdoor concentrations (Spengler, et al. 1981; Spengler, et al. 1985; Sexton, et al. 1984). Indoor air often contains particles produced indoors augmented by particles infiltrating from outdoors. Smoking is considered to be a major source of indoor particles of certain metals, including nickel.

In their long-term measurements of respirable particles in six cities in the United States, Spengler et al. (1981) found that average indoor to outdoor ratios of respirable particulate matter in the absence of smokers was 1.2. With one smoking inhabitant the ratio was 1.7, and with two or more smoking inhabitants it was 3.3. The investigators concluded that the major source of indoor particulate matter is cigarette smoke. This finding is strongly supported by a study of 44 dwellings in Denmark (Revsbech, et al., 1986). The average ventilation rate of the Danish homes was only 0.23 air exchanges per hour. The indoor concentrations of total suspended particulate matter (SPM) averaged 91 ug/m³ in dwellings where no smoking was reported during the measurements. In dwellings with tobacco consumption, indoor SPM concentration averages ranged between 91 and 475 ug/m³, depending upon the amount of tobacco smoking. The average concentration of SPM was 230 ug/m³, which correlated well ($r=0.716$) with tobacco smoking. In Danish residential areas the outdoor air concentrations of SPM are low, with yearly averages of 30-38 ug/m³.

During combustion of tobacco, most metals remain in the ash, but they may be vaporized or carried in micro-fragments of ash and appear in the mainstream (MS) smoke (IARC, 1985). In addition, the more volatile metals may react with volatile gases to form gaseous species such as nickel carbonyl (Jenkins, 1985). One cigarette contains 1 to 3 ug of nickel (Sunderman and Sunderman, 1961; Szadkowski et al., 1969), of which about 10 percent is released into mainstream smoke (Grandjean, 1984), perhaps in part as nickel carbonyl (Stahly, 1973). The smoker inhales both the mainstream gas and particle phase of the smoke, plus some of the smoke that is generated while the cigarette is smoldering between puffs (sidestream smoke, SS).

The non-smoker is also exposed to nickel in cigarette smoke through "passive" inhalation of environmental tobacco smoke (ETS). The amount of this exposure is a very complex issue and may only be inferred at this time. While the burning of a whole non-filter cigarette results in the release of 20 to 80 ng of nickel in the particulate phase of the mainstream smoke, it results in 13 to 30 times as much nickel in sidestream smoke (NRC, 1986). Hoffmann and Wynder (1986) list the release of total nickel as 20 to 3,000 ng/cig. with a ratio of SS to MS of 13 - 30 to one. In addition, the SS particles are an order of magnitude smaller than those of MS smoke: 0.01 to

0.8 μm for SS versus 0.1 to 1.0 μm for MS (NRC, 1986). The SS particles inhaled by the passive smoker will, therefore, reach the deep lung and be absorbed to a greater extent than those in the mainstream smoke.

In general, an average of about 20 ng/m^3 nickel is present in outdoor urban areas and 10 ng/m^3 in rural areas (Bennett, 1981). In light of the high emissions of nickel in sidestream smoke and the amount of time most people spend indoors, it is apparent that cigarette smoking may contribute much more to people's exposure to nickel than does inhaling an urban atmosphere. However, the exact contribution of cigarette smoking to indoor air nickel concentrations cannot be calculated accurately until further research has been completed on nickel levels in tobacco, speciation and apportionment in smoke, and indoor deposition and adsorption.

C. IN-VEHICLE EXPOSURE TO NICKEL

The South Coast Air Quality Management District measured the in-vehicle concentrations of toxic metals and organic gases during commutes on freeways (Shikiya, *et al.*, 1989). Cars were equipped with samplers designed to capture either airborne particulates or gaseous pollutants. Both diesel and non-diesel cars were tested with windows open or closed, air conditioning on or off, and smoking and non-smoking passengers, with parameters recorded by participants in a log book. The in-car average for nickel was about the same as background levels in the basin. The average background (ambient air) concentration of nickel in the basin was 9.0 ng/m^3 (std. dev. = 3). The average in-vehicle concentration of nickel was also 9.0 ng/m^3 , but the standard deviation (6) was larger.

D. NICKEL FROM SUSPENDED SOIL PARTICLES

As mentioned above, an average of about 20 ng/m^3 nickel generally is present in outdoor air in urban areas and 10 ng/m^3 in outdoor air in rural areas (Bennett, 1981). Natural sources contribute about 16 percent of current atmospheric nickel levels (Grandjean, 1984). Natural sources of nickel in the atmosphere, which may reach indoor air through natural infiltration or mechanical ventilation, include wind-blown soils and volcanic emissions (Nriagu, 1980).

Nickel concentrations in soils depend on the composition of sedimentary and igneous rocks (Sunderman, 1986), and levels from decomposition of these rocks range from 5 to 500 ppm ($\mu\text{g}/\text{gm}$; U.S. EPA, 1986). Soils derived from serpentine rocks, however, may contain up to 6,000 ppm nickel. (Serpentine is common in many parts of the State and is the State rock.) The highest levels of nickel in soils are found in soils located near nickel smelters and metal refineries (up to 24,000 ppm). In soils, nickel may exist as inorganic crystalline mineral, as free ion, or chelated metal complexes (U.S. EPA, 1986). Most nickel compounds are relatively soluble at pH values less than 6.5. Nickel exists primarily as insoluble nickel hydroxides at pH values greater than 6.7. Acid rain has a marked tendency to mobilize nickel from soil and to increase nickel concentrations in ground water.

Bennett (1981) estimated that the mean residence time for nickel in soil is 2,400 years. Nickel levels in soil, therefore, change very slowly.

Soil suspension is the major natural source of nickel. Soil is tracked into homes to become indoor dust as well as blown in through doors, windows, and ventilation systems.

E. SUMMARY OF NICKEL IN INDOOR AIR

There is a relative paucity of data concerning metals and metalloids in indoor air compared to a variety of monitoring studies of volatile organic chemicals and simple inorganic compounds (Fishbein and O'Neill, 1987). Major sources of indoor nickel include: cigarette smoke (both mainstream and sidestream), fuel combustion (wood and fossil fuels), and street and soil dusts.

Nickel is one of the prime components of toxic substances in indoor air. Indoor concentrations of respirable, suspended particulates, which often exceed outdoor concentrations, contain particles of respirable nickel. This also is true of particulates suspended in the air of vehicles being driven through heavy traffic. These sources of nickel are particularly important in estimating risk because activity patterns studies show that individuals spend the majority of their time indoors, especially indoors at home.

III. OTHER ROUTES OF EXPOSURE TO NICKEL

A. CUTANEOUS EXPOSURE

Cutaneous exposure to nickel is ubiquitous from stainless steel utensils, and nickel plated materials such as coins, jewelry, clothing fasteners, suspenders, handles, or car doors. This aspect of human exposure to metals does not usually receive much attention, but in the case of nickel (and chromium) it cannot be forgotten. Residual nickel is present in soaps, fats and oils that are manufactured by hydrogenation using nickel catalysts.

Hypersensitivity to nickel is a common cause of allergic contact dermatitis. Positive dermal patch tests for nickel occur in 8 to 11 percent of women and 0.2 to 2 percent of men. Nickel hypersensitivity may cause dermatitis, pulmonary asthma, conjunctivitis, and inflammatory reactions around nickel-containing implants and prostheses (Sunderman, 1987). There is some evidence to show that nickel is the major allergen for women. There has been a two- to three-fold increase in incidence in the last decade. Many people are sensitized to nickel when their ears are pierced with nickel plated needles and when nickel plated earrings are inserted (Fisher, 1987; Iwatsuki *et al.*, 1987).

Although percutaneous absorption seems to be important in the context of nickel sensitivity, its rate has not been established. Only 500 molecules are needed to sensitize the immunologic system (Rondia, 1979). Percutaneous uptake takes place and occurs mainly through sweat ducts and hair follicles (Mushak, 1980). The kinetics of this absorption are unknown, but the process is probably slow.

Divalent nickel penetrates the skin at the sweat duct and hair follicle ostia and binds to the carboxyl groups of keratin. Nickel may penetrate to the dermis, accumulate in the Malpighian layer, sweat glands

and walls of blood vessels or be absorbed into the systemic circulation. Its main importance is its binding with a variety of proteins and apoantigenic factors with resultant contact dermatitis (Nielsen, 1985).

Oral ingestion of nickel can exacerbate hand eczema in nickel-sensitive people (Cronin *et al.*, 1980). Studies have shown that nickel ions can be leached from household items, equipment and prostheses (Samitz and Katz, 1975) by physiologic saline, blood, sweat and other body fluids and produce flare-ups of nickel dermatitis.

B. FOOD INGESTION

The average dietary intake of nickel by adult persons is approximately 165 ug/day (Sunderman, 1987; Bennett, 1981; Myron *et al.*, 1978; Pennington, 1987), although an average daily intake of 300-500 ug of nickel is not unusual (NRC, 1975). However, with diets rich in oatmeal, cocoa, chocolate, leafy vegetables, nuts, and soya products dietary intake may reach 900 ug/day (Nielsen and Flyvholm, 1984). Food ingestion of nickel constitutes, quantitatively, the most important route of exposure to man.

One to ten percent of dietary nickel is absorbed. In a study by Christensen and Langesson (1981) adult human volunteers ingested 5.6 mg of nickel in the sulfate form. Over three days cumulative urinary excretion was 176 ug. This represented a gastrointestinal absorption of 3 percent. The bio-availability of nickel is dependent upon the composition of the diet (Solomons, *et al.*, 1982). Gastrointestinal absorption of nickel is surprisingly high compared to other toxic elements.

Plants absorb nickel through root uptake from the soil. The usual level of nickel in vegetation is less than 1 ppm. If plants grow in nickel-rich soil, concentrations of nickel may reach as high as 100 ppm (U.S. EPA, 1986). Cultivated crops and natural vegetation, however, have concentrations of nickel between 0.05 ppm and 5 ppm. The nickel content of edible parts of crops grown on soil contaminated by smelter fallout of nickel ranges from 15 to 400 ppm.

Food processing may add nickel to levels naturally occurring in foodstuffs. The catalytic hydrogenation of fats and oils with nickel catalysts may add to the nickel content. Consumption of specialty foods such as soya bean products, cocoa, and nuts increase dietary levels of nickel. Vegetables such as peas, beans, lentils, lettuce, spinach and cabbage contain in excess of 1 ug of nickel per gram of vegetable. Even though the daily average intake of nickel may be 200 or 300 ug or less, three or four times that amount will be ingested by a vegetarian, especially if nuts or chocolate are included in the diet (Grandjean, 1984).

Nickel also may enter the diet through leaching from stainless steel kitchen utensils. Stainless steel saucepans and pots treated by boiling water containing four percent acetic acid (three times, 30 minutes each) released an average of 49 ug/l to the acid solution (Rasmussen, 1983). Similar leaching may occur during cooking of acid foods in steel pots and pans. An electric kettle released 36 mg/l nickel when water alone was used for the boiling test but released 137 mg/l when the four percent acetic acid solution was used.

It is difficult to make accurate estimates of ingested metals due to variability of nickel concentrations in foods as well as variability of eating patterns of individuals. Pennington and Jones (1987) recently measured dietary nickel consumption in food samples from one of the U.S. Food and Drug Administration's (FDA's) Total Diet Study collections in 1984. Since 1974, the FDA Total Diet Study has been used to estimate the levels of some elements in the food supply and in the diets of selected age-sex groups. Composites of 234 individual foods obtained from Pennsylvania and New York were analyzed for molybdenum, nickel, cobalt, vanadium, and strontium by plasma emission spectrometry. The 234 foods were selected on the basis of results from the 1977-78 U.S. Department of Food and Agriculture's Nationwide food consumption survey and the Second National Health and Nutrition Examination Survey conducted by the National Center for Health Statistics. The foods were prepared for consumption after three portions of each food were combined to make a single composite. Samples of each composite were analyzed for trace elements at the FDA Center for Food Safety and Applied Nutrition.

Intakes of nickel in this study ranged from 69 to 162 ug/day. The age-sex groups with daily intakes from the lowest to the highest were infants (68.8), toddlers (90.4), older women (99.6), adult women (106), teenage girls (118.9), older men (130.8), adult men (146.2), and teenage boys (162.5).

Of the 234 Total Diet Study foods, 213 (91.0 percent) had nickel concentrations less than 40 ug/100 gm. Only seven foods had values that exceeded 100 ug/100 gm. Some of these foods were nuts, legumes, items with chocolate, canned foods and grain products.

C. WATER INGESTION

The major source of water for California is surface water. The source of nickel in ambient surface water is from chemical and physical degradation of rocks and soils, deposition of particulates from the atmosphere and discharge from industrial processes. Nickel in surface water, usually present as Ni^{+2} (U.S. EPA, 1986) ranges from 5 ug/l to 1000 ug/l (STORET, 1984). The mean nickel concentration in drinking water in the U.S. is 4.8 ug/l as calculated from a survey of 969 water supplies covering eight metropolitan areas (NRC, 1975; U.S. EPA, Oct. 1986). About 90 percent of the waters tested in this survey contained less than 10 ug/l. Los Angeles' water was reported to contain 4.8 ug/l, and San Diego's water contained 7.8 ug/l (U.S. EPA, 1980).

The STORET Data list the nickel content of 85 percent of California surface waters sampled in 1982 as less than 70 ug/l. The level of nickel in California surface water may be high relative to other metropolitan areas due to the abundance of serpentine rock soils in the state. Nickel is commonly associated with asbestos (Schrier, et al., 1986). Drinking water is usually a secondary source of ingestion of nickel compared to food ingestion. Water flowing through mineralized areas (serpentine) or receiving effluents from mining, agricultural or industrial areas may have elevated levels of nickel. Nickel may be transferred to the water from pipes and fixtures containing nickel or plated with nickel. Measurements have shown overnight leaching of 18 to 900 ug nickel from water faucets filled with 15 ml. of deionized water (Grandjean, 1984).

There is growing evidence that the bio-availability of nickel from drinking water may be greater than from food and beverages. Solomons and coworkers (1982) studied the effects of foods and beverages on gastrointestinal absorption of nickel. After post-prandial ingestion of 5 mg of nickel given as nickel sulfate hexa-hydrate there was no significant elevation of plasma nickel. Sustained elevation of plasma nickel occurred when the same dose of nickel was given to fasting subjects. Certain foods or beverages reduce or prevent the absorption of divalent nickel from the alimentary tract. Uptake of nickel may be inhibited by divalent zinc or calcium ion.

D. IATROGENIC EXPOSURE

Recently, nickel-containing dental alloys have led to human nickel exposure (Moffa, 1982). The average daily nickel release to saliva from such materials is about 4.2 ug/cm² of alloy surface.

Various nickel-containing alloys, such as stainless steel (10 to 14 percent nickel) or cobalt alloy (up to 2.5 percent nickel), are implanted for joint prostheses, plates, screws for fractured bones, surgical clips and sutures. The wire probes leading to the heart muscles from nickel-cadmium battery pacemakers may contain 35 percent nickel (Samitz & Katz, 1975). Older commonly used prosthetic heart valves implanted in rheumatic heart patients contained nickel in the framework (Lyell, *et al.*, 1978). Leaching of the nickel may occur from slow corrosion of the alloys.

Following immersion of the alloys in saline, blood and serum, Samitz and Katz (1975) estimated the leaching rate of nickel at several ug/cm²/day. This rate corresponded to Moffa's (1982) rate of leaching of nickel from dental alloys in saliva. In a study of nickel release from steel powder in a Ringer's solution, Marek and Trehagne (1982) estimated the release rate of nickel at 10 ug per year from 100 cm² of surface area of a hip prosthesis.

This results in about:

$$10 \text{ ug}/100 \text{ cm}^2/\text{yr} = 0.1 \text{ ug}/\text{cm}^2/\text{yr} = \frac{0.1 \text{ ug}/\text{cm}^2}{365 \text{ days}} = 0.27 \text{ ng}/\text{cm}^2/\text{day}.$$

The release of nickel from various implants has had significant consequences, such as the failure of implanted heart valves, bone necrosis and loosening of prostheses, and allergic dermatitis secondary to internal exposure to nickel.

Leaching of nickel may contaminate intravenous fluids. In one case dialysate for hemodialysis was heated in a stainless steel water tank. Dialyzed patients became acutely toxic with plasma nickel levels of 3,000 ug/l (Webster *et al.*, 1980). Even during normal dialysis intravenous nickel uptake is estimated at 100 ug/dialysis (Sunderman, 1983). Additional but small amounts of nickel may be dissolved in I.V. fluids from stainless-steel needles.

Sunderman (1983) suggested a maximal permissible amount of nickel in I.V. fluids per day of 35 ug for a 70-kg adult. The limit was set at 35 ug because it was recently found that a 10-fold higher dose (350 ug/day) caused cardiotoxicity in dogs.

IV. ESTIMATES OF EXPOSURE FROM INDOOR AIR AND OTHER ROUTES

Numerous factors must be considered in evaluating exposures of individuals to metals. The major routes of exposure are inhalation and ingestion. The concentrations of metals in environmental media must be considered first, while absorption and retention within the body determine the actual exposure (NRC, 1975). Metals often occur in mixtures in the environment, and transfer rates are determined by various interactions such as chemical form, route of intake, the age of the individual, and the time of exposure. Human exposure to nickel can be assessed by measuring nickel concentrations in man himself, or by measuring the level of nickel in various compartments of his environment (air, water, soil, food, plus iatrogenic exposure such as from dental alloys and prostheses.) Cutaneous uptake may lead to an allergic response. Systemic uptake, however, is not necessarily the critical factor for nickel-induced lung cancer, because respiratory retention of sparingly soluble nickel is associated with the development of respiratory cancer (Grandjean, 1984).

Estimates of presented daily doses of nickel from different environmental media are presented in Table 1. The assumptions and calculations used to arrive at these estimates are discussed below.

A. INDOOR AIR EXPOSURE

Residents and users of buildings with at least one smoker smoking would experience nickel exposure from sidestream and exhaled mainstream smoke. However, nickel concentrations in indoor environments with smoking occurring have not been directly quantified. Developing accurate estimates of indoor exposure to nickel from ETS is problematic at this time due to a lack of information related to the many factors which would affect the indoor air concentrations and individuals' actual exposures. However, since 20 to 3000 ng nickel may be released per cigarette, this may be considered a worst case exposure estimate per cigarette burned, assuming that all nickel released is inhaled (a very unlikely scenario).

If there is a wood burning fireplace present that is in use, a total of 2 to 9 ng/m³ of nickel may be generated in the aerosol produced. Consequently, assuming people inhale about 20 cubic meters of air per day, 40 to 180 nanograms of nickel (2 to 9 ng/m³ X 20 m³/day) could be presented to the airway per day, as a worst case estimate. Since Californians spend 62 percent (about 15 hours) of their time indoors at home, on the average (Wiley, *et al.*, 1990), and usually do not burn wood in a fireplace for a full 24-hour period, a more realistic upper estimate of exposure from woodburning would be about 25 to 112 ng, assuming about 15 hours of exposure (0.62 X 40 = 25 ng; 0.62 X 180 = 112 ng).

If 24 hours per day were spent in a vehicle (a worst case situation), the presented daily dose from in-vehicle inhalation would total about 180 ng (9.0 ng/m³ X 20 m³), assuming inhalation of 20 m³ of air per day. However, Californians who drive cars spend an average of 100 minutes (about 1.67 hours or 100 min./1400 min. per day = 0.07 days) in their vehicle per day (Wiley, *et al.*, 1990). Their presented daily dose of nickel from in-vehicle exposure would total about 12.6 ng (0.07 days X 180 ng per day).

Soil indirectly contributes 16 percent (Bennett, 1981) of ambient levels to dust that may be blown indoors. Indoor concentrations from windblown soils would then be as high as $10 - 20 \text{ ng/m}^3 \times 3.16 = 1.6 - 3.2 \text{ ng/m}^3$, and could contribute up to $1.6 - 3.2 \text{ ng/m}^3 \times 20 \text{ m}^3 \text{ air/day}$, or about 32 to 64 nanograms per day to the presented dose.

This is probably a maximal presented dose. Based on current knowledge, the actual indoor air level may be lower, but is not readily calculable due to significant variation in air exchange rates between indoor and outdoor air. There is also variation in indoor deposition rates. The amount of nickel retained from inhalation of soil dust would depend on the chemical species of nickel present.

For comparative purposes, a 15-hour exposure would result in about 20-40 ng inhaled per day. This estimate might be more realistic than a 24-hour estimate for individuals who work indoors in buildings with relatively low air exchange rates.

B. CUTANEOUS EXPOSURE

Cutaneous exposure has not been measured and would be expected to vary significantly. Cutaneous absorption appears negligible with regards to total intake, but is important with regards to dermatitis. The rate of absorption has not been established, but appears to be small.

C. FOOD INGESTION

The estimate of food ingestion by the FDA Total Diet Study is used. Absorption, however, is only 1 to 2 percent.

Nickel concentrations in beer and wine average about 30 ug/l (Ellen *et al.*, 1978). A few ug/l of nickel are found in mineral water (Rondia, 1978). Cows' milk usually contains less than 100 ug/l, but nickel content in human milk has been found to range between 20 and 500 ug/l, with an average of 70 ug/l (Clemente *et al.*, 1980).

D. WATER INGESTION

The average nickel content of drinking water in California is 10 ug/l. The average person ingests approximately 2 liters of drinking water per day. The presented dose of nickel by drinking water would be:

$$10 \text{ ug/l} \times 2 \text{ liters per day} = 20 \text{ ug/day} (20,000 \text{ ng/day}).$$

There is evidence that nickel from water is absorbed more efficiently than nickel from food. Although the average absorption from the gastrointestinal tract is 1 to 2 percent, during fasting, absorption may reach 4 to 20 percent (Cronin *et al.*, 1980). Soft drinking water and acid beverages may leach nickel from pipes and containers leading to concentrations much higher than 10 ug/l nickel in water.

E. IATROGENIC EXPOSURE

Dental alloys may contribute $4.2 \text{ ug/cm}^2/\text{day}$ ($4200 \text{ ng/cm}^2/\text{day}$). Prostheses add $0.27 \text{ ng/cm}^2/\text{day}$. Dialysis and intravenous medications are responsible for 100 ug and 35 ug per treatment, respectively. The average contribution from all forms of leaching (including that from kitchen utensils) is unknown but could occasionally add 1 mg to the daily intake of nickel (much in excess of that from food and beverages).

TABLE 1

ESTIMATED PRESENTED DAILY DOSES OF NICKEL THROUGH DIFFERENT MEDIA*

<u>Media</u>	<u>24-Hour Exposure</u>	<u>Other Exposure</u>	<u>References</u>
<u>INDOOR AIR**</u>			
Homes with smokers		20 - 3,000 ng released per cigarette***	Szadkowski, <u>et al.</u> , 1969; Grandjean, 1984; Hoffman & Wynder, 1986
Wood Combustion	40 - 180 ng	25 - 112 ng (15 hr. exp.)	Sexton, <u>et al.</u> , 1984
In-Vehicle	180 ng	13 ng (1.67 hr. exp.)	Shikiya, <u>et al.</u> , 1989
Soil and dust	32 - 64 ng	20 - 40 ng (15 hr. exp.)	Grandjean, 1984 Bennett, 1981
<u>CUTANEOUS</u>	Negligible		
<u>IATROGENIC</u>			
Dental alloys		4200 ng/cm ²	Moffa, 1982
Prostheses		0.27 ng/cm ²	Marek & Treharne, 1982
Dialysis		100,000 ng/treatment	Sunderman, 1983
I.V. Solutions		35,000 ng/treatment	Sunderman, 1983
<u>FOOD AND BEVERAGE</u>	62,000-165,000 ng		Pennington & Jones, 1987; NRC, 1975
Beer and Wine		30,000 ng/l	Ellen, <u>et al.</u> , 1978
Milk		100,000 ng/l	Clemente, <u>et al.</u> , 1980
<u>DRINKING WATER</u> (Surface water)	20,000 ng		NRC, 1975; U.S. EPA; 1986; Cronin, <u>et al.</u> , 1980

* Note that estimated doses across media are not directly comparable, since the degree of absorption and effect on the body vary depending on the route of intake.

** Assumes an individual inhales 20 m³ air per day and drinks two liters of water per day.

*** Insufficient data at present time to calculate presented dose.

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APPENDIX A - Total Exposure From All Media

The concentrations of some pollutants have been measured in different environmental media such as air, water, food, pesticides and drugs. Ideally, these measurements can be integrated to estimate the total exposure to those pollutants through all the environmental media. Total exposure data are critical for setting priorities and formulating regulatory actions that can best achieve overall personal risk reduction.

While one of the main objectives of this report is to define exposure through the air medium, personal exposure data through other media are also included. Exposure data are presented according to three basic routes of exposure which are inhalation, ingestion, and skin absorption.

The combination of exposure data from all media will allow the determination of the total human exposure to a toxic air contaminant through the environment. To determine the added risk caused by a particular exposure, both the shape of the dose-response curve and the previously existing exposure level must be known. Although the exposure through a particular medium may be small, its addition to exposures through other media could provide a total dose in excess of a postulated "safe level".

In addition, the pathway of pollutants in the environment is dynamic and complex. Pollutants emitted into the environment in one medium can remain in that medium, transfer to another medium, and/or disperse into a number of media. This results in different routes of exposure. For example, solvents emitted as water pollutants can become airborne and cause exposure through inhalation. Airborne lead particles can be deposit onto food and result in exposure through ingestion. Thus, inclusion of exposure through all media will provide a more accurate exposure estimate for each route of exposure, including inhalation, which is the Board's primary concern.

Documenting exposure to toxic substances through different media can serve as a stimulus for coordinated risk reduction efforts among different regulatory agencies. Other regulatory agencies are more likely to increase their efforts in reducing the overall exposure through other media if they are made aware of such exposure data.

APPENDIX III
DESCRIPTION OF GLEIT'S METHOD

DESCRIPTION OF GLEIT'S METHOD

Gleit's method accounts for the concentrations below the LOD by setting them equal to the "below -LOD mean" μ_{BLOD} , the mean of the portion of the normal distribution below the LOD. Setting the unknown concentrations to their average value seems intuitively reasonable, and the simulations reported in Gleit's paper show that his method is more accurate than other commonly used approximations.

The below-LOD mean of a normal distribution of a variable with a limit of detection L is given, in terms of L and the mean μ and the standard deviation σ of the distribution, by equation 1:

$$\mu_{\text{BLOD}} = \mu - \sigma * [f((L-\mu)/\sigma) / F((L-\mu)/\sigma)] \quad (1)$$

In equation (1), f and F are, respectively, the probability density function and cumulative distribution function of the standard normal distribution. The "Estimated Concentrations for Samples Below the LOD" reported in Table II-2 are the below-LOD means of the assumed lognormal distributions of the concentrations. These below-LOD means are computed from equation (2) in terms of parameters of the associated normal distribution: the LOD L , the mean concentration from Table II-2, and the estimated standard deviation (which is not tabulated).

$$\exp(\mu + 0.5 * \sigma^2) * F((L - \mu - \sigma^2)/\sigma) / F(L - \mu/\sigma) \quad (2)$$

We now describe how Gleit's method estimates the mean and variance of the assumed normal distribution. The mean and variance cannot be estimated by merely substituting into standard formulas, if below-LOD concentrations are to be set to the below-LOD mean. On the one hand, the mean and variance must be known in order to calculate the below-LOD mean from (1); on the other hand,

the below-LOD mean must be known if it is to be used in the calculation of the mean and variance. Statistical theory, by asserting that a "best-fitting" mean and variance for the distribution exist, provides a way out of this dilemma. Gleit uses a simple iterative procedure to compute these best-fitting parameters. Since his procedure can be simply described in words, a written description is given, supplemented where necessary by equations written in a notation more convenient than Gleit's.

Starting with initial guesses $\mu(0)$ and $\sigma^2(0)$ for the mean and variance, the procedure repeatedly generates new estimates of the mean and variance by the two-step computation described below until successive estimates of the mean and variance converge sufficiently (The K-th pair of estimates are denoted by $\mu(K)$ and $\sigma^2(K)$). The two steps are:

(a) The K+1-st below-LOD mean $\mu_{\text{BLOD}}(K+1)$ is computed by substituting $\mu(K)$ and $\sigma(K)$ (the square root of $\sigma^2(K)$) into equation (1).

(b) The K+1-st estimate of the mean, $\mu(K+1)$, is computed in the usual way with $\mu_{\text{BLOD}}(K+1)$ substituted for the sample values below the LOD. The K+1-st estimate of the variance, $\sigma^2(K+1)$, is also computed in the usual way, with an analogous substitution for sample values below the LOD: the squared deviations from the mean of concentrations below the LOD are set equal to the average squared deviation from the mean of the below-LOD portion of the distribution.

Let the N sample items be $X(1), \dots, X(N)$, and let p be the number of sample items below the LOD. $\mu(K+1)$ is computed by:

$$\mu(K+1) = (1/N) \sum Y(J), \text{ where } Y(J) = X(J) \text{ if } X(J) \geq L \\ \text{and } Y(J) = \mu_{\text{BLOD}}(K+1) \text{ otherwise.}$$

$\sigma^2(K+1)$ is computed by:

$$\sigma^2(K+1) = (1/N) \sum D^2(J), \text{ where } D^2(J) = (X(J) - \mu(K+1))^2 \\ \text{if } X(J) \geq L, \text{ and } D^2(J) = \sigma_{\text{BLOD}}^2(K+1) \text{ otherwise.}$$

The quantity $\sigma^2_{\text{BLOD}}(K+1)$, the average squared deviation of the below-LOD portion of the distribution, is computed from the following equation:

$$\sigma^2_{\text{BLOD}}(K+1) = \sigma^2(K) \cdot [1 - Z(K) \cdot (f(Z(K)) / F(Z(K)))],$$

where $Z(K) = (L - \mu(K)) / \sigma(K)$.

Gleit's method nearly always converges in a few steps unless there are only a few distinct values above the detection limit, in which case it may converge very slowly. Gleit's method and closely related methods appear to be the best available estimators of the mean when the sample includes values below the LOD, as is demonstrated by the simulations reported in Gleit's paper.

APPENDIX IV
NICKEL EMISSION RATE CALCULATIONS

APPENDIX IV

STATIONARY SOURCES

1. Fuel Combustion

a. Residual oil:

The total nickel emissions from residual oil combustion was estimated to range from 8.8 tons to 344 tons per year. Area and stationary point sources used approximately 1,442 million gallons of residual oil¹ in 1984 in California (CARB, 1987c; and CARB, 1987d). Area sources¹ used approximately 57 million gallons and stationary point sources used approximately 1,385 million gallons. Of the 1,385 million gallons, oil & gas extraction activities used 912.6 million gallons; power plants used 232.5 million gallons; and others sources such as refineries, sugar manufacturers, chemical manufacturers used 240.4 million gallons.

The average nickel concentrations in residual oils were reported to range from 3.0 ppmw to 118 ppmw (Surprenant et al., 1980; Menczel et al, 1984; Chansky et al., 1974; Sawyer and Higginbotham, 1981; Electric Power Research Institute (EPRI), 1978; Southern California Edison (SCE), 1986a; Tyndall et al., 1978; Shih et al., 1981; PG&E, 1990). Although it is questionable if all of these values are applicable to oil used in California. The lowest and the highest nickel concentrations were used to estimate a range of nickel emissions from residual oil combustion. Brief discussions of the above studies are as follows:

SCE has measured six samples of residual oil at some of its storage tanks and found an average nickel concentration of 4.71 ppmw (SCE, 1986a). However, these oils are foreign oils with relatively low sulfur (0.17% to 0.18%) and ash content (SCE, 1986b). Staff believe that fuel oils used in the SCE study are not representative of oils burned at most stationary sources in California. PG&E also tested several samples of its residual oils in 1984 and again in 1990. Data from these samples show a range of nickel concentrations from 8.4 to 28 ppmw with an average of 17.1 ppmw (PG&E, 1990). Again, these oils are not considered to be representative of all oils used in California.

Chansky et al. reported a range from 3.0 ppmw to 118 ppmw of nickel for residual oil (Chansky et al., 1974). These values were measured before 1974 and may not represent the current fuel oil characteristics.

Sawyer and Higginbotham measured trace metal concentrations in residual oil tested at Pacific Gas and Electric, Moss Landing power plant in California and reported an average nickel concentration of 27.0 ppmw (Sawyer and Higginbotham, 1981).

1. Sources that individually emit less than 25 tpy of any criteria pollutants except mobile sources, and that are not covered in the point source inventory.

Electric Power Research Institute (EPRI) reported a nickel concentration range from 20 ppmw to 90 ppmw. These numbers were specifically for U.S. residual oil (EPRI, 1978).

Menczel et al. measured 16 samples of residual oils in New Jersey and New York for the period from September 1982 through January 1984 and found nickel concentration to range from 12 ppmw to 68 ppmw (Menczel et al., 1984). A value of 42.2 ppmw was reported by both Surprenant et al. and Shih et al. This value, however, was taken from a 1978 EPA report by Tyndall et al., 1978 (Tyndall et al., 1978). Tyndall et al. measured nickel concentration of a composite sample made to represent typical U.S. residual oil (Tyndall et al., 1978).

Equation 1 was used to estimate nickel emissions from residual oil combustion.

$$EMS = PR * D * C_{Ni} * U_f^{-1} * P_i (1-CNTL)_i \quad (1)$$

Where:

EMS = Nickel emissions, tons per year.
 PR = Amount of oil used, million gallons per year.
 D = Density of residual oil, lbs per gallon.
 C_{Ni} = Nickel concentration, ppmw.
 U_f = Unit conversion factor, 2000 lbs per ton.
 P_i = Fraction of oil used, unitless.
 CNTL = Control fraction, unitless.

Subscript i denotes the specific amount being controlled and the control efficiency.

Oil & Gas Extraction

Steam generators which burned residual oil at the oil & gas fields are equipped with scrubbers (CARB, 1986a). Assuming that these scrubbers are 80% efficient in controlling PM emissions, nickel emissions for this category in 1984 are estimated as follows:

$$EMS_{lower} = \frac{(912.6 \text{ million gal/yr}) * [1.0 (1-0.8)] * 8.2 \text{ lbs/gal} * 3 \text{ ppmw} * (2,000 \text{ lbs/ton})^{-1}}{1} = 2.2 \text{ tons Ni/yr}$$

$$EMS_{upper} = \frac{(912.6 \text{ million gal/yr}) * [1.0 (1-0.8)] * 8.2 \text{ lbs/gal} * 118 \text{ ppmw} (2,000 \text{ lbs/ton})^{-1}}{1} = 88 \text{ tons Ni/yr}$$

Utilities

In a study at Moss Landing power plant in California, Sawyer and Higginbotham reported that nickel emissions from the tested utility boiler are concentrated in the vapor phase as opposed to the solid phase (Sawyer and Higginbotham, 1981). Therefore gaseous control devices may also reduce nickel emissions from residual oil combustion. However, it was assumed that

only PM control devices would affect nickel emissions from residual oil combustion. California utility boilers are not equipped with devices to control PM emissions from residual oil combustion (CARB, 1986a). Nickel emissions in 1984 are therefore estimated as follows:

$$\begin{aligned} \text{EMS}_{\text{lower}} &= \frac{(232.3 \text{ million gals/yr}) * [1.0 (1-0)] * 8.2 \text{ lbs/gal} * 3 \text{ ppmw} *}{(2000 \text{ lbs/ton})^{-1}} \\ &= 2.9 \text{ tons Ni/yr} \end{aligned}$$

$$\begin{aligned} \text{EMS}_{\text{upper}} &= \frac{(232.3 \text{ million gals/yr}) * [1.0 (1-0)] * 8.2 \text{ lbs/gal} * 118 \text{ ppmw} *}{(2000 \text{ lbs/ton})^{-1}} \\ &= 112 \text{ tons Ni/yr} \end{aligned}$$

Other Sources

For this category, residual oil is burned in boilers without devices to control PM emissions (CARB, 1986a). Nickel emissions are estimated as follows:

$$\begin{aligned} \text{EMS}_{\text{lower}} &= \frac{(240.4 \text{ million gals/yr}) * [1.0 (1-0)] * 8.2 \text{ lbs/gal} * 3 \text{ ppmw} *}{(2000 \text{ lbs/ton})^{-1}} \\ &= 3.0 \text{ tons Ni/yr} \end{aligned}$$

$$\begin{aligned} \text{EMS}_{\text{upper}} &= \frac{(240.4 \text{ million gals/yr}) * [1.0 (1-0)] * 8.2 \text{ lbs/gal} * 118 \text{ ppmw} *}{(2000 \text{ lbs/ton})^{-1}} \\ &= 116 \text{ tons Ni/yr} \end{aligned}$$

Area Sources

This source category consists of sources that individually emit less than 25 tons per year of any criteria pollutants except mobile sources, and that are not covered in the point source inventory. The Emission Data System (EDS) identified some industrial manufacturers, and ships as area sources. Residual oil burned at these sources are not PM controlled. Nickel emissions are estimated as follows:

$$\begin{aligned} \text{EMS}_{\text{lower}} &\quad \text{Ships at Ports} \\ &= 28.5 \text{ million gallons/yr} * 8.2 \text{ lb/gal} * 3 \text{ ppmw} * (2000 \text{ lb/ton})^{-1} \\ &= 0.35 \text{ ton/yr.} \end{aligned}$$

Similarly, using the high nickel concentration, the upper emission estimate is 14 tons per year.

$$\begin{aligned} \text{EMS}_{\text{lower}} &\quad \text{Ships In-Transit} \\ &= 16.4 \text{ million gallons/yr} * 8.2 \text{ lb/gal} * 3 \text{ ppmw} * (2000 \text{ lb/ton})^{-1} \\ &= 0.20 \text{ ton/yr.} \end{aligned}$$

Similarly, using the high nickel concentration, the upper emission estimate is 7.9 tons per year.

$$\text{EMS}_{\text{lower}} = \text{Industrial Manufacturers} = 12.1 \text{ million gallons/yr} * 8.2 \text{ lb/gal} * 3 \text{ ppmw} * (2000 \text{ lb/ton})^{-1}$$

$$= 0.15 \text{ ton/yr.}$$

Similarly, using the high nickel concentration, the upper emission estimate is 5.9 tons per year.

b. Distillate Oil:

The total nickel emissions from distillate oil combustion was 1.7 tons in 1984. California used approximately 405.4 million gallons of distillate oil for stationary point and area sources in 1984 (CARB, 1987c; and CARB, 1987d). Area sources¹ used 108 million gallons and stationary point sources used 297.4 million gallons. Of the 297.4 million gallons, oil & gas fields used approximately 7.3 million gallons; utilities used approximately 42.5 million gallons; and other sources such as refineries, chemical manufacturers, food processing facilities, etc. used approximately 247.5 million gallons. At oil fields and utilities, distillate oil was burned in boilers without a device to control particulate matter (PM) emissions (CARB, 1986a). For the other sources, various devices such as baghouses, electrostatic precipitators (ESP) and scrubbers are sometimes used to control PM emissions from the combustion of distillate oil. No device is used to control PM emissions from distillate oil combustion at the area sources. Nickel emissions from distillate oil combustion are estimated using equation 2:

$$\text{EMS} = \text{PR} * \text{D} * \text{C}_{\text{Ni}} * \text{U}_f^{-1} * \text{P}_i (1-\text{CNTL})_i \quad (2)$$

Where:

- EMS = Nickel emissions, tons per year.
- PR = Amount of oil used, million gallons per year.
- D = Density of distillate oil, lbs per gallon.
- C_{Ni} = Nickel concentration, ppmw.
- U_f^{Ni} = Unit conversion factor, 2000 lbs per ton.
- P_f = Fraction of oil used, unitless.
- CNTL = Control fraction, unitless.

Subscript i denotes the specific amount being controlled and the control efficiency.

Average nickel concentrations in distillate oil were reported to range from 0.09 ppmw (parts per million by weight) to 1.7 ppmw (Menczel et al., 1984; and Higginbotham et al., 1981). A weighted average of nickel concentration for the two studies was estimated to be 1.4 ppmw. Using equation 1, the nickel emissions from distillate oil combustion are estimated as follows:

Oil & Gas Extraction

1. Sources that individually emit less than 25 tpy of any criteria pollutants except mobile sources, and that are not covered in the point source inventory.

$$\text{EMS} = (7.3 \text{ million gals/yr}) * [1.0(1-0)] * 7.2 \text{ lbs/gal} * 1.4 \text{ ppmw} * (2000 \text{ lbs/ton})^{-1} = 0.037 \text{ ton Ni/yr}$$

Utilities

$$\text{EMS} = (42.5 \text{ million gals/yr}) * [1.0(1-0)] * 7.2 \text{ lbs/gal} * 1.4 \text{ ppmw} * (2000 \text{ lbs/ton})^{-1} = 0.21 \text{ ton Ni/yr}$$

Other sources

Based on the percentage of oil used in equipment with PM-controls and the average control efficiency of various control devices (CARB, 1986a and CARB, 1986b), it was assumed that 30 percent of the distillate oil was used in equipment with control devices having 90 percent control efficiency and 70 percent was used in equipment without control. Nickel emissions for this category are estimated as follows:

Emissions with 90 percent control:

$$\text{EMS} = (247.5 \text{ million gals/yr}) * [0.30 (1-0.9)] (7.2 \text{ lbs/gal}) * 1.4 \text{ ppmw} * (2000 \text{ lbs/ton})^{-1} = 0.037 \text{ ton Ni/yr}$$

Emissions without control:

$$\text{EMS} = (247.5 \text{ million gals/yr}) * [0.70 (1-0)] (7.2 \text{ lbs/gal}) * 1.4 \text{ ppmw} * (2000 \text{ lbs/ton})^{-1} = 0.87 \text{ ton Ni/yr}$$

Area Sources

$$\text{EMS} = (108 \text{ million gals/yr}) * [1.0(1-0)] * 7.2 \text{ lbs/gal} * 1.4 \text{ ppmw} * (2000 \text{ lbs/ton})^{-1} = 0.54 \text{ ton Ni/yr}$$

c. Waste oil:

California used approximately 13 million gallons of waste oil in 1983 (CARB, 1985a). Average nickel concentration in waste oil was measured and reported to range from 2.1 ppmw to 7.84 ppmw (Waite et al., 1982; and Menczel, 1984). A weighted average concentration was estimated to be 7.7 ppmw. Data are not available on how waste oil was used and whether control devices were used on the equipment burning waste oil. To be conservative, the staff has

assumed that waste oil is burned in equipment without a control device. Using the concentration of 7.7 ppmw and assuming that all nickel in waste oil is emitted upon combustion, nickel emissions from waste oil are estimated using equation 3:

$$EMS = PR * D_w * C_{Ni} * U_f^{-1} \quad (3)$$

Where:

EMS = Nickel emissions, tons per year.
 PR = Amount of oil used, million gallons per year.
 D_w = Density of waste oil, lbs per gallon.
 C_{Ni} = Nickel concentration in waste oil, ppmw.
 U_f = Unit conversion, 2000 lbs per ton.

$$EMS = (13 \text{ million gal/yr}) * (7.5 \text{ lbs/gal}) * (7.7 \text{ ppmw}) / (2,000 \text{ lbs/ton})$$

$$= 0.38 \text{ ton Ni yr}$$

d. Coke:

California burned approximately 266,800 tons of coke in 1985 (CARB, 1987a). Based on limited test data on the nickel concentration of petroleum coke, an average of 166 ppmw was calculated (CARB, 1987b). Assuming that facilities burning coke are 90% efficient in controlling PM emissions, the nickel emissions from coke combustion are estimated to be 4.4 tons in 1984.

e. Coal:

The cement industry is the largest coal user in California. In 1986, the California cement industry used approximately 1.16 million tons of coal (Personal communication, 1987) and emitted approximately 0.37 ton of nickel. Based on information from several districts, the California cement manufacturers are equipped with either baghouses or electrostatic precipitators to control PM emissions (Personal communication, 1987). Other sources (such as sugar manufacturers, coal-fired cogeneration facilities) used approximately 372 thousand tons of coal and emitted approximately 0.12 ton of nickel in 1985 (CARB, 1987a).

Several assumptions have been made in order to estimate nickel emissions from coal combustion. First, it is assumed that all sources using coal burn it in coal-fired industrial boilers. Second, the specific types of control used by the sources other than the cement plants are expected to be as equally effective as the ESP or baghouse.

Goldberg et al. reported 6.6×10^{-5} kg Ni/min. at the outlet of an ESP from an industrial boiler burning 3.47 kg coal/sec. (Goldberg et al., 1981). The nickel emission factor from this industrial boiler is calculated as follows:

$$Emfac_{ESP} = 6.6 \times 10^{-5} \text{ kg Ni/min.} * (60 \text{ sec/min})^{-1} * (3.47 \text{ kg coal/sec})^{-1}$$

$$= 3.2 \times 10^{-7} \text{ kg Ni/kg coal (or ton Ni/ton coal)}$$

Assuming that the nickel emission factor for industrial boiler equipped with an ESP is the same as that equipped with a baghouse, nickel emissions in 1986 from coal combustion are estimated using Equation 4:

$$\text{EMS} = \text{PR} * \text{Emfac}_{\text{ESP}}$$

Where:

EMS = Nickel emissions, tons per year.
 PR = Amount of coal used, tons per year.
 $\text{Emfac}_{\text{ESP}}$ = Nickel emission factor for kiln equipped with ESP,
 ton Ni/ton coal.

Other Sources

$$\begin{aligned} \text{EMS} &= 372,000 \text{ tons coal/yr} * 3.2 \times 10^{-7} \text{ ton Ni/ton coal} \\ &= 0.12 \text{ ton Ni/yr} \end{aligned}$$

It was forecasted that the United States will produce approximately 74 million tons and 83 million tons of portland cement in 1990 and 2000, respectively (U.S. DOI, 1985a). Based on the data from 1980 through 1984, approximately 12% of the portland cement was produced in California (U.S. DOI, 1985b). It takes approximately 0.17 ton of coal to produce 1 ton of cement (U.S. DOI, 1985a). Assuming that California would continue to produce the same ratio of U.S. cement and that the amount of coal required to produce cement will be the same in the future, coal usage by the California cement industry is forecasted to be:

$$\begin{aligned} \text{1990 California} \\ \text{coal usage} &= (74,000,000 \text{ tons/yr}) * 0.12 * 0.17 \text{ ton coal/ton cement} \\ &= 1.5 \times 10^6 \text{ tons/yr} \end{aligned}$$

$$\begin{aligned} \text{2000 California} \\ \text{coal usage} &= (83,000,000 \text{ tons/yr}) * 0.12 * 0.17 \text{ ton coal/ton cement} \\ &= 1.7 \times 10^6 \text{ tons/yr} \end{aligned}$$

In addition to the coal - fired cogeneration facilities that have been identified in the Emission Data System (EDS), there are five coal cogeneration facilities operating in California. These facilities have been estimated to emit approximately 0.27 tons of nickel per year.

2. Asbestos Mining/Milling

Approximately 1.5 to 1.8 mg nickel per gram of chrysotile has been reported (U.S. EPA, 1984). Based on an ARB survey, the staff estimated that chrysotile asbestos milling activities emit approximately 150 to 330 pounds asbestos per year while activities at the mine emit approximately 4,500 pounds per year. Assuming asbestos emissions contain 1.65 mg Ni/gram (the average of 1.5 mg/g and 1.8 mg/g), nickel emissions from asbestos mining and milling are estimated as follows:

At the mill:

$$\begin{aligned} \text{EMS} &= 150 \text{ lbs asbestos/yr} * 1.65 \text{ lbs Ni/1,000 lbs asbestos} \\ &= 0.25 \text{ lb Ni/yr} \end{aligned}$$

Similarly, the high estimate is calculated to be 0.54 lb per year.

At the mine:

$$\begin{aligned} \text{EMS} &= 4,500 \text{ lbs asbestos/yr} * 1.65 \text{ lbs Ni/1,000 lbs asbestos} \\ &= 7.5 \text{ lbs Ni/yr} \end{aligned}$$

Total nickel emissions from chrysotile asbestos mining and milling are therefore estimated to be from 7.8 to 8.0 lbs per year or approximately 0.004 ton per year.

3. Municipal Waste Sludge Incineration

Bennett and Knapp reported nickel emissions from a municipal wastewater sludge incinerator to be 0.24% of the particulate matter (PM) emissions (Bennett and Knapp, 1982). The Emission Data System (EDS) shows 11 California municipal waste sludge incineration facilities in 1983 (CARB, 1987e). These facilities emitted approximately 38.6 tons of PM in 1983. In addition, there are 3 Bay Area facilities, not in EDS, that emitted approximately 27.5 tons of PM (Smith, T., 1987). A rough estimate of nickel emissions from municipal waste sludge incinerators, using data from EDS and available data from the Bay Area, is as follows:

$$\begin{aligned} \text{EMS} &= (38.6 + 27.5) \text{ tons PM/yr} * 0.24 \text{ Ni/100 PM} \\ &= 0.16 \text{ ton/yr} \end{aligned}$$

4. Resource Recovery

As of April 1987, only one resource recovery facility was operating in California (CARB, 1987f). This facility burned approximately 340 tons of waste per day (CARB, 1987f). An uncontrolled emission factor of 3.32×10^{-4} lb Ni per ton of waste burned was reported (Cooper Engineers, Inc., 1984). Assuming 99% control by the application of fabric filters, the nickel emission factor is estimated to be 3.32×10^{-6} lb/ton. If the facility operates 7 days/week and 50 weeks/year, nickel emissions are estimated as follows:

$$\begin{aligned} \text{EMS} &= 340 \text{ tons/day} * 350 \text{ days/yr} * 3.32 \times 10^{-6} \text{ lb/ton} \\ &= 0.40 \text{ lb/yr} \end{aligned}$$

MOBILE SOURCES

1. On-Road Motor Vehicles

Currently, data on nickel emissions in vehicular exhaust are very limited. Pierson and Brachaczek studied airborne particulate matter (PM) at two highway tunnels in Pennsylvania and reported emissions factors of 0.003 mg Ni per km driven for gasoline-powered vehicles and 0.03 mg Ni per km driven for heavy-duty diesel trucks (Pierson and Brachaczek, 1983). The Environmental Protection Agency (EPA) reported an emission factor of 0.04 mg Ni/km from a 1978 Ford Pinto equipped with a three-way catalyst (TWC) plus an oxidation catalyst (OC) (U.S. EPA, 1980). Gabele et al. reported an emission factor of 385.2 ug Ni/mile for a 1980 Volkswagen Rabbit-Diesel while no nickel emissions were reported for a 1980 Oldsmobile Diesel (Gabele et al, 1982). A 1975 Mercedes 240D was reported to emit 13.2 ug Ni/mile

while a 1975 Volkswagen Rabbit-Diesel was reported to emit 30 ug Ni/mile (Hare and Baines, 1979). Test data conducted by the California Air Resources Board (CARB) on four heavy-duty diesel trucks show an average of 24.9 ppmw of PM. CARB has tested 10 gasoline-powered vehicles for trace metal emissions. Preliminary data indicated nickel is a component of the gasoline vehicular exhaust (DeVita, J., 1987). However, data on the amount of nickel in the exhaust and on the types of nickel compounds are preliminary and not available at this time.

a. Gasoline-Powered Vehicles

Catalyst: Because available data are lacking, the emission factor derived from tests on a 1978 Ford Pinto was used to estimate nickel emissions for all catalyst equipped vehicles. Activity rates, emission factors, and nickel emissions are shown in Table A-1.

Non-Catalyst: Assuming that the emission factor for catalyst vehicles is also applicable to this category, nickel emissions from non-catalyst vehicles are shown in Table A-1.

b. Diesel-Powered Vehicles

Heavy-Duty Diesel Trucks: An average PM fraction, reported by the CARB for four heavy-duty diesel trucks tested, was used to estimate nickel emissions for this category. Table A-1 shows the PM estimate, PM fraction, and nickel emissions for this category.

Light-Duty Passenger Cars and Light-Duty Trucks: For the lack of better data, emission factors from two Volkswagens and a Mercedes was used to estimate a range of nickel emissions for this category. Emission estimates for this category are shown in Table A-1.

Table A-1. Estimated Nickel Emission from On-Road Vehicles for 1984

	VMT/yr ¹ (10 ⁹ miles)	Emissions (ug/VMT)	(tpy)
Gasoline-Powered			
Light-Duty Passenger Cars			
Catalyst	95.2	25 ²	2.6
Non-Catalyst	33.2	25 ³	0.91
Light-Duty Trucks			
Catalyst	18.0	25 ⁴	0.50
Non-Catalyst	10.9	25 ⁵	0.30
Medium-Duty Trucks			
Catalyst	4.9	25 ⁶	0.14
Non-Catalyst	4.6	25 ⁷	0.13
Heavy-Duty Trucks			
Catalyst	0	25 ⁸	0
Non-Catalyst	6.0	25 ⁹	0.17
Motorcycles	1.3	25 ¹⁰	0.04

ug/VMT: microgram/vehicle miles travelled

-
- 1 CARB, 1987g. EMFAC7C/BURDEN7, run date January 29, 1987.
 - 2 U.S. EPA, 1980.
 - 3 Same as in # 2.
 - 4 Same as in # 2.
 - 5 Same as in # 2.
 - 6 Same as in # 2.
 - 7 Same as in # 2.
 - 8 Same as in # 2.
 - 9 Same as in # 2.
 - 10 Same as in # 2.

Table A-1. Estimated Nickel Emission from On-Road Vehicles for 1984
(Continued)

	VM ¹ _T /yr (10 ⁹ miles)	Emissions (ug/VMT)	(tpy)
Diesel-Powered			
Light-Duty Passenger Cars	3.6	13.2 - 385 ² ₃	0.05- 1.5
Light-Duty Trucks	0.8	13.2 - 385 ⁴ ₃	0.01- 0.34
Medium-Duty Trucks	0.	13.2 - 385 ⁴ ₃	0
Heavy-Duty Trucks	23,491 TPY of PM	24.9 ppm ⁵	0.59

ug/VMT: microgram per vehicle miles travelled.

-
- 1 CARB, 1987g. EMFAC7C/BURDEN7, run date January 29, 1987.
 - 2 Hare and Baines, 1979; Gabele et al., 1982.
 - 3 Same as in # 2.
 - 4 Same as in # 2.
 - 5 CARB, 1987h.

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APPENDIX V
INFORMATION REQUEST LETTER

AIR RESOURCES BOARD

1102 Q STREET
P.O. BOX 2815
SACRAMENTO, CA 95812



December 9, 1986

Dear Sir or Madam:

Request for Information Regarding
Nickel and Nickel Compounds

I am writing to request information on the health effects of nickel and nickel compounds (nickel) as part of our toxic air contaminant program. This program is based on Health and Safety Code Sections 39650, et seq. which require the Air Resources Board (ARB) to prepare a report which would serve as the basis for regulatory action and to determine by regulation, whether a substance is a toxic air contaminant. Once identified as a toxic air contaminant, the law further requires that the ARB prepare a report on the need and appropriate degree of regulation for the substance. After consultation with the staff of the Department of Health Services (DHS), we have selected nickel as a candidate toxic air contaminant to be evaluated in accordance with the provisions of Health and Safety Code Sections 39650, et seq. During our evaluation of nickel, we will consider all available health information regarding this substance.

Before the ARB can formally identify a substance as a toxic air contaminant, several steps must be taken. First, the ARB must request the Department of Health Services to evaluate the health effects of the candidate substance. Second, the ARB staff must prepare a report which includes the health effects evaluation and then submit the report to a Scientific Review Panel for its review. The report submitted to the Panel will be made available to the public. Information submitted in response to this request will be considered in the report to the Panel. I urge you to submit all information at this time for our consideration in the development of the report for the Panel. The Panel reviews the sufficiency of the information, methods, and data used by the DHS in its evaluation. Last, after review by the Scientific Review Panel, the report with the written findings of the Panel will be considered by the Air Resources Board and will be the basis for any regulatory action to identify a substance as a toxic air contaminant.

December 9, 1986

Prior to formally requesting the DHS to prepare a health effects evaluation of nickel, we are providing, pursuant to the provisions of Section 39660(e) of the Health and Safety Code, an opportunity for interested parties to submit information on the health effects of nickel which they believe would be important in DHS' evaluation of nickel as a candidate toxic air contaminant.

In October 1986, we conducted a reference search on nickel health effects using the MEDLINE and TOXLINE data bases available from the National Library of Medicine. These information services include material published from 1965 to mid-1986. The attached bibliography lists the references from this information search. We are requesting pertinent information on nickel health effects, including any material that may not be available to the public and/or that is not included in the attached bibliography.

The information that you provide may be released (1) to the public upon request, except trade secrets which are not emission data or other information which is exempt from disclosure or the disclosure of which is prohibited by law, and (2) to the Federal Environmental Protection Agency, which protects trade secrets as provided in Section 114(c) of the Clean Air Act and amendments thereto (42 USC 7401 et seq.) and in federal regulation and (3) to other public agencies provided that those agencies preserve the protections afforded information which is identified as a trade secret, or otherwise exempt from disclosure by law (Section 91000 Title 17, California Administrative Code and Health and Safety Code Section 39660).

Trade secrets, which are defined in Government Code Section 6254.7, are not considered public records and therefore will not be released to the general public. However, the Public Records Act (Government Code Section 6250 et seq.) provides that air pollution emission data are always public records, even if the data comes within the definition of trade secrets. On the other hand, the information used to calculate air pollution emissions may be withheld from the public if the information is a trade secret.

If you believe that any of the information you are providing is a trade secret or otherwise exempt from disclosure under any other provision of law, you should identify it as such at the time of submission (Health and Safety Code Section 39660(e)). The ARB may ask you to provide documentation of your claim of trade secret or exemption at a later date.

December 9, 1986

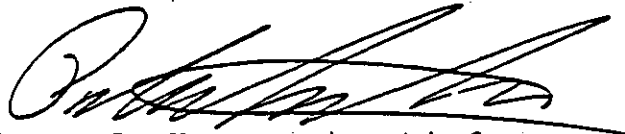
I would appreciate receiving any relevant information you wish to submit by January 26, 1987. Your help in expediting our review will be greatly appreciated. Please send the information in duplicate to the attention of:

William V. Loscutoff, Chief
Toxic Pollutants Branch
Re: Nickel
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

If you have any further questions regarding health effects information, please contact Mr. John Batchelder at (916) 323-1505. For any other questions, please contact Mr. Don Ames at (916) 322-6285.

If you are not the person to whom this request should be addressed, please forward it to the appropriate person in your organization. Also, please let us know whether you would like to continue to receive information inquiries for other candidate substances, and if not, if there is anyone in your organization to whom such requests should be sent.

Sincerely,



Peter D. Venturini, Chief
Stationary Source Division

Attachment

cc: Alex Kelter, DHS
Lori Johnston, DFA
Ed Romano, President, CAPCOA
Jan Bush, Executive Secretary, CAPCOA
David Howekamp, EPA Region IX
Assemblywoman Sally Tanner, Chairwoman
Committee on Toxic Materials
Senator Ralph Dills, Chairman
Committee on Governmental Organization
Senator Art Torres, Chairman, Committee on Toxics
and Public Safety Management
Emil Mrak, Chairman, and Scientific Review Panel Members
APCOs

APPENDIX VI
HEALTH EFFECTS REQUEST TO
DEPARTMENT OF HEALTH SERVICES

Memorandum

Kenneth W. Kizer, M.D., Director
Department of Health Services
714 P Street
Sacramento, CA 95814

Date : June 22, 1987

Subject: Evaluation of
Nickel and
Nickel
Compounds
(Nickel)

James D. Boyd *Jim Boyd*
Executive Officer *J.D.B.*

to : Air Resources Board

I am writing to formally request that the Department evaluate the health effects of nickel and nickel compounds (nickel) as a candidate toxic air contaminant in accordance with Assembly Bill 1807 (Tanner).

According to Health and Safety Code Sections 39660-62, your Department has ninety days to submit a written evaluation and recommendations on the health effects of nickel to the Air Resources Board. If necessary, the Department may request a thirty-day extension.

Attached for your staff's consideration in evaluating nickel are: Attachment I - ambient nickel concentrations which should be used to estimate the range of risk to California residents as required in Health and Safety Code Section 39660(c) and Attachment II - a list of references on nickel health effects which were identified in our letter of public inquiry. A supplemental list of references provided by the public in response to the ARB inquiry letter has been previously transmitted to your staff on February 19, 1987.

My staff is available for consultation in conducting this health effects evaluation and we look forward to continuing to work closely with you and your staff in carrying out this legislative mandate. If you have any further questions regarding this matter, please contact me at 445-4383 or have your staff contact Peter D. Venturini, Chief of the Stationary Source Division, at 445-0650.

Attachments

- cc: Assemblywoman Sally Tanner
- Senator Ralph Dills
- Senator Art Torres
- Jananne Sharpless, Secretary of Environmental Affairs
- Jack C. Parnell, Director, Dept. of Food and Agriculture
- James Kendrick, Chairman and Members of the Scientific Review Panel
- Robin Shimizu, DHS, w/attachments
- Richard Jackson, DHS, w/attachments
- Michael Lipsett, DHS, w/attachments
- Peter D. Venturini, ARB

Attachment I

During 1986, the ARB performed sampling for ambient concentrations of total nickel (nickel) at twenty-three monitoring sites in seven air basins. The maximum concentration of nickel was 77 ng/m^3 ; the minimum concentration was below the detection limit of 1 ng/m^3 . Average concentrations at the monitoring stations ranged from 3.1 ng/m^3 at Citrus Heights to 20.6 ng/m^3 at Bakersfield. For the San Francisco Bay Area, the San Joaquin Valley and the South Coast Air Basins, the average of each basin's total monitoring stations were 4.0 ng/m^3 , 10.6 ng/m^3 and 7.7 ng/m^3 , respectively.

The major source of nickel emissions in California is fossil fuel combustion, specifically residual oil and crude oil. Residual oil is typically used in utility and industrial boiler applications while crude oil is used to generate steam in the oil fields. Estimated nickel emissions from this source range from 14 to 204 tons per year. Other known minor sources of nickel emissions include coal combustion, distillate oil combustion, waste oil combustion, asbestos mining and milling, municipal sludge incineration, electroplating and gasoline and diesel powered vehicles.

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GLOSSARY

Absorption: To take in a substance through a body surface such as lungs, gastrointestinal tract, or skin and, ultimately into body fluids and tissues.

Ambient air: Surrounding; encircling air.

Atmospheric half-life: The time required for one-half of the quantity of an air pollutant to react and/or break down in the atmosphere.

Atmospheric lifetime: The time required for removal of a substance from the atmosphere to the extent that $1/e$ (approximately 37%) of the original material remains.

Cancer: A malignant new growth. Cancers are divided into two broad categories: carcinoma and sarcoma.

Carcinogenic: Able to produce malignant tumor growth.

Carcinogenic risk: The number of potential excess lifetime cancer cases occurring per million persons continuously exposed for 70 years to a given concentration of a TAC.

Confidence limit: The confidence interval is a range of values that has a specified probability (e.g., 95 percent) of containing a given parameter or characteristic. The confidence limit refers to the upper value of the range (e.g. upper confidence limit).

Deposition (wet, dry): Removal of particulate matter from the atmosphere as a result of precipitation or gravitational settling.

Dispersion model: A mathematical model or computer simulation used to predict the movement of airborne pollution. Models take into account a variety of mixing mechanisms which dilute effluents and transport them away from the point of emission.

Excess risk: An increased risk of disease above the normal background rate.

Exposure (E): Contact of an organism with a chemical, physical, or biological agent. Exposure is quantified as the amount of the agent available at the exchange boundaries of the organism (e.g., skin, lungs, digestive tract) and available for absorption.

Gastrointestinal: Pertaining to the intestines and stomach.

Hot spot exposure: Relatively high-level exposure to people living or working near sources of TACs. This is generally based on modeling of emissions data but may also be based on hot spot (near source) ambient air monitoring data.

ISCST Model: Industrial Source Complex Short Term Model is a mathematical model which estimates pollutant ground level concentrations that result from transport of emissions from one or more sources.

Individual cancer risk: The probability, expressed as chances in a million, that a person experiencing 70 years of continuous exposure to a TAC will get cancer.

Limit of Detection (LOD): The concentration at or above which a compound can reliably (at the 99.9 percent confidence level) be detected in the sample.

Mean: A number that represents a set of numbers in any of several ways determined by a rule involving all members of the set; average.

Method of Detection: The method used by which the laboratory staff estimates the LOD.

Standard Deviation: A statistic used as a measure of dispersion in a distribution, the square root of the arithmetic average of the squares of the deviations from the mean.

Troposphere: The lowest region of the atmosphere between the earth's surface and the tropopause, characterized by decreasing temperature with increasing altitude.

Toxic air contaminant (TAC): An air pollutant which may cause or contribute to an increase in serious illness, or which may pose a present or potential hazard to human health.

Unit Risk: The number of potential excess cancer cases from a lifetime exposure to 1 microgram per cubic meter ($\mu\text{g}/\text{m}^3$) of a toxic air contaminant.

XRF method: Analysis for the elements in the sample which is irradiated with monochromatic X-rays, and elements are excited and emit characteristic X-rays unique to the element. The intensity of emitted X-rays is proportional to the amount of element present.

APPENDIX VIII
DESCRIPTIONS OF STATISTICAL TESTS FOR
EXPOSURE DATA

APPENDIX

KRUSKAL-WALLIS TEST

This Kruskal-Wallis Test is a rank statistic defined by the equation:

$$T = 12/(N(N+1)) \sum (R_j - 1/2n_j(N+1))^2/n_j$$

Where N is the total number of data to be ranked, n_j is the number of data in any one group to be ranked and R_j is the sum of the ranks in a group.

The exact distribution of T is found under the assumption that all observations were obtained from the same or identical population. The method is that of randomization which was used also in finding the distribution of the Mann-Witney Test. Under the above assumptions, each arrangement of the ranks 1 to N into groups is equally likely and occur with equal probability which is the reciprocal of the number of ways the N ranks maybe divided into groups being tested. The value of T is computed for each arrangement. The probabilities associated with equal values of T are then added to give the probability distribution of T .

SHAPIRO-WILK TEST

The Shapiro-Wilk Test is an analysis of variance test for normality. The test statistic is obtained by dividing the square of an appropriate linear combination of the sample order statistics by the symmetric estimate of variance. This ratio is both scale and origin invariant and hence the statistic is appropriate for a test of the composite hypothesis of normality.

BOOTSTRAP CONFIDENCE INTERVALS

The Bootstrap Methodology is a way of generating confidence bounds for the sample mean from the empirical distribution using minimal assumptions. The primary assumption made in the Bootstrap is that the sample is representative of the underlying distribution. The fundamental theory behind the Bootstrap is beyond the scope of this memo, so the interested reader may pursue the topic by investigating the following references:

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