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RISK ASSESSMENT FOR NICKEL AND NICKEL COMPOUNDS IN THE AMBIENT AIR FROM EXPOSURE BY INHALATION

REVIEW OF THE EUROPEAN SITUATION

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LIST OF ACRONYMS AND ABBREVIATIONS

AQA/M	Air Quality Assessment and Management					
AQS	Air Quality Standard					
ATMOS/PARCOM	Paris Oslo Commission on Atmospheric pollution					
BAT	Best Available Technology					
CARB	Californian Air Resources Board					
CITEPA	Centre Interprofessionnel Technique de la Pollution					
	Atmosphérique					
CORINAIR	Air emissions inventory in the CORINE EC project					
CORINE	Experimental Programme for gathering, co-ordinating and					
	ensuring consistency of information on the state of the					
	environment and natural resources in the EU					
DG	Directorate General (EC)					
EAE	European Agency for Environment					
EC	European Commission					
EF	Emission Factor					
EIONET	European Environment Information and Observation Network					
EINECS	European Inventory of Existing Commercial Chemical Substances					
ELV	Emission Limit Value					
EMEP	Environmental Monitoring and Evaluation of long range transport					
	of air Pollutants in Europe					
ENERO	European Network of Environmental Research Organization					
EPA	Environmental Protection Agency (USA)					
EQS	Environmental Quality Standards					
ErF	Enrichment Factor					
EU	European Union					
HELCOM	Helsinki Commission (Baltic Sea)					
IARC	International Agency for Research on Cancer (Lyon, France)					
ICNCM	International Committee on Carcinogenesis in Man					
IPPC	Integrated Pollution Prevention Control (Directive)					
IUPAC	International Union of Pure Applied Chemistry					
LCP	Large Combustion Plants					
LRTAP	Long-Range Transport of Toxic Air Pollutants (Geneva), or					
	Long-Range Transboundary Air Pollution					
NTP	US National Toxicology Program					

OECD	Organization for Economic Co-operation and Development		
OPS	Operational Priority Substance		
OSPARCOM	Oslo Paris Commission (North Sea)		
PRTR	Pollutant Release and Transfer Register		
RIVM	Rijkinstitut voor Volksgezondheid en Milieuhygiene (National		
	Institute of Public Health & Environmental Protection, The		
	Netherlands)		
SMR	Standardised Mortality Rate		
TRACE	Trace Toxic Air Concentrations in Europe		
TSP	Total Suspended Particulates		
UNECE	United Nations Economic Commission for Europe (Geneva)		
WHO	World Health Organization (Geneva)		

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EXECUTIVE SUMMARY

The European Union adopted a framework directive on Air Quality Assessment and Management (Directive 96/62/EC) on September 27, 1996. Thirteen agents were listed as priority pollution indicators in Annex 1 of this Directive. « Nickel », which is present at trace levels in the ambient air, is one of these agents, and as such it will be the subject of a sub-directive. This choice was influenced by the World Health Organization Air Quality Guidelines which retained « nickel » as a potentially carcinogenic agent. The preparation of the sub-directive is scheduled to take place in 1998.

The main objective of this « nickel Directive » will be to set an Air Quality Standard (AQS). This AQS will be taken into account by the point source permitting authority when setting emission limit values based on Best Available Technology (BAT), in application of the framework directive on Integrated Pollution Prevention and Control (IPPC).

The objective of this report is to evaluate the risk associated with exposure to nickel in the ambient air, for the general public. The document is divided into three parts, comprising:

- A review of the regulatory context, a description of the physical and chemical characteristics of nickel and certain nickel compounds, a description of certain industrial processes involving nickel, and the characterization of human exposure (emissions, immissions, transport in the atmosphere);
- A risk assessment on the basis of human (occupational exposure) and animal data related to the presumed risk of lung cancer,

An assessment of the risk associated with exposure to nickel in the ambient air for the general public.

ANALYSIS OF HUMAN EXPOSURE TO NICKEL IN THE AMBIENT AIR

The assessment of the risk associated with nickel and nickel compounds for the general public is based on the evaluation of the concentrations of these compounds in the ambient air. By « immission » one must understand the concentration in the ambient air, as opposed to the concentration at the workplace. Due to the relative paucity of direct

immission data, the evaluation was progressively focused on emissions patterns, completed with an attempt to model transport phenomena for both short or long distances. The results must be compared with two other European projects in progress also involving emission inventories: OSPARCOM (Convention of Oslo and Paris for the Protection of the North Sea and North Atlantic) and UNECE-LRTAP (United Nations Economic Commission for Europe/Convention on Long Range Transboundary Air Pollution).

Emission inventories were initiated on a methodical basis at the beginning of the 1980s by Pacyna and Nriagu. The first substance of concern was SO_2 . A nomenclature of various anthropogenic activities was defined. It was progressively extended to other agents including a series of about ten metals (priority being placed on Hg, Pb and Cd). Today, this nomenclature is known as the «ATMOS/PARCOM nomenclature» and its preparation is still in progress for adaptation from the initial SO_2 pattern to a more widespread pattern. The IPPC Directive also envisages the preparation of an emission inventory based on data to be provided by the national authorities responsible for implementing IPPC.

There are two methods of completing the emission inventory table in terms of emitted tonnage. The first is based on direct measurements at the emission point. The measurement results are generally increasingly reported by the industries to their environment authorities. The second method is adopted when measurements have not been performed, and consists of a rough estimate of emissions based on « emission factors ». This latter method is not very satisfactory, especially as most of the emission factors have been established without sufficient involvement of the industries concerned, and above all because inside a specific industrial sector there can be significant differences between the various technologies implemented in dust control equipment.

Three main industrial sectors emerged with respect to significant potential nickel emissions: 1) the nickel production sector 2) the stainless steel production industry as a major nickel user sector 3) heavy fuel oil combustion plants.

There are 7 nickel production plants in the EU and Norway. The two Russian nickel refineries in the Kola Peninsula, near the Scandinavian border, have also been reported. During the last three decades, the tonnage of emitted nickel has been drastically reduced from several hundred tonnes to about 20 tons/y, for the whole EU and Norway. Out of this total of 20 tonnes, the highest individual emission is around 7 tons/y. The

contribution to pollution by nickel in the EU of this sector can be considered negligible. As regards the stainless steel production sector, after re-organization of this industry, there were, at the time this study was performed, about 24 plants distributed in nine member states. This sector, having a high pollution potential, has progressively and considerably reduced its nickel emissions by installing dust control equipment. Today, the corresponding tonnage is expected to become negligible in terms of impact at European level.

As regards fuel oil combustion, this sector is divided into three industrial activities: 1) power generation 2) industrial combustion (these two activities involve « large combustion plants » which fall within the scope of the EU Council Directive on Large Combustion Plants) 3) tertiary and residential combustion. All these combustion units are widely distributed in the EU with variations from one member state to another, depending on energy production policy. In the absence of precise data, the emissions have been estimated by the emission factors method, using the tonnage of heavy fuels consumed by EU Member States appearing in OECD statistics. The value of 28 g/t has been retained, as most representative of the present situation. The estimation for 1990 leads to a total emission for the EU of approximately 1,600 t/y of nickel that can be broken down as follows: 930 t for power plants, 450 t for industrial combustion, and 220 t for tertiary/residential combustion. Italy appears to have the highest emission rate with 640 t in 1990.

These figures probably dropped significantly during the mid-1990s and will decrease further by 2000, when the reduction programme of SO_2 emissions (UNECE protocol) is fully implemented because the emission of nickel, if any, might be related to SO_2 . This decrease will originate mainly in the power generation sector.

At the moment, there is not complete agreement between the emission estimations made in this study and recent estimations made in the course of the UNECE/LRTAP project (giving figures significantly lower than the figures reported in the present study) or those made by TNO.

The chemical description of environmental dusts containing nickel is essential to a toxicity study, according to the European classification of dangerous substances. About 50% of the nickel contained in the particles emitted by oil combustion point sources is in water soluble form (mainly complex sulphate) and 50% is emitted as complex oxides (spinels). Nickel monoxide has not been proved, by limited detection capabilities, to exceed 8% of

total nickel forms. Similarly, nickel sulphides have not been evidenced in these dusts. Immission data have been measured mainly in Germany and Great-Britain. Such measurements have been performed for about two decades and confirmed the down trend in immission values. These values are generally classified into four types of areas: remote, rural, industrial and urban.

Table 1.	Classification of the immission values collected by type of
	area (over the last 25 years)

Type of area	Range of concentration values (ng/m ³)	Number of measurement points	Mean value (ng/m ³)
Urban (*)	3 - 25	35	11.5
Industrialized (+)	2.3 - 50	70	7
Rural (**)	0.7 - 5.5	13	2.5
Remote	0.44 - 0.92	4	0.74

(*) Data from Rotterdam (1970) and from Belgium (site 19, 1980) excepted.

(+) One value from Finland (1990) excepted.

(**) Two values from Belgium (1980) excepted.

The collected data tend to confirm the fact that the immission values in rural areas are mostly below 5 ng (Ni) /m³ and below 1 ng (Ni) /m³ in remote areas. As it is almost impossible to clearly differentiate urban from industrial sites in the collected data, these two areas must be considered as one. The table presented below sums up the data collected from various countries during the last 25 years in urban sites.

Table 2. Immission values for urban sites during the last 25 years

Average immission value (ng/m³)		Decades		Date not available
Country	1970	1980	1990	
Germany	-	16	6	27
Belgium	19	6	-	-
Denmark	_	7	-	-
Spain	-	6	-	10
France [*]	25	_ 15	-	-
Greece	-	12	ŀ	-
Netherlands	1	-	-	-
United-Kingdom	19	10	7	55

Data from Strasbourg excepted.

It appears that, until the beginning of the 1980s, the annual average immission values for urban sites could reach 30 ng (Ni) $/m^3$. At the beginning of the 1990s, values of less than 10 ng (Ni) $/m^3$ were observed.

Data on the last five years are too scarce to derive representative values related to current exposure to nickel in the various areas. Some indications may however be retained:

- For Germany, in five large cities (Mannheim, Stuttgart, Karlsruhe, Freiburg, Dortmund), values range from 1 to 6 ng/m³ (the latter value refers to Dortmund).
- For Belgium, values around 6 ng/m³ were measured in Antwerp and Gent.
- For France, a mean annual value of 10 ng/m³ was observed in Paris in 1992.

According to these first results, it can be expected that current annual average concentrations of nickel in European urban areas are comprised between 1 and 10 ng/m³. As a comparison, in Tokyo, yearly averages were approximately constant, around 5 ng/m^3 for the last five years, and in Canada, during the period 1987-1990, the average ranged from 1 to 5 ng/m³ in ten large cities.

The principal characterization in terms of particle size remains relatively unclear. Data on size distribution of nickel-containing particulate is still limited. Our knowledge is also incomplete in the field of nickel compound speciation analyses, with respect to the chemical properties of nickel compounds, which are expected to be different at emission sources from those in the ambient air.

RISK ASSESSMENT OF NICKEL COMPOUNDS

At present, the only clearly demonstrated end point associated with exposure to nickel is respiratory cancer (nose, lung). Nevertheless, no epidemiological study has been performed on the general public. Thus, in the absence of such human data, the risk assessment for low levels of exposure to nickel in the ambient air (of the order of a few nanograms per cubic meter of nickel) can be derived by extrapolation from occupational human data and animal data, both associated with higher levels of exposure and different chemicals forms of nickel compounds.

Risk assessment of nickel and compounds in the ambient air on the basis of occupational human exposure

The levels of exposure observed in available epidemiological studies were often one million times higher than the nickel exposure levels observed today in the general environment. An epidemiological study of a total of approximately 70,000 workers revealed an excess of nasal and lung cancers (nasal cancers being associated with high level exposures and coarse particles).

All the epidemiological data were reviewed and updated by the International Committee on Nickel Carcinogenesis in Man (ICNCM). The report of this committee, based on the analysis of ten cohorts, was published in 1990. It should be noted that only one sub-cohort in each of the three following studies enables deriving dose-effect relationships: Clydach (UK), Kristiansand (Norway) and Copper Cliff (Canada).

As regards the Clydach cohort, before 1930 (the date when the process was changed), a standardized mortality rate (SMR) of 393 for lung cancer was found. After 1930, the risk of lung cancer was no longer observed (the modified process has led to a drastic decrease in exposure, and also to a chemical change in the nature of exposure, in particular a decrease in sulphur, copper and arsenic levels). The data used in this cohort are those updated by the ICNCM study.

The exposed population of the Kristiansand cohort was relatively stable. The mobility of the workers between workplaces inside the plant was very low. The risk of lung cancer is multiplied by a factor of 3 for workers employed before 1956, but is still significant in the cohort after this period. Soluble nickel exposure is confirmed as being associated with an increase in the risk of lung cancer and questions have been posed as to the role of oxidic nickel in combination with soluble nickel. A specific analysis (published at the end of 1996) was performed by Andersen *et al* on the role of tobacco among the exposed workers. This study was not considered for the present study.

The clearest dose-response relationship was observed in the Copper Cliff cohort. Workers were essentially exposed to nickel sub-sulphide. Exposures were very high before 1951 (up to 100 mg (Ni) $/m^3$). An SMR of 850 was found in a subgroup of 495 workers.

From the analysis of the ten cohorts, the main conclusions pointed out by the ICNCM study are as follows:

"...it appears that more than one form of nickel gives rise to lung and nasal cancer. Although much of the respiratory cancer risk seen among the nickel refinery workers could be attributed to exposure to a mixture of oxidic and sulfidic nickel at very high concentrations, exposure to large concentrations of oxidic nickel in the absence of sulfidic nickel was also associated with increased lung and nasal cancer risks. There was also evidence that soluble nickel exposure increased the risk of these cancers and that it may enhance risk associated with exposure to less soluble forms.

There was no evidence that metallic nickel was associated with increased lung and nasal cancer risks, and no substantial evidence was obtained to suggest that occupational exposure to nickel or any of its compounds was likely to produce cancers elsewhere than in the lung or nose..."

Because of the lack of knowledge concerning effects at low levels of exposure to nickel in the ambient air, extrapolations from the epidemiological studies presented above were performed by the three following organizations to estimate the risk associated with one unit of exposure $(1 \ \mu g \ (Ni) \ /m^3)$:

- US Environment Protection Agency (EPA) 1986 Health Assessment Document for Nickel,
- WHO-Europe (World Health Organization) 1987 Air Quality Guidelines for Nickel currently under revision in 1994-96,
- CARB (Californian Air Resources Board) 1991.

Furthermore, one of the studies was reviewed by Nickel Producers Environmental Research Association (NiPERA) in 1990 for the CARB. This assessment was expanded for NiPERA by Seilkop in 1995. Because of the existence of these risk assessments performed by different organizations, it was not judged necessary to perform new risk calculations in this report.

In the absence of scientific evidence on the existence or not of effects at low levels of exposure, the prudent approach of using a linear model has been adopted. The following table summarizes the unit risk adopted by the various organizations according to the cohort considered in the calculations.

Organization		Clydach	Kristiansand*	Copper Cliff
wнo	1987	5.7 10-4	5.9 10-4	1.5 10-4
	1995		9.6 10-4	
CARB	1991			2.57 10-4
EPA	1986	8.1 10 ⁻⁵ to 4.6 10 ⁻⁴	1.9 10 ⁻⁵ to 1.9 10 ⁻⁴	8.9 10 ⁻⁵ to 1.2 10 ⁻⁴
NiPERA	1995			9.1 10 ⁻⁵

Table 3.Estimates of excess of lung cancer for a life span exposure
to 1 μ g (Ni) /m³ published by four organizations

*The updated data produced by Andersen et al. (1996) have not been considered

All these values are calculated using the linear multiplicative method (relative risk) and using average exposure, except in the case of NiPERA, which proposes a multiplicative model that calculates exposure using the maximum likelihood. It should be kept in mind that these figures are based on the extrapolation of the results of three cohorts that underwent nickel exposures of slightly different chemical nature. Kristiansand workers were exposed to a mixture of insoluble and soluble nickel compounds, whereas workers in the two other cohorts were mainly exposed to insoluble compounds, in particular to nickel sub-sulphide. The chemical species considered in these situations do not completely reflect the composition of dusts present in the ambient air inhaled by the general public.

According to the available results of epidemiological studies for occupational exposures, the maximum excess of risk of lung cancer for a full life span of continuous exposure to $1 \mu g$ (Ni) /m³ ranges from 10⁻⁴ to 4.6 10⁻⁴. An average value of 2.5 10⁻⁴ is proposed.

Risk assessment of nickel and compounds in the ambient air on the basis of animal data

Animal carcinogenesis bioassays provide various data of interest for the identification and the quantification of the potential risk resulting from environmental exposure to nickel compounds. These data include:

• The specific carcinogenic potency of different nickel compounds (speciation)

• An ascertainement of the dose-effect relationship, taking into account the characteristics of the aerosol, the lung burden, and exposure-induced physiopathological changes.

Three main parameters are critical from the methodological point of view:

- The duration of the study which should extend to the greater part of the life expectancy of the species under study, since it is well known that in mammalian species, the age-specific prevalence of cancer rate is a power function of age,
- The size of experimental groups which, as well as the spontaneous incidence of cancers, determines the statistical power of the study,
- The survival rate, which should reach an acceptable level, i.e., a sufficient number of animals should be at risk during most of their life span.

Taking into account these parameters, it can be concluded that:

- Oral administration does not reveal any carcinogenic effect of inorganic nickel compounds,
- Inhalation demonstrates the carcinogenicity of nickel sub-sulphide in rats, and of nickel oxide in rats and presumably in female mice; on the other hand, no carcinogenic effect is observed in rats and mice following exposure to nickel sulphate,
- Non-relevant routes demonstrate *in situ* carcinogenicity for most of the insoluble nickel compounds under study, but, whatever the route of administration, it appears that no primary tumours occur in remote organs.

The exposure of the population to environmental airborne nickel results in the continuous inhalation of low doses during the human life span. The evaluation of human risk at these dose levels using experimental data (only inhalation results will be considered since inhalation is the only relevant route for extrapolation from animal to man) requires adjustments based on pragmatic assumptions:

- A linear dose-effect relationship for carcinogens, when shifting from discontinuous experimental exposures at high aerosol concentrations to continuous exposures at low aerosol concentrations during the whole human life span,
- A constant absorption factor among species (one can evaluate the mean daily human equivalent from the body surface which is proportional to (weight)^{2/3} and which follows a constant relationship among species).

Only the most recent results obtained by the US National Toxicology Program (NTP) in rats have to be considered. As previously reported, inhaled soluble NiSO₄ did not significantly increase lung tumour incidence in rats and mice. Because animals were sacrificed at 24 months, the cancer risk (carcinoma) was underestimated, and the upper limit should be given by the total tumour risk (carcinoma + adenoma). Thus, after correcting for the spontaneous incidence of tumours observed in controls, the mean risk, excluding the negative value observed for the lowest NiO aerosol concentration, expressed as equivalent continuous human exposure, is 0.4 10⁻³ µg (Ni) /m³ for NiO and 3.0 10⁻³ µg (Ni) /m³ for Ni₃S₂.

The environmental airborne physical and chemical form of nickel is not nickel subsulphide (Ni_3S_2), which is emitted in low quantities by certain industrial environments. Therefore, experimental results obtained on NiO should be used to assess the maximum value of the risk, but it is strongly expected that the behaviour of environmental airborne nickel is different from NiO, since it is a different chemical form and associated with other chemicals such as metal compounds or hydrocarbons. In this respect, its solubility would be higher than NiO, but no correcting factor has been proposed to take these phenomena into account.

Experimental results were obtained following exposure to aerosols of selected size (median aerodynamic diameter = $2.4 - 2.8 \ \mu m$, σg =2) to achieve an optimal lung deposition rate. The particle sizes used in animal experiments differ from those measured for most environmental aerosols, which could exhibit a different particle size distribution and thus different lung deposition characteristics. Therefore, it seems advisable to reduce the deposition rate by an arbitrary factor of 5 compared to experimental data, in order to take into account possible differences in the physical characteristics of the aerosol which may occur in the ambient air. Accordingly, the human risk would be: 0.8 10⁻⁴ μg (Ni) /m³.

In rat, carcinogenicity of NiO is only observed for exposure concentrations inducing severe changes in pulmonary clearance. Therefore, the rat lung burden determined at 15 months is overestimated by a factor of 2 to 4. After 2 years, this factor is at least 5 with an upper value of 10. Similar correction factors should be applied to carcinogenic effects. However, because pulmonary clearance parameters are different in rat and in man, a correction factor of 2 for humans seems reasonable. The inhibition of rat lung clearance is related to particle overload but its role during the carcinogenic process is not clear and has to be investigated further.

Finally, assuming a non-threshold linear dose effect relationship, the value of 0.4 10^{-4} for an exposure of 1 µg (Ni) /m³ seems acceptable for NiO, taking into consideration the correction factors mentioned above. In the case of Ni₃S₂, a similar risk estimate can be performed, giving the value of 3 10^{-4} for an exposure of 1 µg (Ni) /m³, a value very similar to the value extrapolated from epidemiological studies performed on workers.

RISK ASSOCIATED WITH NICKEL COMPOUNDS IN THE AMBIENT AIR FOR THE GENERAL PUBLIC

As for most toxic substances, the results from epidemiological studies concerning exposures to nickel do not provide a direct estimate of the risk for very low levels of exposure. Considering the fact that it is impossible to demonstrate the existence of a limit exposure value, below which no side effects are expected, a precautionary attitude is adopted, assuming that a risk exists as long as the exposure is not nil. Risk assessment is no longer a matter of scientific knowledge, but relies greatly on risk management (i.e. including social, economic and ethical considerations). Adopting a precautionary approach, the above analyses on human and animal data permit proposing a risk coefficient for exposure to nickel in the ambient air, keeping in mind that in view of the scientific uncertainties, this value is a result of a theoretical construction of the risk.

The epidemiological studies on occupational exposure led to a unit risk of lung cancer for a full life span of continuous exposure to 1 μ g (Ni) /m³ of 2.5 10⁻⁴. The immission values measured in various European areas (a few ng (Ni) /m³) are not comparable with values of a few μ g (Ni) /m³ to a few mg (Ni) /m³. A first simple linear extrapolation of the results obtained for an exposure of 1 μ g (Ni) /m³ would lead to a unit risk of 2.5 10⁻⁷ for an exposure of 1 ng (Ni) /m³. But the physical and chemical characteristics of the nickel compounds in workplaces are also different from those expected in the ambient air. The unit risk calculated for the ambient air must take these differences into account. This adjustment was performed using the results from animal studies, which permitted distinguishing between the effects of NiO and Ni₃S₂, leading to a unit risk of 0.4 10⁻⁴ for Ni₀ O and 3 10⁻⁴ for Ni₃S₂ respectively, for an exposure of 1 μ g (Ni) /m³.

Considering the fact that in the case of ambient air exposures, Ni_3S_2 is not the relevant nickel compound, and that there is a maximum of a few percents of total nickel as NiO, if any, contrary to the occupational exposures considered in most of the epidemiological studies (essentially Ni_3S_2 and oxidic nickel), the unit risk of lung cancer of 10^{-7} for an

exposure of 1 ng (Ni) $/m^3$ is proposed as a precautionary value for assessing the risk in the ambient air for the general public.

In order to characterize the current risk in the ambient air, the three following values have been adopted on the basis of the data on immission values collected in this study, and some complementary surveys conducted in Paris and in the United-Kingdom.

 Table 4.
 Characterization of areas and corresponding immission rates

Representative value	Type of area	
1 ng/m ³	Rural, low economic activity	
10 ng/m ^{3 *}	Urban, industrial activities	
30 ng/m ^{3**}		

*Areas with an active protective policy regarding air pollution **Areas without an active protective policy regarding air pollution

Assuming an average life expectancy of 70 years, the following figures are obtained for the various ranges of lifetime exposure:

Lifetime exposure level (ng/m ³)	Lifetime risk of lung cancer	Average annual risk of lung cancer
1	10-7	1.4 10 ⁻⁹
10	10-6	1.4 10 ⁻⁸
30	3 10-6	4.3 10-8

Table 5. Calculated risk of lung cancer

Both the individual risk and the collective risk have to be considered insofar as they should provide information for any decision-making process.

Concerning the individual level of risk derived from the previous calculations, it clearly appears that the values are far below the level considered as significant. An annual risk of death in the range of 10^{-6} to 10^{-7} is generally considered as a negligible level of risk.

On the other hand, in a public health perspective, decision-makers may have to consider the collective exposure associated with nickel in the ambient air. A rough calculation was performed for the 1990 European population and led to an expected annual risk of about 4 to 5 cases of lung cancer in excess per year for the whole European population.

1. INTRODUCTION

The European Union adopted a framework directive on Air Quality Assessment and Management (AQA/M directive 96/62/EC) on September 27, 1996. Thirteen agents were listed as priority pollution indicators in Annex 1 of this directive. Nickel, which exists at trace levels in the ambient air, is one of these agents, and will consequently be the subject of a specific sub-directive. This decision was influenced by the World Health Organization Air Quality Guidelines, which retained nickel as a potentially carcinogenic agent. The preparation of the sub-directive is scheduled to take place in 1998. The main objective will be to set an Air Quality Standard (AQS). This AQS will be taken into account by the authority in charge of establishing emission limit values at the level of the emission point sources. These limit values will be based on Best Available Technology (BAT) recommendations, according to the framework directive on Integrated Pollution Prevention and Control (IPPC).

1

The present document was devised at the request of the European industry as a contribution to the preparation of the specific nickel sub-directive, planned by the European Commission in 1998. The objective of the present report is to make an evaluation of the risk associated with the exposure to nickel in the ambient air, for the general public. At present, the only clearly demonstrated end point associated with exposure to nickel is respiratory cancer (nose, lung). The study on the effects of the deposition of suspended nickel-containing particles on the environment (or ecotoxicity) does not fall within the scope of the present report.

The document is divided into three parts. In the first part, a brief review of the state of the art is presented. It includes an inventory of the different actions being conducted for reducing air pollution associated with certain usual polluting gases or particulate matters. Priority is given to European programmes, although international actions such as those conducted by the Organization for Economic Co-operation and Development (OECD) are also considered. The physical and chemical properties of nickel, as well as certain industrial processes using nickel, are briefly described. Some atmospheric measurement networks are listed. The characterization of human exposure to nickel in the ambient air is presented in terms of « air quality values », or « immission » values, with a description of the major emission sources and intermediate transport mechanisms.

Secondly, the unit risk associated with low levels of exposure to nickel in the ambient air (of the order of a few nanograms per cubic meter of nickel) is calculated, derived by extrapolation from occupational human data and animal data, both corresponding to higher levels of exposure and different chemicals forms of nickel compounds that are expected in the ambient air.

Finally, an assessment of the risk associated with nickel in the ambient air for the general population is presented, on the basis of the unit risk calculated above and the exposure levels estimated in the first part of the present report.

1.1. Regulatory context

The major regulatory documents of the European Union for controlling air pollution and related to nickel are listed below.

- The Council Directive 80/779/EEC of July 15, 1980 on the air quality limit values and the guidelines values for sulphur dioxide and suspended particulates. It imposes the creation of measuring stations and the reporting of measurement results to the Commission.
- The Council Decision 81/462/EEC of June 11, 1981 on the conclusions from the Convention on long-range transboundary air pollution.
- The Council Decision 82/459/EEC of June 24, 1982 calling for exchanges of information and data between networks and independent stations measuring air pollution within member states.
- The Council Directive 84/360/EEC of June 28, 1984 on the limitation of air pollution from industrial plants. Nickel indirectly appears in the annexes including: 1) Energy industry 2) Production and processing of metals 3) Waste disposal 4) List of more polluting substances such as « Heavy metals and their compounds ».
- The Council Decision 86/277/EEC of June 12, 1986 on the conclusions from the Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution (LRTAP) related to the long-term financing of the co-operative programme for Environmental Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP).
- The Council Directive 88/609/EEC of November 24, 1988 on the limitation of emissions of certain pollutants from large combustion plants into the air. Nickel is

indirectly involved through the emission limit values related to dusts.

- The Council Directive 89/369/EEC of June 8, 1989 on the prevention of air pollution from new municipal waste incineration plants. Nickel is specifically concerned through an emission limit value.
- The Council Directive 89/429/EEC of June 21, 1989 on the reduction of air pollution from existing municipal waste incineration plants. Nickel is indirectly concerned through an emission limit value on total dust.
- The Council Directive 96/61/EC of September 24, 1996 on « Integrated Pollution Prevention and Control (IPPC) » setting the concepts of Best available Technique (BAT), Emission Limit Value (ELV) and Environment Quality Standard (EQS).
- The Council Directive 96/62/EC of September 27, 1996 on Air Quality Assessment and Management. Nickel is one of the 13 agents listed in Annex 1, and for each of these a sub-directive will be prepared.

In addition, a proposal for a general directive concerning « Integrated Pollution Prevention and Control » (IPPC) is in progress. It is currently the subject of « Common Position » (EC) No. 5/96 adopted by the Council on November 30, 1995. This upcoming directive quotes the « Emission Limit Value » (ELV) and the « Environmental Quality Standard » (EQS) concepts. The AQA/M directive will contribute to the implementation of the IPPC Directive.

1.2. International survey programmes

International programmes have been set up in Europe to deal with the protection of various maritime or terrestrial areas, potentially polluted by the deposition of air pollutants.

- The UNECE Long Range Transport of Air Pollutants was initiated at the end of the 1970s, and has been proposing « conventions » to the member states since its creation. A convention for Hg, Cd and Pb is in preparation. Nickel could be subsequently included.
- The OSPARCOM Convention is a combination of two conventions the Oslo Convention ratified in 1972 and the Paris Convention ratified in 1978. Its objective is to protect the North Sea and North Atlantic Ocean. In 1978, PARCOM created the subgroup ATMOS, a network for the survey of atmospheric pollution.

- HELCOM is a Commission for the Baltic Sea.
- OECD is also involved in this field through its « Air Management Policy Group », which has initiated a research programme on the elaboration of « Air Quality Trends Indicators ».

The first two programmes are closely linked to the present study because they also encompass the nickel emissions inventory (see Section 3.2.1).

Some atmospheric emission or concentration measurement networks have also been set up in Europe:

- EMEP (Environmental Monitoring and Evaluation Programme), linked to UNECE,
- CORINAIR (Air emissions inventory in the CORINE/EC project),
- EIONET (European Environment Information and Observation Network), associated with the European Agency for the Environment (EAE),
- ENERO (European Network of Environmental Research Organization), working in cooperation with CORINAIR.

Most European countries have their own national programmes, partly linked to these European programmes.

1.3. Risk assessment calculations

In addition to the measurement programmes, some complementary risk assessments with respect to nickel have been performed by various institutions such as the Environment Protection Agency (EPA), the World Health Organization (WHO), and the California Air Resources Board (CARB). These calculations have led to risk units related to an average lung cancer incidence (number of cases) as a function of the exposure to nickel, assuming a conventional life span.

PART 1

ANALYSIS OF HUMAN EXPOSURE TO NICKEL IN THE AMBIENT AIR

2. DESCRIPTION OF NICKEL

2.1. General characteristics of nickel

Nickel is the 24th element in order of importance in the terrestrial crust, together with other metals (Mn: 14th, Zn: 25th, Cu: 28th), with an average content of 75 mg/kg (0.0075%). Nickel is a metallic element belonging to the group of « transition metals » (Group VIII) in the Mendeleïev table, like iron and cobalt. Pollution by nickel is generally expressed using this generic term, due to the fact that the analytical methods used to analyse the air samples do not allow any chemical speciation. For the same reason, nickel appears under this generic name in most of the lists of environmental pollutants.

2.2. Chemical speciation of nickel compounds

A distinction must be made between the various nickel-containing compounds which may be encountered in the environment. This speciation is necessary to take into account the possibility of different toxicity and ecotoxicity properties for each species.

2.2.1. Chemical speciation

Speciation is used to differentiate nickel metal and its compounds. Generally, nickel in compounds has a valence of II, while the metallic form has valence of zero. Nevertheless, an important exception exists for the sulphidic forms of nickel, either as simple compounds (combination of nickel and sulphur), or as complex compounds (additional presence of other metallic elements such as iron and/or copper). In this case, a number of sulphides have been identified in nickel-sulphur or nickel-copper-iron-sulphur diagrams. They are non-stoechiometric compounds (such as pentlandite $(Ni,Fe)_9S_8$). In some exceptional situations, nickel can be found at higher valencies (III and IV), but these forms are not of interest in the present report. The official chemical speciation of nickel compounds can be found in the International CAS Register and the IUPAC Nomenclature, which have been extended on a practical basis into the European Inventory of Existing Commercial Chemical Substances (EINECS).

2.2.2. Regulatory speciation

This speciation, based on toxicological assessment, is acknowledged in regulatory terms in directive 67/548/EEC and its 15th adaptation (91/632/EEC), in which ten nickel-containing substances are classified as dangerous substances, each being identified with an individual EEC Number.

2.2.3. Other speciations of nickel compounds

Practically, the use of a specific speciation is often made for certain compounds.

- Inorganic compounds vs. organic compounds (organic nickel compounds are not considered in the present study);
- Simple nickel substances (such as NiO) vs. complex nickel substances (complex ironnickel oxide NiFe₂O₄/trevorite or ammonium-nickel sulphate [(NH₄)₂(NiSO₄)₂ 6H₂O]);
- Water soluble vs. water insoluble (or slightly soluble) compounds. The concept of water solubility is complex because of the kinetics which may play an important role. The British institutions in charge of occupational regulations have defined water solubility as follows: « A water soluble nickel compound is regarded as any single nickel compound or complex which has a solubility greater than 10% by weight in water at 20°C »;
- Water soluble (sulphates, chlorides) vs. water insoluble (carbonates) nickel salts;
- Natural vs. anthropogenic nickel compounds. Natural nickel substances are minerals having complex chemical structures, either « sulphidic » forms (pentlandite [(Ni, Fe)₉S₈]), or « oxidic » forms (complex oxides or complex silicates, such as garnierites [MgO, FeO, (NiO)_x (SiO₂)_y]). Anthropogenic nickel compounds are either « tailor-made substances » for commercial uses, generally simple nickel substances (NiO/monoxide, NiSO₄, 6H₂O/sulphate) or other sub-products emitted in the air. Generally, the latter have a complex chemical structure (complex oxides, double salts). A detailed description of commercial (simple) nickel substances is given in recent monographs [1];
- The ICNCM speciation: a classification into four groups was made in the context of an international epidemiological study conducted by the International Committee on Nickel Carcinogenesis in Man. It considers metallic nickel, soluble nickel, sulphidic

nickel and oxidic nickel. This speciation does not make any distinction between the various oxidic forms of nickel (NiO monoxide vs. a large variety of complex nickel oxides).

2.2.4. The particular case of nickel monoxide (NiO)

This nickel substance is well-known in the field of catalysis. Its catalytic properties depend considerably upon the way it is produced and especially on the temperature at which it is obtained (500 to 1200°C). A large variety of nickel monoxides is commercially available. The toxicological properties of nickel oxides can vary widely.

2.3. Properties of nickel and nickel compounds

These compounds can be characterized by various parameters:

- Water solubility extended to biological fluid solubility,
- Particle size vs. behaviour in the various compartments of the respiratory tract, associated with the morphology of the particles and their specific surface area,
- Degree of crystalline state of water insoluble compounds,
- Nature of the superficial electric charge of the particles,
- Chemical heterogeneity of the particles (example: a nickel compound embedded/encapsulated in a different compound containing nickel or non-nickel-containing),
- Concentration of nickel in the particles ultimately contacting target organs in the human body.

A consideration of the physical properties of nickel-containing substances present in the ambient air must first encompass the multiple possibilities of their physical and chemical transformations during the period of their residence time in the ambient air.

The description below is limited to nickel (the substance), and to some simple nickel compounds relevant to the present study, and for which there are both of commercial interest and literature.

- Nickel metal - Ni (CAS No. 7440-02-0)

This substance is marketed in the form of dark grey powders of various particle sizes for a use as a usual chemical or as a massive (non-dispersible) form for metallurgical uses. Most often it is used as a component of alloys, such as stainless steels or high nickel alloys (super-alloys, etc.). This substance is insoluble in water, but very fine powders may react with water and biological fluids, such as blood, resulting in the formation of Ni²⁺ ions.

- Nickel oxide - NiO (« monoxide ») (CAS No. 1313-99-1)

This substance is marketed either as powders of various particle sizes for use as a chemical, or as a « sinter » whose coarse particles or roundels are used in metallurgy. There are two main categories: « low temperature oxides », generally black in colour, used as chemicals, and « high temperature oxides », grey-green in colour, used in metallurgy. These forms are all crystalline in structure. Nickel monoxide can be encountered in the fumes produced when pure nickel or high nickel alloys are melted. In this case, its crystalline structure is sometimes difficult to detect. Nickel oxide (NiO) is insoluble in water and biological fluids, except for sub-micronic particles present in fumes for which some « bio-solubility » may be observed. The black and grey-green forms are known to have dramatically different chemical reactivities.

- Nickel sub-sulphide-Ni₃S₂ (CAS No. 12035-72-2)

This compound is not present in the ambient air at significant levels. Its main interest comes from its role in the toxicology chapter related to « nickel ». Nickel sub-sulphide has no commercial application. It is an intermediate component of nickel refining. To some extent it is the representative substance of the subgroup of « sulphidic nickel » species.

- Nickel sulphate $NiSO_4, 6H_2O$ (CAS No. 10101-97-0) [7786-81-4 for $NiSO_4$ anhydrous form]

This substance is the representative compound of « water soluble » nickel substances. It is higly soluble in water and biological fluids. Once « solubilized » in biological fluids, nickel is no longer combined as a sulphate, but transformed into various nickel organic compounds or complexes involving various « ligands ». Nickel sulphate may be encountered at the workplace either as droplets (mist) or as dust, but in the ambient air it is in solid particulate form. The main use of nickel sulphate is in metal finishing (nickel plating).

Other nickel-containing (simple) substances are of minor interest for the present study, but are known in metallurgical fields (nickel refining), commercial fields, and toxicological studies:

- Water insoluble compounds

- Nickel mono-sulphide NiS (CAS No. 16812-54-7) (in nickel-refining and toxicological studies);
- Nickel hydroxide-Ni(OH)₂ (CAS No. 12054-48-7) (in nickel-refining and nickel-cadmium batteries);
- Nickel (basic) carbonates NiCO₃, xNi(OH)₂, (with various CAS Nos. -only one is retained in Directive 67/548: 3333-67-3);
- Water soluble compounds
 - Nickel chloride-NiCl₂, 6H₂O (CAS No. 7791-20-0) [7718-54-9 for NiCl₂ anhydrous] (encountered in nickel-refining (electrolytic processes), nickel-plating, and in a few toxicological studies);
 - Nickel nitrate-Ni(NO₃)₂, $6H_2O$ (mainly encountered as an intermediate component in the production of nickel chemicals).
- Nickel carbonyl-Ni(CO)₄ (CAS No. 13463-39-3)
 - This nickel compound has a specific reputation because of its very acute toxicity when inhaled. It may be encountered as a gas in a very specific nickel-refining process. Very unstable under normal conditions (half-life of a few minutes), the presence of this compound in the ambient air is very unlikely.

2.4. Nickel in the ambient air

The chemical forms of nickel in contaminated ambient air, from natural and anthropogenic sources, are generally much more complex than the species described above. These forms pertain to complex oxides (or silicate oxides) or to the complex sulphates group.

2.5. Nickel in ultimate receptive media

The « ultimate receptive medium » considered here is the human body. The nickel chemical species transient transported by the ambient air may reach the human organism in which they are likely to be dissolved in biological fluids. In this case, a significant part

of these nickel-containing substances (molecules) is destroyed, and nickel is released as a divalent ion Ni⁺⁺ which combines with organic ligands. However, a part of these nickel substances may remain at the impact site in particulate form and develop a biological action towards target cells.

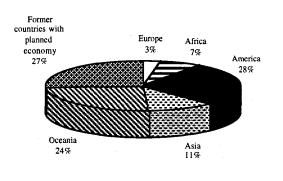
2.6. The nickel industry

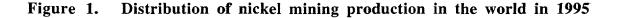
The nickel industry is described below with a distinction made between:

- nickel mining,
- nickel extractive metallurgy,
- nickel-using industries,
- non-specific industries or activities as potential sources of nickel emissions.

2.6.1. Nickel mining

Nickel, which is very abundant in meteorites and in the core of the terrestrial globe (fifth element by order of abundance), is less abundant in the terrestrial crust. It was used 3000 years BC in alloyed forms. Industrial extraction of nickel began in the 19th century in Norway. Detailed descriptions of nickel reserves and mining production are given in the UNEP Technical Guide - Environmental Management of Nickel Production, 1993, and in the « Eramet Statistical Yearbook ». In summary, there are two forms of nickel ore: sulphidic and oxidic. Sulphidic ores are generally extracted from underground mines, while oxidic ores are extracted by « strip mining ». Current reserve estimations are 40% sulphidic nickel and 60% oxidic nickel. Sulphidic ore reserves are available in decreasing order of quantity in Canada, Russia, Australia and South Africa. In the EU, Finland is the only country with such reserves. Oxidic ore (garnierites and/or laterites) reserves are located in New Caledonia, the Philippines, Cuba, Indonesia, Greece, Russia and the Dominican Republic, in decreasing order of quantity. In the EU, in addition to Greece, some significant reserves also exist in former Yugoslavia. Nickel mining is carried out in Finland for sulphidic ores and in Greece for oxidic ores. Intermittently, oxidic ores are also mined in small tonnages in former Yugoslavia. At the border of the EU, in the Kola Peninsula (Russia), sulphidic ores are mined in two different sites: Pechenga and Monchegorsk. Figure 1 represents the distribution of nickel mining production in the world in 1995.





2.6.2. Nickel extractive metallurgy

The production of nickel comprises various complex processes determined by the nature of the orebody. Processes applied to sulphidic ores include two main steps. A first smelting step is applied to a flotation concentrate of iron nickel-copper sulphides, leading to the production of a nickel-copper matte. This step is the most potentially air-polluting. A second « nickel refining » step is then applied to this matte. Modern hydrometallurgy/electrowinning or vapometallurgy (via nickel carbonyl) processes have very low air pollution potential. These processes lead to the production of pure nickel and nickel compounds (oxide/NiO and sulphate). The processes, directly applied to oxidic ores, are similar to steelmaking processes using electric furnaces. They lead to either ferronickel production (an alloy containing roughly 25% Ni and 75% Fe) or to matte production (a metallurgical intermediate made up of nickel-iron-cobalt sulphides). Their polluting potential is not negligible, but the dusts emitted have a very low nickel content. Detailed descriptions of these processes [1] are available in UNEP « Nickel Production », in the OSPARCOM document in preparation, and in the BAT-DG XI. The geographic situation of nickel production plants in Europe is supplied in Figure 2 and Figure 3 provides nickel-production data for Europe. Table 6 provides nickel-production data for various countries of the world.

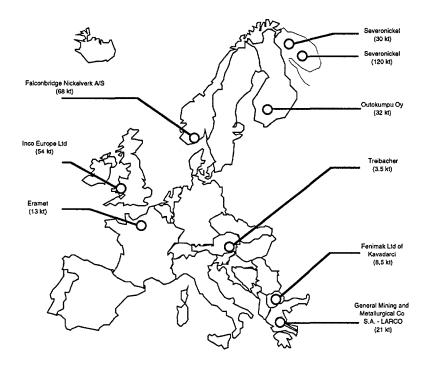


Figure 2. Principal sites of nickel production in Europe and annual capacity

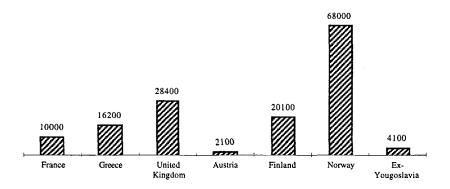


Figure 3. Metallurgical production of nickel in Europe in 1994 (in metric tons)

Region	Production (tons)
Europe	148 900
Africa	46 600
America	170 700 (Canada 102 600)
Asia	127 200
Oceania	98 400
Subtotal	591 800
Former Eastern European Countries	233 300 (CIS 188 000)
World Total	825 100

Table 6.World metallurgical production of nickel in 1994
(in metric tons)

2.6.3. Nickel-using industries

There are two categories of metallurgical industries:

- 1. Industries using « primary nickel » (pure nickel or sinter oxide, ferronickel) for the production of nickel-containing alloys (stainless steels, etc.),
- 2. Industries using these nickel-containing alloys for the manufacture of various equipment or products.

Figure 4 shows the major stainless steel production centres in Europe. Among these nickel-using industries, the production of nickel-containing stainless steels has the greatest potential for air pollution in the absence of dust/fume controlling equipment. Table 7 gives the estimated production amounts for the nine EU Member States having such an activity.

Country	1994	1996
Austria	24	28
Belgium	523	552
Finland	410	442
France	492	529
Germany	1049	839
Italy	640	648
Spain	566	714
Sweden	578	545
The UK	471	488
Total EU	4753	4785

Table 7.Estimated annual productions of nickel-containing stainless
steel (austenitic) of EU Member States, in 1 000 tons [2]

The downstream manufacturing industries have no air pollution potential insofar as they do not involve any melting operations at high tonnage. In addition to these nickel metallurgical industries, nickel and some nickel compounds are used in the chemical industry (catalysts, pigments), the production of nickel-cadmium batteries, nickel plating, the glass industry, etc. None of these industries have a significant air pollution potential specific to nickel. Figure 5 gives the distribution in percentages of nickel consumption in the world. Figure 6 gives the distribution of this nickel consumption among the major industrial sectors and Figure 7 shows distribution between end uses.





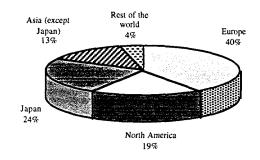


Figure 5. World nickel consumption in 1995

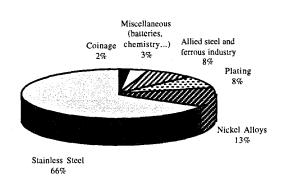


Figure 6. Nickel consumption by activity sector in 1995

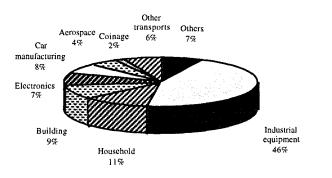


Figure 7. Distribution of nickel consumption by end uses in 1995

2.6.4. Other industries (non-specific)

The extractive pyrometallurgy of non-ferrous metals such as copper and lead may produce some atmospheric emissions of nickel, but are of very small significance. The steel production industry (mild steel) is also a source of atmospheric emissions of nickel.

Fossil fuel combustion, especially liquid fuels, is a considerable potential source of nickel emissions. The nickel content in fossil fuels depends on their geographic origin. Recent nomenclatures have classified different operations having this nickel emission potential:

- Petroleum refining (refining process)
- Power plant fuel combustion

- Industrial combustion
- Residential and urban heating
- Road, fluvial transport

Coal burning is another potential source of nickel emission [1]. Incineration of municipal wastes is also the subject of nickel emission surveillance, but this sector is not yet well documented. It should be noted that emission rates depend directly on the existence and efficiency of fume treatment equipment.

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3. CHARACTERIZATION OF EMISSIONS AND TRANSPORT

3.1. Sources

Sources are characterized by their potential « giving off of environmental pollutants » (WHO 1979), quantified by the emission rate of the pollutant in the air. « Point sources » are either fixed sources (chimneys) or mobile sources (transport vehicles), and must be differentiated from « diffuse sources », where dust or fumes may rise from doors, roofs, or may be raised from soil by wind or traffic. Generally, « point source » emissions can be measured directly, while « diffuse source » emissions are evaluated by modelling, mass balance calculations, etc.

A complete definition of a source must include other information, such as the height of the stack, which plays an important role in the dispersion and transport of the pollutant in the atmosphere, or the seasonal variability of the emission rate (oil-fired power plants or residential heating having greater activity in winter than in summer). « Emission factors » [3] are generally used to calculate the emission rate from a source. Principles of calculation using emission factors related to different processes are presented in [1].

Sometimes, the origin of a contaminant is natural and can be identified by application of the « enrichment factor » (ErF) concept, introduced by Rahn in 1971 [4]. ErF compares the ratio of the concentration of the considered element in a sample, to that of a reference element, selected to be almost entirely of crustal origin, and to the corresponding ratio in the average composition of the Earth's crust, i.e.:

$$ErF = \frac{[c_{x,s}]/[c_{ref,s}]}{[c_{x,c}]/[c_{ref,c}]}$$

where :

 $\begin{bmatrix} c_{x,s} \end{bmatrix} : & \text{concentration of the element x in the sample,} \\ \begin{bmatrix} c_{x,c} \end{bmatrix} : & \text{concentration of the element x in the terrestrial crust,} \\ \begin{bmatrix} c_{ref,s} \end{bmatrix} : & \text{concentration of the selected reference element in the sample} \\ \begin{bmatrix} c_{ref,c} \end{bmatrix} : & \text{concentration of the selected reference element in the terrestrial crust.} \\ \end{array}$

These enrichment factors must be interpreted with caution. In 1976, Rahn suggested that a clear « anthropogenic » source could be concluded for ErF > 10 and a « crustal source » for ErF < 7. However, « crustal » may not systematically mean « natural ». A local increase in an element of natural origin may be encountered as the result of human activity (transport, agriculture, mining, etc.).

3.2. Transport

The dispersion of pollutants may occur at various distances from the source, depending on source characteristics, the physical and chemical properties of the pollutant, and geographical and meteorological conditions. Several approaches for modelling these phenomena have been developed. At the beginning of the 1980s, programmes were conducted to study the transport of heavy metals to remote regions of Scandinavia. The first model calculations of heavy metal transport from central Europe to Scandinavia [5] were made soon after the European emission survey was completed, using a model developed in the OECD programme on the long-range transport of sulphur in Europe [6], [7]. The results of the calculations were compared to the results from measurements made in Norway, Sweden and Finland. The comparison was relatively satisfactory, the difference between the two results being within a factor of 2. In 1990, Bartnicki [8], [9], [10] developed a model of Eulerian type applied to the transport of arsenic and lead in Europe.

Some models of the transport and deposition of heavy metals over the seas have also been developed. A tridimensional model based on the Monte Carlo method was used for cadmium and lead in the North Sea by Krell in 1988 [11], [12]. Similar calculations were made for the Baltic Sea in 1989, in the context of the GESAMP programme [13]. Particular attention can be focused on two models: the OPS (Operational Priority Substances) model for local calculations, and the TRACE (Trace Toxic Air Concentrations in Europe) model for long distances. The OPS model was described in a report published in 1992 by the Dutch « National Institute of Public Health & Environmental Protection » (RIVM) [14]. The objective of this model was to calculate the concentration in the air and deposition on the soil of particles emitted at a given point. This model was considered to be valid for an area within a few kilometres from the emission source and for a permanent emission regime. The TRACE model was designed in 1991 by Alcamo for dispersions on a large scale at the European level [15]. A comparative summary of the different models applied for heavy metals in Europe was made by Pacyna, and is presented in [16].

A specific study on long-range transport possibilities was described in a 1994 publication by a laboratory of Antwerpen University [17]. A series of measurements centred on the North Sea was carried out for several heavy metals, including nickel, over a period of five years. Figure 8 shows a selection of results related to nickel as measured in the ambient air. The influence of the origin of air masses appears clearly; the nickel content differs by several orders of magnitude depending upon the existence of extensive industrial activities (Great-Britain, Germany, France) for measurement points 2, 3 and 4 or areas without anthropogenic emissions (north of the North Sea, the Arctic Ocean) for measurement points 1 and 5.

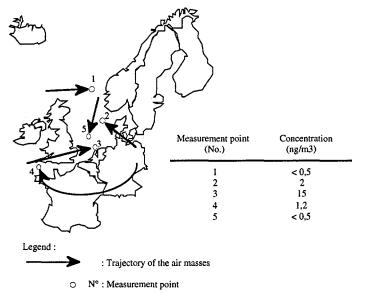


Figure 8. Influence of long range transport phenomena on nickel contents and their concentration over the North Sea [17]

3.2.1. Physical and chemical changes

Once emitted, the solid nickel-containing particles may stay in suspension several days for the finest sizes. During this period, they may undergo physical and chemical changes. One physical change is generally their agglomeration into clusters with particles of other mineral natures and origins, but these are still fine enough to remain suspended. Information on the heterogeneity of the structure of the solid particles (in particular possible encapsulation with different successive layers) is required with a view to assessing the possible impact on the human respiratory tract. Seasonal parameters, including meteorological conditions, strongly influence the evolution of the particles released in the atmosphere, in terms of transportation and chemical reactions. "Dry" and "wet" depositions appear as key processes for scrubbing the atmosphere. Dry deposition is computed conventionally as the product of air concentration and dry deposition velocity as a function of particle diameter, friction velocity, and surface roughness. Dry deposition is mainly associated with Brownian diffusion and gravitational settling [15]. Wet deposition is due to precipitation and involves water-soluble particles. The corresponding scavenging ratio, the ratio of the concentration of metal in precipitation to its concentration in air, is deduced by experimental calculations [18]. According to the major conclusions drawn from the application of models to study the long-range transport of heavy metals to various remote locations [16], wet deposition dominates dry deposition throughout most of Europe, except in some high emission areas and outlying dry areas.

On the other hand, re-suspension has the opposite effect, since it contributes to the enrichment of the atmosphere with ground dust, via, either natural (wind) or anthropogenic mechanical processes.

Physical changes are generally accompanied by a chemical transformation, especially in wet atmospheres, e.g. by reaction with acids (mainly sulphuric acid) or with ammonia. With respect to nickel, this reaction may lead to very complex substances, either complex oxides or complex sulphates in particles of overall acidic or basic reactivity. It should be noticed that it is thermodynamically impossible for a substance such as NiO to be produced during these chemical transformations, whereas it is highly probable that a simple substance such as nickel sulphate is transformed into a complex nickel sulphate + ammonium + magnesium + \ldots , which is still water soluble.

3.2.2. Exposure of the general public

The exposure of the general public to a pollutant in the ambient air is associated with the concentration of pollutant in the inhaled air of the exposed person, everywhere except at the workplace. « Immission » is a term currently used in France and Germany. In the USA and Great Britain, « air quality concentration » is preferred, while the recent issue from the « OECD Guidance Manual for Governments on Pollutant Release and Transfer Registers » (PRTR, 1996) has retained the term « exposure ». The term « immission » has been retained, being more closely associated with the exposure of the general public to air pollution.

Finally, complete exposure characterizing requires a detailed description of the emission and immission values in terms of chemical speciation, physical properties (size of particles), bio-availability for the target cells in the respiratory tract (degree of encapsulating), etc.

3.2.3. Measurement methods

Various measurement methods exist. The first problem is to define, at the sampling stage, the particle size to be monitored. Traditionally, « total suspended matter » is sampled, but PM10 (particulate matters of less than 10 μ m), PM5 and PM2.5 are also used. The selection of the cutting size is extremely relevant in view of further toxicological risk assessment (behaviour in the respiratory tract). In the context of ambient air quality, the terminology « black smoke » and « Diesel fumes » is also encountered.

As regards the measurements, two kinds of analytical methods can be envisaged:

- 1. The determination of total nickel as traces: particles are collected on filters, then analysed,
- 2. The identification of the chemical species (speciation).

The seasonal variability of the immission values requires averaging, starting from minimum measurements made during one year in order to be as representative as possible of the cumulative exposure of the populations of concern. The expression of the results must take into account both the large variability of the real situation and the details of the analytical methods used.

3.3. Calculation principles for atmospheric nickel emissions

The following collection of data on emission and immission are in principle limited to EU countries. However, interest will be placed on Scandinavian regions near non-EU regions, which have a number of large nickel production sites. References to publications or reports related to the USA and other places will be also provided.

As regards chronology, in order to study the general trend in the evolution of emission/immission data, information will be provided, as far as possible, for the last three decades.

3.3.1. Existing measurements programmes

Tables 8 & 9 summarize the different national and international heavy metal survey programmes.

Institution	Programme	Objectives	References
European Commission DG XI	Regulation	Proposal directive COM(94)109 final - 94/0106(SYN)	« Environment and quality of life/Heavy metals » (1986)
	CORINAIR	Inventories of atmospheric emissions in Europe	
	OSPARCOM, HELCOM	Convention on the evaluation of marine pollution Programme ATMOS : Evaluation of the atmospheric pollutants contribution	 « Draft Report of results of CAMP measurements made at coastal stations » ATMOS/PARCOM : - « Emission factors manual (1992) » - « 1987-1992 annual meetings »
EAE		Information on the European environment	Dobris report (1995)
Organization of Economic Co- operation and Development (OECD)	« Air Management Policy Group »	Inventory of European atmospheric emissions	« Emission Inventory of Major Air Pollutants in OECD Countries (1990) »
	ENERO - « European Network of Environmental Research Organizations » EMEP - « Environment	European atmospheric emissions Evaluation of river	
	Monitoring and Evaluation Programme »	pollution in rural areas Evaluation of pollution and long-range transport	
United Nations/Economic Commission for Europe	« Working Group on Technology/Task Force on Heavy metals »	Inventory of European emissions	Rapport « Heavy metal emissions (1991) »

Table 8.International programmes

		······································		
Country	Centre	Connections to other programmes and institutions		
Austria	Umweltbundesamt (Wien)	EAE		
	Amt des Steiermarkischen Landesregierung (Graz)	Measurements in metallurgical production site environments (Leoben- Donawitz)		
Belgium	Institut d'Hygiène et d'Epidémiologie (Bruxelles)			
Denmark	National Agency for Environment Protection			
Finland	Finnish Meteorological Institute	Measurement stations		
Netherlands	RIVM, RijksInstituut voor Volkgezondheid en Milieuhygiene (Bilthoven)			
Norway	NILU (Norsk Institutt for Luft-forskning)	EMEP, OSPARCOM, AMAP, CORINAIR		
France	Institut Français de l'Environnement, IFEN (Orléans)	EAE		
	CITEPA (Centre Interprofessionnel Technique d'Etudes de la Pollution Atmosphérique)	Emissions inventories CORINAIR		
	INERIS (Institut National de l'Environnement industriel et des risques)	ENERO		
	Ecole des Mines (Douai)	EAE, RIVM (Bilthoven)		
	Laboratoire d'Hygiène de la Ville de Paris			
	Laboratoire Central de la Préfecture de Police (Paris)	Measurements in Paris		
	Association pour la Surveillance et l'Etude de la Pollution Atmosphérique en Alsace, ASPA (Strasbourg)	Measurements in Strasbourg		
	AIR NORMAND (Rouen)	Regional measurements (Normandie)		
Germany	UmweltBundesAmt (Berlin)			
	Meteorological Institute (Hamburg)	HHLRT (Long-Range Transboundary Program)		
	GKSS (Research center Geesthacht)	EMEP Programme (North and Baltic Seas)		
	Gesellschaft für Umweltmessungen und Umwelterhebungen, Karlsruhe (BW.)	Measurements in Baden-Wurtenberg		
United Kingdom	Quality of Urban Air Review Group QUARG	Coordinator		
	Warren Spring Laboratory	Supervision programmes		
	AEA Technology	Urban measurements		
	National Environment Technology Centre	Rural measurements		

Table 9.National programmes

3.3.2. Natural nickel sources

Both natural and anthropogenic sources contribute to atmospheric emissions of nickel. An estimation made by Rasmussen [19] gives a ratio of 93% natural to 7% anthropogenic sources for the annual emissions of primary particulate matter in the atmosphere. For nickel, values in the range of 16% to 36% for the natural part of atmospheric nickel are reported in [20], [21]. This distribution may vary widely from one geographical area to another, depending on human activities.

As for many other heavy metals, nickel can enter the atmosphere from various natural sources, such as windblown soil dusts, seaspray, volcanic ash, biogenic material (plants) and forest fire debris [22] (see Figure 9).

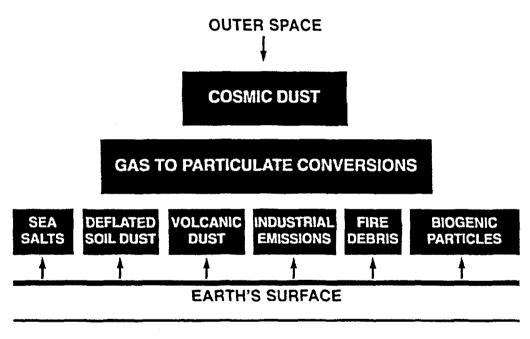


Figure 9. Sources of atmospheric particulate [19]

The average content of nickel in the terrestrial crust is estimated to be 75 ppm (0.0075%). For rural areas, this content may vary from 3 to 3000 ppm. Generally, soil and volcanoes are the major source of atmospheric nickel and may contribute 40-50% to airborne nickel from natural sources [22].

Estimations of global nickel emissions from natural sources have been made and the results are presented in Table 10.

Source	Nriagu	Schmidt & Andren	Barrie
	(1980)	(1980)	(1981)
Soil dust	20	4.8	7.5-37.5
Volcanoes	3.8	2.5	10-60
Vegetation	1.6	0.82	1.5-20
Forest fires	- ^a	0.19	0.3-15
Meteoric dust	-	0.18	-
Sea salt	-	-	27
Sea aerosol	-	0.009	-
Total	26 ^b	8.5	46-160

Table 10.Global atmospheric emission of nickel from natural sources
 (10^6 kg/year) [22]

^a No available data.

^b Total includes 0.6 for "others".

A rough estimation of the global emission of nickel from anthropogenic sources was performed by Schmidt & Andren in 1980 [22]. The results are presented in Table 11.

The estimation of the relative proportion of nickel emitted from natural vs. anthropogenic sources remains a controversial issue. In addition to the uncertainty associated with natural sources, assessment of anthropogenic sources relies heavily on the accuracy of the emission factors. However, natural processes that favour the accumulation of metals tend to be more effective in smaller particles because of the relatively greater surface area available. Thus, the assumption that fine particle size provides sole identification of anthropogenic heavy metal sources may have resulted in a systematic overestimation of this proportion. It is therefore difficult, for the time being, to directly assess the tonnage of nickel emitted in the atmosphere from natural sources in each area of EU.

Source	Emission rate (10 ⁶ kg/year)
Residual oil combustion	17
Fuel oil combustion	9.7
Nickel mining and refining	7.2
Municipal incinerators	5.1
Steel production	1.2
Gasoline and diesel fuel combustion	0.9
Nickel alloy production	0.7
Coal burning	0.66
Cast iron production	0.3
Sewage sludge incineration	0.048
Copper-nickel alloy production	0.04
Total	42.85

Table 11.Global emission of nickel from man-made sources to the
atmosphere [22]

3.3.3. Anthropogenic sources of nickel

3.3.3.1. General points

A quantitative assessment of the anthropogenic sources of nickel was performed according to existing nomenclatures. The best estimation is the collection of emission rates measured directly or calculated at the emission point (industrial sectors of concern). For most of these sectors, such figures are not available. In these cases, the only way to evaluate yearly nickel emissions is to refer to calculations on the basis of emission factors, despite the inaccuracy of this method.

The European industries of concern are facing this problem of emission inventories in the framework of two projects in addition to the current study: OSPARCOM and UNECE/LRTAP (as mentioned above). Most of these industries are working on updating the emission factors to be transmitted to the competent authorities. Consequently, the collection of data has been relatively limited in the course of this study, which necessitated using published values (sometimes dating back to more than 10 years ago) for emission factors. Several adjustments, mainly based on industrial/professional judgements, were

made. Some of the estimations provided in this study may be revised by the industries concerned, which are expected to produce new data in the future.

The first quantitative estimation of heavy metal emissions in the air was performed by Pacyna and Nriagu in 1989 [16]. The first nomenclature associated with the emission factors was prepared in the early 1980s in the scope of OSPARCOM. Pacyna and Axenfeld used this nomenclature for a first inventory of 16 metals including nickel in Europe. A geographic gridding system was designed at that time and was used for five metals (As, Cd, Hg, Pb, Zn), excepted nickel. This first nomenclature was revised in the form of a manual of emission factors by the Dutch delegation to OSPARCOM, to be used in the UNECE/LRTAP programme [1].

The inventory of metals in Europe is far from complete because emission data are still lacking for several EU countries, particularly for nickel. The UNECE/LRTAP project led to the conclusion that:

- Emission rates from sources such as electric power plants, central heating plants and primary smelters should be based on measurements not calculated on the basis of emission factors;
- Emissions from other sources, e.g., iron and steel manufacturing, could be derived from emission factors.

Table 12 summarizes the nomenclature adopted today for the categories of metal emission sources selected by the UNECE/LRTAP project, consistent with the CORINAIR/EMEP network.

Sou	Irce	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn
1)	Public power, co-generation and district heating	xx	х	x	xx	XX	XX	x	xx	x
2)	Commercial, institutional and residential combustion	X	x	x	x	XX	x	x	x	x
3)	Industrial combustion	x	х	x	x	XX	x	x	x	х
4)	Production processes	xx	хx	xx	xx	XX	x	xx	х	xx
5)	Extraction and distribution of fossil fuels				x		x	x		x
6)	Solvent use									
7)	Road transport		x		x		x	xx		x
8)	Other mobile sources and machinery		x		x		х	xx		x
9)	Waste management and disposal	x	xx	x	x	xx	x	x	x	xx
10)	Agriculture	x								x
11)	Nature	x			x	x		х	x	x

Table 12.CORINAIR/EMEP Common Source Sector Split of Heavy
Metal Emissions [16]

Note: Relevant source sectors are given by 'x' and major source sectors are presented by 'xx', although this classification may not hold true in all countries

Table 13 summarizes the nomenclature proposed by Nriagu in 1988.

Table 13.	Estimated	atmospheric	emission	of	nickel	in	1983
-----------	-----------	-------------	----------	----	--------	----	------

Source category	Estimated atmospheric emission of		
	nickel in 1983 (in t/year)		
1. Coal combustion:			
- Electric utilities	1395-9300		
- Industry and domestic	1980-14850		
2. Oil combustion:			
- Electric utilities	3840-14500		
- Industry and domestic	7160-28640		
3. Wood combustion	600-1800		
4. Mobile sources	-		
5. Non-ferrous metal industry	8781		
6. Steel and iron manufacturing	36-7100		
7. Cement production	89-890		
8. Other anthropogenic sources	269-1289		
Total emissions	24150-87150		
Median value	55650		
Percentage of atmospheric emissions due to fossil	sil 75.5%		
fuel combustion			

A review of various categories and associated emission factors is presented in [1]. Several of these will be quoted in the following descriptive review of emission sources. As far as nickel emissions are concerned, a distinction has to be made between:

- 1. « Specific » and « non-specific » sources,
- 2. « Point sources » and « diffuse sources ».

The list of industrial sectors retained as « point sources » is extracted from the following categories:

• Specific sources/industries:

- 1. Nickel mining,
- 2. Nickel extractive metallurgy,
- 3. Nickel-using industries.

• Non-specific sources/industries/activities:

- 4. Non-ferrous metal production,
- 5. Steel production,
- 6. Oil combustion or assimilated (power stations, industrial combustion, residential/urban heating, transport/traffic),
- 7. Coal combustion,
- 8. Other non-specific sources (glass industry, cement industry, municipal waste incineration, etc.).

Below, an attempt is made to describe each of these sectors in terms of:

- Process chemistry (speciation of nickel in raw materials and in emissions),
- Fume control/abatement capabilities,
- Chimneys,
- Geographic location,
- Quantities,
- Chronology and trends.

3.3.3.2. Specific sources/industries

Specific sources include nickel mining, extractive metallurgy and various nickel-using industries.

In the EU, there are currently two active mining sites. One in Finland (underground sulphidic ore), without atmospheric emission potential. The second is located in Greece (oxidic ore in an open pit) and its emissions are diffuse and non-quantifiable.

The main nickel refineries are presented below. Their principal characteristics are summarized in Table 15, with the corresponding emission rates directly derived from measurements and not from emission factors.

Finland. One refinery is located in Harjavalta, in south-east Finland (see Figure 10). The plant was commissioned in 1960. The process is described in [1]. The only potential airpolluting operation is the smelting process, which includes flashsmelting and matte converting. This results in the emission of dust from a single stack. The chemical nickel forms are mostly of oxidic nature (complex oxides), with a smaller proportion of sulphidic nature. The rest of the process is based on hydrometallurgy and electrowinning, both of which have a very low air pollution potential. The chronological evolution of nickel emissions is summarized in Table 15.

Norway. One refinery began operation in 1910 at Kristiansand, in south-east Norway (see Figure 10). It treats a nickel-copper matte produced in Ontario, Canada. Until 1978, an « old process » was used, with a significant air pollution potential (in a multi-hearth furnace), followed by electro-refining. Since 1978, the transition to a purely hydrometallurgical + electrowinning process has considerably decreased the tonnage of emitted nickel. The emissions are released through a single stack. The chemical forms of emitted nickel are mainly oxidic (complex nickel-copper oxides), with a small sulphidic proportion. The two processes are described in [1].



Figure 10. Geographical location of the Harjavalta and Kristiansand plants

France. An old plant operated in Le Havre (Sandouville) since the beginning of the century until 1977 (see Figure 11). The feed was a nickel matte, first roasted in horizontal furnaces, secondly in a fluosolid furnace, and then in a rotary kiln. Dusts were emitted through a single stack. The chemical nickel form was predominantly pure nickel oxide with a proportion of nickel sub-sulphide. Since 1977 this process has been replaced by a purely hydrometallurgical + electrowinning process. The emissions, mostly nickel sub-sulphide, are released during the matte crushing step, through a small chimney. It is assumed that most of the particles fall inside the perimeter of the plant, with a negligible impact on the surrounding areas. The different processes are described in [1].



Figure 11. Geographical location of the Sandouville plant

Great-Britain. A nickel refinery has been operating in Clydach, South Wales, since 1902 (see Figure 12). In a first period, up to 1948, the feed was a nickel-copper matte and the most polluting step was matte roasting. The emitted dust was mainly nickel-copper oxide and some nickel sub-sulphide. Since 1948 the feed has been replaced by impure nickel oxide. This is the only plant in Europe with the potential of emitting nickel

carbonyl, but the effective emission rate of this substance is practically nil.



Figure 12. Geographical location of the Clydach plant

<u>Greece</u>. There is a smelter in Larco, on the eastern coast. It smelts an oxidic nickel ore. The process is described in [1]. Nickel-containing dust and fumes (complex oxides/spinels - no nickel oxide) are emitted through a single chimney.

Austria. The Treibacher plant treats nickel-containing alloys scraps and nickel-cadmium batteries. It produces ferronickel at the rate of about 3000 t/y. The smelting operation is performed in an electric furnace. Emissions of nickel may be of the order of 1 t/y.

Former Yugoslavia. The processes used in the two Yugoslav plants are similar to those used in Greece. No data on the nickel emissions are available, mostly due to frequent and long periods of inactivity.

Country		1975	1985	1995
FINLAND	Capacity			32 000 t
	Emissions		50 t	2 t
	Chimney height			
FRANCE	Capacity	10 000 t	15 000 t	
	Emission	50 t	7 to 10 t	5 t
	Chimney height	63 m		
GREAT-BRITAIN	Capacity			40 000 t
	Emission			7 t
	Chimney height			100 m
GREECE	Capacity			21 000 t
	Emission	7 t		3 t
	Chimney height	60 m		156 m
NORWAY	Capacity		· · · · · · · · · · · · · · · · · · ·	68 000 t
	Emission	6 t		2 t
	Chimney height	100 m		
AUSTRIA	Capacity			3 000 t
	Emission			1
	Chimney height			
Former Yugoslavia	Capacity			13 000 t
	Emission			
	Chimney height			

Table 14.Recapitulation of nickel emissions by European nickel
production plants, in averaged tons/year [23]

The main nickel-using sector is the production of stainless steel, which represents more than 65% of nickel uses in terms of tonnage. The equipment involved in the various processes of interest are electric furnaces and Argon Oxygen Decarburization (AOD) converters. The raw materials are ferronickel (ingots or granules), pure nickel (in massive forms), nickel oxide in roundels or coarse particles, or recycled stainless steel scraps. Fumes containing nickel-iron complex oxides (spinels) are emitted during melting operations. Fume and dust abatement equipment has been progressively installed in the plants during the past decade.

Information on the emissions from the stainless steel production sector is very scarce. The emission factors (EF) found in the literature present very large ranges, and it was very difficult to find any general agreement on a « best estimate » EF for this sector. Thus the

tonnage of nickel emitted by this sector has been calculated on the basis of two direct emission values. One value of 12.7 t (Ni) /y for France was proposed in 1994, associated with a total production of stainless steel of 492 000 t [24], leading to an estimated EF of 25.8 g/t. For Germany, the value of 6.4 t (Ni) /y was proposed in 1990 for a production of about 900 000 t [25], giving an EF of 7.1 g/t. An average of 16.5 g/t has been retained, independently of the differences between each installation and the improvement of dust abatement equipment.

A total emission of $4785 \times 16.5 = 79 \text{ t}$ (Ni) was so estimated for 1996 in Europe.

	1990	1994	1996 (estimate*)
	t (Ni) /y	t (Ni) /y	t (Ni) /y
Austria			0.5
Belgium			9.1
Finland			7.3
France	53	12.7	8.7
		(prod. 492 000 t)	
Germany	6.4		13.8
	(prod. 900 000 t)		
Italy			10.7
Spain			11.8
Sweden			9.0
United-Kingdom			8.0
Total Europe			79
			(prod. 4 785 000 t)

Table 15.Estimation of nickel emissions by stainless steel production
in Europe

* Assuming a constant EF of 16.5 g/t and the stainless steel production tonnage from [23]

3.3.3.3. Non-specific sources/industries

Non-specific sources include non-ferrous metal production, steel production and oil and coal combustion.

The smelting of lead-copper concentrates during lead and copper production may present a potential for emitting oxidic nickel. But today, due to the control of lead emissions, these smelters are all equipped with dust emission control devices, and nickel emissions have become non-significant. France, Belgium, Germany, Italy, Great-Britain and Sweden each have one smelter. Table 16 summarizes the EF calculated for some non-ferrous metal production processes.

Metal produced	Process	Nickel emission factor (g/t of metal produced)	Reference
Copper	Primary copper-	9000	PACYNA 1983 [26]
(nickel)	nickel production		
	Cu, Ni	900	NRIAGU 1987-1988 [27]
	production		
Lead	Primary lead	85	PACYNA 1983 [26]
	production		
	Lead production	85	NRIAGU 1987-1988 [27]
Aluminium	Primary	10	ATMOS/PARCOM 1992 [28]
	aluminium		
	production		· · · · ·

Table 16.Nickel emission factors for some non-ferrous metal
production processes

The EFs for copper are calculated for Canadian smelters which have no equivalent in Europe. The corresponding process includes a primary step (roasting of the Ni-Cu concentrate) which leads to the nickel-copper matte, used as a feed for European refineries (Norway). The Finnish nickel-copper smelter has a modern flash smelting process that should lead to a much lower EF. Therefore, the EF for copper production may not be adapted to the situation in the European context.

Table 17 presents the emission factors corresponding to mild-steel production. Direct emission values are available for the French steel-making industry. In 1990, the emission of nickel was about 3 t/y, and about 2 t/y in 1994 [29].

Process	Nickel Emission factors (g/t of steel produced)	Reference
Iron and steel production / oxygen furnace	0.1	ATMOS/PARCOM 1992 [28]
Steel and iron manufacturing	0.05-10	NRIAGU 1987-1988 [27]
Steel works	0.9	PACYNA 1983 [26]
« Sidérurgie »	1.5	CITEPA 1992 [27]

Table 17. Emission factors for mild steel production

In this sector the EF is heavily dependent on the type of process (electric arc furnace (EAF), basic oxygen furnace (BOF) or open hearth furnace). The EF proposed by Pacyna (0.9 g/t) is determined by the type of furnace used in Europe (EAF or BOF). ATMOS PARCOM proposes a specific EF for each type of process. CITEPA proposes an EF which is a combination of different sources: US/EPA, Reinders, Germany, UNEP.

The next sections deal with the potential emission of nickel from the combustion of fossil fuels (oil and coal and derived products). Nickel may be present in crude oils in significant amounts. Nickel abundance depends on the geographic origins of the crude oils. Tables 18 and 19 illustrate this fact.

Element	Concentration range (ppm)	Average concentration (ppm)
As	0.046 - 1.11	0.263
Cd	-	0.03
Co	0.032 - 12.751	1.71
Cr	0.0016 - 0.017	0.008
Fe	3.365 - 120.84	40.67
Hg	0.023 - 30	3.240
Mn	0.630 - 2.54	1.17
Мо	0.008 - 0.053	0.031
Ni	<2 - 344.5	165.8
Pb	0.17 - 0.31	0.24
Se	0.026 - 1.396	0.53
V	<2 - 298.5	88.5
Zn	3.571 - 85.8	29.8

Table 18.Trace metal contents of crude oil [Source HMIP, United
Kingdom]

Table 19.	Averag	ge concenti	rations of	nickel	and vanad	lium in c	rude oil
	from	different	source	areas	[Source	HMIP,	United
	Kingd	om]					

Element (ppm)	North Africa	North Sea	Middle East	North America	South America
Ni	<2	4	13	13	177
V	<2	8	50	25	14 - 15

Nickel and vanadium are present in crude oil as complex organic molecules. Generally these two metals are found in the heaviest residual fractions of oil refining. Consequently nickel is found in different distillation fractions, in the following order of increasing content, (asphalt > residual oil > heavy fuel HTS > heavy fuel BTS > residential fuel > diesel oil > gasoline).

Combustion processes take place at around 1300-1400°C. At this temperature, the nickel porphyrines present in crude oil are decomposed, and nickel is transformed into oxidic forms, complex nickel oxides with other metal oxides (iron oxides, nickel vanadates). By reaction with SO₂ or SO₃ present in the fume, at a temperature lower than 800°C, nickel sulphides or sulphates may be produced.

The size of the emitted particles is determined by the design of the pulverization system in the burner component. Opposed burners produce finer particles than a simple mechanical system. Furthermore high pressure conditions lead to lower emissions of particles.

An estimation of nickel emissions resulting from the combustion of oil and derived products is based on the following nomenclature:

- 1. Combustion in energy production and energy transformation,
- 2. Combustion in industry,
- 3. Combustion in commercial, institutional and residential sectors, agriculture, forestry and fishing.

For each of these activity sectors, the objective is to present the adapted emission factors and to determine emission rates when available. 1) Combustion in energy production and energy transformation

Three main parameters govern the emission of nickel:

- Fuel quality in terms of sulphur contents
- The general flowsheet of the station (technological design)
- The type of boiler (burner, etc.)

The general flowsheet considers four possible outlets for nickel:

- boiler slags, progressively formed on water pipes and periodically collected,
- bottom ashes (or « fouling ashes »), settling in gaps between the boiler and the dust collector,
- soots or fly ashes, collected in the dust collector, when this exists,
- flue dusts or effective emissions at the stack.

The influence of the type of boiler on particulate matter emission is not as well documented as for coal combustion. The design of the oil spray system (atomization/pulverization) is an important factor. High pressure atomization leads to lower particulate matter emissions. The variety of parameters which affect the emission of nickel makes it difficult to define a valid emission factor for all the power stations in Europe. Table 20 gives various published emission factors.

	Nickel emission factor	
Source	(g/t of fuel consumed)	Reference
Fuel power plants	28	CITEPA 1996 [Pers.Com.]
Combustion of fossil fuel/heavy oil	30	ATMOS/PARCOM 1992 [28]
Oil-fired Power Plants	42	PACYNA 1983 [26]
Fuel power plants	12.9 - 15	EDF 1993 [Pers.Com.]

Table	20.	Emission	factors	for	fossil	fuel	combustion	-	Oil/Power	plants
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The emission factor proposed by Pacyna was calculated on the basis of a heavy fuel containing 1% of sulphur. Pacyna also considered in his calculations that 90% of the nickel present in crude oil was still present in the heavy fuels used in power stations. This EF is specifically estimated for Europe. The ATMOS/PARCOM EF was calculated on the

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basis of Dutch and German data, with the assumption that all the nickel contained in the heavy fuel is emitted at the stack. The individual EFs are 35 g (Ni) /t of fuel for the Netherlands and 25 g (Ni) /t for Germany. The average of 30 g/t was used by ATMOS/PARCOM (1992). The EDF emission factor (12.9 g/t) was calculated on the basis of five measurements made in 1993 at the stack of the Porcheville power station (nickel content of the emission of 0.79 to 1.5 mg/m³, heavy fuel HTS). The EF CITEPA 1996 (28 g (Ni) /t) was proposed by UFIP on the basis of measurements made in the oil refineries where heavy fuel is also used for steam power generation. Specific and local estimations for 1987 were made in France for two power stations, both using heavy fuel N°2 (2.5 to 4% sulphur). The figures presented in Table 21 are calculated on the basis of the EFs themselves, which were calculated from series of measurements carried out in 1982 on both stations.

Measurements	Aramon	Martigues-Ponteau		
	(dust collection with cyclone)	(no dust collection)		
Nickel emission (kg)	101	827		
Heavy fuel consumption (kt)	20	110		
Power (MW)	2 x 700	4 x 250		
Emission factor (g/t)	5	7.5		

Table 21.Atmospheric releases of nickel estimated for two French
power stations, in 1987 [33]

The EF for Martigues-Ponteau (7.5 g/t) can be considered as a sort of « worst case », due to the lack of dust collection, combined with the use of heavy fuel. The average for the three power stations cited above (Porcheville, Aramon and Martigues-Ponteau) gives an EF of 12.9 g/t, as shown in Table 20.

As regards France, it appears that the proposition of nuclear power in French energy production limits seasonal variations in particulate emissions from oil and coal combustion plants. At the European level, economic factors (prices of crude oils) may also play an important role in the fluctuations of emission rates. It should also be noted that power plants are systematically equipped with high stacks, resulting in possible long distance transport of emitted particles.

2) Industrial combustion

This terminology includes the «no contact» combustion of flames and/or combustion gases with materials used in industry, such as in power generators (including refineries) and steam generators, and «contact» combustion. A long list of activities is included in these two groups. The only data available are the emission factors shown in Table 17.

	Nickel emission factor	
Process	(g/t of fuel consumed)	Reference
Combustion of fossil fuel/heavy oil	30	ATMOS/PARCOM 1993 [30]
Combustion of fossil fuel/heavy oil	35 (Netherlands)	ATMOS/PARCOM 1992 [28]
Combustion of fossil fuel/heavy oil	25 (Germany)	ATMOS/PARCOM 1993 [30]
Conventional power plants, industries	28	CITEPA 1996 [Pers.Com.]

Table 22. Emission factors for oil/industrial combustion

The ATMOS/PARCOM EFs were set in the same way as for power stations. Industrial combustion units are usually equipped with significantly lower stacks than those of power plants. This may result in transport over smaller distances.

Due to the lack of specific analyses, the same methodology was used for estimating nickel emissions by oil-fired industrial combustion plants as for power stations. However, «contact» combustion may lead to a particulate of still more complicated chemistry, and is expected to produce complex oxides.

3) Residential/urban heating (units of < 50 MW)

The calculation of emission rates was performed using the same model as for industrial combustion. However, it is highly probable that there is less dust control equipment in these units. The published EFs are presented in Table 23.

Process	Nickel emission factor (g/t of fuel consumed)	Reference
	28	CITEPA 1996 [Pers. Com.]
Oil combustion/Industry and domestic	20-80	NRIAGU 1987-1988 [27]
Oil-fired commercial and residential units	27	PACYNA 1983 [26]

Table 23. Emission factors for oil/Tertiary & residential heating

On the basis of these estimated emission factors, a first rough estimate was derived from OECD data giving the annual tonnage of heavy fuel consumed by EU countries for each type of sector (power plants, industrial consumption of heavy fuels, tertiary consumption of heavy fuels) [31], [32]. The estimation was performed for the last 25 years, with the same emission factor for each sector (28 g/t). The results are presented in Table 24.

The calculations of the estimated tonnage of emitted nickel for the fossil fuel combustion sectors (Tables 24, 25, 26, 27, 28 and 30) were made as follows:

$$Q_{tNi/y} = EF x C_{tFuel/y}$$

where:

Q _{tNi/y}	yearly nickel emission rate
C _{tFuel/y}	yearly heavy fuel oil consumption
EF	Emission factor (here 28 g/t for each sector)

Table 24.Average annual nickel emissions of the 16 countries
considered, by the three major oil combustion sectors

Sector (t (Ni) /y)	1970-1980	1975-1985	1980-1990	1985-1995
Combustion in energy production and energy transformation	1922	1393	1094	929
Combustion in industry	827	624	512	448
Combustion in commercial, institutional and residential sectors, agriculture, forestry and fishing	603	417	323	229

In Tables 25, 26, 27 and 28 the detailed emissions for the four major European countries (France, Germany, Great-Britain and Italy) are shown.

Sector (t (Ni) /y)	1970-1980	1975-1985	1980-1990	1985-1995
Combustion in energy production and energy transformation	320	134	60	18
Combustion in industry	132	91	69	47
Combustion in commercial, institutional and residential sectors, agriculture, forestry and fishing	83	69	52	45

Table 25.Average annual nickel emissions, by the three major oil
combustion sectors in France

Table 26.Average annual nickel emissions, by the three major oil
combustion sectors in Germany

Sector (t (Ni) /y)	1970-1980	1975-1985	1980-1990	1985-1995
Combustion in energy production and energy transformation	140	72	46	39
Combustion in industry		120	89	71
Combustion in commercial, institutional and	56	48	42	25
residential sectors, agriculture, forestry and fishing				

Table 27.Average annual nickel emissions, by the three major oil
combustion sectors in United-Kingdom

Sector (t (Ni) /y)	1970-1980	1975-1985	1980-1990	1985-1995
Combustion in energy production and energy transformation	312	283	221	157
Combustion in industry	153	118	102	94
Combustion in commercial, institutional and residential sectors, agriculture, forestry and fishing	82	65	49	39

Sector (t (Ni) /y)	1970-1980	1975-1985	1980-1990	1985-1995
Combustion in energy production and energy transformation	493	464	466	520
Combustion in industry	181	148	115	85
Combustion in commercial, institutional and residential sectors, agriculture, forestry and fishing	132	79	57	36

Table 28.Average annual nickel emissions, by the three major oil
combustion sectors in Italy

4) Road transport

Currently, there is no agreement between the various experts with respect to the road transport potential of emitting nickel into the atmosphere. Thus, the values presented in Table 29 have to be considered with caution and should be of interest for future investigation.

Table 29. Emission factors for Oil/Road transport

Substance	Nickel emission factor (g/t of fuel consumed)	Reference	
Automotive fuels/gasoline	0.5 g/t	ATMOS/PARCOM 1992 [28]	
Automotive fuels/diesel	1-10 g/t	ATMOS/PARCOM 1992 [28]	
Diesel oil	15 g/t	PACYNA 1983 [26]	

The results of the estimations for the 16 countries concerned are presented in Table 30.

Table 30.Average annual nickel emissions by the road/transportsector of the 16 countries considered

Sector (t (Ni) /y)	1970-1980	1975-1985	1980-1990	1985-1995
Gasoline	47	49	51	56
Road-gas/Diesel oil	213	261	301	379

As regards coal combustion, nickel is present in coal in smaller amounts than in crude oils, in general between 20 and 40 ppm (see Table 31). The principal mineral structure of fly ash is a vitreous substance made of silico-aluminate. Some enrichment has been observed between coal and fly ash. Nickel will therefore be present in silicate form [21].

Origin	Nickel concentration (in mg/kg dry coal)
n°1/RUS	27.20
n°2/SAF	24.90
n°3/SAF	40.80
n°4/SAF	23.70
n°5/USA	21.90
n°6/SAF	42.00
n°7/SAF	39.20
n°8/USA	27.70
n°9/CHI	17.80
n°10/SAF	28.60
n°11/SAF	28.30
n°12/AUS	39.90
n°13/SAF	28.80
n°14/SAF	29.50
Average	30.02

 Table 31.
 Nickel concentrations in 14 coal samples [33]

RUS = Russia, SAF = South Africa, USA = United States, CHI = China, AUS = Australia.

In order to estimate the quantity of nickel emitted by coal combustion, the following categories were considered:

- 1. Combustion in energy production and energy transformation,
- 2. Combustion in industry,
- 3. Combustion in the commercial, institutional and residential sectors, agriculture, forestry and fishing.

For each of these activity sectors, the objective is to present the adapted emission factors and to sum up emission rates when available.

All coal-fired power plants are equipped with sophisticated dust control devices such as electrostatic precipitators (ESP). The percentage of emissions for nickel is around 1% of the nickel contained in the coal. All emission factors are reported in Table 32.

Sector	Source	Nickel Emission factors (g/t of coal consumed)	Reference
Power plant	Coal power plant	0.2	CITEPA 1996 [Pers.Com.]
	Coal power plant	0.15	CITEPA 1992 [27]
Industrial	Combustion of	0.85 (Germany)	ATMOS/PARCOM 1992 [28]
combustion	fossil fuel/coal		
· · · · · · · · · · · · · · · · · · ·	Combustion of	0.11 (Netherlands)	ATMOS/PARCOM 1993 [30]
	fossil fuel/coal		
	Combustion/ coal	0.2	CITEPA 1996 [Pers.Com.]
	industry		
	Industrial coal	0,15	CITEPA 1992 [27]
	combustion		
· · · · · · · · · · · · · · · · · · ·	Coal-fired	14.5	PACYNA 1983 [26]
	industrial boilers		
	(stoker)		
Tertiary/	Coal	2-15	NRIAGU 1987-1988 [27]
Residential	Combustion/Indus		
heating	try and domestic		
	Coal-fired	5.12	PACYNA 1983 [26]
	commercial and		
	residential units		

 Table 32.
 Emission factors for coal combustion

There is apparently no reason to make any distinction between the three sectors of power plant, industrial combustion and residential/urban heating in terms of emission factors. The Pacyna EFs were calculated for coals with a collection of dusts of 99% for power plants and 85% for industrial combustion.

Generally, the potential for nickel emission by coal-fired combustion units is much lower (about 100 times less) than by fuel-fired units. However, a rough first estimate for power plants was made from OECD data, giving the annual tonnage of coal consumed by EU countries for the production of electricity. It was made for the last 25 years. The EF was set at 0.2 g/t, as an average figure for all countries. There are too data lacking to permit a good evaluation of the emissions from these sectors (power plants + industry + tertiary and residential heating). The emitted tonnage of nickel for the last decade was estimated to reach 30 t/y of nickel as a total for the three sectors previously mentioned. The evolution of coal consumption in EU and several member states are also of interest and are described in Table 33.

Table 33.Evolution of the coal consumption in the EU (10^6 TEP) and
some member states [33]

	1973	1979	1989	1990	1991
EU (12 countries)	284	291	291	286	274
- Germany	139	138	136	129	115
- France	29	32	21	20	21
- United-Kingdom	76	74	63	64	64

Table 34 summarizes emission factors given up to now for some other non-specific sources. The glass industry is the only one intentionally having nickel present, the latter been introduced as nickel oxide in the reaction mixture as a pigment for a certain quality of glass. ATMOS/PARCOM emission factors were also used by CITEPA, on the basis of tonnage of nickel emitted. For France, it has been concluded that all these activities will not be considered in the present risk assessment.

With respect to these emission factors, the CITEPA proposed tonnage for nickel emissions in France in 1990. These results are presented in Table 35.

Sector	Source	Nickel emission factors (g/t)	Reference
Cement industry	Cement production	0.1-1	NRIAGU 1987-1988 [27]
	Cement production	0.111	ATMOS/PARCOM 1992 [28]
Glass industry	Glass production	1.9	ATMOS/PARCOM 1992 [28]
Municipal waste incineration	Refuse incineration/municipal incinerators	0.33	PACYNA 1983 [26]
	Waste incineration/municipal	0.2	ATMOS/PARCOM 1992 [28]
	Refuse incineration/municipal	0.7 - 3	NRIAGU 1987-1988 [27]
	Municipal waste	0.2	CITEPA 1996 [Pers.Com.]
Industrial waste incineration	Industrial waste	1.2	CITEPA 1996 [Pers.Com.]
	Incineration of wastes, other than municipal waste and sewage sludge	1.2	ATMOS/PARCOM 1992 [28]
Sewage sludge incineration	Sewage sludge incinerators	0.001	PACYNA 1983 [26]
	Sewage sludge incineration	0.5	ATMOS/PARCOM 1992 [28]
	Sewage sludge incineration	0.5	CITEPA 1996 [Pers.Com.]
	Refuse incineration	10 - 50	NRIAGU 1987-1988 [27]

 Table 34.
 Emission factors for other non-specific sources

Table 35. Ni tonnage emitted in France in 1990 [Source CITEPA 1996]

Sector	Emission factor	Ni (t/y)
Glass industry	1.9	8.2
Cement industry	0.1	2
Municipal waste incineration	0.2	1
Industrial waste incineration	1.2	1
Sewage sludge incineration	0.5	0.1

3.4. Summary of nickel emissions in EU

3.4.1. Emission rates by sector

This estimation has excluded non-specific sources which appear negligible in terms of yearly tonnage of nickel emitted over the past 25 years. The results correspond to the preselection of three major activities whose average emission rates during the last 25 years are compared:

- Oil combustion [power generation, industrial combustion, and heating (urban)],

- Primary nickel production,

- Stainless steel production.

The nickel and stainless steel production sectors have been submitted to greater more control of emitted nickel-containing dusts than oil combustion processes. This has resulted in a significant decrease in nickel emissions between the 1970s and the 1990s. This is shown in Table 36 for France. For the nickel and stainless steel sectors, the emission rates which are presented correspond to a rough estimate, made on the basis of values provided by different experts in the industrial field of concern.

Table 36.Recapitulation of estimated annual emissions by main
nickel emission sources in Europe

Sector (t (Ni) /y)	1970-1980	1975-1985	1980-1990	1985-1995	1996 (estimate)
- Nickel production					20 (1995)
Oil combustion					
- Power generation	1922	1393	1094	929	929
- Industrial	827	624	512	448	448
- Tertiary/residential	603	417	323	229	229
- Stainless steel production					79 (1996)
Total*					1705

* These estimates are indicative, assuming for simplification that nickel emission rates have not been significantly changed in the second part of the 1990s

It should be kept in mind that the presented emission rates are estimated with a large margin of uncertainty, which could be of 100%, especially for oil combustion processes. However, some conclusions can be drawn:

- Oil combustion processes have a higher potential for nickel emission than metallurgical processes involving nickel;
- The trend for nickel reduction emission over the past 25 years clearly appears to be the direct result of the decreasing consumption of heavy fuel oils in combustion processes in the whole EU. This decrease has been about 50% in 25 years;
- In 1996, it is expected that the respective contribution of each of the relevant sectors in the total annual emission of nickel is ≈2% for the nickel production sector, ≈5% for the production of nickel-containing stainless steel and ≈93% for the oil combustion sector, out of total amount of ≈1 700 t (Ni) /y for Europe.

The present inventory can be compared with inventories made in the scope of the UNECE/LRTAP project. This inventory should logically be established using the ATMOS/PARCOM category/emission factors. Some figures provided by EU member countries of this project appear systematically inferior to those calculated in the present study.

It appears (see Tables 24, 25, 26, 27 & 28) that the « urban heating » sector of the oil combustion process has a high potential for nickel emission. To this observation must be added the fact that these units are not equipped with dust control devices and that their nickel emissions were calculated using an EF estimated from combustion units from the oil refining sector which implies the use of dust collection.

Industrial combustion involves certain «contact» combustion processes (the flames are in contact with the materials treated in the course of these processes). This induces a potential emission of dust arising from these materials, leading to the installation of dust control equipment to reduce nickel emissions from fuel oil combustion. This has not been considered in the present study, in which an EF of 28 g/t has been considered, the same as for power generation units.

Table 37 presents the data related to the three sectors for the four EU countries among the highest heavy fuel oils consumers. Clear differences between these countries can be

observed, mainly in the sector of urban heating.

Source	FRANCE	GERMANY	UNITED-KINGDOM	ITALY
Power plants	18	39	157	520
Industrial combustion	47	71	94	84
Tertiary/residential heating	45	25	39	36
Total	160	135	290	640
Results from CITEPA combustion without contact	250			
Results from TNO 95	177	277	161	191

Table 37.Estimates of nickel emissions by oil combustion sector for
four EU countries in t (Ni) /y - 1990

3.4.2. Geographic and seasonal analysis

Significant variations in power generation and residential/urban heating should be considered with a view to any research on the correlation between emission and immission values.

A first distinction can be made on the basis of seasonal variations:

(1) industrial activities with a yearly constant emission rate:

- primary nickel production,
- stainless steel production,
- industrial combustion (fuel),
- transport/traffic.
- (2) activities with an expected seasonal aspects:
 - power stations,
 - residential/urban heating.

A second distinction can be made between rural and urban areas, especially related to transport/traffic emissions and residential/urban heating.

3.4.3. Chemical and physical characterization of emitted nickel-containing particles

As demonstrated above, most of the nickel emissions from anthropogenic sources result from oil combustion. Very few investigations have been conducted on these dusts. The most relevant is the analysis made by Zatka on fly ashes collected at the top of the stack of an oil-fired power plant. Those fly ashes contained 5-6% Ni, 9% Fe and 11.3% C. The fraction of nickel was about 50% in water soluble form (sulphate group). The 50% water insoluble forms were in majority complex oxides (spinel group), such as mixed iron-nickel oxides. The presence of nickel monoxide NiO « bunsenite » could not be evidenced because of the detection limit of 8% of the total nickel present in the sample [1].

3.5. Findings and lack of data

The characterization of nickel sources in the ambient air, either natural or anthropogenic, is a crucial issue. It is made very complicated by possible long-range transport mechanisms, and by particle re-suspension phenomena at the earth's surface, by wind or human activities. Most authors have estimated that the natural fraction ranged from 16% to 36% [20], [21] in the mid 1980s, but these values greatly depend on geographical factors. There are very few industrial sectors for which potential nickel emissions have been recently clearly evaluated. The use of emission factors remains necessary to evaluate most the emission rates and their evolution during the past 25 years.

Despite the uncertainties on the estimated rates, the preponderance of the heavy fuel oil combustion sector in nickel emissions appears clearly. The emissions of nickel by this sector (power generation, industrial combustion, urban/residential heating) have decreased by about 50% over the past 25 years, and other sectors, such as primary nickel and stainless steel production industries have become non-significant, mainly due to the installation of dust control equipment. However, some regional variations can be observed from one EU country to another, depending on the national energy-production strategies.

The emissions of SO_2 from oil combustion plants can be related to the potential emission of nickel for this sector, because both nickel and sulphur are contained in crude oils. The seasonal characteristics of these activities (power generation and heating) should be taken into consideration.

With respect to the chemical species of nickel compounds in the ambient air, it can be

noted that nickel arising from natural origins is very likely to be of silicate-oxidic nature (complex oxides), known to be water insoluble. On the contrary, nickel coming from anthropogenic source (oil combustion) is likely to be, at the point sources, half in water-soluble forms (sulphates) and half in water-insoluble forms (complex oxides with no more than 8% nickel as NiO, if present at all).

In terms of particle size (medium aerodynamic diameter), too little information was available concerning nickel. It is generally accepted that the fine particles of nickel resulting from anthropogenic sources are fixed onto coarser particles.

4. NICKEL CONCENTRATIONS IN THE AMBIENT AIR

4.1. Introduction

4.1.1. Methodological measurement aspects

A nickel immission value (concentration in the ambient air) at a precise geographic location is the result of an extremely complex combination of processes. These processes involve both nearest anthropogenic and natural emission point sources, meteorological parameters (wind, dry or wet conditions), re-suspension due to human activities (transport, etc.) or by wind (long-range transport-LRT).

Long-range transport within air masses from major source regions in Europe or North America to regions a few thousand kilometres away has been recognized for nickel as for other heavy metals having similar behaviours (Cd, Cr, Zn, etc.) [16]. About 30 to 50% of nickel entering the North Sea or the Baltic Sea come from atmospheric depositions. It is estimated [16] that more than 30% of heavy metals deposition (except Hg) to the Lake Superior come from sources which are located 500 to 1.000 km away. In the Arctic region, during winter, 60% of the heavy metal present in the atmosphere are transported from sources in the former Soviet Union and the rest comes from Europe and North America. In summer, this rate can reach 75% for Europe alone. A number of heavy metals, including nickel, are concentrated on fine particles (i.e. below 2 μ m), which can be transported on a regional scale (i.e. a couple of thousand kilometres) [16].

In light of the possibility of LRT, the average residence time of aerosols in the atmosphere is also of great importance. In the lower atmosphere, the longest residence time (around 10 days) is for aerosols of 0.1 μ m to 1 μ m. The coarsest particles (above 10 μ m) and ultra-fine aerosols (10⁻⁴ to some 10⁻³ μ m) have the shortest residence time (a few minutes to a few hours). An aerosol may stay in the stratosphere several years [34].

The characterization of particle size is also of great importance, and depends on the cutting size of the selected sampling device (total suspended particles - TSP, or particle matter - $PM<10 \mu m$, or $PM<2.5 \mu m$). Discussion on this fundamental point has been engaged in the context of the EC-DG XI Technical Groups for sub-directives on « particles » and « lead » and the trend would be for PM10, to be in accordance with

health effects. Nevertheless it should be noticed that most of immission values reported in the literature are related to TSP methods.

It is generally considered that coarser particles (above 2.5 μ m) are of natural origin whereas finer particles come from anthropogenic sources [35]. It has also been estimated that 90% of the elements of anthropogenic origin are mostly carried (more than 90%) on particles whose median aerodynamic diameter is less than 10 μ m [36]. This means that TSP sampling will not significantly overestimate nickel contents (most of anthropogenic origin), in comparison with values calculated from PM10 or lower sampling.

Because of strong geographic and seasonal variations, the reliability of the measurements relies heavily on numerous factors such as the geographic distribution of the measurement points (isolated, local, regional or national network), sampling time frequency (hourly, daily, monthly, seasonal, average for a determined period), the sampling method as mentioned above (cutting size), etc. Other parameters have also to be taken into account, such as the height of the sampling point or the distance to high traffic areas (resuspension), for example.

Figure 13 shows the geographic distribution of nickel deposited on moss in northern European countries around 1991-92. It illustrates the transport of nickel away from the emission sources, clearly identified on the map [37].

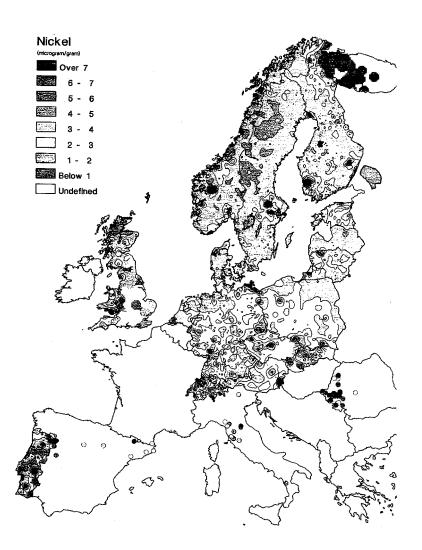


Figure 13. Nickel in moss $(\mu g/g)$

4.1.2. Presentation of the results

From a general point of view, there is still a relative paucity of data on nickel immission values. This substance has not been considered, up to now, as a priority in the measurement programmes implemented by the organizations in place. This considerably affects the quality of the results available at the time of the present study. These results will be presented for different types of areas, characterized by demographic aspects:

- 1. Urban areas,
- 2. Industrialized areas,
- 3. Rural areas,
- 4. Remote areas (for comparison).

It should be noted that some of these areas can result from a combination (urbanindustrialized for example).

The first data collected result from analyses made at the very beginning of the 1970s (France, Netherlands and Great-Britain). The upper values come from Germany and Great-Britain. Table 38 gives an order of magnitude of some nickel immission values compared with some other heavy metals.

	Antwerpen Jan-Feb 1987	Athens April-June 1986	Tokyo Oct-Nov 1986	Paris 1986-1988
Metal	<30 µm	2.5 μm	TSP	TSP
Fe	275	1100	2200	750
Zn	64	273	370	220
Mn	11	21	100	20
Cu	13	50	3100	35
Pb	74	699	170	500
Ni	5.8	11.8	10	10
Cd	-	220	3.1	5
Cr	0.6	-	15	3
As	15	-	4.1	2

Table 38. Immission values for some heavy metals (ng/m³) [36]

TSP : Total Suspended Particles

4.2. Summary of immission values

4.2.1. Immission values in urban areas

The immission values related to urban areas were taken from [1] and are presented in Table 39. Data are available for nine large towns in Germany and nine in Great-Britain.

Average immission value (ng/m ³)		Decade		No date
Recording site (country)	1970	1980	1990	
Germany	-	16	6	27
Belgium	19	6	-	-
Denmark	-	7	-	-
Spain	-	6	-	10
France	25	15	-	-
Greece	-	12	-	-
Netherlands	1 ·	-	-	-
United-Kingdom	19	10	7	55

Table 39. Immission values for urban sites

* Data from Strasbourg excepted

Paris was submitted to a detailed analysis by the Laboratoire d'Hygiène de la Ville de Paris, in the course of a surveillance campaign for about 15 metallic elements [36]. A summary of this article is presented in [1]. It gives a description of the chronological evolution of nickel immission values from 1976 to 1989 for a network of five measurement stations, and also a comparison of nickel immission values and detailed chemical analyses of the particles between winter and summer of 1992. The major conclusions from this survey highlighted the difficulty in identifying the direct contribution of close emission points (such as refuse incinerators) at the sampling point. The relative homogeneity of the values from the five stations also suggested that LRT could affect the concentration of heavy metal in the aerosols sampled in Paris.

It appears that, until the beginning of the 1980s, the annual average immission values for urban sites could reach 30 ng/m³. At the beginning of the 1990s, values of less than 10 ng/m³ can be expected according to the available data. This shows a significant decrease, which has to be related to emission reduction.

Data on the last five years are too scarce to derive representative values related to current exposure to nickel in the various areas. Some indications may however be retained:

• For Germany, in five large cities (Mannheim, Stuttgart, Karlsruhe, Freiburg, Dortmund), values range from 1 to 6 ng/m³ (the latter value refers to Dortmund). This range of levels is very likely when looking at similar levels observed in industrial

areas, also in Germany.

- For Belgium, values around 6 ng/m³ have been measured in Antwerp and Gent,
- For France, a mean annual value of 10 ng/m³ was observed in Paris in 1992.

According to these first results, it can be expected that current annual average concentrations of nickel in European urban areas are in the range of 1 to 10 ng/m^3 . As a comparison, in Tokyo, yearly averages were approximately constant, around 5 ng/m³ for the last five years [38], while in Canada, yearly averages for the period 1987-90 in ten large cities ranged from 1 to 5 ng/m³, except for one city (Halifax), where the value reached 20 ng/m³ for the same period [39].

4.2.2. Immission values in industrialized areas

The immission values related to industrialized areas were taken from [1] and are presented in Table 40.

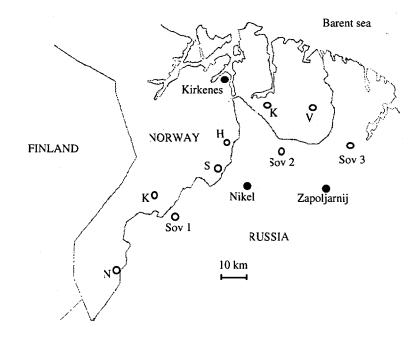
Average Immission value (ng/m ³)		Decade		No date
Recording site (country)	1970	1980	1990	
Germany	-	10	5	-
Belgium	-	27	-	-
Finland	-	-	1	-
France*	-	-	17	-
Italy	-	-	-	30
United-Kingdom	23	-	-	99

Table 40.Immission values for industrialized sites

* Data from Strasbourg excepted

In Germany, the immission rates corresponding to the beginning of the 1980s ranged from 10 to 20 ng/m³ in the North Rhine Westphalia. In Great-Britain, levels between 10 and 30 ng/m³ were observed in the 1970s. In Belgium, levels at the beginning of the 1980s ranged from 10 to 50 ng/m³.

A specific study was performed in Scandinavia at the border of the Kola Peninsula in order to check the possible influence of two nickel-producing plants known for their high pollution potential (about 500 t of nickel emitted in the atmosphere in 1989). Figure 14 represents its geographic location.



Norseth - Sci. Total Environ. (1994) - This map shows cities (filled circles) and other measuring stations (open circles). Letters denote the following stations: Noatun (N), Kobbfoss (K), Svanvik (S), Holmfoss (H), Karpdalen (K)) and Viksjrfjell (V) - Slightly modified from Sivertsen (1991).

Figure 14. Part of the Kola Peninsula - Vicinity of two nickel production plants (Nikel and Zapoljarnij)

The nickel emission levels measured in five stations are presented in Table 41.

Recording site	Ni (ng/m ³)
Noatun (N)	1.59
Svanvik (S)	3.26
Karpdalen (K)	4.95
Viksjefjell (V)	13.34
Birkenes 1985 - 1986	1.1

Table 41.Impact of industrial emissions in NW part of the KolaPeninsula (by reference to Figure 14)

Note: Concentrations given as mean values for the period January 1990 to March 1991

The measurement stations are located from 10 to 70 km from the emission sources. The most contaminated area is about 30 km from the nearest emission point which is influenced by wind direction. The corresponding yearly average nickel concentration is about 13 ng/m³, while the most distant measurement point, which is also in the opposite direction of prevailing winds, is about 1.6 ng/m³.

This measurement campaign is an interesting reference for assessing the direct impact of potentially polluting regions or highly polluting neighbouring regions (influence of Poland on Western Germany for example). An article by Chan and Lusis (1986) [40] reported nickel immissions values obtained in the early 1980s in the proximity of the Inco and Falconbridge smelters, both in the Sudbury area (Ontario). These values ranged from 10 to 124 ng/m³ within the 39 km radius circle around the Inco smelter, and from 3 to 36 ng/m³ within the 37 km-radius circle around the Falconbridge smelter.

To conclude, it can be stated that current nickel exposure for the general population in industrial areas in most EU countries is now in the range of 5 to 20 ng/m³. This has to be confirmed by measurements in areas not yet investigated, and where there is still considerable industrial combustion of heavy fuels.

4.2.3. Immission values in rural areas

The immission values related to rural areas were taken from [1] and are presented in Table 42.

Average Immission value (ng/m ³)		Decade		No date
Recording site (country)	1970	1980	1990	
Germany (8 stations)*	-	2 - 4	1.1 - 2.7	-
Belgium (2 stations)	-	≈ 10	-	-
Denmark	-	4	-	-
Finland (2 stations)	-	-	0.65 - 1.2	-
Italy	-		-	20
United-Kingdom (4 stations)	≈ 5	≈ 3	-	11
Sweden (1 station)	-	-	1.1	-

Table 42.Immission values for rural sites

Data from Willstät excepted

It should be noticed that the classification of the areas as rural, industrialized or urban is very qualitative and approximate.

4.2.4. Immission values in remote areas

Immission values in remote areas are summarized in Table 43.

The term « remote area » can be interpreted in two ways: either an area where human activity is nil because impossible (North or South Poles, and vicinity or middle of the Pacific Ocean), or an isolated area in an industrialized country.

Average Immission value (ng/m3)	Decade	
Recording site (country)	1970	1980
Norway	0.70	0.92
Pacific	0.14	-
Spitzbergen	1997 <mark>-</mark>	0.45

Table 43.Immission values for remote sites

It appears that nickel concentration in remote areas ranges from 0.1 to 1 ng/m^3 .

4.3. Characterization of nickel-containing atmospheric aerosols

Atmospheric aerosols have to be characterized for both their physical and chemical aspects.

4.3.1. Physical characterization

Studies made in the station of Birkenes, Norway, have shown that nickel is fairly uniformly distributed in various sizes of particles [41, 42].

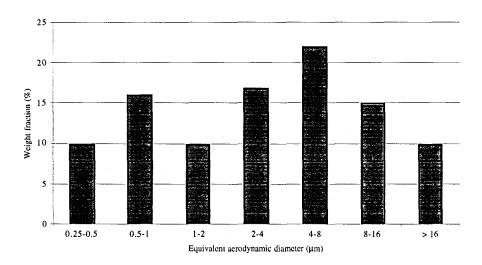


Figure 15. Distribution of particle sizes in the samples analysed in Birkenes

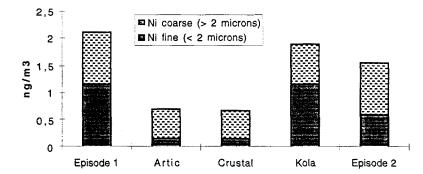


Figure 16. Contribution of particles of different size (coarse and fine) in the total atmospheric concentration of nickel at Birkenes (summer 1987)

These studies confirmed the fact that the majority of nickel of anthropogenic origin is contained in particles of less than $2 \,\mu m$, as presented in Figure 16.

These data must be compared with observations made by Zatka on flue dusts from an oilfired power station describing these nickel-enriched dusts at particle sizes of 1 to 2 μ m, most of them being agglomerates of individual particles of 1 μ m in diameter or less.

4.3.2. Chemical characterization

Very few data are available. A first estimate of the total nickel content when the concentration of TSP (in μ g/m3) and nickel (in μ g/m3) are given simultaneously. This allows estimating the nickel content in atmospheric aerosols to be around 0.01%, which is very low.

Precise analyses were made by the Laboratoire d'Hygiène de la Ville de Paris [36], and are presented in [1]. It appears that the nickel content ranges from 0.009% to 0.021% in summer. This is quite consistent with the estimation made above.

It seems reasonable to retain an average content of 0.01% Ni for these atmospheric dusts. This has to be compared with the 5% found by Zatka in the flue dust emitted by a power station burning residual fuel oil with a particularly high nickel content. It should be kept in mind that these flue dusts, once emitted, are diluted by aerosols of various origins. This dilution factor is evaluated to be about 100.

Other elements of interest are also present in significant amounts, such as iron (around 1%) which is consistent with the presence of nickel in spinel form (complex oxides).

Despite the absence of detailed studies on atmospheric aerosol speciation, it seems reasonable to estimate that the same nickel species, as identified by Zatka and mainly spinels/complex oxides, are still present because of their high stability. Nickel is also present in very complex sulphate forms (soluble forms), with possibly interference with chloride and nitrate anions.

4.4. Conclusions and lack of data

For the time being, it is difficult to draw a precise image of the situation with respect to ambient air exposure to nickel, both in terms of concentration and of chemical and physical analysis (chemical species, particle size, etc.).

Immission values expressed in yearly averages have decreased during the last few decades, from about 30 ng/m³ in urban and industrialized areas in the 1970s to about 5 ng/m³ in urban areas and 5-10 ng/m³ in industrialized areas today. In the region of Scandinavia, bordering the Kola Peninsula, despite the proximity of a Russian nickel production industry, the impact seems finally very low.

In rural areas, nickel exposure is about 1 to 2 ng/m³ and 0.2 to 1.0 ng/m^3 in remote areas. For urban and industrial areas, current programmes of reduction of SO₂ emissions may have an indirect effect on nickel emission and immission. The benefical effects of these programmes have not yet been fully determined. The period 1993-96 should probably be characterized with a significant progress in comparison with the period 1992-93 and it can be expected that nickel immission values for urban and industrialized areas are now in the range of 3 to 6 ng/m³, and at least below 10 ng/m³.

Particles contain around 0.01% of nickel, extremely diluted in comparison with dust emitted by some nickel refining processes associated with respiratory cancer risk (1 to 50% Ni). Nickel is probably present in these dusts as complex oxides (water insoluble) and complex sulphates (water soluble) in equivalent proportions.

The data on nickel immission values published in EU presented in the previous sections for the various urban, industrial and rural areas have to be completed by more regular measurement surveys to better improve their reliability. At the moment, it is not possible to draw up a clear correlation between exposure levels and demographic aspects. PART 2

RISK ASSESSMENT OF NICKEL COMPOUNDS

5. RISK ASSESSMENT OF NICKEL COMPOUNDS

5.1. Introduction

The objective of this section is to calculate the risk associated with a unit exposure to nickel in the ambient air for the general public. At present, the only clearly demonstrated end point associated with exposure to nickel is respiratory cancer (nose, lung). Nevertheless, no epidemiological study has been performed on the general public. Thus, in the absence of such human data, the risk assessment for low levels of exposure to nickel in the ambient air (of the order of a few nanograms per cubic meter of nickel) can be derived by extrapolation from occupational human data and animal data, both associated with higher levels of exposure and different chemical forms of nickel compounds.

5.1.1. Mechanistic considerations

The carcinogenicity of nickel as an element, or ion « Ni²⁺ », has not yet been clearly established. During the last two decades, studies on the mechanisms of the action of nickel on DNA and target cells have been extensively conducted, but our understanding of these mechanisms remains incomplete. Furthermore, the toxicity of nickel and nickel-containing particles depends on their chemical form and on their combination with other substances¹. For example, their combination with magnesium may protectively affect the migration of nickel to target cells.

Finally, the risk assessment of exposure to nickel or nickel-containing particles in the ambient air requires a good knowledge of their chemical characteristics. In regulatory terms, this has made it necessary to differentiate the toxicities of the various nickel-containing substances, and to take into consideration the particular case of mixtures/preparations (Directive 88/379 for Dangerous Preparations).

¹ An analysis of dust composition performed in Paris in 1992 illustrates the presence of various metallic components in the ambient air: Ni (0.01-0.02%), Mg (0.5-0.6%), As (0.006%), Cu (0.06%), Mn (0.04-0.05%), Cd (0.005%), Fe (1.6-1.9%).

5.1.2. Hazard identification

The following classification, performed in the scope of Directive 67/548 on Dangerous Substances, gives a first appreciation of the toxicity of ten different nickel compounds, and illustrates the importance of their chemical speciation in hazard identification.

Category 1 Carcinogens by inhalation (R 49: may cause cancer by inhalation):

- nickel monoxide (NiO) CAS No.1313-99-1/EEC N°028-003-00-2
- dinickel trioxide (Ni₂0₃) CAS No. 1314-06-3/EEC N°028-005-00-3
- nickel dioxide (NiO₂) CAS No. 12035-36-8/EEC N°028-004-00-8
- nickel subsulfide (Ni₃S₂) CAS No.12035-72-2/EEC N°028-007-00-4
- nickel sulfide (NiS) CAS No. 16812-54-7/EEC N°028-006-00-9

Category 3 Carcinogens (R 40: possible risks of irreversible effects):

- nickel metal (Ni) CAS No.7440-02-0/EEC N°028-002-00-7
- nickel sulphate (NiSO₄, 6H₂O) CAS No.7786-81-4/EEC N°028-009-00-5
- nickel carbonate (NiCO₃) CAS No. 333312035-36-8/EEC N°028-010-00-0
- nickel hydroxide Ni(OH)₂ CAS No.12054-48-7/EEC N°028-008-00-x
- nickel carbonyl Ni(CO)₄ CAS No.13463-39-3/EEC N°028-001-00-1

Assessments of the toxicity of nickel compounds were made by the European Union and by IARC approximately at the same time, and were both based on the conclusions of the ICNCM report. At that time, the results from the NTP experiments on NiO, Ni_3S_2 , and $NiSO_4, 6H_2O$ were not considered.

5.2. Analysis of the dose-response relationship

5.2.1. Risk assessment of nickel and compounds in ambient air on the basis of human data

5.2.1.1. Introduction

There are no epidemiological data on the respiratory risk associated with exposure to nickel in the ambient air in rural, urban or industrial areas, even in the vicinity of an industrial site. Available epidemiological studies were performed in the context of the nickel industry, referring to a time when occupational hygiene was not well developed in nickel-production and nickel-using industries. Exposure to nickel dusts at workplaces was extremely high (up to 100 mg (Ni) $/m^3$), about one million times higher than that expected today in the general environment, and was combined with other compounds, such as arsenic compounds, acid mists, polyaromatic hydrocarbons, etc. Moreover, the chemical composition of dusts in the work place differs from that of the ambient air.

Epidemiological studies on a total of approximately 70 000 workers revealed an excess of nasal and lung cancers, excluding excess of other cancers. Nasal cancers were associated with high level exposures and coarse particles, while lung cancers were more frequent and observed in cohorts with lower exposures. A few cases of pulmonary fibrosis were reported, but their relation to nickel exposure is not totally demonstrated. As regards skin allergies associated with nickel exposure, these result from skin contact and not from inhalation. Finally, asthmetiform respiratory problems due to occupational exposure to certain nickel compounds were relatively rare, and no relevant incidence was noted. Therefore, the risk assessment carried out in the present study will focus on lung (bronchial) cancer.

5.2.1.2. Review of the cohorts

All the epidemiological data were reviewed and updated by the International Committee on Nickel Carcinogenesis in Man (ICNCM). The committee's report [43], based on the analysis of ten cohorts, was published in 1990. A detailed presentation of these studies is provided in [1] and the ten cohorts are described in Table 35.

Only three sub-cohorts among the studies from Clydach (UK), Kristiansand (Norway) and Copper Cliff (Canada) allow deriving dose-effect relationships. Nevertheless, durations and exposure rates are not completely detailed in all the studies, so the possibility of comparing the different cohorts is restricted.

As regards the Clydach cohort, before 1930 (the date when the process was changed), a standardized mortality rate (SMR) of 393 for lung cancer was found. After 1930, a risk of lung cancer was no longer observed (the modified process led to a drastic decrease in exposure, and also to a chemical change in the nature of exposure, in particular a decrease in sulphur, copper and arsenic levels). The data used in this cohort are those updated by the ICNCM study.

The exposed population of the Kristiansand cohort was relatively stable. The mobility of the workers inside the plant was very low. The risk of lung cancer was multiplied by a factor of 3 for workers employed before 1956, but was still significant in the cohort after this period. Soluble nickel exposure is confirmed as being associated with an increase in the risk of lung cancer and questions were posed concerning the role of oxidic nickel in combination with soluble nickel. A specific analysis (published at the end of 1996) [44] was performed by Andersen *et al* on the role of tobacco among the exposed workers. This study was not considered in the present analysis.

The clearest dose-response relationship was observed in the Copper Cliff cohort [45]. Workers were essentially exposed to nickel sub-sulphide. Exposures were very high before 1951 (up to 100 mg (Ni) $/m^3$). An SMR of 850 was found in a subgroup of 495 workers.

Cohorts	Size (workers)	Comments	Dose-effect relationship
Clydach	2,521	- First positive study (before 1930)	Yes
(Ni refining)		- Subgroup of 726	
		- Matte roasting	
Kristiansand	3,250	- Updated study (including tobacco	Yes
(Ni refining)		smoking)	
		- Matte roasting	
Ontario-Inco		- Only the Copper Cliff cohort	
(Ni refining)		reveals a dose-effect relationship (on	
- Roasting Sudbury	2,097	a subgroup of 495)	No
- Sintering/roasting Copper Cliff	1,754		Yes
- Roasting Coniston	343		No
- Sudbury others	48,361		No
- Port Colborne	4,288		No
(Sintering + electrorefining)			
Ontario - Falconbridge	11,594		
(Nickel matte production)			
Oregon	1,510	- Slight excess (SMR: 147)	No
(Ferronickel smelter)			
Oak Ridge	813	- Negative study in the nickel-using	
(Powder metallurgy)		industry	
		- Exposure to pure nickel metal	
Huntington	3,108	- Negative study in the nickel-using	
(Ni alloys)		industry	
Harjavalta - Finland	129	- Too small cohort	
(Ni refinery)			
Hereford - UK	1,907	- Negative study in the nickel-using	
(Ni refinery)		industry	
New Caledonia	Case	- Negative study	
(Ferronickel and nickel matte	control		
production)	study		
	(79/223)		

Table 44. Main available worker cohorts [43]

The main conclusions pointed out by the ICNCM study were:

"...it appears that more than one form of nickel gives rise to lung and nasal cancer. Although much of the respiratory cancer risk seen among the nickel refinery workers could be attributed to exposure to a mixture of oxidic and sulfidic nickel at very high concentrations, exposure to large concentrations of oxidic nickel in the absence of sulfidic nickel was also associated with increased lung and nasal cancer risks.

There was no evidence that metallic nickel was associated with increased lung and nasal cancer risks, and no substantial evidence was obtained to suggest that occupational exposure to nickel or any of its compounds was likely to produce cancers elsewhere than in the lung or nose...

Although the investigation did not provide dose specific estimates of risks for individual nickel species, it is possible to comment on the cancer risks associated with the level of airborne nickel to which the general population is exposed. The evidence from this study suggests that respiratory cancer risks are primarily related to exposure to soluble nickel at concentrations in excess of 1 mg (Ni) /m³ and to exposure to less soluble forms at concentrations greater than 10 mg (Ni) /m³. With excess risks being confined to these high levels of exposure and the absence of any evidence of hazard from metallic nickel, it can be concluded that the risk to the general population from exposure to the extremely small concentrations (less than 1 μ g (Ni) /m³) to which it is exposed in the ambient air is minute, if indeed there is any risk at all..."

5.2.1.3. Different models used for extrapolation

Calculations of the risk associated with exposure to nickel in the ambient air on the basis of the epidemiological studies presented above were performed by the following three organizations:

- US EPA (Environmental Protection Agency) 1986 Health Assessment Document for Nickel [46]
- WHO-Europe (World Health Organization) 1987 Air Quality Guidelines for Nickel currently under revision in 1994-96 [47, 48]
- CARB (Californian Air Resources Board) 1991 [49].

Furthermore, one of these studies was reviewed by the NiPERA (Nickel Producers Environmental Research Association) in 1990 for CARB. Seilkop made his own assessment for NiPERA in 1995, as an extension to the ICNCM Report.

The extrapolation is divided into two parts. In a first part, the past exposure of the considered cohorts is determined. For that purpose two methods are available: the average estimate and the maximum likelihood (estimated from regression curves slope of SMR as a function of exposure, fitted minimizing the sum of the squares). In a second part, two linear extrapolation models were tested:

- A linear extrapolation using an additive risk model (absolute risk model), based on the principle that the mortality excess, by reference to the background rate, is proportionally increased with the exposure (cumulative exposure). This model was first used by EPA in order to assess the Huntington cohort, but was not retained;
- A linear extrapolation using a multiplicative model (relative risk model) based on the assumption that the studied agent acts by reference to a basic risk (combination of different causes contributing to the risk associated with nickel).

The risk assessment performed by the various organizations is based on a combination of these methods (see Table 45).

	Additive model	Multiplicative model		
Average exposure		EPA:	Copper Cliff, Clydach, Kristiansand	
		WHO:	Kristiansand	
		CARB:	Copper Cliff	
		NiPERA:	Copper Cliff	
Maximum likelihood	EPA: Huntington	EPA:	Copper Cliff	
		NiPERA:	Copper Cliff	

Table 45. The risk assessment methods adopted by variousorganizations

5.2.1.4. Results

The extrapolation of the results from epidemiological studies related to occupational exposures to the case of environmental exposures requires using conversion factors and uncertainty factors which were considered in these studies.

EPA

As regards the Clydach cohort, the extrapolation led to an average relative risk associated with a lifetime exposure of 1 μ g (Ni) /m³ ranging from 8.1 10⁻⁵ to 4.6 10⁻⁴ for levels of exposure respectively ranging from 10 to 50 mg (Ni) /m³.

As regards the Kristiansand cohort, EPA proposed an average relative risk based only on a subgroup of workers exposed to matte sintering/roasting dusts containing mainly nickel sub-sulphide and oxidic nickel. The extrapolation led to an average relative risk associated with a lifetime exposure of 1 μ g (Ni) /m³ ranging from 1.9 10⁻⁵ to 1.9 10⁻⁴ for levels of exposure respectively ranging from 3 to 30 mg (Ni) /m³.

For the Copper Cliff cohort, EPA used two methods to evaluate the risk for a level of exposure of 200 mg (Ni) /m³ prior to 1951 and 100 mg (Ni) /m³ after that date. The first method (maximum likelihood) led to a risk increase of 1.2 10^{-4} for a lifetime exposure, while the second one (average relative risk) gave a risk increase of 8.9 10^{-5} .

A fourth cohort (Huntington) was considered by EPA. The additive model did not result in a any dose-effect relationship, while the multiplicative model led to an average relative risk of 3.1 10^{-5} for a life span exposure of 1 µg (Ni) /m³. This cohort was not retained by the other organizations.

WHO

For the Kristiansand cohort, a first calculation, performed in the 1987 publication of WHO, resulted into a unit risk of 5.9 10^{-4} associated with a life span exposure to 1 µg (Ni) /m³ (the corresponding exposure level of the cohort was estimated at 3 mg (Ni) /m³). This calculation was revised in the 1995 publication of the WHO, and the new estimate gave a unit risk of 9.6 10^{-4} for an exposure level of the cohort estimated at 0.5 mg (Ni) /m³.

As regards the Copper Cliff cohort, the WHO calculated a unit of risk of 5.7 10^{-4} for an exposure level of 10 mg (Ni) /m³.

CARB

CARB only used the Copper Cliff cohort (on the basis of old epidemiological data) for its assessment. The unit risk derived from the relative risk method and the maximum likelihood was $2.57 \ 10^{-4}$ for a life span exposure of $1 \ \mu g$ (Ni) /m³.

NiPERA

The calculation performed by the CARB was updated by NiPERA on the basis of the new epidemiological data from ICNCM. Using the same methodology, the unit risk was estimated to be $1.2 \ 10^{-4}$ (the adoption of a different methodology leads to an estimate of a unit risk of 9.1 10^{-5}).

Due to this diversity of risk assessments from different organizations, new calculations were not performed in this report. A critical review of the various studies presented above is proposed in [1]. In the absence of scientific evidence of the existence or absence of effects at low levels of exposure, the prudent approach of using a linear model was adopted. Figure 17 presents the relative risk, according to the lifetime exposure of the cohort, derived from the epidemiological studies described in [1].

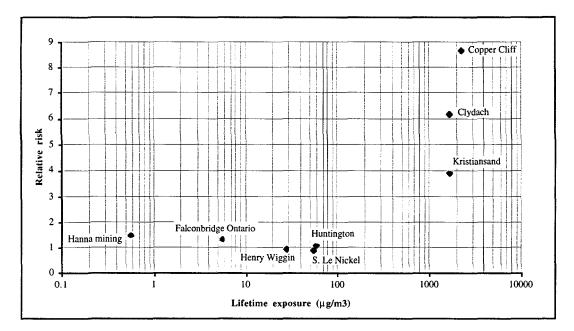


Figure 17. Relative risk of lung cancer derived from epidemiological studies

Taking into account the lack of precise information in the different studies, the results shown in Figure 17 must be considered carefully, as a rough estimation. It must be kept in mind that, as mentioned above, only three epidemiological studies were considered for extrapolating the relative risk to low levels of exposure. In the other studies, the available information on the level and duration of exposure was too limited and/or the results of these epidemiological studies did not permit driving dose-effect relationship. The values presented in Figure 17, related to Hanna mining, Henry Wiggin, S. Le Nickel and

Falconbridge Ontario were calculated assuming a duration of exposure of 17.5 years (1/4 of worker's life). Table 46 summarizes the unit risks adopted by the different organizations according to the cohort considered for the calculations.

Organization		Clydach	Kristiansand*	Copper Cliff
wнo	1987	5.7 10-4	5.9 10 ⁻⁴	1.5 10-4
	1995		9.6 10-4	
CARB	1991			2.57 10-4
EPA	1986	8.1 10 ⁻⁵ to 4.6 10 ⁻⁴	1.9 10 ⁻⁵ to 1.9 10 ⁻⁴	8.9 10 ⁻⁵ to 1.2 10 ⁻⁴
NiPERA	1995			9.1 10 ⁻⁵

Table 46.	Estimates of excess of lung cancer for a life span exposure
	to 1 μ g (Ni) /m ³ published by the various organizations

* The updated data produced by Andersen et al. (1996) were not considered

All these values were derived using of the linear multiplicative method (relative risk) using average exposure, except in the case of NiPERA which proposes a multiplicative model with a calculation of exposure using the maximum likelihood. It should be kept in mind that these figures are based on the extrapolation of the results of three cohorts that underwent nickel exposures of slightly different chemical nature. Kristiansand workers were exposed to a mixture of insoluble and soluble nickel compounds, whereas workers in the two other cohorts were mainly exposed to insoluble compounds, in particular nickel sub-sulphide. The chemical species considered in these situations do not completely reflect the composition of the dusts present in the ambient air inhaled by the general public.

According to the available results of epidemiological studies for occupational exposures, the maximum excess of risk of lung cancer for a full life span of continuous exposure to $1 \mu g$ (Ni) /m³ ranges from 10⁻⁴ to 4.6 10⁻⁴. An average value of 2.5 10⁻⁴ is proposed.

5.2.2. Risk assessment of nickel and compounds in the ambient air on the basis of animal data

Animal carcinogenesis bioassays provide various data of interest for the identification and quantification of the potential risk resulting from environmental exposure to nickel compounds [1]. These data include:

- The specific carcinogenic potency of various nickel compounds (speciation)
- The ascertainement of the dose-effect relationship taking into account the characteristics of the aerosol, the lung burden and the exposure-induced physiopathological changes.

Three main parameters are critical from the methodological point of view:

- The duration of the study which should extend to the greater part of the life expectancy of the species under study, since it is well known that in mammalian species, the age-specific prevalence of cancer rate is a power function of age,
- The size of experimental groups which, as well as the spontaneous incidence of cancers, determines the statistical power of the study,
- The survival rate, which should reach an acceptable level, i.e., a sufficient number of animals should be at risk during most of their life span.

Taking into account these parameters it can be concluded that:

- Oral administration does not result in any carcinogenic effect of inorganic nickel compounds,
- Inhalation demonstrates the carcinogenicity of nickel sub-sulphide in rats, and of nickel oxide in rats and presumably in female mice; on the other hand, no carcinogenic effect is observed in rats and mice following exposure to nickel sulphate,
- Non-relevant routes demonstrate *in situ* carcinogenicity for most of the insoluble nickel compounds under study, but, whatever the route of administration, it appears that no primary tumours occur in remote organs.

The exposure of the population to environmental airborne nickel results in the continuous inhalation of low doses during its life span. The evaluation of the risk for humans at these dose levels, using experimental data (only inhalation results will be considered since it is the only relevant route for extrapolation from animal to man), requires adjustments based on pragmatic assumptions:

• A linear dose-effect relationship for carcinogens, when shifting from discontinuous

experimental exposures at high aerosol concentrations to continuous exposures at low aerosol concentrations during a whole human life span,

• A constant absorption factor among species (one can evaluate the mean daily human equivalent from the body surface which is proportional to (weight)^{2/3} and which follows a constant relationship among species).

5.2.2.1. First estimation of human carcinogenic risk

Tumour rates observed in various experiments on nickel compounds are presented in Figure 18.

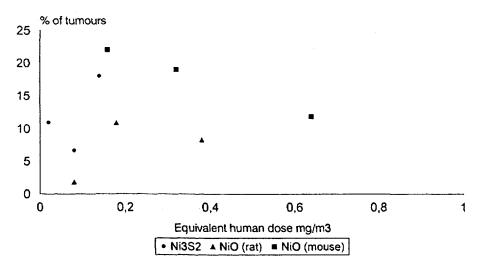


Figure 18. Tumour rates observed in various experiments for different nickel compounds

Only the latest results obtained by the US National Toxicology Program (NTP) in rats have to be considered. They are presented in Table 47. As previously reported, inhaled soluble NiSO₄ did not significantly increase lung tumour incidence in rats and mice. Because animals were sacrificed at 24 months, the cancer risk (carcinoma) was underestimated and the upper limit should be given by the total tumour risk (carcinoma + adenoma). Thus, after correcting for the spontaneous incidence of tumours observed in controls, the mean risk, excluding the negative value observed for the lowest NiO aerosol concentration, expressed as equivalent continuous human exposure, is 0.4 10⁻³ µg/m³ for NiO and 3.0 10⁻³ µg/m³ for Ni₃S₂.

	Carcinoma		Carcinoma + adenoma	
NiO				
0.5 mg (Ni) /m ³	0/53	0/53	1/53	0/53
1 mg (Ni) /m ³	3/53	5/53	6/53	6/53
2 mg (Ni) /m ³	2/52	1/54	4/52	5/54
Ni ₃ S ₂				
0.11 mg(Ni)/m ³	3/53	1/53	6/53	6/53
0.73 mg(Ni)/m ³	6/53	4/52	11/53	9/52
Controls				
	0/53-1/54	0/53-0/53	0/53-1/54	2/53-1/53

Table 47.Results from NTP in rats

5.2.2.2. Factors modifying the dose-effect relationship

The environmental airborne physical and chemical form of nickel is not nickel subsulphide (Ni_3S_2), which is emitted in small quantities by certain industrial environments. Therefore, experimental results obtained on NiO should be used to assess the maximum value of the risk, but it is expected that the behaviour of environmental airborne nickel is different from NiO, since it is in a different chemical form and associated with other chemicals, such as metal compounds or hydrocarbons. In this respect, its solubility would be higher than NiO, but no correction factor has been proposed to take these phenomena into account.

Experimental results were obtained following exposure to aerosols of selected size (median aerodynamic diameter = $2.4 - 2.8 \mu m$, $\sigma g=2$) to achieve an optimal lung deposition rate. The particle sizes used in animal experiments differ from those measured for most environmental aerosols, which could exhibit a different distribution of particle size and thus different lung deposition characteristics. Therefore, it seems advisable to reduce the deposition rate by an arbitrary factor of 5 compared to experimental data, in order to take into account possible differences in the physical characteristics of the aerosol which may occur in the ambient air. Accordingly, the human risk would be $0.8 \ 10^{-4} \mu g/m^3$.

In rat, the carcinogenicity of NiO is only observed for exposure concentrations inducing severe changes in pulmonary clearance. Therefore, the rat lung burden determined at 15 months is overestimated by a factor of 2 to 4. After two years, this factor is at least 5 with an upper value of 10. Similar correction factors should be applied to carcinogenic effects. However, because pulmonary clearance parameters are different in rat and in man, a correction factor of 2 for humans seems reasonable. The inhibition of rat lung clearance is related to particle overload, but its role during the carcinogenic process is not clear and has to be further investigated.

5.2.2.3. Proposal for an estimation of the carcinogenic risk of environmental airborne nickel

Finally, assuming a non-threshold linear dose-effect relationship, the value of 0.4 10^{-4} for an exposure of 1 µg (Ni) /m³ seems acceptable for NiO, taking into consideration the correction factors mentioned above. In the case of Ni₃S₂, a similar risk estimate can be performed, giving a value of 3 10^{-4} for an exposure of 1 µg (Ni) /m³, which is similar to the value extrapolated from epidemiological studies performed on workers.

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PART 3

RISK ASSOCIATED WITH NICKEL COMPOUNDS IN THE AMBIENT AIR FOR THE GENERAL PUBLIC

6. RISK ASSOCIATED WITH NICKEL COMPOUNDS IN THE AMBIENT AIR FOR THE GENERAL PUBLIC

Like most toxic substances, the results from epidemiological studies concerning exposures to nickel do not provide a direct estimate of the risk with respect to very low levels of exposure. Considering the fact that it is impossible to demonstrate the existence of a limit exposure value, below which no side effects are expected, a precautionary attitude is adopted, assuming that a risk exists as long as the exposure is not nil. Risk assessment is no longer a matter of scientific knowledge but relies much on risk management (i.e. includes social, economic and ethical considerations). Adopting the precautionary approach, the above analyses on human and animal data permit proposing a risk coefficient for exposure to nickel in the ambient air, keeping in mind that this value is a result of a theoretical construction of the risk in view of the scientific uncertainties.

6.1. Foundations of the precautionary principle

The reference to the precautionary principle is the starting point for risk management, in the absence of scientific evidence of a nil risk. This principle was introduced in the eighties for the protection of the environment (adopted by the Rio Conference on the Environment and Development - June 1992, as well as in the European Union Maastricht Treaty - Chapter 16, article 130-B2) [50].

Schematically, the principle considers that the uncertainty associated with the side effects, on man or on the environment, of specific actions, leads to the need to take into account a potential risk in the decision framework, in so far as it is impossible to exclude this risk on the basis of scientific knowledge. This is considered as a responsible attitude with respect to the safety of the population or the environment, especially in the case of irreversible actions [51, 52]. As mentioned by O. Godard [53], this opens an area for public debate, economic analysis, and social and ethical considerations. The French law on the environment (Law 95-101, 1995) re-enforces these considerations, stating that the protection strategies to be adopted have to refer to an acceptable cost.

6.2. "Construction" of the risk for very low levels of exposure to nickel in the ambient air

The epidemiological studies on occupational exposure led to a unit risk of 2.5 10^{-4} for lung cancer, for a full life span of continuous exposure to $1 \mu g$ (Ni) /m³. The immission values measured in various European areas (a few ng (Ni) /m³) are not comparable with values of a few μ g (Ni) /m³ to a few mg (Ni) /m³. A first simple linear extrapolation of the results obtained for an exposure of 1 μg (Ni) /m³ would lead to a unit risk of 2.5 10⁻⁷ for an exposure of 1 ng (Ni) /m³. But the physical and chemical characteristics of the nickel compounds in workplaces are also different from those expected in the ambient air. Nickel sub-sulphide (Ni_3S_2) , the main constituent of nickel-copper matte, has been considered as the main cause for respiratory cancers excess among workers exposed during certain nickel refining steps. However, this substance cannot be present at significant levels in the ambient air dusts. Nickel monoxide (NiO) may have been associated with nickel sub-sulphide in those refining steps. In the ambient air, nickel monoxide cannot exceed 8% of total nickel [1]. Nickel sulphate has been retained as the surrogate of the water soluble nickel-containing substances in the ambient air (about 50% of nickel compounds in the ambient air). The other compounds have not been considered in this study because they do not contribute to a significant exposure level in the ambient air.

The unit risk calculated for the ambient air must take these differences into account. This adjustment was performed using the results from animal studies, which permitted distinguishing between the effects of NiO and Ni₃S₂, leading to a unit risk of 0.4 10⁻⁴ for NiO and 3 10⁻⁴ for Ni₃S₂ respectively, for an exposure of 1 μ g (Ni) /m³.

Considering the fact that, in the case of the ambient air exposures, Ni_3S_2 is not the relevant nickel compound, and that there is a maximum of a few percents of total nickel as NiO, if any, the unit risk of lung cancer of 1 10⁻⁷ for an exposure of 1 ng (Ni) /m³ is proposed as a precautionary value for assessing the risk in the ambient air for the general public.

6.3. Proposed reference values for immissions in European areas

The present study led to a first appraisal of little human exposure to the ambient air nickel in some European countries. In spite of very few available data related to systematic atmospheric nickel analyses, it seems reasonable to consider different exposure levels on which the risk assessment will be based. These values are summarized in Table 48.

It is relatively difficult to associate the data collected with any precise geographic region. In most cases, the locations of the measurements are not clearly identified (50 noncharacterized measurements out of the 220 values collected in [1]), and the classification is mainly based on logical assumptions. Some measurements campaigns may have produced a rough image of the situation for some cities in France (Paris) and in the United-Kingdom (London). Special attention must also be paid to the results of measurements related to the Ruhr region in Germany (industrialized area).

Table 48.Classification of the immission values collected by type of
area

Type of area	Range of concentration value (ng/m ³)	Number of measurement points	Mean value (ng/m ³)
Urban (*)	3 - 25	35	11.5
Industrialized (+)	2.3 - 50	70	7
Rural (**)	0.7 - 5.5	13	2.5
Remote	0.44 - 0.92	4	0.74

(*) The data from Rotterdam (1970) and from Belgium (site 19, 1980) excepted

(+) One value from Finland (1990) excepted

(**) Two values from Belgium (1980) excepted

The relatively high value for urban sites compared with industrialized ones can be explained by the abundance of recent measurements from the Ruhr region (industrialized area). Data for urban sites is less documented for the last decade. In any cases, the uncertainty on these figures is greater than the difference between the two values.

It should be noted that the improvement of the industrial processes during the last decade should lead to a decrease in the immission values.

Figure 19 presents the distribution of the immission values related to the sector identified as "urban".

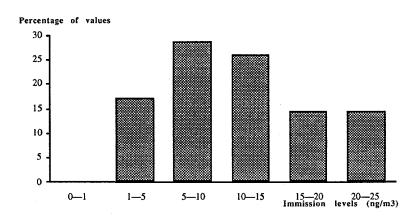


Figure 19. Distribution of immission values in urban areas

Several studies referenced in this report provide some data on the range of the immission values in urban areas in France and United-Kingdom [36]. The first study gives a range from 8 to 45 ng/m³ (period 1969 - 1992), the lowest value corresponding to 1992. The second one gives a range from 5 to 17 ng/m³ (period 1984 - 1993).

Table 49 presents a synthesis of the immission values collected from different industrialised areas of Europe [1].

Country	Range (ng/m ³)	NB of values	Mean (ng/m ³)
Germany	2.3 - 13	63	5
Belgium	10 - 50	3	27
France	16.5	1	16.5
United-Kingdom	13 - 31	3	25

Table 49.	Immission	values	in	some	industrialised	areas of	European
	countries						_

In order to characterize the current risk in the ambient air, the following three values (see Table 50) were adopted on the basis of the data on immission values collected in this study, and some complementary surveys conducted in Paris and in the United-Kingdom [36]. These values are a preliminary proposal for the characterization of current exposure, in so far as they do not really reflect the current situation in all of Europe (restricted

number of measurements), and they are derived from various measurement campaigns spread over the last three decades. Further data has to be obtained to confirm these trends.

Representative value	Type of area
1 ng/m^3	Rural, little economic activity
10 ng/m ^{3*}	Urban, industrial activities
30 ng/m ³ **	

 Table 50.
 Selection of representative immission values

*Areas with an active protective policy regarding air pollution **Areas without an active protective policy regarding air pollution

7. CONCLUSION

Assuming an average life expectancy of 70 years, the figures presented in Table 51 are obtained for the various ranges of lifetime exposure.

Lifetime exposure level (ng/m ³)	Lifetime risk of lung cancer	Average annual risk of lung cancer
1	10.7	1.4 10 ⁻⁹
10	10-6	1.4 10 ⁻⁸
30	3 10-6	4.3 10 ⁻⁸

Table 51. Evaluation of the potential risk

Both the individual risk and the collective risk have to be considered insofar they should provide information for a decision-making process.

Concerning the individual level of risk derived from the previous calculations, it clearly appears that the values are far below the level considered as significant. An annual risk of death in the 10^{-6} to 10^{-7} range is generally considered as a negligible level of risk [54], [55].

On the other hand, in a public health perspective, decision-makers may have to consider collective exposure to nickel in the ambient air. A rough calculation was performed for the 1990 European population (327 million) and led to an expected annual collective risk of about 4 to 5 cases of lung cancer in excess per year for the whole European population for an exposure level of 10 ng (Ni) /m³, which can be compared with the 120,000 lung cancers per year in Europe.

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