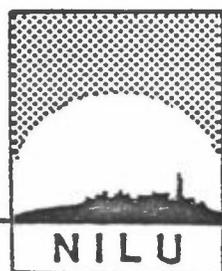


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ESTIMATION OF EMISSION FACTORS
OF TRACE METALS FROM OIL-FIRED
POWER PLANTS

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ESTIMATION OF EMISSION FACTORS OF TRACE
METALS FROM OIL-FIRED POWER PLANTS

1 INTRODUCTION

In many industrialized countries oil-fired power plants are still the most important source of energy (1). The trace metal contents of oil is significantly lower than for coal (particulate emissions from oil-fired boilers are about 1 per cent of emissions from similar coal-fired equipment (2)), but considering the large quantities of oil burned, oil-fired power plants still represent a significant source of trace metal emissions. In the present report emission factors of trace metals from oil power plants are estimated, using available data on concentration of pollutants in the fuels. Ideally, emission factors should be related to plant design and operating conditions as well as fuel composition in order to permit a definite statement as to the emissions characterizing a given plant. Unfortunately, the numerous and expensive studies (for instance stack testing studies) needed to completely characterize a source have not generally been performed. The emission factors used in this work were compiled from an extensive literature survey.

2 DESCRIPTION OF A TYPICAL OIL-FIRED PLANT

The oil is injected by burners located in the boiler combustion chamber or furnace. Each burner also injects air, and the air and oil streams become thoroughly mixed within the furnace. Basically two different designs of furnaces are used. The tangentially fired unit is constructed to produce a spiral upward motion of the flame and combustion products around the walls of the cylindrical firebox.

In horizontally fired units the flames are usually at right angles to the walls of the firebox, but may also be used at different angles. The burners may be mounted on one or more sides, or at the bottom of the firebox.

Emission rates of particulate matter from tangential and horizontal units working under similar conditions are comparable. In modern boilers the oil must be introduced at high flow rates. To accomplish this, each burner contains an atomizer which sprays the oil into the furnace as a fine mist. The two most widely used systems for atomizing the oil are steam or air atomizers and mechanical atomizers.

Oil-fired boilers do not require ash hoppers and ash pits (3). Fly ash removal equipment is not generally required (4), although such equipment is used at some oil-burning plants (3,5). Dust collectors are, however, used during soot blowing. This equipment serves principally to collect particulate matter larger than 10 μm . The emission of particulate matter from an oil-fired unit without stack gas cleaning is comparable to a coal-fired unit of better than 99 per cent collection efficiency (6).

3 FUEL OIL REQUIREMENTS

The amount of fuel oil consumed per day by an oil-burning, i.e., its daily fuel oil requirement (DFOR), is given by the formula (3):

$$\text{DFOR} \left(\frac{\ell}{\text{day}} \right) = \left(\frac{P}{100} \right) \times C(\text{MWe}) \times 10^3 \frac{\text{kW}}{\text{MW}} \times 24 \frac{\text{h}}{\text{day}} \times 3412 \frac{\text{Btu}}{\text{kWh}} \\ \times \frac{100}{E} \times \frac{1 \text{ gal. fuel oil}}{B_{fo}(\text{Btu})} \times 3.785 \frac{\ell}{\text{gal}} \quad (1)$$

where: C = the capacity of the plant in megawatts (MWe).
P = the capacity or plant factor, i.e., the percentage of capacity at which the plant operates, averaged over one year. A typical value for P is 70 per cent.
E = the efficiency of the plant, in terms of kWh electrical energy output from the plant per kWh of coal energy input. Typically E ranges from 36-40 per cent. For the subsequent calculations a constant efficiency of 38 per cent has been assumed.
 B_{fo} = the heat content in Btu per gallon of fuel (in this work 145.800 Btu/gal) oil.

The daily oil requirements of the four model plants considered in this work are given in Table 1.

Table 1: Daily oil requirements of the four model power plants.

Plant size (MWe)	Fuel oil consumed liters/day
100	392.000
350	1.372.000
700	2.744.000
2100	8.232.000

4 METALS IN OILS

4.1 Metals in crude oils

Both crude oils and refinery products contain varying amounts of numerous metals. The metals content of crude oils is shown in Table 2 (8,9,10).

Table 2: Metal content in crude oils (8,9,10).

Element	Concentration range (ppm)	Average concentration (ppm)
As	0.046 - 1.110	0.263
Cd		0.030
Co	0.032 - 12.751	1.710
Cr	0.0016- 0.017	0.008
Cu	0.130 - 6.330	1.320
Fe	3.365 - 120.840	40.670
Hg	0.023 - 30.000	3.240
Mn	0.630 - 2.540	1.170
Mo	0.008 - 0.053	0.031
Ni	< 2.000 - 344.5000	165.800
Pb	0.170 - 0.310	0.240
Se	0.026 - 1.396	0.530
V	< 2.000 - 298.500	88.500
Zn	3.571 - 85.800	29.800

Table 2 shows that fuel oil is a significant source only for nickel and vanadium.

For a region, "average concentrations" is a difficult term. The average concentrations of trace elements listed in Table 2 were calculated on the basis of oil resources and trace element concentrations in oils from particular areas.

To obtain suitable weighted mean concentrations for Western Europe, figures of crude oil import from different areas will have to be used together with distillate yields and trace element concentrations. Average nickel and vanadium concentrations in crude oils imported to Western Europe from different source areas are given in Table 2a (7).

Table 2a: Average concentrations of nickel and vanadium in crude oils from different source areas (?).

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

The concentrations of nickel and vanadium generally increase with the asphalt content or weight of the crude oil. Most metal atoms are chelated within large hydrocarbon complexes.

According to (10), refineries treat crude oils by acid extraction and fractionation to reduce the metal content prior to catalyst treatments. Little is known about the chemical form of metallic compounds in crude oils, other than vanadium and nickel.

Refining tends to concentrate about 90 per cent of the original metals content in the heavy distillate residuals, such as residual fuel oils and asphalts, and in the liquid and solid waste streams.

4.2 Metals in oil burned in oil-fired plants

Refining may concentrate trace metals in the heavy distillate residuals by a factor of 5 to 10 or more (10). Hence, potentially hazardous trace metals may be discharged by combustion of residuals in both electric utility and industrial boilers.

From among more than 60 detectable trace elements in residual oils, only about 12 are normally analyzed: As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, V and Zn. These elements are either the most toxic or appear in the highest concentrations.

Physiological, effects and toxicity data for some metals found in oils are given in Table 3 (9).

Table 3: Physiological effects of trace metals found in oils (9).

Element 1	Human Effects 2	Toxicity Data 3
Arsenic	Dermatitis, bronchitis, skin cancer. Damages the heart, kidney, nerves, and possibly the liver. GI symptoms in acute systemic poisoning.	Normal ingestion 0.1 mg/day. Toxic level 5-50 mg/day. Smallest fatal dose recorded 130 mg.
Cadmium	Cumulative poison. Pulmonary emphysema, hypertension, kidney damage. Cardiovascular disease. Interferes with Zn and Cu metabolism. Inhalation of 0.03-35 mg/m ³ significantly reduced children's weight. GI symptoms.	LD (oral) for rabbits 200-600 mg. LD50 CdO ₃ fume 500 mg/m ³ for rats to 1.500 mg/m ³ for monkeys.
Chromium	Dermatitis, ulceration of skin, perforation of nasal septum, chronic catarrh, emphysema, carcinogenesis when inhaled. Cr(VI) extremely toxic. Not cumulative. Apparently essential in glucose metabolism.	Normal ingestion 0.05 mg/day. Toxic level 200 mg/day. No ill effects from well water with 1.0-25.0 mg/liter. LD (oral) K chromate in rabbits 1.9 g within 2 hrs.
Cobalt	Goitrogenic, lung effects disputed. Dermatitis. No injury from Co ₂ (CO) ₈ . Affects heart and GI tract. ~7 mg/day. beneficial. Liver and kidney damage.	Normal ingestion 0.002 mg/day; toxic level 500 mg/day. Co metal dust more toxic than salts in lung irritation; lethal dose of either relatively high. LD Co ₂ (CO) ₈ in animals by inhalation 100 ppm.

Table 3 cont.

Element 1	Human Effects 2	Toxicity Data 3
Copper	Antagonistic to Zn toxicity. Not cumulative. Require 1-2 mg/day. Inhalation of Cu-contg. dust causes lung and GI disturbances. Affects erythrocytes and liver. Skin and mucous membrane irritants.	Normal ingestion 2-5 mg/day; 65-130 mg CuSO ₄ dangerous and 648-972 mg highly toxic. 27 g CuSO ₄ fatal.
Lead	Brain damage, convulsions, behavioral disorders, death	Oral toxicity of Pb naphthenate 3.5-5.1 g/kg. Normal Pb ingestion 0.4 mg/day.
Manganese	Chronic Mn poisoning and/or Mn pneumonitis. Reduces Fe absorption. Requirement 3-9 mg/day. Primarily a nerve toxin. CNS symptoms often result in permanent disability.	Represents data not available.
Molybdenum	No indication of even an industrial hazard. Not cumulative.	Ingestion of <500 mg/day MoS ₂ nontoxic to animals. 8.1 mg MoS ₂ /ft ³ nontoxic to guinea pigs. MoO ₃ at 5.8 mg/ft ³ very irritating with high mortality. MoO ₃ dust more toxic than fume.

Table 3 cont.:

Element 1	Human Effects 2	Toxicity Data 3
Nickel	Rarely gives systematic toxic effects even from therapeutic doses (65-195 mg NiSO ₄ and 324-454 mg NiBr ₂). Dermatitis, respiratory disorder, carcinogenesis (nose and lung).	Normal ingestion 0.3-0.5 mg/day. 30-73 mg NiSO ₄ · 6H ₂ O toxic in humans. ²
Selenium	May cause caries. Prevents teratogenic effects of Cd and As. Affects kidneys, liver, marrow, and CNS. Se compounds are potent skin and mucous membrane irritants.	Industrial selenosis symptoms when Se in air <0.2 ppm. Liver damage in humans from 5-7 mg/liger in food. Liver cancer in animals from food containing 10 ppm Se. H ₂ Se and SeO ₂ more toxic than S analogs. LD by inhalation of SeO ₂ 10 ppm for 2 hrs. ² Normal ingestion 0.2 mg/day; toxic level 5 mg/day. Extreme tolerance limit in food (dry weight) 20 ppm.

Table 3 cont.:

Element 1	Human Effects 2	Toxicity Data 3
Vanadium	Cardiovascular disease, carcinogenesis. Main toxic effects on respiratory system. V_2O_5 residues from fuels irritating to those who clean oil-fired burners, renew fire-brick linings, and clean heat-exchanger tubs (dusts contain 6-20% V).	10 mg/kg fatal to rat. Sublethal doses 92-368 ppm. 49 $\mu\text{g/ml}$ drinking water highly toxic. 0.205 mg/liter causes lung changes in animals. LD (IV) in humans 30 mg V_2O_5 as tetra-vanadate.
Zinc	Dermatitis, hypertension, arteriosclerotic and heart diseases. 675-2.280 mg/liter is emetic. Causes mineral loss from bones. Most Zn compounds not particularly toxic at moderate concentrations orally. Zn inhibits the teratogenic, embryocidal, and neo-plastic effects of Cd. Essential.	LD50 (oral) Zn dithiophosphates 2.13-3.7 g/kg. LD50 (skin) 11.3 g/kg for rabbits (24-hr contact). Mixed Mg-Zn phenolate LD50 (oral) 9.5 mg/kg. LD50 (oral) $ZnCl_2$ in guinea pigs, rats, and mice 200-350 mg/kg. Normal ingestion Zn 10-15 mg/day.

Notes: LD50 = the dose at which 50 per cent of the best animals die.

CNS = central nervous system

Table 4 presents average concentrations of trace metals in residual oils, estimated on the basis of literature data (10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20).

Table 4: Metal content in residual oils.

Element	Concentration range, ppm	Average concentration, ppm	Element	Concentration range, ppm	Average concentration, ppm
As	0.17-1.28	0.80	Mo	0.23-1.55	0.95
Cd	1.59-2.27	1.93	Ni	12.50-86.13	42.20
Co	0.26-12.68	2.11	Pb	2.49-4.55	3.52
Cr	0.26-2.76	1.33	Se	0.40-1.98	0.75
Cu	0.28-13.42	2.82	V	7.23-540.00	160.00

Average concentrations were calculated by EPA (19). Concentration range is wide due to variation in imported crude oils and the common refinery practice of blending the bottoms from different crudes into one final residual oil.

4.3 Trace metal behaviour during fuel combustion

Of the more abundant trace metal compounds formed, only the amounts of silicon dioxide and vanadium pentoxide emitted remain constant for combustion temperatures in the range from 500^oK to 1800^oK. Nickel comes out predominately as the oxide at 1800^oK, but mostly as sulphate at lower temperatures. Other metals form sulfates. When the SO₂ concentration increases at higher temperatures, there are less metal sulfates; at lower temperatures there are more metal sulfates and less SO₂.

5 EMISSION OF TRACE METALS FROM OIL-FIRED PLANTS

The particulate loading of stack gases depends primarily upon the efficiency of combustion and the build-up of boiler deposits. Poor mixing, low flame temperatures, and short residence time in the combustion zone, result in larger particles with a higher content of combustibles and higher particulate loadings (21). Low-pressure atomization in the burner produces larger fly ash particles and a higher particulate loading. High-pressure atomization produces smaller particles, fewer cenospheres, and

lower particulate loadings (21). The size distributions of the emitted particles which are mostly cenospheres and ash residues, vary greatly. By way of example, particle size data (22) from five different oil-fired sources gave a mass mean diameter of about 15 μm . However, results vary widely, partly because of different sampling and analyses techniques. For instance, Barrett and Putman (23) report mass mean diameters for different fuels and equipment varying from 0.36 μm to 5.2 μm with up to 20 wt per cent smaller than 0.1 μm , whereas Goldfarb (24) finds volume median diameters varying from 22 μm to 119 μm .

On the other hand, under the same combustion conditions the weight of particulates emitted from heavy fuels is roughly proportional to their asphalt and ash content. The asphalt content plays a major part in determining the level of large (>10 μm) and intermediate (1-10 μm) size particulate emissions; the fuel ash content plays an important part in determining the level of submicron particulates. Most low-S fuels are low in their content of ash and asphalt. Consequently, the use of low-S fuel oil reduces particulate emissions in all size ranges. This is also the basis of the empirical relationship between the particulate emission and sulphur content derived by EPA (25):

$$e_p = 1.25 \times S + 0.38 \quad (2)$$

where: e_p = the particulate emission factor, kg of dust/
10³ liters

S = the percentage by weight of sulphur in the crude oil

The sulphur content in crude oils from major production areas is shown in Table 5 (26,27,28).

Table 5: Sulphur contents in the oil.

Region	Sulphur content, %		
	max.	Average	min.
Middle East	4.6	1.6	1.3
Africa	0.5	0.2	0.1
Latin America	2.4	1.4	0.2
Western Europe	1.0	0.3	0.2
Other	0.1	0.1	0.1

Using the particulate emission factor of equation (2), the daily dust emission can be estimated from the oil consumption when the sulphur concentration of the oil is known. If the concentration of trace metals in dust from the oil fired is known, the trace metal emission can be determined. Calculation for oil-fuel, contained 1 per cent of sulphur were made using equation:

$$E = \text{DFOR} \times e_p \cdot C \quad (3)$$

where: E = the trace metal emissions, mg of trace metal/day
DFOR = daily fuel oil requirements, liters/day
 e_p = the particulate emission factor, kg of dust/
 10^3 liters
C = trace metal content in dust emitted, mg of trace metal/kg of dust.

The trace metal content in dust emitted from oil-fired power plants varies. Table 6 presents mean concentrations of trace metals in dust emitted from European oil-fired power plants.

Table 6: Trace elements in dust from European oil-fired power plants.

Element	Concentration range, ppm	Average concentration, ppm	Element	Concentration range, ppm	Average concentration, ppm
As	120-480	330	Mo	200-400	380
Cd	75-190	158	Ni	12,200-20,000	13,800
Co	1250-2000	1750	Pb	700-1,800	1,700
Cr	20-840	585	Se	100-320	250
Cu	1100-2600	2350	V	1,000-70,000	50,000
Mn	200-600	550	Zn	350-2,000	1,200

The average concentrations of trace metals in dust listed in Table 6 were calculated on the basis of measurements of trace elements in dust emitted from oil power plants in some European countries (15,29,30) and figures of crude oil import from different areas to Europe (31) together with distillate yields and trace element concentrations in crude oils (Tables 2 and 2a).

Using data from Tables 1 and 6, the trace metal emissions can be estimated. Table 7 present data on trace metal emissions from a 100 MWe power plant, burning oil, with 1 per cent of sulphur.

Table 7: Trace metal emission from a 100 MWe power plant (g/day).

Element	Emission	Element	Emission
As	210.9	Mo	242.8
Cd	110.9	Ni	8817.6
Co	1118.2	Pb	1086.2
Cr	373.8	Se	159.7
Cu	1501.6	V	31948.0
Mn	351.4	Zn	766.7

For larger plants (i.e., 350, 700 or 2100 MWe) and different sulphur (ash) contents similar results can be estimated using data from Table 1 and equation (2).

On the basis of results as shown in Table 7, average emission factors of trace metals have been calculated dividing the trace metal emission from a 100 MWe power plant by the daily energy production in this plant being $8.64 \cdot 10^6$ MJ. Table 8 presents the trace metal emission factors for power plant burning oil with 1 per cent of sulphur. For different sulphur contents similar results can be estimated using equation (2).

Table 8: Emission factors of trace metals ($\mu\text{g}/\text{MJ}$).

Element	Emission factor	Element	Emission factor
As	24.4	Mo	28.1
Cd	11.6	Ni	1020.6
Co	129.4	Pb	125.7
Cr	43.3	Se	18.5
Cu	173.8	V	3697.7
Mn	40.7	Zn	88.7

6 CONCLUDING REMARKS

The emission factors, calculated in this work allow us to assess the trace metal emissions from oil-fired power plants. National emissions and their spatial distribution in European countries will be calculated.

The emission factors obtained will be used together with available statistical data to estimate an emission field for trace metals in the same grid as the EMEP emission survey.

This field will be used to assess the contamination of Arctic areas by sub-micron particles from mid-European power plants.

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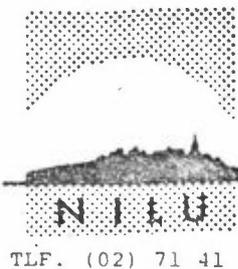
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TITLE Estimation of emission factors of trace metals from oil-fired power plants.		
ABSTRACT (max. 300 characters, 5-10 lines) The emission factors of trace metals from oil-fired power plants are estimated for different operating conditions using data for the same trace metal concentrations in the fuel. Fuel oil requirements and behaviour of trace metals during oil combustion are discussed. The emission factors obtained, will be used to calculate national emissions and their spatial distribution in European countries.		

**Kategorier: Åpen - kan bestilles fra NILU A
 Må bestilles gjennom oppdragsgiver B
 Kan ikke utleveres C