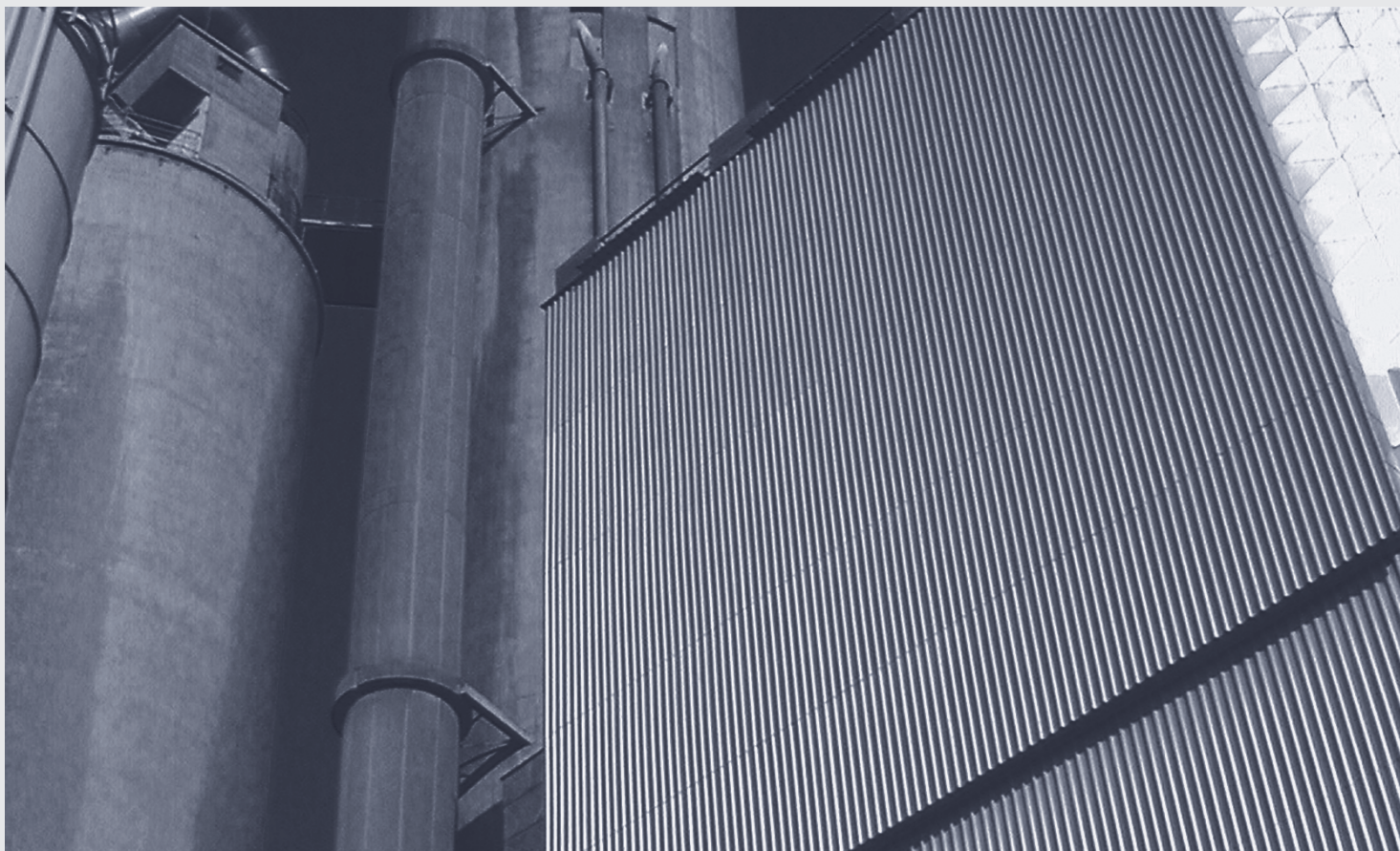


Environmental Data of the German Cement Industry 2007

2007



Verein Deutscher Zementwerke e.V.
Forschungsinstitut der Zementindustrie



Contents

Contents	2
Foreword	3
1 Cement manufacture	4
2 Production and structural data	6
3 Input materials	8
3.1 Raw materials	8
3.2 Fuels	10
4 Energy	12
5 Emissions	14
5.1 Greenhouse gases / carbon dioxide	17
5.2 Dust	18
5.3 Nitrogen oxides	19
5.4 Sulphur dioxide	21
5.5 Carbon monoxide and total organic carbon	22
5.6 Dioxins und Furans	24
5.7 Polychlorinated biphenyls	25
5.8 Polycyclic aromatic hydrocarbons	26
5.9 Benzene, toluene, ethylbenzene, xylene	27
5.10 Benzene	28
5.11 Gaseous inorganic chlorine compounds	29
5.12 Gaseous inorganic fluorine compounds	30
5.13 Trace elements	31
Literature	50
Additional literature	50
Imprint	51

In September 2000 the German Cement Works Association presented the “Environmental Data of the German Cement Industry” for the first time.

The present ninth edition updates the data and continues the report. Extent and contents remain largely unchanged. Again all clinker producing works in Germany took part in the survey on which these figures are based. As a consequence, a complete documentation of both the results of continuous emission monitoring and of individual measurements of trace elements and organic exhaust gas constituents can be presented for the year 2007.

Düsseldorf, in September 2008

Verein Deutscher Zementwerke e. V.

1 Cement manufacture

Cement is a construction material that sets automatically as a consequence of chemical reactions with water and subsequently retains its strength and soundness both when exposed to air and submerged in water.

Cement consists of finely ground Portland cement clinker and calcium sulphate (natural gypsum, anhydrite or gypsum from flue gas desulphurisation). In addition, cement may contain other main constituents, such as granulated blast furnace slag, natural pozzolana (e.g. trass), fly ash, burnt oil shale or limestone. Fig. 1-1 depicts the manufacturing process schematically.

What is known as Portland cement clinker is made from a raw material mix mainly consisting of calcium oxide (CaO), silicon dioxide (SiO₂), aluminium oxide (alumina (Al₂O₃)), and iron oxide (Fe₂O₃). These chemical constituents are supplied by limestone, chalk and clay or their natural blend, lime marl. Limestone and chalk are composed of calcium carbonate (CaCO₃). The major constituents of clay, which is a natural product of weathering processes, are fine-grained mica-like minerals and smaller quantities of quartz and feldspar, which constitute residues of the starting material. Clay minerals and feldspar are compounds of aluminium oxide and silicon dioxide (aluminosilicates) with alkalis, such as sodium and potassium. The iron oxide required for melt formation is either contained in the clay minerals in the form of ferrous hydroxide or it is added in the form of iron ore. For the cement to conform to the quality requirements stipulated, a precisely defined raw material composition must be complied with. Only a small margin of deviation can be tolerated.

The raw material mix is heated up to a temperature of approximately 1,450 °C in a rotary kiln until it starts sintering. This results in the starting materials forming new compounds known as clinker phases.

These are certain calcium silicates and calcium aluminates which confer on the cement its characteristic features of setting in the presence of water.

The clinker burnt in the rotary kiln is subsequently ground to cement in finish mills with calcium sulphate and, if necessary, with further main constituents being added. The calcium sulphate serves to adjust the setting behaviour of the cement in order to obtain optimum workability of the product during concrete production.

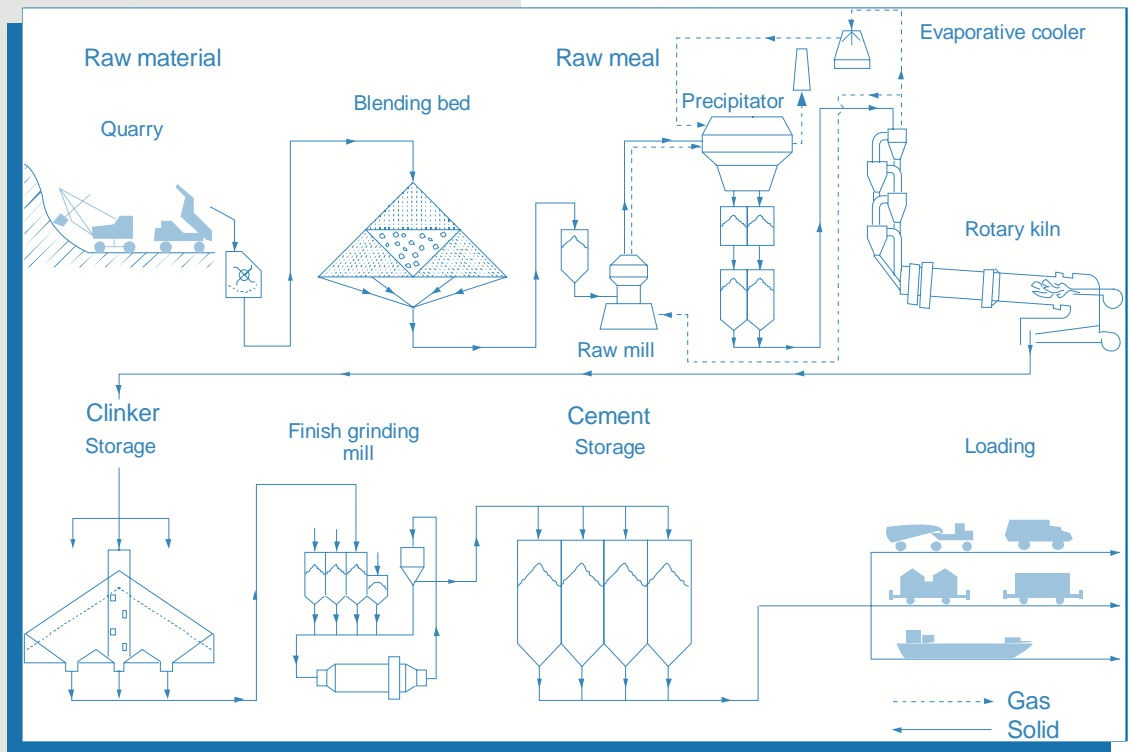


Fig. 1-1: Schematic presentation of the cement manufacturing process from quarry to dispatch

Apart from cement clinker, substances of silicate, aluminate or calcareous nature represent the further main constituents. They contribute to the setting of the cement or have favourable effects on the physical properties of the concrete.

2 Production and structural data

Cement is a homogeneous bulk commodity that, given the high cost of transport, is almost exclusively delivered to local markets. Production facilities of the German cement industry are spread evenly all over the Federal Republic of Germany and located in the immediate vicinity of the respective limestone deposits. In 2007, 22

companies with their 56 works produced about 33.4 million t of cement in Germany (Fig. 2-1).

Tables 2-1 and 2-2 give an overview of the clinker output in Germany and the cement made from it. The ready-mixed concrete industry (53% of cement output) and the manufacturers of concrete elements (25% of cement output) are among the principal buyers of cement. 8% of the cement is dispatched as bagged cement.

In Germany most of the cement clinker is nowadays produced in rotary kilns with cyclone preheaters applying the dry process. Kilns equipped with grate preheaters account for a significantly lower share of output (Table 2-3).



Fig. 2-1: Cement works in the Federal Republic of Germany in the year 2007

	Unit	2005	2006	2007
Clinker output	1,000 t	24.379	24.921	26.992
Cement sales (incl, clinker export)	1,000 t	32.364	34.714	34.076
of which: domestic sales	1,000 t	25.615	27.428	26.064
export incl, clinker	1,000 t	6.749	7.286	8.012
Cement import	1,000 t	1.427	1.492	1.144

Table 2-1: Output, sales and import [1, 2]

Cement type	Group	Unit	2005	2006	2007
Portland cement	CEM I	1,000 t	13.226	11.189	8.932
Portland-slag cement	CEM II	1,000 t	3.701	5.170	5.229
Portland-pozzolana cement		1,000 t	34	32	30
Portland-fly ash cement		1,000 t	5	0	0
Portland-burnt shale cement		1,000 t			
Portland-limestone cement		1,000 t	3.878	3.946	3.837
Portland-composite cement		1,000 t	437	1.480	2.203
Blastfurnace cement	CEM III	1,000 t	3.621	4.764	4.883
Other cements		1,000 t	193	263	308
Total		1,000 t	25.095	26.843	25.422

Table 2.2: Domestic sales classified by cement types [1]

	As at: 01. Jan 2006			As at: 01. Jan 2007			As at: 01. Jan 2008		
	Number	Capacity t/d	%	Number	Capacity t/d	%	Number	Capacity t/d	%
Kilns with cyclone preheaters	42	103,650	91.0	41	100,550	90.8	41	101,000	92.1
Kilns with grate preheaters	11	8,970	7.9	11	8,970	8.1	9	7,500	6.8
Shaft kilns	8	1,200	1.1	8	1,200	1.1	8	1,200	1.1
Total	61	113,820	100	60	110,720	100	58	109,700	100
Average kiln capacity in t/d									
Rotary kilns		2,124			2,106			2,170	
Shaft kilns		150			150			150	

Table 2-3: Number and capacity of kilns with operating permits in the Federal Republic of Germany in the years from 2005 to 2007 [2].

3 Input materials

3.1 Raw materials

Limestone or chalk and clay or their natural blend – lime marl – constitute the most important raw materials for the production of Portland cement clinker. Depending on the raw material situation at the location of a cement works, it

Group	Raw material	Input quantity 1,000 t/a
Ca	Limestone / marl / chalk	40,207
	Others, such as: - lime sludge from drinking water and sewage treatment - hydrated lime - foam concrete granulates - calcium fluoride	118
Si	Sand	1,399
	Used foundry sand	164
Si-Al	Clay	1,114
	Bentonite / kaolinite	48
	Residues from coal pre-treatment	
Fe	Iron ore	158
	Other input materials from the iron and steel industries, such as: - roasted pyrite - contaminated ore - iron oxide/fly ash blends - dusts from steel plants - mill scale	128
	Granulated blastfurnace slag	6,602
	Fly ash	387
	Oil shale	233
Si-Al-Ca	Trass	28
	Others, such as: - paper residuals - ashes from incineration processes - mineral residuals, e. g. soil contaminated by oil	91
	Natural gypsum	625
	Natural anhydrite	547
	Gypsum from flue gas desulpherisation	389
S	Input materials from the metal industry, such as: - residues from reprocessing salt slag - aluminium hydroxide	62

may be necessary to add pure limestone, iron ore, sand or other corrective substances to the raw material mix in order to compensate for the lack of certain chemical constituents.

Apart from natural raw materials, also alternative raw materials can be utilised, such as lime sludge, used foundry sand and fly ash. They contain silicon dioxide, aluminium oxide, iron oxide and/or calcium oxide as main constituents as well and are combined with the raw materials in quantities apt to ensure compliance with the clinker composition specified. The preconditions to be met by the material composition of an alternative raw material primarily depend on the raw material situation prevailing at a cement works, i.e. the composition of the limestone and marl deposits, respectively.

Table 3-1 lists the raw materials utilised in the year 2007. They can be classified into different groups, according to their chemical composition. Most of them are utilised as raw material components in the clinker burning process. Blastfurnace slag, a small proportion of the limestone, oil shale (burnt) and trass are used as main constituents of cement.

Table 3-1: Raw materials input in 2007 [3]

The cement industry is making efforts to increase the share in the cement of constituents other than clinker. This allows to modify the quality of the product purposefully, to improve the economic efficiency of the manufacturing process, to conserve natural resources, and to utilise materials generated by other processes in a useful manner, as stipulated by the German Waste Management and Recycling Act.

The materials, having industrial importance as potential substitutes for cement clinker in the cement in Germany, are chiefly (granulated) blastfurnace slag and also limestone. Blastfurnace slag is a spin-off of pig iron production and is used in the manufacture of Portland-slag and blastfurnace cements.

Natural gypsum and/or anhydrite cover about 70% of the demand for sulphate agents, which serve to adjust the working properties of the cements. Gypsum from flue gas desulphurisation accounts for the remaining share.

3.2 Fuels

Cement clinker burning uses up most of the fuel energy consumed in cement manufacture. To a lesser extent thermal energy is also used for drying raw materials and other major cement constituents, such as granulated blastfurnace slag. Since the mid-70ies, the traditional fuels of the cement industry have been coal and lignite and, on a smaller scale, also heavy fuel oil. A significant portion of coal has been replaced by petcoke since the 90ies. Petcoke is a coal-like fraction of mineral oil generated in crude oil processing. In addition to that, light and heavy fuel oil and gas are used for kiln start-up and drying processes. Table 3-2 lists all the energy sources exploited in the German cement industry.

Fuel	2005 million GJ/a	2006 million GJ/a	2007 million GJ/a
Coal	8.7	11.4	13.9
Lignite	29.1	27.6	25.1
Petcoke	4.2	4.3	5.6
Heavy fuel oil	2.2	1.9	2.1
Fuel oil EL	0.2	0.2	0.2
Natural gas and other gases	0.5	0.3	0.1
Other fossil fuels	0.5	0.3	0.3
Total fossil fuels	45.4	46.0	47.3
Total alternative fuels	43.3	46.1	52.2
Total thermal energy consumption	88.7	92.1	99.5

Table 3-2: Fuel energy consumption classified by energy sources [2]

Apart from fossil fuels, the use of alternative fuels in the clinker burning process is gaining in importance nowadays. Alternative fuels accounted for about 50% of the total fuel energy consumption of the German cement industry in 2007. Table 3-3 lists the alternative fuels utilised and their average calorific values.

Alternative fuel	1,000 t/a	MJ/kg
Tyres	289	26
Waste oil	85	26
Fractions of industrial and commercial waste:	-	-
- Pulp, paper and cardboard	236	7
- Plastics	452	23
- Packaging	0	0
- Wastes from the textile industries	0	0
- Others	907	20
Meat and bone meal and animal fat	293	18
Mixed fractions of municipal waste	186	15
Scrap wood	13	13
Solvents	100	23
Fuller earth	0	0
Sewage sludge	254	4
Others, such as:	90	7
- oil mud		
- organic distillation residues		

Table 3-3: Consumption and average calorific value of alternative fuels in 2007 [3]

4 Energy

The production of one tonne of cement consumed an average of 2,915 MJ fuel energy and 99.7 kWh electrical energy in 2007 (Tables 4-1 and 4-2). Fuel energy is primarily required for clinker burning, while electrical energy is chiefly used for raw material pre-treatment (about 35%), for burning and cooling the clinker (about 22%) and for cement grinding (about 38%).

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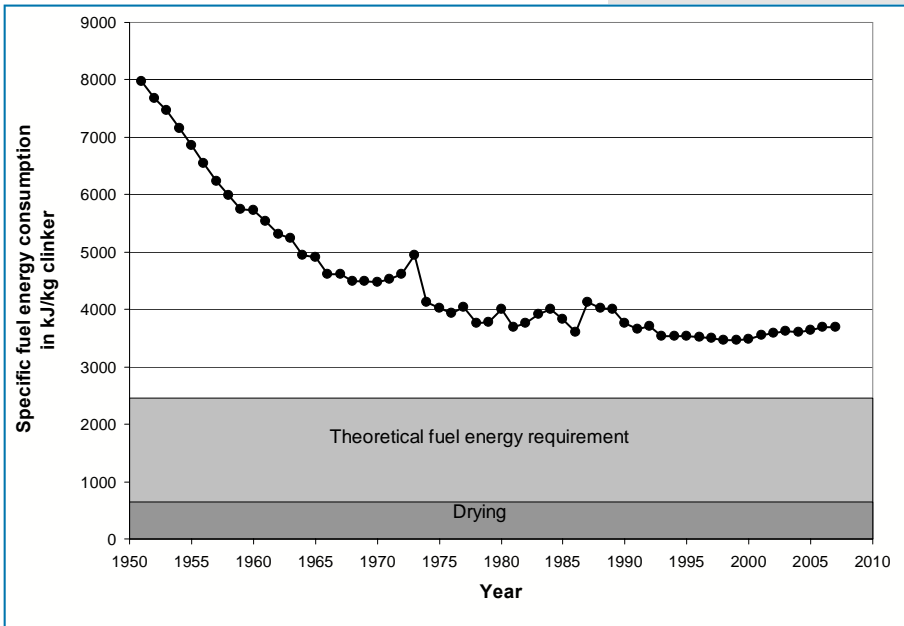


Fig. 4-1: Development of the specific fuel energy consumption (New Federal States included since 1987) [2]. Note: Fuel energy is relative to clinker in this chart.

Specific thermal energy consumption in the cement industry has declined significantly over the past 50 years. This is mainly attributable to improvements in plant and process technology. After 1990, the modernisation of the cement works in the New Federal States was one of the factors contributing to a further decrease in specific fuel energy consumption.

Since some years the clinker specific fuel energy consumption is stabilized at 3,500 to 3,700 kJ/kg clinker. Taking the utilization of the heat in the kiln exhaust gases for the drying processes (raw material, pulverized coal, blastfurnace slag) into account the overall efficiency of rotary kiln plants is more than 70%. This demonstrates the high level of energy efficiency of the clinker burning process [4].

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Year	Fuel energy consumption	
	absolute in million GJ/a	specific in kJ/kg cement
2005	88,7	2785
2006	92,1	2674
2007	99,5	2915

Table 4-1: Absolute and specific fuel energy consumption [2]

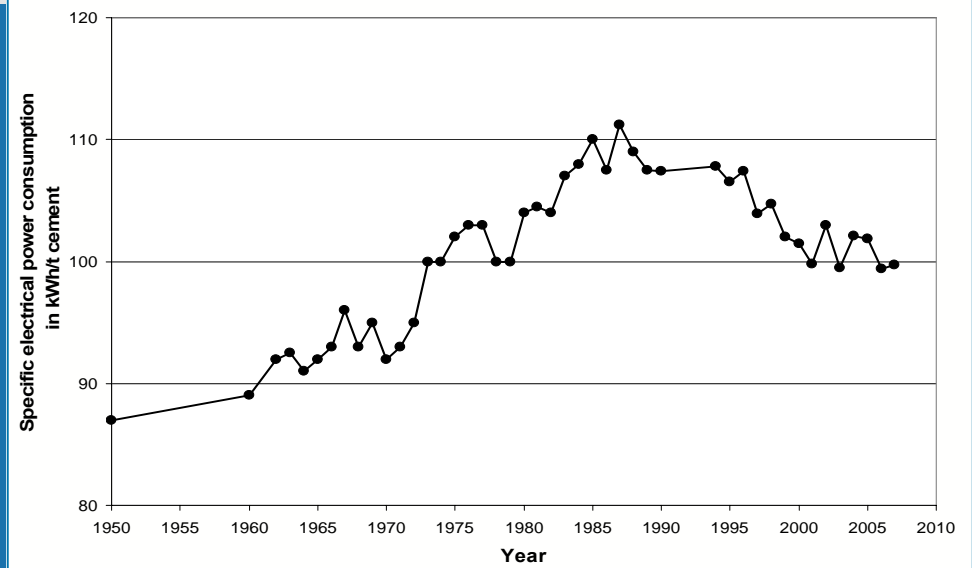


Fig. 4-2: Development of the specific electrical power consumption (New Federal States included since 1987) [2]

More demanding specifications for product quality and measures aimed at improving environmental protection were the major causes for the upward tendency in electrical power consumption over the past decades (Fig. 4-2). Among other things, improvements in grinding technique have contributed to a stabilisation of the specific electrical energy consumption most recently.

Year	Electrical power consumption	
	absolute in million MWh/a	specific in kWh/t cement
2005	3,24	101,9
2006	3,42	99,4
2007	3,40	99,7

Table 4-2: Absolute and specific electrical power consumption [2]

5 Emissions

The erection and operation of cement works are subject to the provisions of the Federal Ambient Pollution Protection Act. Depending on the type of fuel utilised, different

Object of measurement	Standard, guideline
Total dust	DIN EN 13284-1
Heavy metals - Sampling - Analysis	DIN EN 13211, 14385 VDI 3868, Sheet 1 VDI 2268, Sheets 1 - 4
Sulphur dioxides	DIN EN 14791
Nitrogene oxides	VDI 2456
Carbon monoxide	DIN EN 15058
Gaseous inorganic chlorine compounds	DIN EN 1911, Parts 1 - 3
Gaseous inorganic fluorine compounds	VDI 2470, Sheet 1
Dioxins, furans - Sampling - Analysis	DIN EN 1948, Part 1 DIN EN 1948, Parts 2 - 3
Polycyclic aromatic hydrocarbons - Sampling - Analysis	DIN EN 1948, Part 1 VDI 3873, Sheet 1
Organically bound carbon	DIN EN 12619,13526
Benzene, toluene, ethylbenzene, xylene	DIN EN 13649

Table 5-1: Emission measuring methods

specifications for the emission concentrations to be complied with are laid down. If standard fuels are used exclusively, the regulations of the Clean Air Act (TA Luft) are decisive. If a proportion of the standard fuels is replaced by waste used as alternative fuels, the provisions of the German regulation on waste incineration (17th BImSchV) apply additionally. Proceeding from this legal basis, the competent authorities can

order both measurements for special reasons and first-time and recurrent measurements to be carried out by accredited measuring bodies only.

Emissions from cement works can be determined both by continuous and discontinuous measuring methods, which are described in corresponding VDI guidelines and DIN standards (Table 5-1). Continuous measurement is primarily used for dust, NO_x and SO₂, while the remaining parameters relevant pursuant to ambient pollution legislation are usually determined discontinuously by individual measurements.

The measurement results [3] presented in this chapter are based on the emission measurements at the rotary kiln plants of the German cement industry required by law. The emissions measured continuously (dust, NO_x, SO₂) were converted to annual averages. In the case of emissions measured discontinuously, the values are derived from the respective individual measurements. All measured values relate to 1 m³ of dry gas under standard conditions with an oxygen content of 10%.

In some of the Figures the ranges for detection limits are marked in grey to facilitate assessment. Detection limits depend on sampling, sample preparation and analysis methods and are thus not identical for all measurements. The ranges indicated in the charts were determined, among other things, applying the performance characteristics given in the pertinent technical standards. Although significantly lower detection limits are cited in measurement reports in some cases, these generally refer to the analytical part of the measuring method only.

In the last few years, the European Union has increasingly set the course in environmental policy. For example, Commission decision 2000/479/EC instituting an European Pollutant Emission Register (EPER) came into force on July 28, 2001. It is to comprise the emission data on 37 air pollutants and 26 water pollutants emitted by about 20,000 industrial plants in the European Union. The data will be compiled specifically for each plant and published on the internet regularly, with the plant name being quoted. This compilation also covers all European cement plants having an output of more than 500 t clinker per day. The first reports by member states on the reference year 2001 had to be submitted to the Commission by June 2003. In Germany, these reports have been established on the basis of the emission declarations filed for 2000. In 2007 the EPER system was substituted by the even more complex PRTR system (PRTR: Pollutant Release and Transfer Register).

Pollutant	Threshold value kg/year
Carbon monoxide (CO)	500,000
Carbon dioxide (CO ₂)	100,000,000
Non-methane volatile organic compounds (NMVOC)	100,000
Nitrogen oxides (NO _x)	100,000
Sulphur dioxide (SO ₂)	150,000
Arsenic	20
Cadmium	10
Chromium	100
Copper	100
Mercury	10
Nickel	50
Lead	200
Zinc	200
Dioxins and furans (PCDD/F)	0.001
Benzene	1,000
Polycyclic aromatic hydrocarbons (PAH)	50
Chlorine and inorganic chlorine compounds (HCl)	10,000
Fluorine and inorganic fluorine compounds (HF)	5,000
Fine dust (PM ₁₀)	50,000

Table 5-2: Threshold values for mandatory reporting on 19 of the 37 air pollutants covered by the European Pollutant Emission Register (sector-specific list for the industrial plants of the cement industry [5])

The figures supplied for the register refer to quantities emitted, i.e. the quantity of a certain substance that an industrial plant emits annually (kg/year). In order to record significant sources only, emissions below certain threshold values need not be indicated. Accordingly, the emissions of only 19 of the 37 air pollutants are considered relevant in the case of cement works (Table 5-2).

In the following, the concentration of a pollutant in the clean gas of rotary kiln systems is supplemented by the associated emission quantity, which is presented in an additional Figure. It is calculated on the basis of the clean

gas volume flow emitted per year (m³/year) and the pollutant concentration it contains (g/m³). If the pollutant is detectable in the clean gas, it is possible to supply definite figures, the accuracy of which can be described by the measuring uncertainty, for example. If, however, this is not the case (e.g. values not secured or measurements below the detection limit), only a theoretical upper limit for the emissions released can be indicated. It is calculated on the basis of the assumption that the pollutant concentration in the clean gas reaches the detection limit. The quantity actually emitted, however, is lower. In the Figures, the range of possible values is represented by a broken line.

Evaluation of the measurement results shows that emissions from rotary kiln plants in the cement industry undershoot the thresholds for mandatory reporting pursuant to EPER, in some cases even significantly so.

5.1 Greenhouse gases / carbon dioxide (CO₂)

During the clinker burning process climatically relevant gases are emitted. CO₂ accounts for the main share of these gases. Other climatically relevant gases, such as dinitrogen monoxide (N₂O) or methane (CH₄), are emitted in very small quantities only.

CO₂ emissions are both raw material-related and energy-related. Raw material-related emissions are produced during limestone decarbonation (CaCO₃) and account for about 60% of total CO₂ emissions. Energy-related emissions are generated both directly through fuel combustion and indirectly through the use of electrical power. Table 5-3 lists the proportions of CO₂ emissions accordingly.

In the year 1995, the German cement industry committed itself to make its contribution to global warming prevention and lower its specific fuel energy consumption by 20% between 1987 and 2005. This commitment has been updated into a negotiated agreement and, since November 9, 2000, has provided for a 28% reduction in energy-related

specific CO₂ emissions from 1990 to 2008/2012.

On January 1, 2005 a trading system for CO₂ emissions was introduced in the EU. Direct CO₂ emissions from the combustion of all fuels (without biogenous compounds) and decarbonation of limestone are part of this trading system. In contrast the negotiated agreement of the cement industry also contains emissions deriving from the electrical energy consumption. CO₂ emissions from the combustion of alternative fuels are not taken into account, because they substitute fossil fuels and thereby reduce CO₂ emissions elsewhere. Since the emissions trading scheme further on refers only to the clinker burning process, but the agreement to the whole cement production, different emission values occur in the corresponding reporting systems.

Specific CO ₂ emissions					
Year	Thermal energy-related ¹⁾	Electrical energy-related	Raw-material-related	Total	Unit
2005	0,132	0,068	0,406	0,606	t CO ₂ / t cement
2006	0,123	0,067	0,383	0,573	t CO ₂ / t cement
2007	0,128	0,067	0,419	0,614	t CO ₂ / t cement

Table 5-3: CO₂ emissions by the cement industry [2]
1) only regular fuels

5.2 Dust

To manufacture 1 t of Portland cement, about 1.5 to 1.7 t raw materials, 0.1 t coal and 1 t clinker (minus

other main constituents and sulphate agents) must be ground to dust fineness during production. In this process, the steps of raw material preparatory processing, fuel preparation, clinker burning and cement grinding constitute major emission sources for particulate components. While particulate emissions of up to 3,000 mg/m³ were measured at the stack of

cement rotary kiln plants as recently as in the 50ies, these can be limited to 20 mg/m³ today.

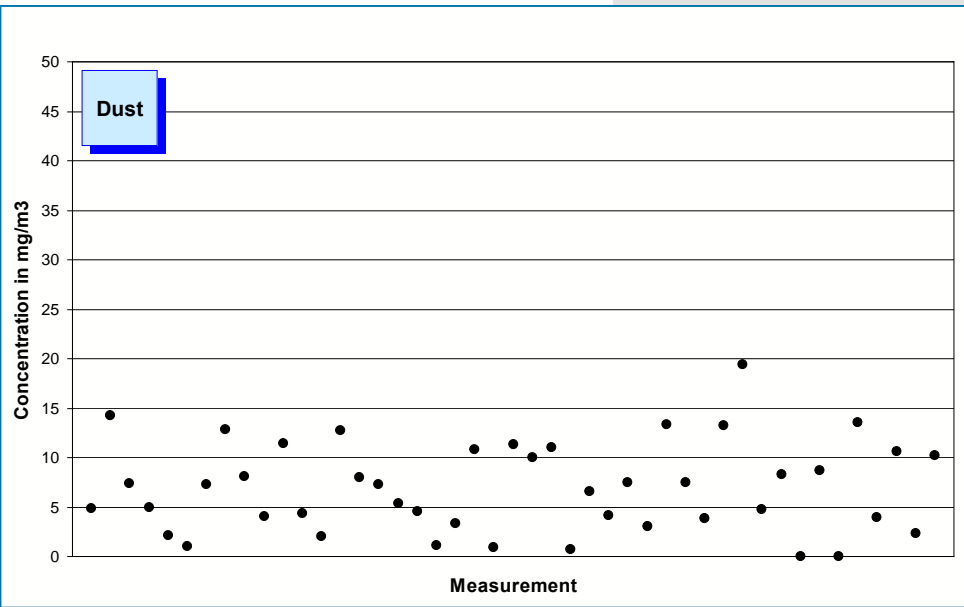


Fig. 5-1: Average (year 2007) dust concentrations in the clean gas of 45 rotary kilns

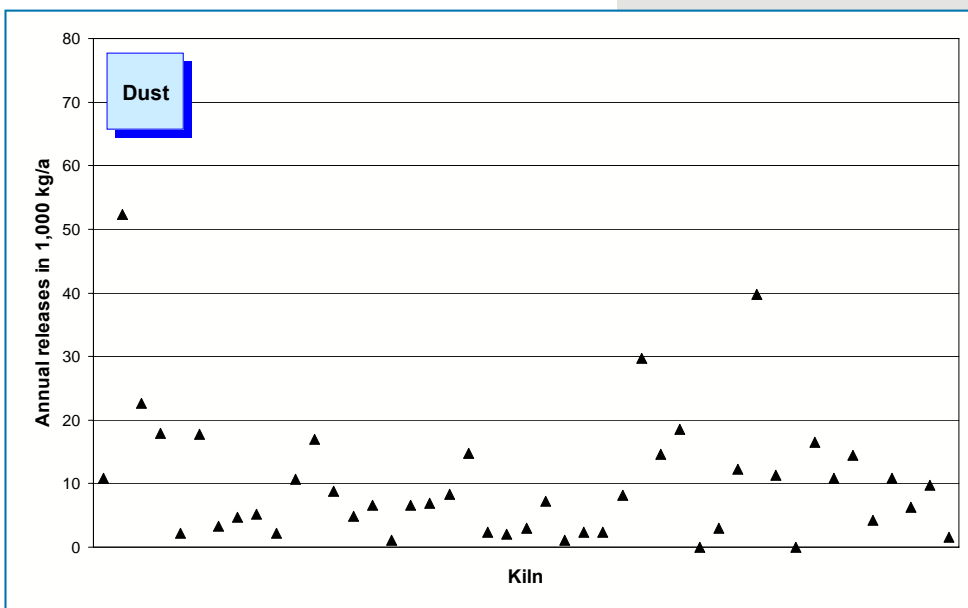


Fig. 5-2: Dust emissions (annual releases in 2007) of 45 rotary kilns

5.3 Nitrogen oxides (NO_x)

The clinker burning process is a high-temperature process resulting in the formation of nitrogen oxides (NO_x). Nitrogen monoxide (NO) accounts for about 95%, and nitrogen dioxide (NO₂) for about 5% of this compound present in the exhaust gas of rotary kiln plants. As most of the NO is converted to NO₂ in the atmosphere, emissions are given as NO₂ per m³ exhaust gas.

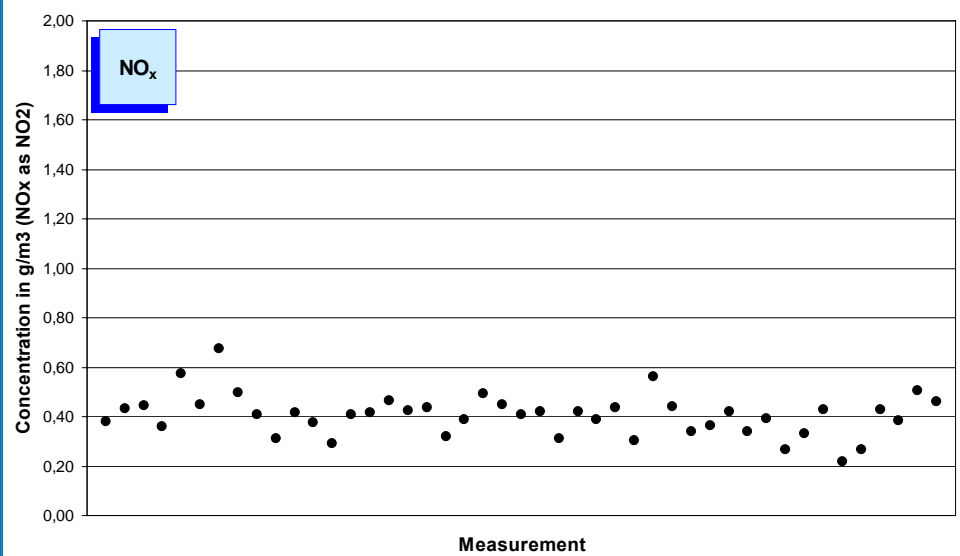


Fig. 5-3: Average NO_x concentrations (year 2007) in the clean gas of 45 rotary kilns. Note: In 2007, the emissions of several kilns exceeded the emission values for cement plants specified by the Clean Air Act now. The operating permits for these works are based on higher NO_x limits. Some of these plants have been or will be retrofitted with NO_x reduction devices.

Without reduction measures, process-related NO_x contents in the exhaust gas of rotary kiln plants would considerably exceed the current specifications of the Clean Air Act of 0.50 g/m³. Reduction measures are aimed at smoothing and optimising plant operation. Furthermore, considerable efforts were made to achieve compliance with the demanding NO_x values in different ways. In 2007, eight plants were equipped with staged combustion, and the SNCR technique was applied at about 35 plants.

High process temperatures are required to convert the raw material mix to Portland cement clinker. Kiln charge temperatures in the sintering zone of rotary kilns range at around 1,450 °C. To reach these flame temperatures of about 2,000 °C are necessary.

For reasons of clinker quality the burning process takes place under oxidising conditions under which the partial oxidation of the molecular nitrogen in the combustion air resulting in the formation of nitrogen monoxide dominates. This reaction is also called thermal NO formation.

At the lower temperatures prevailing in a secondary firing unit, however, thermal NO formation is negligible: here the nitrogen bound in the fuel can result in the formation of what is known as fuel-related NO.

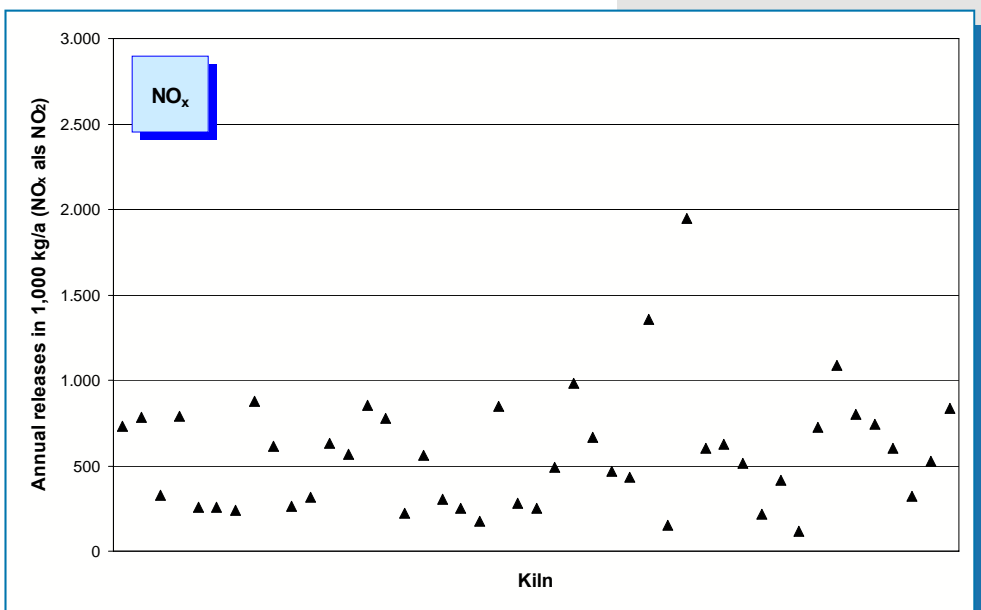


Fig. 5-4: NO_x emissions (annual releases in 2007) of 45 rotary kilns

5.4 Sulphur dioxide (SO₂)

Sulphur is fed into the clinker burning process via raw materials and fuels. Depending on their respective deposits, the raw materials may contain sulphur bound as sulphide or sulphate. Higher SO₂ emissions by rotary kiln systems of the cement industry might be attributable to the sulphides contained in the raw material, which become oxidised to form SO₂ at the temperatures between 370 °C and 420 °C prevailing during the kiln feed preheating process. Most of the sulphides are pyrite or marcasite contained in the raw materials.

Given the sulphide concentrations found in German raw material deposits, SO₂ emission concentrations can total up to 1.2 g/m³ depending on the site location. The cement industry has made great efforts to reduce SO₂ emissions. For example, lime hydrate is utilised at 15 kiln systems to lower SO₂ emissions. The sulphur input with the fuels is completely converted to SO₂ during combustion in the rotary kiln. In the area of the preheater and the kiln, this SO₂ reacts to form alkali sulphates, which are bound in the clinker.

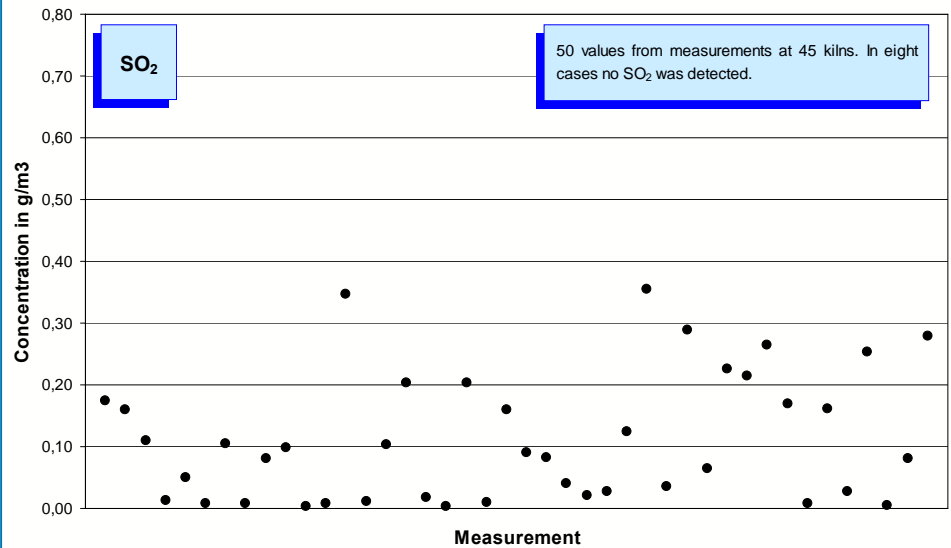


Fig. 5-5: Average SO₂ concentrations (year 2007) in the clean gas of 45 rotary kilns.

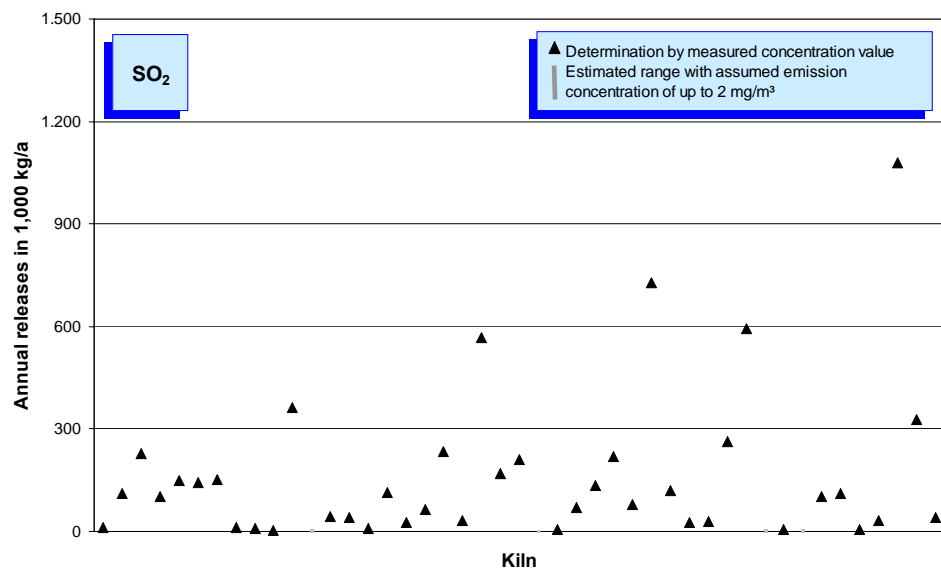


Fig. 5-6: SO₂ emissions (annual releases in 2007) of 45 rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 2 mg/m³.

5.5 Carbon monoxide (CO) and total carbon (ΣC)

The exhaust gas concentrations of CO and organically bound carbon are a yardstick for the burn-out rate of the fuels utilised in energy conversion plants, such as power stations.

By contrast, the clinker burning process is a material conversion process that must always be operated with excess air for reasons of clinker quality. In concert with long residence times in the high-temperature range, this leads to complete fuel burn-up.

The occurring emissions of carbon monoxide and total carbon do not result from combustion, but from

the thermal decomposition of organic compounds of the raw material in the preheater.

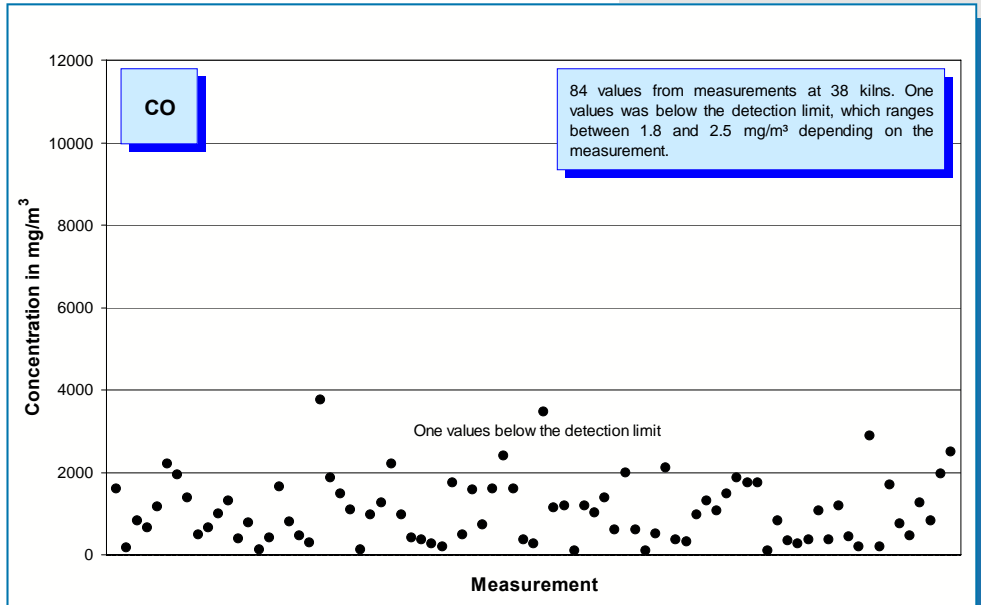


Fig. 5-7: CO concentration values (year 2007) measured in the clean gas of 38 rotary kilns.

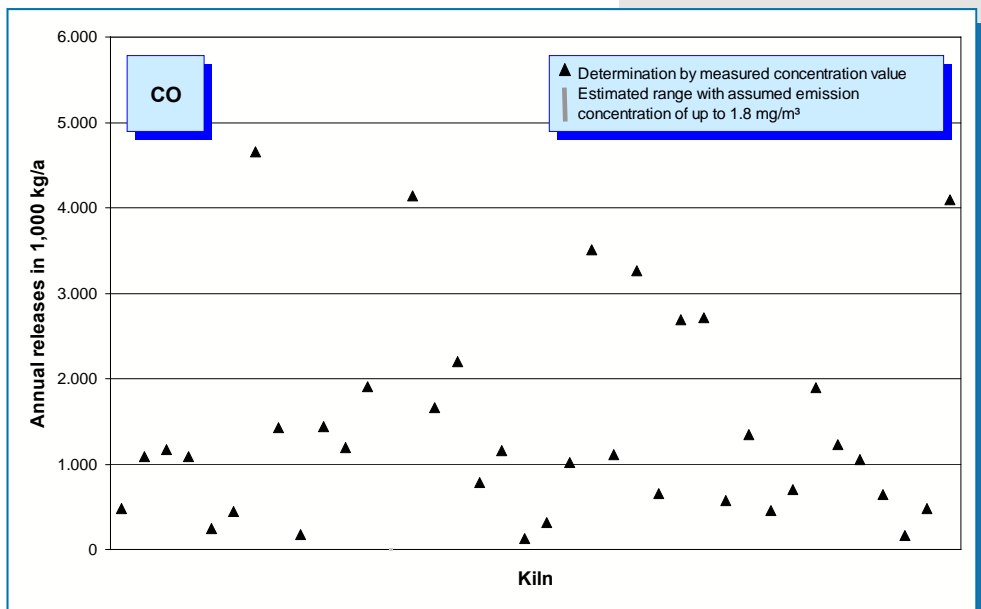


Fig. 5-8: CO emissions (annual releases in 2007) of 38 rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 1.8 mg/m³.

The emissions of CO and organically bound carbon during the clinker burning process are caused by the small quantities of organic constituents input via the natural raw materials (remnants of organisms and plants incorporated in the rock in the course of geological history). These are converted during kiln feed preheating and become oxidised to form CO and CO₂. In this process, small portions of organic trace gases (total organic carbon) are formed as well. In case of the clinker burning process, the content of CO and organic trace gases in the clean gas therefore does not permit any conclusions on combustion conditions.

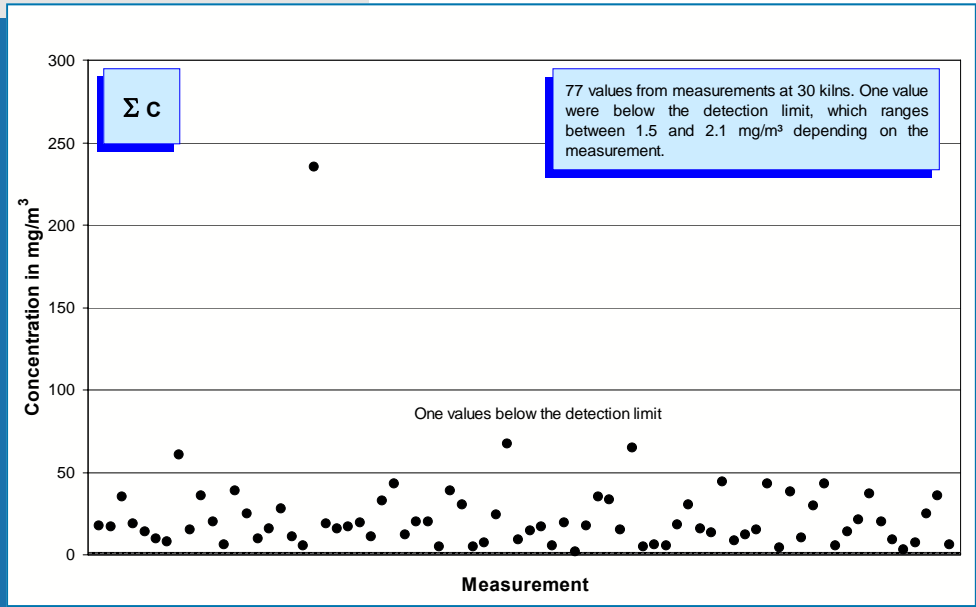


Fig. 5-9: Total organic carbon concentration values (year 2007) measured in the clean gas of 30 rotary kilns.

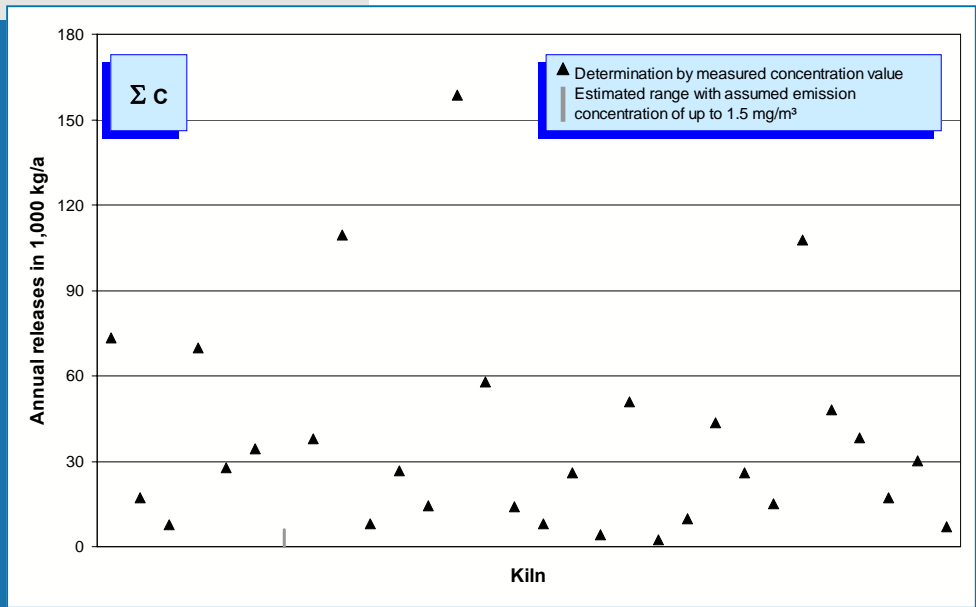


Fig. 5-10: Total organic carbon emissions (annual releases in 2007) of 30 rotary kilns. If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 1.5 mg/m³.

5.6 Dioxins and furans (PCDD/F)

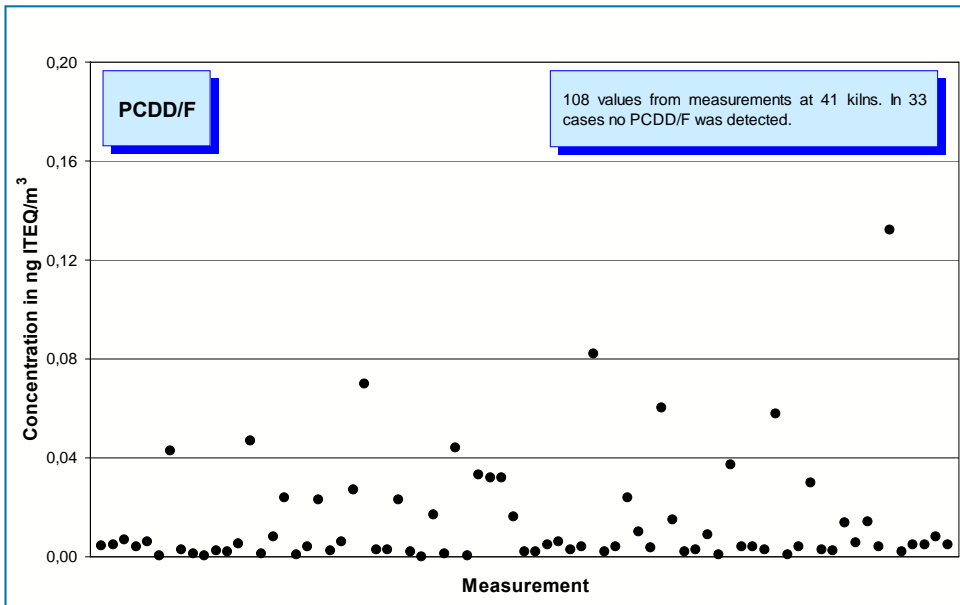


Fig. 5-11: Dioxin and furan (PCDD/F) concentration values (year 2007) measured in the clean gas of 41 rotary kilns. In 33 cases no PCDD/F was detected ¹⁾. Note: No detection limit can be deduced from the standard. To evaluate the measurement results, inter-laboratory variation of the method (comparison between different laboratories) can be referred to. Pursuant to DIN EN 1948 it amounts to ± 0.05 ng ITEQ/m³. (ITEQ: international toxicity equivalent)

for organic compounds, introduced either via fuels or derived from them, to be completely destroyed. For that reason, only very low concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans (in short: dioxins and furans) can be found in the exhaust gas from cement rotary kilns. Investigations have shown that their emissions are independent of the type of input materials used

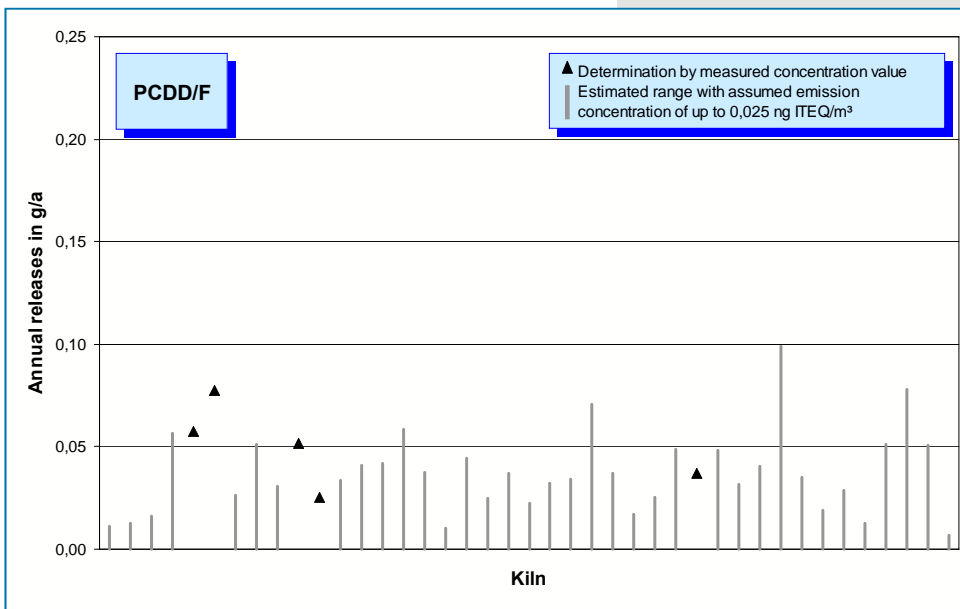


Fig. 5-12: Dioxin and furan emissions (annual releases in 2007) of 41 rotary kilns.

If the values measured are within the range of the external deviation of the method, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.025 ng ITEQ/m³.

and cannot be influenced by process technology measures.

¹⁾ In one case an increased PCDD/F value was measured due to a technical modification during the measurement. It was an unique outlier that could be attributed to the trial conditions which were not consistent with the usual operation.

5.7 Polychlorinated biphenyl (PCB)

The emission behaviour of PCB is comparable to that of dioxins and furans. PCB may be introduced into the process via alternative raw materials and fuels. The rotary kiln systems of the cement industry guarantee a virtually complete destruction of these trace components.

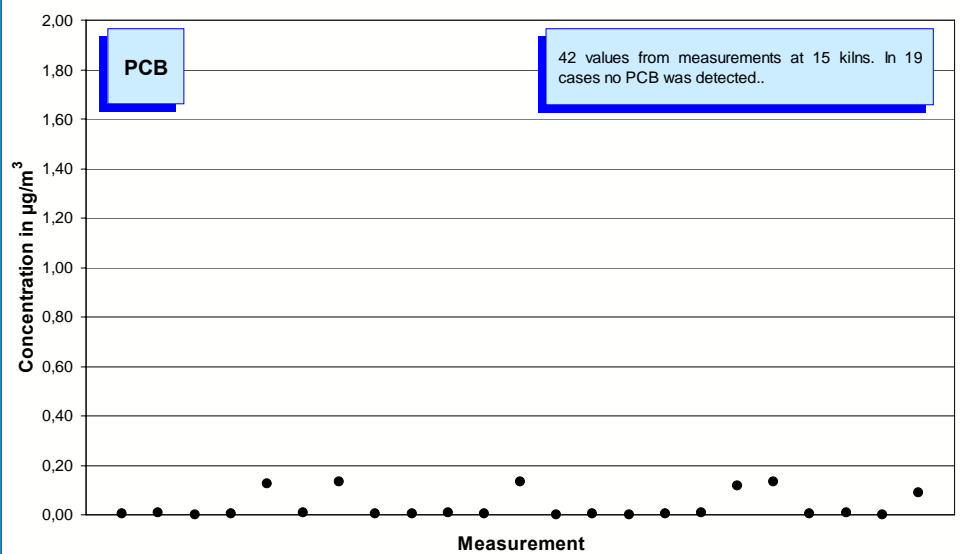


Fig. 5-13: Polychlorinated biphenyl (PCB according to DIN 51527) concentration values (year 2007) measured in the clean gas of 15 rotary kilns. In 19 cases no PCB was detected. Note: there is no standardised test specification indicating the performance characteristics of the measuring method used for measuring PCB in the clean gas of rotary kilns. For that reason, no detection limit is given here. below $0.02 \mu\text{g}/\text{m}^3$ the methods currently used do not provide secured emission concentrations.

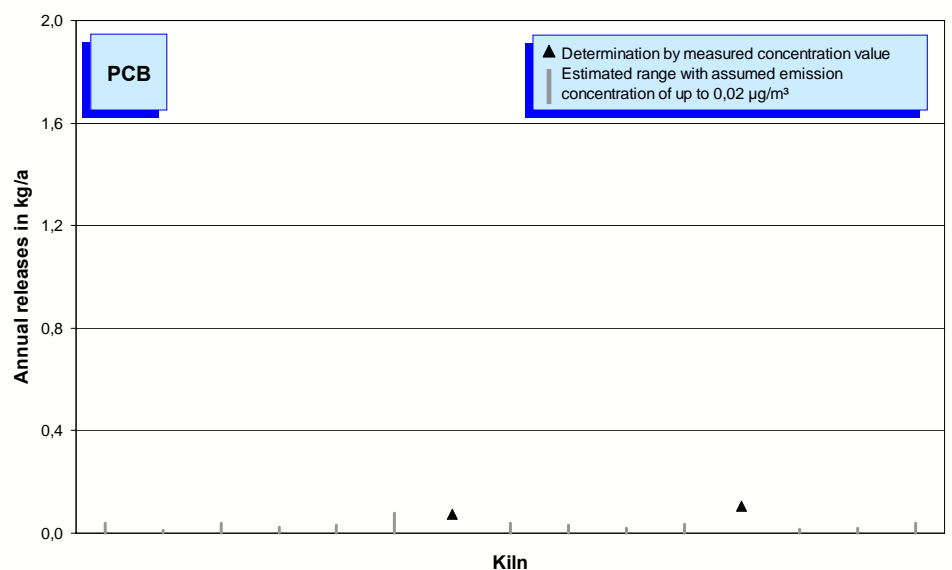
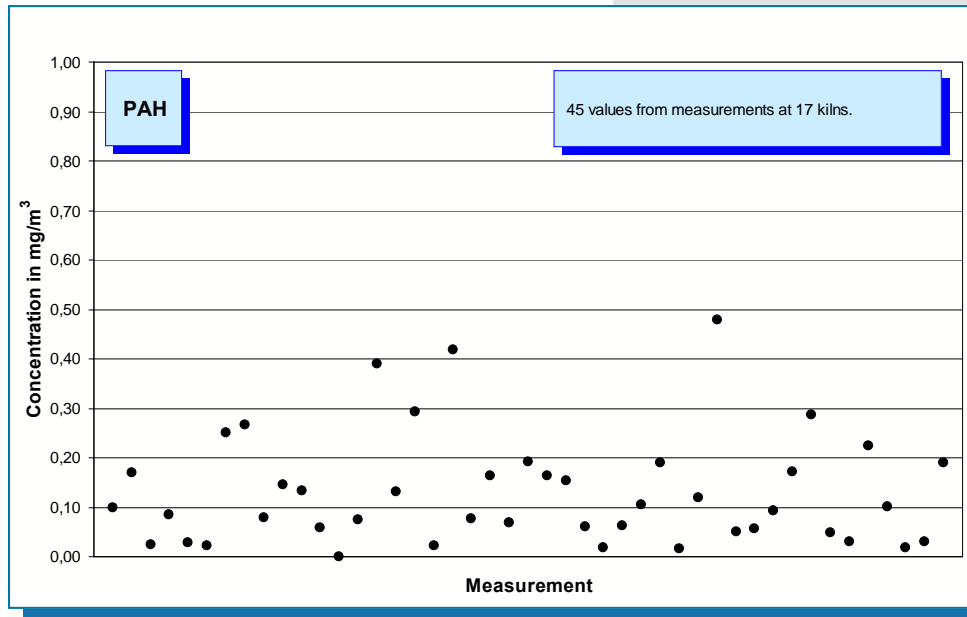


Fig. 5-14: PCB emissions (annual releases in 2007) of 15 rotary kilns.

If the measurements are not secured, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of $0.02 \mu\text{g}/\text{m}^3$.

5.8 Polycyclic aromatic hydrocarbons (PAH)



PAHs (according to EPA 610) in the exhaust gas of rotary kilns usually appear at a distribution dominated by naphthalene, which accounts for a share of more than 90% by mass. The rotary kiln systems of the cement industry guarantee a virtually complete destruction of the PAHs input via fuels. Emissions are caused by organic constituents in the

raw material.

Fig. 5-15: Polycyclic aromatic hydrocarbon (PAH according to EPA 610) concentration values (year 2007) measured in the clean gas of 17 rotary kilns. No detection limit can be deduced from the standard. Below 0.01 mg/m³ the measuring methods currently used do not provide secured emission concentrations.

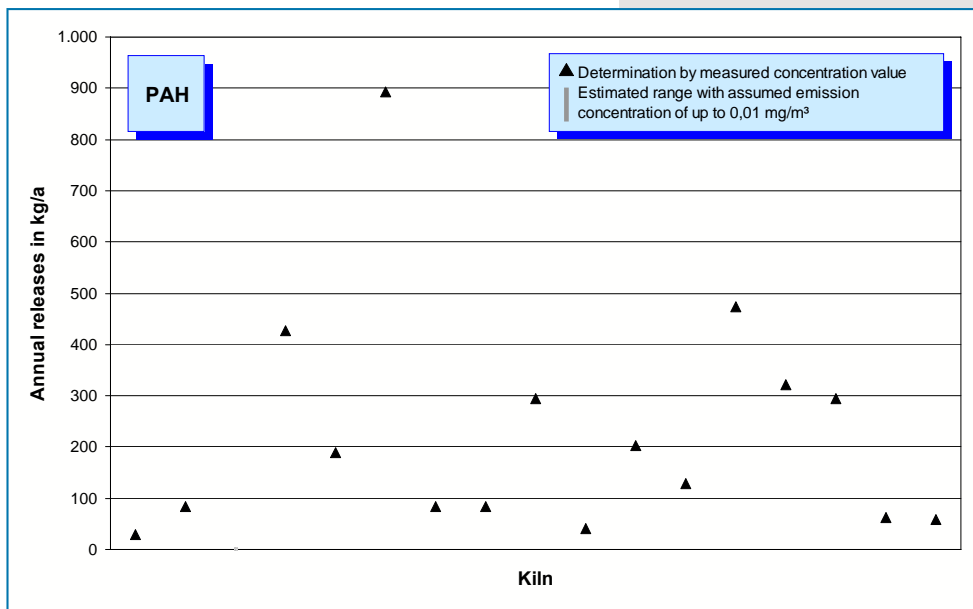


Fig. 5-16: PAH emissions (annual releases in 2007) of 17 rotary kilns. If the measurements are not secured, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.01 mg/m³.

5.9 Benzene, toluene, ethylbenzene, xylene (BTEX)

As a rule the above compounds are present in the exhaust gas of rotary kilns in a characteristic ratio. BTEX is formed during the thermal decomposition of organic raw material constituents in the pre-heater. They account for about 10% of total carbon emissions.

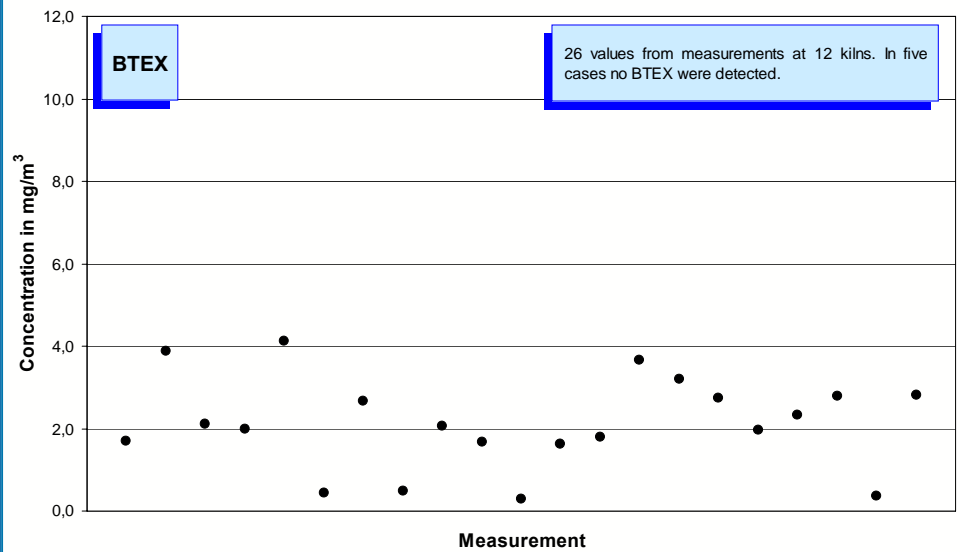


Fig. 5-17: BTEX concentration values (year 2007) measured in the clean gas of 12 rotary kilns. In five cases no BTEX were detected.

No detection limit can be deduced from the standard. Below 0.013 mg/m³ the measuring methods currently used do not provide secured emission concentrations.

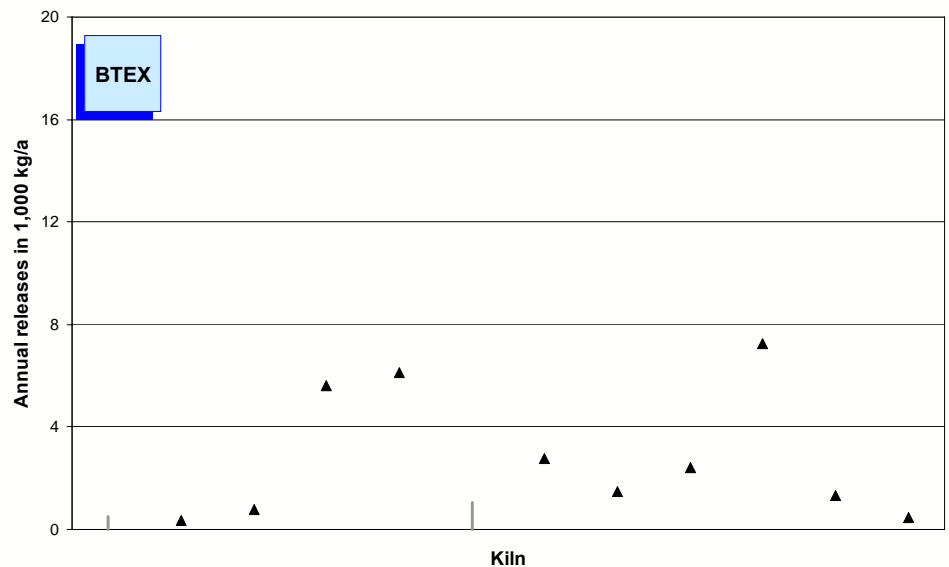
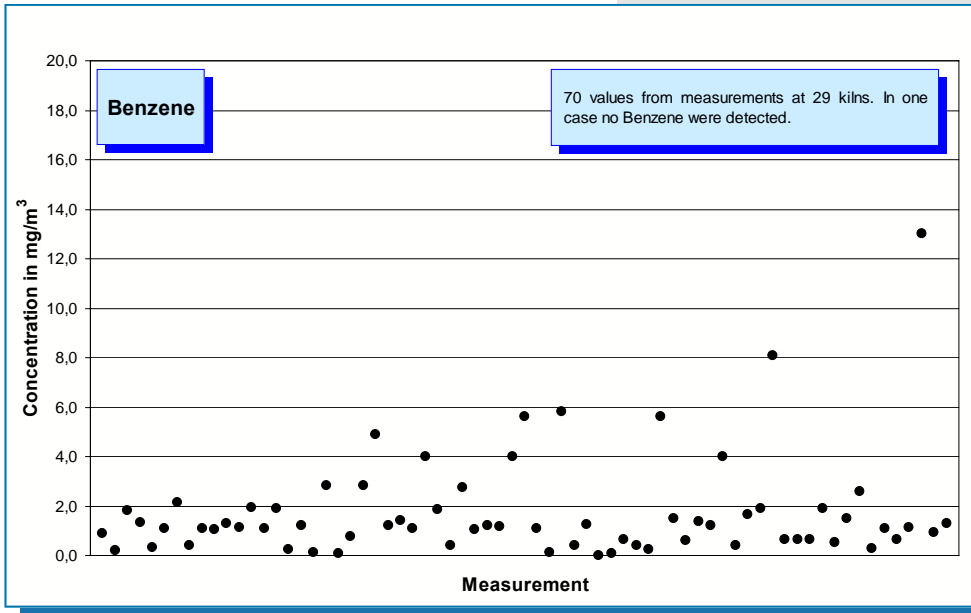


Fig. 5-18: BTEX emissions (annual releases in 2007) of 12 rotary kilns.

5.10 Benzene



Benzene is produced during the thermal decomposition of organic raw material constituents in the preheater. As a rule, it accounts for more than half of the BTEX emissions.

Fig. 5-19: Benzene concentration values (year 2007) measured in the clean gas of 29 rotary kilns. In one case no Benzene were detected.

No detection limit can be deduced from the standard. Below 0.013 mg/m^3 the measuring methods currently used do not provide secured emission concentrations.

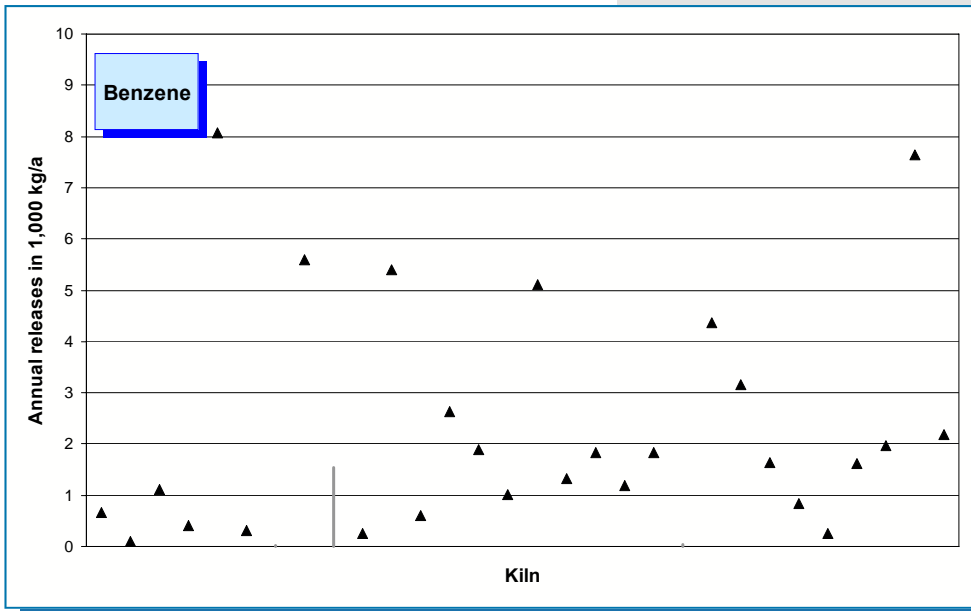


Fig. 5-20: Benzene emissions (annual releases in 2007) of 29 rotary kilns.

5.11 Gaseous inorganic chlorine compounds (HCl)

Chlorides are minor additional constituents contained in the raw materials and fuels of the clinker burning process. They are released when the fuels are burnt or the kiln feed is heated and primarily react with the alkalis from the kiln feed to form alkali chlorides. These compounds, which are initially vaporous, condense on the kiln feed or the kiln dust, respectively, at temperatures between 700 °C and 900 °C, subsequently re-enter the rotary kiln system and evaporate again. This cycle in the area between the rotary kiln and the preheater can result in coating formation. A bypass at the kiln inlet allows to effectively reduce alkali chloride cycles and to thus diminish operational malfunctions.

During the clinker burning process gaseous inorganic chlorine compounds are either not emitted at all or only in very small quantities. Owing to the alkaline kiln gas atmosphere, the formation of hydrogen chloride (HCl) in the exhaust gas can be virtually ruled out. Gaseous inorganic chlorides detected in the exhaust gas of rotary kiln systems are generally attributable to ultra-fine grain size fractions of alkali chlorides in the clean gas dust. They can pass through measuring gas filters, thus feigning the presence of the gaseous compounds.

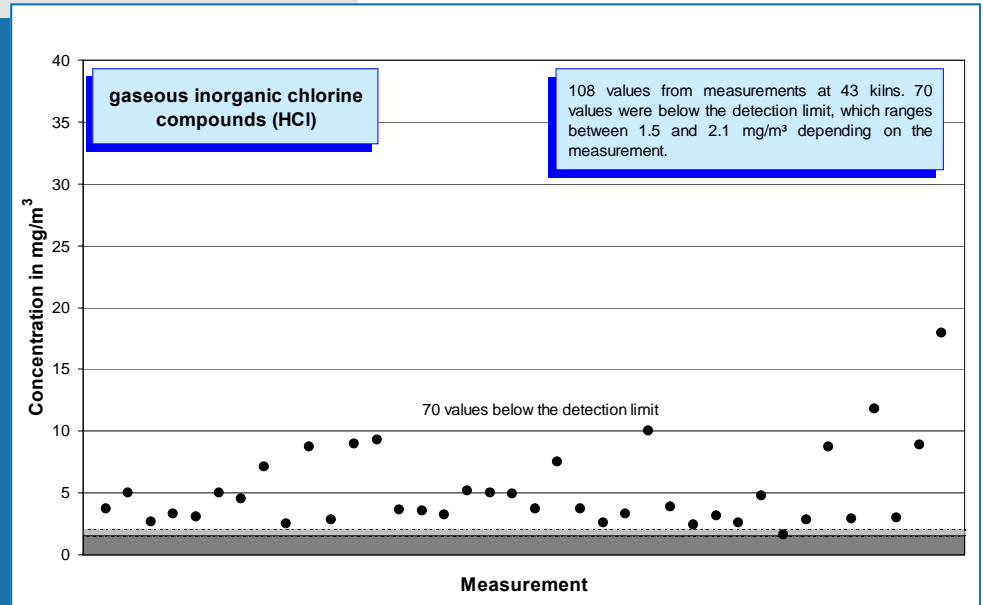


Fig. 5-21: Gaseous inorganic chlorine compound concentration values (year 2007) measured in the clean gas of 43 rotary kilns and given as HCl.

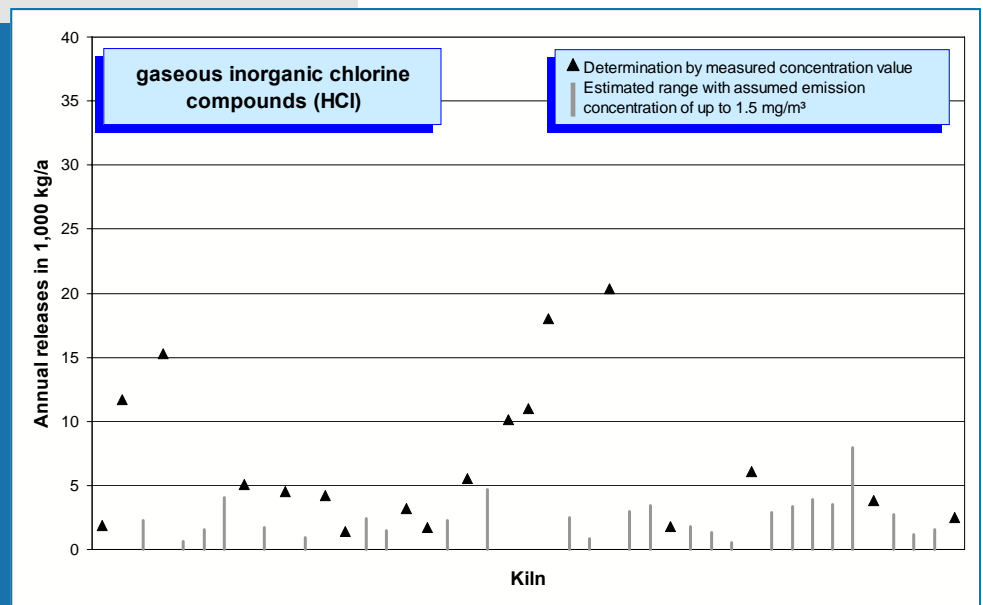


Fig. 5-22: HCl emissions (annual releases in 2007) of 43 rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 1.5 mg/m³.

5.12 Gaseous inorganic fluorine compounds (HF)

Of the fluorine present in rotary kilns, 90 to 95% is bound in the clinker and the remainder is bound with dust in the form of calcium fluoride stable under the conditions of the

burning process. Owing to the great calcium excess, the emission of gaseous fluorine compounds and of hydrogen fluoride in particular, is virtually excluded. Ultra-fine dust fractions that pass through the measuring gas filter may simulate low contents of gaseous fluorine compounds in rotary kiln systems of the cement industry.

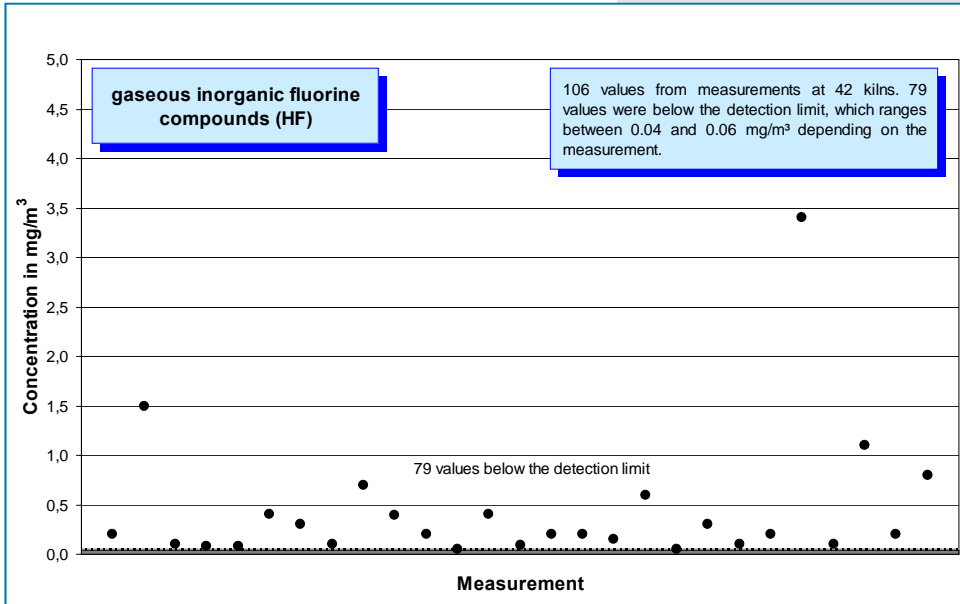


Fig. 5-23: Gaseous inorganic fluorine compound concentration values (year 2007) measured in the clean gas of 42 rotary kilns and given as HF.

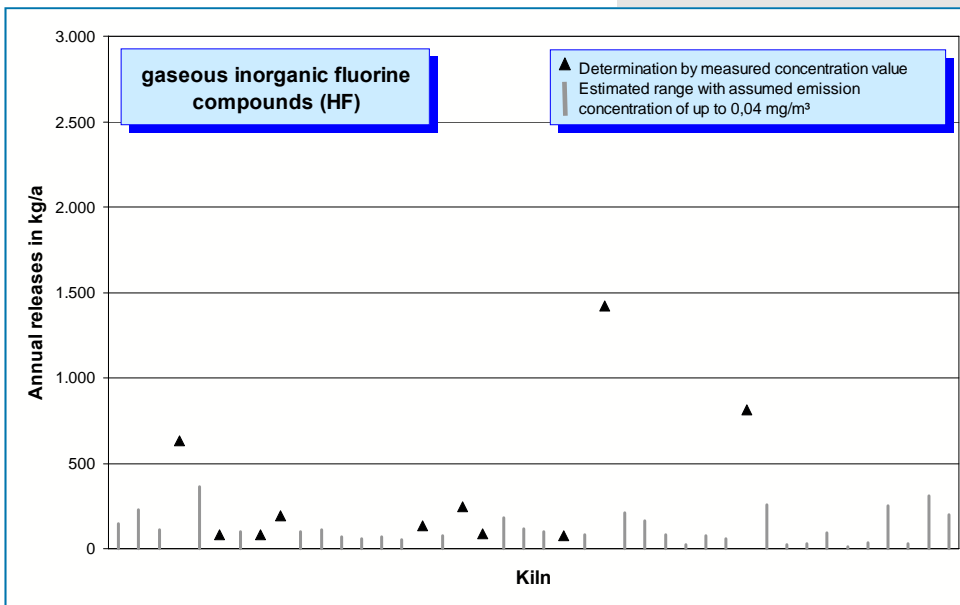


Fig. 5-24: HF emissions (annual releases in 2007) of 42 rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.04 mg/m³.

5.13 Trace elements

The emission behaviour of the individual elements in the clinker burning process is determined by the input scenario, the behaviour in the plant and the precipitation efficiency of the dust collection device. The trace elements introduced into the burning process via the raw materials and fuels may evaporate completely or partially in the hot zones of the preheater and/or rotary kiln depending on their volatility, react with the constituents present in the gas phase and condense on the kiln feed in the cooler sections of the kiln system. Depending on the volatility and the operating conditions, this may result in the formation of cycles that are either restricted to the kiln and the preheater or include the combined drying and grinding plant as well.

Trace elements from the fuels initially enter the combustion gases, but are emitted to an extremely small extent only owing to the retention capacity of the kiln and the preheater. Table 5-4 gives representative transfer coefficients for rotary kiln systems equipped with cyclone preheaters. These coefficients serve to calculate the proportion of trace elements from fuels emitted with the clean gas.

By contrast, the emission factors listed in the Table are higher than the corresponding transfer coefficients. Apart from fuel-related emissions, they also take into account raw material-related emissions, which usually predominate by a significant margin. The bandwidths indicated for the emission factors result from inventory investigations. No values are given for mercury since measurement results primarily depend on the respective operating conditions.

Component	EF in %	TC in %
Cadmium	< 0.01 to < 0.2	0.003
Thallium	< 0.01 to < 1	0.02
Antimony	< 0.01 to < 0.05	0.0005
Arsenic	< 0.01 to 0.02	0.0005
Lead	< 0.01 to < 0.2	0.002
Chromium	< 0.01 to < 0.05	0.0005
Cobalt	< 0.01 to < 0.05	0.0005
Copper	< 0.01 to < 0.05	0.0005
Manganese	< 0.001 to < 0.01	0.0005
Nickel	< 0.01 to < 0.05	0.0005
Vanadium	< 0.01 to < 0.05	0.0005

Table 5-4: Emission factors (EF, emitted portion of the total input) and transfer coefficients (TC, emitted portion of the fuel input) for rotary kiln systems with cyclone pre-heater

Under the conditions prevailing in the clinker burning process, non-volatile elements (e.g. arsenic, vanadium, nickel) are completely bound in the clinker. Elements such as lead and cadmium preferably react with the excess chlorides and sulphates in the section between the rotary kiln and the preheater, forming low-volatile compounds. Owing to the large surface area available, these compounds condense on the kiln feed particles at temperatures between 700 °C and 900 °C. In this way, the low-volatile elements accumulated in the kiln-preheater-system are precipitated again in the cyclone preheater, remaining almost completely in the clinker.

Thallium and its compounds condense in the upper zone of the cyclone preheater at temperatures between 450 °C and 500 °C. As a consequence, a cycle can be formed between preheater, raw material drying and exhaust gas purification.

Mercury and its compounds are not precipitated in the kiln and the preheater. They condense on the exhaust gas route due to the cooling of the gas and are partially adsorbed by the raw material particles. This portion is precipitated in the kiln exhaust gas filter.

Owing to trace element behaviour during the clinker burning process and the high precipitation efficiency of the dust collection devices, trace element emission concentrations are on a low overall level. For example, the average values measured in 2006 of the trace elements listed in the German regulation on waste incineration (17th BImSchV) were above the detection limit in merely about 20% of all cases.

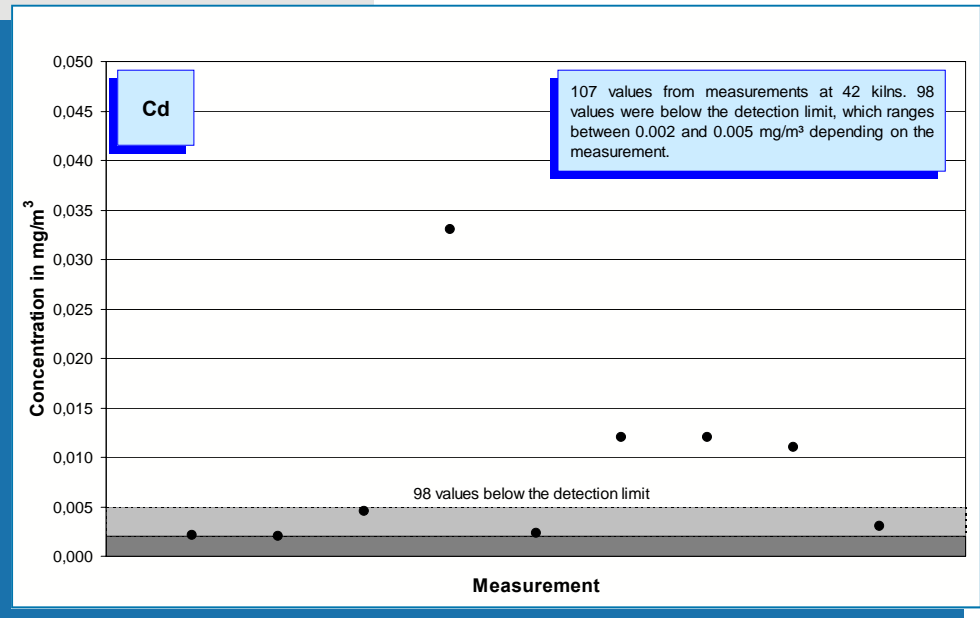


Fig. 5-25: Cadmium concentration values (year 2007) measured in the clean gas of 42 rotary kilns.

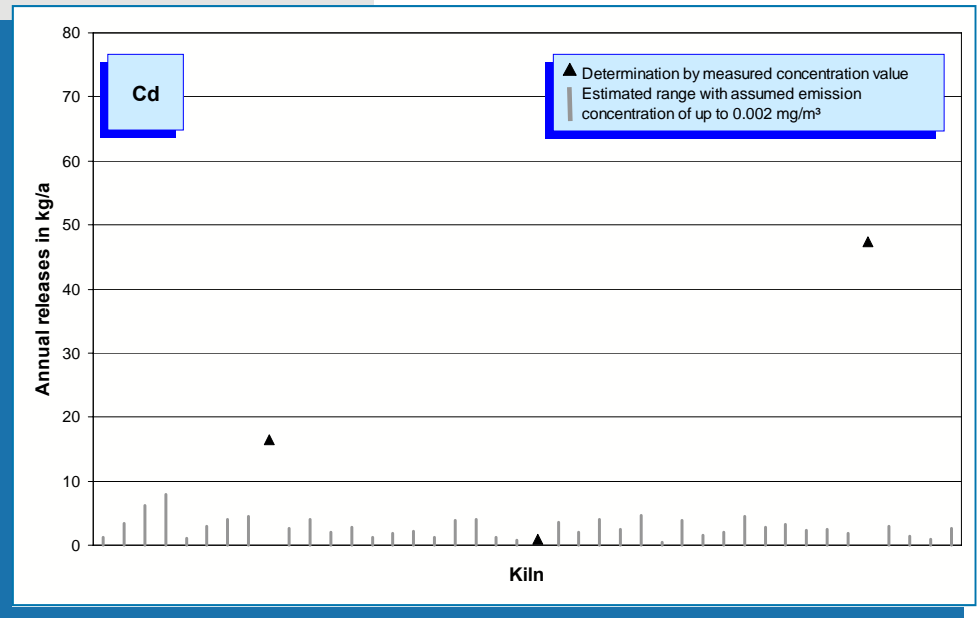


Fig. 5-26: Cadmium emissions (annual releases in 2007) of 42 rotary kilns. If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.002 mg/m³.

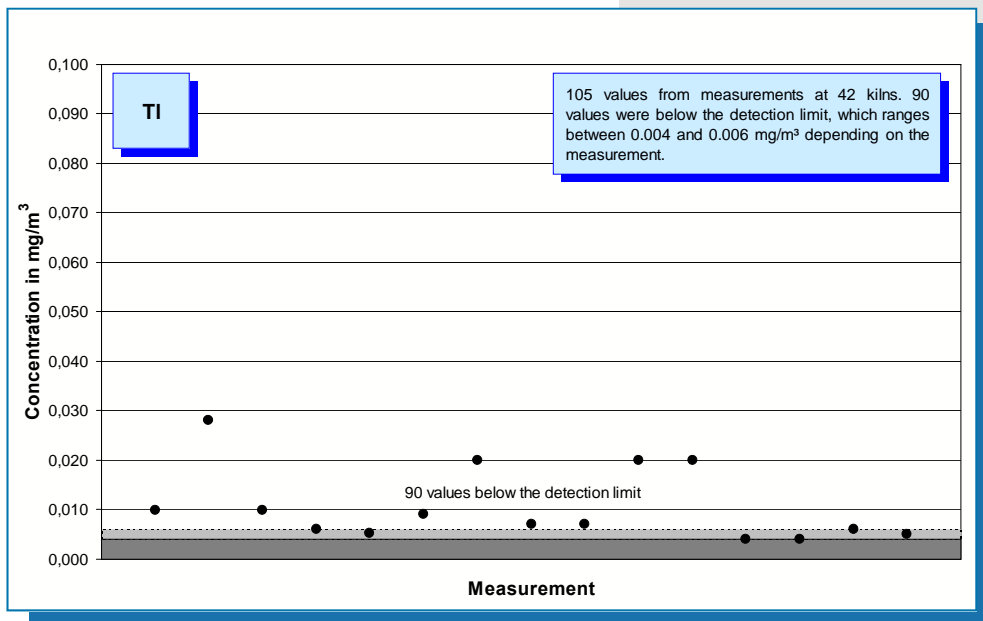


Fig. 5-27: Thallium concentration values (year 2007) measured in the clean gas of 42 rotary kilns.

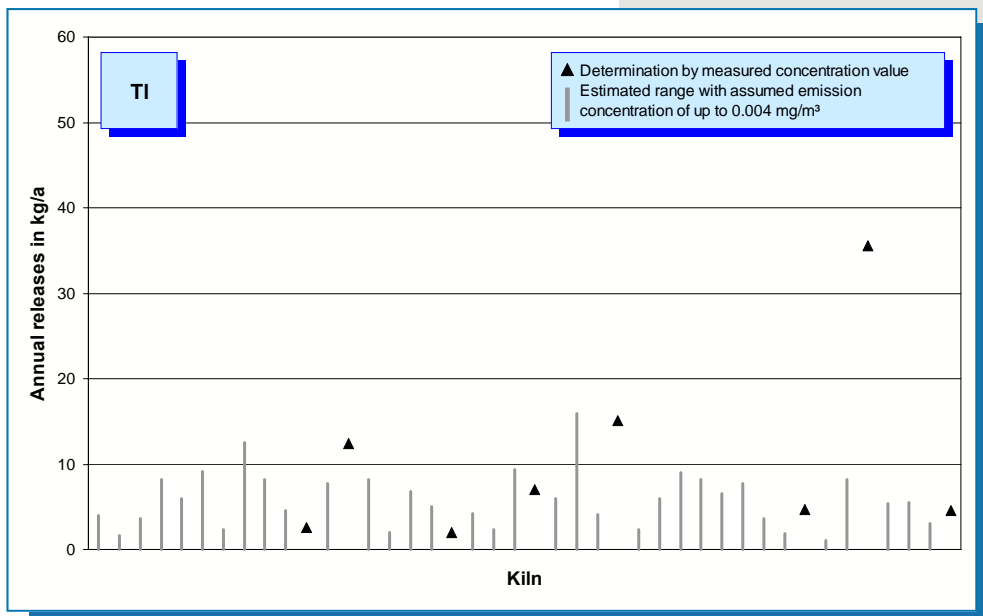


Fig. 5-28: Thallium emissions (annual releases in 2007) of 42 rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.004 mg/m³.

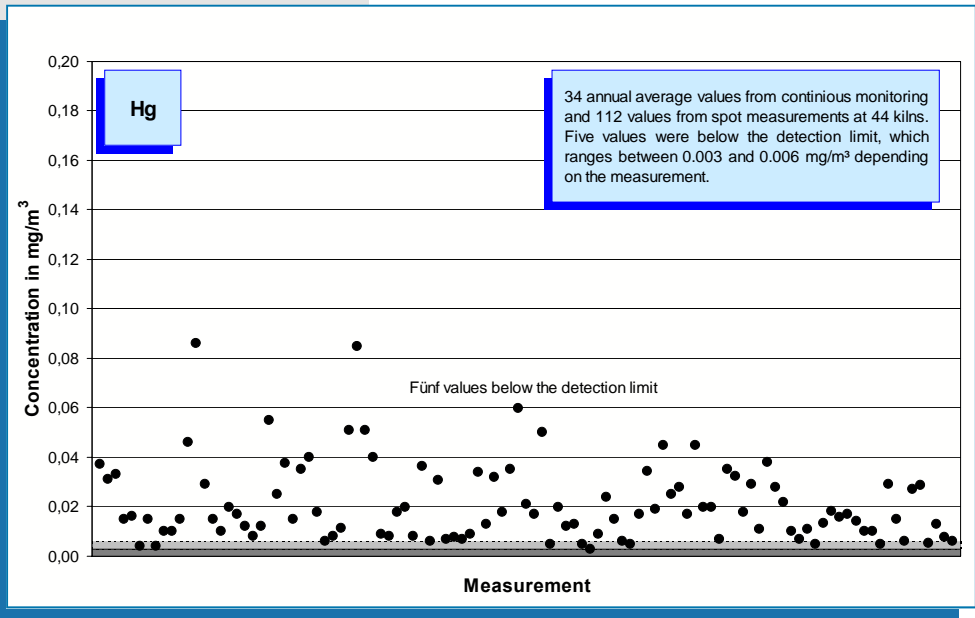


Fig. 5-29: Mercury concentration values (year 2007) measured in the clean gas of 44 rotary kilns.

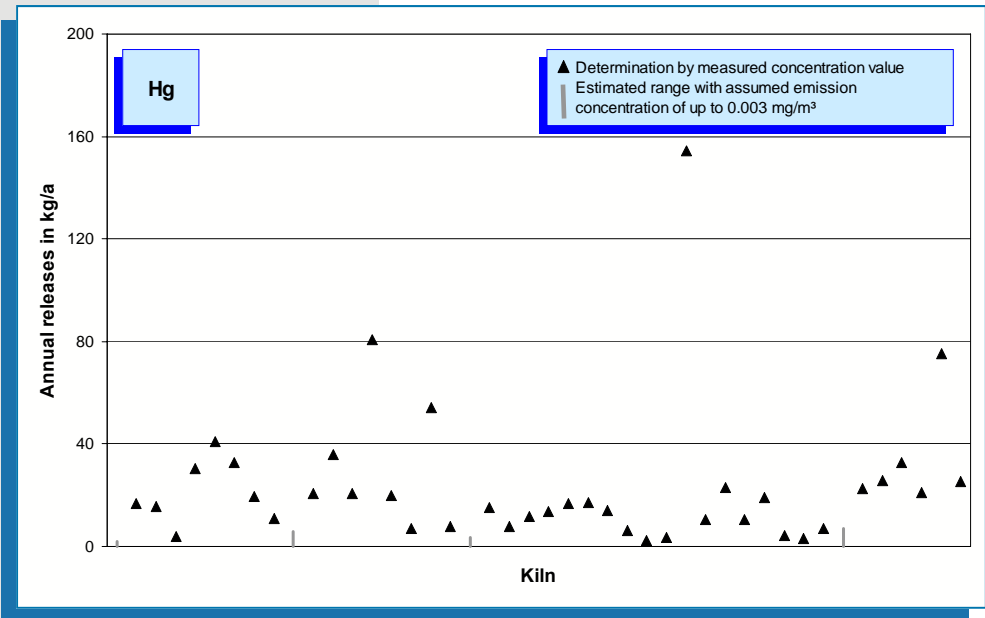


Fig. 5-30: Mercury emissions (annual releases in 2007) of 44 rotary kilns.
 If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.003 mg/m³.

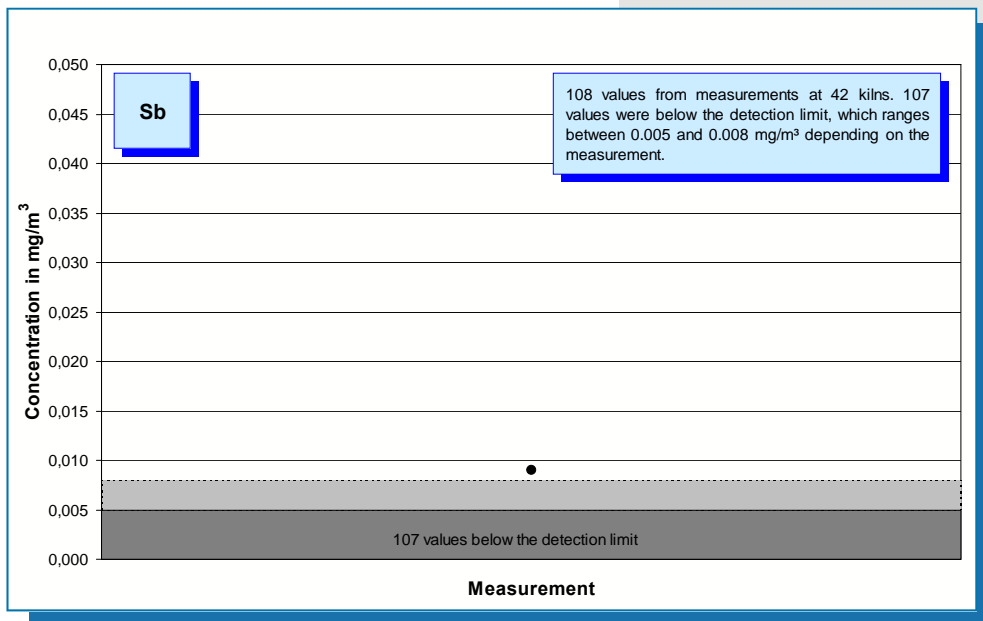


Fig. 5-31: Antimony concentration values (year 2007) measured in the clean gas of 42 rotary kilns.

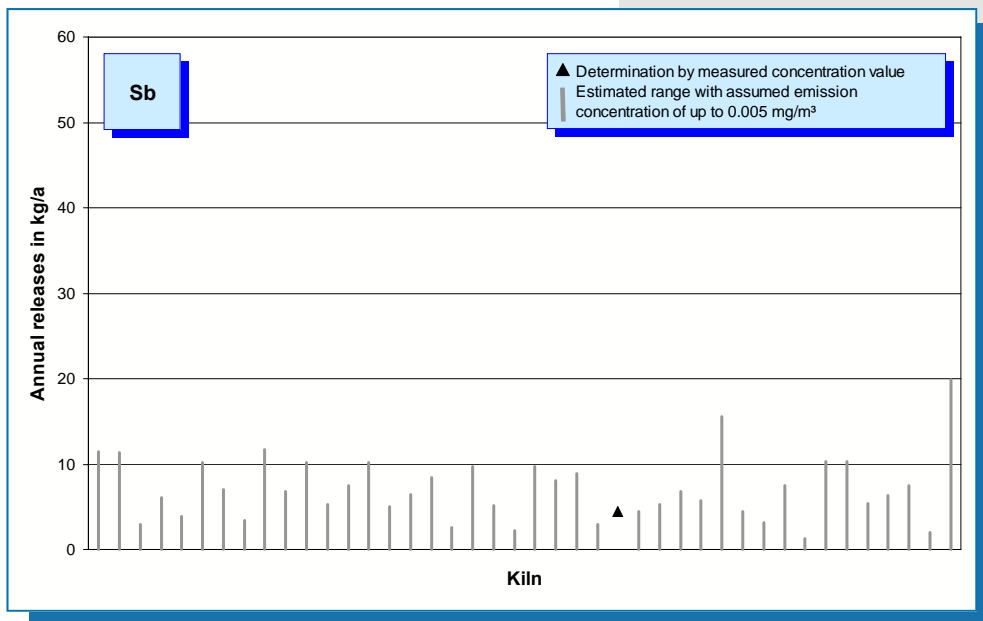


Fig. 5-32: Antimony emissions (annual releases in 2007) of 42 rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.005 mg/m^3 .

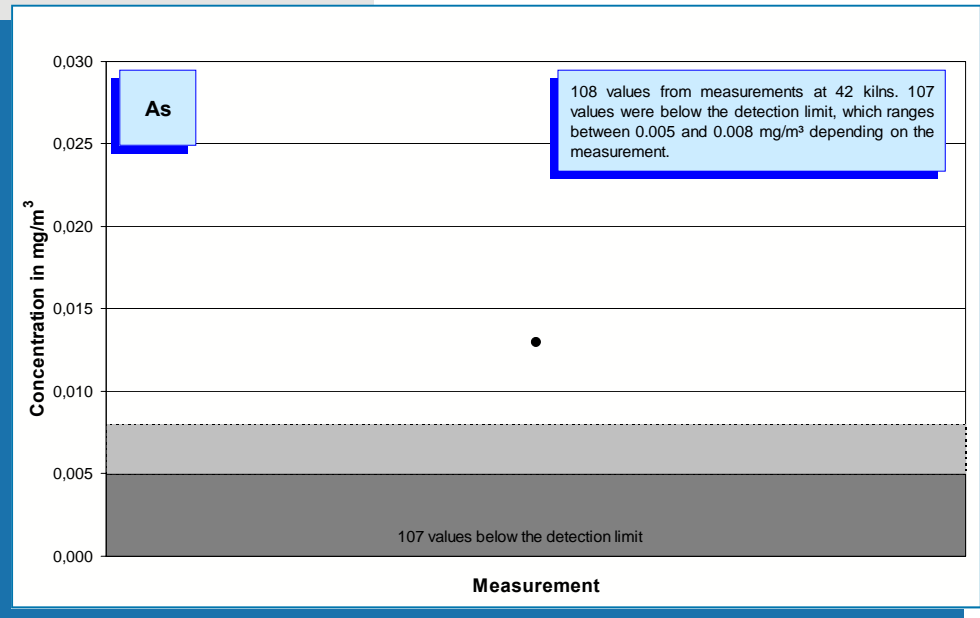


Fig. 5-33: Arsenic concentration values (year 2007) measured in the clean gas of 42 rotary kilns.

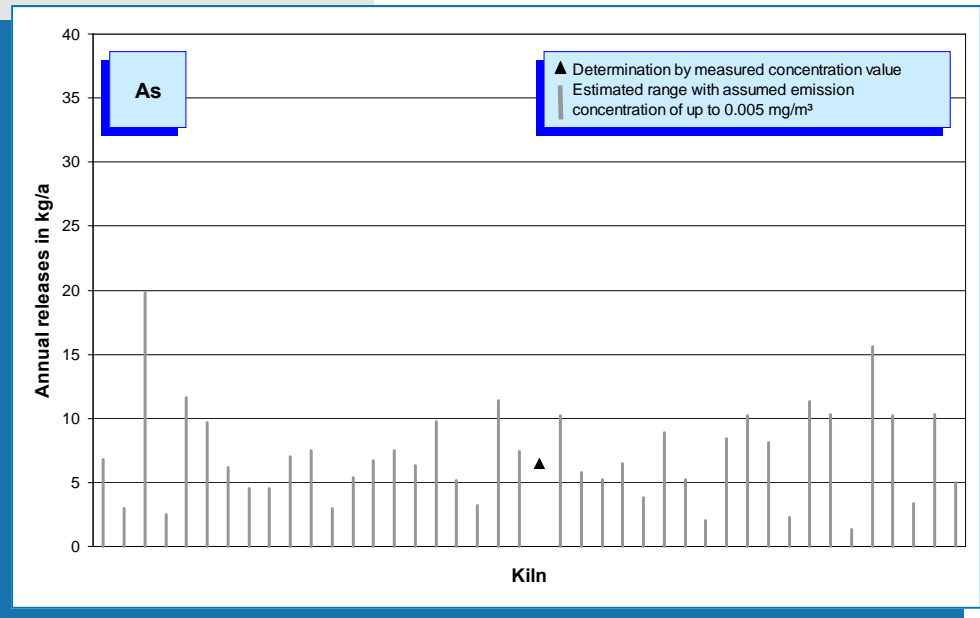


Fig. 5-34: Arsenic emissions (annual releases in 2007) of 42 rotary kilns.
 If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.005 mg/m³.

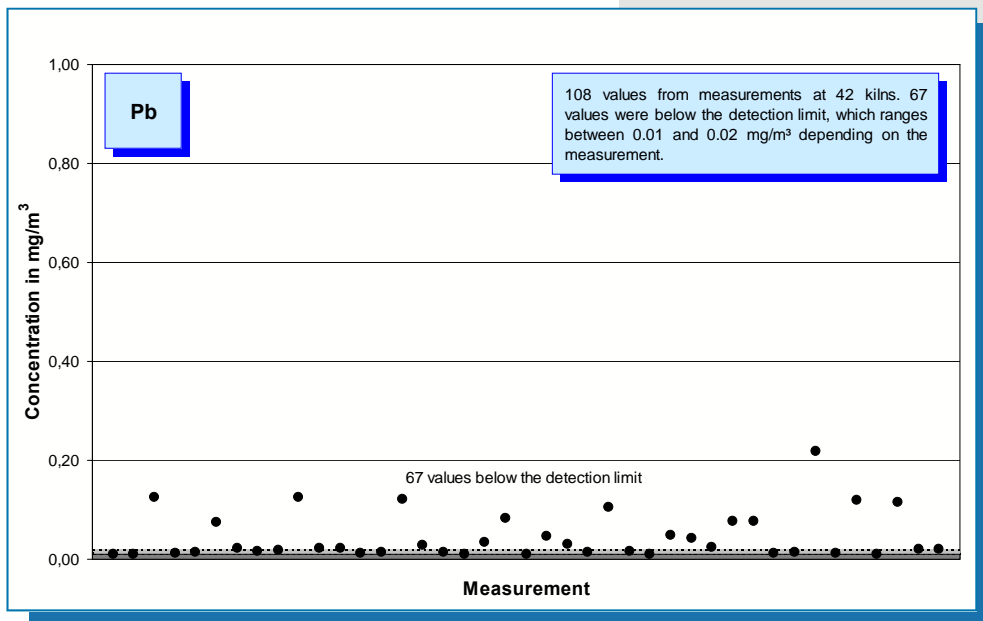


Fig. 5-35: Lead concentration values (year 2007) measured in the clean gas of 42 rotary kilns.

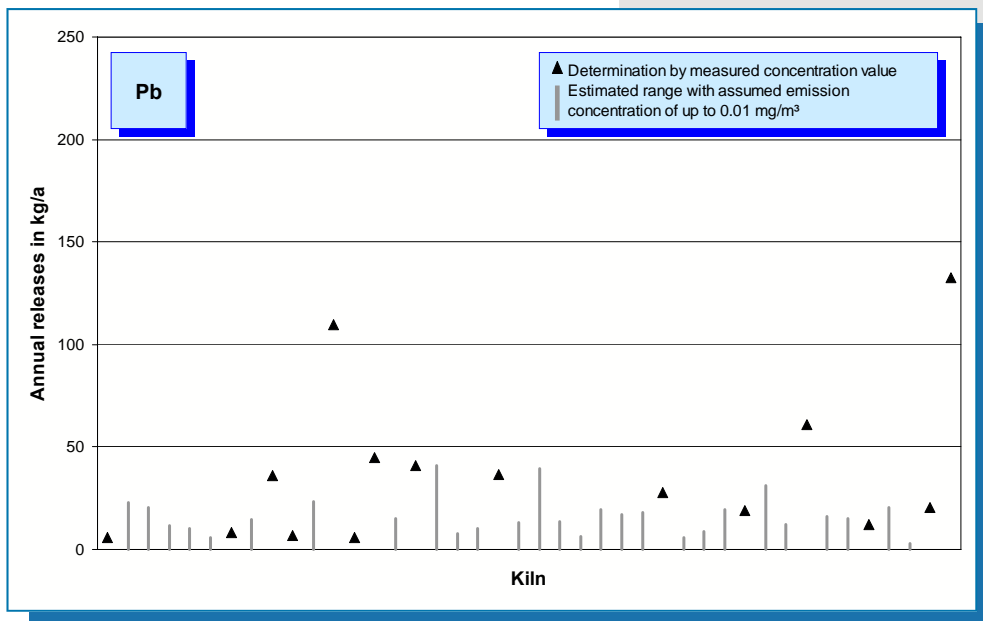


Fig. 5-36: Lead emissions (annual releases in 2007) of 42 rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.01 mg/m^3 .

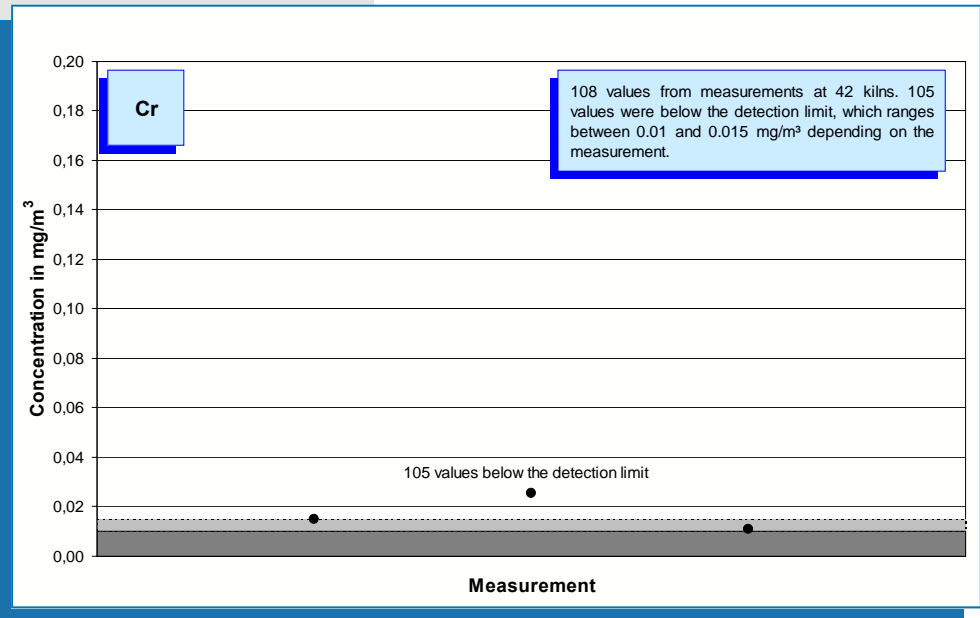


Fig. 5-37: Chromium concentration values (year 2007) measured in the clean gas of 42 rotary kilns.

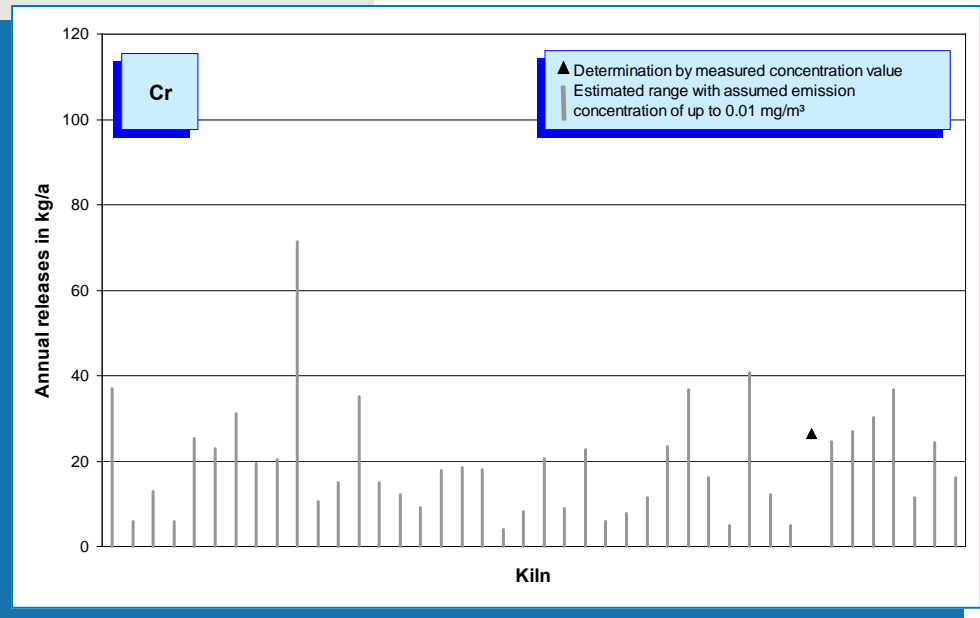


Fig. 5-38: Chromium emissions (annual releases in 2007) of 42 rotary kilns. If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.01 mg/m³.

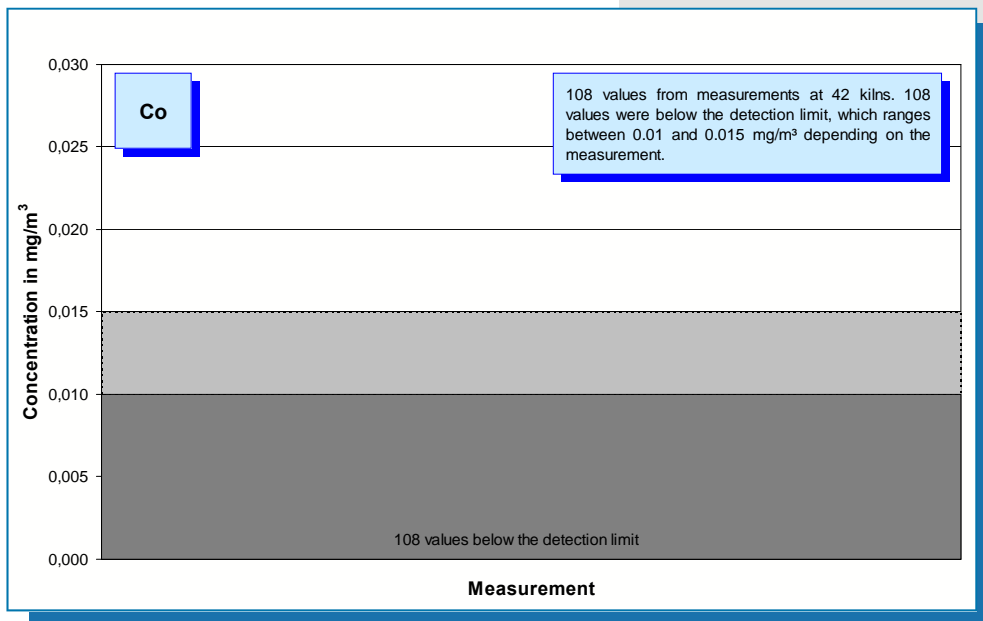


Fig. 5-39: Cobalt concentration values (year 2007) measured in the clean gas of 42 rotary kilns.

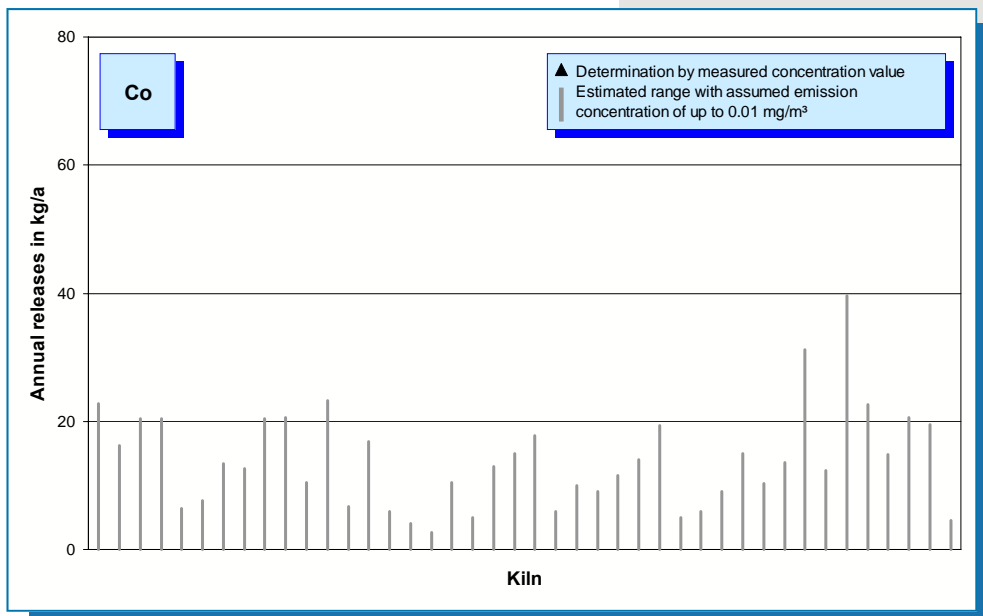


Fig. 5-40: Cobalt emissions (annual releases in 2007) of 42 rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.01 mg/m³.

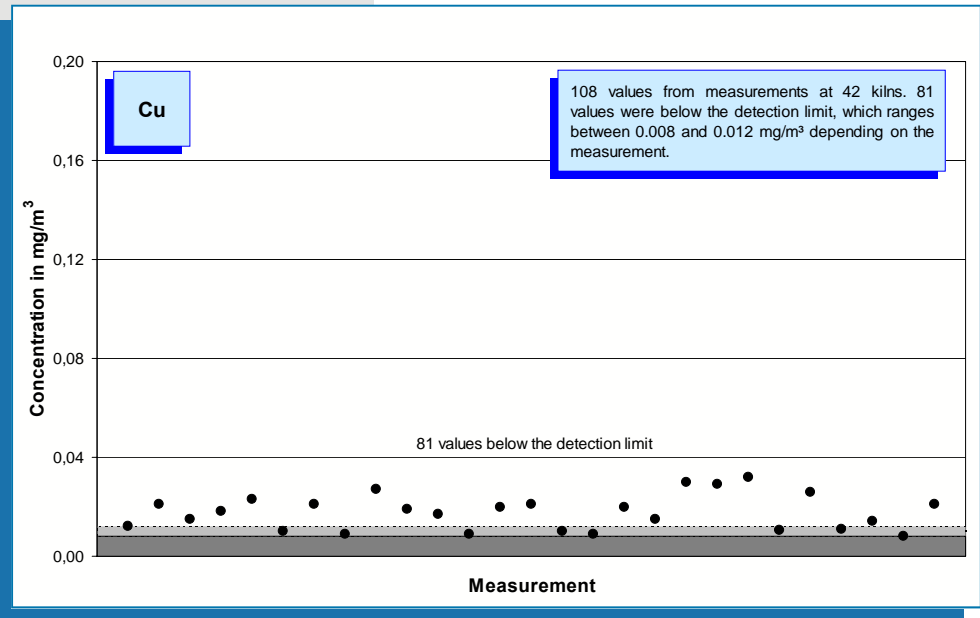


Fig. 5-41: Copper concentration values (year 2007) measured in the clean gas of 42 rotary kilns.

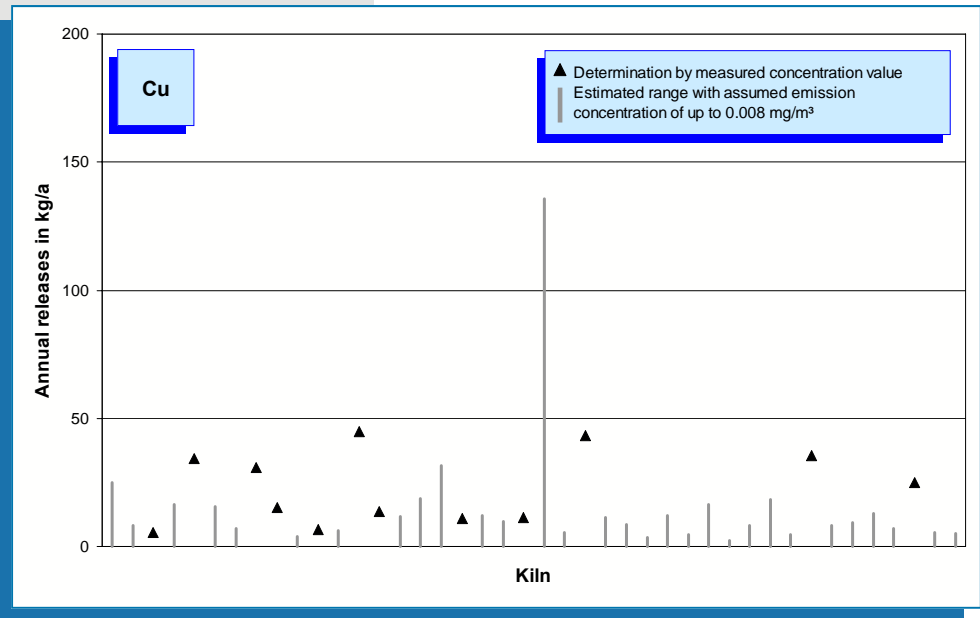


Fig. 5-42: Copper emissions (annual releases in 2007) of 42 rotary kilns.
 If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.008 mg/m³.

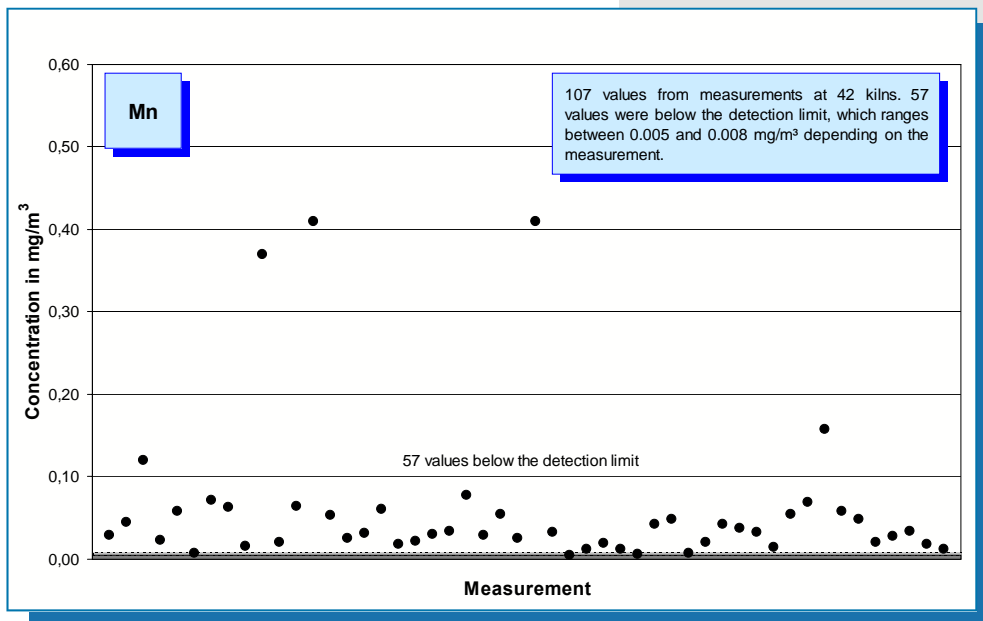


Fig. 5-43: Manganese concentration values (year 2007) measured in the clean gas of 42 rotary kilns.

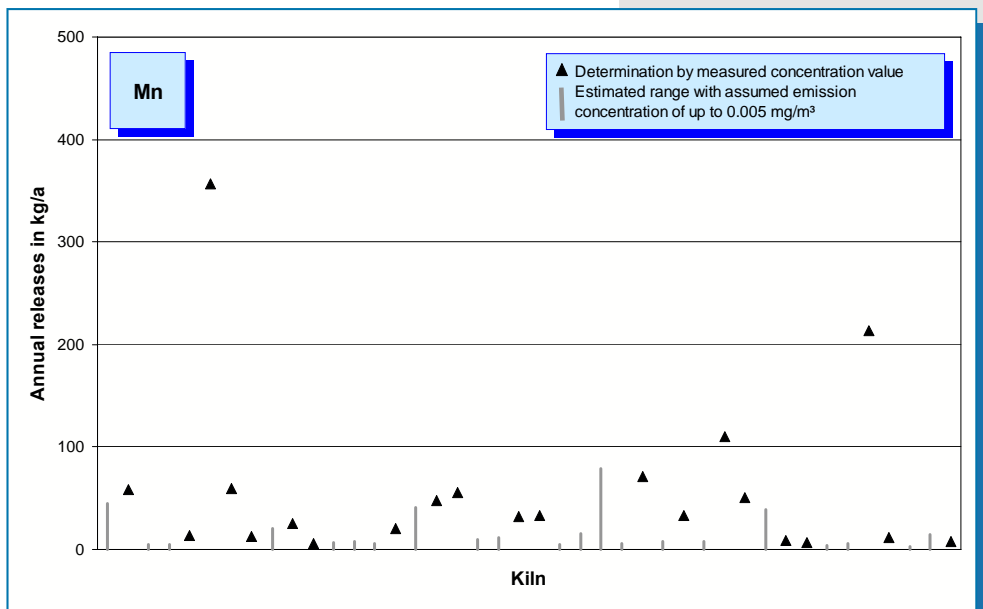


Fig. 5-44: Manganese emissions (annual releases in 2007) of 42 rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.005 mg/m³.

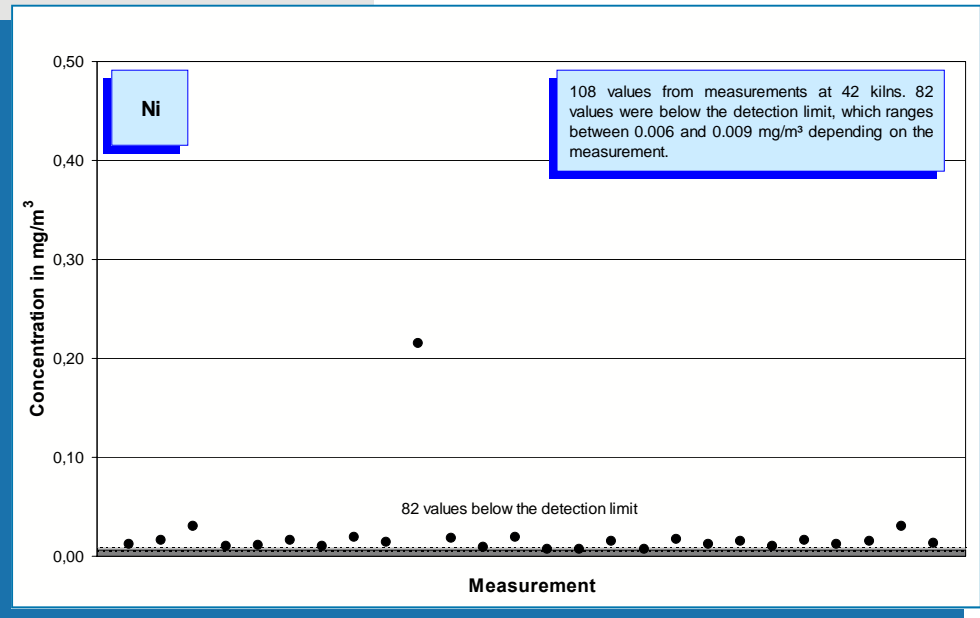


Fig. 5-45: Nickel concentration values (year 2007) measured in the clean gas of 42 rotary kilns.

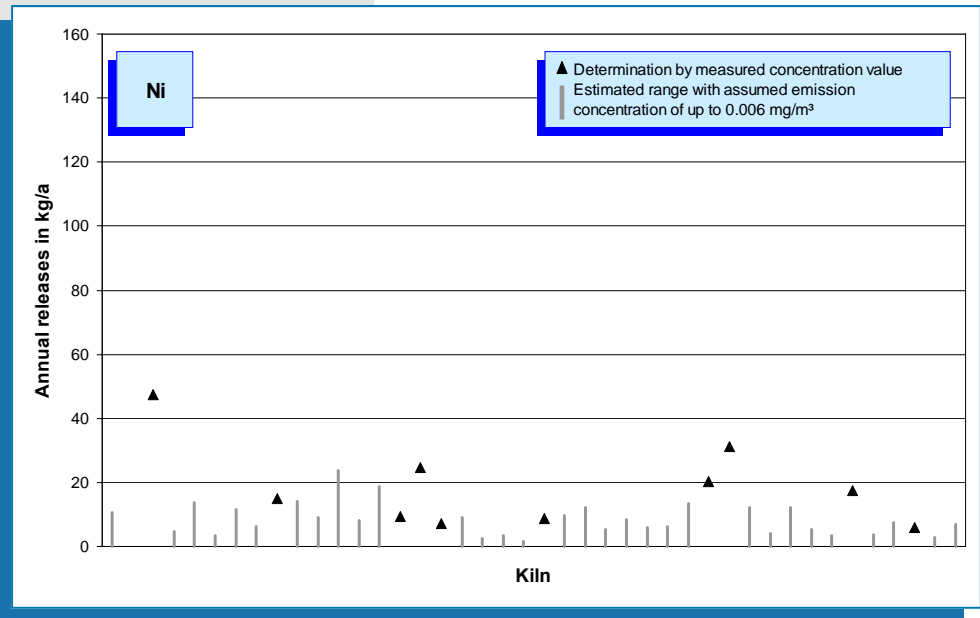


Fig. 5-46: Nickel emissions (annual releases in 2007) of 42 rotary kilns.
 If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.006 mg/m³.

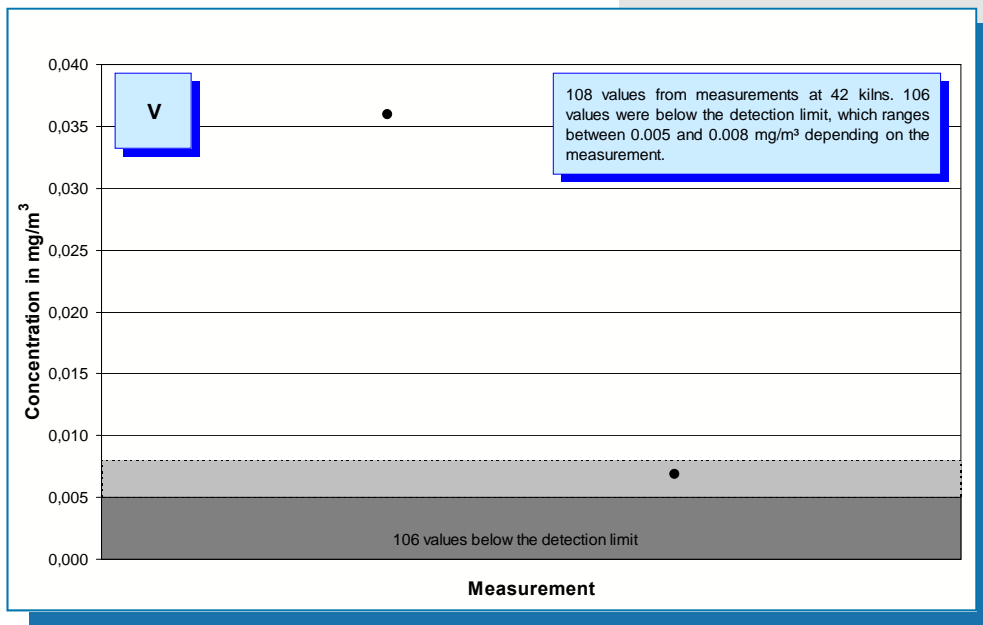


Fig. 5-47: Vanadium concentration values (year 2007) measured in the clean gas of 42 rotary kilns.

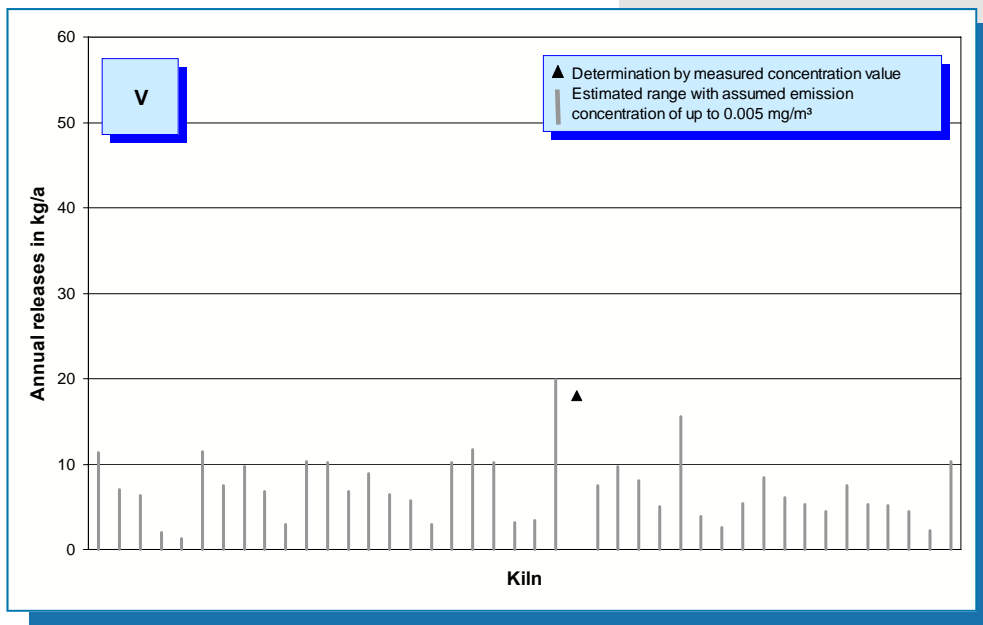


Fig. 5-48: Vanadium emissions (annual releases in 2007) of 42 rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.005 mg/m^3 .

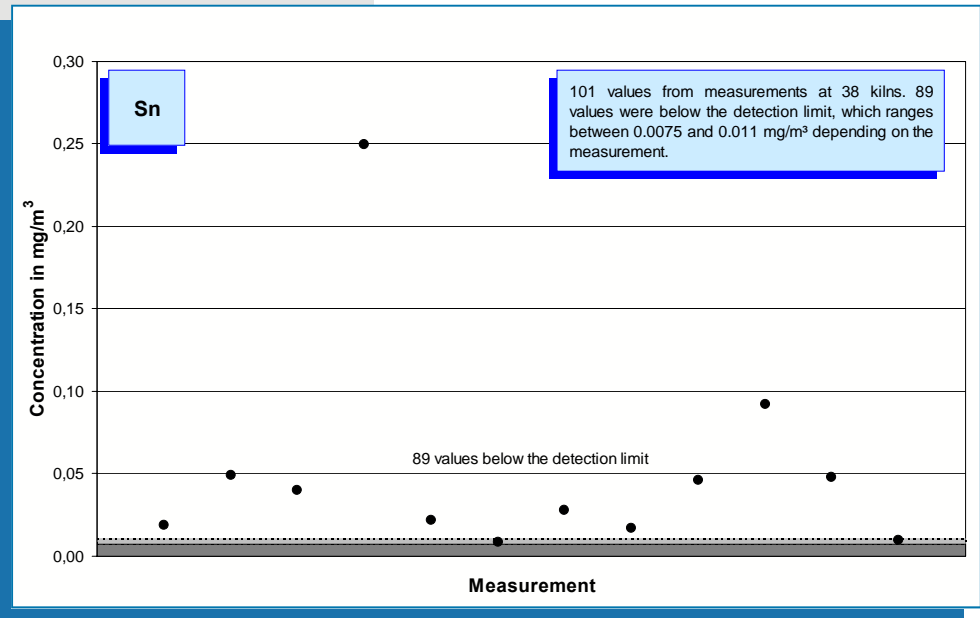


Fig. 5-49: Tin concentration values (year 2007) measured in the clean gas of 38 rotary kilns.

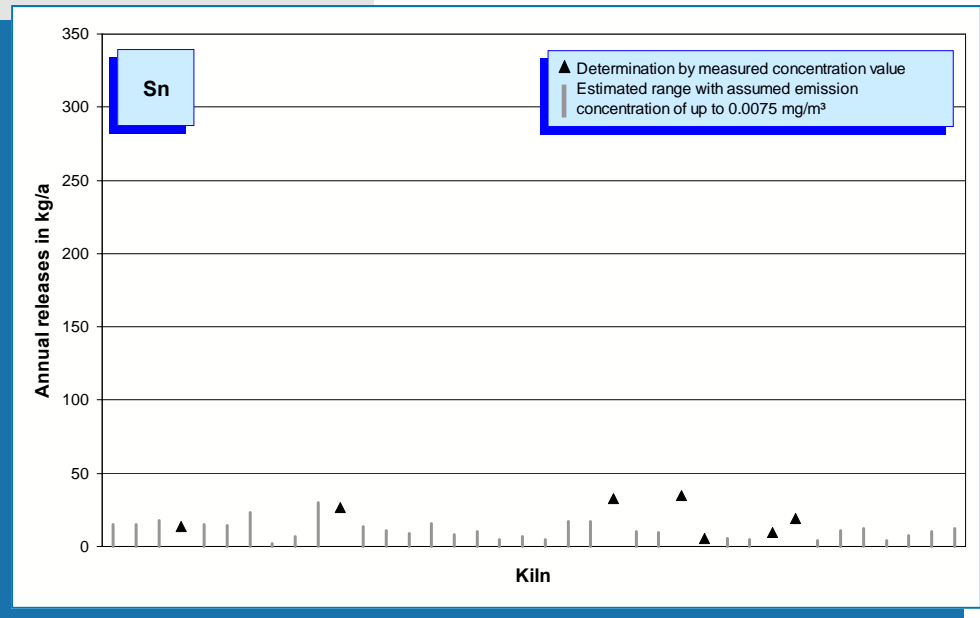


Fig. 5-50: Tin emissions (annual releases in 2007) of 38 rotary kilns.
 If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.0075 mg/m^3 .

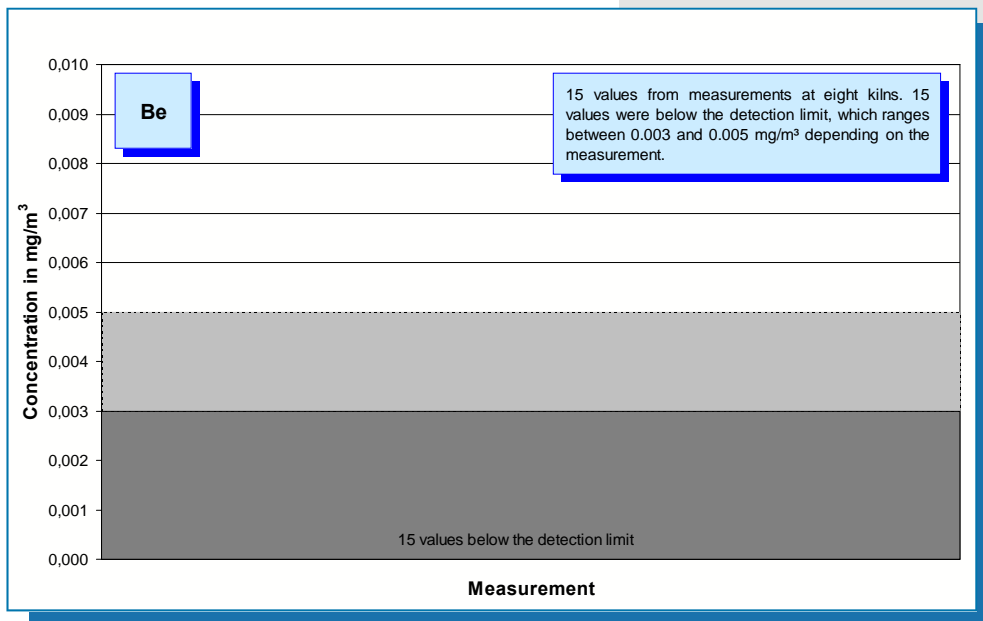


Fig. 5-51: Beryllium concentration values (year 2007) measured in the clean gas of eight rotary kilns.

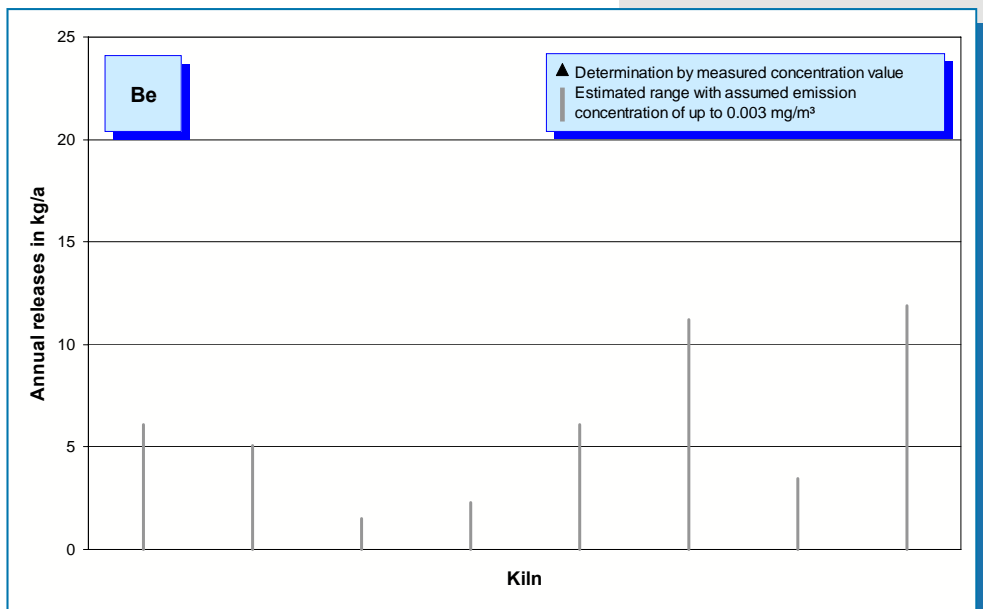


Fig. 5-52: Beryllium emissions (annual releases in 2007) of eight rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.003 mg/m³.

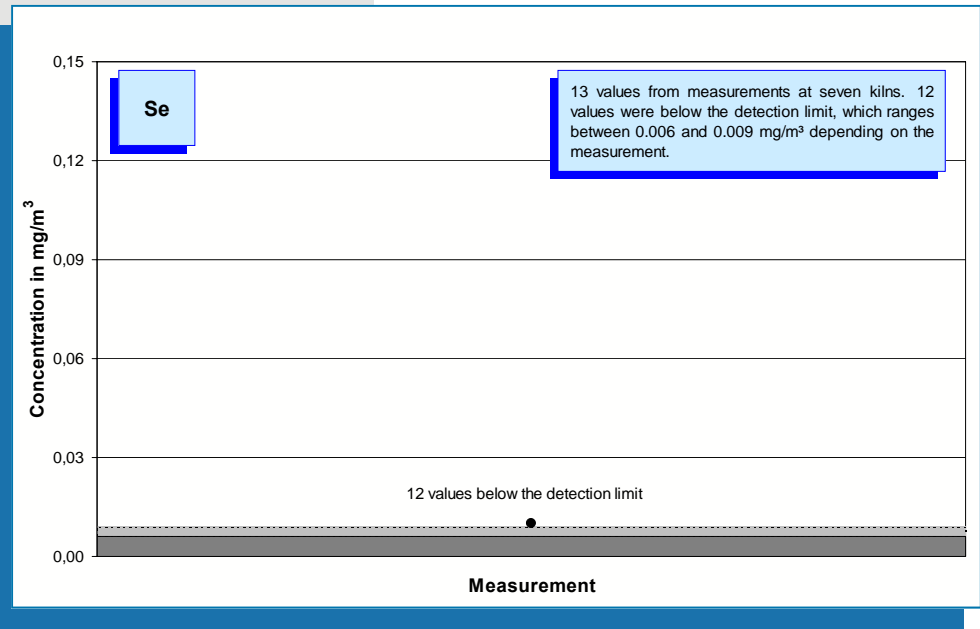


Fig. 5-53: Selenium concentration values (year 2007) measured in the clean gas of seven rotary kilns.

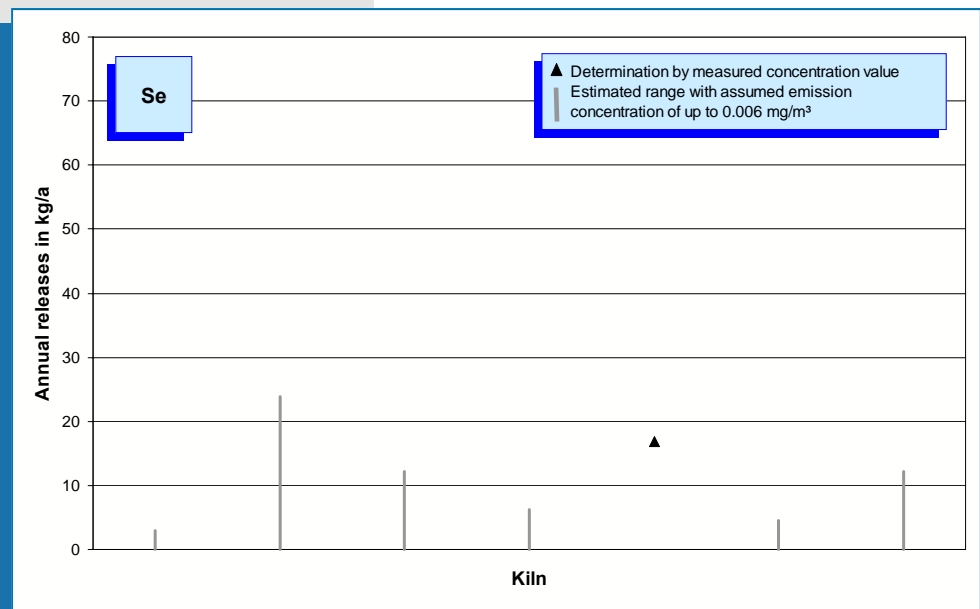


Fig. 5-54: Selenium emissions (annual releases in 2007) of seven rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.006 mg/m^3 .

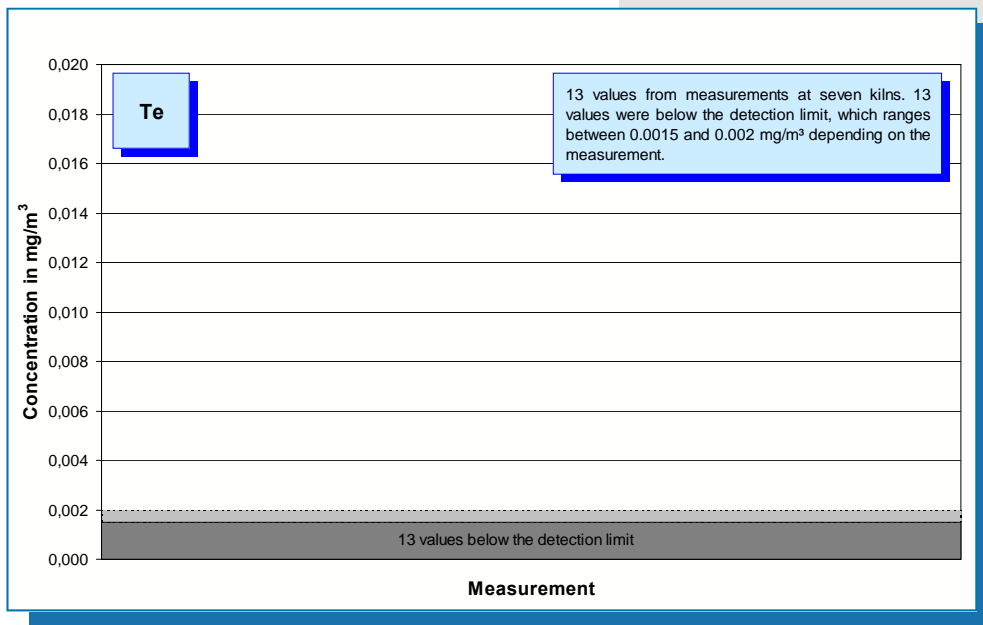


Fig. 5-55: Tellurium concentration values (year 2007) measured in the clean gas of seven rotary kilns.

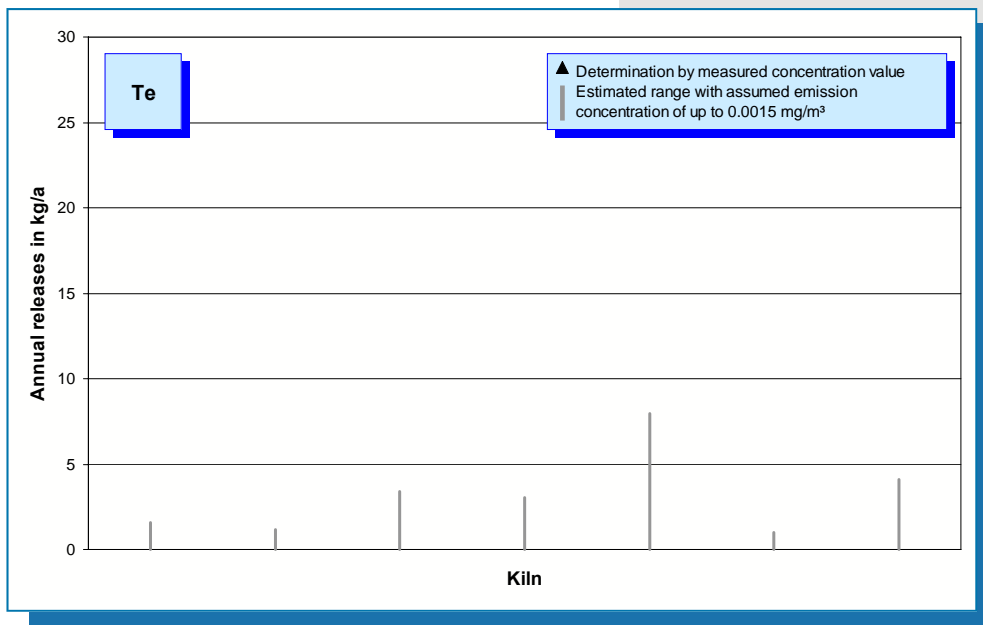


Fig. 5-56: Tellurium emissions (annual releases in 2007) of seven rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.0015 mg/m³.

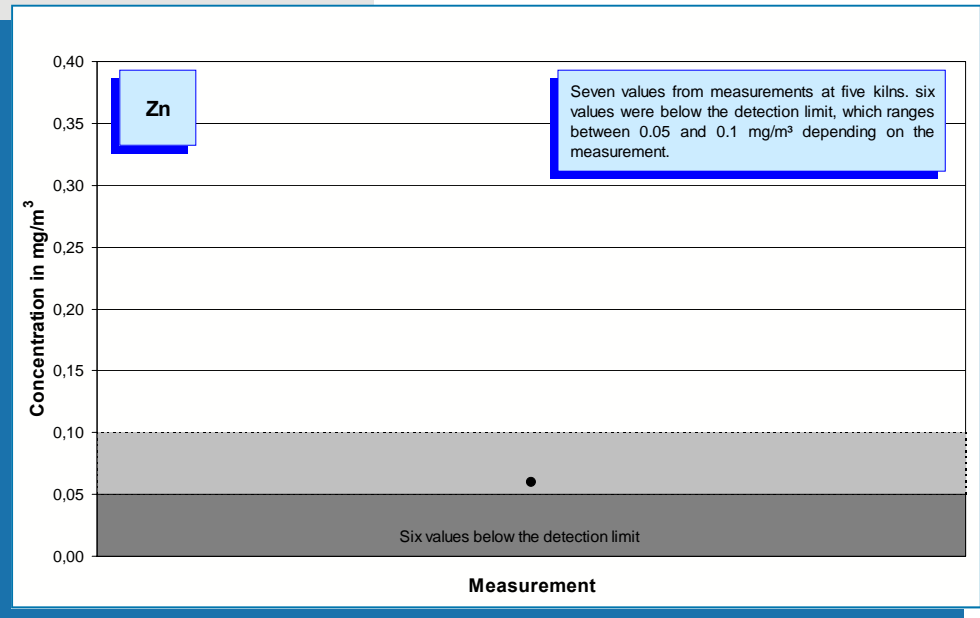


Fig. 5-57: Zinc concentration values (year 2007) measured in the clean gas of five rotary kilns.

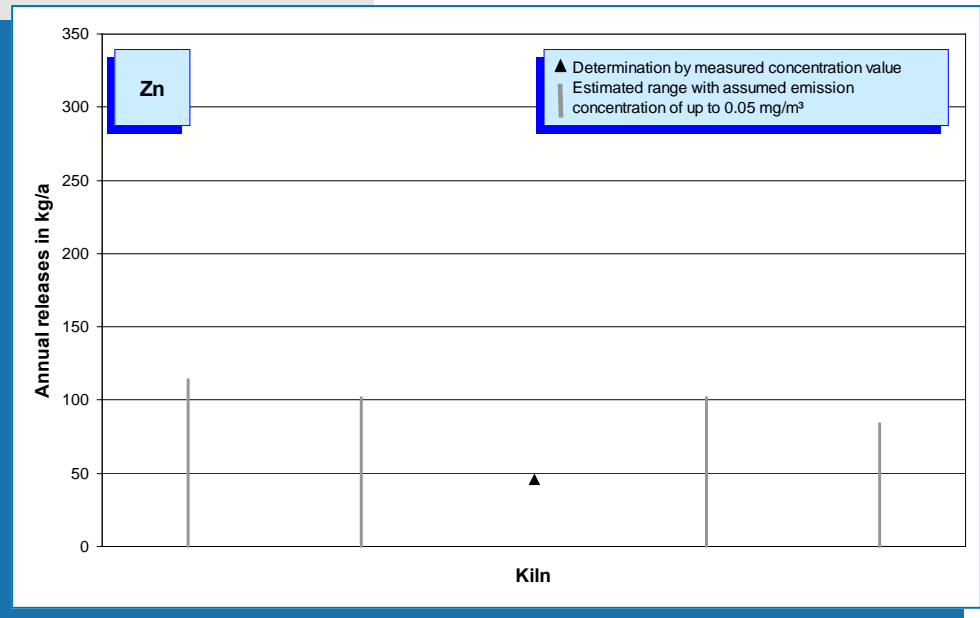


Fig. 5-58: Zinc emissions (annual releases in 2007) of five rotary kilns.

If the values measured are below the detection limit, the releases can only be estimated. In these cases, the range of possible emissions is represented by a broken line, the upper limit of which was calculated using a concentration of 0.05 mg/m^3 .

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