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COMPARATIVE ANALYSIS OF THE ENVIRONMENTAL IMPACTS OF ALUMINUM SMELTING TECHNOLOGIES

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Abstract

This paper focuses on the global warming potential (GWP) of primary aluminum production analyzing the hotspots of greenhouse gas (GHG) emission. The major GHG emission of primary aluminum production is caused by aluminum smelting. Inert anodes or non-consumable anodes are considered as a solution to mitigate GHG emission of the Hall-Héroult process.

A comparative cradle-to-gate life cycle assessment (LCA) was conducted to estimate the environmental impact of primary aluminum production considering conventional and inert anode smelting, including the production technology of the anodes themselves as well as the influence of the energy mix used to produce the electrical power.

Introduction

The major greenhouse gas (GHG) emission of primary aluminum production is caused by aluminum smelting due to the use of carbon anodes and the high electrical energy consumption of the Hall-Héroult process. However alumina and anode production have also a significant share in the GHG emissions.

Inert anodes or non-consumable anodes are claimed to be a revolution of the Hall-Héroult process, as retrofitting existing cells with such anodes will lower GHG emission and may reduce energy consumption as well. Inert anodes are therefore considered as a solution to mitigate the global warming potential (GWP) of the Hall-Héroult process reducing CO, CO_2, SO_2, Perfluorocarbons (PFC) and Polycyclic Aromatic Hydrocarbons (PAH) emissions.

The GWP of primary aluminum production is significantly influenced by the source of electrical power, as half or even more of the GWP can be derived from power generation.

Are inert anodes really favorable from a global environmental point of view? What is their effect on GWP and other environmental impacts of primary aluminum production in the light of the source of power generation?

To answer these questions a simplified comparative cradle-to-gate life cycle assessment (LCA) was conducted to estimate the environmental impact of primary aluminum production considering traditional and inert anode smelting, including the production technology of the anodes themselves as well as the influence of the energy mix used to produce the electrical power.

Theoretical Considerations

A simplified "cradle to-gate" LCA model was built focusing on the hot spots of GHG emissions thus excluding some processes of the complete "cradle-to-gate" life cycle of primary aluminum production. The following processes were considered:

- Bauxite mining
- Alumina production
- Anode production
- Aluminum smelting
- Ingot casting
- Power generation

The comparative LCA was conducted considering traditional anodes and inert anodes in the light of the source of power generation. Beside electricity intensity [kWh/kgAl] the source of electrical power is a critical parameter that can significantly influence the environmental impact of primary aluminum production.

Unlike most other manufacturing industries where the electrical power usually comes from a general grid, the primary aluminum smelting companies get their electrical power either through purchasing directly from electric utility companies or through building and owning their own power generation facilities near which the smelting facility itself is usually located [1]. To analyze the effect of the source of electrical power, different energy mixes were considered in this study.

Anodes

Traditional Anodes

The traditional consumable carbon anodes on one hand reduce the electrical energy required in Hall-Héroult process, as the thermal energy of carbon burning to CO_2 saves electrical energy, thus the theoretical minimum voltage necessary to produce 1 kg aluminum considering the ohmic resistances of the cell and the heat losses is only 4,2V. That corresponds to 13,18 kWh for a hypothetical 200 kA cell operating at 95% CE, 960°C, 10% alpha alumina, and one-third alumina saturation [2]. There are two types of anodes used in the smelting process: Søderberg and prebake.

Søderberg Anodes

Søderberg design uses a single anode, which covers most of the top surface of a reduction cell. Anode paste is fed to the top of the anode and as the anode is consumed in the process, the paste feeds downward by gravity. Heat from the pot bakes the paste into a monolithic mass before it gets to the electrolytic bath interface [3].

Prebake Anodes

The prebake design uses prefired blocks of solid carbon suspended from metallic anode beams. The anode beams both hold the anodes in place and carry the current for electrolysis. Baking furnace technology has evolved from simple pits that discharged volatiles to atmosphere during the baking cycle to closed loop type designs that convert the caloric heat of the volatile into a process fuel that reduces energy consumption for the process [3]. Prebaked anodes need to be replaced during the electrolysis process when approximately one-fourth remains of the original size [4].

There are several harmful emissions during traditional anode production and consumption in the electrolysis process. Fluorides arise not just from the molten bath, but from recovered anode butts which are recycled within prebake anode production. PAH, including benzo-a-pyrene, are air emissions generated from the basic anode production process and from anode consumption as well, along with CO_2 and CO. PFCs are generated during anode effects. SO_2 is generated from consumption of anode material as well as particulates and NOx from fuel combustion [5]. Moreover, the anode changing process causes not only excess emissions in the potroom, but it is the greatest disturbance of the operation of the cell [2].

Inert Anodes

Retrofitting existing cells with inert anodes will cause a voltage penalty in the cell that results in higher energy consumption, namely 5,11V that corresponds to 16,03kWh for a hypothetical 200 kA cell operating at 95% CE, 960°C, 10% alpha alumina and two-thirds alumina saturation. On the other hand cells equipped with inert anodes will not emit any CO_2 and CO from the electrolysis process, and there will be no emissions of PFCs, PAH, or SO_2. The fluoride and dust emissions will be reduced considerably in the potrooms. The emissions from hot carbon anode butts into the potroom after anode changing will be eliminated as well. Inert anode cells should never have anode effects (if they had one, the anode material would dissolve rapidly). The only regular automatic work done on these cells will be alumina feeding and anode-beam adjustment, however, the use of aluminum-wetted and drained cathodes eliminates the need for anode adjustments. The main manual work will be metal tapping.

Inert anodes will not remove all the environmental problems from the electrolysis process. The fluoride-containing electrolyte will still generate HF (g), and vaporization of $NaAlF_4$ (g) will continue. In addition, alumina dust may still be a problem inside the potrooms of many smelters. The workers' exposure to fluorides, dust and heat, as well as local air pollution will remain; but at a considerably lower level [2].

There are three types of inert anodes considered for retrofitting existing cells.

Ceramic Anodes

Initially most of the inert anode research focused on ceramic materials because of their chemical stability. A typical material that has been the subject of extensive research was tin oxide, usually doped with Sb_2O_3 and CuO [6].

Cermet Anodes

These anodes consist of a mixture of ceramic phase and a metal phase. Cermet anodes are attractive since they combine the advantages of ceramics that are desirable for their chemical inertness and metals that are desirable for their high electrical conductivity and mechanical properties. Cermet anodes represent the Alcoa approach, and include sintered nickel oxide, iron oxide and copper [6,7].

Metallic Anodes:

Metals or alloys have several advantages compared to ceramic materials because they are easy to manufacture, non-brittle, good conductors, and provide good electrical connections. But metals tend to be chemically unstable in the presence of oxygen and high temperatures, so it is crucial that the metals remain permanently covered with a coherent, relatively thin self-repairing oxide layer [6,7].

After laboratory tests it was realized that ceramic anodes are not suitable for the Hall-Héroult process due to their limited electrical conductivity, weak thermal shock resistance and the limited manufacturing capacity of industrial scale ceramic anodes.

During recent years research focused on the development of $NiFe_2O_4$-based cermets and NiFe-based alloys. Alcoa and Chinese scientists chose cermet, while other western laboratories and Rusal chose the metal alloy solution. After developing a new cell design Rusal is convinced it can improve NiFe-alloy manufacture by 2015, and then equip the first industrial electrolysis cell of 100 kA with alloyed anodes, which should be in operation by 2017. [8]

To achieve all the benefits of inert anodes from the global environmental point of view it would be desirable to maintain the original energy demand of the Hall-Héroult process, as the increased energy demand has to be generated with the existing energy mix. The excess emissions of power generation, and thus the possible increase of environmental impact of primary aluminum production with inert anodes, strongly depend on the composition of the energy mix used to generate the electrical power.

Electricity mixes

Two extreme electricity mixes were considered in this study to emphasize the important role of the source of electrical power on the environmental impact of primary aluminum production. The renewable energy mix is based on hydro power and fossil energy mix is based on coal.

Hydro Based Power Generation

Hydro power is one of the most reliable and large scale renewable power sources, therefore it is preferred for electricity generation. The chosen electricity mix is based on data of Statistics Canada for Quebec, year 2010 [10, 11, 12]. The composition of the hydro based energy mix is:

Heavy fuel oil	0,2%
Natural gas	0,18%
Nuclear	1,79%
Biomass	0,47%
Wind	0,2%
Hydro	97,16%

Coal Based Power Generation

Coal burning has the highest GWP and is therefore the least favorable solution for electricity production. The chosen electricity mix was based on IEA statistics for China year 2010 [9]. The composition of the coal based energy mix is:

Hard coal	76,7%
Coke gas	0,61%
Heavy fuel oil	0,7%
Natural gas	0,9%
Nuclear	2,06%
Biomass	0,07%
Photovoltaic	0,01%
Wind	0,42%
Hydro	18,6%

Electricity Mix for Smelting and Casting.

As the primary aluminum smelting companies purchase the electrical power directly from electric utility companies, or in special situations have their own power generating system, special energy mixes were used within fossil and renewable based power generation for smelting and casting. The renewable based energy mix for smelting is based on the aluminum industry of Quebec, where practically all the electrical power consumed by smelting is produced from hydro power. The fossil based energy mix for smelting comes from IAI statistics of China where 90% of the electricity is generated from coal and the remaining 10% from hydro power [13].

LCA Model

A simplified "cradle-to-gate" LCA model was built to estimate the environmental impact of primary aluminum production considering traditional and inert anode smelting, including the production technology of the anodes themselves, as well as the influence of the energy mix used to produce the electrical power. The model was based on LCI reports of IAI for the primary aluminum industry [3, 5]. Figure 1. shows the flow chart of considered processes of the LCA model of primary aluminum production.

This study is focusing on the hot spots of GHG emissions, thus not all the processes of the "cradle-to-gate" life cycle are included in the analysis, such as the production of some materials of alumina, aluminum, anode and ingot production or water use and fuel production of the system. The dotted line shows the system boundary on Figure 1.

However a simplified "cradle-to-gate" analysis was conducted, the comparative analysis focused only on the effect of different anode types and sources of electrical power. Table I. shows the considered scenarios. The base of comparison was the electrolysis with a prebaked anode. In the case of inert anodes the following two sub-scenarios were investigated:

I. pessimistic: voltage penalty cannot be eliminated, thus the electricity consumption of the cell is higher
II. optimistic: electricity consumption of the cell is the same as one of with a carbon anode

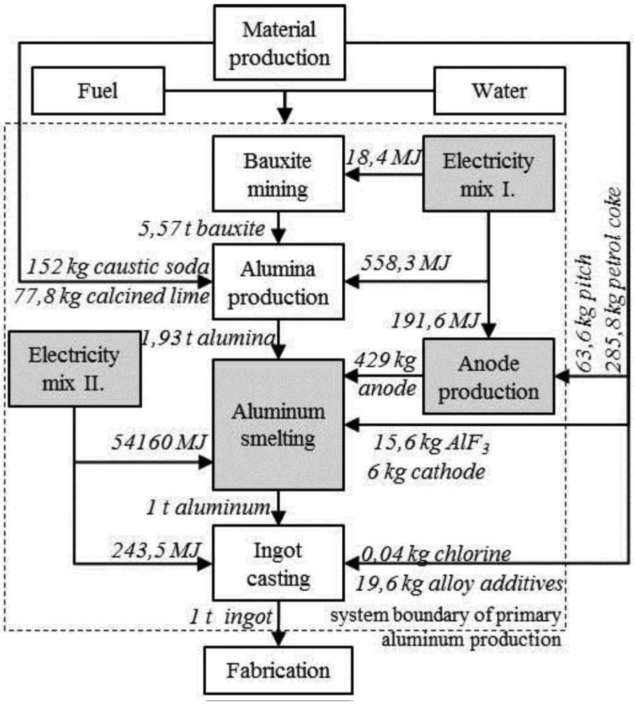

Figure 1. Unit process flow chart of primary aluminum production with prebake anode

Table I. Scenarios of comparative LCA

Scenario	electricity mix	anode type
1	hydro based	prebake
2		Søderberg
3		inert I.
4		inert II.
5	coal based	prebake
6		Søderberg
7		inert I.
8		inert II.

Life Cycle Inventory (LCI)

To determine the environmental impact of primary aluminum production all material and energy flows (in- and outputs) through the "cradle-to-gate" life cycle of primary aluminum production need to be collected and quantified. The LCI analysis was based on previous LCA studies of IAI, AA and EAA [1, 3, 5, 7, 14, 15]. The emission factors of the energy mixes were based on different country specific LCI – LCIA data of ProBas [16].

In case of conventional anodes the mass and energy flows are based on IAI and EAA LCI data for primary aluminum industry year 2010 [3,14, 15].

In the case of inert anodes a casted 55% Cu – 20% Ni – 20% Fe alloy was used in this study, as Rusal is convinced it will have the first industrial electrolysis cell of 100 kA with alloyed anodes in operation by 2017 [8]. Rusal claims that Cu-Ni-Fe alloys are the most suitable material for the inert anode. [17]. As no LCI data was available for cells equipped with inert anodes, the factors of mass and energy flows were determined considering the following assumptions:

- Required inert anode mass was estimated from the necessary area of the conventional anode considering the different shapes of conventional and inert anodes assuming similar current density.
- Rusal tests showed less than 2 cm/year wear rate of inert anodes [17], therefore an optimistic one year lifetime of the inert anode was considered.
- Anode change related emissions were lowered proportionally to the anode change frequency, but not completely eliminated.
- No change was made in the cathode and in other material needs of the smelting process.

Results and Discussion

Life Cycle Impact Assessment (LCIA) results are presented for 1 metric ton of primary aluminum ingot. Unlike the LCI, which only reports sums for individual emissions, the LCIA includes methodologies (CML [18] and UBA [19]) for weighting and combining different emissions into a metric for the potential impacts of significant LCI. Through LCIA the environmental impacts of primary aluminum production were categorized [1]. Table III. shows the results of the analyzed impact categories.

The GWP is represented in the light of primary energy demand (PED) of primary aluminum production. The GWP is a measure of the emission of greenhouse gases (GHG) such as CO_2, PFC, and CH_4, and is expressed as kilogram of CO_2-equivalent and spans a time horizon of 100 years. GHG emissions are found to cause an increase in the absorption of radiation emitted by the sun and reflected by the earth, magnifying the natural greenhouse effect [1, 14].

The PED is a measure of the total amount of primary energy extracted from the earth, including both non-renewable and renewable resources, taking into account the energy needed for extractions and fuel conversions, the efficiency of electrical power generation and heating methods, as well as transmission and distribution losses. Thus PED is the amount of total energy that primary aluminum production consumes. It is measured in primary energy format [1].

The PED of 1 metric ton of primary aluminum ingot is mainly affected by the source of electrical power. The PED is only 1,05 MJ_{pe}/MJ_e for hydroelectric power while it is around 2,76 MJ_{pe}/MJ_e for coal based electrical power, therefore the PED results are nearly two and a half times higher with coal based electricity mixes. Table III. shows that in the case of inert anodes the PED is higher than the PED with prebake anodes even without the voltage penalty.

The LCIA results in Table III. show that the GWP related to 1 metric ton of primary aluminum ingot is significantly affected by the structure of the source of electrical power.

In the case of prebake anodes the breakdown of GWP by individual processes is shown in Figure 2.

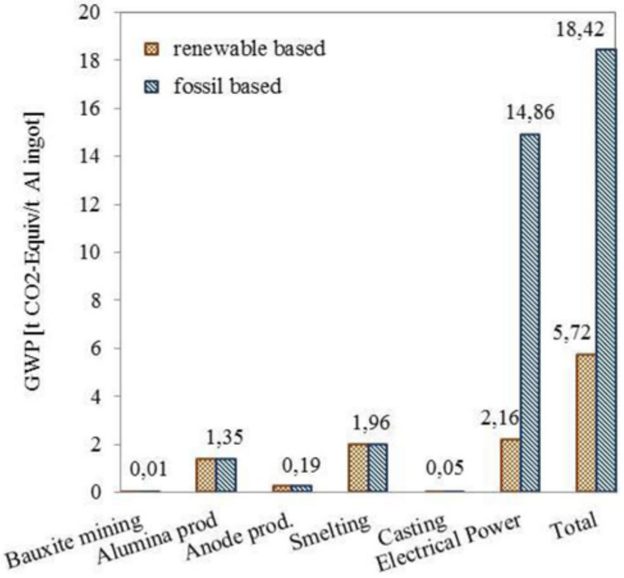

Figure 2. GWP of primary aluminum production with prebake anode

The total GWP is 5,72 t CO_2 equivalent with renewable based energy mix;38% of total GWP comes from power generation. The next largest contributor is smelting with a 34% share of total GWP. Alumina production has significant share too as it is responsible for 24% of total GWP. Anode production has less than a 4% share of total GWP.

The total GWP and the rates are different with fossil based electricity. The total GWP is much higher; 18,42 t CO_2 equivalent. Power generation is still the largest contributor but with a much higher share (81%) of total GWP. The net GWP of smelting is still 1,96 t CO_2 equivalent but its share is only 11% while the share of alumina production decreases to 7% while anode production has only a 1% share of total GWP.

Table III. LCIA results of the considered impact categories of primary aluminum production

Scenario	GWP $t\ CO_{2,eq}/t\ Al$	PED GJ/t Al	AP $kg\ SO_{2,eq}/t\ Al$	EP $kg\ PO_4^{3-}{}_{,eq}/t\ Al$	POCP $kg\ C_2H_{4,eq}/t\ Al$
1	5,72	58,63	23,04	0,52	3,98
2	6,62	66,65	24,03	0,60	4,52
3	4,30	74,84	48, 96	1,23	3,39
4	3,88	63,47	48,84	1,20	3,20
5	18,42	141,40	71,60	6,28	59,49
6	21,10	160,98	79,36	7,16	67,78
7	19,47	173,65	106,90	8,10	69,65
8	16,54	145,99	97,24	6,94	58,84

From the point of view of GWP, not only the direct GHG emission of smelting, but the indirect emission of electrical power generation is equal to or even more important. The indirect GHG emission of anode production has very low share in the total GWP of aluminum production. Therefore the comparative analysis focused only on the GHG emission of smelting and power generation.

Table IV. shows the GWP of smelting and power generation in conventional and inert anodes. The GWP of smelting is practically zero in the case of inert anodes, as no GHG emission is produced. If the voltage penalty can be avoided with modification of the design of the electrolysis cells, then inert anodes are no doubt favorable from the point of view of global warming. But if the voltage penalty leads to increased electricity demand, depending on the source of electricity, the GWP can be higher than that with using prebake anodes. With fossil based electricity the GWP of smelting with inert anodes can be 5% higher than that of prebake anodes, but on a renewable based energy mix the GWP is approximately 40% lower even with the voltage penalty.

Table IV. GWP of smelting and electricity generation, [t CO_2 equivalent]

Scenario	GWP of smelting	GWP of power generation	total GWP
1	1,96	2,16	4,12
2	2,76	2,46	5,22
3	0,00	2,58	2,58
4	0,00	2,15	2,15
5	1,96	14,86	16,82
6	2,76	16,94	19,70
7	0,00	17,74	17,74
8	0,00	14,82	14,82

Although the GWP is the most demanded environmental impact of the energy sector, the primary aluminum production was characterized with other environmental impacts as well. Table III. shows AP, EP and POCP of primary aluminum production in the examined scenarios. All environmental impacts are highly affected by the source of electrical power.

The acidification potential (AP) is a measure of emissions that cause acidifying effects to the environment, and is expressed as kilogram SO_2-equivalent. The major acidifying emissions are NOx and SO_2, as well as ammonia emissions that lead to ammonium deposition. Hydrogen fluoride and hydrogen chloride also have their share in the total AP of primary aluminum production [1]. Table III. shows that the total AP of primary aluminum production can be up to three times higher with a fossil based energy mix, as the AP of fossil based power generation is two orders of magnitude higher than that AP of renewable based power generation. The AP of inert anode production is one order of magnitude higher than the AP of conventional anode production. Thus the total AP of primary aluminum production with inert anodes can be more than two times higher than the total AP with prebake anodes; depending on the source of electrical power. Therefore inert anode use is not favorable from the point of view of AP.

The eutrophication potential (EP) is a measure of emissions that cause eutrophying effects to the environment and is expressed as kilograms of phosphate equivalent. The eutrophication of aquatic systems is primarily caused by excessive inputs of nitrogen and phosphorus. Over-fertilization can cause excessive growth of algae, thus reducing the oxygen level and damaging the ecosystem. Over-fertilization of soil is related to the increased growth of biomass that can change the biodiversity of the soil habitat [1, 14]. Figure III. shows that the total EP of primary aluminum production is one order of magnitude higher with fossil based energy mixes due to the higher eutrophication impacts of fossil based power generation. Inert anode use is not necessarily favorable from the point of view of EP as the total EP with inert anodes, depending on the power mix, can be up to 1,82 kg phosphate equivalent (29%) higher than the total EP with prebake anodes.

The photochemical ozone creation potential (POCP) is a measure of precursor emissions that contribute to low level smog (summer smog), produced by the reaction of NOx and volatile organic compounds (VOC) under the influence of ultra violet light. It is expressed as kilogram ethylene-equivalent [1, 14]. As total EP, total POCP is also one order of magnitude higher with a fossil based energy mix. Inert anode use is favorable with a renewable based energy mix as the total POCP is at most 85% of the POCP of prebaked anode use, while with a fossil based power mix the total POCP with inert anodes can be 10,16 kg ethylene-equivalent (17%) higher due to the voltage penalty.

In addition to environmental impacts, the human health hazard of primary aluminum production needs to be considered as well. The human toxicity potential (HTP) is a measure of toxic emissions that have impacts on human health and can cause carcinogenic or non-carcinogenic diseases. It is expressed as kilogram of 1,4-dichlorobenzene-equivalent [20]. The referenced IAI, AA and EAA LCA studies had no information about human toxicity, nor did they contain sufficient information to estimate HTP, thus the LCI data of primary aluminum production of ProBas [16] was used to estimate HTP. The calculated total HTP of 1 metric ton of primary aluminum ingot produced with conventional smelting technology is 17100 kg 1,4-dichlorobenzene-equivalent. The calculated HTP of 1 kg of the investigated metallic inert anode production is 282 kg 1,4-dichlorobenzene-equivalent. Depending on the actual inert anode demand of the smelting process, the estimated HTP of metallic inert anode production can vary from ten up to tens of thousands of kilograms of 1,4-dichlorobenzene-equivalent. Thus the HTP of metallic inert anode production itself is comparable to the total HTP of 1 metric ton of primary aluminum ingot produced with conventional smelting technology.

Conclusion

This study focused on the global warming potential of primary aluminum production analyzing the hotspots of greenhouse gas emission.

The LCIA results of primary aluminum production considering traditional and inert anode smelting, including the production technology of the anodes themselves as well as the influence of the energy mix used to produce the electrical power, showed that inert anodes can be an effective solution to lower the global warming potential of primary aluminum production, as the greenhouse gas emission of smelting with inert anodes is practically zero. However, due to a voltage penalty the indirect greenhouse gas emission of electrical power generation can be higher compared to conventional smelting technology, depending on the source of electrical power. Thus the actual environmental impact of primary aluminum production with inert anodes highly depends on the source of electrical power.

Cell modifications to maintain or lower the original electrical power demand of a smelter, even with a hydro based energy mix, may not be enough to achieve an environmentally beneficial primary aluminum production. Although the global warming potential and the photochemical ozone creation potential of primary aluminum production with inert anode smelting can be lower, the acidification potential, eutrophication potential and human toxicity potential may be higher when compared to the primary aluminum production with conventional smelting technology.

Acronyms and Chemical Compounds

AA	The Aluminium Association
AP	Acidification Potential
CML	Institute of Environmental Sciences, Leiden University
CO	Carbon monoxide
CO_2	Carbon dioxide
CuO	Cupric oxide
EAA	European Aluminium Association
EP	Eutrophication Potential
GHG	Greenhouse gas
GWP	Global Warming Potential
HF	Hydrogen fluoride
HTP	Human Toxicity Potential
IAI	International Aluminium Institute
IEA	International Energy Agency
LCA	Life Cycle Assessment
LCI	Lice Cycle Inventory
LCIA	Life Cycle Impact Assessment
$NaAlF_4$	Sodium fluoroaluminate
NiFe	Nickel-iron
$NiFe_2O_4$	Nickel ferrite
NOx	Nitrogen oxides
PAH	Polycyclic Aromatic Hydrocarbons
PED	Primary Energy Demand
PFCs	Perfluorocarbons
POCP	Photochemical Ozone Creation Potential
Sb_2O_3	Antimony trioxide
SO_2	Sulfur dioxide
UBA	Umweltbundesamt
VOC	Volatile Organic Compounds

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