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Atmospheric SF₆: Trends, Sources, and Prospects

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Sulfur hexafluoride (SF₆) is the most potent greenhouse gas known. Its atmospheric concentration has increased by 2 orders of magnitude since industrial production started in 1953. Once released into the atmosphere, SF₆ will only be removed exceedingly slowly due to its atmospheric lifetime of about 3200 yr. These features have brought SF₆ into the climatic impact discussion aimed at reduction of emissions. The dominant uses of SF₆ are in gas insulated switchgear (GIS) and in blanketing or degassing molten aluminum and magnesium. From 1978 onward, the rapidly growing global SF₆ burden is well-documented by atmospheric observations. Concerning the SF₆ applications responsible for that, a vast range of speculations is circulating. The underlying information gap—which preempts the design of any reduction program—will be bridged for the first time. Recently reported global sales of SF₆ for end-use applications form the basis of this investigation but need various revisions. The good agreement between emissions modeled out of revised sales data and atmospheric observations since the 1970s allows the extrapolation of the atmospheric SF₆ record further back to the 1950s. Our analysis also shows that the natural background of SF₆ is lower than 0.04 ppt. A geographical analysis of SF₆ uses suggests that the North American market needs to be better specified. With certain technological efforts, a global reduction of SF₆ releases of up to 90% seems feasible, equivalent to 5500 t for the year 1995, and climatically equivalent to 132 million ton of CO₂.

Introduction

Sulfur hexafluoride (SF₆) is an extremely stable gas with unique physical and chemical properties that make it ideally suited for some specialized applications. It is a heavy, inert, nontoxic, and nonflammable gas. Worldwide, the dominant uses of SF₆ are in gas-insulated equipment for electrical transmission and distribution systems and in blanketing or degassing of molten reactive metals such as magnesium and aluminum. The industrial production of SF₆ began in 1953 with the market introduction of SF₆-insulated circuit breakers in the United States. Since then, production has grown steadily but at an increased rate since 1972 when the use of SF₆ in gas-insulated switchgear (GIS) became widespread. Releases from these “closed” and other more recent “open” applications have increased the atmospheric burden from virtually zero in 1953 to 85 700 t of SF₆ in 1995.

Atmospheric measurements reveal a clear and distinct increase of the global mean surface concentration of SF₆,

from 0.6 ppt (10⁻¹² mol/mol in dry air) at the beginning of 1978 to 4 ppt today. Being a strong electron capturer, extreme low detection limits (<0.01 ppt) are achieved. A concentration increase of approximately 7%/yr, due to main sources located in the industrialized northern midlatitudes, generates distinct vertical and meridional concentration gradients in the atmosphere. These features have made SF₆ one of the most attractive tracers for atmospheric transport and mixing studies (cf. refs 1–8). Meanwhile a large database of atmospheric measurements is available, which is essential for the present study. Despite the usefulness as an atmospheric tracer, the potential climatic impacts of SF₆ are troubling.

SF₆ is very long-lived in the atmosphere, absorbs effectively in radiatively important windows in the infrared region (9, 10), and thus is a very efficient greenhouse gas. According to refs 11 and 12, the atmospheric lifetime of SF₆ is most likely about 3200 yr, determined solely by atmospheric destruction processes that take place above 60 km. Oceanic uptake rates are negligible due to the low solubility of SF₆ in water combined with the relatively slow oceanic deep-water formation rate. No microbiological process is known that could destruct SF₆ in soils or plants at an appreciable rate. This all implies an irreversible accumulation of any released SF₆ for thousands of years, with sources outweighing sinks by orders of magnitude. The Intergovernmental Panel on Climate Change (IPCC) has adopted the use of a 100yr time horizon merely to express the Global Warming Potential (GWP) of SF₆ relative to CO₂. It estimates the GWP₁₀₀ for SF₆ to be about 23 900 times larger than that of CO₂ (13), which is by far the highest value evaluated by this panel. The actual situation is only less dramatic because of the present low concentrations of SF₆ being a factor 10⁸ below that of CO₂. Hence to date the contribution of all atmospheric SF₆ to the total man-made global warming effect of CO₂ is only 0.1%. The radiative forcing of the present SF₆ emissions, ≈6500 ton/yr, corresponds to 0.155 GtCO₂/yr (using GWP₁₀₀ = 23 900) or 0.7% of the present CO₂ emissions of 22 GtCO₂/yr. This is pretty small but already about 14% of the reductions agreed at the Kyoto Summit on Climate Change, where SF₆ was included into the basket of the six “greenhouse gases” for negotiation: CO₂, CH₄, N₂O, HFCs, PFCs, and SF₆. Anyhow, it is desirable that users of SF₆ establish a policy aimed at minimizing the—in contrast to CO₂—virtually irreversible releases of SF₆ to the atmosphere. The United Nations’ Framework Convention on Climate Change has encouraged the assessment and regulation of SF₆ emissions (14). In the proceedings of a conference, organized in this context by the United States Environmental Protection Agency (12), it is recognized that (a) the only hard data to date are the atmospheric SF₆ observations; (b) it remains unknown where most of the observed annual emissions are coming from; and (c) a prerequisite for a proper policy is a true and accurate picture of how much is produced and where the products go.

The present study includes several goals: (a) On the basis of observations, the long-term trend of SF₆ in the atmosphere is described first, since it serves as almost ideal tracer for studying global scale tropospheric mixing and serves further as dating reference for mixing and transport studies in linked compartments such as the stratosphere, the hydrosphere, and the cryosphere. (b) Reported SF₆ sales data are combined, evaluated, and revised. (c) Revised sales are split up into emitting applications and those where SF₆ is banked, to match the observed annual atmospheric increases since the 1970s and the accumulation of man-made emissions

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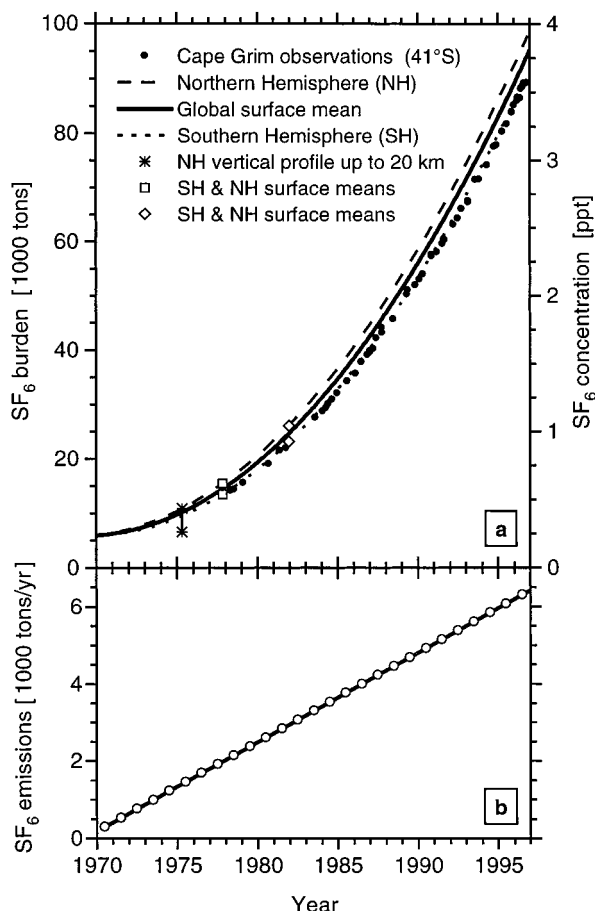


FIGURE 1. (a) Atmospheric history of SF_6 as inferred from observations at Cape Grim (3, 15). Also shown are mean hemispheric surface concentrations reported by Singh et al. (16, 17), which have been scaled by a factor of 1.16 and 2.00 for December 1981 and September–December 1977, respectively. From the mean NH vertical profile reported by Krey et al. (18), the value for <10 km and at 20 km altitude is shown, scaled by a factor of 1.45. Fit curves show the long-term trends of mean surface concentrations, globally and for both hemispheres. A second scale on the left side gives the conversion of global mean surface concentrations in ppt to the corresponding atmospheric burden in 1000 t of SF_6 . (b) Annual SF_6 release rates to the atmosphere as inferred from the trend of the global burden in panel a.

since the 1950s. (d) The year 1995 is singled out for a geographical market analysis, which suggests a higher SF_6 demand by the magnesium industry and reveals that some application sectors within the North American market need further clarification. (e) The potential of future emission reductions is addressed using the 1995 market structure as reference.

Databases

Observed Atmospheric SF_6 Concentrations. The long-term trend of atmospheric SF_6 is best described by measurements on air samples from Cape Grim (Tasmania, 41° S, 145° E), which have been archived since 1978. These data from Maiss et al. (3) are shown in Figure 1a together with an update for the years 1995 and 1996 (15). Both data sets are based on analyses performed at the University of Heidelberg (Institut für Umwelphysik) and refer to the same calibration scale. By chance, the observed long-term trend seems to follow closely a single functional quadratic time dependency over a time period of more than 20 yr. Such a least-squares fit—with terms and formalism as used by ref 3—was performed with the extended data set of Figure 1a. But by introducing

the parameter $c_0(t_0)$, the fit was no longer forced to zero in times before 1978. The result for the Cape Grim data set is as follows (not shown in Figure 1a):

$$c_{\text{CG}}(t) = c_0(t_0) + u(t - t_0)^2 \quad [\text{ppt}] \quad (1)$$

$$= 0.2373(\pm 0.0344) + 4.628(\pm 0.100) \times 10^{-3} \{t - 1969.91(\pm 0.41)\}^2$$

with time t in years AD (e.g., $t = 1992.0 \Leftrightarrow$ January 1, 1992) and the Cape Grim SF_6 concentration, $c_{\text{CG}}(t)$, in ppt. The derived fit values for parameter u and t_0 differ from that given by Maiss et al. (3) for $c_{\text{SH}}(t)$ since (a) the database is different and (b) the offset c_0 is introduced. The latter betters the whole fit, and the values obtained for c_0 and t_0 indicate that any extrapolation prior to 1978 might be valid back to around 1970 but will not be zero. The SF_6 concentrations in the Northern Hemisphere (NH) are persistently higher when compared to the Southern Hemisphere (SH). This is due to the fact that emissions of SF_6 occur predominantly in the NH and have first to be transported to the SH. From meridional profiles of SF_6 and time-series of SF_6 from other sites at various latitudes (3, 5), linear time-dependent surface concentration offsets with respect to the Cape Grim record can be defined. Although details of such an analysis will be published elsewhere, the global and hemispheric means of these offsets are given by:

$$\Delta c_{\text{NH}}(t) = 11.65 \times 10^{-3}t - 22.95 \quad [\text{ppt}] \quad (2)$$

offset of the NH to Cape Grim

$$\Delta c_{\text{G}}(t) = 6.548 \times 10^{-3}t - 12.90 \quad [\text{ppt}] \quad (3)$$

offset of the global mean to Cape Grim

$$\Delta c_{\text{SH}}(t) = 1.450 \times 10^{-3}t - 2.856 \quad [\text{ppt}] \quad (4)$$

offset of the SH to Cape Grim

Adding these offsets to eq 1 yields long-term trends for SF_6 , both global and for each hemisphere with an error of $\approx \pm 0.005$ ppt (Figure 1a).

The first observations in the NH, which are determined against the present SF_6 calibration scale, are from November 1990 (3). Earlier interhemispheric gradients in Figure 1a are only a back extrapolation of the situation in the 1990s. Also the trend prior to 1978 is extrapolated and needs further evidence. Historical measurements in the 1970s and early 1980s, gathered by Maiss and Levin (1), fit as a whole the picture in Figure 1a. But their considerable scatter, mainly due to untraceable calibration differences, renders them virtually unuseable. Exceptions are three historical measurements of concentration differences (Figure 1a) that can provide, after recalibration to the actual scale, accurate additional information: Two interhemispheric differences reported by Singh et al. (16, 17) fit well into the present interhemispheric trend analysis for November 1977 and December 1981. Next, a mean vertical profile up to 20 km altitude reported by Krey et al. (19) for the NH in April 1975 is scaled to the NH trend using its tropospheric value. Then, applying the same factor to the lower concentrations at 20 km altitude yields a value equal to the surface trend about 5 yr earlier. Since such a stratospheric time delay is reasonable (8), the quadratic trend extrapolation prior to 1978 gets some further indirect support. In summary, it can be stated that a clear long-term trend for SF_6 , globally and for each hemisphere, has been established. The global mean surface concentration shows a strong increase from around 0.24 ppt at the beginning of 1970 to 3.81 ppt at the end of 1996.

Atmospheric SF₆ Inventory. An total atmospheric inventory can be obtained by multiplying the global mean surface concentrations (in ppt) with the molar weight of SF₆ and with a fraction $\beta \approx 93\text{--}96.5\%$ of the total number of moles in the atmosphere (1.771×10^{20}). Because SF₆ is inert below the mesosphere, β differs from unity approximately by half the tropospheric increase rate ($\approx 14\%/yr$ in 1978; $\approx 7\%/yr$ in 1995) and thus compensates the time-lag of concentrations at higher altitudes. As a rule of thumb, the global surface mean values in ppt have to be multiplied by a factor of 25.0 in order to get the atmospheric SF₆ mass inventory in Gigagram (Gg) or thousand metric tons. This conversion is described by a second scale in Figure 1a. It is accurate to within $\pm 1\%$ for the time since 1988 and slightly overestimates the inventory (at maximum by 3.5%) prior to 1988. Until the end of 1996, a cumulative mass of 95 250 ton of SF₆ was observed in the atmosphere. The derivative of the cumulative record gives the annual SF₆ release into the atmosphere (Figure 1b), which shows a linear increase from 300 ton/yr in 1970 to 6300 ton/yr in 1996. It is a major task in the following sections to match these observed annual rates and their corresponding accumulation by a SF₆ sales data analysis.

SF₆ Sales by End-Use Applications. An independent consulting firm, Science & Policy Services Inc. (SPS) from Washington, DC, was ask by SF₆ producers to conduct a compilation of worldwide SF₆ sales data by end-use markets. The following six companies, inclusive of any subsidiaries and/or joint venture, participated: (a) AGA Chemicals (USA) + Asahi Glass Chemicals (Japan), (b) Air Products & Chemicals (USA) + Air Products Canada (CDN); Air Products PLC (UK), (c) AlliedSignal (USA) + AlliedSignal Canada (CDN), (d) Ausimont (Italy), (e) Kanto Denka Kogyo (Japan), (f) Solvay Fluor und Derivate (Germany).

These major manufacturers of SF₆ (missing are mainly Russian and Chinese manufacturers) reported annual sales for the period 1961–1996 following pre-defined end-use categories (for a better understanding of these categories, corresponding major applications are given in parentheses and will be discussed in greater depth below). (a) Utilities and Accelerators (UA) (refill and leakage compensation of SF₆-insulated electrical installations), (b) Original Equipment Manufacturers (EQ) (switchgear manufacturers), (c) Magnesium Industry (MI) (blanketing molten magnesium) (d) End-Use Utilizing SF₆ Adiabatic Properties (AP) (filling of tires and soles of sport shoes), (e) Electronics Industry (EI) (plasma-etching of tungsten), (f) All Other Uses (OU) (filling of sound-insulating windows, degassing of molten aluminum), and (g) Additional quantities not specified (AD).

Data on these applications have been recently published by SPS in aggregated form (19) and are shown in Figure 2 as time records. This enables for the first time an insight into market shares and their temporal development. Sales for utilities and accelerators are strongly dominant (46% mean for the period 1992–1996), followed by sales to switchgear manufacturers (33%), whereas all other applications share the remaining 21% of the market among each other (5% MI, 4.5% AP, 3.5% EI, 8% OU). At a first glance, the commonly cited figure of “80% of production going into the market of electrical equipment” seems to be supported but will questioned later. The above-noted preliminary mean end-use fractions for the period 1992–1996 have been used to split up the additional Chinese and Russian production among given categories, in lieu of no other reliable data being available. Solvay (20) estimates the total annual sales of these two countries to have increased from 400 ton in 1992 to 880 ton in 1996 (Figure 2).

For the years 1966–1974, the SPS study also gives additional quantities for which reporting companies cannot provide a breakdown by end-use. Since these quantities are larger than any nonelectrical application at that time, it is

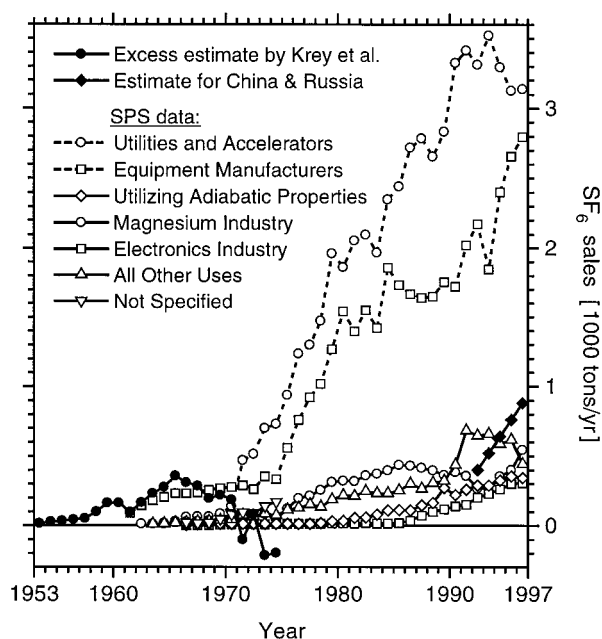


FIGURE 2. Annual sales of SF₆ as reported by SPS (19) for end-use applications described in the legend. Additionally shown are estimates for the total of the Chinese and Russian production (20) and from 1953 to 1974, an earlier global production estimate by Krey et al. (21) expressed as excess with respect to the total of the SPS data.

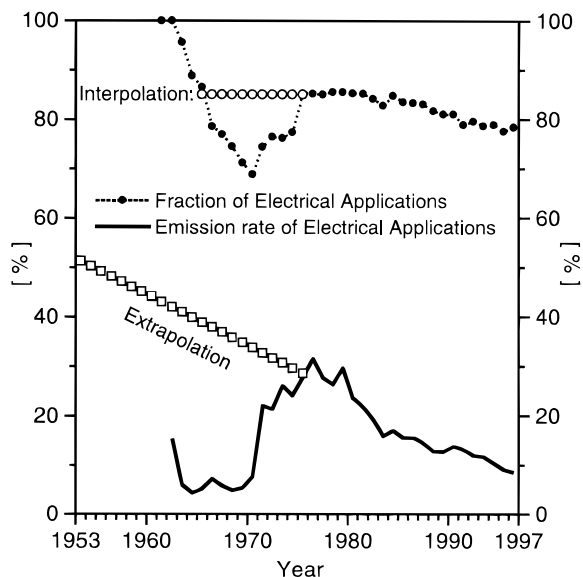


FIGURE 3. Rates and fractions as derived from the original SPS data set and their assumed inter- and extrapolations used for a revision of given data (see text for a detailed discussion).

most probable that they belong mainly to the sector of electrical applications (UA + EQ). In Figure 3, a time-series of the fraction of electrical applications (UA + EQ to total sales) provides additional evidence. It starts in 1961 when the switchgear industry, the only end-use at that time, absorbed 100% of the SF₆ production and continues to decline to its present value of 79%. Exactly for the period of the nonspecified quantities, 1966–1974, this decline shows an unrealistic discontinuity, which, the other way round, allows us to split up the not specified additional quantities: It is reasonable to assume that, like before and after this period, around 85% of the sales have gone into electrical applications (interpolation indicated by open circles in Figure 3). Consequently, the nonspecified quantities were distributed

between the pool of (UA + EQ) and the pool of OU in such a way that the 85% assumption is fulfilled.

Another conspicuous point in Figure 2 is that the UA market is virtually nonexistent prior to 1970, rises sharply in 1970, and dominates thereafter. The ratio of UA sales to the cumulative EQ sales may be identified (as a first approach) with a global mean emission rate of all quantities purchased for and banked in insulated electrical equipment. A time-series of such an emission rate of electrical applications, calculated from the original SPS data, is included in Figure 3. It declines from 1976 onward approximately from 30% to 10%, which can be seen as a result of an improving handling and/or tightness of gas-insulated installations. However, the ratio's drop prior to 1976 has no technological explanation and is probably introduced by a different splitting between UA and EQ in the early years. At the beginning of the EQ market, the entire maintenance was provided by the equipment manufacturers themselves. Only later on, when operators of the larger utilities started to purchase SF₆ for refill and leakage compensation by their own, does the UA market appear in books. To correct for this, the total of UA + EQ will be redistributed among the single pools under the constraint, where the resulting emission rate of electrical installations equals the assumed back-extrapolation indicated by open squares in Figure 3.

A further shortcoming of the SPS data set is that sale figures do not start at the beginning of industrial production of SF₆ in 1953 and are probably underestimated for the period 1961–1970. Fortunately, in 1975 the Allied Chemical Company (USA) has given another compilation of total SF₆ sales for the period from 1953 to 1974 (21). This historical data set is presented in Figure 2, expressed as excess or additional quantity with respect to the total of the SPS sale numbers. By that, it can be easily derived that the total sales from 1961 to 1970 according to SPS are on average by a factor of 2 lower when compared to the older report. There are some qualitative arguments that speak for the older data set. Prior to 1961, there is no alternative. For the period 1961–1974, it was certainly more feasible to accurately compile sales figures in 1975 and without the political or economical pressure of today. Until 1970, SF₆ was produced virtually only by Allied Chemicals in the United States, and data should be best overviewed by the producer himself. In fact, the old U.S. compilation underestimates the global market (negative excess values in Figure 2 from 1971 onward) exactly at a time when upcoming foreign producers have to be taken into account. So it was decided here to rely on the older data set, at least until 1970. Consequently, the corresponding positive excess quantities in Figure 2 were added to the total of the SPS pools UA and EQ and distributed among these under the constraint assumed for the emission rate in Figure 3.

Results and Discussion

Annual Sales Numbers and the Atmospheric Rate of Increase. The preceding revision of the original SPS data set provides the modified picture given in Figure 4 (and Table 1). The annual sales by end-use are shown now in an additive manner. That enables the comparison of the releases inferred from the atmospheric observations (Figure 1b) with the shares of total sales. The temporal development of the total sales can be roughly divided into two phases: prior to 1972 when the major uses were more or less confined to the American market and after 1972 when industrial uses of SF₆ had spread noticeably worldwide. In this second phase, emissions based on sale volumes can be directly compared with release rates inferred independently from atmospheric observations. Globally, the total sales of SF₆ increased approximately from 1000 ton in 1972 to 8500 ton in 1996. These annual sales are generally larger than the observed increase rates of the

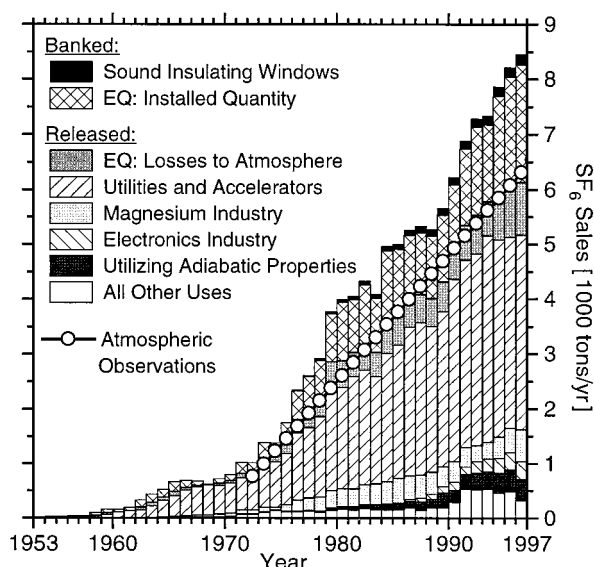


FIGURE 4. Revised sales of SF₆. Annual accumulations differentiated for end-use applications and for banked or released quantities as described by the legend (see also Table 1 for data). The annual release rates inferred from atmospheric observations (Figure 1b) are shown for comparison.

atmospheric inventory, which grew approximately from 760 to 6300 ton/yr over the same time period. Thus, only a fraction of sales has been emitted within the same year.

To match the undisputed atmospheric record, the banked fraction of the total sales must be quantified. In case of refill and of leakage compensation of electrical installations (UA), an equivalent quantity emitted within the same year is a reasonable assumption. Magnesium (MI) and electronics industry (EI) are directly emitting users. In case of tires and sport shoes (AP), some time delay for releases may be given but will be neglected for the moment. The bump of the mixed pool OU in the 1990s (Figure 4) seems to be mainly made up by aluminum degassing and thus is seen as direct emission. The dominant fraction of the remaining OU pool is used for filling sound-insulating windows in Europe. This market is approximately described by a linear increase from zero in 1975 to 350 ton/yr in 1996 (20), from which about one-half is actually banked in windows and the rest is lost during the filling process (22). The various other minor applications in the pool of OU are assumed to be emitted within the same year. In summary, the total of {(reduced OU) + AP + EI + MI + UA} should make up the annual emissions. Figure 4 clearly shows that this second picture (after the full release model) however underestimates the releases inferred from atmospheric observations. That can be corrected when the assumption is given up, where all quantities sold to equipment manufacturers are enclosed in installations. Here, an emitted fraction of 31% of the sales to EQ best fits the atmospheric observations as a long-term mean (least-squares fitting, Figure 4). This figure gets strong independent evidence from the manufacturers, who (start to) distinguish by themselves between SF₆ enclosed really on a long-term basis and emissions arising from by-packed SF₆ spares and from the construction and commissioning phase. On the basis of their practical experience, European manufacturers estimated recently the nonbanked fraction of their purchased SF₆ to be about 29–33% (23, 24), whereas the Japanese manufacturers report for their own production fractions of 31–40% in the years 1990–1995 (25). Thus, regarding 31% of the sales to EQ as additional emissions fits both the technical practice and the atmospheric observations. However, it reduces also the quantity banked in electrical equipment.

TABLE 1. Data Summary of Revised SF₆ Sales, Inferred and Observed Atmospheric Inventories (t)^a

year type cf. Figure	sales banked		sales released						SF ₆ in the atmosphere		
	EQ	OU ^b	EQ	UA ^c	MI	EI	AP	OU	sales- inferred inventory ^d	observed global inventory ^d	observed global emissions ^d
	4	4	4	4	4	4	4	4	5c	5c	4
1953	10	0	5	0	0	0	0	0	1001		
1954	14	0	6	8	0	0	0	0	1010		
1955	12	0	5	17	0	0	0	0	1027		
1956	12	0	5	26	0	0	0	0	1053		
1957	12	0	5	34	0	0	0	0	1087		
1958	41	0	18	41	0	0	0	0	1132		
1959	66	0	30	67	0	0	0	0	1204		
1960	37	0	16	109	0	0	0	0	1311		
1961	39	0	18	130	0	0	0	0	1443		
1962	120	0	54	151	0	0	0	0	1610		
1963	142	0	64	221	0	0	0	0	1845		
1964	138	0	62	299	14	0	0	14	2170		
1965	172	0	77	372	23	0	0	18	2593		
1966	116	0	52	459	27	2	5	22	3109		
1967	76	0	34	510	32	5	9	13	3688		
1968	16	0	7	537	36	5	14	9	4293		
1969	78	0	35	530	41	7	14	12	4911		
1970	103	0	46	554	44	9	14	24	5568		
1971	191	0	86	588	71	10	14	58	6304		
1972	140	0	63	662	63	11	14	65	7148	7113	762
1973	327	0	147	704	83	11	14	100	8086	7991	993
1974	238	0	107	826	46	12	14	135	9171	9099	1224
1975	386	4	173	937	120	13	14	107	10386	10439	1455
1976	524	13	326	1236	195	13	14	113	11897	12009	1686
1977	638	22	286	1299	214	13	14	129	13753	13810	1917
1978	703	31	316	1473	256	13	20	103	15784	15843	2148
1979	874	39	393	1962	312	15	32	149	18192	18106	2379
1980	1064	48	478	1861	321	16	35	168	21060	20601	2610
1981	964	57	433	2055	320	17	54	153	23990	23327	2841
1982	1070	66	481	2096	360	18	59	180	27076	26283	3072
1983	980	74	441	1966	374	17	80	159	30218	29471	3303
1984	1283	83	576	2348	397	16	108	149	33440	32890	3534
1985	1196	92	538	2440	437	20	111	162	37072	36539	3765
1986	1150	101	516	2717	431	38	110	199	40881	40420	3996
1987	1132	109	509	2784	415	73	146	156	44916	44532	4227
1988	1138	118	511	2654	398	100	162	189	48976	48875	4458
1989	1210	127	543	2832	363	117	270	196	53092	53449	4689
1990	1188	136	534	3323	385	140	220	299	57607	58253	4920
1991	1395	144	627	3414	357	151	260	538	62657	63289	5151
1992	1590	153	715	3496	286	215	308	524	68069	68556	5382
1993	1393	162	626	3762	300	247	313	538	73693	74054	5613
1994	1803	171	810	3589	386	284	354	468	79514	79783	5845
1995	2008	179	902	3476	437	327	390	498	85452	85743	6076
1996	2129	188	956	3544	588	338	384	324	91516	91934	6307

^a All values refer to the middle of the calendar year noted. ^b Fraction of sector OU assumed to be banked in windows. ^c Includes unknown quantities for the magnesium industry, cables, military, and space sector. ^d Divide by 25 000 to obtain concentration values in ppt or changes in ppt/yr.

The Cumulative Picture of Sales-Modeled Emissions.

The previous sections were restricted to annual turnovers and budgets, especially from the 1970s onward for which atmospheric data are available. It will be interesting to see what can be learned additionally from a cumulative picture that includes the time prior to the 1970s. First, in Figure 5a the cumulative total sales as reported originally by SPS are compared with the atmospheric inventory. Also the ratio of both records is given by an inset. It appears, that until 1972 the accumulation of these sales amounts only to 75% of the atmospheric inventory. This obvious underestimation supports independently the revision made for missing historical sales above. Figure 5a also shows the accumulation of the revised sales taken from Figure 4. These values are always larger than the atmospheric inventory. In 1996, the sum of revised sales amounts to 136% of what was registered by the atmosphere or to a total of 124 600 ton of SF₆.

The emission scenario, which was inferred on the basis of annual sales from 1972 onward, is already shown back-

extrapolated in time in Figure 4. Figure 5b shows that its accumulation from 1953 onward agrees quite well with the atmospheric record. Remaining sales, assumed to be banked in sound-insulating windows and in electrical equipment, are also given in a cumulative manner. How realistic these curves are depends on the rate of replacement and on the lifetime of installations. For windows, a lifetime of 20–30 yr is estimated (22). Manufacturer of electrical equipment state that nearly all installations of the past are still in use. In this case, a quantity equal to around 30% of the total atmospheric SF₆ burden is actually banked, mainly in electrical installations.

An inspection of the ratio of cumulative emissions to the atmospheric value (inset of Figure 5b) reveals some small but interesting features: The ratio shows an approximately constant offset to the 100% value from 1980 onward, whereas prior to 1980 it decreases continuously. This indicates that a constant factor in combination with a small emission offset seems to be missing generally. Reasonable explanations for

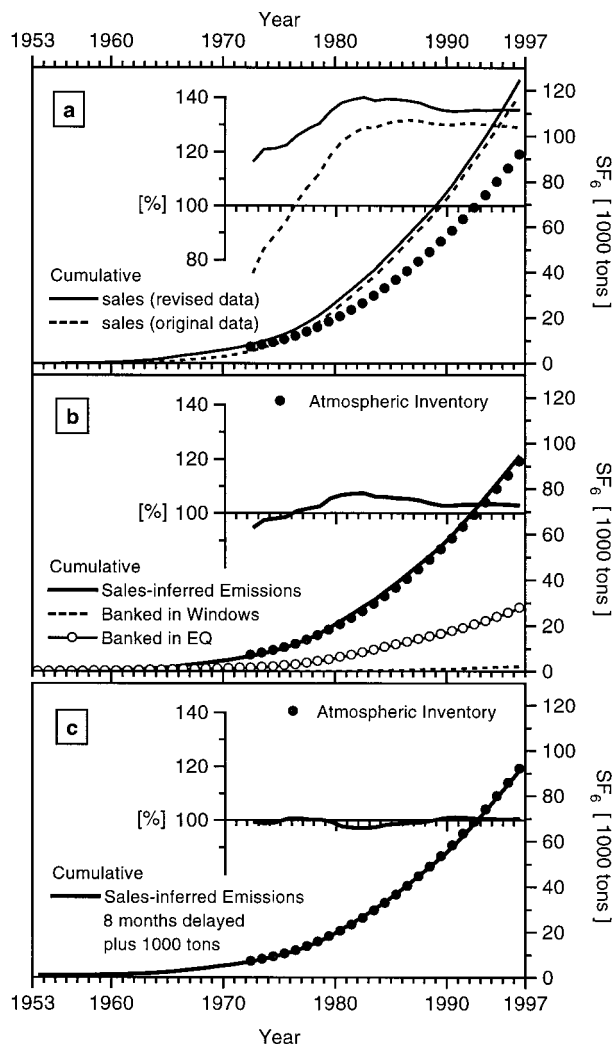


FIGURE 5. Observed atmospheric SF_6 inventory from Figure 1a compared with cumulative sales and modeled emissions. (a) Cumulative sales according to the original and the revised SPS data. The inset shows the respective ratio to the atmospheric inventory. (b) Cumulative emissions inferred from the revised sales data and their ratio to the atmospheric observations. The remaining sales, banked in sound insulating windows or electrical equipment (EQ), are shown by additional cumulative curves. (c) Like panel b but with emissions delayed by 8 months and starting at a background of 1000 of SF_6 in 1953 (see also Table 1 for data).

both are as follows: Some small systematic errors in the deduction of emissions from sales numbers or in the conversion of the atmospheric surface observations to a global atmospheric burden cannot be excluded. However, that should be no longer noticeable after fitting one approach to the other on an annual base like what was done in Figure 4. It remains the only factor delay-time to be optimized, which is more precisely felt by an integral analysis. Indeed a much better consistency in the 1990s is obtained when allowing the emissions to be delayed. The concomitant increased discrepancy in the comparison of the early years has to be compensated then by an additive and constant offset for the emissions. The best agreement is obtained by applying a delay of 8 months between the time of sale and emission and a constant emission offset of 1000 ton (least-squares fitting to 100%, Figure 5c). For all open uses in one pool, such an average time-delay is not unreasonable. There are several reasons for the added emission offset of 1000 ton of SF_6 (equal to 0.04 ppt in the atmosphere). First, a full release of the total SF_6 production prior to 1972 (which cannot be excluded by atmospheric observations) has the potential

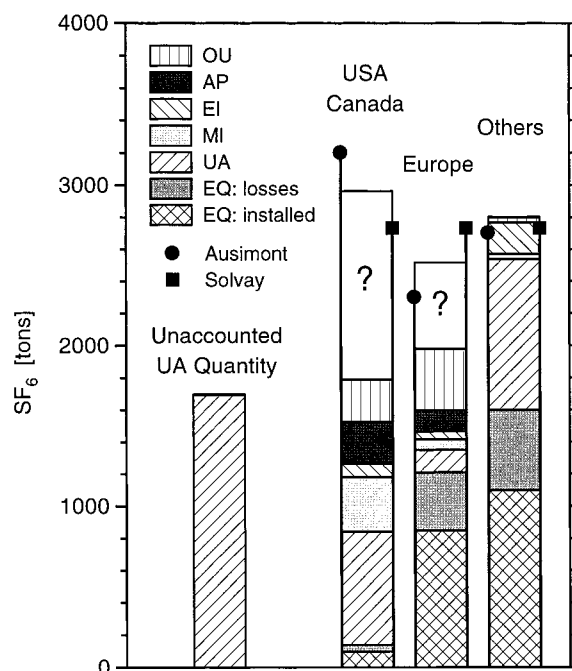


FIGURE 6. Geographical distribution of SF_6 end-use applications in 1995. Symbols describe independent estimates of the total geographical market shares given by two major SF_6 producers: Ausimont (28) and Solvay (20). These estimates should be matched by the indicated accumulation of SF_6 applications based on user's information. This approach leaves a significant gap of unaccounted uses within the North American market. At the same time, it remains a comparable quantity of produced SF_6 , which is attributed by the producers to the sector "utilities and accelerators" (see text for a discussion of this mismatch).

to explain an offset of 1000 ton partly, up to a maximum of 800 ton. The remaining quantity of at least 200 ton (equal to 0.008 ppt) might be due to unreported productions or due to an unknown SF_6 formation as byproduct of another industrial process. Anyhow, the offset of 1000 ton also includes the natural background of SF_6 for which Harnisch and Eisenhauer (26) have given recently an estimate of 0.001–0.01 ppt. Harnisch et al. (27) showed unambiguously that SF_6 has a small but natural source since it is produced, like CF_4 , radiochemically in natural fluorite (CaF_2) minerals. However, the quality of the numbers in the present study is not appropriate to prove or to quantify such a small natural background exactly. Nevertheless, its absolute value can be constrained to be below 0.04 ppt. Only analysis of air from ice cores will provide the final proof here. Anyhow, the inferred emission history prior to 1972 extends the atmospheric SF_6 record as based on observations (Figure 1) by about 2 decades (Figure 5c, Table 1). Altogether, a reliable chronology of the accumulation of SF_6 in the atmosphere over the past 45 yr is obtained, which is the longest atmospheric SF_6 record available to date.

The SF_6 Market Structure in 1995. Except for the sales to the equipment manufacturers, the end-use specification given by the SPS study has not been evaluated so far. This will be done here by having a detailed look at the market structure for the reference year 1995. The sale volumes of end-uses in 1995 are as in Figure 4. They will be split up into applications within three geographical regions, USA & Canada, Europe, and the rest of the world, using independent information from SF_6 users. The goal of this exercise is to match the geographical SF_6 market sharing according to two major SF_6 producers, Ausimont (Italy) (28) and Solvay (Germany) (20), as indicated in Figure 6. The estimated market shares by Ausimont have been modified by adding

a Chinese and Russian SF₆ production of 760 ton, resulting in a total volume of 8200 ton (from Figure 4) which then splits up as follows: 39% (3200 ton, USA & Canada), 28% (2300 ton, Europe), and 33% (2700 ton, Others). Solvay estimates the sharing between the three geographical regions to be one-third each. The end-use quantities behind these total geographical volumes will now be estimated from user's information. This detailed step-by-step analysis for the reference year 1995 will explain the information given in Figure 6 and reveal a partly unclarified sharing between open applications within the North-American market.

Electrical Equipment (EQ). The major manufacturers are located in Asia and Europe. Comparatively small quantities of SF₆-insulated electrical equipment are produced in the United States and China. The Russian production is thought to be even smaller but cannot be quantified (29). The U.S. National Electrical Manufacturer Association (30) reports a nationally purchased quantity of 140 ton of SF₆ for new installations in 1995, from which 100 ton is assumed to be finally banked, and the rest is released. For Japan, a volume of 1000 ton was reportedly banked in new installations, and 400 ton was released during development, testing, and installation (31). According to Bitsch (29), in 1995 the Chinese equipment production can be assumed to be around 100 ton with the same quantity released until final installation. The remaining quantities of the total EQ volumes of Figure 4 are 850 (EQ installed) and 360 ton (EQ lost). That equals the European share, for which, independently, a total purchased quantity of 1200 ton is reported (32).

Utilities and Accelerators (UA). In case of the United States and Canada, the annual refill and leakage compensation for all existing power installations was recently estimated for 1995 to be 700 ton or 20% of a total installed quantity of 3500 ton (30). Outside North America, the market is dominated by Japanese and European technology for which the manufacturers regard an overall refilling rate (leakage plus handling) of 3%/yr already as a conservative upper limit. All equipment produced since 1980 should need less refilling by at least a factor of 2. Using the 3%/yr assumption enables the estimation of the quantities used for the sector "utilities". With a volume of 4500 ton installed in Europe (32, 29) and 18 000 ton in the rest of the world (without America) (29), the demand of utilities in 1995 will be 135 and 540 ton, respectively. Furthermore, SF₆ is used also, predominately in Japan, for insulating high-voltage cables. This market share of 400 ton in 1995 (31) is included in the sector utilities of the rest of the world. The use of SF₆ in accelerators is (e.g., in Germany with 3 ton/yr (22)), of minor relevance, which might not be the case for North America.

Magnesium Industry (MI, Preliminary Estimate). A total of around 440 ton of SF₆ used by the magnesium industry is obtained from Figure 4. It is used throughout the western world for blanketing molten magnesium, whereas in China and Russia mainly SO₂ is used for this purpose. The worldwide sum of primary and secondary magnesium production in 1995, except for China and Russia, is estimated to be 329 000 ton (33) and is taken as the total annual molten and SF₆-blanketed quantity. That results in a mean global consumption rate of 1.3 kg of SF₆/molten ton of magnesium. In a first approach, the geographical distribution of all molten magnesium, 78% (USA & Canada), 15% (Europe), and 7% (rest of the world), is used to split up the total of the 440 ton of SF₆ used, which yields 340, 70, and 30 ton of SF₆, respectively (Figure 6).

Electronics Industry (EI). The geographical distribution of the semiconductor production is the only information available for splitting up the 330 ton of SF₆ used globally in this sector in 1995 (Figure 4). With estimates (29) of 25% of semiconductor production in USA & Canada, 15% in Europe, and 60% in the rest of the world (mainly Japan and southeast

Asia) the 330 ton of SF₆ split up into 80, 50, and 200 ton, respectively (Figure 6).

Utilizing SF₆ Adiabatic Properties (AP). SF₆ for filling the tires of cars is a more or less German speciality for which a quantity of around 130 ton was purchased in 1995 (22). Furthermore, a consumption of 288 ton of SF₆ in 1997 by one major American sport shoe producer was recently reported (34). For 1995, we assume 260 ton for this application to balance the total of 390 ton of SF₆ attributed to the whole sector AP in 1995.

All Other Uses (OU). This application pool with a total of 680 ton of SF₆ in 1995 includes numerous small and specialized applications, but two major applications, aluminum degassing (USA & Canada) and SF₆-insulated windows (Europe), can be identified and roughly quantified. Disregarding the bump from 1990 to 1995, the time-series of OU is approximately described by a linear increase from 100 ton/yr in 1975 to 450 ton/yr in 1995 (Figure 4). Over the same period, the use of SF₆ as filling gas of sound-insulating windows increased from zero to around 350 ton/yr (20). The balance of around 100 ton for all other smaller applications is assumed to split up equally over the three geographical regions of Figure 6. With respect to the general linear increase, an additional temporal limited rise of sales to the sector OU is observed between 1990 and 1995. Its absolute value and temporal occurrence falls well together with figures reported for the use of SF₆ for degassing aluminum in North America (20). Thus we attribute the remaining quantity of 230 ton of OU in 1995 to this sector.

General. Figure 6 shows, that the sum of the geographically distributed applications from above matches the market estimates of SF₆ producers partly. The agreement is very good for the rest of the world. The European market is slightly underestimated by the sum of applications. However, the observed discrepancy is not very significant since the total of basing estimates for applications and the producer's estimates are certainly accurate only by ± 400 ton. But the gap between both approaches observed for North America is significant. This gap equals approximately the uncertainty of a recently published experimental study of Bakwin et al. (35), who independently estimated the source strengths of SF₆ for North America to be 2400 ± 500 ton in 1995. According to the specification by SPS, the unaccounted North American gap of 1200 ± 400 ton should be filled by remaining sales to the UA sector (Figure 6). But the sales for compensating leakage and handling of utilities in the United States and Canada are already considered with the reported 700 ton in 1995 (30). It is unlikely that this number is wrong by such a degree. Also questioning the demand by the assumed 3%/yr refilling rate of SF₆-insulated electrical equipment outside North America is unable to solve the discrepancy. The sales of SF₆ to accelerators have been so far not quantified. Furthermore, uses in the military and space sector may play an, until present, unquantifiable important role in the pool of UA. The present discrepancy will be reduced by these unquantified applications, but an annual market as large as 1200 ton seems unlikely. Among all applications, only a revision of the SF₆ demand by the magnesium industry has the potential to solve the remaining mismatch.

Questioning the Demand of SF₆ by the Magnesium Industry. The total magnesium smeltered in primary and secondary foundries is shown in Figure 7a. Numbers for China and Russia are excluded since, in contrast to the Western World, mainly SO₂ and not SF₆ was used for blanketing. In Figure 7b, the total sales to the MI from Figure 4 are shown. In case of Norway, the SF₆ sales to the MI are reported independently (10, 36) and are highlighted in Figure 7. The consumption of SF₆ (in kg/ton of molten magnesium) has decreased in Norway approximately from 4 kg/ton in the 1980s to 0.7 kg/ton in 1996. The cost factor and the climatic

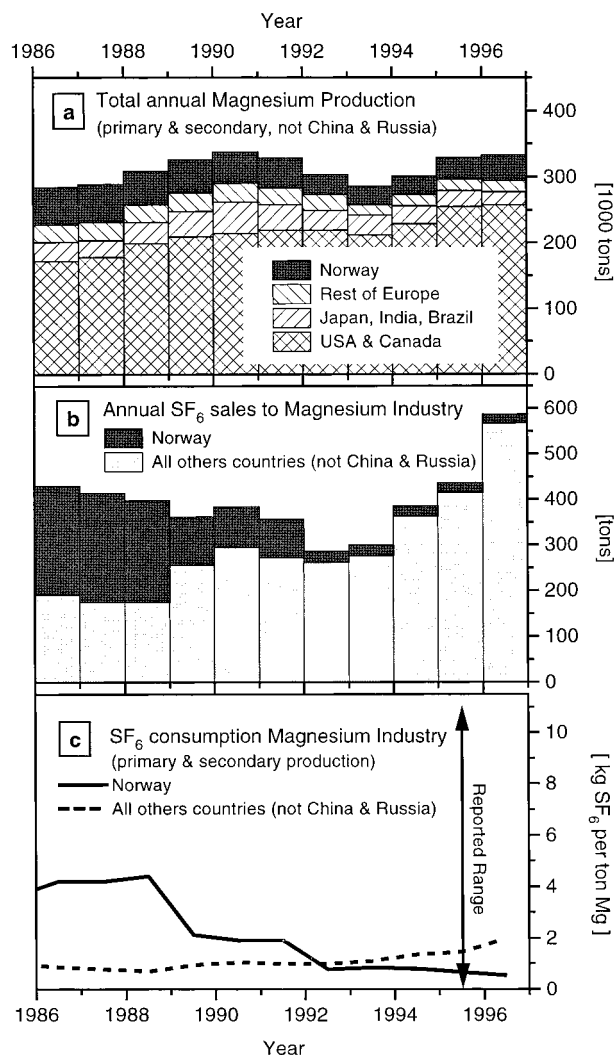


FIGURE 7. Reported SF_6 consumption by the magnesium industry. (a) Total of primary and secondary magnesium produced by the major manufacturing countries (33). (b) Total sales of SF_6 to magnesium industry from Figure 4, split up into volumes for Norway (10, 36) and remaining countries, China and Russia excluded. (c) Resulting SF_6 consumption rate for Norway and remaining countries, China and Russia excluded. A vertical bar indicates the range of consumption rates reported for diecasters (37, 38).

impact of SF_6 have motivated the Norwegian magnesium producer Norsk Hydro to reduce the SF_6 waste by technological improvements as one of the first worldwide (37, 38) to do so. It is thus hard to understand that outside Norway magnesium should have been produced at a low SF_6 consumption rate already as implied by Figure 7c. It is more likely that on average the SF_6 consumption rate in all other countries is at least as high as the formerly 4 kg/ton in Norway. A survey by Norsk Hydro revealed that the consumption rate of diecasters (secondary foundries) varies between 0.1 and 11 kg/ton worldwide (37, 38). Nothing is reported for the dominating use of SF_6 in the primary foundries. It thus might be allowed to speculate that the sales of SF_6 to the MI are so far largely underestimated. That might be possible since some companies are producing both electricity and magnesium. SF_6 suppliers might have been unable to distinguish between these uses when reporting their sales numbers. If the total of the so far unaccounted UA quantity (1700 ton, Figure 6) is attributed to the sector MI outside Norway, the mean MI consumption of all other countries (mainly North America) would increase to around 7 kg/ton. The real MI consumption will be somehow lower, reduced by that North

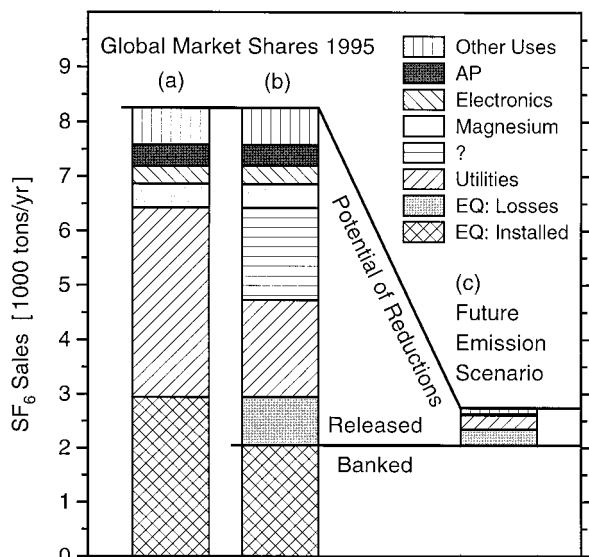


FIGURE 8. Global SF_6 market shares in 1995 by end-use applications. (a) Market structure according to the SPS study but with a Russian and Chinese production of 760 ton included. (b) Revised structure: the category with the question mark stands for additional applications by the magnesium industry in accelerators and in the military and space sector. (c) Future scenario showing the potential of emission reductions of open applications (see text for a detailed discussion).

American UA sales that are actually sales to the sectors military and space, accelerator, and insulated power transmission cables.

Revised Market Structure by End-Uses. Nearly independent of the correct SF_6 consumption by the MI, the picture of the global end-use applications alters strongly with respect to the electrical applications. This is shown in Figure 8 for the year 1995. The "old" structure, according to data from Figure 4, represents the commonly cited mix with about 80% of the total SF_6 produced used in heavy electrical equipment (39). Based simply on the purchased quantity by equipment manufacturers, the truly banked quantity is considerably overestimated. Furthermore, the sector UA as reported by SPS seems to include substantial quantities of others, mainly North-American applications, which have nothing to do with the leakage compensation of existing electrical installations. The present new analysis suggests a 40%/60% mix of nonelectrical to electrical application, with the later half banked and half released. Note that this new "revised" picture is certainly not uniquely for the year 1995. If further information becomes available, the whole time records of the sectors UA and MI have to be respecified. The internal end-use sharing of these sectors in Figures 2–4 is thus preliminary and probably subject to future revision.

The Potential of Future Emission Reductions. A third column in Figure 8 shows the enormous potential of reducing SF_6 emissions from open applications. The existing and newly banked quantities will convert to future emissions only to a small extent, if appropriate recycling techniques are used during replacement and maintenance of equipment. Here, already available reuse techniques and concepts might allow a nearly closed-loop handling (40).

Concerning the open applications, the questionable use of SF_6 for filling tires and soles of sport shoes could be given up. For the degassing of aluminum, SF_6 should be replaced. For the filling of sound-insulating windows, the use of SF_6 will be phased out (20). That reduces already releases from the sector OU to an annual 100 ton (Figure 8). In case of blanketing molten magnesium, Norsk Hydro has shown that reducing the SF_6 consumption by a factor of 10 (Figure 8) is

feasible with trained personnel and relatively moderate technical modifications. Furthermore, Norsk Hydro promotes the return to the climatically more acceptable SO₂ technique (38). In case of plasma etching in the electronics industry, closed systems with thermal destruction of SF₆ residuals could reduce emissions to virtually zero (22). The SF₆ losses before the final installation of new electrical equipment are also susceptible to a significant reduction (in Figure 8, a factor of 3 is assumed). The refilling rate of SF₆-insulated electrical equipment can be reduced globally to below 1%/yr by modernizing old installations using state-of-the-art technology and by training personnel on the SF₆ problem. Releases from the 26 000 ton SF₆ banked in 1995 will then amount to less than 260 ton/yr (Figure 8). In summary, the future market scenario of Figure 8 describes a 90% reduction of the total of open SF₆ applications, which is equal to a quantity of 5500 ton/yr.

Reported SF₆ sales have been differentiated according to directly emitting open applications and closed applications, in which SF₆ is banked for a longer time. As a long-term global mean, about 70% of the SF₆ purchased by the electrical equipment manufacturers seems to be really banked. All other sales are more or less directly released to the atmosphere. Their annual and cumulative values agree well with the increase of SF₆ observed over decades in the atmosphere. Thus, for the first time, sales data and end-use modeling are brought into line with atmospheric observations. A geographical analysis of end-uses suggests that remaining uncertainties are most likely traceable to an unclarified sharing between open applications within the North American market. Information on that will be available with the future national assessment report on SF₆ applications in the United States, a project within the U.S. Climate Action Plan. Anyhow, a considerable reduction potential of SF₆ emissions can already be identified. The above-described global reduction scenario of an annual 5500 ton SF₆ will be equivalent to 132 million ton of CO₂ (base: GWP₁₀₀ = 23 900 for SF₆). Especially in case of the large North American SF₆ market, about 90% of all applications seem to be more or less open uses. Here, a reduction by a factor of 10 or ≈2900 ton/yr is feasible and will equal to 69 million ton of CO₂ per year, a quantity that equals 17% of the total U.S. national reduction share of the Kyoto protocol. The various data gathered and analyzed in the present study will be of interest to atmospheric scientists, will help politicians with future policies, and will guide industry in modifying/optimizing current practices.

Acknowledgments

The authors thank representatives of Solvay, Norsk Hydro, RWE, and Siemens for their open information policy. Without them the SF₆ puzzle would not have been solved so far. Jeff and Shari Johnston and two anonymous reviewers are acknowledged for their helpful remarks on the manuscript.

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Received for review March 19, 1998. Revised manuscript received July 27, 1998. Accepted July 28, 1998.

ES9802807