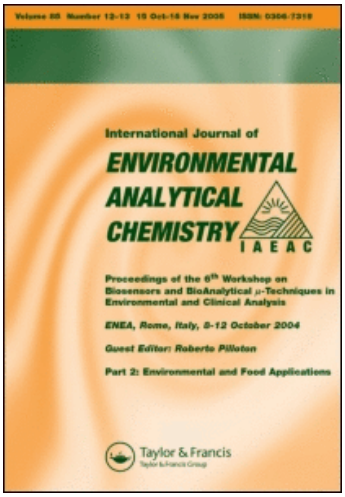

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Lead Concentration in Wet Deposition Results of a Ten Year Time Series in Saltzburg, Austria

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LEAD CONCENTRATION IN WET DEPOSITION RESULTS OF A TEN YEAR TIME SERIES IN SALZBURG, AUSTRIA

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Since 1984 wet precipitation is sampled in Salzburg, Austria, by a wet only technique on a daily basis to get information about the seasonal and temporal trends of ionic concentrations and wet deposition loads. Today 4 sampling sites are operated being part of the Austrian wet precipitation network. Annual volume weighted mean concentrations of lead in wet precipitation have decreased from 4.3 to 2.8 µg/l at Nuβdorf (520 m a.s.l., 1984–1993), from 3.6 to 0.9 µg/l at Werfenweng (940 m a.s.l., 1984–1993), from 2.6 to 1.8 µg/l at Kolm Saigurn (1600 m a.s.l., 1990–1993) and from 5.0 to 1.9 µg/l at Sonnblick (3106 m a.s.l., 1988–1993). The decrease of the lead concentration in wet precipitation is well correlated with the reduction of lead emissions due to combustion of leaded gasoline. The correlation coefficients for the 4 sampling sites range from 0.69 to 0.87, respectively. The highest deposition loads for lead in Salzburg are found at the Sonnblick sampling site with values between 70 and 29 g/ha (1988–1993) caused by the memorable precipitation depth at the high elevated site. The decadal reduction of the wet deposition load of lead in Central Austria is in the order of 50-70%.

Keywords: Lead; lead emission; precipitation; wet deposition; AAS

INTRODUCTION

Lead is a naturally occuring element, which represents an almost ever present constituent of the earth's crust. It can be found in all environmental media such as air, soil, rock, sediments or water and in all components of the biosphere. The major part of lead found in the atmosphere results from combustion of leaded gasoline (about 90%[1,2,3]). Because lead introduced into the environment by

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human activities is a stable compound and accumulates locally and in biological organisms, children especially are at greater health risk if they inhale or intake orally lead components[4,5]. Due to medical warnings and the scientific work, eg. by C. Patterson and his coworkers presenting lead concentrations in Greenland ice increasing from prehistoric times to the 1960s of about a factor of 200[6], several countries limited their use of lead alkyl additives in gasoline starting in the early 1970s[2,3,7,8,9]. Figure 1 shows the gasoline consumption in kilotons together with the lead emissions in tons between 1960 and 1993 for Austria [10]. Limitations prescribed by law were seen in the early 1970s (0.40g lead per liter), the early 1980s (0.15g lead per liter) and in 1993 (prohibition of lead in gasoline, except 0.013g lead per liter "Eurosuper 95"). Lead may be removed from the atmosphere either by dry, occult or wet deposition. The most efficient clearing mechanism is assumed to be wet deposition[1,11,12].

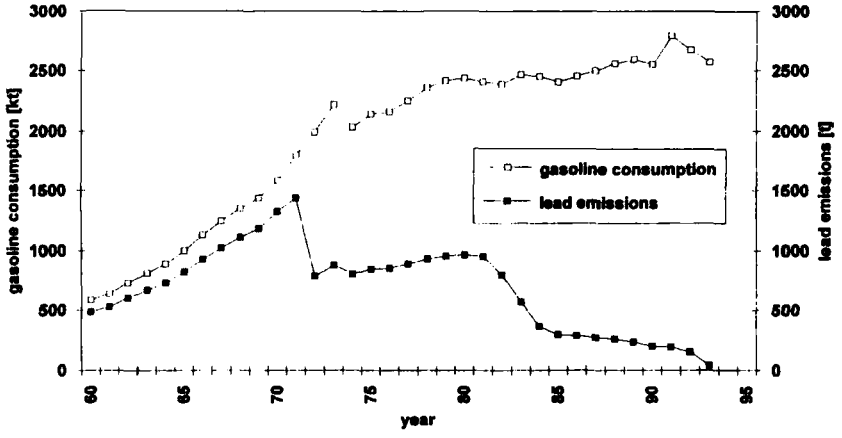

FIGURE 1 Gasoline consumption and lead emissions, 1960-1993, Austria[10]

EXPERIMENTAL

Since 1984 wet precipitation is sampled in Salzburg, Austria, by a wet only technique on a daily basis to get information about the seasonal and temporal trends of ionic concentrations and wet deposition loads[13]. Today 4 sampling sites are operated being part of the Austrian wet precipitation network (Nußdorf, 520 m a.s.l., Werfenweng, 940 m a.s.l., Kolm Saigurn, 1600 m a.s.l. and Sonnblick, 3106 m a.s.l.). Figure 2 shows the 4 sampling sites in Salzburg being part of the Austrian wet precipitation network. All sites are equipped with the WADOS

("Wet and dry only precipitation sampler"). The daily control of the samples is carried out by local observers usually in the morning hours. The samples are stored in polyethylene bottles at 0-4°C, transported at biweekly intervals to the central laboratories and analysed generally within 1-4 weeks of receipt[14,15].

FIGURE 2 Wet only stations in the Austrian precipitation network, 1993

Lead is analysed by AAS (Perkin Elmer 370 without modifier, wavelength 283.3 nm, low slit 0.7 nm) using a graphite tube and a Perkin Elmer AS-I autosampler (sample volume 10 µl). After a drying time of 10s at 100°C and an ashing time of 10s at 450°C atomization occurs at 2000°C (7s) followed by a 2s clean-out step at 2500°C. The Argon flow is interrupted at the atomization stage. A linear range is yielded up to 100 ppb with a detection limit of 0.3 ppb[16,17].

In this study the annual volume weighted mean concentrations of lead in wet precipitation are presented as results of a ten year time series in Salzburg starting at the stations Nußdorf and Werfenweng in 1984. The Sonnblick sampling site has been equipped with the WADOS in 1988. Kolm Saigurn, a sampling site located at the bottom of a steep wall descending from the Sonnblick Observatory (about 1600 m hight difference), has been integrated into the wet precipitation network in 1990 to give information about the hight dependence of ionic concentrations in direct comparison to the Sonnblick sampling site.

RESULTS AND DISCUSSION

Lead Concentrations

The results of the ten year time period are shown in table I as annual volume weighted mean concentrations of lead in wet precipitation at the 4 sampling sites in Salzburg. Due to its location the highest concentration levels of each particular year are to be found at the Nuβdorf sampling site. Nuβdorf is located in a rural area influenced by the city of Salzburg and two main Highways through Austria while the other sampling sites are located at inneralpine valleys (Werfenweng and Kolm Saigurn) and remote high alpine areas (Sonnblick) respectively[13,18]. The two main transit routes through the country of Salzburg are found to be a North to South transect (A10, "Tauernautobahn") and an East to West transect (A1, "Westautobahn") as to be seen in Figure 2. For the year 1993 the lead concentration in leaded gasoline in the neighbouring countries Germany, Italy and Hungary was 0.15 g/l by law[19]. In Germany about 90% of the used gasoline in 1993 was unleaded[19], while Molnar et al.[20] published the respective number for Hungary to be only 25%. The percentage of cars of "Eastern Countries", where leaded gasoline is not as yet prohibited, using the Austrian transit routes is not available at that time. The higher lead concentration at the traffic exposed station Nuβdorf compared to the other stations indicates however an influence from emissions from cars using leaded gasoline.

TABLE I Annual volume weighted mean concentrations of lead in wet precipitation and annual wet deposition loads of lead in Salzburg, 1984-1993

Year	*Precipitation [µg/l]*				*Deposition [g/ha]*			
	Werfen-weng	Hauns-berg	Kolm Saigurn	Sonn-blick	Werfen-weng	Haunsberg	Kolm Saigurn	Sonn-blick
1984	3.6	4.3			24.7	39.5		
1985	3.2	5.4			30.2	63.8		
1986	4.2	5.2			31.1	52.6		
1987	2.3	3.5			23.8	43.6		
1988	2.4	5.2		5.0	26.1	66.9		69.8
1989	2.8	3.8		3.9	27.9	40.7		51.3
1990	2.1	2.9	2.6	2.3	19.5	36.5	24.3	28.4
1991	1.9	3.0	2.4	1.8	19.1	31.3	20.9	28.2
1992	1.7	3.2	2.7	2.4	16.8	29.6	18.1	35.7
1993	0.9	2.8	1.8	1.9	9.2	21.4	20.0	29.4

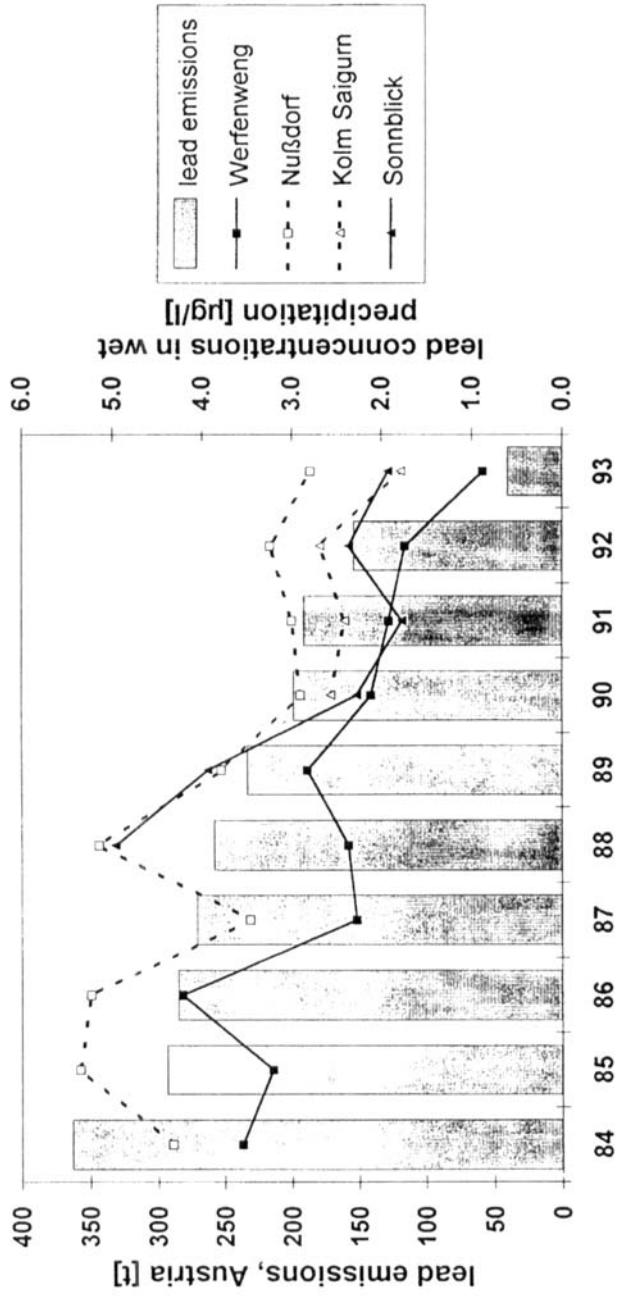

FIGURE 3 Lead concentrations in wet precipitation in Salzburg together with lead emissions due to combustion of gasoline in Austria, 1984-1993

The comparison of the lead concentrations in wet precipitation at the Salzburg sampling sites with the lead emissions in Austria is shown in Figure 3. The decrease of the lead concentrations in wet precipitation is well correlated with the reduction of lead emissions due to combustion of leaded gasoline. The correlation coefficients between lead emissions and lead concentrations for the 4 sampling sites range from 0.69 for Nußdorf and Sonnblick up to 0.86 for Werfenweng and 0.87 for Kolm Saigurn respectively. This decrease in lead concentrations due to the massive decrease in the use of lead alkyl additives in gasoline starting at the early 1970s, which brings the 1992 values back to the concentrations observed in the mid 19th century, is also documented in central Greenland snow and ice as well as in European glacier fields [9,21].

TABLE II Comparison of lead concentrations in wet precipitation at different urban, rural and remote sites

Site/Country	*Year*	*Lead [µg/l]*	*Reference*
Vienna/Austria	1988	27	Kovar et al., 1990[20]
Vienna/Austria	1993	7	Kalina et al., 1995[21]
Essex/U.K.	1986	22	Radojevic et al., 1987[22]
Zagreb/Croatia	1989	7–20	Mikac and Branica, 1994[23]
Belgrade/Serbia	1993	38	Vukmirovicet al., 1996[24]
Minnesota/USA	1983	1.5	Eisenreich et al., 1986[2]
ATMOS S2/Sweden	1992	2.6	Cabon and Bihan, 1996[12]
ATMOS GB4/U.K.	1992	1.4	Cabon and Bihan, 1996[12]
ATMOS F1/France	1992	1.2	Cabon and Bihan, 1996[12]
Bermudas/U.K.	1982	0.7	Church et al., 1984[25]
Monte Rosa/Switzerland	1993	0.5	Wagenbach et al., 1994[19]
Central Greenland	1992	0.02	Candelone et al., 1995[9]

The comparison of the Salzburg data set with lead concentrations of other studies at urban, rural and remote sites is presented in Table II. The comparison of an urban sampling site in Vienna[22,23] with the Salzburg site Haunsberg shows the characteristic West to East concentration gradient in Austria with values by a factor of 5 higher in the Eastern part of the country[14]. The decrease in the lead concentrations as mentioned above for the Salzburg sites is also to be seen for the Viennese sampling site (about 75% between 1988 and 1993). The concentration levels at the urban sites in Europe are in the same order of magnitude for the

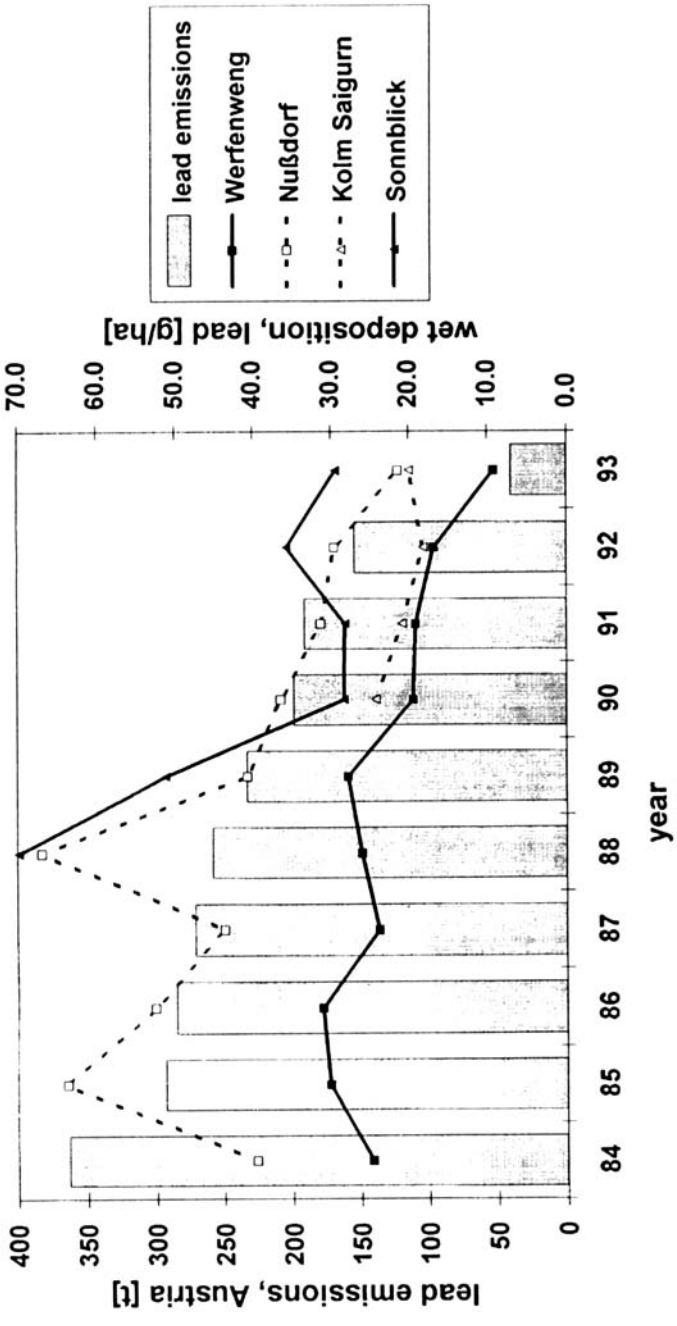

FIGURE 4 Wet deposition of lead in Salzburg together with lead emissions due to combustion of gasoline in Austria, 1984-1993

results of the mid 80th[22,24,25]. Measurements in Belgrade[26] yielded by a factor of 5 higher 1993 values than respective data of the Viennese site[23] indicating the higher content of lead in East European petrol. The rural site in the USA[2] shows a 1983 concentration level that is comparable with concentration levels of the early 90th in Europe which reflects the earlier start of the massive lead reduction in the US compared to Europe[2,7,8,9]. The concentration levels at the ATMOS stations in Sweden, Great Britain and France which are mostly influenced by clean Atlantic air are of comparable magnitude with the results of the Salzburg study[12]. Remote regions represented by the measurements at the Bermudas or the European glacier fields show by a factor of 2 to 3 lower levels compared to the Salzburg study, while younger results of measurements in Greenland yielded by 1 to 2 magnitudes lower concentration levels[9,21,27].

Wet Deposition Loads

Atmospheric annual lead fluxes are calculated by multiplying the volume weighted mean concentrations by the respective precipitation amount. The wet deposition data for the Salzburg sampling sites are presented in g/ha in Table I. Sevaral studies in Italy, Croatia and Austria have pointed out the problem of increasing lead concentrations in soil with increasing height above sea level[28,29,30]. Although there is a difference of about 1500 m in height the concentration levels in wet precipitation at the Sonnblick (3106 m a.s.l.) and the Kolm Saigurn sampling site (1600 m a.s.l.) are of comparable magnitude (eg. 2.4 and 2.7 µg/l in 1992, 1.8 and 1.9 µg/l in 1993). Although no height dependence of the lead concentration is to be seen the highest wet deposition loads of lead in Salzburg are calculated for the Sonnblick sampling site with average wet deposition loads between 70 and 29 g/ha from 1988 to 1993. These results are yielded caused by the memorable precipitation depth at the high elevated site (eg. 1506 mm at the Sonnblick compared to 674 mm at Kolm Saigurn in 1992). Figure 4 shows the lead deposition due to wet precipitation at the 4 sampling sites in Salzburg in g/ha together with the lead emissions in Austria in tons. Thus the decadal reduction of the wet deposition load of lead in Central Austria is in the order of 50-70%. The Austrian values of 1992 are comparable to that levels determined at the ATMOS stations with 21 g/ha in Sweden (S2) and 20 g/ha in Britain (GB4) [12].

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