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Fureneset Forskingsstasjon

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KARL-JAN ERSTAD

HEAVY METAL AND ACCESSORY ELEMENT CONTENTS IN LIMING MATERIALS OF CARBONATE ORIGIN MARKETED IN NORWAY.

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Utdrag: Det er i dag stor merksemd retta mot sporelement i miljø og materialemne. Generelt er kalkingsmiddel ei underordna kjelde for tungmetall og andre uønska følgestoff. Av det som finst i kalk, er berre 10-30% lettløyseleg (karbonatbunde). Nokre kalkingsmiddel inneheld likevel ein del av desse sporelementa. Dette gjeld særleg dei industrielle sideprodukta som ODDA-kalk (Ni, V, Cd, F) og konverteringskalk (Cd, F). Dessutan er det relativt mykje Cd i FAXE korallkalk, og litt Pb i kvartbrent dolomitt (import frå England).
Dei strengaste krava vert stilt i samband med vassdragskalking. I samsvar med grenseverdiane fastsett av det svenske Naturvårdsverket ville einskilde av kalktypane truleg ikkje verte godtatte til vassdragskalking.
Vurdering av akseptable nivå må omfatte toksiske grenseverdiar samt mogleg nytte.

4 emneord, norske	4 emneord, engelske
1. Tungmetall	1. Heavy metals
2. Følgestoff	2. Accessory elements
3. Kalkingsmiddel	3. Liming materials
4. Karbonat	4. Carbonates

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FURENESET RESEARCH STATION
REPORT 6/1992

PREFACE

Environmental contamination is evoking a steady concern at all levels of society, and there is kept a sharp watch on all possible sources of toxic substances, which might be a future danger due to accumulation. This concerns mainly agricultural soils with their high buffering capacity, whilst there might be an **acute** risk of toxification by liming in watersheds against acidification.

This project regarding the contents of heavy metals and accessory elements in liming materials of carbonate origin marketed in Norway was initiated by STIL (The National Agricultural Inspection Service), resulting in a joint project with Fureneset Research Station.

There is no exact definition of these elements of our periodic system, but they are occurring in minor amounts, and a properly covering term might be **trace elements**. In appropriate concentrations some of these treated in this report are plant micronutrients (Fe, Cu, Mn, Zn, B, Mo) - not to mention the macronutrients N, P, K, Ca, Mg, S (and sometimes Na).
V is under consideration as a plant nutrient, Co is essential for animals.
Al is toxic to biological life at low pH, and Ba, Ni, Cr and Ti under certain circumstances (concentrations, compounds and fixation). No beneficial effects have been confirmed of "the terrible three", Pb, Cd and Hg.

Several companies of the lime industry have contributed with their own results of analysis, performed at different laboratories.

STIL and NORSK HYDRO have covered the expenses of the current analyses at Landbrukets Analysesenter in 1992. Analytical parameters and samples were jointly selected by STIL and Fureneset Research Station.

Fureneset Research Station has been in charge of the scientific treatment and publication of the data.

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SAMANDRAG

Element som i mindre mengder opptrer i råstoff og allment i miljøet vårt, vekker interesse som næringsstoff for det biologiske liv og samstundes som giftstoff ved auka mengder.
Definisjonen av tungmetall er svært vag, og omgrepet sporstoff er meir dekkande, idet det omfattar normalt alle element som førekjem i mindre mengder enn jern, og dekkar då både tungmetall og andre følgestoff.

Eit stort tal sporstoffanalyser i kalkingsmiddel er vortne gjennomført dei to siste tiåra, dels p.g.a. kontrollar og krav frå styresmaktene si side, og dels grunna trongen for dokumentasjon og sertifisering innan sjølve industrien.
Men hovudproblemet har vore at ei mengde forskjellige laboratorium har nytta eit heilt spekter av analysemetodar, med særleg varierande prosedyrar andsynes oppslutning og ekstraksjon av kalkprøvene.

Denne rapporten har samanstilt fleire analyseseriar gjennomført etter oppdrag frå kalkindustrien, og til sist presentert ei fersk undersøking (B-serien) utført i samarbeid mellom STIL (Statens Tilsynsinstitusjonar i Landbruket) og SFL Fureneset.
For å kunne samanlikne resultata har analysemetodane vorte grundig omtalt. Særleg må ein vere klar over at nokre framgangsmåtar er gjennomført for å ekstrahere dei lettløyselege fraksjonane, for det meste karbonatbundne, medan dei røffe oppslutningane med kongevatn, alkaliske og sure smelter vil gje totalinnhald.

Sett i høve til mineralgjødsel, atmosfærisk nedfall og kloakkslam er kalkingsmidla normalt underordna kjelder for sporstoff til jordbruksjord.
Generelt er berre 10-30% av totalinnhaldet av sporstoff lettløyseleg, d.v.s. hovudsakleg karbonatbunde og kan dermed føre til auka konsentrasjonar ved mineralnedbryting.
Samanlikna med anlyseresultata frå Nordkalottprosjektet (Fennoskandia) er konsentrasjonane av sporelement i karbonata lågare enn bakgrunnsverdiane i morene og elvesediment.

Like fullt må ein kunne vise til nokre unntak som kan ha verknad også for velbufra jordbruksjord.
M.o.t. Cd synte det seg forholdsvis høge verdiar for ODDA brent kalk (prøve B4), ODDA-kalk (prøve B5), konverteringskalk (prøve B10) og særleg FAXE korallkalk (prøve B17).
Engelsk kvartbrent dolomitt (prøve B2) framviste forholdsvis store mengder Pb.
Innhaldet av Hg kunne ein sjå bortifrå for alle kalkprodukta.

Ganske store mengder F vart tilført jorda ved bruk av ODDA-kalk (prøve B5) og konverteringskalk (prøve B10).
Litt As vart også tilført med kalktypane frå ODDA, men desse nivåa skulle ikkje vekke uro.

Truleg utanfor biologisk fareområde viste 3 kalktypar seg å vere ein viss kjelde for V, nemleg engelsk kvartbrent dolomitt (prøve B2), ODDA-kalk (prøve B5) og GAUSDAL kalkdolomitt.
Ba vart særleg funne i kvartbrent dolomitt og konverteringskalk.

Ba vert normalt felt og inaktivert i jord, t.d. som barytt ($BaSO_4$).

Dei lågaste toleransenivåa for sporelement vert sett ved bruk av kalk ved innsats mot forsura vassdrag.
I samsvar med krava til det svenske Naturvårdsverket var Cd-innhaldet for høgt i FAXE korallkalk. I ODDA-kalken var Ni-innhaldet nær oppunder grenseverdiane, og V-innhaldet for høgt. Jamvel utan deklarerte krav til F-innhald var nivåa truleg for høge i ODDA-kalken og konverteringskalken til å verte godtatt for vassdragskalking.

SUMMARY

Minor elements in materials and generally in our environment are creating interest as nutrients in biology, and simultaneously as toxic substances in elevated quantities.
The definition of heavy metals is very vague, and the term trace elements would fit better, normally including all elements occurring in smaller quantities than iron, thus covering heavy metals and accessory elements.

Several analyses of trace elements in liming materials have been performed during the last two decades, partly due to controls and requirements of the authorities, and partly due to need of documentation and certification in the industry itself.
The main problem has been, however, that a lot of different laboratories have been applying a wide range of analytical methods, in particular with respect to digestion and extraction of the lime samples.

This report has compiled many series of analyses initiated by the lime industry, and ultimately presented a recent investigation (the B series) performed by STIL (The National Agricultural Inspection Service) and Fureneset Research Station.
To compare the results the analytical procedures have been thoroughly described. In particular we must be aware that some methods have been effected to extract the easily soluble fractions, mainly fixed to the carbonates, whereas the digestions with aqua regia, alkali melts (basic fluxes) and acidic fluxes are yielding total contents.

Relatively to mineral fertilizers, atmospheric fallout and sewage sludge the liming materials are generally minor sources of trace elements to agricultural soils.
In general only 10-30% av the total contents would be easily soluble, i.e. mainly fixed to the carbonates and thus enrich the soil by decomposition of the compounds.
Compared with the analytical results from the Nordkalott Project (Fennoscandia) the contents of trace elements in liming materials would in most cases be lower than the background levels in till and stream sediments.

Still, some exceptions must be pointed out, which might be of importance also for well buffered agricultural soils.
With respect to Cd the ODDA burnt lime (sample B4), the ODDA lime (sample B5), the carbonate converter lime (sample B10) and in particular FAXE coral lime (sample B17) were containing substantial amounts.
The English quarterly burnt dolomite (sample B2) contributed with a substantial amount of Pb.
The contents of Hg were negligible for all liming materials.

Quite large amounts of F were added to soils by using ODDA lime (sample B5) and carbonate converter lime (sample B10).
Some As was also provided by the ODDA products (sample B4 and B5), although beyond any concern.

Probably outside the range of anxiety three liming materials, the English quarterly burnt dolomite (sample B2), the ODDA lime (sample B5) and the GAUSDAL magnesian limestone (sample B13) proved to be sources of V.
Ba was found particularly in the quarterly burnt dolomite and in the carbonate converter lime. Ba is normally precipitated and inactivated in soil, e.g. as barytes ($BaSO_4$).

The lowest levels of tolerance with respect to trace elements are stated when liming materials are used as a remedial measure in acdified watercourses.
According to the requirements of the Swedish Naturvårdsverket (National Swedish Environmental Protection Board) the Cd contents were too high in FAXE coral lime. In ODDA lime the Ni contents were close to the threshold values, and the V contents too high. Even without any declared requirements to F contents the levels would possibly not be accepted for ODDA lime and the carbonate converter lime when liming acidified waters.

INTRODUCTION

GEOLOGICAL BACKGROUND LEVELS OF ELEMENTS IN CONCERN

Within the Nordkalott Project Bølviken et al. (1986) made geochemical investigations (Subproject 4) in the northern part of the Precambrian Baltic Shield bordered by the Caledonian fold belt towards the north and west. The contents of trace elements could be considered as natural background levels in areas of old bedrocks (notwithstanding some Ni surface fallout from Russian side of the border), and four important sample types were till, stream sediments, stream organic matter and stream moss. These were sampled at the apex (downstream end) of each drainage area. Acid soluble elements were digested in 7 N HNO_3 (383 K, 3 h) followed by ICP analyses, of total elements by the means of X-ray fluorescence techniques.

The geochemical maps showed broad distribution patterns including regions and provinces with characteristic element concentrations. Enrichment factors were calculated for each of 22 elements, and these varied between 0.1 and 3.0. Concerning geochemical anomalies, chalcophile elements such as Cu, Co and Zn were enriched in the fine fraction of till and drainage samples from a number of the lithological zones.

Still, average values including their minimum/maximum levels, standard deviations and 50%/95% percentiles yielded good estimates of expected background levels. The glacial displacement of the geochemical patterns in the fine fractions of till and, consequently, in stream sediments and organic samples seemed to be negligible. The minus 0.06 mm grain size fraction of till had generally been displaced no more than a few hundred metres. Podzolization in the soils was normally quite scarce, with a podzolic E layer of only a few millimetres.
Regarding plant uptake of indicated elements, for some the fine fraction of mineral samples and the ash of organic samples (stream organic matter and mosses) produced similar distribution patterns (e.g. Cr).

Tab. 1 is presenting the total contents of some vital elements in till (<0.062 mm), tab. 2 of some partly rare elements in combined samples of till (<0.062 mm), and tab. 3 of HNO_3 soluble elements in stream sediments (<0.18 mm).

Tab. 1. Total contents of elements in till (fraction <0.062 mm) in northern Fennoscandia (n=5400), analyzed by optical emission spectrography (Bølviken et al. 1986).

Element	Minimum	Maximum	Mean	Stand. dev.	Percentiles 50%	 95%
Co, ppm	10	117	25.4	7.54	25	38
Cr, ppm	13	4120	103.49	104.04	84	250
Cu, ppm	1	978	17.2	25.67	11	48
K, %	0.01	7.9	1.68	0.99	1.48	3.65
Mg, %	0.01	6.31	1.47	0.75	1.43	2.77
Mn, ppm	1	7430	605.34	546.04	483	1600
Ni, ppm	1	1670	40.84	47.09	31	90
Pb, ppm	2	224	17.49	8.16	16	29
Ti, ppm	1000	24000	6101.51	1724.59	6090	8600
V, ppm	10	1950	224.45	109.93	218	360
Zn, ppm	1	208	29.77	18.67	24	67

Tab. 2. Total contents of elements in combined samples of till (fraction <0.062 mm) in northern Fennoscandia (n=1040), analyzed by neutron acitvation analysis (Bølviken et al. 1986).

Element	Minimum	Maximum	Mean	Stand. dev.	Percentiles 50%	 95%
As, ppm	<1	74	2.4*	3.52*	1.3	8.5
Au, ppb	<3	436	**	**	**	9.5
Ba, ppm	<100	1200	636.11*	153.29*	630	900
Br, ppm	<0.3	98	11.28*	11.12*	7.8	33
Cs, ppm	<0.6	13	1.85*	1.39*	1.6	4.7
Fe, %	<0.5	10.4	4.86*	1.27*	4.8	7
La, ppm	<1.8	133	36.72*	14.67*	33	61
Na, %	<0.01	4.99	2.44*	0.57*	2.5	3.2
Rb, ppm	<15	182	64.36*	20.41*	61	99
Sb, ppm	<0.1	115	0.41*	3.58*	0.2	0.9
Sc, ppm	<0.6	130	19.84*	5.71*	20	28
Sm, ppm	<0.1	37	6.28*	2.52*	6	10.4
Ta, ppm	<0.5	39	1.22*	1.25*	1.1	1.8
Th, ppm	<0.3	45	10.11*	4.06*	9.5	18
W, ppm	<0.6	9	**	**	**	1.9
U, ppm	<0.2	11	3.01*	1.28*	2.8	5.2

* Contents below the detection limit (DL) constituting less than 10% of the values were defined as 2/3*DL and included in the calculations of the mean and standard deviation.

** Mean and standard deviation were not calculated because the number of values below the detection limit constituted more than 10% of the total number of samples.

Tab. 3. Contents of HNO_3 soluble (7N, 383 K, 3 h) elements in streams sediments (fraction <0.18 mm) in northern Fennoscandia (n=5773), analyzed by ICP (Bølviken et al. 1986).

Element	Minimum	Maximum	Mean	Stand. dev.	Percentiles	
					50%	95%
Ag, ppm	<0.8	6	**	**	**	1.3
Al, %	0.07	5.4	0.79	0.49	0.66	1.7
Ba, ppm	1	1700	40.77	55.12	27.9	113.5
Ca, %	0.03	7.12	0.33	0.23	0.3	0.65
Ce, ppm	3	721	55.47	45.62	43.6	131
Co, ppm	0.6	242	6.83	6.99	5.3	16.4
Cr, ppm	0.3	668	19.04	22.2	14.2	44.1
Cu, ppm	<10	741	**	**	**	28.3
Fe, %	<0.05	31.9	1.59	2.02	1.1	4
La, ppm	3.5	317	29.65	20.31	24.6	64.3
Li, ppm	0.3	62	6.85	6.58	4.7	19.8
Mg, %	0.01	4.38	0.29	0.24	0.24	0.7
Mn, ppm	6.5	118000	317.97	1741.1	141	828.2
Mo, ppm	<1	117	**	**	**	4.4
Ni, ppm	1	617	9.99	12.87	6.99	26.4
P, ppm	29	21500	539.45	559.42	442	1200
Sc, ppm	0.1	24	2.41	1.28	2.21	4.5
Sr, ppm	1.6	569	14.85	13.81	12.1	32.9
V, ppm	1	225	23.33	14.77	19.8	50.3
Zn, ppm	1.2	608	23.27	24.85	15.6	66.6
Zr, ppm	<5	51	**	**	**	17

** Mean and standard deviation were not calculated because the number of values below the detection limit constituted more than 10% of the total number of samples.

THRESHOLD VALUES IN SOILS IN THE NETHERLANDS, AND NORWEGIAN AND GLOBAL AVERAGE LEVELS

In Norway there are no directives to evaluate the contents of environmentally toxic substances in soils or ground waters, but very often Dutch threshold values for contamination are referred to as a basis, as also done by NOTEBY (1992) in the report to Hole Kalkverk.

In the Dutch system values A, B, and C are presented. The A values are closely corresponding to non polluted nature conditions, and these values are listed for some elements in tab. 4, with Norwegian average agricultural soil contents, and assumed global average figures.

In European perspective the Norwegian soils are generally considered as non contaminated, exhibiting slightly lower trace element contents than the estimated global average.

On the other hand, the A values of the Netherlands are revealing the historical high loads on agricultural land within this densely industrialized area of Europe.

Tab. 4. A-values for element contents in soil (ppm) in the Netherlands (ref. NOTEBY 1992), Norwegian average agricultural soil contents (Bærug & Aasen 1991, Kongshaug et al. 1992), and assumed global average (Kongshaug et al. 1992), all verified in ppm in DM soil.

Elements	A-values Netherlands	Norwegian aver. soil contents	Assumed global average
copper (Cu)	50	15	22
zinc (Zn)	200	55-60	70
barium (Ba)	200		
lead (Pb)	50	14	22
cadmium (Cd)	1	0.07	0.4
nickel (Ni)	50	20-25	23
cobalt (Co)	20	7.3	9
chromium (Cr)	100	40	60
mercury (Hg)		0.05	0.08
arsenic (As)		6	9
manganese (Mn)		377	500
molybdenum (Mo)			1.3
tungsten (W)			1.5
vanadium (V)			90
uranium (U)			2.5
thorium (Th)			8.0

THE EUROPEAN COMMUNITY

Current EC directives are limiting the accepted heavy metal contents in soils, in sewage sludge, and annual heavy metal supplies to agricultural soils as an average of 10 years. One of these directives is numbered 86/278.

Threshold values in soils

Tab. 5. is showing the threshold values in soils. According to details given by the EC Commission these limits may be exceeded if sewage sludge is used and the agricultural area is used for animal production only.

Tab. 5. Threshold values for heavy metal concentrations in representative soils (ppm in DM) of pH 6-7 in the European Community.

Elements	Recommended values	Maximum values
cadmium (Cd)	1	3
copper (Cu) ¤	50	140
nickel (Ni) ¤	30	75
lead (Pb)	50	300
zinc (Zn) ¤	150	300
mercury (Hg)	1	1.5
chromium (Cr)	100	200

Tab. 5. cont.

¤ Until 50% higher concentrations of these metals are acceptable if pH>7.

Threshold values in sewage sludge

Tab. 6A is presenting the threshold values within the European Community in sewage sludge intended supplied to soils. These requirements are very liberal compared with the actual contents of Norwegian sludge products for agriculture, and proposed requirements from SFT (The Norwegian State Pollution Control Authority) (tab. 6B). In Norway these heavy metals were divided into groups due to toxicity and danger of the elements.

Tab. 6A. Threshold values for heavy metal concentrations in sewage sludge utilized on agricultural land (ppm in DM) in the European Community.

Elements	Recommended limit values	Maximum limit values
cadmium (Cd)	20	40
copper (Cu)	1,000	1,750
nickel (Ni)	300	400
lead (Pb)	750	1,200
zinc (Zn)	2,500	4,000
mercury (Hg)	16	25
chromium (Cr)	1,000	1,750

Tab. 6B. Threshold values for heavy metal concentrations in sewage sludge utilized on agricultural land and green open spaces (ppm in DM) as proposed by SFT (The Norwegian State Pollution Control Authority).

Elements	Agricultural and forest land	Green open spaces
GROUP 1		
cadmium (Cd)	4	10
GROUP 2		
lead (Pb)	100	300
mercury (Hg)	5	7
GROUP 3		
nickel (Ni)	80	100
zinc (Zn)	1,500	3,000
copper (Cu)	1,000	1,500
chromium (Cr)	125	200

Annual heavy metal supplies to agricultural soils

The limits for annual heavy metal supplies to agricultural soils are exhibited in tab. 7 as an average of 10 years.
Regarding details given by the EC Commission these limits might be exceeded if sewage sludge is used and the agricultural areas simultaneously are producing only animal fodder.

Tab. 7. Threshold values for annual heavy metal supplies (kg*ha^{-1}*year^{-1}) to agricultural land in the European Community.

Elements	Recommended limit values
cadmium (Cd)	0.15
copper (Cu)	12
nickel (Ni)	3
lead (Pb)	15
zinc (Zn)	30
mercury (Hg)	0.1
chromium (Cr)	4.5

THRESHOLD VALUES IN LIMING MATERIALS AS REMEDIAL MEASURES FOR ACIDIFIED WATERS IN SWEDEN

Naturvårdsverket (National Swedish Environmental Protection Board) (1988) has stated a list of acceptable levels of metal elements in liming materials for liming acidified waters, as presented in tab. 8. The analytical method is stated as dissolved in HNO_3 (probably according to the recommendations of SS 028150 [Swedish Standard], and analyzed by AAS or ICP.

Tab. 8. Limits (ppm in DM) of metal element contents in liming materials for liming acidified waters in Sweden, according to Naturvårdsverket (1988).

Elements	Accepted upper limit values
aluminium (Al)	20,000
zinc (Zn)	50
chromium (Cr)	50
nickel (Ni)	20
cobalt (Co)	20
copper (Cu)	20
vanadium (V)	20
lead (Pb)	20
cadmium (Cd)	0.5
mercury (Hg)	0.05

The limits with respect to Al might look a little strange, because most of the Al occurs tightly bound in silicates, and there will generally be waste amounts of Al in sediments. In general their solubility and toxicity are entirely pH dependent.

PREVIOUS INVESTIGATIONS OF CARBONATE AND SILICATE LIMING MATERIALS AND SOILS IN GERMANY

At several German universities and research stations there are currently running scientific projects regarding heavy metal contamination of soils and plants.

Rex (pers. comm. 1992) presented the wide variation in heavy metal contents of several mineral nutrients to soil, and the EC limiting values for these elements in sewage sludge for agriculture, as shown in tab. 9. It must be noticed that rock powder (for instance of basalt) might have higher contents than silicate and carbonate liming materials. The plant availability of these heavy metals is, however, a wider question. In addition to their disposition of weathering from minerals, their hydratization energy and polarity in soils, the Germans are stressing the importance of boiling point, mainly related to the processes of the steel industry. Elements with low boiling points will easily evaporate during these treatments.

Concerning silicate liming materials there is particularly paid attention to the Cr contents. Cr^{6+} is a toxic ion, but is to a large extent and rapidly reduced to Cr^{3+}, which is quite firmly fixed to soil colloids. Tab. 10 is showing the influence of longterm fertilization with convert slag on Cr contents of soils and plants. Certainly there was a slight increase in soil contents, nevertheless rarely any significant increase in plant uptake was confirmed.

Similarly Munk (1990) presented results from longterm fertilizer experiments with Thomas phosphates and sewage sludge in Germany. The method used to discriminate between Cr^{3+} and Cr^{6+} was a precipitation of Cr^{3+} and aluminium hydroxide in the presence of a phosphate buffer in the pH range 7.0-7.2, according to DIN 83405. The results are presented in tab. 11, and showed that in spite of a moderate increase in total Cr contents, the soluble contents of Cr, and in particular Cr^{6+} did not demonstrate any relationship to the supply of Thomas phosphates, and only to a small extent when sewage sludge was added.

Tab. 9. **Heavy Metal Contents in Slags and Natural Limestones** (ppm)

Fertilizer	n	Cd	Cu	Ni	Pb	Zn	Hg	total Cr	Cr (VI)
basic oxygen slag (converterslag)	39	<0,1	11- 36	<0,5-21	2-41	10-98	<0,01-0,16 (n = 5)	727-2630	<0,3-0,32
mode		-	18	3	9	17	~0,04	1924	-
blast furnace slag	30	<0,1-0,35	2-10	<0,5- 4	1-29	3-166	<0,01-0,14 (n=7)	22-206	<0,3
mode		<0,1	3	<0,9	13	7	~0,03	68	-
natural limestone	32	0,1-1,5	1-14	1-34	1-51	22-145	<0,01-0,11 (n = 16)	9-62	?
rock powder	11	<0,1-5,0	4-73	3-392	1-109	46-268	<0,01-2,0	14-357	?
boiling point °C		770	1083	2340	1540	907	357	2200	
EC limiting values for heavy metals in sewage sludge for use in agriculture (mg/kg dry substance)									
recommended		20	1000	300	750	2500	16	1000	
maximum		40	1750	400	1200	4000	25	1750	

temperature range in the blast furnace 1500 - 2000 °C, in the converter 1600 - 2000 °C

(Rex, pers. comm. 1992)

Tab. 10.

Influence of longterm fertilization with converter slag on Chromium contents of soils and plants

location	institute	duration years	ppm Cr in soil range	 increase	ppm Cr in the plant without Cr	 with Cr
1. Dikopshof	Bonn university	88	23 - 29	6	0,14 - 1,24	0,15 - 1,11
2. Ernsthofen	LUFA Darmstadt	69	42 - 50	8	0,80 - 1,70	1,10 - 1,40
3. Weihenstephan	Munich university	53	37 - 42	5	0,51 - 3,25	0,69
4. St. Peter*	VA Kamperhof	33	28 - 43	15	0,40 - 3,20	0,40 - 3,20
5. Meckenheim	Bonn university	29	26 - 32	6	0,40 - 2,90	1,40 - 1,70
6. Kolsaßberg*	Vienna, ÖDB	15	257 - 273	16	0,30 - 1,00	0,60 - 2,50
7. Uelzen	VA Kamperhof	11	15 - 22	7	0,50 - 0,60	0,40
8. Meckenheim	VA Kamperhof	12	33 - 43	10	1,50 - 1,90	1,80
				mean	0,55 - 1,81	0,77 - 1,48

*grassland

(Rex, pers. comm. 1992)

Tab. 11. **Total Chromium and Chromium (VI) in Soil Extracts (mg Cr/kg soil dry weight)**

	total chromium		Cr (III) + Cr (VI) at pH***			Cr (VI) at pH***		
	*	**	1	2	H_2O-soluble	1	2	H_2O-soluble
Dikopshof (88 years)								
without Cr	26	81	< 0,25	-	< 0,01	-	-	< 0,25
with Cr	29	82	0,59	< 0,25	< 0,01	< 0,25	< 0,25	< 0,25
Weihenstephan (53 years)								
without Cr	37	79	< 0,25	< 0,25	0,54	-	-	< 0,25
with Cr	42	81	0,47	-	< 0,01	-	-	< 0,25
Darmstadt (69 years)								
without Cr	54	112	1,36	< 0,25	< 0,01	-	-	< 0,25
with Cr	57	96	1,11	< 0,25	< 0,01	< 0,25	-	< 0,25
Uelzen (11 years)								
without Cr	16	60	0,80	< 0,25	-	< 0,25	< 0,25	-
with Cr	22	63	1,20	< 0,25	-	< 0,25	< 0,25	-
sewage sludge soils								
1	108		4,60	< 0,25	0,37	< 0,25	< 0,25	< 0,25
2	440		44,50	2,80	0,36	< 0,25	< 0,25	< 0,25
3	1107			10,10	0,65			0,26
4	49		1,90	< 0,25	0,10	< 0,25	< 0,25	< 0,25

means of dissolution: * aqua regia
** alkaline melting

(Munk 1990)

*** pH stat 30 min

PREVIOUS INVESTIGATIONS IN SWEDEN

Statens Lantbrukskemiska Laboratorium (SLL) (1985) made an investigation upon quality parameters of liming materials in Sweden intended for use as a remedial measure against acidified waters. The project was performed on behalf of Naturvårdsverket (National Swedish Environmental Protection Board). This was a preliminary report, to a large extent based upon information from the lime industry, as indicated in tab. 12.
Most of the companies in 1985 are now included in the three larger companies in Sweden: The Finnish PARTEK, and the Swedish ERNSTRÖM MINERAL AB and SVENSKA MINERAL AB (Gåsgruvan).

Tab. 12. Liming materials analyzed at Statens Lantbrukskemiska Laboratorium (SLL) (1985) on behalf of Naturvårdsverket (National Swedish Environmental Protection Board) Results of trace element analyses (ppm in DM). All analyses were performed by AAS.

Product no.	**Brand name**	**Type of liming material**	**Origin**
1	T lime	Silicate liming material	Steel industry
2	Agricultural lime 0-0.5 mm	Fine limestone	Silurian limestone
3	C 25	Fine dolomite	Precambrian dolomite
4	C 45	Fine dolomite	Precambrian dolomite
5	Fine limestone 0-0.5 mm	Fine limestone	Precambrian limestone
6	Fine limestone 0-0.1 mm	Fine limestone	Precambrian limestone
7	Fine limestone 0-0.05 mm	Fine limestone	Precambrian limestone
8	Fine chalk 0-0.2 mm	Fine chalk	Cretaceous chalk
9	Moist fine limestone 0-0.2 mm	Fine limestone	Ordovician limestone
10	Mesa lime, Delary	Non designated liming material	By-product from the Sulfate process (Kraft) pulp plants
11	Fine limestone 0-0.5 mm	Fine limestone	Silurian limestone
12	Glanshammar dolomite 0-0.3 mm	Fine dolomite	Precambrian dolomite
13	Glanshammar dolomite, filter dust	Fine dolomite	Precambrian dolomite
14	Larsbo dolomite 0-0.3 mm	Fine dolomite	Precambrian dolomite
15	Larsbo limestone 0-0.3 mm	Fine limestone	Precambrian limestone
16	Fine limestone for environment and and lakes 1	Fine limestone	Precambrian limestone
17	Fine limestone for environment and and lakes 2	Fine limestone	Precambrian limestone
18	Fine limestone 0-0.2 mm	Fine limestone	Silurian limestone

Tab. 12. cont.

Product no.	**Companies of delivery**	**Quarries**
1	FERROLEGERINGAR, TROLLHÄTTEVERKAN AB	
2	YXHULT MINERAL AB	Hällabrottet, Kumla
3-4	NORDISKA MINERALPRODUKTER AB	Stråbruken, Sala
5-7	CEMENTA	Forsby, Köping
8	CEMENTA	Ignaberga
9	CEMENTA	Skövde
10	CEMENTA	
11	St. Stohlans Kalkindustri AB	Uddagården
12-13	ERNSTRÖM MINERAL AB	Glanshammar
14-15	ERNSTRÖM MINERAL AB	Larsbo
16-17	NORDISKA MINERALPRODUKTER AB	Gåsgruvan, Filipstad
18	DALA KALK AB	Orsa

Tab. 12. cont.

	Product no.	**Heavy metal contents**										
		Pb	Cd	Ni	Co	Cu	Zn	Ti	Cr	V	Hg	
	1	excluded from the analyses, not recommended for lake liming										
ß	2	<10	<1	10	<10	<10	10		30	20	<0.1	*
ð	3-4	0.06	<0.2	<0.05		<0.01	0.27		0		0.002	¤
Þ	5-7	<5	<0.4	<1	2	3	41	<1	9	<10	<0.4	
Þ	8	<5	0.5	<1	1	2	19	<1	4	<10	<0.4	
	9	not analyzed										
¶	10	5-7	0.1-0.5	5-10	1.3-2.5	10-20	50-60	<1	25-30	<10	<0.03	@
ß	11A	10	<1	20	10	<10	10		30	20	<0.1	$
ß	11B	<5	<1			<10					<0.1	£
©	12-13	1	<0.11	<0.6	<0.6	2.2	22.3		<1	<4	<0.02	µ
©	14	<0.6	<0.07	<0.6	<0.6	2.3	26.5		<1	<4	<0.02	
©	15	5.9	<0.29	<0.6	<0.6	2.3	57.9		<1	<4	<0.02	
	16-17	4	0.4		18	3			30		<0.02	
©	18	<2	<0.1	8.5	3.0	5.0	8.0		2.0	<10.0	<0.01	

* Product information 1985/Certificate of analysis 1981
¤ Information by letter 1985
@ Product declaration 1982
$ Certificate of analysis 1981
£ Product declaration 1984
µ Written product information

ANALYTICAL METHODS:

ß Analyzed in another laboratory, analytical methods unknown

ð Analyzed at SLL, digestion with aqua regia (HCl : HNO_3 = 3:1)

Þ Analyzed in laboratories of the lime industry, digestion with aqua regia (HCl : HNO_3 = 3:1) + HNO_3

¶ Analyzed in laboratories of the lime industry, digestion with HNO_3

© Analyzed at SLL, digestion with HNO_3, to dissolve Cr also addition of HF, which might yield higher figures (+50% for silicate liming materials)

Tab. 12. cont.

Product no.	**Accessory element contents**									
	P	S	Ag	As	Be	Bi	Mn	Mo	Sb	Sn	
1	excluded from the analyses, not recommended for lake liming										
2			<1	<50	<3	<10	1500	<10	<100	<10	*
3-4											
5-7	<0.01	0.01									
8	0.04	0.02									
9	not analyzed										
10		0.1									@
11A											$
11B			<1	<50	<3	<10	2300	<10	<100	<10	§
12-13											
14-15											
16-17	0.004	0.005									
18	0.01	0.02									

* Journal of analysis SLL 1981
@ Journal of analysis SLL 1982
$ Product information 1984
§ Journal of analysis SLL 1981

Relating these results to the requirements of Naturvårdsverket (1988), the Mesa lime (sample 10) was particularly contaminated with heavy metals. Only for Zn the figure was, however, higher than the acceptable upper limit.
Agricultural lime 0-0.5 mm (sample 2) was a little high in Cr and V, the Precambrian limestone from Forsby, Köping (samples 5-7) with respect to Zn, the fine limestone 0-0.5 mm from Uddagården (sample 11) regarding Cr and V, and the fine limestones for environment and lakes (samples 16-17) concerning Cr, but all these parameters were below the critical levels.
Merely the Zn content of the Larsbo limestone 0-0.3 mm (sample 15) was slightly above the critical value.

MATERIALS AND METHODS

SAMPLING OF LIMING MATERIALS

The certificates of analysis from the different lime industry companies reflected the industrial priority and requirements of their customers.
Tab. 13 is presenting these products (series A) as analyzed by initiative of the industry, accompanied by names of applied laboratories. The analytical methods of these laboratories are described in detail in the next chapter.
The analytical data (fundamental carbonate analyses) for the samples A16-A25 are general figures and were not checked for these trace element investigations.

Tab. 13. Liming materials delivered for analysis by lime industry companies, accompanied by fundamental carbonate analyses and names of applied laboratories for heavy metal and accessory element analyses. Series Ann and series Axn. NV = neutralizing value. The chemical analyses 'as delivered.'

Tab. 13A.

Product no.	**Brand name**	**Type of liming material**	**Origin**
A1	Fine limestone	Fine limestone	Ordovician-Silurian limestone
A2	Fine limestone	Fine limestone	Ordovician-Silurian limestone
A3	Hydrated lime	Hydrated lime	Silurian limestone
A4	Fine limestone	Fine limestone	Silurian limestone
A5	Fine limestone	Fine limestone	Silurian limestone
A6	Fine limestone	Fine limestone (dust from drilling)	Cambro-Silurian limestone
A7	Carbonate converter lime	Non designated liming material	Raw phosphate
A8	Half-burnt dolomite	Burnt dolomite	Ordovician dolomite
A9	Coarse dolomite	Coarse dolomite	Ordovician dolomite
A10	Coarse dolomite	Coarse dolomite	Ordovician dolomite
A11	Hydrated lime	Hydrated lime	Silurian limestone
A12	Fine limestone	Fine limestone	Ordovician-Silurian limestone
A13	FAXE lime	Non designated liming material	Tertiary coral lime (Faxe Kalk, Denmark
A14	Fine limestone	Fine limestone	Ordovician-Siluran limestone
A15	Carbonate converter lime	Non designated liming material	Raw phosphate
A16	FAXE fodder lime	Non designated liming material	Tertiary bryozo lime (Faxe Kalk, Denmark)
A17	FAXE Rollovit (paint industry)	Non designated liming material	Tertiary bryozo lime (Faxe Kalk, Denmark)

Tab. 13A. cont.

Product no.	Brand name	Type of liming material	Origin
A18	Aggersund fine chalk	Non designated liming material	Cretaceous chalk
A19	Granulated dolomite	Granulated dolomite	Ordovician dolomite
A20	Very fine limestone	Very fine limestone	Silurian limestone
A21	Coarse dolomite	Coarse dolomite	Ordovician dolomite
A22	Fine limestone	Fine limestone	Ordovician-Siluran 0imestone
A23	Carbonate converter lime	Non designated liming material	Raw phosphate (ca. 50 % Kola ph., ca. 50 % Israel ph.)
A24	Carbonate converter lime	Non designated liming material	Raw phosphate (100 % Kola ph.)
A25	Shell sand	Shell sand	Quaternary carbonate marine organisms
A26	Carbonate converter lime	Non designated liming material	Raw phosphate
Samples A27-A30: Industrial qualities			
A27	Microdol Super	Very fine dolomite	Ordovician dolomite
A28	Microdol Extra	Very fine dolomite	Ordovician dolomite
A29	Microdol 1	Very fine dolomite	Ordovician dolomite
A30	Microdol 200	Very fine dolomite	Ordovician dolomite
A31	Coarse dolomite	Coarse dolomite	Ordovician dolomite
A32	Microdol 1	Very fine dolomite	Ordovician dolomite
A33	ODDA lime	Non designated liming material	By-product from dicyandiamid production+burnt lime
A34	TORPE lime	Non designated liming material	By-product from the Sulfate process (Kraft) pulp plants
A35-A38	Carbonate converter lime	Non designated liming material	Raw phosphate

Tab. 13A. cont.

Product no.	Date of sampling(S) /analysis(A)	Fundamental carbonate analyses			
		% DM	NV	% Ca	% Mg
A1	31st Jan. 1990 (A)	100	53.1	34.1	2.29
A2	12th Jun. 1989 (A)	100			
A3	29th Apr. 1988 (A)	100	74.4	50.9	0.45
A4	10th Oct. 1990 (S)	99.96	54.3		
A5	1987 (A)	100	49.7	34.4	0.67
A6	3rd Oct. 1991 (S)	100			
A7	4th Sep. 1990 (A)	100			
A8	27th Dec. 1989 (A)	100			
A9	18th Jun. 1987 (A)	100	60.2	22.4	12.4
A10	18th Jun. 1987 (A)	100	57.5	22.3	11.3
A11	1989 (A)	100			0.42
A12	1989 (A)	100			2.10
A13	1989 (A)	100			0.19

Tab. 13A. cont.

Product no.	**Date of sampling(S) /analysis(A)**	**Fundamental carbonate analyses** % DM	NV	% Ca	% Mg
A14	1989 (A)	100			2.50
A15	1989 (A)	100			0.0030
A16	1990 (A)	99.9	55.9	38.9	0.42
A17	1990 (A)	99.9	55.9	38.9	0.42
A18	1990 (A)	93.1	52.4	36.8	0.32
A19	1990 (A)	91.19	57.5	22.3	11.3
A20	1990 (A)	99.70	51.0	34.3	1.3
A21	1990 (A)	98.40	61.0	21.6	13.0
A22	1990 (A)	99.87	44.2	30.9	0.58
A23	1990 (A)	89.24			
A24	1990 (A)	85.65			
A25	1990 (A)	98.80	50.4	35.5	0.4
A26	23rd Oct. 1987 (A)				
A27-A30	6th Jun. 1983 (S)	100.0	61.0	21.6	13.0
A31	Feb. 1989 (A)	100			
A32	20th Jul. 1990 (S)	100.0	61.0	21.6	13.0
A33	30th Mar. 1990 (A)	89.5		(12.6)	(0.00138)
A34	13th Sep. 1991 (S)	90.5	46.0	31.8	0.66
A35	18th Apr. 1991 (S)	91.4	50.6	36.2	
A36	20th Sep. 1991 (S)	90.3	47.3	33.8	
A37	24th Sep. 1991 (S)	88.3	45.9	32.8	
A38	11th Oct. 1991 (S)	90.3	47.4	33.9	

Tab. 13A. cont.

Product no.	**Companies of delivery**
A1	Hole Kalkverk, Hans Sandbakken A/S, N-2840 REINSVOLL
A2	Steens Kalkverk A.S., N-2320 FURNES
A3	Mjøndalen Kalkfabrik A.S., N-3050 MJØNDALEN
A4-A5	Franzefoss Bruk A/S, Sect. Rud, N-1351 RUD
A6	Franzefoss Bruk A/S, Sect. Hylla/Verdal, N-7672 RØRA
A7-A8	NORSK HYDRO A.S./Franzefoss Bruk A/S, Sect. Rud, N-1351 RUD
A9-A10	Franzefoss Bruk A/S, Sect. Ballangen, N-8540 BALLANGEN
A11	Mjøndalen Kalkfabrik A.S., N-3050 MJØNDALEN
A12	Steens Kalkverk A.S., N-2320 FURNES
A13	Råde Mølle og Kornsilo A/S, N-1640 RÅDE
A14	Hole Kalkverk, Hans Sandbakken A/S, N-2840 REINSVOLL
A15	NORSK HYDRO A.S./Franzefoss Bruk A/S, Sect. Rud, N-1351 RUD
A16-A17	FAXE Kalk, P.O.Box 2183, DK-1017 COPENHAGEN K
A18	DANKALK, Aggersund Kalkværk A/S, DK-9670 LØGSTØR
A19	Franzefoss Bruk A/S, Sect. Ballangen, N-8540 BALLANGEN
A20	Store Stohlans Kalk AB, S-52100 FALKÖPING (now PARTEK AB)
A21	Hammerfall Dolomitt A.S., N-8200 FAUSKE
A22	AKER-NORCEM A.S., P.O.Box 38, N-3901 BREVIK
A23-A24	NORSK HYDRO A.S./Franzefoss Bruk A/S, Sect. Rud, N-1351 RUD

Tab. 13A. cont.

Product no.	**Companies of delivery**
A25	Hordaland Skjellsandtørkeri A/S, P.O.Box 53 Holmen, 0322 OSLO
A26	NORSK HYDRO A.S./Franzefoss Bruk A/S, Sect. Rud, N-1351 RUD
A27-A30	A/S NORWEGIAN TALC - now: NORWEGIAN TALC, ERNSTRÖM MINERALS AB, N-5355 KNARREVIK Dolomite delivered from Hammerfall Dolomitt A.S.
A31	Hammerfall Dolomitt A.S., N-8200 FAUSKE Dolomite delivered from Løgavlen Quarry, Fauske
A32	RAPRA TECHNOLOGY LTD., GREAT BRITAIN - A/S NORWEGIAN TALC - now: NORWEGIAN TALC, ERNSTRÖM MINERALS AB, N-5355 KNARREVIK Dolomite delivered from Hammerfall Dolomitt A.S.
A33	Odda Smelteverk A/S, N-5750 ODDA
A34	Knut Knutsen A/S, Lilleborgveien 9, N-1650 SELLEBAKK
A35-A38	NORSK HYDRO A.S./Franzefoss Bruk A/S, Sect. Rud, N-1351 RUD

Tab. 13A. cont.

Product no.	**Laboratories for heavy metal and accessory element analysis**
A1	Department of Geology and Mining Technics, Univ. of Trondheim/NTH, N-7034 TRONDHEIM
A2	Section of Technical Chemistry/Group of Sensing Tecnhology, SINTEF/NTH, N-7034 TRONDHEIM (Project no. 213000,01, J.no. 98144)
A3	ANALYTICA AB, P.O.Box 511, S-183 25 TÄBY (J.no. 88-47834)
A4	KEMISKA STATIONEN AB, S-532 00 SKARA (Project. no. 90-563, J.no. 13381-90)
A5	NORDISK ANALYSE CENTER/NORSK ANALYSESENTER, P.O.Box 24, N-1361 BILLINGSTAD (J.no. 257/87)
A6	EUROC RESEARCH, Box 104, S-620 30 SLITE (J.no. 51653/91)
A7	NORSK HYDRO A.S., HYDRO Porsgrunn
A8	NORSK HYDRO A.S., HYDRO Porsgrunn, (Mg-Norge/ Teknologi, T. Haugerød/bee)
A9-A10	NORDISK ANALYSE CENTER/NORSK ANALYSESENTER, P.O.Box 24, N-1361 BILLINGSTAD (J.no. 93/87)
A11-A15	NORSK HYDRO A.S., HYDRO Porsgrunn, (Johnsen (1989), Doc. no. 89B.FG8)
A16-A25	NORSK HYDRO A.S., HYDRO Porsgrunn, (Melgård (1990), Proj. no. L51550.001, Doc. no. 89B.FG8)
A26	Chemical Analytical Laboratory, P.O. Box 5031, 1432 ÅS (Jo.no. 870664)
A27-A30	CHEMLAB SERVICES A.S., P.O.Box 1517, N-5035 BERGEN-SANDVIKEN (J.no. 41952-41956)
A31	SINTEF-MOLAB, N-8600 MO I RANA
A32	Unknown British laboratory (NAMAS approved)

Tab. 13A. cont.

Product no.	**Laboratories for heavy metal and accessory element analysis**
A33	Landbrukets Analysesenter, P.O.Box 5091, N-1432 ÅS (J.no. 10,320/90)
A34	Landbrukets Analysesenter, P.O.Box 5091, N-1432 ÅS (J.no. 8,225/91)
A35-A38	Landbrukets Analysesenter, P.O.Box 5091, N-1432 ÅS (J.no. Ay2: 91120, Ay3: 91230, Ay4: 91234, Ay5: 91252)

In sample A33 there were also made analyses of Ca and Mg, but these represented only a fraction of the total contents, due to a rather weak dissolving agent (dilute HNO_3).

Tab. 13B.

Product no.	**Site in the quarries**	**Type of liming material**	**Origin**
Ax1	Hanseberget 1	Fine limestone	Silurian limestone
Ax2	Hanseberget 2	Fine limestone	Silurian limestone
Ax3	Hanseberget 3	Fine limestone	Silurian limestone
Ax4	Hanseberget 4	Fine limestone	Silurian limestone
Ax5	Fredly 1	Fine limestone	Silurian limestone
Ax6	Fredly 2	Fine limestone	Silurian limestone
Ax7	Fredly 3	Fine limestone	Silurian limestone
Ax8	Fredly 4	Fine limestone	Silurian limestone
Ax9	Residue (non dissolved portion) of samples Ax1-Ax4.		

Tab. 13B. cont.

Product no.	**Date of sampling**	**Fundamental carbonate analyses**			
		% DM	**NV**	**% Ca**	**% Mg**
Ax1	1991	100.0	51.5	34.8	1.2
Ax2	1991	100.0	47.5	30.8	1.9
Ax3	1991	100.0	54.1	37.2	0.88
Ax4	1991	100.0	54.0	34.9	2.2
Ax5	1991	100.0	54.5	36.6	1.4
Ax6	1991	100.0	53.4	37.0	0.67
Ax7	1991	100.0	54.2	37.5	0.71
Ax8	1991	100.0	24.8	15.9	1.1
Ax9	Residue (non dissolved portion) of samples Ax1-Ax4.				

Tab. 13B. cont.

Product no.	**Companies of delivery**
Ax1-Ax9	Hole Kalkverk, Hans Sandbakken A/S, N-2840 REINSVOLL

Tab. 13B. cont.

Product no.	**Laboratories for heavy metal and accessory element analysis**
Ax1-Ax9	Landbrukets Analysesenter, P.O.Box 5091, N-1432 ÅS (J.no. Ax1-Ax8: 10,008-10,015, Ax9: Residue)

The samples of liming materials analyzed at Landbrukets Analysesenter in spring 1992 were sampled according to priority of STIL and Fureneset Research Station.
These (series B) are shown in tab. 14.

Tab. 14. Liming materials delivered for analysis of heavy metal and accessory element contents at Landbrukets Analysesenter, P.O. Box 5091, N-1432 ÅS in spring 1992, accompanied by fundamental carbonate analyses. NV = neutralizing value. The chemical analyses 'as delivered.'

Product no.	**Brand name**	**Type of liming material**	**Origin**
B1	Coarse limestone	Coarse limestone	Silurian limestone
B2	Quarterly burnt dolomite	Non designated liming material	75% Maglime + 25% burnt dolomite (Steel Ltd., England)
B3	Fine limestone	Fine limestone	Ordovician-Silurian limestone
B4	OODA burnt lime	Burnt lime	Dusty lime drained off by calcium carbide production
B5	ODDA lime	Non designated liming material	By-product from dicyandiamid production+burnt lime
B6	K2 Agricultural Lime	Coarse limestone	Precambrian limestone (marble)
B7	Coarse limestone - Special product	Coarse limestone	Cambro Silurian limestone
B8	Coarse dolomite - Fine variant	Coarse dolomite	Ordovician dolomite
B9	Fine limestone	Fine limestone	Silurian limestone
B10	Carbonate converter lime	Non designated liming material	Raw phosphate
B11	Coarse dolomite	Coarse dolomite	Ordovician dolomite
B12	Coarse dolomite	Coarse dolomite	Ordovician dolomite
B13	Coarse magnesian limestone	Coarse magnesian limestone	Late Precambrian limestone & dolomite
B14	Fine limestone	Fine limestone	Silurian limestone
B15	Coarse limestone	Coarse limestone	Silurian limestone
B16	Simontorps coarse dolomite	Coarse dolomite	Precambrian dolomite (Ernström Mineral AB, Sweden)
B17	FAXE lime	Non designated liming material	Tertiary coral lime (Faxe Kalk, Denmark

Tab. 14 cont.

Product no.	Brand name	Type of liming material	Origin
B18	Coarse limestone - Fine variant	Coarse limestone	Silurian limestone (Uddagård lime, Sweden)

Tab. 14 cont.

Product no.	Date of sampling	Fundamental carbonate analyses			
		% DM	NV	% Ca	% Mg
B1	15th Jan. 1992	99.5	49.2	34.2	0.58
B2	24th Apr. 1991	86.3	52.1	21.1	9.70
B3	22nd Nov. 1991	99.9	50.6	31.3	2.90
B4	23rd Dec. 1991	-	89.0	62.6	0.58
B5	23rd Dec. 1991	92.1	52.8	37.4	0.20
B6	21st June 1991	99.3	55.4	38.9	0.40
B7	26th Sep. 1991	96.7	53.3	37.6	0.30
B8	27th Jan. 1992	100.0	58.5	22.7	11.50
B9	10th Dec. 1991	99.9	47.9	32.2	1.20
B10	7th Feb. 1992	86.7	46.9	33.0	0.32
B11	4th Dec. 1991	99.7	60.4	21.4	13.10
B12	29th Jan. 1992	100.0	58.3	21.7	12.00
B13	11th Nov. 1991	99.9	53.8	24.0	8.70
B14	27th Sep. 1991	99.9	51.0	35.5	0.57
B15	14th Oct. 1991	97.1	44.6	31.2	0.51
B16	27th Feb. 1992	99.9	54.6	20.6	11.10
B17	19th Oct. 1991	92.9	50.9	35.8	0.33
B18	18th Apr. 1991	96.8	47.2	33.1	0.35

Tab. 14 cont.

Product no.	Companies of delivery	Journal number at Landbrukets Analysesenter
B1	Mjøndalen Kalkfabrik A.S., N-3050 MJØNDALEN	91284
B2	Mjøndalen Kalkfabrik A.S., N-3050 MJØNDALEN	91133
B3	Steens Kalkverk A.S., N-2320 FURNES	91267
B4	Odda Smelteverk A/S, N-5750 ODDA	91281
B5	Odda Smelteverk A/S, N-5750 ODDA	91280
B6	Visnes Kalk- og Marmorbrudd A/S, N-6493 LYNGSTAD	91200
B7	Franzefoss Bruk A/S, Sect. Hylla/Verdal, N-7672 RØRA	91240
B8	Franzefoss Bruk A/S, Sect. Ballangen, N-8540 BALLANGEN	91296
B9	Franzefoss Bruk A/S, Sect. Rud, N-1351 RUD	91274
B10	Franzefoss Bruk A/S, Sect. Rud, N-1351 RUD	91305
B11	Hammerfall Dolomitt A/S, N-8200 FAUSKE	91271
B12	Nymineral A/S, N-8120 NYGÅRDSJØEN	91302
B13	Gausdal Kalk A/S, N-2622 SVINGVOLL	91263
B14	Nysether Kalkmølle, N-7160 BJUGN	91241
B15	Sando Kalk- og Pukkservice A/S, N-3070 SANDE I VESTFOLD	91250
B16	Simontorps a.s, N-3157 BARKÅKER	91318
B17	Råde Mølle og Kornsilo A/S, N-1640 RÅDE	91259
B18	Halden Kalkservice A/S, N-1750 HALDEN	91227

Tab. 14 cont.

Sample no.	**The Norwegian Forest Research Institute (NISK)**
B4	1572/1992
B5	1571/1992
B10	1573/1992

CHEMICAL ANALYTICAL METHODS

Each laboratory adopted its own procedures of analyses, or modified different standard methods.

I. DEPARTMENT OF GEOLOGY AND MINING TECHNICS, UNIV. OF TRONDHEIM/NTH, N-7034 TRONDHEIM

Only a few details were given about methods at this laboratory. The procedures were, however, stated to be X-ray fluorescence spectroscopy and atomic absorption for total element analysis. The fluorimetric method was probably used for Cd (Cd^{2+} with 2-(o-Hydroxyphenyl)-benzoxazole as a complexing agent) and Zn (Zn^{2+} with Benzoin as a compl. ag.), according to Skoog & West (1982). For mineral analyses X-ray diffractometry was used.

II. SECTION OF TECHNICAL CHEMISTRY/GROUP OF SENSING TECHNOLOGY, SINTEF/NTH, N-7034 TRONDHEIM

The procedure used was a method for a total analysis.

The digestion of the sample prior to atomic absorption spectroscopy (AAS) was a two-step operation:

Step I.
1. The sample was added conc. HCl : conc. HF = 2:1, and vapoured to dryness.
2. This operation was repeated twice with only conc. HCl to remove the HF.
3. The dried sample was dissolved in 5% HCl.

Step II.
1. Potassium pyrosulfate ($K_2S_2O_7$) as a potent acidic flux was added to the residue, heated 5 min. to 1000-1100 K using a gas burner. This attacked the more intractable metal oxides, and partly silicates and sulfides.

After filtration both the solutions were measured by atomic absorption spectroscopy (AAS), and the total result presented.

The sample was digested and analyzed by a separate procedure for Hg:

1. Conc. HNO_3 : dist. H_2O = 1:1 was added to the sample, ensued by heating on plate for 1 hour.
2. Filtering the sample, followed by atomic absorption spectroscopy (AAS) using cold vapour technics.

III. ANALYTICA AB, P.O.Box 511, S-183 25 TÄBY

This method was mainly dissolving the carbonate materials and their derivatives (for instance hydroxides):

1. Digestion with HNO_3 according to the recommendations of SS 028150 (Swedish Standard), directed by the National Swedish Environmental Protection Board (Naturvårdsverket 1987).
2. Hg analysis by the means of AAS cold vapour technics, analyses of other elements using ICP.

When handling samples of hydrated lime the analyses of loss by ignition were performed at 1233 K.

IV. EUROC RESEARCH, Box 104, S-620 30 SLITE

The methods were similar to those at ANALYTICA AB, not dissolving the more intractable compounds, referring to Swedish Standards, as directed by Naturvårdsverket (1987):

* SS 028150 - Metal contents in water, sludge and sediments. Determinations by flame AAS - general principles and regulations.
* SS 028151 - Metal contents in water, sludge and sediments. Determinations by flame AAS - particular directives for Al.
* SS 028152 - Metal contents in water, sludge and sediments. Determinations by flame AAS - particular directives for Pb, Fe, Cd, Co, Cu, Ni and Zn.
* SS 028157 - Metal contents in water, sludge and sediments. Determinations by flame AAS - particular directives for Mn.
* SS 028173 - Metal contents in water, sludge and sediments. Determinations by flame AAS - particular directives for Cr.
* SS 028183 - Metal contents in water, sludge and sediments. Determinations by non-flame AAS - electrothermic atomization in graphite oven - general principles and regulations.

The procedures at this laboratory deviated from the Swedish Standard by applying a teflon bomb instead of an autoclave for digestion of the sample (1 g of the sample, 20 ml conc. HNO_3 : dist. H_2O = 1:1, 30 min. at 393 K).
Due to the concentration levels of these samples of liming materials Mn and Cu were analyzed by AAS, Cr, Pb and Cd by graphite oven, Hg as a hydride, and S by LECO aparatus.

V. KEMISKA STATIONEN AB, S-532 00 SKARA

The analyses performed were in accordance with the Swedish Standards cited for EUROC RESEARCH.

VI. NORDISK ANALYSE CENTER, P.O.Box 47 Grorud, N-0917 OSLO
From 1st June 1991: NORSK ANALYSESENTER, P.O.Box 24,
N-1361 BILLINGSTAD

The samples were decomposed in two steps:

Step I. Easily soluble elements: quite a large portion digested in perchloric acid + nitric acid, heated until 453 K for 16 h.

Step II. Total element contents: 100-500 mg decomposed in 2 ml conc. aqua regia (conc.HCl : conc.HNO_3 = 1:3) + 2 ml conc. HF, diluted to 50 ml with dist. H_2O, reacting in an autoclave or a teflon bomb at 413 K for 4 h.

Hg analyses were performed by the means of AAS cold vapour technics, analyses of other elements using ICP.
The analyses of loss by ignition were performed at 973 K.

VII. NORSK HYDRO A.S., HYDRO PORSGRUNN, P.O.Box 110, N-3901
PORSGRUNN

Different laboratories/factories at HYDRO PORSGRUNN considered varying approaches to decomposition of analytical materials.

PROCEDURE 1 (Mg DIVISION HYDRO PORSGRUNN/T. Haugerød).

Two methods of dissolution were applied, firstly to determine the water soluble elements, secondly to establish the level of elements dissolved in acid.

1.1. Water soluble:
25.00 g dry sample was weighed into an Erlenmeyer flask, added 200 ml double dist. H_2O, boiled for 10 min. with reflux, cooled, diluted to 250 ml and filtered.

1.2. Soluble in acid:
10.00 g dry sample was weighed into an Erlenmeyer flask, added 100 ml double dist. H_2O and 40 ml aqua regia (conc. HCl : conc. HNO_3 = 3:1), boiled for 10 min. with reflux, cooled, diluted to 200 ml and filtered.

Acid soluble Hg was extracted by the means of aqua regia, 20 ml added to 2.00 g sample.

All elements were determined by AAS. Hg analyses were performed by the means of AAS cold vapour technics and CVAAS/Au amalgamation.

F^- and Cl^- were analyzed with ion sensitive electrodes in moist samples.

PROCEDURE 2 (THE RESEARCH CENTER HYDRO PORSGRUNN).

The procedures 2.1. and 2.2 described by Melgård (1990) were applied to assess trace elements dissolved in water succeeding liming of acidified waters, in addition to elements dissolved in a fairly strong acid solution.

In accordance with methods used by SI (Center of Industrial Research) in Oslo two dissolution techniques were utilized:

- 2.1. The samples of 0.100 g were dissolved in 1 l H_2O pH 5.0, steadily kept at this fixed level by adding H_2SO_4 to counteract the dissolution effect. This chemical environment should be similar to the conditions of acidified waters.
- 2.2. Parallel samples were dissolved in 1 l 1 N (0.5 M) H_2SO_4 to determine the total level of readily soluble elements of the liming materials.

All elements were determined by ICPAES plasma analysis, except fluoride, which was assessed by ion selective electrodes. Due to sensitivity to acids, these F^- determinations were performed only at constant pH 5.

Procedure 2.3. described decomposition of samples in a fairly strong acid, but without intentional dissolution of the silicates:

2.3.
Digestion of samples for ICP analysis of elements except Hg:

1. 2.5 g of the sample was dissolved in a teflon beaker containing 25 ml double dist. and deionized H_2O and 25 ml conc. supra pure HCl (>99.9%).
2. The beaker was carefully heated to boiling, and kept at this point for 20 min., filtrated og diluted to 500 ml with dist. H_2O (less dilution if the element conc. was low).

Analyses of Hg in samples:
Digestion for Hg analyses was effected by adding 5 ml aqua regia to 2-2.5 g sample, and instrumentally performed by the means of AAS cold vapour technics and CVAAS/Au amalgamation.

VIII. CHEMICAL ANALYTICAL LABORATORY, P.O.Box 5031, 1432 ÅS

Methods were applied for water soluble and total contents of elements, at these investigations for Cl and F, and in addition total contents of Pb.

Method 1. Water soluble Cl^- and F^-

1. 5 g sample dissolved in 100 g deionized H_2O, and shaked for 4 h.
2. Filtered and analyzed by autoanalyzator (Cl^-) and ionselective electrode (F^-).

Method 2. Total Cl^-

1. 5 g sample dissolved in 100 g deionized H_2O.
2. Transferred to a porcelain crucible, added 2 ml 10% Na_2CO_3 and heated on a plate to dryness.
3. Ignited in a muffle furnace (823-873 K) for 2 h.
4. The ash of the sample was heated in deionized H_2O, and filtered into a volumetric flask.
5. The steps 1-3 were repeated for the residue on the filter paper, in step 3 ignited for 1 h, dissolved in 15 ml 6 N HNO_3 : H_2O = 1:3.

6. The two solutions were mixed, and carefully shaken to expel CO_2. Filtrated after 1 h, diluted to fixed volume, and analyzed by autoanalyzator.

Method 3. Total F^-

1. 5 g sample dissolved in 100 g deionized H_2O.
2. Transferred to a nickel crucible, added 10 ml NaOH solution (400 $g*l^-$ deion. H_2O), and mixed thoroughly with a glass rod.
3. Heated on a plate at 373-393 K to dryness.
4. Ignited in a muffle furnace (623--->748 K) overnight.
5. The ash of the sample was heated in deionized H_2O, and filtered into a 100 ml volumetric flask, also containing 1 ml citrate solution (192 g Na-citrate and 73.6 g citric acid * 1^- deion. H_2O).
6. 18 ml conc. HCl : H_2O = 1:2 was added. pH should be just below 6.0, if higher, then added some more HCl.
7. Diluted to 100 ml (deion. H_2O), standing 2 h. before analyzing by ion selective electrode.

Method 4. Total Pb

1. 0.5 g sample added 2.5 ml conc. HNO_3, and decomposed in a teflon bomb.
2. Dissolved with deion. H_2O to 25 ml, and analyzed by AAS.

Blank sample determinations were made for all methods.

IX. CHEMLAB SERVICES A.S., P.O.Box 1517, N-5035 BERGEN-SANDVIKEN

The procedure applied was a method for a total analysis.

1. The sample was dissolved in conc. HF added some drops of conc. H_2SO_4, disintegrating the carbonates, whereas the silicates remained.
2. It was followed by the flux sodium carbonate (Na_2CO_3), using a temperature of 1300-1500 K, decomposing some silica- and alumina-containing samples, and sparingly soluble phosphates and sulphates.
3. Li-borate managed the decomposition of the most resistant silicates and oxides (1000-1200 K).

The laboratory had not been precise calculating the final results, making faults upon the decimals, but with a careful consideration the results could be interpreted.

X. SINTEF-MOLAB, N-8600 MO I RANA

This method was undertaken to yield analytical figures of total contents. The procedure was adopted to the requirements of this laboratory:

1. 10 ml conc. supra pure HCl (>99.9%) was added to 1-2 g of the sample, heated 0.5-1 h on a plate, filtered (paper filter). S was analyzed just in this solution.
2. The filter paper was ignited, dissolved in 5 ml conc. HF +

a few drops of conc. H_2SO_4 : H_2O = 1:1, and filtered.

3. The two solution samples were mixed together, and analyzed by AAS for the rest of the elements.

XI. Unknown British laboratory (NAMAS approved)

The method as stated by RAPRA TECHNOLOGY Ltd., Great Britain, was very short and unprecise, bringing into solution the easily soluble elements:

1. A portion of the sample was dissolved in 2 M HCl, heated and filtered. The filter was once washed through with dist. H_2O.
2. The trace elements were quantified by ICP emission spectrometry (plasma emission).

XII. LANDBRUKETS ANALYSESENTER (LAS), P.O.Box 5091, N-1432 ÅS

The most approved method was adopted by Landbrukets Analysesenter including dissolution of the samples in two steps:

Step I (easily soluble elements):

1. 5 g (<0.063 µm) of the sample was weighed to the nearest 0.001 g.
2. 100 ml diluted HNO_3 (7.5 ml conc. HNO_3 to 100 ml H_2O) was added to the sample.
3. The flasks were shaken several times and left overnight.
4. The solutions were filtered through a folded filter paper, and then analyzed by ICP. If the levels were very low and non detectable by ICP, analyses by graphite oven were done to establish absolute figures (concerned Cd).

Step II (total element contents):

1. To include the contents of the residual 1 g of the sample was weighed to the nearest 0.001 g.
2. The sample was added aqua regia (conc.HCl : conc.HNO_3 = 1:3), except for Hg, to which was added conc.HNO_3, boiled and vapoured to dryness.
3. The sample was dissolved in 5% HNO_3.
4. As in Step I.

It was of major interest to determine the contents of elements easily dissolving in nature (Step I), accompanying the dissolution of carbonates and other unstable minerals when added to soils and acidified waters.
The residuals (included in Step II) might also gradually weather, but elements are trapped in the lattice of hardly soluble silicates and small fractions of sulfides and oxides.

Step I was used for several samples of the A series:
* ODDA lime (A33) (J.no. 10320/90, 30th March 1990)
* Hole fine limestone, 8 samples from the quarries (Ax1-Ax8)
* TORPE lime (A34)
* carbonate converter limes (sample A35-A38)
* The entire B series

Step II was used for quite a number of samples:
* Hole fine limestone, 1 compound portion of samples Ax1-Ax8.
* The entire B series

The ODDA lime sample (A33) was also analyzed for N compounds. Kjeldahl-N was analyzed by CHN analyzer, and watersoluble NO_3-N and NH_4-N were measured after 1 h shaking.

XIII. THE NORWEGIAN FOREST RESEARCH INSTITUTE (NISK)

The analyses of F were performed according to methods for plant dry matter, and this procedure concerned some samples of the B series (ODDA burnt lime [B4], ODDA lime [B5] and carbonate converter lime [B10]):

1. Fluoride in the samples reacted with hexamethyldisiloxane, HMDS, in 3.4 M $HClO_4$ to produce trimethylfluorosilane, TMFS.
2. The volatile TMFS was trapped hydrolyzed in 0.1 M NaOH. The reaction took place in a sealed Petri dish containing separate cups for sample and trapping solution.
3. The sample solution was neutralized with 0.1 M HCl and analyzed.
4. The fluoride solution was analysed as fluoride in water, determined by a flow injection method (Tecator application note ASN 102-01/88). The sample was injected into a carrier stream, mixed with a buffer and the fluoride-concentration measured potentiometrically by an ion selective fluoride electrode.
   Reagents:
   Carrier: 0.1 mg $F*l^{-1}$ in 0.05 M NaCl.
   Buffer: 58 g NaCl and 2 g Titriplex III dissolved in 500 ml de-ionised water. 57 ml conc. acetic acid added pH adjusted to 5.1 with 5 M NaOH. About 150 ml required. Diluted to 1000 ml with de-ionised water.
   Electrolyte solution: 3 M KCl.
   Detection limit: 0.05 $mg*l^{-1}$ F.

STATISTICAL METHODS

These investigations had mainly the character of being a survey, and in spite of establishing replicates of chemical methods to declare precision and replicability, there was scarcely made any parallel sampling within the quarries. Thus statistical differences between liming materials could not be stated, merely chemical features and trends being indicated, referring with caution to the different chemical procedures.

Nevertheless, some graphs could be drawn by the means of the SAS Graph (SAS INSTITUTE 1987b), and transferred to WP Version 5.1.

All documents were printed on an IBM Laserprinter.

RESULTS AND DISCUSSION

The results are presented in accordance with the methods operated at the different laboratories.

A. LIMING MATERIALS OF THE A SERIES

I. ANALYSES AT DEPARTMENT OF GEOLOGY AND MINING TECHNICS, UNIV. OF TRONDHEIM/NTH, N-7034 TRONDHEIM

At the laboratory of the Dep. of Geology and Mining Technics, Univ. of Trondheim/NTH there was made an obvious, and subsequently admitted, misinterpretation by calculating the analytical results for Pb and Cd.
This was corrected in tab. 15, reducing the figures in the presented certificate of analysis to 1/10.

Tab. 15. Contents (ppm of DM) of heavy metals and accessory elements in the sample of Hole limestone (sample A1), analyzed at Dep. of Geology and Mining Technics, Univ. of Trondheim/NTH.

TOTAL ELEMENT CONTENTS

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Sr	Hg	As
A1	2.3	0.5	25		14		10		199		

Tab. 15. cont., tot. elem. cont.

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
A1				18						3200

Tab. 15. cont., tot. elem. cont.

Sample no.	Kjeldahl-N	NO_3-N	NH_4-N	DM%	Ca, %	Mg, %	CO_2, %	RESIDUE, %
A1				100	34.1	2.29	41.06	7.00

Tab. 15. cont., mineral analyses, constituents, %

Sample no.	calcite	dolomite	quartz	feldspars	micas	Fe_2O_3	FeS
A1	73	21	3	------minor quantities------			

The minor quantities of Sr were of particular interest, due to the

Ca/Sr antagonism by plant uptake. Moreover, stable nuclides of Sr also compete with the radioactive ones (in particular ^{90}Sr), a very important concern succeeding the nuclear bomb fallouts in the 1960's.

II. ANALYSES AT SECTION OF TECHNICAL CHEMISTRY/GROUP OF SENSING TECHNOLOGY, SINTEF/NTH, N-7034 TRONDHEIM

Tab. 16. is presenting the analytical results of Steen limestone (sample A2) as analyzed by SINTEF 1989.

Tab. 16. Contents (ppm of DM) of heavy metals and accessory elements in the sample of Steen limestone (sample A2), analyzed at Section of Technical Chemistry/Group of Sensing Technology, SINTEF/NTH.

TOTAL ELEMENT CONTENTS

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Sr	Hg	As
A2	3.6	<0.1	5.6	28.2			3.9			<0.005	

Tab. 16. cont., tot. elem. cont.

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
A2				8.5						

The content of Pb was slightly higher and the contents of Cd, Ni, Cu and Zn some lower than found in sample A1 (Hole limestone) of similar geological depositional environments.

III. ANALYSES AT ANALYTICA AB, S-183 25 TÄBY

Tab. 17. is presenting the analytical results of Mjøndalen hydrated lime (sample A2) as analyzed by ANALYTICA AB 1988.
Fe, Al, Ca, Mg, Ti and Mn were all stated in the oxide form, but were recalculated for this presentation.

The trace element contents were fairly low. Loss by ignition would mainly be the hydrous fraction of the hydrated lime.

This hydrated lime is not the current one of today, because Mjøndalen Kalkfabrik is not running its own oven for burning, but is buying burnt lime from Franzefoss Bruk A.S., Sect. Hylla/Verdal, for hydratization.

Tab. 17. Contents (ppm of DM) of heavy metals and accessory elements in the sample of Mjøndalen hydrated lime (sample A3), analyzed at ANALYTICA AB, S-183 25 TÄBY.

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Sr	Hg	As	Ti
A3	1.0	<0.5	5.0	5.5	<1	5	2.5			<0.05		18

Tab. 17. cont.,

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S	Tl
A3	280	250	54	6.5						1400	<10

Tab. 17. cont., additional analyses

Sample no.	DM%	Ca, %	Mg, %	Loss by ignition, %
A3	100	50.9	0.45	24.0

IV. ANALYSES AT KEMISKA STATIONEN AB, S-532 00 SKARA

Tab. 18. is presenting the analytical results of Franzefoss limestone (Sect. Rud) performed at KEMISKA STATIONEN AB, Skara in Sweden.
The trace element levels were in the same range as found for the other Ordivician-Silurian limestones.

Tab. 18. Contents (ppm of DM) of heavy metals and accessory elements in the sample of Franzefoss limestone, Section Rud (sample A4), analyzed at KEMISKA STATIONEN AB, S-532 00 SKARA.

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Sr	Hg	As
A4	1.3	0.13	2.2	4.8	<0.62	1.2	5.2			<0.005	

Tab. 18. cont.

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
A4	1180			5.7						

V. ANALYSES AT NORDISK ANALYSE CENTER/NORSK ANALYSESENTER, P.O.Box 24, N-1361 BILLINGSTAD

The analytical results for the sample of Franzefoss limestone, Section Rud (sample A5) and the two dolomite samples (samples A9 and A10) from Franzefoss, Section Ballangen are shown in tab. 19A and 19B for easily soluble elements and total element contents respectively. These analyses were effected at NORDISK ANALYSE CENTER/NORSK ANALYSESENTER.
The sample A5 might be compared with the sample A4, in spite of some differences in methods. Sample A5 exhibited slightly higher levels of Ni, Cr, V and Zn than found in sample A4, but simultaneously a little less Cu.
The dolomites were generally very poor with respect to trace elements arising environmental concern.

Tab. 19. Contents (ppm in DM) of heavy metals and accessory elements in Franzefoss limestone, Sect. Rud (sample A5), and Franzefoss dolomites, Sect. Ballangen (samples A9-A10), performed at NORDISK ANALYSE CENTER/NORSK ANALYSESENTER.

Tab. 19A.

EASILY SOLUBLE ELEMENTS

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Sr	Hg	As	Ti
A5	<2	<0.5	10	17	<1	11	2.7	29	380	<10		400
A9	<1	<0.2	<0.5	0.4	<0.2	<0.5	<0.1	4		<0.01		
A10	<1	<0.2	<0.5	0.7	<0.2	<0.5	<0.1	4		<0.01		

Tab. 19A. cont.

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
A5	6900	7900	260	13	<1		15	3100	170	
A9	22	120	7.8		<0.5		44	9	9.3	
A10	73	120	7.9		<0.2		49	20	9.3	

Tab. 19A. cont.

				ADDITIONAL ANALYSES		
Sample no.	Si	Sn	Zr	Ca, %	Mg, %	Loss by ignition, %
A5	1100	<10		28.2	0.42	36.3
A9	20	4	<0.1	17.3	10.6	
A10	50	2	<0.1	17.3	10.3	

Tab. 19B.

TOTAL ELEMENT CONTENTS

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Sr	Hg	As	Ti
A5	<10	<5	12	28	<5	20	<5	90	490	<25		1000
A9						<5		11				<5
A10						<5		11				<5

Tab. 19B. cont.

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
A5	16300	11400	330	13	<5		<50	7000	1800	
A9	80	250	16		<5		ca. 50			
A9	180	210	14		<5		ca. 50			

Tab. 19B. cont.

Sample no.	Si	Sn	Zr	Ca, %	Mg, %
				ADDITIONAL ANALYSES	
A5	52000	<50		34.4	0.67
A9	2400			22.4	12.4
A10	1700			22.3	11.3

VI. ANALYSES AT EUROC RESEARCH, Box 104, S-620 30 SLITE

Tab. 20 i giving the analytical results of the Franzefoss limestone, Section Hylla/Verdal (sample A6), performed at EUROC RESEARCH.
The contents of trace elements were generally very low, merely the Cu demonstrated a slightly higher level than found among many other carbonates.

Tab. 20. Contents (ppm of DM) of heavy metals and accessory elements in the sample of Franzefoss limestone, Section Hylla/Verdal (sample A6), analyzed at EUROC RESEARCH, S-620 30 SLITE.

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Sr	Hg	As
A6	1.3	<0.05		<0.5			9			<0.03	

Tab. 20. cont.

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
A6			11							140

VII. ANALYSES AT NORSK HYDRO A.S., HYDRO PORSGRUNN, P.O.Box 110, N-3901 PORSGRUNN

PROCEDURE 1.

Table 21 is firstly (table 21A-21B) presenting the analytical results of carbonate converter lime (sample A7) and half-burnt dolomite (sample A8), performed at HYDRO PORSGRUNN, according to Procedures 1.1 and 1.2.

The contents of heavy metals in sample A7 of the carbonate converter lime were fairly low, whereas the Ba and Sr contents were rather high, and there were also a substantial quantity of F^-. The Cd content was much lower than recently found by Landbrukets Analysesenter (samples A35-A38), and also in sample A15.
The acid soluble Pb level in half-burnt dolomite (sample A8) was slightly higher than expected. The contents of other analyzed elements were rather small.

Secondly table 21 is showing (table 21B) the analytical results of the project run by Johnsen (1989) at NORSK HYDRO A.S., HYDRO Porsgrunn, applying procedure 2.3 for Mjøndalen hydrated lime (sample A11), Steen fine limestone (sample A12), FAXE coral lime (sample A13), Hole fine limestone (sample A14) and carbonate converter lime (A15).
In these analyses there were high Cd levels in carbonate converter lime and Faxe coral lime, and in the former also apparently high levels of fluoride.

Tab. 21. Contents (ppm in DM) of heavy metals and accessory elements in carbonate converter lime (sample A7), half-burnt dolomite (sample A8), and the series A11-A15 (Johnsen 1989) performed at MgO DIVISION HYDRO PORSGRUNN, according to Procedure 1 (n.d.=non detectable).

Tab. 21A.

WATER SOLUBLE ELEMENTS (PROCEDURE 1.1)

Sample no.	Pb *	Cd *	Ni	Cr *	Co	V	Cu	Ba	Sr	Hg #	As	Ti
A8	n.d.	n.d.		n.d.						n.d.		

Tab. 21A. cont.

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
A8										

Tab. 21A. cont.

Sample no.	Be	Si	Sn	Mg	F^-	Cl^-
A8						

Tab. 21B.

ELEMENTS SOLUBLE IN ACID

Sample no.	Pb	Cd *	Ni	Cr	Co	V	Cu	Ba	Sr	Hg ©	As	Ti
PROCEDURE 1.2												
A7	1	<0.2	<2	<1	<1		2	100	340	<10		60
A8	3.4	n.d.		0.4						n.d.		
PROCEDURE 2.3												
A11	<1	<0.2	<10	17	<10		2	12	600	<0.01		190
A12	5	<0.2	20	13	<10		6	25	200	<0.01		11
A13	4	1.7	<10	7	<10		4	15	500	<0.01		50
A14	4	<0.2	10	10	<10		6	45	200	<0.01		9
A15	0.6 -1.8	3.5	<2	10	<1		2	90	360			6.5

Tab. 21B. cont.

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
PROCEDURE 1.2										
A7	70	70	30	<1			1600			
A8										
PROCEDURE 2.3										
A11	4000	3000	200	<10			<100			
A12	2000	6000	250	20			<100			
A13	1000	900	100	15			<100			
A14	1000	5000	200	15			<100			
A15	400	1300	30	17			3300			

Tab. 21B. cont.

Sample no.	Be	Si	Sn	Mg	Cl^-	F^-
PROCEDURE 1.2						
A7	<0.1	360$		20	<3	2200
A8						
PROCEDURE 2.3						
A11	<0.2	11000		4200	<10	<300
A12	<0.2	1500		21000	180	300
A13	<0.2	1600		1900	350	300
A14	<0.2	1300		25000	110	300
A15	<0.2	260		30	- @	2700

$ acid soluble Si (more left in the residue)

Tab. 21B. cont.

Levels of detection limit:
* 0.1 ppm
\# 0.0001 ppm
© 0.01 ppm
@ 10 ppm

PROCEDURE 2.1 AND 2.2

Table 22 is giving the condensed analytical results of dissolved trace elements in water at constant pH 5.0 (H_2SO_4 addition) for samples A16-A26, as presented by Melgård (1990).
The contents of F, Sr and Cu from many of the liming materials were in fact surprisingly high, possibly higher than the total determined contents of the liming materials.
There was a remarkably large amount of Sr dissolved from the shell sand material (sample A25).

Tab. 22. Trace elements dissolved ($mg*g^{-1}$) in water at constant pH 5.0 (H_2SO_4 addition) for the samples A16-A26, performed at RESEARCH CENTER HYDRO PORSGRUNN, according to Procedure 2.1 as presented by Melgård (1990).

Sample no.	F	Sr	Cu	Cd	Zn	Cr
A16	1.0	0.38	0.04	<0.05	<0.05	<0.05
A17	1.0	0.46	0.04	<0.05	<0.05	<0.05
A18	1.1	0.84	<0.01	<0.05	<0.05	<0.05
A19	1.1	0.14	<0.01	<0.05	<0.05	<0.05
A20	1.0	0.16	<0.01	<0.05	<0.05	<0.05
A21	1.0	0.32	0.09	<0.05	<0.05	<0.05
A22	1.0	0.20	<0.01	<0.05	<0.05	<0.05
A23	1.6	0.76	<0.01	<0.06	<0.06	<0.06
A24	2.2	0.86	<0.01	<0.06	<0.06	<0.06
A25	1.0	1.18	<0.01	<0.05	<0.05	<0.05

Melgård (1990) estimated the heavy metal contribution to very acid waters by adding the maximum 9 g * m^{-3} effective Ca-carbonate-equivalents would approach the critical level of good water quality only with respect to Cd in carbonate converter lime. In this 'worst case' there would be 0.54 µg $Cd*l^{-1}$, whereas the limit figure was 1.0 µg $Cd*l^{-1}$. Using this liming material for liming against water acidification, each quantity would have to be controlled by analysis.

VIII. ANALYSES AT THE CHEMICAL ANALYTICAL LABORATORY, P.O.Box 5031, 1432 ÅS

Tab. 23 is showing the data of the carbonate converter lime analyzed at the Chemical Analytical Laboratory. Only a few

elements were determined in this investigation, but water soluble as well as total contents were checked.
The total Cd and F contents were low, whereas the Pb level was abnormally high. The origin of the raw phosphate for this lime was not known.

Tab. 23. Contents (ppm in DM) of heavy metals and accessory elements in carbonate converter lime (sample A26), analyzed at the Chemical Analytical Laboratory, P.O. Box 5031, 1432 ÅS.

Tab. 23A

WATER SOLUBLE ELEMENTS

Sample no.	Pb	Cd	Cl	F
A26			<10	87

Tab. 23B

TOTAL ELEMENT CONTENTS

Sample no.	Pb	Cd	Cl	F
A26	10	<0.1	<10	460

Comparing this carbonate converter lime with other important sources in agriculture, it must be considered that normal compound fertilizers contain 780-1550 ppm F, ca. 5 ppm Pb and 2-12 ppm Cd, all stated as total figures.

IX. ANALYSES AT CHEMLAB SERVICES A.S., P.O.Box 1517, N-5035 BERGEN-SANDVIKEN

The carefully interpreted analytical results (total element contents) of dolomite products from NORWEGIAN TALC (samples A27-A30) are presented in tab. 24.
Cd and Hg levels, which were analyzed with a high degree of precision, were very low. Concerning Zn some variation was confirmed - at generally a low level.
These analyses of dolomite from NORWEGIAN TALC were coinciding with the analyses of dolomite from Franzefoss Bruk A/S, Sect. Ballangen, and Nymineral A/S in Nygårdsjøen.

Tab. 24. Total element contents (ppm in DM) of heavy metals and accessory elements in dolomite products from NORWEGIAN TALC (sample A27-A30), analyzed at the CHEMLAB SERVICES A.S., P.O.Box 1517, N-5035 BERGEN-SANDVIKEN.

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Sr	Hg	As	Ti
A27	0.11	0.002	0.33	<0.1			0.36			0.00025	<1	10
A28	0.10	0.003	0.20	<0.1			0.27			0.00016	<1	22
A29	0.12	0.002	0.21	<0.1			0.28			0.00027	<1	10
A30	<0.02	0.003	0.17	<0.1			0.36			<0.00002	<1	8

Tab. 24A. cont.

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
A27		300	39	1.0						
A28		300	38	0.9						
A29		300	39	0.9						
A30		300	33	12.8						

Tab. 24A. cont.

Sample no.	Si	Sn	Zr	Sb
A27		5		2.9
A28		4		1.9
A29		5		8.2
A30		5		2.8

X. ANALYSES AT THE SINTEF-MOLAB, N-8600 MO I RANA

Tab. 25 is presenting the analytical results of the heavy metals and accessory elements in the Løgavlen dolomite (Hammerfall Dolomitt A.S.) (sample A31) as analyzed at the SINTEF-MOLAB. The detection limits of these analyses were fairly high, and there were only a few absolute figures. The results were, however, in agreement with the other analyses of the dolomites of the same geological origin (samples A27-A30, B8 and B11-B12).

Tab. 25. Total element contents (ppm in DM) of heavy metals and accessory elements in Løgavlen dolomite (Hammerfall Dolomitt A.S) (sample A31), analyzed at the SINTEF-MOLAB, N-8600 MO I RANA.

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Sr	Hg	As	Ti
A31	<5	<1	<1	<1	<1		<1	<6.5	67	<0.02	<1	

Tab. 25. cont.

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
A31				1						0.2

Tab. 25. cont.

Sample no.	F
A31	57

XI. ANALYSES AT AN UNKNOWN BRITISH LABORATORY (NAMAS APPROVED)

The analytical results of easily soluble heavy metals and accessory elements in the NORWEGIAN TALC dolomite (Microdol 1) sample (sample A32) by the initiative of RAPRA Technology Ltd. at an unknown British laboratory is given in tab. 26.
The detection limits were very low, but none of the results represented any contrast with other analyses performed on the same dolomitic materials.

Tab. 26. Easily soluble element contents (ppm in DM) of heavy metals and accessory elements in NORWEGIAN TALC dolomite (Hammerfall Dolomitt A.S) (sample A32), analyzed at an unkown British laboratory (NAMAS approved).

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Sr	Hg	As	Ti
A32	<1	<0.5		<0.5				<10		<5	<10	

Tab. 26. cont.

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
A31										

Tab. 26. cont.

Sample no.	Si	Sn	Zr	Sb	Se
A31				<10	<5

XII.A. ANALYSES AT LAS (LANDBRUKETS ANALYSESENTER, P.O.Box 5091, N-1432 ÅS): ODDA LIME, TORPE LIME, CARBONATE CONVERTER LIME AND HOLE LIMESTONES.

Tab. 27.A. is presenting the analytical results of the liming materials analyzed according with the LAS analytical method (Landbrukets Analysesenter).

Tab. 27.A. Contents (ppm in DM) of heavy metals and accessory elements in ODDA Lime (sample A33), TORPE Lime (sample A34), carbonate converter limes (sample A35-A38), and Hole limestones (sample Ax1-Ax8).

Tab. 27.A.Sol.

EASILY SOLUBLE ELEMENTS

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Hg	As	Ti
A33	8.0	<0.2	0.4	<0.5	0.4		0.33		0.0066		
A34	8.4	0.12							0.006		
A35		0.63									
A36		0.67									
A37		0.28									
A38		0.40									
Ax1	<0.5	<0.5	1.4	3.0	<0.5	1.0	0.80	5.8			<0.2
Ax2	<0.5	<0.5	3.0	6.2	<0.5	1.0	3.0	3.2			2.0
Ax3	<0.5	<0.5	1.0	0.80	<0.5	0.80	1.4	2.8			<0.2
Ax4	<0.5	<0.5	1.2	1.8	<0.5	0.60	0.60	3.4			<0.2
Ax5	<0.5	<0.5	0.40	0.80	<0.5	0.80	0.60	11.4			<0.2
Ax6	<0.5	<0.5	0.60	0.80	<0.5	0.60	0.60	3.8			<0.2
Ax7	<0.5	<0.5	0.20	0.40	<0.5	0.60	0.60	2.8			<0.2
Ax8	4.2	<0.5	0.20	15.6	4.2	2.6	8.8	8.2			8.0

Tab. 27.A.Sol. cont.

Additional element analysis of A series samples

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
A33	320	68.5	9.68	1.25	0.121	2.4	3340	6.005	47.3	166
A34						wat.	tot.			
A35						10	3500			
A36						10	3100			
A3						10	3200			
A38						10	3200			

Tab. 27.A.Sol. cont.

Additional element analysis of A series samples

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
Ax1	51.4	1090	74.0	1.2	<0.2	<1.0	21.8	86.8	37.6	88.0
Ax2	148	1280	67.0	1.8	<0.2	<1.0	27.0	247	45.6	141
Ax3	14.4	746	49.4	1.0	<0.2	<1.0	18.4	191	40.0	186
Ax4	23.0	1262	74.6	0.80	<0.2	<1.0	13.0	53.2	53.6	107
Ax5	<0.5	979	63.6	1.4	<0.2	<1.0	13.4	38.8	39.6	58.0
Ax6	<0.5	842	58.0	2.2	<0.2	<1.0	10.2	41.0	28.2	51.0
Ax7	<0.5	608	45.2	0.60	<0.2	<1.0	8.4	24.6	33.6	47.0
Ax8	1153	11640	119	15.2	<0.2	<1.0	142	486	66.4	7240

Tab. 27.A.Sol. cont.

Sample no.	Kjeldahl-N	NO_3-N	NH_4-N	DM%	Ca, %	Mg, %	RESIDUE, %
A33	17200	4900	5140	89.5			
A34					31.8	0.66	
		water soluble					
A35	11000	2600		91.4	36.2		
A36	10000	5600		90.3	33.8		
A37	16000	8100		88.3	32.8		
A38	13000	9200		90.3	33.9		
Ax1					34.8	1.2	17.5
Ax2					30.8	1.9	23.2
Ax3					37.2	0.88	12.8
Ax4					34.9	2.2	14.1
Ax5					36.6	1.4	13.5
Ax6					37.0	0.67	13.5
Ax7					37.5	0.71	12.2
Ax8					15.9	1.1	59.3

When considering the level of Kjeldahl-N in sample Ax (ODDA lime), other components of N ,besides NO_3-N and NH_4-N, would be amid-N and nitrid-N.
As previously mentioned, in sample Ax there were also made analyses of Ca and Mg, but these represented only a fraction of the total contents, due to a rather weak dissolving agent (dilute HNO_3).

Regarding the sites of the quarries of Hole Kalkverk A/S there were no apparent differences between the two quarries Hanseberget (samples Ax1-Ax4) and Fredly (Ax5-Ax8) with respect to the trace elements. Even sample Ax8, demonstrating a low content of $CaCO_3$, did not present any levels evoking anxiety.
Moreover, the residues represented only a small fraction of these carbonate rocks.

Tab. 27.A.Tot.

TOTAL ELEMENT CONTENTS **IN THE RESIDUAL**

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Hg	As	Ti
Ax9	6.5	<1.0	36.4	45.7	5.7	13.1	75.1	12.6			8.9

Tab. 27.A.Tot. cont.

Additional element analysis of A series samples

Sample no.	Al	Fe	Mn	Zn	Mo	B	P	K	Na	Tot-S
Ax9	11654	14290	82.5	53.5	<1.0	7.4	17.5	3990	56.8	1360

Tab. 27.A.Tot. cont.

Sample no.	Kjeldahl-N	NO_3-N	NH_4-N	DM%	Ca, %	Mg, %	RESIDUE, %
Ax9					0.14	0.60	-

In samples Ax1-Ax9 (samples from different sites at Hole Kalkverk) the contents of trace elements (heavy metals and accessory elements) were generally low in the carbonates. There was, however, a marked increase of these elements with elevated levels of non carbonate minerals. These minerals were probably sulfides and oxides, and the total S contents of these samples accompanied the increase of these elements.
The trace elements of the non carbonate minerals are quite fixed in the lattice of these minerals, and are not readily soluble as they would be from the carbonates. Moreover, the residue is only a minor constituent of these rocks, with an exception of one sample (Ax8).

Considering the element Pb, Skjeseth (pers. comm. 1992) indicated the abundant enrichment of galena (PbS) in the carbonate rocks of the area Dokka-Gjøvik-Hamar, and in particular in the Vang geological formation. It is also found in the quartzite further eastwards.
Within this area of the Oslo geological formation there was an abruption in sedimentation in the 3rd floor (Ordovicium-Silur) due to sea regressions. Pb enriched bentonite was deposited at river estuaries of shallow marine waters. Thus quite a lot of this Pb bentonite is found between the limestone beds, especially in Ringerike. Now the surface exposed bentonite is weathering.

B. LIMING MATERIALS OF THE B SERIES

XII.B. ANALYSES AT LAS (LANDBRUKETS ANALYSESENTER, P.O.Box 5091, N-1432 ÅS) AND NISK (THE NORWEGIAN FOREST RESEARCH INSTITUTE, N-1432 ÅS): THE B SERIES.

Tab. 27.B. is presenting the analytical results of the liming materials analyzed according with the LAS analytical method (Landbrukets Analysesenter) and the NISK analytical method of fluoride (The Norwegian Forest Research Institute).

Tab. 27.B. Contents (ppm in DM) of heavy metals and accessory elements in the B series.

EASILY SOLUBLE ELEMENTS

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Hg	As	F
B1	<0.5	<0.010	0.57	<0.5	<0.5	<0.5	<0.5	1.6	<0.002		
B2	5.5	0.057	1.6	<0.5	<0.5	6.5	<0.5	19.1	<0.002		
B3	<0.5	<0.010	1.3	<0.5	<0.5	0.79	1.0	10.3	<0.002		
B4	<0.5	<0.010	<0.5	<0.5	<0.5	<0.5	<0.5	2.8	<0.002	<0.002	
B5	<0.5	0.10	7.4	1.3	<0.5	3.3	<0.5	4.2	<0.002	0.90	
B6	<0.5	<0.010	<0.5	<0.5	<0.5	<0.5	<0.5	0.94	<0.002		
B7	<0.5	<0.010	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.002		
B8	<0.5	<0.010	<0.5	<0.5	<0.5	<0.5	<0.5	2.0	<0.002		
B9	<0.5	<0.010	0.94	0.55	<0.5	0.76	<0.5	3.2	<0.002		
B10	<0.5	0.15	<0.5	<0.5	<0.5	0.76	<0.5	30.2	<0.002	0.071	
B11	<0.5	<0.010	<0.5	<0.5	<0.5	<0.5	<0.5	2.6	<0.002		
B12	<0.5	<0.010	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.002		
B13	<0.5	0.012	<0.5	<0.5	<0.5	3.9	0.70	7.3	<0.002		
B14	<0.5	0.012	<0.5	<0.5	<0.5	0.79	<0.5	1.6	<0.002		
B15	1.9	<0.010	<0.5	<0.5	<0.5	<0.5	0.56	2.3	<0.002		
B16	<0.5	<0.010	<0.5	<0.5	<0.5	<0.5	<0.5	0.92	<0.002		
B17	<0.5	0.67	1.1	<0.5	0.54	1.7	1.9	9.6	<0.002		
B18	<0.5	0.015	0.74	<0.5	0.68	<0.5	0.86	10.9	<0.002		

Tab. 27.B.Tot.

TOTAL ELEMENT CONTENTS

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Hg	As	F
B1	<0.5	0.015	4.9	4.2	1.1	3.4	2.6	5.1	<0.002		
B2	15.2	0.096	4.6	1.0	<0.5	14.6	2.1	74.1	0.004		
B3	1.6	0.014	5.7	2.2	1.1	3.3	4.8	23.9	0.005		
B4	2.3	0.78	1.1	2.5	<0.5	4.5	2.2	5.7	<0.002	1.2	210
B5	0.78	0.27	19.2	3.9	1.1	29.7	4.5	9.0	0.006	2.1	2085
B6	2.0	0.010	0.86	<0.5	<0.5	1.1	1.0	1.5	<0.002		
B7	2.0	0.010	<0.5	<0.5	<0.5	0.85	0.91	0.92	<0.002		
B8	<0.5	0.017	<0.5	<0.5	<0.5	<0.5	0.96	4.1	<0.002		
B9	1.0	0.015	4.6	4.1	1.3	3.8	2.4	8.8	0.003		
B10	1.8	0.33	<0.5	<0.5	<0.5	2.0	0.65	61.5	<0.002	0.16	2415

Tab. 27.B.Tot.

Sample no.	Pb	Cd	Ni	Cr	Co	V	Cu	Ba	Hg	As	F
B11	0.83	<0.010	<0.5	<0.5	<0.5	<0.5	0.63	4.8	<0.002		
B12	<0.5	<0.010	<0.5	0.85	<0.5	0.58	1.0	0.99	<0.002		
B13	<0.5	0.037	1.1	3.1	0.78	15.9	2.8	20.3	<0.002		
B14	<0.5	0.035	1.1	0.78	0.92	3.1	4.7	3.4	0.006		
B15	1.9	0.034	4.2	2.9	1.7	3.5	4.8	5.3	0.002		
B16	<0.5	0.034	<0.5	<0.5	<0.5	<0.5	1.4	2.8	<0.002		
B17	<0.5	1.3	3.6	1.1	1.2	4.1	4.8	19.3	0.003		
B18	2.3	0.033	5.5	1.2	3.7	3.0	6.1	25.2	0.003		

The levels of trace elements were generally very low.
Rather high levels of Pb, V and Ba were, however, found in the English quarterly burnt dolomite. The largest quantity of Cd was analyzed in the Danish coral lime.
The Ordovician-Silurian limestones in the Oslo geologocial area reflected the same carbonate depositional environments as mentioned by Skjeseth 1992 (pers. comm.) for the Hole limestones (samples Ax1-Ax9), characterized by slight enrichments of Pb, Ni, V, Cu and Ba.
The Silurian limestones from Mjøndalen Kalkfabrik A.S. (sample B1) and Franzefoss Bruk A.S., Sect. Rud (sample B9) were very similar. The analysis of the B3 sample (Steen limestone) was in accordance with the SINTEF analysis (sample A2), with an exception of Cr, which was measured to be much higher at the SINTEF laboratory.

The dolomites were very pure. The magnesian limestone from Gausdal (sample B13) contained a little Cd and a remarkably high level of V.

The carbonate converter lime was now much less contaminated than previously manifested (sample A15, A35-A38). The Ba contents were a little high.
On the other hand, the ODDA lime contained more Ni and V than any other of the analyzed materials. The Ni content was much higher than found in 1990 (sample A33), but simultaneously there was much less Pb.
The F contents were quite high for both the carbonate converter lime and the ODDA lime. A little As was found in these two materials.

All the liming materials contained merely a few ppb Hg.

Burnt limes as sample B4 and partly sample B1 are concentrated materials, and in spite of trace metal enrichment by production these are added in smaller quantities to the soils.

Comparing the results of tab. 27.B.Sol (easily soluble elements - in approx. 1 N HNO_3 - of the B series) with the contents of elements in stream sediments of tab. 3 (7 N, 383 K, 3 h), these elements of the liming materials are far below the background levels. Even by decomposition of the carbonates resulting from the neutralization processes there will be only a faint soil enrichment of these elements. Carbonate diagenesis in nature is normally disposing for lower trace element contents than most other rock formations.

A parallel comparison of tab. 27.B.Tot. (total element contents of the B series) with the contents of elements in till (tab. 1-2), revealed that the comprehensive element contents of the liming materials were lower than the background levels in northern Fennoscandia. The same observation was valid when comparing with average Norwegian agricultural soils in tab. 4 (Bærug & Aasen 1991).
An exception was probably F, which was found in relatively large amounts in sample B5 (ODDA lime) and sample 10 (carbonate converter lime). These liming materials and phosphate fertilizers will undoubtly enrich the agricultural soils with F.
Moreover, the same sources might slightly increase the As contents of soils.

In general the liming materials would, however, yield no enrichment in neither agricultural nor uncultivated soils, because the trace element contents in the carbonate fractions are low, and the somewhat elevated levels in the residue fractions are normally also below or equal to the background figures, as stated by comparison with the analytic results of the Nordkalott Project (Bølviken et al. 1986).

C. SOURCES AND QUANTITATIVE ESTIMATIONS OF HEAVY METAL AND ACCESSORY ELEMENT SUPPLIES TO AGRICULTURAL SOILS

According to Kongshaug et al. (1992) fig. 1-3 are showing average soil contents of several trace elements in Europe, and the effects of accumulation by different sources during 250 years. All these figures are markedly higher than common in Norway, due to higher previous accumulations in soils, larger atmospheric loads, and more contaminated fertilizers and sewage sludge.

Tab. 28 is presenting the calculated input of different trace elements to soil by fertilization, atmospheric deposition and sewage sludge, differentiating between global average values (mainly the industrialized countries in West Europe, North America and Japan) and available Norwegian figures (Kongshaug et al. 1992). The effects of another 100 and 250 years of continued inputs were also forecasted.

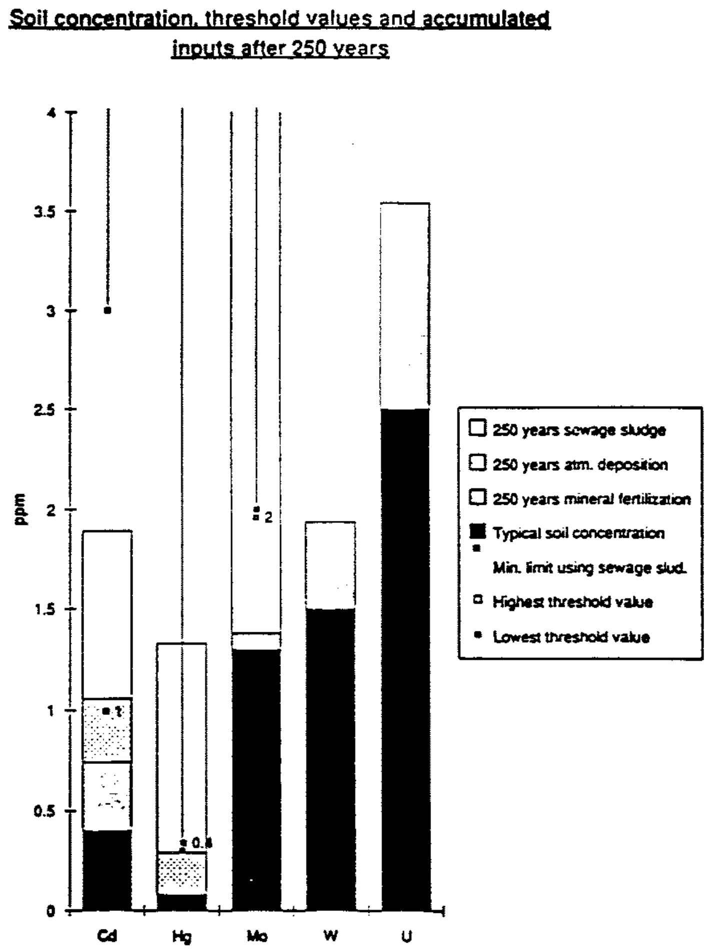

Fig. 1. Tendencies of soil concentration developments for trace elements at low levels (Kongshaug et al. 1992).

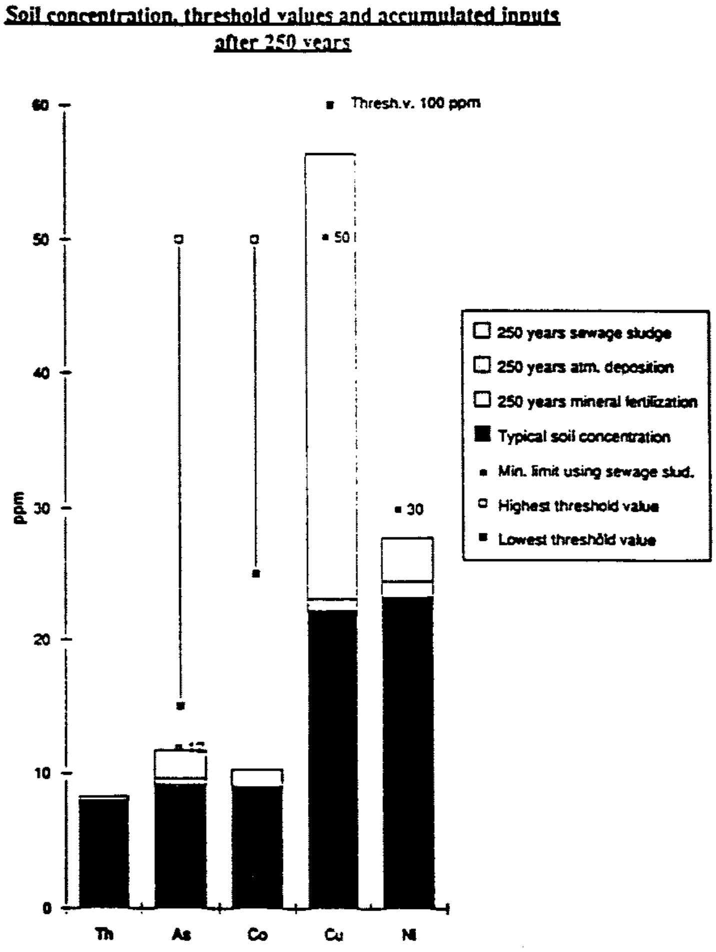

Fig. 2. Tendencies of soil concentration developments for trace elements at medium levels (Kongshaug et al. 1992).

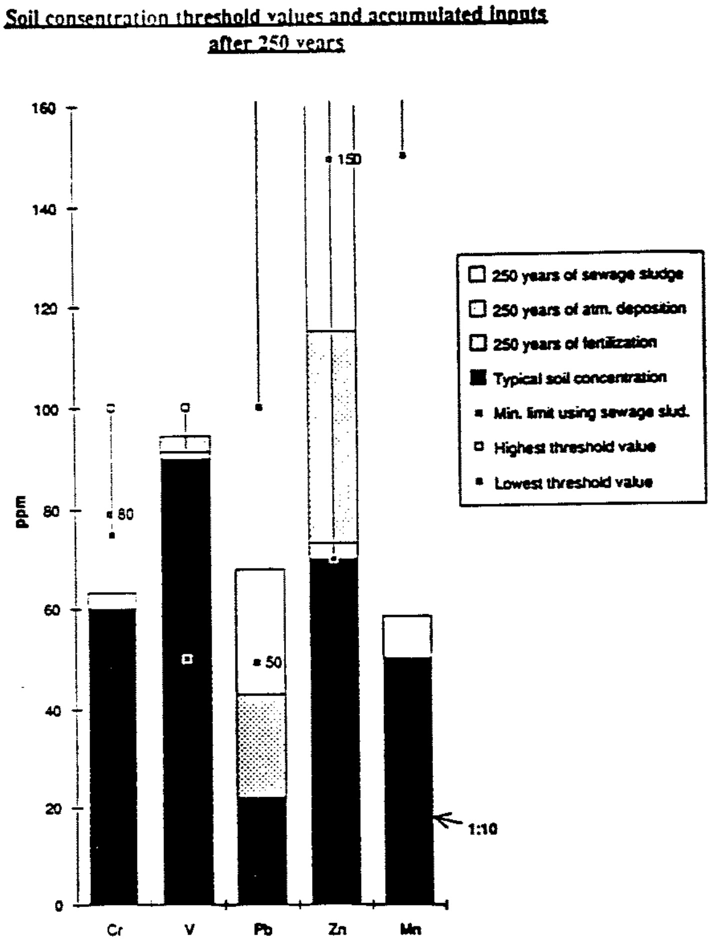

Fig. 3. Tendencies of soil concentration developments for trace elements at slightly higher levels (Kongshaug et al. 1992).

Tab. 28. Soil background levels, inputs of trace elements to soil by fertilization, atmospheric deposition and sewage sludge, differentiated between average global levels and available Norwegian figures, and forecasting trends of accumulation (according to Kongshaug et al. 1992). Soil concentrations and accumulated inputs stated in pmm, inputs in g*ha^{-1}*year^{-1}.

ELEMENTS	As	Cd	Cr	Co	Cu	Pb	Mn	Hg
Soil concentr.								
levels - Norway	**6**	**0.07**	**40**	**7.3**	**15**	**14**	**377**	**0.05**
- global average	9	0.4	60	9	22	22	500	0.08
Input by fertilizers								
- global average	1.4	3.3	24.5	0.2	4.2	1.3	8.4	0.01
Atmospheric fallout								
- Norway	**0.5**	**0.2**	**0.7**	**0.06**	**2.5**	**50**	**3**	**0.004**
- global average	4.5	3	4	1	20	200	40	2
Sewage sludge								
- Norway (*)	**5**	**0.22**	**7**	**8**	**56**	**6**	**200**	**0.28**
- global average	20	8	300	30	800	240	800	10
ASSUMED TOTAL INPUTS								
- Norway, max.	**6.9**	**3.7**	**35.5**	**8.3**	**62.7**	**57.3**	**211.4**	**0.30**
- global average	25.9	14.3	328	31.2	824	441	848	12
Long term accumulated								
input (ppm) - global								
100 years of fert.	0.06	0.14	1.02	0.01	0.18	0.05	0.35	0.0004
100 years atm. dep.	0.19	0.13	0.17	0.04	0.8	8.3	1.7	0.08
100 years sew. sl.	0.83	0.33	13	1.25	33	10	33	0.42

Tab. 28. cont.

ELEMENTS	Mo	Ni	Zn	W	V	U	Th
Soil concentr.							
levels - Norway		**25**	**55**				
- global average	1.3	23	70	1.5	90	2.5	8
Input by fertilizers							
- global average	0.8	3.8	31.2	4.2	11.6	10	2.7
Atmospheric fallout							
- Norway		**12**	**30**		**1.9**		**0.01**
- global average	1	30	400	1.0	30	0.1	0.2
Sewage sludge							
- Norway (*)	**10**	**4.5**	**83**				
- global average	40	80	1250				
ASSUMED TOTAL INPUTS							
- Norway, nax.	**11.8**	**20.3**	**144**		**13**		
- global average	42	114	1680		42		
Long term accumulated							
input (ppm) - global							
100 years of fert.	0.03	0.16	1	0.18	0.48	0.42	0.11
100 years atm. dep.	0.04	1.3	17	0.04	1.3	0.004	0.008
100 years sew. sl.	1.7	3.3	52				

(*) Norwegian inputs by sewage sludge were preliminarily calculated by these authors by multiplying the new Norwegian threshold values forwarded by the Norwegian SFT, as presented in tab. 6B, with the 1992 supply to Norwegian agricultural land, i.e. 50,000 tons DM sewage sludge, equivalent to 50% of the total production (Holdhus 1992), evenly distributed on 900,000 ha. The assumed contents of heavy metals would definitely be too high, but simultaneously there is an intention of the authorities to increase the supply to agriculture from 50% to 75% of the total production, and new sewage sludge plants are steadily constructed.
On the other hand, the sewage sludge is not evenly distributed, and in particular areas with cereal production are receiving far more than indicated in tab. 28.
For elements where no limits were declared by the SFT, the figures of input were fixed to 1/4 of the global average. These assumptions were probably too high.

Hauken (1991) indicated that the Cd levels were fairly lower from fertilizers than calculated as a global average, as demonstrated i in tab. 29, regarding an agricultural area of 900,000 ha.

Tab. 29. Cd supplies by mineral fertilizers from NORSK HYDRO A.S. 1986-89 (Hauken 1991).

Cd source	1986	1987	1988	1989
Compound fertilizers		803	614	615
PK and P fertilizers imported from Sweden	27	26	15	19
Calcium nitrate			24	16

According to information from NORSK HYDRO A.S. (A. M. Justad, pers. comm. 1992) there was a substantial drop in Cd contents in mineral fertilizers of this company during the period 1990-91, approximately 44 kg Cd as a total level in 1991. Calculating 49 kg Cd in imported fertilizers there was only 0.054 g Cd*ha^{-1}*year^{-1} added to 900,000 ha agricultural land in Norway, based on analyses and estimations by STIL.

There would also be a certain input of trace elements from manure, too, but these are mainly in an internal agricultural cycle, with exception of purchased concentrates, additional fodder stuffs and animal mineral supplies. Some figures were given by Kongshaug et al. (1992).
Holdhus (1992) mentioned that a Swedish investigation confirmed a heavy metal increase of 15-50% in manure the last 20 years.

Tab. 30 is presenting the calculated supplies of trace elements, choosing between different liming materials marketed in Norway, assuming an average need of 800 kg*ha^{-1}*year^{-1} lime generally yielding an ENV(5 years)=50.
When the contents were measured to be below the detection limit, these figures were fixed to half of this limit.

Tab. 30. Calculated **total** supplies of trace elements (g*ha^{-1}*year^{-1}) by choosing different liming materials from the B series (tab. 27.B.Tot.), adding 800 kg*ha^{-1}*year^{-1} lime. Contents below the detection limit were fixed to half of this limit.

	ELEMENTS							
LIMING MATERIALS Sample no.	As	Cd	Cr	Co	Cu	Pb	Mn	Hg
B1 Mjøndalen Limest.		0.012	3.4	0.88	2.1	0.2		0.001
B2 Mjønd., quar.b.dol.		0.077	0.8	0.2	1.7	12.2		0.0032
B3 Steen Limestone		0.011	1.8	0.9	3.8	1.3		0.004
B4 ODDA burnt lime	1.0	0.62	2.0	0.2	1.8	1.8		0.001
B5 OODA Lime	1.7	0.22	3.1	0.9	3.6	0.62		0.0048
B6 Visnes Limestone		0.008	0.2	0.2	0.8	1.6		0.001
B7 Franzefoss Hylla Lim.		0.008	0.2	0.2	0.73	1.6		0.001
B8 Franzefoss Ball. Dol.		0.014	0.2	0.2	0.77	0.2		0.001
B9 Franzefoss Rud Lime.		0.012	0.2	0.2	1.9	0.8		0.0024
B10 Fr. Carb. Conv.	0.13	0.26	0.2	0.2	0.52	1.4		0.001
B11 Hammerfall Dol.		0.004	0.2	0.2	0.50	0.66		0.001
B12 Nymineral Dol.		0.004	0.68	0.2	0.8	0.2		0.001
B13 Gausdal Magn. Lime.		0.030	2.5	0.62	2.2	0.2		0.001
B14 Nysether Limestone		0.028	0.62	0.74	3.8	0.2		0.0048
B15 Sando Limestone		0.027	2.3	1.4	3.8	1.5		0.0016
B16 Simont./Ernst. Dol.		0.027	0.2	0.2	1.1	0.2		0.001
B17 FAXE Coral Limest.		1.04	0.88	0.96	3.8	0.2		0.0024
B18 Uddagården Limest.		0.026	0.96	3.0	4.9	1.8		0.0024

Tab. 30. cont.

	ELEMENTS								
LIMING MATERIALS Sample no.	Mo	Ni	Zn	W	V	U	Th	Ba	F
B1 Mjøndalen Limest.		3.9			2.7			4.1	
B2 Mjønd., quar.b.dol.		3.7			11.7			59.3	
B3 Steen Limestone		4.6			2.6			19.1	
B4 ODDA burnt lime		0.9			3.6			4.6	168
B5 OODA Lime		15.2			23.8			7.2	1668
B6 Visnes Limestone		0.69			0.9			1.2	
B7 Franzefoss Hylla Lim.		0.2			0.68			0.74	
B8 Franzefoss Ball. Dol.		0.2			0.2			3.3	
B9 Franzefoss Rud Lime.		3.7			3.0			7.0	
B10 Fr. Carb. Conv. Lime		0.2			1.6			49.2	1932
B11 Hammerfall Dol.		0.2			0.2			3.8	
B12 Nymineral Dol.		0.2			0.2			0.79	
B13 Gausdal Magn. Lime.		0.88			12.7			16.2	
B14 Nysether Limestone		0.88			2.5			2.7	
B15 Sando Limestone		0.2			0.2			2.2	
B16 Simont./Ernst. Dol.		0.2			0.2			2.2	
B17 FAXE Coral Limest.		2.9			3.3			15.4	
B18 Uddagården Limest.		4.4			2.4			20.2	

It must be stressed that tab. 30 is showing **the total contents** of heavy metals and accessory elements annually supplied by normal use of actual liming materials. Normally would only 10-30% of these trace elements be easily soluble (HNO_3).

Still, a few of the liming materials would be important sources of some trace elements.
With respect to Cd the ODDA burnt lime (sample B4), the ODDA lime (sample B5), the carbonate converter lime (sample B10) and in particular FAXE coral lime (sample B17) were containing substantial amounts.
The English quarterly burnt dolomite (sample B2) contributed with a substantial amount of Pb.
The contents of Hg were negligible for all liming materials.

Quite high contents of F were added to soils by using ODDA lime (sample B5) and carbonate converter lime (sample B10), amounts equivalent to the supply of mineral fertilizers.
Some As was also provided by the ODDA products (sample B4 and B5).

The contents of V in sewage sludge in Norway was not confirmed, and thus we lacked a proper comparison, but three liming materials, the English quarterly burnt dolomite (sample B2), the ODDA lime (sample B5) and the Gausdal magnesian limestone (sample B13) proved to be important V sources.
The effects of Ba supply is not entirely cleared up, but elevated levels were in particular found in the English quarterly burnt dolomite (sample B2) and in the carbonate converter lime (sample B10). Ba is normally precipitated and inactivated in soil, e.g. as barytes ($BaSO_4$).

Comparing these results with tab. 1-2 (total contents of elements in till in Fennoscandia) the contents of trace elements will generally be lower in the liming materials than found as background levels. The products with the largest amounts of Cd (samples B4, B5, B10 and B17), Pb (sample B2) and Ni (sample B5) would, however, slightly enrich the soils by decomposition of the carbonate constituents.

The biological effects and acceptable levels of these trace elements is another topic, but "the horrible triplets" Cd, Pb and Hg have no beneficial biological functions, and must be minimized regarding supplies and concentrations.
Cr is required in small amounts to the animal and human diet, and considering its toxic levels it is rapidly reduced to Cr^{3+} as explained in the introduction chapter.
F must also be kept at acceptable levels, but is steadily increasing in soil also due to P fertilization. It is, however, prone to precipitate with Ca, and partly exposed to leaching.
Arsenic contents of crop plants are normally not an issue.

In small amounts Ni and V have important biological functions, but might readily approach toxic levels.
Co, Cu, Mn, Mo and Zn are important minor nutrients for biological life in proper quantities.

D. HEAVY METAL CONTENTS OF LIMING MATERIALS USED IN NORWAY AND SWEDISH REQUIREMENTS WHEN APPLIED TO ACIDIFIED WATERS

The lowest levels of tolerance with respect to trace elements are stated when liming materials are used as a remedial measure in acdified watercourses.
As presented in Introduction there are fixed requirements to these liming materials in Sweden (Naturvårdsverket 1988), and these are also often referred to by the Directorate for Nature Management in Norway.
The tolerance limits are based on decomposition of the samples in HNO_3 according to Swedish Standard SS 028150 (Naturvårdsverket 1987). This method is at an intermediate position concerning extractibility of the elements, compared with the two digestion methods used at Landbrukets Analysesenter, nevertheless some closer to the procedure of total contents (aqua regia).

Fig. 4-7 are showing the distribution of Pb, Cd, Ni and V contents of the B series, including both decomposition methods, with a lower reference line of detection limit and an upper of the Swedish requirements to lake liming materials.
With respect to Cd the detection limit was 0.010 ppm, but in figure 2 the levels were fixed at 0.005 ppm if the analyzes proved Cd contents below this limit, because a few samples also exhibited contents identical with the analytical sensitivity. Regarding the three other elements the lowest levels were fixed at the detection limit (0.5 ppm).

Estimating the Pb levels the English quarterly burnt dolomite (sample B2) was just below the critical lake liming level of the Swedish environmental authorities, at least based upon the total content analysis.
The Cd contents were for most liming materials very low, but FAXE coral lime (sample B17) was definitely unacceptable according to Swedish requirements. ODDA burnt lime (sample B4) demonstrated too high contents, too, although concentrated by the calcination process. Still, as a burnt product it will normally not be used for lake liming purposes. The ODDA lime (sample B5) and the carbonate converter lime (sample B10) showed elevated levels of Cd, but simultaneously below the critical limit. The Cd content of the English quarterly burnt dolomite (sample B2) was positioned just above the detection limit.

The Ni contents were close to the critical level only for the ODDA lime (sample B5). The Cambro Silurian limestones (samples B1, B3, B9, B15 and B18) contained slightly more Ni than the purest recrystallized carbonates (marble limestones and dolomites), and the same concerned the English quarterly burnt dolomite (sample B2) and FAXE coral lime (sample B17).

Too high levels of V were only found in the ODDA lime (sample B5), remarkably large quantities were also confirmed in the English quarterly burnt dolomite (sample B2) and GAUSDAL magnesian limestone (sample B13).

Related to the Swedish criteria there were only small contents of the other metals. With respect to an accessory element, F, the contents were, however, quite high (>0.2% as a total figure) in the

ODDA lime (sample B5) and the carbonate converter lime (sample B10), and these would probably not be recommended for use in acidified waters.

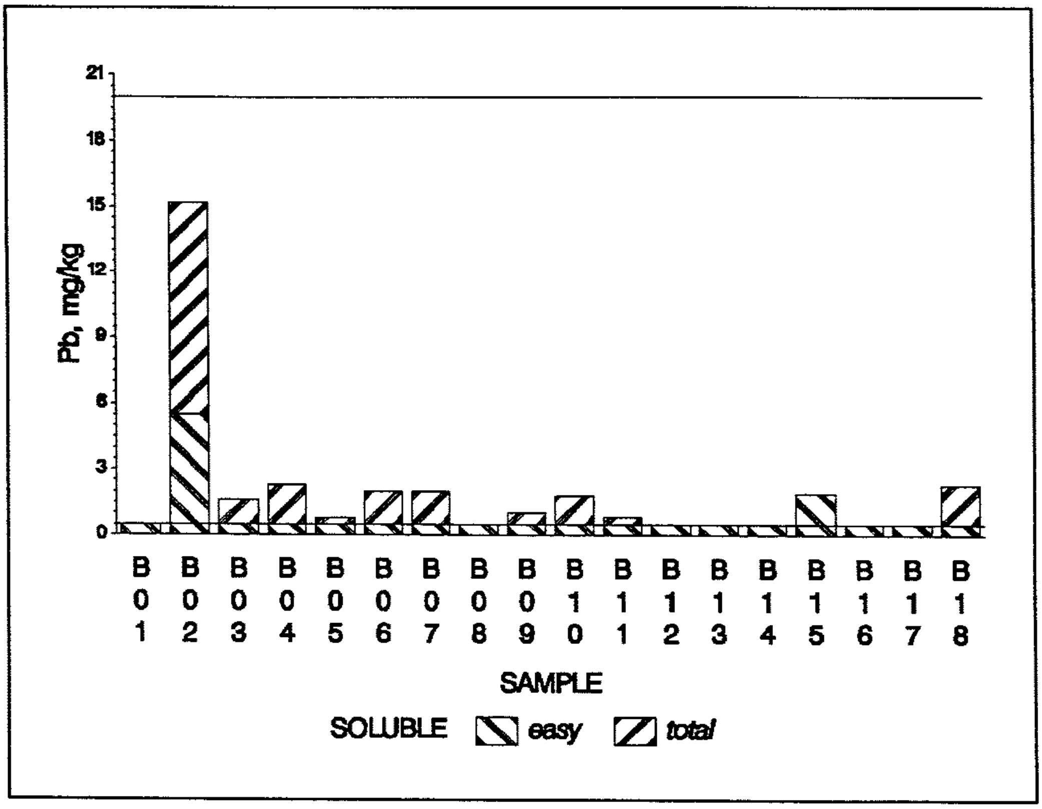

Fig. 4. Easily soluble and total Pb contents in liming materials of the B series, analyzed at Landbrukets Analysesenter, N-1432 ÅS. The lower reference line is showing the detection limit, the upper the limit for lake liming materials in Sweden (analyzed according to Swedish Standard SS 028150).

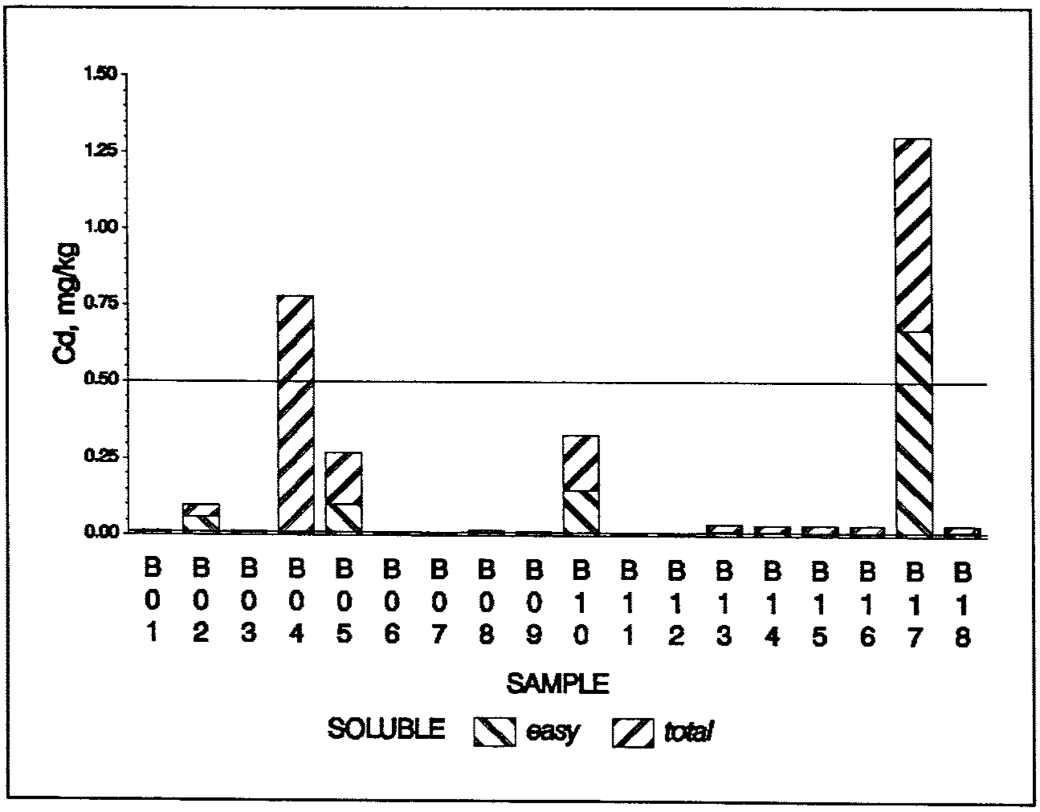

Fig. 5. Easily soluble and total Cd contents in liming materials of the B series, analyzed at Landbrukets Analysesenter, N-1432 ÅS. The lower reference line is showing the detection limit, the upper the limit for lake liming materials in Sweden (analyzed according to Swedish Standard SS 028150).

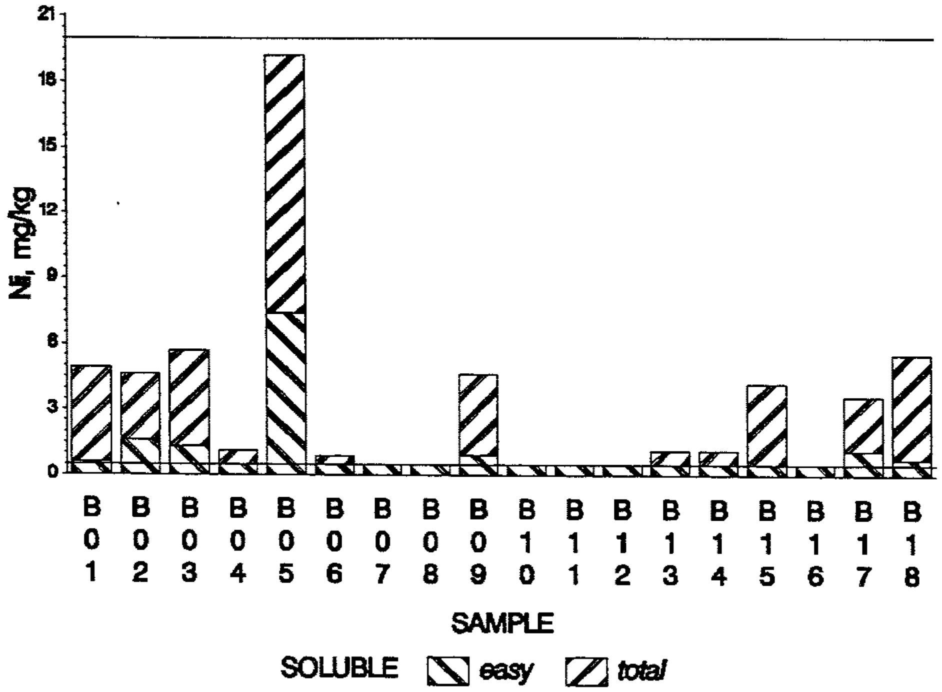

Fig. 6. Easily soluble and total Ni contents in liming materials of the B series, analyzed at Landbrukets Analysesenter, N-1432 ÅS. The lower reference line is showing the detection limit, the upper the limit for lake liming materials in Sweden (analyzed according to Swedish Standard SS 028150).

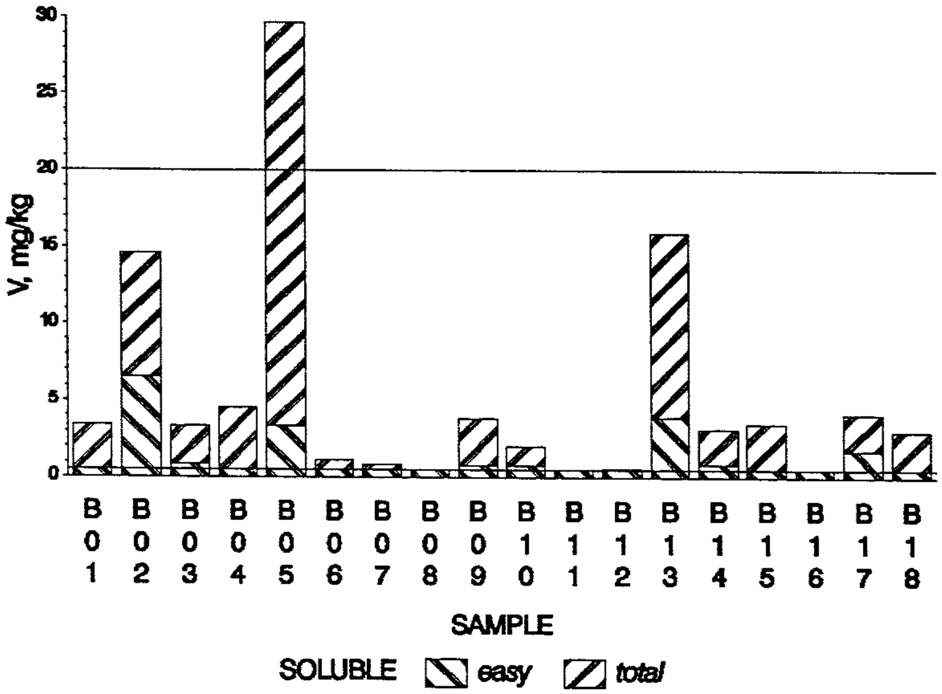

Fig. 7. Easily soluble and total V contents in liming materials of the B series, analyzed at Landbrukets Analysesenter, N-1432 ÅS. The lower reference line is showing the detection limit, the upper the limit for lake liming materials in Sweden (analyzed according to Swedish Standard SS 028150).

CONCLUSIONS

With respect to trace elements liming materials marketed in Norway would normally be a minor source to agricultural soils.
In a global and industrialized perspective the contents and supplies of trace elements are very low in average Norwegian soils. Normally they are considered as non contaminated. Yet there are gradients within the country, with soils demonstrating higher contents far south and far north in Norway, exposed to atmospheric fallouts from the Continent (East and West), Great Britain and Russia.
Moreover, we will find different buffering capacities and plant uptake mechanisms between soils, with higher retention of most of the trace elements with increased colloid contents (organic matter and in particular clay minerals) and elevated pH levels.

In general the contents of heavy metals and accessory elements are lower in liming materials than found as background levels, as verified by comparison with the Nordkalott Project (Fennoscandia).

With respect to some elements there were, however, a few products which might contribute to slight enrichments of certain elements. This concerned Cd (ODDA products, carbonate converter lime and FAXE coral lime), Pb (English quarterly burnt dolomite), Ni (ODDA lime) and possibly F (ODDA lime and carbonate converter lime).

Strict regulations are arranged for liming materials used as remedial measures in Sweden. The method of extraction was a little weaker as prescribed by Naturvårdsverket than stated by these analyses of total contents, but the FAXE coral lime would definitely not be accepted with respect to its Cd contents under Swedish conditions. The same concerned the ODDA lime considering its Ni and V contents. Relatively high values were also stated in some products viewing their contents of Pb (English quarterly burnt dolomite) and V (English quarterly burnt dolomite, GAUSDAL magnesian limestone).
The F contents of the ODDA lime and the carbonate converter lime would probably make it unacceptable for liming of acidified waters.

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