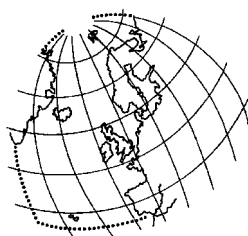


**Emissions and Discharges of  
Polycyclic Aromatic Hydrocarbons (PAHs)  
from Primary Aluminium Electrolysis,  
Soederberg Technology**



OSPAR Commission  
2002

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the “OSPAR Convention”) was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. It has been ratified by Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland and the United Kingdom and approved by the European Community and Spain.

*La Convention pour la protection du milieu marin de l'Atlantique du Nord-Est, dite Convention OSPAR, a été ouverte à la signature à la réunion ministérielle des anciennes Commissions d'Oslo et de Paris, à Paris le 22 septembre 1992. La Convention est entrée en vigueur le 25 mars 1998. La Convention a été ratifiée par l'Allemagne, la Belgique, le Danemark, la Finlande, la France, l'Irlande, l'Islande, le Luxembourg, la Norvège, les Pays-Bas, le Portugal, le Royaume-Uni de Grande Bretagne et d'Irlande du Nord, la Suède et la Suisse et approuvée par la Communauté européenne et l'Espagne.*

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## EXECUTIVE SUMMARY

OSPAR Recommendation 98/2 on Emission and Discharge Limit Values for Existing Aluminium Electrolysis Plants requires that the Commission evaluate the need and timing of an additional OSPAR measure concerning limit values with respect to discharges of Polycyclic Aromatic Hydrocarbons (PAHs) (as Borneff<sub>6</sub>) to the aquatic environment from Soederberg plants.

This report includes a presentation of the results of a monitoring campaign, a description of technologies used at plants and the conclusions from the measuring campaign, and a justification for setting discharge limit values for PAHs into water.

Over the period 1996 - 1999, standardised sampling of PAH emissions to air and discharges into water have been conducted at six Norwegian aluminium plants with Soederberg technology. The focus has been on emissions in pot room ventilation air and discharges into water from seawater scrubbers. For comparison between plants of PAH emissions to air and discharges to water, it was imperative that standardised procedures for sampling, sample preparation and analysis were followed at all stages. Based on relevant Norwegian Standards, a description of practical methods for sampling, sample preparation and analysis of PAHs at aluminium plants has been produced, a description of which is attached to this report.

The average level of emissions to air of particulate PAH<sub>16</sub> from all six plants was 280 g per tonne aluminium produced and the average level of total PAH<sub>16</sub> was 638 g per tonne aluminium. The variations in emissions to air have been large from plant to plant and from year to year. All the components in PAH<sub>16</sub> could be detected in the particulate fraction of the emissions to air. The component benzo(a)pyrene constituted on average 5% of PAH<sub>16</sub> in the particulate fraction. The components fluoranthene and benzo(bjk)fluoranthene constituted each 15-20% and dominated quantitatively the particulate fraction. In the gaseous fraction of the emissions to air, only four of the most volatile components in PAH<sub>16</sub> could be detected. On average for all plants, the component phenanthrene alone constituted 66% of the gaseous PAH emissions to air. No benzo(a)pyrene could be detected in the gaseous fraction of the emissions to air. Due to analytical difficulties, the Oslo<sub>11</sub> selection of PAH components should be omitted in future reporting of PAH emissions to air from aluminium electrolysis plants.

When using a single component as an indicator for PAH emissions or discharges, it must be remembered that the inaccuracy in analysis is far greater for one single component than for the sum of a selection of components. Because of the short half-lives of the gaseous components, it may be advantageous to focus the future emission sampling of ventilation air from Soederberg pot rooms on particulate emissions only. Future reporting of PAH emissions to air should be based on PAH<sub>16</sub> / benzo(a)pyrene.

From the three aluminium plants with seawater scrubbing of ventilation air, the discharges of total PAH<sub>16</sub> were on average 84, 72 and 17 g per tonne aluminium, respectively. The corresponding values for Borneff<sub>6</sub> were 28, 25 and 6 g per tonne aluminium. A considerable amount (50-70%) of the PAHs in the discharge water is in the dissolved fraction. It has been previously documented that the dissolved fraction of PAHs in effluents may be harmful to marine organisms in the recipient. It is therefore necessary to employ sampling methods that include the dissolved fraction of PAHs in effluents. Reporting should be based on Borneff<sub>6</sub> / PAH<sub>16</sub>.

On the basis of the findings in this report, the Commission has adopted a supplementary measure: OSPAR Recommendation 2002/1 on Discharge Limit Values for Existing Aluminium Electrolysis Plants.

## RÉCAPITULATIF

La Recommandation OSPAR 98/2, sur les plafonds d'émission et de rejet applicables aux installations existantes de fabrication de l'aluminium par électrolyse, porte que la Commission appréciera s'il y a lieu d'adopter une mesure complémentaire OSPAR concernant les plafonds de rejet de HAP (dits 6 de Borneff) dans le milieu aquatique par les installations Soederberg, ainsi que le moment où il y aura lieu d'adopter une telle mesure.

Dans le présent rapport figurent les résultats d'une campagne de surveillance, une description des techniques appliquées dans les usines, ainsi que les conclusions de la campagne de mesures et l'argumentaire justifiant les plafonds fixés pour les rejets de HAP dans l'eau.

De 1996 à 1999, il a été procédé, dans six installations norvégiennes de fabrication de l'aluminium faisant appel à la technologie Soederberg, à un échantillonnage normalisé des émissions de HAP dans l'atmosphère et des rejets de HAP dans les eaux. L'on s'est concentré sur les émissions dans l'air de ventilation des ateliers des creusets ainsi que sur les rejets dans les eaux des épurateurs à l'eau de mer. Pour pouvoir comparer les émissions atmosphériques et les rejets de HAP dans les eaux entre les usines, il était impératif que des procédures normalisées d'échantillonnage, de préparation des échantillons et d'analyse soient suivies à tous les stades. Sur la base des normes norvégiennes correspondantes, une description des méthodes concrètes d'échantillonnage, de préparation des échantillons et de dosage des HAP dans les installations de fabrication d'aluminium a été élaborée, cette description étant jointe au présent rapport.

Le niveau moyen des émissions atmosphériques des 16 HAP en particules dans les six usines s'est avéré être de 280 g par tonne d'aluminium produit, tandis que le niveau moyen des 16 HAP totaux était de 638 g par tonne d'aluminium. Les variations des émissions atmosphériques se sont avérées importantes tant d'une usine à l'autre que d'une année à l'autre. Tous les composants des 16 HAP ont pu être décelés dans la fraction particulaire des émissions atmosphériques. La composante benzo(a)pyrène représentait en moyenne 5% des 16 HAP dans la fraction particulaire. Les composantes fluoranthène et benzo(bjk)fluoranthène représentaient chacune entre 15 et 20%, et dominaient quantitativement la fraction particulaire. Dans la fraction gazeuse des émissions atmosphériques, seuls 4 des composants les plus volatiles des 16 HAP ont pu être décelés. En moyenne, et pour l'ensemble des installations, à elle seule, la composante phénanthrène représentait 66% des émissions de HAP à l'état gazeux dans l'atmosphère. Aucun benzo(a)pyrène n'a pu être décelé dans la fraction gazeuse des émissions atmosphériques. En raison des difficultés d'analyse, la sélection des 11 composants de HAP dits d'Oslo devrait être omise dans la notification des émissions atmosphériques de HAP des installations de fabrication de l'aluminium par électrolyse.

Lorsque l'on ne se sert que d'un seul composant comme indicateur des émissions ou des rejets de HAP, il est impératif d'être conscient du fait que le manque de précision de l'analyse est beaucoup plus important dans le cas d'un seul composant que pour la somme des composants, ou pour une série de composants. Du fait de la brièveté de la demi-vie des composants à l'état gazeux, il se peut qu'il soit avantageux, dans l'avenir, de ne centrer l'échantillonnage des émissions dans l'air de ventilation des ateliers des creusets Soederberg que sur les émissions de particules. Il conviendrait que dans l'avenir, la notification des émissions atmosphériques de HAP soit basée sur les 16 HAP/le benzo(a)pyrène.

Dans les trois usines d'aluminium dans lesquelles l'air de ventilation est épuré à l'eau de mer, les rejets des 16 HAP totaux se sont avérés s'élever respectivement et en moyenne à 84, 72 et 17 g par tonne d'aluminium. Les valeurs correspondantes des 6 de Borneff étaient de 28, 25 et 6 g par tonne d'aluminium. Une proportion considérable (entre 50 et 70%) des HAP dans les eaux rejetées se trouve dans la fraction dissoute. Il a déjà été dit, dans la bibliographie, qu'il se pouvait que la fraction de HAP dissoute dans les effluents soit nocive pour les organismes marins présents dans le milieu récepteur. Il est par conséquent nécessaire de faire appel à des méthodes d'échantillonnage qui englobent la fraction dissoute des HAP dans les effluents. Il conviendrait de notifier les teneurs des 6 de Borneff/16 HAP.

Se basant sur les constatations du présent rapport, la Commission a adopté une mesure supplémentaire, à savoir la Recommandation OSPAR 2002/1 sur les plafonds de rejet applicables aux installations existantes de fabrication de l'aluminium par électrolyse.

## **1. INTRODUCTION**

Section 3.2 of the OSPAR Recommendation 98/2 on Emission and Discharge Limit Values for Existing Aluminium Electrolysis Plants Discharges to water states that:

*“With respect to discharges of PAHs (as Borneff<sub>6</sub>) to the water environment from Soederberg plants, Contracting Parties concerned should collaborate in preparing:*

- *A measuring programme for an intercalibration exercise between different Soederberg plants and;*
- *Descriptions of technologies (including treatment facilities, relevant design criteria, flows) used in Soederberg plants for wet cleaning of pot gas and ventilation air.*

*Based upon the results of these activities, which should be available by 1 January 2000, the Commission will evaluate the need for and timing of an additional OSPAR measure concerning limit values with respect to discharges of PAHs (as Borneff<sub>6</sub>) to the water environment from Soederberg plants.”*

Norway presented to the 1999 meeting of the Working Group on Point Sources (POINT 1999) a progress report on the intercalibration exercise including a preliminary report (Results from intercalibration of PAH measurements at aluminium electrolysis plants in Norway 1996-1999, National Institute of Technology report no 99-44649).

This background paper includes a presentation of the results from the measuring campaign, description of technology used at the plants, conclusions from the measuring campaign and justification for setting discharge limit values for PAHs to water.

With regard to PAHs to air, some comments on the results and possible future follow up are discussed.

Comments made at POINT 1999, PDS 2000 and PDS 2001 (Working Group on Point and Diffuse Sources) have been taken into account, and the report has been updated accordingly. Norway has not received data from other Contracting Parties, and has therefore based the report on Norwegian data only.

## **2. INTERCALIBRATION EXERCISE IN NORWAY**

Six out of the seven Norwegian aluminium electrolysis plants use Soederberg technology in their pot rooms. Five of these plants have both Soederberg and prebake technology, and one plant is operating only Soederberg pots. Three plants use seawater for scrubbing of the ventilation air from Soederberg pot rooms.

Each year from 1996 to 1999, intercalibration of PAH measurements has been conducted at the Soederberg electrolysis plants. Using standardised methods for sampling, sample preparation and analysis, PAH emissions to air and discharges to water from Soederberg pot rooms and anode paste factories have been measured.

This intercalibration project has been a co-operation between the aluminium producers Hydro Aluminium, Elkem Aluminium and the National Institute of Technology. The PAH analysis have been performed by the Norwegian Institute for Water Research (NIVA) and at SINTEF Kjemi, a research institution attached to the University of Oslo.

According to OSPAR Recommendation 98/2 on Emission and Discharge Limit Values for Existing Aluminium Electrolysis Plants, the intercalibration project should have included all Soederberg plants within the convention area. At present, data from other countries have not been made available.

### 3. SUMMARY OF RESULTS FROM THE INTERCALIBRATION EXERCISE

#### 3.1 Purpose

This report summarises the results of the intercalibration of measurements of PAH emissions and discharges from the Soederberg aluminium electrolysis plants in Norway, 1996-1999.

The purpose of the intercalibrations was:

- to establish common procedures for sampling, sample preparation and analysis of PAHs;
- to gather comparable data from each plant on levels of PAH emissions to air and discharges to water.

#### 3.2 Scope

The intercalibrations have been conducted each year as 2-3 days sampling campaigns. The three plants with seawater scrubbing of pot room ventilation air were of special interest. Sampling at these plants has taken place each year during the four-year intercalibration period. At the three plants with no seawater scrubbing, sampling of emissions to air was done twice during the same period. In addition, samples were taken of PAH discharges to water from the anode paste plants. No samples were taken from the discharges to water from the plants without ventilation air scrubber.

#### 3.3 Summary of results

a. *Emissions to air*

Average level (all plants, all four years) of emission to air of particulate PAH<sub>16</sub> was 280 g/tonne Al, and average level of total PAH<sub>16</sub> was 638 g/tonne Al.

The variations differed greatly from year to year and from plant to plant;

b. *Discharges to water*

From the three plants with seawater scrubbing of pot room ventilation air, the discharges of total PAH<sub>16</sub> were on average 84, 72 and 7 g/tonne Al, respectively. Or, as total Borneff<sub>6</sub>, 28, 25 and 6 g/tonne Al;

c. In the particulate fraction of the PAH emissions to air, the component benzo (a) pyrene constituted on average 5% of the PAH<sub>16</sub> selection of components. Other components, such as fluoranthene and benzo(bjk)fluoranthene were present in greater concentrations by 3-4 times. The inaccuracy in analysis is far greater when reporting a single indicator component compared with a selection of several components;

d. Because of analytical difficulties, the use of the Oslo<sub>11</sub> selection of PAH components should be omitted in future reporting of PAH emissions to air.

### 4. DESCRIPTION OF TECHNOLOGY

#### 4.1 Description of plants, technology and sampling points

##### 4.1.1 Elkem Aluminium Lista

*Plant*

The plant uses only Soederberg technology. The annual production is approximately 80 000 tonnes. The pot gas is collected and goes to an alumina scrubber and then to a seawater scrubber.



The pot room ventilation air is forced through seawater scrubbing towers. Ventilation airflow is about 15 million Nm<sup>3</sup>/h, and seawater flow approximately 6000 m<sup>3</sup>/h. There is no treatment of the discharge water after the seawater scrubber.

The plant has developed the Soederberg technology. This development includes collection and scrubbing of anode fumes and closed point feeding for part of the plant. Additional measures are improved gas skirts and gas burners, and increased height of the anode casing. Some of this development has also been going on during the measurement campaign period, and is therefore reflected in the results. The total rebuilding of the plant has however not yet been completed.

#### *Sampling*

Emissions to air were sampled at points situated after the fans of the scrubbing towers. Samples of discharge to water were taken from the main duct leading to the recipient.

### **4.1.2 Elkem Aluminium Mosjøen**

#### *Plant*

The annual production from the Soederberg pot rooms is approximately 50 000 tonnes. The pot gas is collected and lead through an alumina scrubber and subsequently to a seawater scrubber.

Soderberg pot room ventilation air is scrubbed in towers similar to those at Elkem Aluminium Lista. Ventilation airflow is 6,8 million Nm<sup>3</sup>/h, and the seawater flow is approximately 5600 m<sup>3</sup>/h. Effluence from the scrubbing towers flows through a sedimentation pond before it reaches the recipient water. Measures to improve the Soederberg part of the plant have not been installed.

#### *Sampling*

Emissions to air were sampled at points situated after the fans of the scrubbing towers. Samples of discharge water were taken at the outlet of the sedimentation pond.

### **4.1.3 Hydro Aluminium Karmøy**

#### *Plant*

The annual production from the Soederberg pot rooms is about 118 000 tonnes. The pot gas is collected and goes to an alumina scrubber and then to a seawater scrubber.

The pot room ventilation air is scrubbed in rooftop scrubbers. Ventilation airflow is 17 million Nm<sup>3</sup>/h. Two separate sedimentation ponds handle the discharge water from the pot rooms.

Point feeders were installed for the Soederberg pot rooms in 1997.

#### *Sampling*

Emissions to air were sampled from a selection of the rooftop scrubbers. Discharge water was sampled from outlet of sedimentation pond. One of the ponds has no defined outlet, and samples were drawn from the recipient on the outside of the barrier of the pond.

### **4.1.4 Hydro Aluminium Årdal**

#### *Plant*

This is the only aluminium electrolysis plant in Norway not located by the sea. The annual production from the Soederberg pot rooms is approximately 50 000 tonnes. The pot gas is collected and lead through an alumina scrubber and subsequently to wet scrubber (using lye). There is no cleaning of pot room ventilation air. Rooftop fans provide ventilation with a total airflow of some 10,6 million Nm<sup>3</sup>/h. There is no treatment of discharge water after the wet scrubber, and it is transported and discharged into the sea. Point feeders were installed for the Soederberg pot rooms in 1999.

### Sampling

Samples of emissions to air were drawn from the rooftop ventilators.

#### 4.1.5 Hydro Aluminium Sunndal

##### Plant

The Soederberg pot rooms produce approximately 59 000 tonnes annually. The pot gas is collected and led through an alumina scrubber and subsequently a seawater scrubber. Fans blow fresh air into the cellar thus providing ventilation of the pot rooms. There is no cleaning of pot room ventilation air. The airflow is approximately 8 million Nm<sup>3</sup>/h. Measures to improve the Soederberg part of the plant have not been installed.

##### Sampling

Manifolds and fans are mounted to draw sampling air from the pot room down to floor level. Samples were taken at sampling points in the manifold pipes.

#### 4.1.6 Hydro Aluminium Høyanger

##### Plant

The plant has a small Soederberg pot room with an annual production of 23 000 tonnes. The pot gas is collected and led through an alumina scrubber and subsequently a seawater scrubber. There is no treatment of the discharge water after the seawater scrubber.

There is no forced ventilation and no cleaning of ventilation air. Ventilation airflow from convection is estimated to approximately 3 million Nm<sup>3</sup>/h. Point feeders were installed for the Soederberg pot rooms in 1998.

##### Sampling

Emissions to air were taken at the slits in the pot room roof, where the ventilation air escapes the pot room.

#### 4.1.7 Overview of Soederberg aluminium plants in Norway

Table 4 gives an overview of the Soederberg electrolysis plants in Norway. All the plants except Lista also employ prebake technology. In addition, there is one plant, Sør-Norge Aluminium at Husnes, which employs prebake technology solely. This plant has not been included in the intercalibrations.

**Table 1 Soederberg pot rooms at aluminium electrolysis plants in Norway**

	<b>Annual Al production, Soederberg</b>	<b>Pot room ventilation/ gas scrubbing</b>	<b>Ventilation airflow (Nm<sup>3</sup>/h)</b>	<b>Seawater flow (m<sup>3</sup>/h)</b>
Elkem Aluminium Lista	80 000 tonnes	Seawater scrubbers	15 000 000	6000
Elkem Aluminium Mosjøen	50 000 tonnes	Seawater scrubbers	6 800 000	5600
Hydro Aluminium Karmøy	118 000 tonnes	Seawater scrubbers	17 000 000	7500
Hydro Aluminium Årdal	50 000 tonnes	Rooftop fans	10 600 000	-
Hydro Aluminium Sunndal	59 000 tonnes	Cellar fans	8 000 000	-
Hydro Aluminium Høyanger	23 000 tonnes	No forced ventilation	3 000 000	-

## 5. RESULTS FROM MEASUREMENTS OF PAHS TO WATER

### 5.1 Discharges to water

#### 5.1.1 Discharges from seawater scrubbers for pot room ventilation air

Tables 2 and 3 give the specific levels of discharge from the plants at Lista, Mosjøen and Karmøy.

Table 2 shows the levels that were established for each year of sampling. Table 3 gives the average values for all three years.

"Part", "Diss" and "Tot" denote the particulate fraction, the dissolved fraction and the total PAH values. The results are given as specific discharges of both PAH<sub>16</sub> and Borneff<sub>6</sub>.

**Table 2 Discharges to water of PAHs from scrubbing of Soederberg pot room ventilation air**

		Discharges to water (gram PAHs / tonne Al)								
		1997			1998			1999		
		<i>Part.</i>	<i>Diss.</i>	<i>Tot.</i>	<i>Part.</i>	<i>Diss.</i>	<i>Tot.</i>	<i>Part.</i>	<i>Diss.</i>	<i>Tot.</i>
Elkem Aluminium Lista	PAH <sub>16</sub>	35	78	113	25	45	70	33	35	68
	Borneff <sub>6</sub>	15	20	35	11	14	25	12	11	23
Elkem Aluminium Mosjøen	PAH <sub>16</sub>	25	35	60	49	48	97	23	36	59
	Borneff <sub>6</sub>	11	7	18	20	16	36	8	13	21
Hydro Aluminium Karmøy	PAH <sub>16</sub>	3	9	12	6	17	23	5	9	14
	Borneff <sub>6</sub>	1	3	4	2	7	9	2	2	4

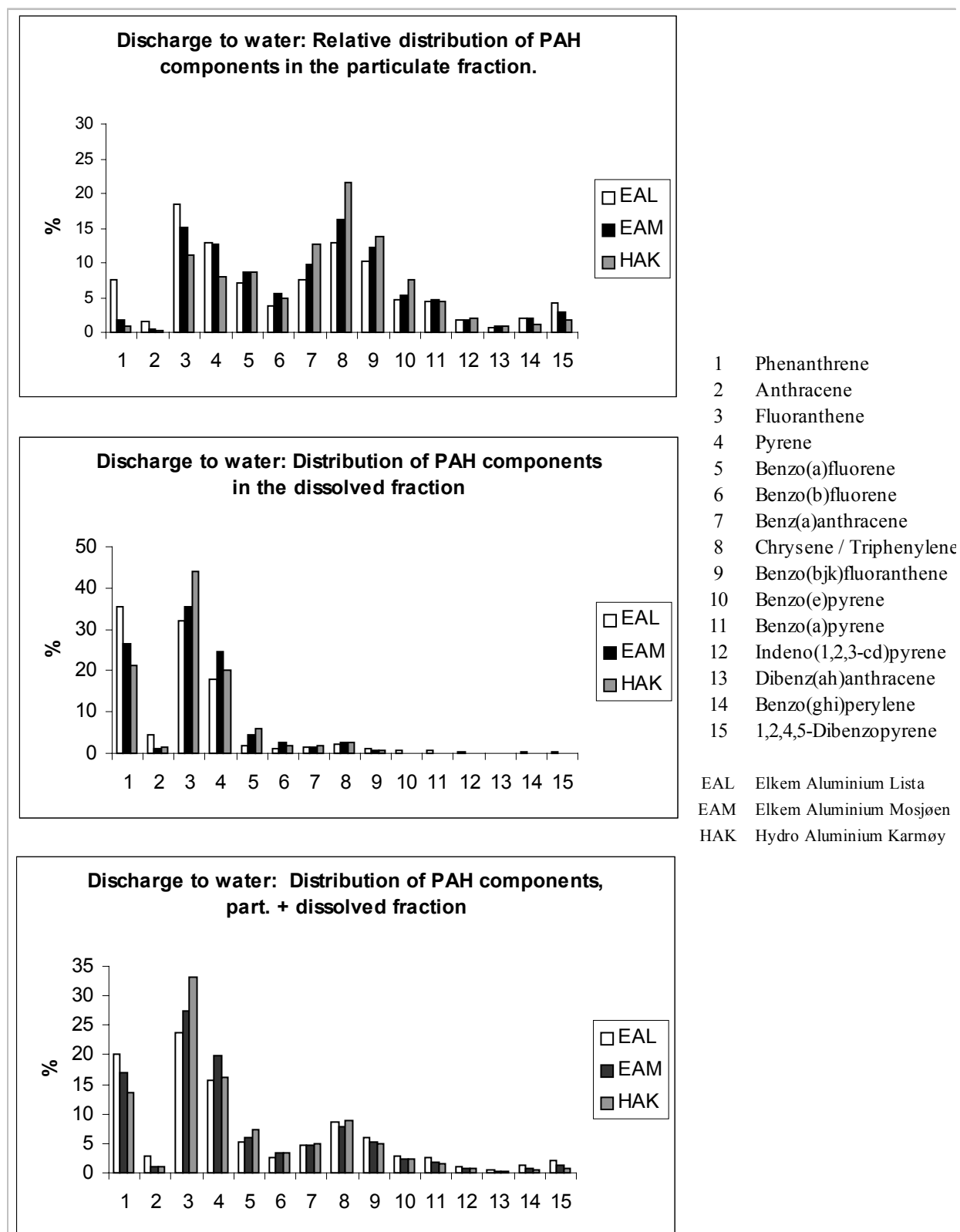
**Table 3 Average levels, specific PAH discharges to water from Soederberg pot room ventilation air scrubbing**

		Average levels, discharge to water (gram PAHs / tonne Al)		
		<i>Part.</i>	<i>Diss.</i>	<i>Tot.</i>
Elkem Aluminium Lista	PAH <sub>16</sub>	31	53	84
	Borneff <sub>6</sub>	13	15	28
Elkem Aluminium Mosjøen	PAH <sub>16</sub>	32	40	72
	Borneff <sub>6</sub>	13	12	25
Hydro Aluminium Karmøy	PAH <sub>16</sub>	5	12	17
	Borneff <sub>6</sub>	2	4	6

In the particulate fraction of the effluent from the seawater scrubbers, the dominating PAH components were phenanthrene, fluoranthene, pyrene and benzo(bjk)fluoranthene. These components accounted for between 50% and 68% of PAH<sub>16</sub> in the particulate fraction. The component benzo(a)pyrene constituted on average 5% of the particulate PAH<sub>16</sub>.

In the dissolved fraction, the components phenanthrene, fluoranthene and pyrene were dominating. They constituted at all plants some 90% of the total PAH values in the dissolved fraction, although there was some variation in the reciprocal distribution of the components. All the other components of PAH<sub>16</sub> could also be detected.

Figure 1 shows the distribution of PAH components in the effluent from the three plants with seawater scrubbing of pot room gas. For each plant, the distribution of components was constant from year to year.



**Figure 1** Relative distribution of PAH components in effluent from seawater scrubbing of pot room ventilation air

## 6. RESULTS FROM MEASUREMENTS OF PAHS TO AIR

### 6.1 PAH emissions to air from Soederberg pot rooms

Table 4 shows the results of the samplings of the PAH emissions to air from the Soederberg pot rooms. "Part", "Gas" and "Tot" denote the amounts of particulate, gaseous and total PAHs. The results are given as specific emissions; i.e. grams of PAHs per tonne of primary aluminium produced at the Soederberg electrolysis plant.

**Table 4 Specific emissions of PAHs to air (g PAH<sub>16</sub>/tonne of aluminium produced)**

	1996			1997			1999†		
	<i>Part.</i>	<i>Gas</i>	<i>Tot</i>	<i>Part.</i>	<i>Gas</i>	<i>Tot</i>	<i>Part.</i>	<i>Gas</i>	<i>Tot</i>
Elkem Aluminium Lista	229	89	318	182	262	444	240/17	264/0	504/17
Elkem Aluminium Mosjøen	380	126	506	185	110	295	479/40	254/0	733/40
Hydro Aluminium Karmøy	308	883	1191	565	358	923	375/16	348/0	723/16
Hydro Aluminium Årdal	671	655	1326	231	188	419			
Hydro Aluminium Sunndal	180	1003	1183	78	157	235			
Hydro Aluminium Høyanger 1	116	294	410						
Hydro Aluminium Høyanger 2*	115	207	322						

\* Sampling in Høyanger on two separate occasions in 1996.

† PAH<sub>16</sub>/B(a)P /tonne aluminium produced.

The campaign in 1999 included measurements of PAHs to air from conventional and "new" Soederberg at Elkem Aluminium Lista. The results show a significant reduction of PAHs from "new" Soederberg. Table 5 shows the results from one measurement in 1999. The results must therefore be used with caution. Based on the results from regular monitoring at the plant we see at this time that a reduction of 60-70%, compared to the figures in table 4, in PAH emissions from "new" Soederberg can be achieved.

**Table 5 Specific emissions of PAHs to air (g PAH<sub>16</sub>/tonne of aluminium produced and B(a)P/tonne aluminium produced)**

"New" Soederberg cells with complete hood coverage of the anode top, which is connected to a separate gas exhaust and dry aluminium scrubber, measurements carried out in flue gases in stacks after scrubbing. This will result in additional discharges to water.

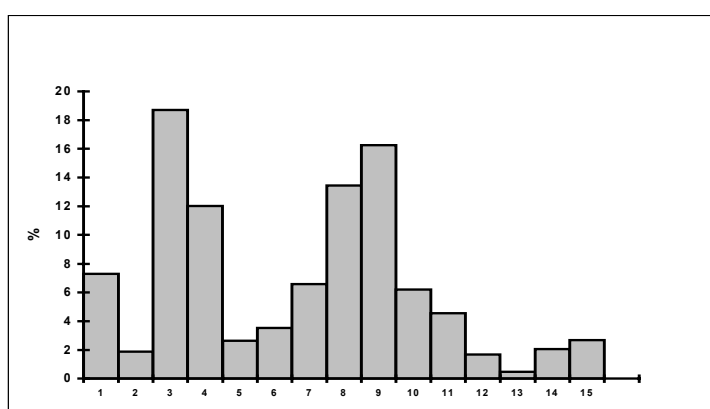
	1999 PAH <sub>16</sub>			1999 BaP		
	<i>Part.</i>	<i>Gas</i>	<i>Tot</i>	<i>Part.</i>	<i>Gas</i>	<i>Tot</i>
Elkem Aluminium Lista						
"new" Soederberg	49	50	99	4	0	4

Arithmetic average emission levels for each plant are given in table 6. The average values are calculated based on the data given in table 4.

**Table 6 Arithmetic average levels for samplings 1996-1999. Specific PAH emissions to air, Soederberg pot rooms**

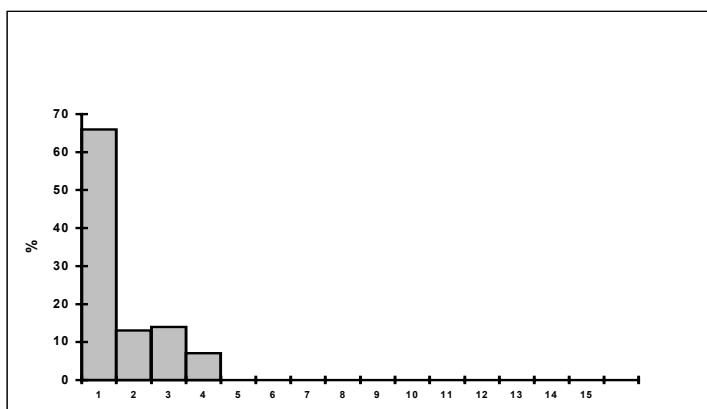
	Average emission level (grams PAH <sub>16</sub> / tonne Al)		
	Particulate	Gaseous	Total
Elkem Aluminium Lista	217	205	422
Elkem Aluminium Mosjøen	348	163	511
Hydro Aluminium Karmøy	416	529	945
Hydro Aluminium Årdal	451	422	873
Hydro Aluminium Sunndal	129	580	709
Hydro Aluminium Høyanger	116	251	367
<b>Average, all plants</b>	<b>280</b>	<b>358</b>	<b>638</b>

The average relative distribution of PAH components in emissions to air is illustrated in figures 2 and 3.



- 1 Phenantrene
- 2 Anthracene
- 3 Fluorantene
- 4 Pyrene
- 5 Benzo(a)fluorene
- 6 Benzo(b)fluorene
- 7 Benz(a)anthracene
- 8 Chrysene / Triphenylene
- 9 Benzo(bjk)fluoranthene
- 10 Benzo(e)pyrene
- 11 Benzo(a)pyrene
- 12 Indeno(1,2,3-cd)pyrene
- 13 Dibenz(ah)anthracene
- 14 Benzo(ghi)perylene
- 15 1,2,4,5-Dibenzopyrene

**Figure 2 Relative distribution of particulate PAHs in emissions to air**



- 1 Phenantrene
- 2 Anthracene
- 3 Fluorantene
- 4 Pyrene
- 5 Benzo(a)fluorene
- 6 Benzo(b)fluorene
- 7 Benz(a)anthracene
- 8 Chrysene / Triphenylene
- 9 Benzo(bjk)fluoranthene
- 10 Benzo(e)pyrene
- 11 Benzo(a)pyrene
- 12 Indeno(1,2,3-cd)pyrene
- 13 Dibenz(ah)anthracene
- 14 Benzo(ghi)perylene
- 15 1,2,4,5-Dibenzopyrene

**Figure 3 Relative distribution of gaseous PAHs in emissions to air.  
Average for all plants (1996-1999)**

As Figure 2 shows, the dominating components in the particulate fraction were fluoranthene, pyrene, chrysene/triphenylene and benzo(bjk)fluoranthene. These components accounted for between 53% and 68% of the total particulate PAH emissions. All of the other components in PAH<sub>16</sub> were also present. The component benzo(a)pyrene constituted between 2% and 8% of PAH<sub>16</sub> in the particulate emission to air. The average value for all plants was 5%.

In the gaseous fraction, only the component phenanthrene, anthracene, fluoranthene and pyrene could be detected. Among these components, phenanthrene was clearly dominant, ranging from 26% to 70%. Average level of phenanthrene in the gaseous fraction was 66%.

## 7. DISCUSSION

### 7.1 Sampling

Description of methods used for sampling and analysis is given in Appendix 1. The method description is based on the relevant Norwegian Standards.

At several plants, the only available sampling points for emissions to air were immediately before or after ventilation fans. This made it difficult to fully achieve isokinetic sampling conditions, a problem these plants also face when taking routine emission samples.

### 7.2 Analysis

#### 7.2.1 Benzo(a)pyrene, B(a)P

Inaccuracy in analysis of single components may be as much as 25% and 10% for the sum of PAH<sub>16</sub>. The confidence intervals and distribution of inaccuracy in the analysis are uncertain, but with several samples, normal distribution can be assumed. Thus, the overall inaccuracy in analysis will decrease with increasing number of analysed PAH components. In other words, the inaccuracy in analysis is far greater when reporting only one component, such as benzo(a)pyrene, than when reporting a selection of components, such as PAH<sub>16</sub>.

The concentration of benzo(a)pyrene in the particulate fraction of both emissions to air and discharges to water was approximately 5% of PAH<sub>16</sub>.

#### 7.2.2 Oslo<sub>11</sub>

In some contexts, a selection of components called Oslo<sub>11</sub> are referred to for reporting PAH emissions to air.

**Table 7 Definition of the Oslo<sub>11</sub> selection of PAH components**

1	Phenanthrene	7	Benzo(k)fluoranthene
2	Anthracene	8	Benzo(a)pyrene
3	Fluoranthene	9	Indeno(1,2,3-cd)pyrene
4	Benzo(b)anthracene	10	Benzo(g,h,i)perylene
5	Chrysene	11	Dibenzo(a,h)anthracene
6	Benzo(b)fluoranthene		

The principle of gas chromatographic analysis is to separate components in a sample based on different retention times for each component as it flows through a capillary column. For analytical purposes, the retention time for each component is set as a time interval. If two components or two isomers of the same component have overlapping retention time intervals, it is not possible to distinguish between them.

SINTEF Kjemi has experienced some problems regarding analysis of the Oslo<sub>11</sub> selection of components:

- it was not possible to separate chrysene from triphenylene. These components are reported as the sum of both;
- benzo(b)fluoranthene and benzo(k)fluoranthene could not be separated from benzo(j)fluoranthene. These isomers are reported as the sum of all three;
- dibenzo(a,h)anthracene was difficult to separate from the isomer dibenzo(a,c)anthracene.

Because of these analytical problems, the use of Oslo<sub>11</sub> for reporting PAH emissions to air has been omitted. Emissions were reported as PAH<sub>16</sub> with benzo(a)pyrene as an indicator component.

Section 4.2.4. of the OSPAR Recommendation 98/2 on Emission and Discharge Limit Values for Existing Aluminium Electrolysis Plants makes reference to Oslo<sub>11</sub> PAHs analysed for emissions to air. The supplementary OSPAR Recommendation 2002/1 makes reference to 16 PAHs analysed for emissions to air. It is proposed that these 16 PAHs replace Oslo<sub>11</sub> PAHs and for consistency they should also be referred to in any future revision of PARCOM Recommendation 92/1 for BAT for Plants Producing Anodes, a review of which is foreseen in 2006. It should be noted that any emission values contained in the EC IPPC BAT Reference Document for aluminium production may need to be adjusted when taking into account 16 PAHs rather than the previously agreed Oslo<sub>11</sub>.

## **7.3 Distribution of PAH components**

### **7.3.1 Emissions to air from Soederberg pot rooms**

The amount of gaseous PAHs in emissions to air could vary greatly. For example, at Sunndal, this was 1003 g/tonne Al in 1996 and 157 g/tonne Al in 1997. Also at the plants with seawater scrubbing of pot room ventilation air variations for gaseous PAHs were found, e.g. at Lista 89 g/tonne Al in 1996 and approximately 260 g/tonne in 1997 and 1999.

In the gaseous fraction of the PAHs, only the components phenanthrene, anthracene, fluoranthene and pyrene could be detected. The half-lives of these gaseous components in air are short on account of rapid photo oxidation. /1/

It is believed that variations in ambient temperature can influence the emission level of PAHs. This may explain some of the variations that were observed, especially for the gaseous PAHs. Operating procedures in the pot rooms and anode top temperatures are also believed to influence the emissions of PAHs.

### **7.3.2 Discharges to water from Soederberg pot rooms**

The discharge levels at the plants in Mosjøen and at Lista were similar. Although the plant in Mosjøen has a sedimentation pond, measurements have shown that it is not very efficient: 25% efficiency for particulate PAH<sub>16</sub> and 6% for dissolved PAHs (16% for total PAH<sub>16</sub>), determined in 1998. The sedimentation ponds at Karmøy have, due to their size and construction, higher overall efficiency (93% for one and 61% for the other, total PAH<sub>16</sub>). Hence the level of PAH discharges to water was significantly lower at Karmøy than at the two other plants with seawater scrubbing of Soederberg pot room ventilation air.

As figure 3 shows, the relative distribution of PAH components in the effluents from the pot room gas scrubbing showed the same tendency at the three plants.

In the total PAH discharges to water from the plants, the contribution from the dissolved fractions dominated quantitatively. This is also confirmed by research performed by the Norwegian Institute for Water Research. /2/

It has been previously documented that the dissolved fraction of PAHs in effluents from aluminium plants may have effect on marine organisms. /3/



## **8. CONCLUSIONS FROM THE MEASUREMENT CAMPAIGN**

Based on the PAH surveys conducted at the Soederberg aluminium electrolysis plants during 1996-1999, the following can be concluded:

- (i) standardised sampling of PAH emissions to air and discharges to water have been conducted at six Norwegian aluminium plants with Soederberg technology. Focus has been on emissions in pot room ventilation air and discharge to water from seawater scrubbers.
- (ii) For comparison between plants of PAH emissions to air and discharges to water, it is imperative that standardised procedures for sampling, sample preparation and analysis are followed at all stages.
- (iii) Based on relevant Norwegian Standards, a description of practical methods for sampling, sample preparation and analysis of PAHs at aluminium plants has been produced. A description of these methods is given in Appendix 1.
- (iv) The average levels of emission to air of particulate PAH<sub>16</sub> from all six plants was 280 g/tonne Al, and the average level of total PAH<sub>16</sub> was 638 g/tonne Al. The variations in emissions to air differed greatly from plant to plant and from year to year.
- (v) All the components in PAH<sub>16</sub> could be detected in the particulate fraction of the emissions to air. The component benzo(a)pyrene constituted on average 5% of PAH<sub>16</sub> in the particulate fraction. The components fluoranthene and benzo(bjk)fluoranthene constituted each 15-20% and dominated quantitatively the particulate fraction.
- (vi) In the gaseous fraction of the emissions to air, only four of the most volatile components in PAH<sub>16</sub> could be detected. On average for all plants, the component phenanthrene alone constituted 66% of the gaseous PAH emissions to air. No benzo(a)pyrene could be detected in the gaseous fraction of the emissions to air.
- (vii) Due to analytical difficulties, the Oslo<sub>11</sub> selection of PAH components should be omitted in future reporting of PAH emissions to air from aluminium electrolysis plants.
- (viii) When using a single component as an indicator for PAH emissions or discharges, it must be remembered that the inaccuracy in analysis is far greater for one single component than for the sum of a selection of components.
- (ix) Because of the short half-lives of the gaseous components, it may be advantageous to focus the future emission sampling of ventilation air from Soederberg pot rooms on particulate emissions only. Future reporting of PAH emissions to air should be based on PAH<sub>16</sub> / benzo(a)pyrene.
- (x) From the three aluminium plants with seawater scrubbing of ventilation air, the discharges of total PAH<sub>16</sub> were on average 84, 72 and 17 g/tonne Al, respectively. The corresponding values for Borneff<sub>6</sub> were 28, 25 and 6 g/tonne Al.
- (xi) A considerable amount (50-70%) of the PAHs in the discharge water is in the dissolved fraction. It has been previously documented that the dissolved fraction of PAHs in effluents may be harmful to marine organisms in the recipient. It is therefore necessary to employ sampling methods that include the dissolved fraction of PAHs in effluent water. Reporting should be based on Borneff<sub>6</sub> / PAH<sub>16</sub>.

## 9. CONCLUSIONS AND PROPOSAL FOR DISCHARGE LIMIT VALUES

### 9.1 OSPAR Strategy and decisions on a way forward

The objective stated in the OSPAR Strategy with regard to Hazardous Substances, which was adopted in Sintra in 1998 and endorsed by Ministers is as follows:

*"to prevent pollution of the maritime area by continuing to reduce discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances".*

Furthermore the basis for OSPAR's work to achieve this objective is also set out in the Strategy, which also includes a timeframe which states that

*"every endeavour will be made to move towards the target of cessation of discharges, emissions and losses of hazardous substances by the year 2020".*

PAHs are on the OSPAR list of hazardous substances already identified for priority action set out in Annex 2 of the Strategy, and the OSPAR Action Plan for 1998 – 2003.

Primary aluminium industry is considered a significant source of PAH emissions.

Section 3.4 of the PARCOM Recommendation 96/1 on Best Available Techniques and Best Environmental Practice for Existing Electrolysis Plants states that:

*"The long-term objective with regard to emission values from all plants should be to achieve the values for new prebake plants (cf PARCOM Recommendation 94/1 on Best Available Techniques for New Aluminium Electrolysis Plants). A time schedule for achieving the long-term objective should be developed before year 2000 within the framework of the Paris Commission or its successor, as appropriate."*

OSPAR defined prebake technology as BAT in OSPAR Recommendation 94/1. OSPAR Recommendation 98/2 has set short-term emission limit values for, among others, PAHs to air (2005/2007), as well as long-term targets (2010).

Based on the OSPAR strategy, the OSPAR Recommendations mentioned above and the results of the measuring campaign, the need for addressing PAH discharges to water from existing Soederberg plants is well documented.

### 9.2 Discharge Limit Values for PAHs (Borneff<sub>6</sub>)

It was decided in OSPAR Recommendation 98/2, that Borneff<sub>6</sub> total should be used as PAH components included in the future discharge limit values.

When considering setting limit values it is important to see the strong connection between the emissions of PAHs to air and discharges to water. For the Soederberg plants with ventilation air scrubbers more PAHs will be collected and transferred from air to water.

In OSPAR Recommendation 98/2 the long-term target limit value for PAHs to air is divided into plants with and without ventilation air scrubber. A more stringent limit value is set for emissions to air from plants with ventilation air scrubbers. When setting the discharge limit value to water it therefore seems relevant to use the same approach.

Development of improved Soederberg technology has shown that the emissions of PAHs to air and discharges to water can be reduced substantially. This includes measures like automatic point feeders, collection and scrubbing of anode fumes, improved gas burners and gas skirts and increased height of the anode casing. If these measures do not give the desired effect regarding discharges to water, an end of pipe solution may be needed in addition.

The results from the measuring campaign give a good basis for setting discharge limit values for PAHs to water from Soederberg plants with ventilation air scrubbers. The discharges from plants without ventilation air scrubbers, and where the PAHs arises from the wet scrubber and from the primary gas, are not included in the campaign. The proposed limit values are based on reported discharges in the regular control of the plants in Norway.

Annual average discharge limit values by 1 January 2007 and, if possible, Contracting Parties should aim to achieve them by 1 January 2005.

Plant/Technology	Discharge Limit Values (annual average in kg per tonne of aluminium produced)
	PAHs (as Borneff <sub>6 total</sub> )
Soederberg without ventilation air scrubber	0,010
Soederberg with ventilation air scrubber	0,015

Contracting Parties should aim to achieve the target limit values for discharges to water by 1 January 2010 as follows.

Plant/Technology	Target discharge Limit Values (annual average in kg per tonne of aluminium produced)
	PAHs (as Borneff <sub>6 total</sub> )
Soederberg without ventilation air scrubber	0,006
Soederberg with ventilation air scrubber	0,008

### 9.3 Emission Limit Values for PAHs to air

Experience shows that there are some problems with the PAH components chosen in OSPAR Recommendation 98/2 (B(a)P and Oslo<sub>11</sub>). These problems may result in difficulties reporting on the measure. Norway therefore proposes that Oslo<sub>11</sub> is replaced by PAH<sub>16</sub> (particulate).

**APPENDIX 1****METHODS****Sampling and analysis**

At all plants, the same equipment was used for sampling, sample preparation and analysis. Some adjustments in sampling methods had to be made according to local conditions.

A more detailed description of methods for sampling, sample preparation and analysis is given in Appendix 2.

**Emissions to air**

Sampling trains were used with Versapore 800 filter for the particulate PAHs and XAD-2 as absorbent for the gaseous PAHs.

The sampling period for emissions from pot rooms was 24 hours.

The filters and the XAD-2 were extracted separately using soxhlet extraction. A gas chromatograph with mass selective detector (GC/MS) was used for analysis. Quantification was based on addition of internal standard prior to extraction.

**Discharges to water**

Three of the plants have seawater scrubbing of pot room gas. Samples were taken of effluent water from the scrubbers. The samples were taken momentarily as grab samples. In addition, some samples were taken from cooling water in the paste plants.

In order to separate the particulate from the dissolved PAHs, the samples were filtered through GF/C filters. PAHs on the filters and in the filtrate were analysed and reported as respectively particulate and dissolved PAHs.

Analysis was performed at NIVA by means of GC/MS using internal standard for quantification.

**Extent of sampling**

Table 1 shows the number of samples taken at each plant. Figures given in brackets indicate the number of samples taken from the anode paste plants.

**Table 1 Number of samples taken at each plant**

		Number of samples			
		1996	1997	1998	1999
Elkem Aluminium Lista	Emissions to air	7	3		10
	Discharges to water		13	12 (3)	12 (1)
Elkem Aluminium Mosjøen	Emissions to air	8	4		10
	Discharges to water		6 (2)	10 (2)	9 (1)
Hydro Aluminium Karmøy	Emissions to air	8	4		10
	Discharges to water		8 (1)	9 (2)	9 (1)
Hydro Aluminium Årdal	Emissions to air	8	4		
	Discharges to water		(2)	(1)	
Hydro Aluminium Sunndal	Emissions to air	10	4		
	Discharges to water		(4)	(2)	
Hydro Aluminium Høyanger	Emissions to air	16			
	Discharges to water				

## PAH components

The PAH<sub>16</sub> and Borneff<sub>6</sub> selections of components were reported. In addition, the component benzo(a)pyrene was reported separately. Application of the Oslo<sub>11</sub> selection of components is discussed in section 7.2.2.

### PAH<sub>16</sub>:

**Table 2 Definition of the PAH<sub>16</sub> selection of PAH components**

1	Phenanthrene	9	Benzo(bjk)fluoranthene
2	Anthracene	10	Benzo(e)pyrene
3	Fluoranthene	11	Benzo(a)pyrene
4	Pyrene	12	Indeno(1,2,3-cd)pyrene
5	Benzo(a)fluorene	13	Dibenz(ah)anthracene
6	Benzo(b)fluorene	14	Benzo(g,h,i)perylene
7	Benzo(a)anthracene	15	1,2,4,5-Dibenzopyrene
8	Chrysene/triphenylene		

### Borneff<sub>6</sub>:

**Table 3 Definition of the Borneff<sub>6</sub> selection of PAH components**

1	Fluoranthene	4	Indeno(1,2,3-cd)pyrene
2	Benzo(k)fluoranthene	5	Benzo(a)pyrene
3	Benzo(b)fluoranthene	6	Benzo(ghi)perylene

## Detection limits and analysis inaccuracy

For each component, the detection limit is between 0,05 and 0,1 µg per component per sample.

SINTEF Kjemi states that the inaccuracy in analysis of single components is maximum 25%, and for the sum of PAH<sub>16</sub> in a sample maximum 10%.

## REFERENCES

- 1 Mackey, D. et al: "Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals", Lewis Press, 1992.
- 2 Næs, K. et al: "Role of Soot and other Carbon Matrices in the Distribution of PAHs among particles, DOC, and the Dissolved Phase in the Effluent and Recipient Waters of an Aluminium Reduction Plant", Environmental Science and Technology, vol. 32, no. 12, pp. 1786-1792.
- 3 Knutzen, J.: " Effects on marine organisms from polycyclic aromatic hydrocarbons (PAHs) and other constituents of waste water from aluminium plants with examples from Norway", Science of the Total Environment, no 163, pp. 107-122.

## APPENDIX 2

### METHODS FOR SAMPLING AND ANALYSIS OF PAH EMISSIONS AND DISCHARGES FROM ALUMINIUM PLANTS

#### 1. BACKGROUND

PAH measurements at Norwegian plants are at present conducted in different ways. The relevant Norwegian Standards (henceforth referred to as "NS") are in some areas difficult to comply with during routine measurements. Also, in some areas NS provide little or no guidance to specific problems, which are encountered when sampling at aluminium plants.

Comparison between plants of PAH emission levels requires the use of the same methods for sampling and analysis at all plants. A standardised procedure for sampling and analysis of PAH emissions from all Norwegian plants has thus been required. Emphasis has been on equipment and procedures that are practical to use for routine measurements.

#### 2. REFERENCES

Norwegian Standard:

- |           |  |
|-----------|--|
| NS 9808   | Sampling of emission from stationary sources for the determination of PAHs;          |
| NS 9813   | Sample preparation for the determination of PAHs;                                    |
| NS 9805   | Sampling of water for the determination of PAHs;                                     |
| NS-EN 872 | Determination of suspended solids. Method by filtration through glass fibre filters; |
| NS 9810   | Water analysis. Clean up procedure of water samples for the determination of PAHs;   |
| NS9815    | Water and air analysis. Gas chromatographic analysis for the determination of PAHs.  |

#### 3. PAH EMISSIONS TO AIR

##### 3.1 Sampling equipment

Metal filter holder  
Gelman Versapore filter, pore diameter 0,8 µm  
Stainless steel probe, shape and size adjusted to the sampling points at each plant  
Sampling pump  
Gas meter  
Flexible tubes to connect pump, gas meter and sampling equipment.

For sampling of gaseous PAHs, the following must be used in addition:

XAD-2 as adsorbent  
XAD-2 holder. A cylindrical holder of metal is recommended.  
Cellulose pads to keep the XAD-2 in its holder.  
Short metal pipe to connect the filter holder to the XAD-2 holder.

For sample preparation and analysis, the following is required:

Internal standard (e.g. 3,6-dimethylphenanthrene and β,β-binaphtyl)  
Soxhlet extraction apparatus  
Rotor evaporator  
Centrifuge  
Misc. glass equipment  
Solvents: Dichloromethane and cyclohexane  
Gas chromatograph with flame ionisation detector (GC/FID)

### **3.2 Method for sampling**

If only sampling of particulate PAHs is required, use the filter holder and probe. If also gaseous PAHs is to be sampled, connect the XAD-2 holder to the sampling train after the filter holder.

In order to obtain representative samples, it may be required to conduct the sampling over 24 hours. The sampling time must be adjusted to the activities in the pot room. To check the XAD-2 adsorbent for saturation, two XAD-2 holders can be connected in series.

At plants with seawater scrubbing of pot room gas, it may be necessary to place the filter holders in a warm container in order to avoid clogging of the filter due to moisture from the seawater. The temperature on the filter should not be higher than what is required to keep the filter dry, 40-50 °C should be sufficient. The XAD-2 holder is placed outside the heated container.

### **3.3 Sample preparation**

It is important that PAH samples are extracted as soon as possible after sampling. If immediate extraction is not possible, the samples (filters and XAD-2) must be stored in a freezer.

After sampling, the inside of the probe is washed with dichloromethane. This solvent is later used to extract the corresponding filter. In this way, residue of particulate PAHs is included in the measurement of particulate PAHs.

Filter and XAD-2 is extracted in dichloromethane in a soxhlet extraction apparatus. Before extraction, internal standard is added to the samples. The amount of internal standard is adjusted according to the assumed PAH concentration of the sample. Minimum extraction time is 16 hours. After extraction, the solvent volume is reduced by controlled evaporation in rotor evaporator. Using centrifuge subsequently separates any particles from the solvent.

After preparation is completed, the samples are analysed on GC as described in section 5.

## **4. PAH DISCHARGES TO WATER**

### **4.1 Equipment**

Vessel for sampling (bottle with wide neck)

Filtration apparatus

Glass bottles for extraction

Internal standard (e.g. 3,6-dimethylphenanthrene and  $\beta,\beta$ -binaphtyl)

Filter: Whatman GF/C

Shaking table

Separating funnel

In addition:

Equipment for sample preparation and analysis as described in section 3.1 of this appendix.

### **4.2 Method for sampling**

All samples must be taken as grab samples. The sampling frequency must be adjusted to variations in pot room operations. Sample volume should be adjusted to the expected concentration level, but should not be less than 1 litre. PAH contents in intake water should also be checked.

The sample is filtered immediately after being taken. The filter is treated in the same way as filters used for sampling of emissions to air, see section 3.3 above.

For analysis of the dissolved PAH fraction, the filtrate is treated as follows:

- a. transfer the filtrate to glass extraction bottles, add cyclohexane and internal standard. Approximately 50 ml of solvent should be added for each litre of sample. Place the bottle on the shaking table. Allow the bottle to shake in such a way that the solvent is distributed evenly in the body of water. Alternatively, a magnetic stirrer can be applied instead of a shaking table. Extraction time is minimum 12 hours.
- b. after extraction, the sample is transferred to the separating funnel for separation of water and solvent. Afterwards, the extract is evaporated using a rotor evaporator to a volume of approximately 0,5 ml. 2-3 ml of pure cyclohexane may be added. A centrifuge may be used to separate small droplets of water. The sample is then analysed as described in section 5.

## **5. ANALYSIS**

The samples are analysed on gas chromatograph with flame ionisation detector (GC/FID).

When the sample is ready for final analysis, the method of analysis is in principle the same for all samples, regardless of their origin. However, different concentration levels may dictate different operating parameters on the GC, and the operating parameters must therefore be chosen based on concentration level. Emphasis must be placed on selecting operating parameters that ensure the detection and sufficient separation of all PAH components present.

## **6. DEVIATIONS FROM NORWEGIAN STANDARD**

### **6.1 PAH emissions to air**

#### **6.1.1 Sampling**

Relevant standard is NS 9808, which describes "Method B: Simplified method with XAD-2" and "Method C: Simplified method with ethanol". Method B describes sampling equipment, which is unpractical for routine measurements. The use of such equipment is extremely labour intensive and incompatible with the plants' sampling strategies.

NS 9808 states no requirements for filters used for sampling. The smallest measured particle size in the particulate emission is partly determined by the pore diameter of the sampling filter. It should therefore be specified that a filter with pore opening of 0,8 µm be used. Also, NS 9808 does not mention the problems connected to sampling of gas from seawater scrubbers and how to avoid the problem of clogging due to moisture.

At aluminium plants with forced pot room ventilation, the only available sampling points are often in the proximity of the fans. This can make it difficult to achieve fully isokinetic sampling.

NS 9808 states that when sampling under varying operating conditions, the sampling period should be chosen to incorporate these variations. Further more, NS 9808 recommends that the sampling period does not exceed two hours. To satisfy both these conditions may be difficult without having to take an unreasonable large number of samples. When sampling PAH emissions to air from pot room ventilation air, the necessary sampling period may be as much as 24 hours. The use of ethanol as absorbent will then cause problems because of evaporation. It is therefore better to take samples as described in NS 9808 Method C, but with XAD-2 as adsorbent instead of ethanol.

#### **6.1.2 Sample preparation**

Relevant Norwegian Standard is NS 9813 - There are no significant deviations from this standard.



## **6.2 PAH discharges to water**

### **6.2.1 Sampling**

Relevant Norwegian Standard is NS 9805 - NS 9805 describes sampling of water for PAH analysis, without separating the particulate from the dissolved fraction. Samples can then be taken directly in the extraction bottle. For separation of the two fractions, the sample must be filtered before extraction, thus making extraction directly in the sample vessel impossible.

### **6.2.2. Sample preparation**

Relevant Norwegian Standards are NS-EN 872 and NS 9810 - NS 9810 describes preparation of samples without filtration. NS-EN 872 describes filtration of samples on glass fibre filters for determination of suspended solids. Such a filtration is required in order to separate the particulate fraction of PAHs from the dissolved. However, it is not necessary to comply with NS-EN 872 in the areas which describe drying and weighing of the filters.

## **6.3 Analysis**

Relevant Norwegian Standard is NS 9815 which is specific concerning certain technical data. The standard does not take into consideration the concentration level of the sample, nor the distribution of the PAH components in the sample. E.g.: In some cases, it may be required to inject samples using "split" injection, where as NS 9815 only allows for "splitless" or "on column" injection. Split ratio must be adjusted to the concentration level of the sample. The same applies to other parameters described in NS 9815, such as the temperature programme for the capillary column of the gas chromatograph.