

## Monitoring air fluoride concentration around ALUAR smelter in Puerto Madryn (Chubut Province, Argentina)

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### Abstract

The emissions of Total Fluoride (gaseous + particulate) (F<sup>-</sup>) are one of the significant environmental aspects of the aluminum industry. Therefore the government has established regulations aimed at controlling the environmental performance of smelters through monitoring of F<sup>-</sup> emissions.

Chubut Province (Argentina), sets emission limits, 1 kg F/ton Al and following recommendations from the World Health Organization, a 16.0 µg F/m<sup>3</sup> guideline for inmission has been established.

In this paper we present: i) the monitoring network that ALUAR deployed in Puerto Madryn, 12 air sampling stations; ii) sampling procedures and analysis adopted; iii) the results of air fluoride concentration from July 2009 to June 2010; iv) the validation of these results by three scientific institutes of Argentina.

The results show that in Puerto Madryn (100000 inhabitants; 2 km to the South of ALUAR's Plant), the median concentration in air was 1.61 µg F/m<sup>3</sup> (N = 471 - p95 = 5.32). These values met the inmission guideline level determined by the supervisory authority.

### Introduction

The ALUAR smelter was originally started in 1974 with 400 SWPB and open pots, working at 150 kA. Starting at 1987 the original pots were transformed to PFPB and gas treatment centers were installed. This and other technical improvements allowed the original potlines to reach now 200 kA, with a high current efficiency and a good general performance [1]. In 1999, ALUAR started its expansion using AP18 pots, later upgraded to AP22. This expansion process is still underway.

ALUAR site (42° 44' 21.35'' S - 65° 02' 46.73'' W) (4 potlines, 736 PFPB cells and 36,000 ton Al/month), is located at 2 km to the North of the city of Puerto Madryn, with 100000 habitants, in the Province of Chubut.

Puerto Madryn is located in an environmentally sensitive area of the Atlantic coast of Argentina, characterized by the presence of flagship species of marine mammals like the Southern Right Whale.

Due to the presence of these species, some of which are endangered, in 1999 the UNESCO inscribed the Península Valdés, very close to Puerto Madryn, on the World Heritage List [2]. The region is also a very important touristic area.

The climate of Puerto Madryn is characterized by low rainfall (200 mm/year), prevailing winds from the southwest and an annual average temperature of 13.6 °C.

The emission of Total Fluoride (gaseous + particulate) (F<sup>-</sup>) is a significant environmental aspect of the aluminum industry. Therefore the government have established regulations aimed at controlling the environmental performance of smelters through monitoring of F<sup>-</sup> emissions and inmission.

The Authority of Chubut Province (Argentina), sets emission limits at 1 kg F/ton Al and following recommendations from the World Health Organization, a 16.0 µg F/m<sup>3</sup> guideline for inmission has been established [3].

Although measurements were started years before, since 1998 ALUAR has been operating an Air Quality Monitoring Net (RMCA stands for its initials in Spanish), with the purpose of systematically measuring the air Total F<sup>-</sup> concentration in the city of Puerto Madryn and surroundings.

Sampling and analysis are based on ASTM D3267 [4] and ASTM D3270 standards. However some modifications have been made on sampling in order to simplify the procedures. Two samples are taken every week from each and every one of the RCMA stations, sampling periods being of 72 and 96 hours. The results are then recalculated for an average of 24 hours.

In this context some doubts were publicly raised concerning the accuracy of the information get by ALUAR. These doubts were mainly based on the fact that the sampling was not made following in all the details an international standard. Some objections were also made to the design and location of the monitoring stations

Therefore, and in order to ensure the quality of the information sent to the authorities and communicated to the residents of the city, Aluar decided to ask to three well known research centers in Argentina (CNEA [5], INQUIMAE [6], PLAPIQUI [7]), to make independent monitoring of the F<sup>-</sup> in air around the smelter.

It was required to each Institute to select points close to some of the existing monitoring stations, to design and install sampling stations at these points, to take samples representing at least 1500 hours and to analyze them. The sampling and analysis procedures should be selected by each Institute. The ASTM D3267, ASTM D3268, ASTM D3269 and ASTM D3270 standards were used.

The monitoring by the three Institutes, which made their work in a completely independent way and without exchange of information between them, was made between July 2009 and June 2010. During that time, ALUAR made his own monitoring as usual allowing a direct comparison of the results.

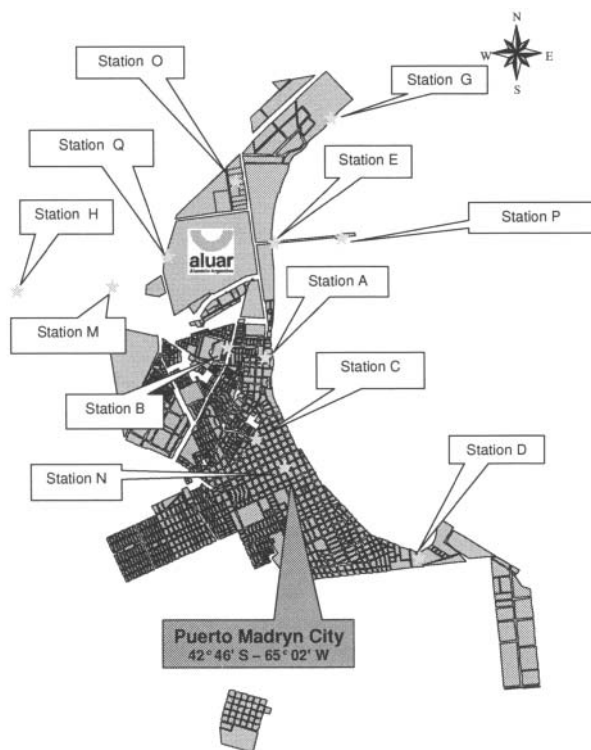


Figure 1. ALUAR air sampling network at Puerto Madryn city.

### Results

The results produced by the RMCA show that in Stations A, B, C, N and D located at urban areas in Puerto Madryn city (100000 inhabitants; 2 km to the South from ALUAR's Plant), the median of concentration of F in air is  $1.61 \mu\text{g}/\text{m}^3$  ( $N = 471 - p95 = 5.32$ ). These values met the inmission guideline level determined by the supervisory authority ( $16 \mu\text{g F}/\text{m}^3$ ).

The average concentrations of these urban stations do not differ significantly between them and it was not possible to link the temporal evolution of these F concentrations to the wind performance.

Tables 1, 2 and 3 show the results of air F concentration obtained by the Research Centers and those obtained by the ALUAR RMCA, taken simultaneously and at points very close between them, for different periods of monitoring.

In most cases the ALUAR values are higher than those obtained by the Institutes. These differences can partially be explained by two reasons:

- The ALUAR values are corrected in order to take into account the loss of absorbent liquid during the sampling. The ASTM D3267 does not consider any correction for this loss.

- Due to practical reasons the ALUAR sampling is made for 72 or 96 hours, while the regulations consider the average concentration for 24 hours. Therefore, the values are affected by a factor  $>1$  to take into account the difference in the sampling time [8]

Purposely, both corrections tend to increase the final result. In this way, ALUAR always takes a "safe" position with reference to the adherence to the environmental regulation. The reported concentration could be overestimated but never underestimated.

Table 1: CNEA validation of results from the ALUAR-RMCA. Monitoring period from July the 28<sup>th</sup> to November the 13<sup>th</sup> of 2009.

Research Center: CNEA	RMCA – ALUAR
Station H (3.8 km to the West of ALUAR)	
Median: $0.34 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 5: $0.21 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 95: $2.34 \text{ F } \mu\text{g}/\text{m}^3$ N: 67	Median: $1.35 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 5: $0.21 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 95: $4.10 \text{ F } \mu\text{g}/\text{m}^3$ N: 32
Station E (0.7 km to the East of ALUAR)	
Median: $1.03 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 5: $0.32 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 95: $6.79 \text{ F } \mu\text{g}/\text{m}^3$ N: 67	Median: $1.79 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 5: $0.84 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 95: $3.82 \text{ F } \mu\text{g}/\text{m}^3$ N: 31
Station O (0.8 km to the North of ALUAR)	
Median: $0.48 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 5: $0.31 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 95: $3.45 \text{ F } \mu\text{g}/\text{m}^3$ N: 65	Median: $1.12 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 5: $0.60 \text{ F } \mu\text{g}/\text{m}^3$ Percentile 95: $2.60 \text{ F } \mu\text{g}/\text{m}^3$ N: 31
The number of samples for station differs between CNEA and the RMCA since CNEA took samples of 24 hours of duration, while RMCA Net covers periods of 72 and 96 hours.	

All the air F concentration values shown in tables 1, 2 and 3 proves that the emission generated by ALUAR operations, do not exceed the corresponding guideline for inmission ( $16 \mu\text{g F}/\text{m}^3$ ), set by the environmental authorities of the province of Chubut (Argentina).

At the same time it is worth mentioning that the three research centers that participated in the validation of data systematically report concentration values that are lower than those reported by RMCA in each instance.

### Conclusion

- The monitoring by three independent and prestigious Institutes has confirmed the correctness of the F inmission values reported by ALUAR
- The values reported by ALUAR tend to be higher than those obtained by the Institutes. This is explained by the use of corrections that ensure that the concentrations can be overestimated but cannot be underestimated.

- The results of this study validate the immission results reported by ALUAR to the authorities since 1998.
- The F concentrations around the ALUAR smelter satisfy the regulations sets by the authorities for the environmental protection
- The results confirm that the potroom operating procedures and emission control equipment, originally started in 1988, are still operative for the environmental protection, in spite of the large increase in the production of the plant.

Table 2: INQUIMAE validation of results from the ALUAR-RMCA. Monitoring period from December the 4<sup>th</sup> of 2009 to March the 19<sup>th</sup> of 2010.

Research Center: INQUIMAE	RMCA - ALUAR
Station O (0.8 km to the North to ALUAR)	
Median: 1.44 F $\mu\text{g}/\text{m}^3$ Percentile 5: 0.47 F $\mu\text{g}/\text{m}^3$ Percentile 95: 2.31 F $\mu\text{g}/\text{m}^3$ N: 24	Median: 1.66 F $\mu\text{g}/\text{m}^3$ Percentile 5: 0.54 F $\mu\text{g}/\text{m}^3$ Percentile 95: 2.84 F $\mu\text{g}/\text{m}^3$ N: 26
Station C (3.5 km to the South to ALUAR)	
Median: 0.84 F $\mu\text{g}/\text{m}^3$ Percentile 5: 0.46 F $\mu\text{g}/\text{m}^3$ Percentile 95: 1.58 F $\mu\text{g}/\text{m}^3$ N: 27	Median: 1.44 F $\mu\text{g}/\text{m}^3$ Percentile 5: 0.20 F $\mu\text{g}/\text{m}^3$ Percentile 95: 5.15 F $\mu\text{g}/\text{m}^3$ N: 30
Station D (3.5 km to the South-East to ALUAR)	
Median: 1.11 F $\mu\text{g}/\text{m}^3$ Percentile 5: 0.38 F $\mu\text{g}/\text{m}^3$ Percentile 95: 1.91 F $\mu\text{g}/\text{m}^3$ N: 26	Median: 1.98 F $\mu\text{g}/\text{m}^3$ Percentile 5: 0.73 F $\mu\text{g}/\text{m}^3$ Percentile 95: 9.82 F $\mu\text{g}/\text{m}^3$ N: 27
Both INQUIMAE and RMCA samples were taken covering periods of 72 and 96 hours.	

Table 3: PLAPIQUI validation of results from the ALUAR-RMCA. Monitoring period from June the 2<sup>nd</sup> to August the 9<sup>th</sup> of 2010.

Research Center: PLAPIQUI	RMCA - ALUAR
Station E (0.7 km to the East to ALUAR)	
Median: 2.69 F $\mu\text{g}/\text{m}^3$ Percentile 5: 0.66 F $\mu\text{g}/\text{m}^3$ Percentile 95: 8.13 F $\mu\text{g}/\text{m}^3$ N: 29	Median: 1.95 F $\mu\text{g}/\text{m}^3$ Percentile 5: 1.17 F $\mu\text{g}/\text{m}^3$ Percentile 95: 6.90 F $\mu\text{g}/\text{m}^3$ N: 20
Station C (3.5 km to the South to ALUAR)	
Median: 0.21 F $\mu\text{g}/\text{m}^3$ Percentile 5: 0.04 F $\mu\text{g}/\text{m}^3$ Percentile 95: 0.99 F $\mu\text{g}/\text{m}^3$ N: 27	Median: 1.53 F $\mu\text{g}/\text{m}^3$ Percentile 5: 0.52 F $\mu\text{g}/\text{m}^3$ Percentile 95: 4.28 F $\mu\text{g}/\text{m}^3$ N: 20
Station G (2.8 km to the North-East to ALUAR)	
Median: 0.19 F $\mu\text{g}/\text{m}^3$ Percentile 5: 0.09 F $\mu\text{g}/\text{m}^3$ Percentile 95: 0.40 F $\mu\text{g}/\text{m}^3$ N: 22	Median: 2.46 F $\mu\text{g}/\text{m}^3$ Percentile 5: 1.13 F $\mu\text{g}/\text{m}^3$ Percentile 95: 8.51 F $\mu\text{g}/\text{m}^3$ N: 20
Both PLAPIQUI and RMCA samples were taken covering periods of 72 and 96 hours.	

## References

- [1] P. Navarro, C. Daviou, L. Daurade. "ALUAR'S al20 PROJECT: A SUCCESSFUL WAY UP TO 200kA". IV International Aluminium Congress (May 18th, 19th and 20th, 2010 - São Paulo): 594-609.
- [2] <http://whc.unesco.org/en/decisions/2534>
- [3] World Health Organization. "Air Quality Guidelines for Europe 2<sup>nd</sup> Edition", WHO Regional Publications, European Series, No. 91 (2000): 143-145.
- [4] American Society for Testing and Materials (ASTM) ([www.astm.org](http://www.astm.org)).
- [5] CNEA [http://www.cnea.gov.ar/cac/utt\\_nuevo/unidades1.htm](http://www.cnea.gov.ar/cac/utt_nuevo/unidades1.htm)
- [6] INQUIMAE - <http://www.inquimae.fcen.uba.ar>
- [7] PLAPIQUI - <http://www.plapiqui.edu.ar>
- [8] D. Bruce Turner. "Workbook of Atmospheric Dispersion Estimates". (1994): 4-8 to 4-9.