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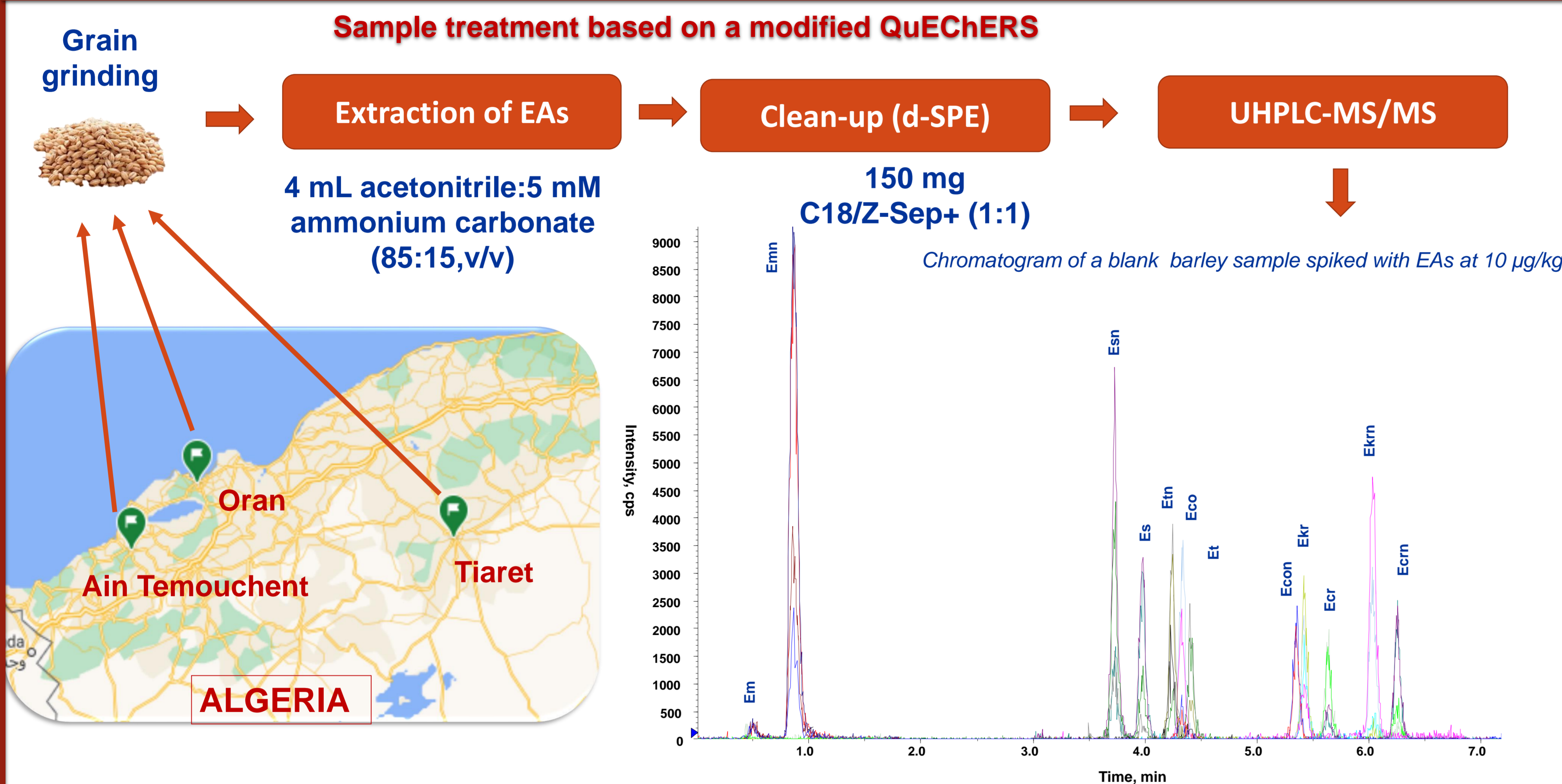
INTRODUCTION

Mycotoxins are fungal secondary metabolites naturally present in different food and feed with toxic effects to humans and animals. Among them, ergot alkaloids (EAs), produced mainly by fungi of the *Claviceps* genus, as *Claviceps purpurea*, are present in cereals such as rye, triticale, wheat and barley. Improvements in agricultural practices have significantly reduce the risk of severe epidemic outbreaks of ergotism, however, EAs can be found in cereal-based food and feed. The European Commission has established a maximum content of 0.5 g/kg of ergot sclerotia in unprocessed cereals (with the exception of corn and rice), but the maximum content for EAs is still under study. Moreover, other countries (as Algeria) has no legislation regarding mycotoxin contamination.



In this study, the natural occurrence of six major EAs, ergometrine (Em), ergosine (Es), ergotamine (Et), ergocornine (Eco), ergokryptine (Ekr) and ergocristine (Ecr), as well as their corresponding epimers; ergometrinine (Emn), ergosinine (Esn), ergotaminine (Etn), ergocorninine (Econ), ergokryptinine (Ekrrn) and ergocristinine (Ecrn) were investigated in 60 cereal samples (barley and wheat) from Algerian markets using a QuEChERS-UHPLC-MS/MS method.

ANALYTICAL METHOD



CHROMATOGRAPHIC CONDITIONS	
Organic solvent (B)	Methanol + 0.3% formic acid
Aqueous solvent (A)	Ultrapure water + 0.3% formic acid
Temperature	35 °C
Flow rate	0.4 mL/min
Injection volume	5 µL
Column	Zorbax Eclipse Plus RRHD C18 (50×2.1 mm, 1.8 µm)
Gradient	0-6 min 30-60% B; 6-9 min 60% B; 9-10 min 60-30% B; 10-12 min 30% B
MS Conditions	
Ionization mode and polarity	ESI +
Scan type	MRM
Target scan time	1s

RESULTS

Method validation

- ✓ Procedural calibration curves were established in wheat and barley samples and good linearity was obtained ($R > 0.993$)
- ✓ LOQs were below 3.3 µg/kg (wheat) and 3.9 µg/kg (barley).
- ✓ The precision, evaluated in terms of repeatability and intermediate precision, was lower than 11% (RSD%) in all cases.
- ✓ Recovery experiments were carried out at two level of concentration (5 and 50 µg/kg) ranging between 85 and 109%.
- ✓ Matrix effects were lower than 20% in most cases.

Occurrence study

		Concentration of Ergot Alkaloids ((µg/kg))												Total EA content
		Em	Emn	Esn	Es	Etn	Eco	Et	Econ	Ekr	Ecr	Ekrrn	Ecrn	
BARLEY		30.4	<LOQ	-	-	-	-	<LOQ	-	-	-	-	-	30.4
		50.0	<LOQ	-	-	-	-	3.90	-	-	-	-	-	53.9
		34.2	<LOQ	-	-	-	-	2.34	-	-	-	-	-	36.5
		17.8	<LOQ	-	-	-	-	-	-	-	-	-	-	17.8
	Mean	33.1						3.12						34.7
WHEAT		13.6	-	-	-	-	-	-	-	-	-	-	-	13.6
		24.9	1.42	-	0.62	<LOQ	<LOQ	3.71	<LOQ	17.71	16.13	3.45	8.03	76.0
		-	-	<LOQ	1.66	-	8.68	-	3.84	13.2	-	3.28	-	30.7
		<LOQ	<LOQ	<LOQ	1.61	-	-	1.15	-	4.76	2.54	<LOQ	<LOQ	10.1
		<LOQ	-	-	-	-	-	-	-	1.56	2.10	<LOQ	<LOQ	3.66
		11.8	0.44	-	1.30	-	-	-	-	-	2.75	-	1.50	17.8
		3.52	<LOQ	-	-	2.91	-	13.6	-	-	28.6	-	12.2	60.8
		-	-	<LOQ	3.30	-	12.4	-	4.90	26.2	-	5.88	-	52.7
Mean	13.4	0.93		1.80	2.91	10.5	6.15	4.37	12.7	8.69	4.20	7.24	33.2	

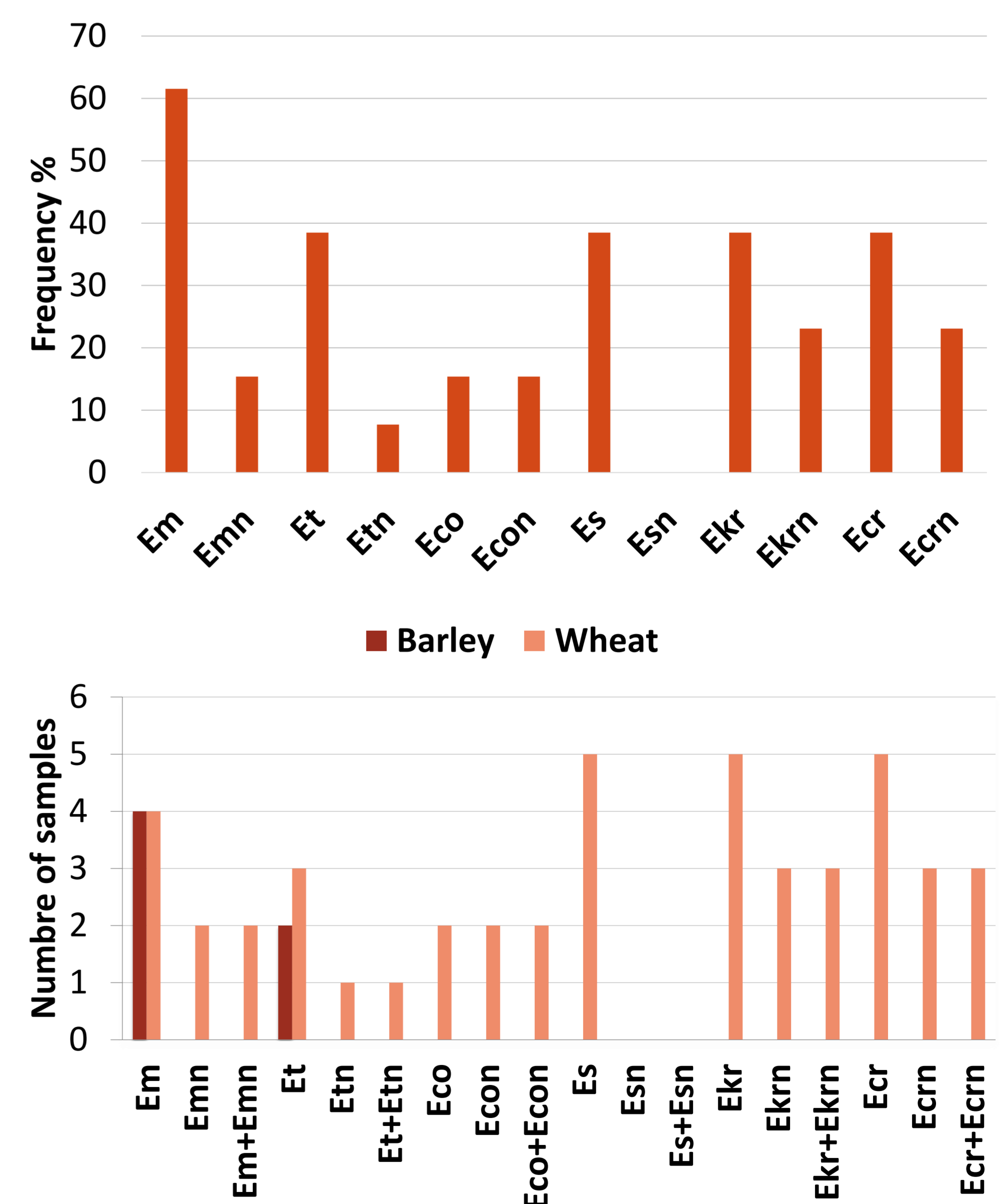
8 positive samples in wheat

Higher contamination (up to 8 EAs above the LOQ) with total EAs contents ranging from 3.66 to 76.0 µg/kg

4 positive samples in barley

All of them were contaminated with Em and Emn, and 3 of them showed also contamination by Et, with total EAs contents ranging from 17.8 to 53.9 µg/kg

Frequency of EAs in positive samples



CONCLUSIONS

- The occurrence of EAs in 60 samples of wheat (30) and barley (30) collected from different points of Algeria have been investigated.
- There are variability in the pattern of EAs and in most cases the epimer appears with the main EA, highlighting the importance of quantifying both forms.
- Em shows the highest incidence (aprox. 60% of positive samples), followed by Et, Es, Ekr and Ecr.
- This study concluded that there is a low risk linked with the EAs intake through the consumption of barley and wheat in Algeria.