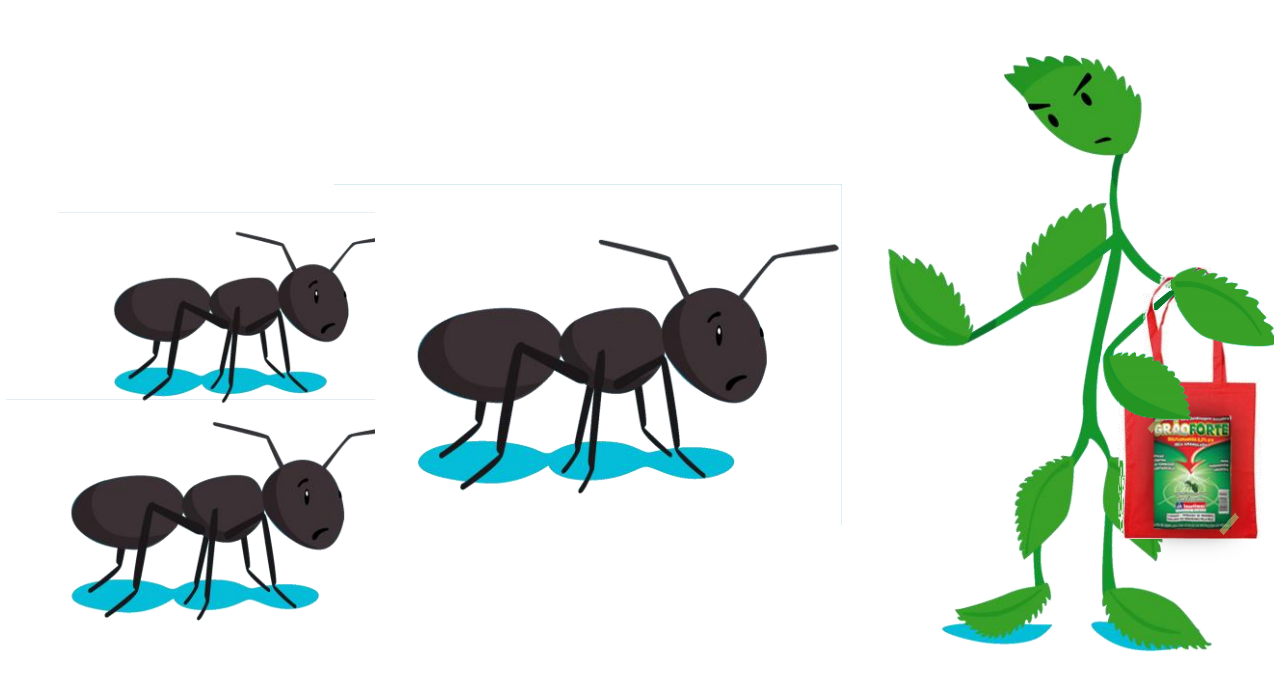


Biodegradation and uptake of the pesticide Sulfluramid in a soil/carrot mesocosm



E. Bizkarguenaga, I. Zabaleta, D. N. Nunoo,
L. Schultes, J. Leonel, A. Prieto, O. Zuloaga, J. P. Benskin

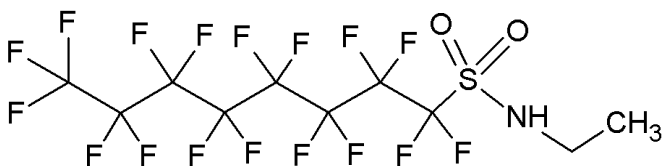
Oslo, 21st June 2017



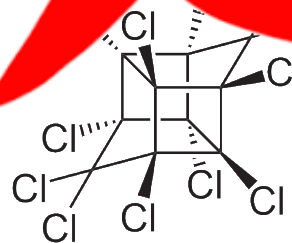
1	Introduction
2	Objectives
3	Experimental design and analysis
4	Results
5	Conclusions

Why study Sulfluramid?

- Sulfluramid is a pesticide used in Brazil for the control of leaf-cutting ants.
- Sulfluramid was introduced in Brazil in 1993 following phase-out of Mirex.
- EtFOSA (PFOS-precursor) is the active ingredient of Sulfluramid (~0.01-0.1 %).



EtFOSA

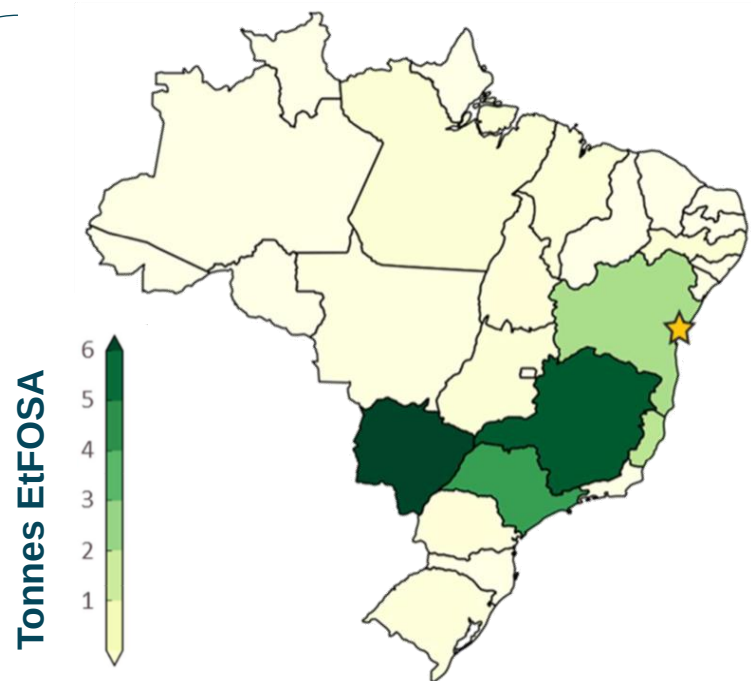


1. Introduction

Sulfluramid use in Brazil

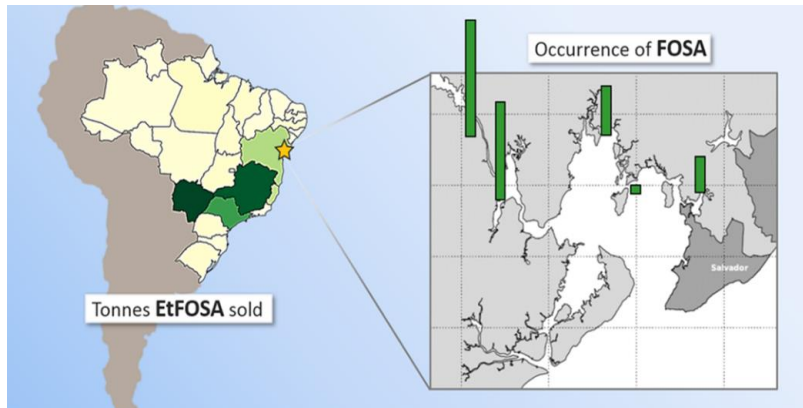
- Brazil holds an exemption from the Stockholm Convention for manufacture/use of Sulfluramid for control of leaf cutting ants.
- Sulfluramid contained baits represents up to 95 % formicide market.
- ~380 t of EtFOSA manufactured / imported into Brazil from 2004 - 2015.

Sales of Sulfluramid in Brazil

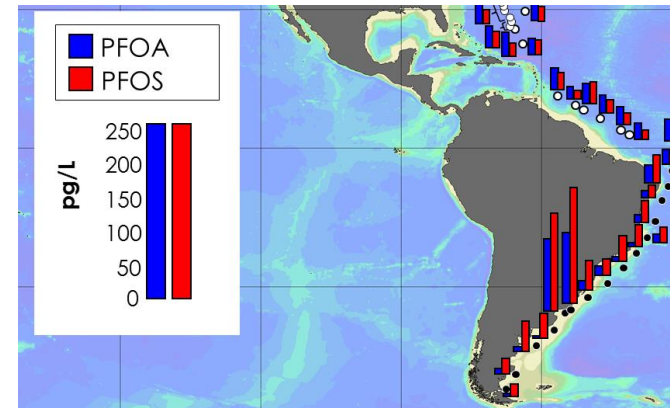


What's going on in Brazil coast?

- PFOS in surface water and dolphin livers elevated in coastal Brazil relative to other locations.
- Sulfluramid speculated as a source, but no conclusive evidence.



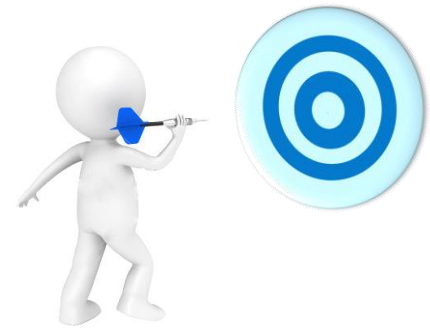
Gilljam et al. 2015



Benskin et al. 2012

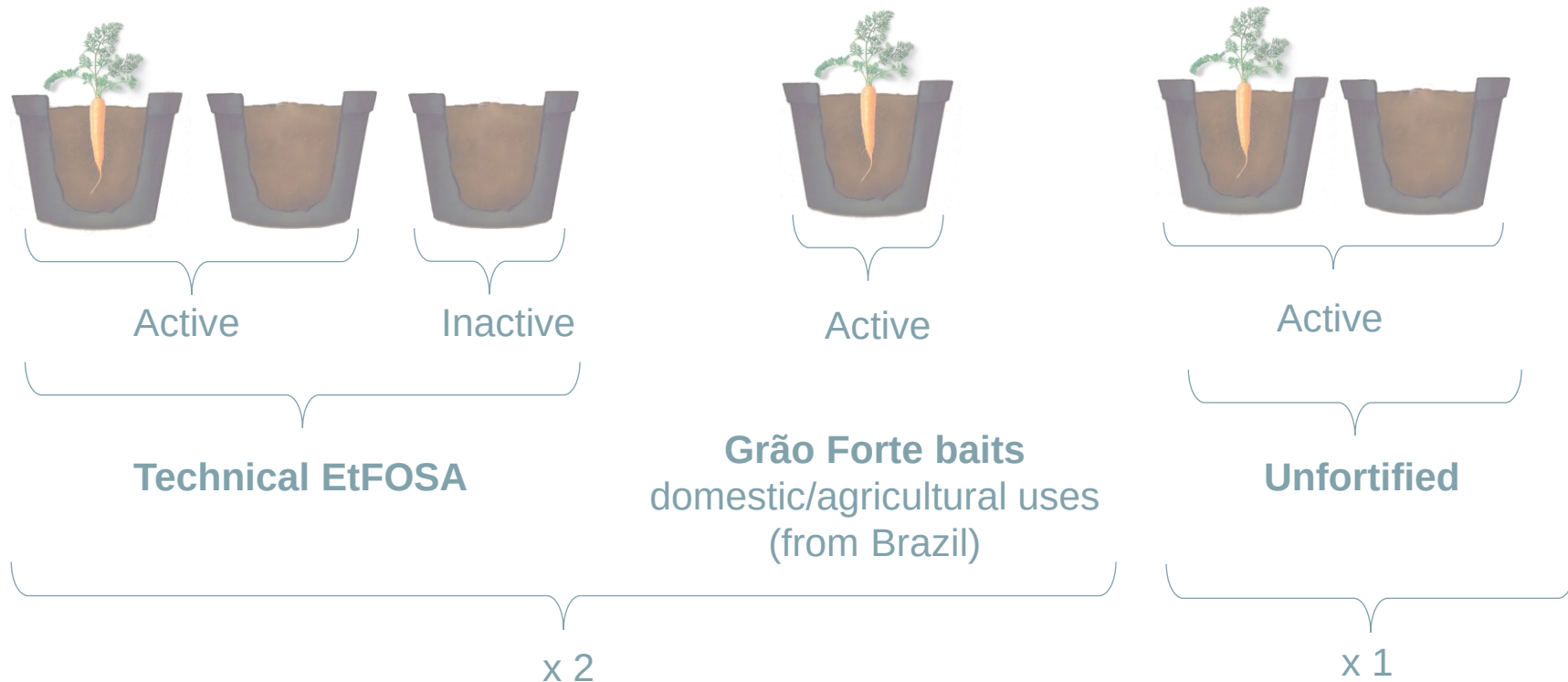
Understanding the importance of Sulfluramid to the Brazilian environment requires knowledge of:

- Occurrence of PFASs around sites where Sulfluramid has been deployed.
- Degradation yields of EtFOSA (currently ~4 % PFOS estimated from soil biodegradation experiments (Avendaño and Liu 2015)).



- Biodegradation of EtFOSA in the presence and absence of carrot.
- Uptake of EtFOSA and transformation products in carrot.
- Technical vs Grão Forte commercial Sulfluramid formulation.

Experiments



- Experiments with EtFOSA: $n=2$ pots/ time point; 5 time points.
- Experiments without EtFOSA: $n=1$ pot/ time point; 5 time points.
- Soil & composite water collected on $t=0, 14, 28, 56, 81$ days.
- Carrots harvested at $t = 56, 81$ days.

Greenhouse conditions

- **PFDA** included as negative control

- Greenhouse conditions



25 °C for 14-h

Relative humidity of 50 %



18 °C for 10-h

Relative humidity of 60 %

- Watering

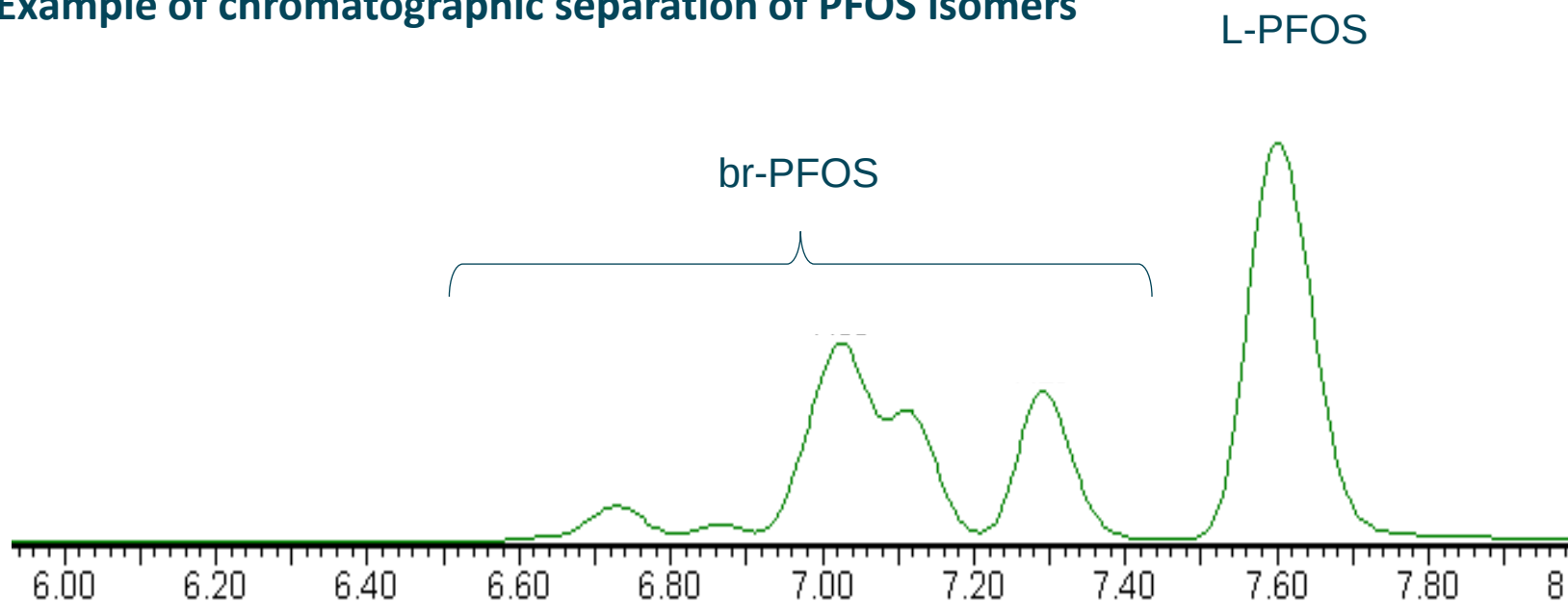
Hoagland nutritive solution

Deionized water

Sample processing

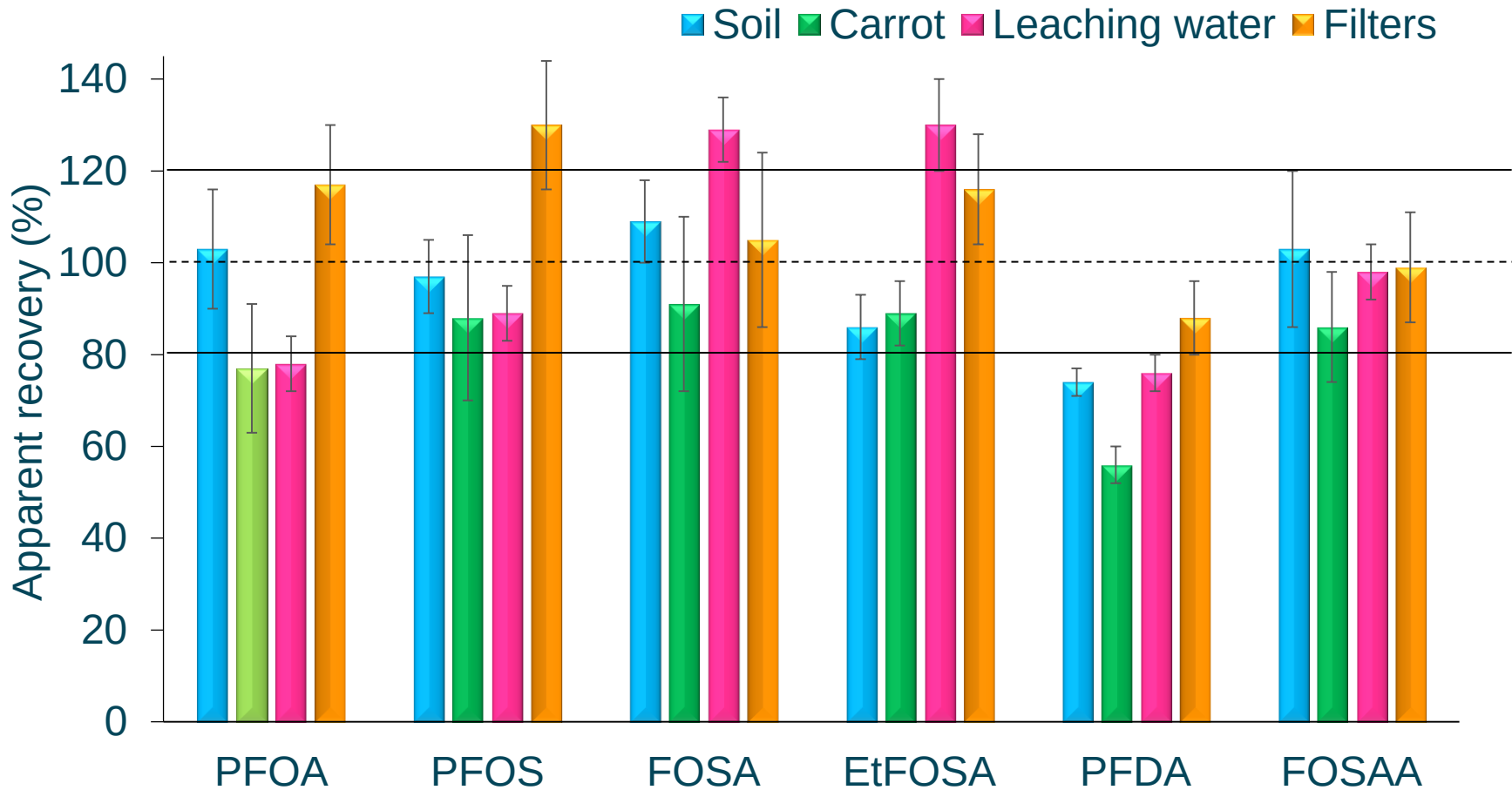
- Samples extracted according to Avendaño and Liu 2015.
- Isomer-specific analysis by UPLC-MS/MS using method modified from Benskin et al 2012.

Example of chromatographic separation of PFOS isomers



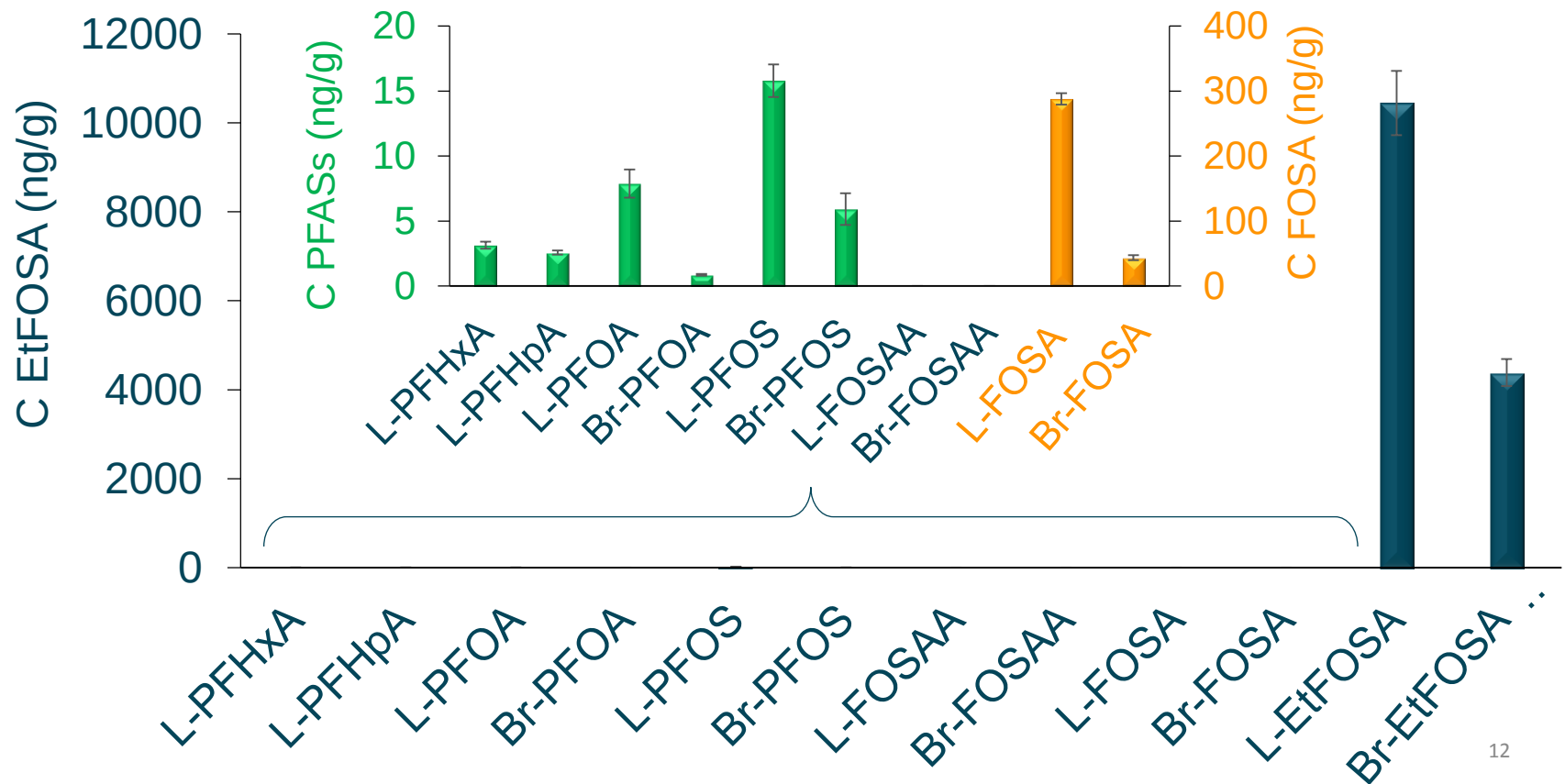
Quality control

- Spike/recovery experiments were performed by fortifying each matrix with native standards and extracting together with real samples.



Grão Forte baits characterisation

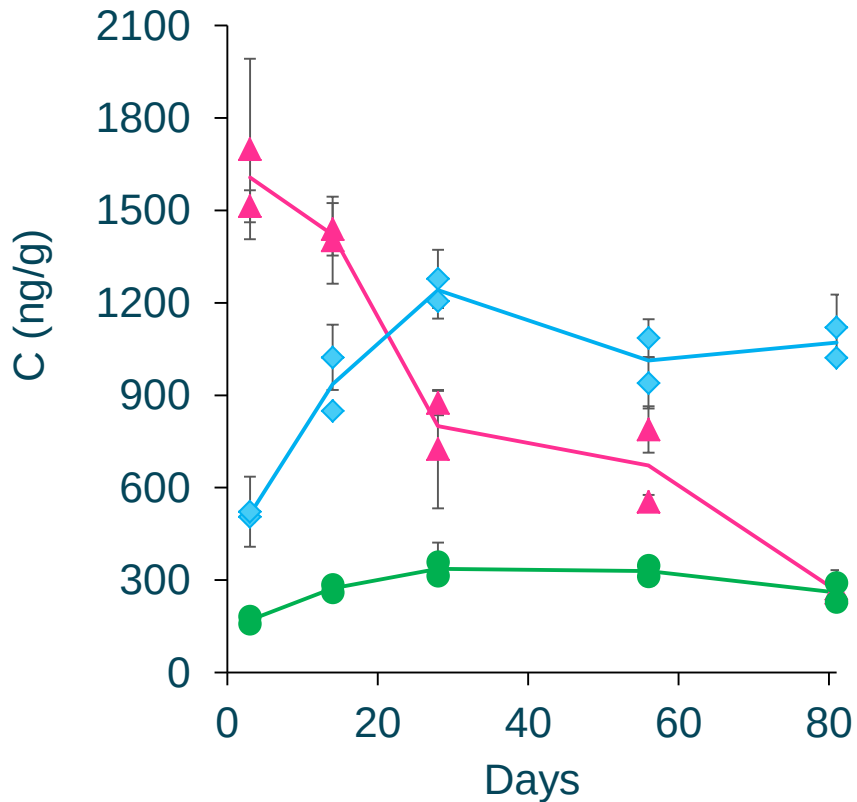
- 0.0017 % EtFOSA in Grão Forte baits (compared to 0.01-1 % EtFOSA reported by manufacturers).
- FOSA, PFOS, PFCAs also present at low concentrations.



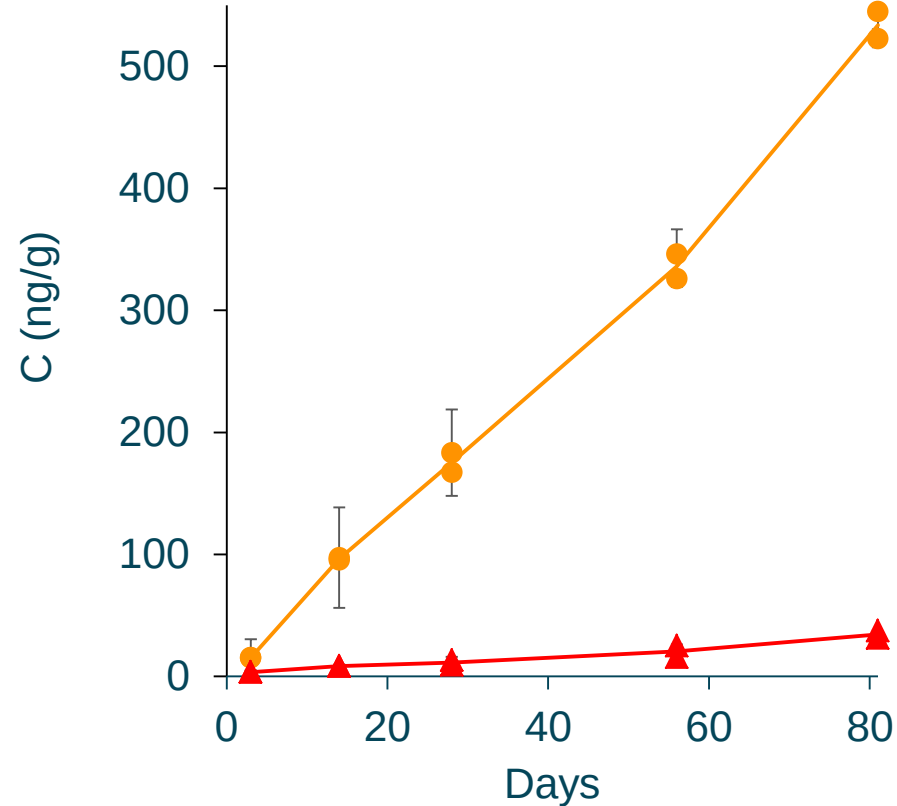
EtFOSA degradation

Results from Technical EtFOSA + Carrot + Active soil experiments

▲ L-EtFOSA ◆ L-FOSA ● L-FOSAA



● L-PFOS ▲ L-PFOA



EtFOSA degradation

Experiment		$t_{1/2}$ (days)	
Technical	Carrot + Active soil	35.8 ± 3.7	
	Active soil	33.6 ± 9.0	
	Inactive soil	40.0 ± 7.8	

- 2.5-fold lower half-lives
- PFOS yield > 4 %

} reported by Avendaño & Liu Chemosphere (2015)

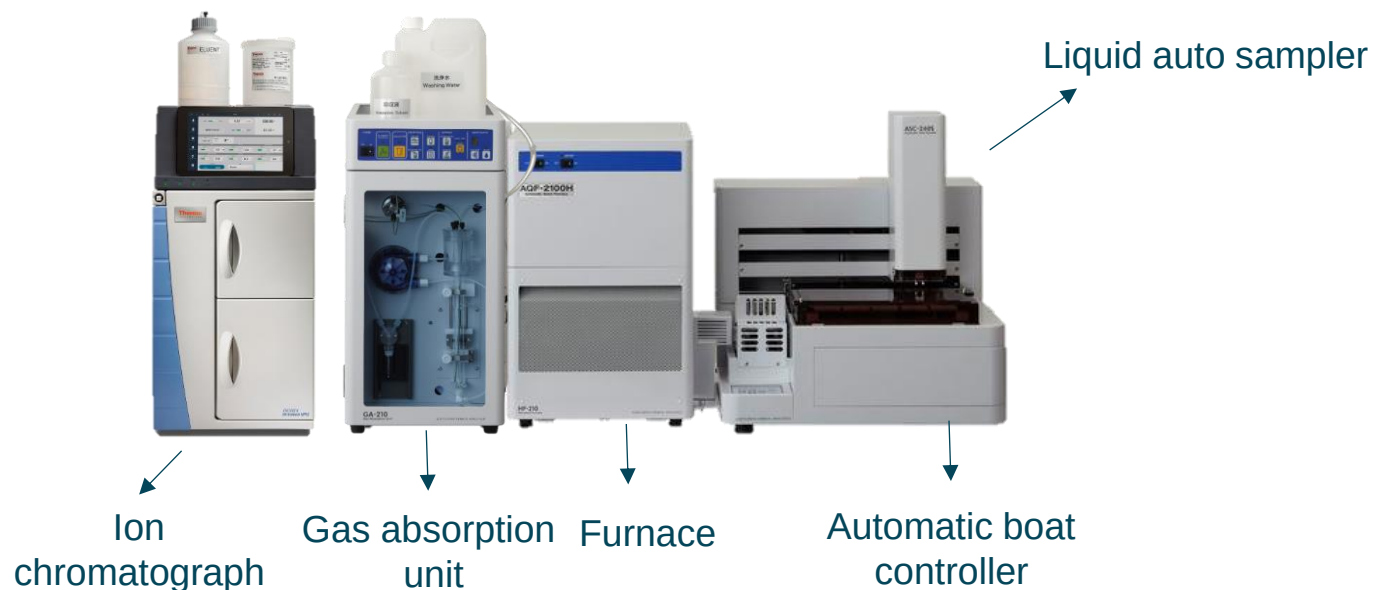
EtFOSA degradation

Experiment		$t_{1/2}$ (days)	PFOS yield (%)	Mass balance relative to T0 (%)
Technical	Carrot + Active soil	35.8 ± 3.7	34	100 ± 5
	Active soil	33.6 ± 9.0	24	110 ± 1
	Inactive soil	40.0 ± 7.8	12	83 ± 3
	Carrot + Active soil	11.5 ± 2.1	277	176 ± 11



- **PFOS yield > 100 %** was achieved when soil was fortified with commercial bait formulation.
- Mass balance does not fit.

Fluorine content using combustion ion chromatography—preliminary results



	C $\mu\text{g F/g}$
TF (CIC)	61 ± 7
EOF (CIC)	47 ± 7



24 % Using LC-MS/MS

- Inorganic or non-extractable organic fluorine content are negligible in the baits.
- More PFOS-precursors than EtFOSA are present in Grão Forte baits.



Plant uptake



PFOS, PFOA

EtFOSA, FOSA, FOSAA

High

Water solubility

Low

Remarkable results



- EtFOSA application will lead to PFOS occurrence in crops.
- PFOS yield is dependent on soil characteristics and crop presence.
- EtFOSA is not the only PFOS-precursor present in Grão Forte commercial baits.

Future work

- Baits characterisation.
- PFAS analysis in environmental samples from Brazil.



Acknowledgements

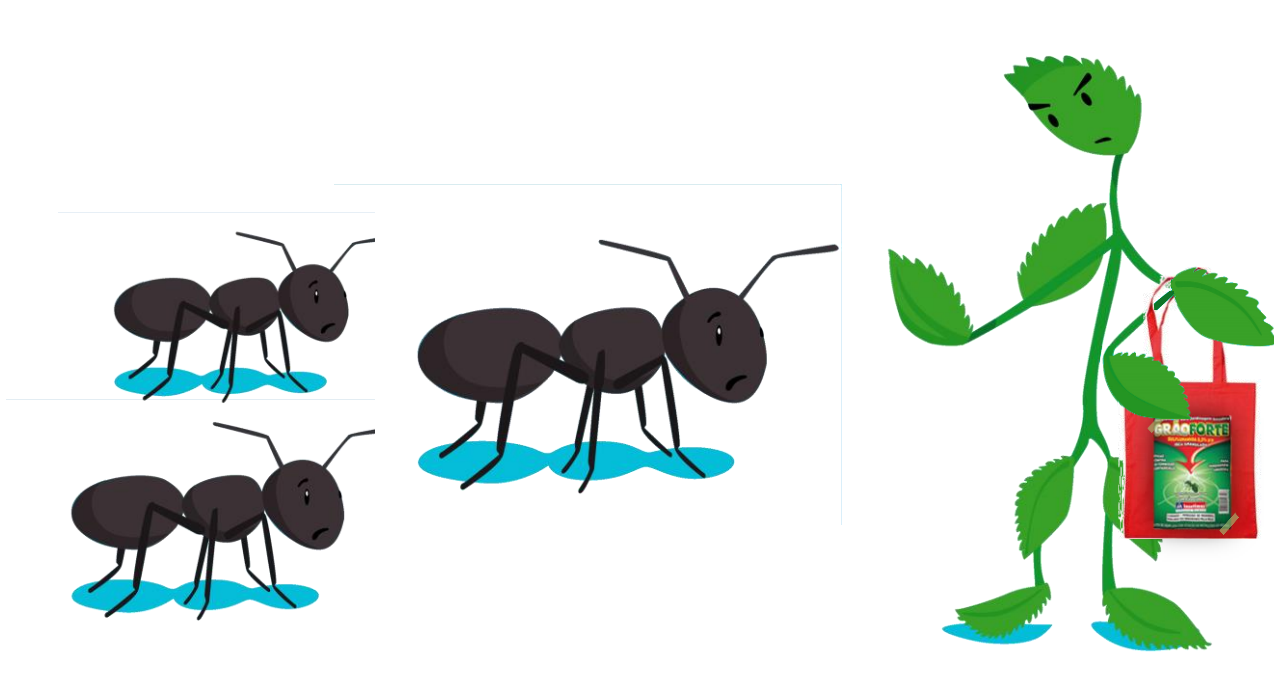


Funding from the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS; grant number 219-2013-794) is gratefully acknowledged.



I. Zabaleta and E. Bizkarguenaga are grateful to the University of the Basque Country (UPV/EHU) for their pre-doctoral and post-doctoral fellowships, respectively.

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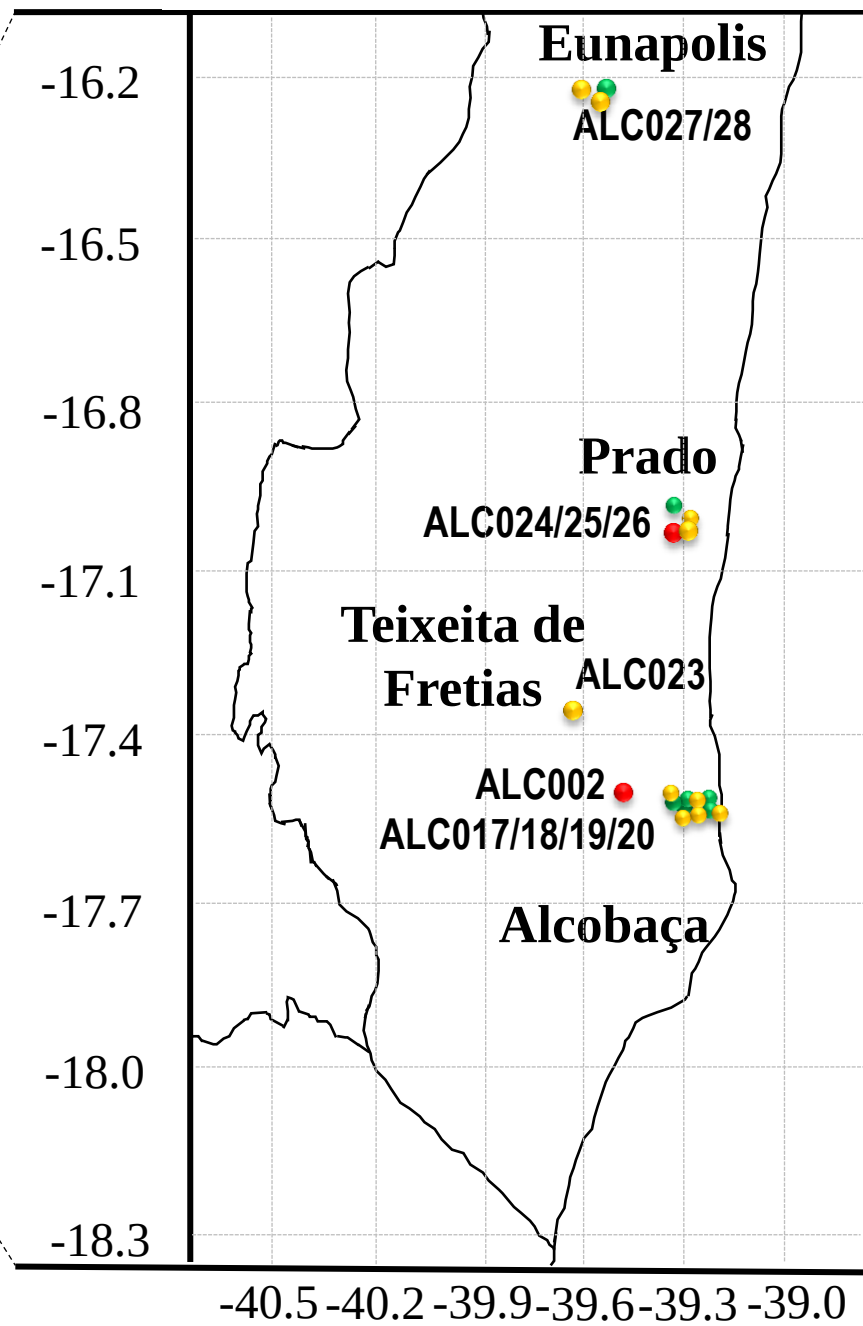


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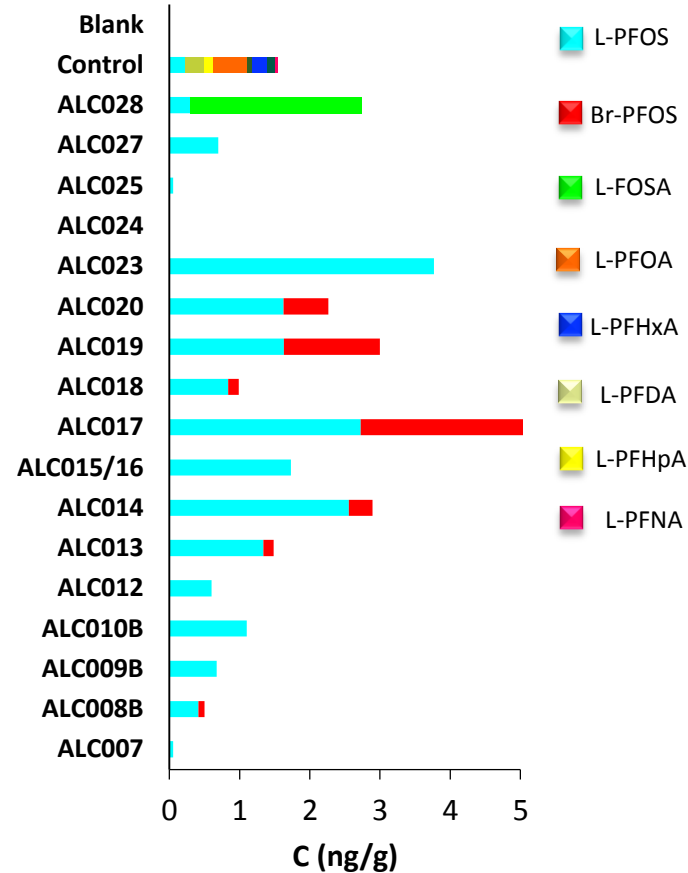
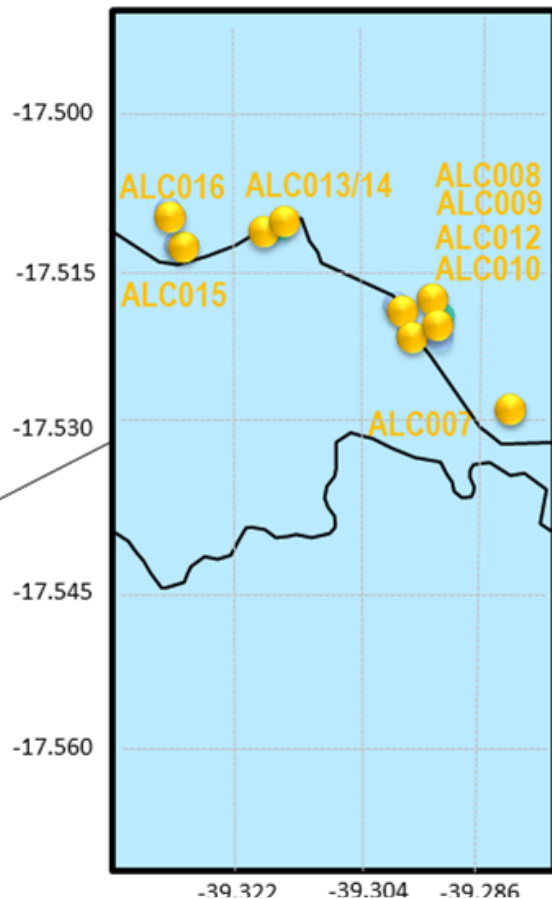
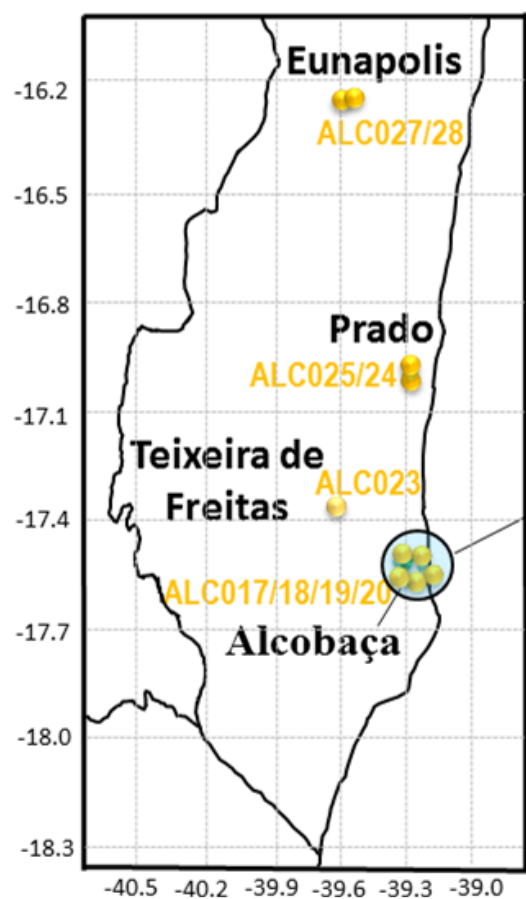


Soil samples from Brazil





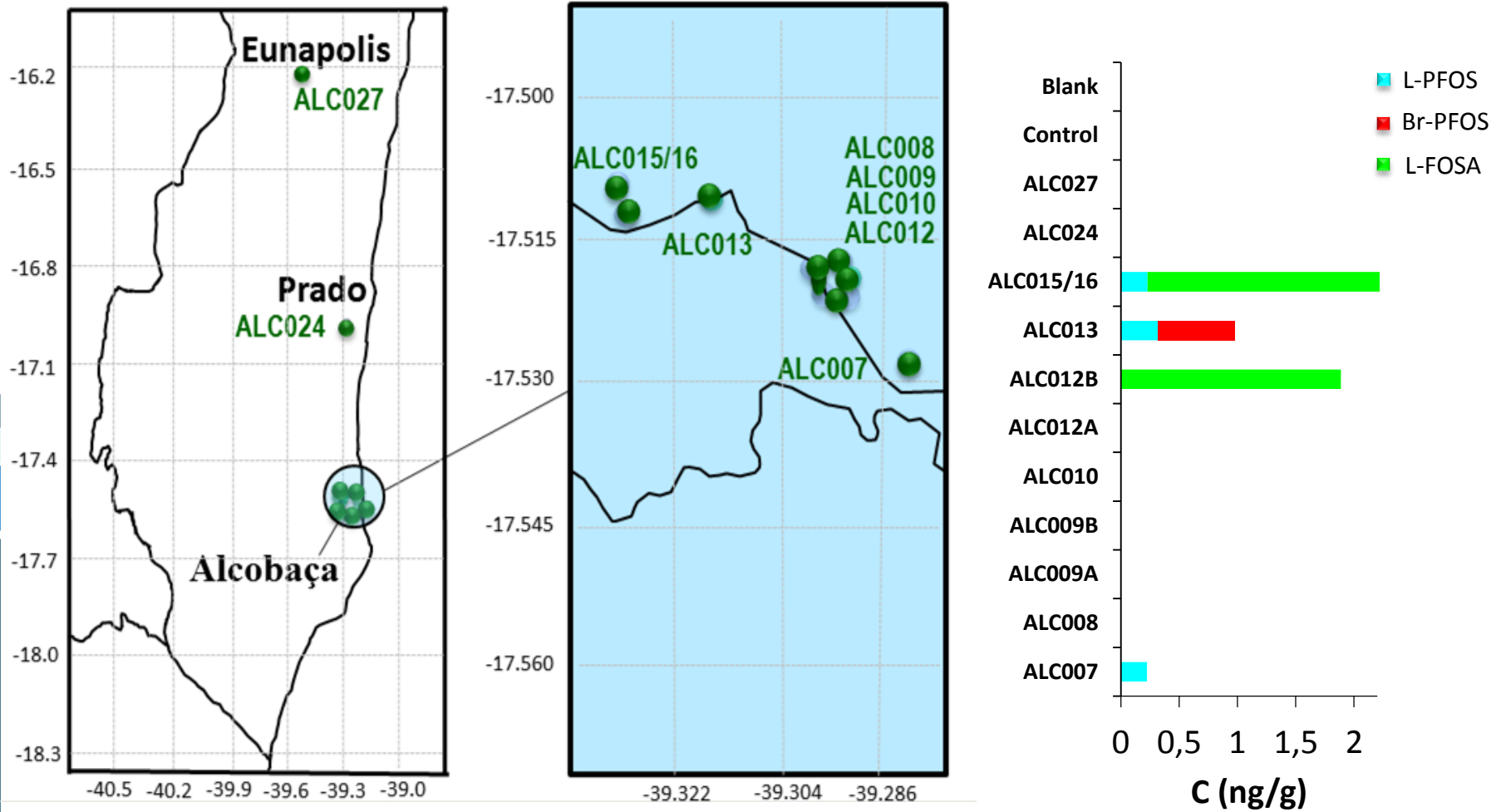
Soil samples from Brazil





Eucalyptus leaf from Brazil

6. Ongoing work



Degradation pathway

