Instituto Universitario de Plaguicidas y Aguas (IUPA)

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Universitat Jaume I / Catedrático de Química Analítica

Universitat de València · Universitat Politècnica de València · Universitat d'Alacant / Universidad de Alicante · Universitat Jaume I · Universitas Miguel Hernández · Universidad Católica de Valencia San Vicente Mártir · CSIC Consejo Superior de Investigaciones Científicas

Universitat Jaume I · Institut Universitari de Plaguicides i Aigües

This study forms part of the ThinkInAzul programme and was supported by MCIN with funding from European Union NextGenerationEU (PRTR-C17.I1) and by *Generalitat Valenciana*

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Descripción del Grupo de Trabajo

IUPA. 25+ investigadores del ámbito de la Química Analítica. Técnicas Crom-MS avanzadas en Medio Ambiente, Seguridad Alimentaria, Toxicología..

Juan V Sancho Llopis (IP)
Maria Ibáñez Martínez
Tania Portolés Nicolau
Miriam González Hernández

UHPLC-ESI-IMS-QTOFMS
GC-EI-QOrbitrap MS (SPME, TDU)
Screening (Target, Suspect, Nontarget)
Metabolomics/Volatolomics

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Objetivos y tareas

- **Objetivo 5.1. (L.A2.13, L.A2.16)** Caracterizar **materias primas** para piensos, incluyendo fuentes de proteína alternativa, y los **piensos formulados** para **dorada** (*Sparus aurata*) de acuicultura. Evaluar el efecto de la alimentación con esos piensos a lo largo del ciclo completo de vida en la calidad nutricional, funcional y sensorial de dorada. Incluye identificar compuestos bioactivos y posibles contaminantes en las porciones comestible y vísceras (UMH1 metales pesados, **UJI1 contaminantes orgánicos**).

- **Tarea 5.1.1 (M1-14) - Caracterización de materias primas y piensos formulados para dorada**

- **Tarea 5.1.2 (M6-36) - Caracterización de doradas obtenidas de los diferentes sistemas de alimentación y en diferentes etapas del desarrollo**

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Resultados obtenidos hasta el momento (target-ingred)

		INGREDIENTS																
	COMPOUND (µg/kg)	CGM	WHP	SFM	SBM	WHM	PS	FMSP	FM60	FPH	PM	FMH	NT70	RP	AO	FO	SO	IM
PESTICIDES	Acenaphthene	0.91		1.67		1.80	3.20	1.76	3.42				2.53				2.10	0.55
	Azaconazole	0.25	0.18		0.23	0.26	0.22	0.52										
	Carbaryl			0.89			0.77	0.94	1.74	0.93	0.49				2.35	1.41	1.05	1.16
	Carbendazim							1138.01										
	Chrysene																	
	DDE																15.32	
	DEET						2.09											
	Deltamethrin	3.72				11.25												
	Diphenylamine			0.29		0.51	0.61			0.55		0.78					1.06	0.24
	Ethoxyquin	0.07																
	Ethoxyquin DIMER																	
	Etofenprox	2.27																
	Fenpropimorph			0.04	0.03	0.04	0.04	0.13	0.13									
	Metalaxyl	67.51																
	Methoxychlor							37.35		0.47	1225.43	2.70				117.55	5.97	
	Pirimiphos methyl	1.51																
	Terbutryn							0.68										
	Thiabendazole		0.87		1.29	1.67												
PAHs	Anthracene	2.30		2.74	2.78	3.72	9.33	7.31	6.11	5.36	4.92	3.96	3.65	8.40	4.71	10.79	18.78	3.38
	Benz[a]anthracene																1.24	
	Benzo[b]fluoranthene	0.17	0.09			0.07		0.25	0.09			0.10						
	Benzo[j]fluoranthene	0.17	0.09			0.07		0.25	0.09			0.10						
	Fluoranthene	0.30	0.21			0.44	0.73	2.66	1.65	0.35		0.61	0.23	1.12				0.81
	Fluorene	1.23		1.28		2.41	4.11	3.02	2.55	2.63	2.30	1.72	2.70	5.04		7.24	9.29	0.87
	Phenanthrene	2.29	2.52	2.74	2.77	3.72	9.09	7.31	6.11	5.35	4.95	3.80	3.61	8.40	4.62	10.79	19.04	3.38
	Pyrene	0.47	0.23	0.70		0.60	0.73	2.40	2.14	0.36	0.62	1.35	0.36	1.41	1.48	7.61	1.55	
UV-FILTER	EHMC	0.51	0.43	4.16	4.18	4.61	12.09	3.27	3.14	5.70	8.05	0.83	26.41	23.93				4.13
	Octocrylene	2.20	2.86	6.57	38.26	7.88		10.49	16.38	8.78	6.99	1.05	66.41	19.39	15.80	5.14	19.12	23.64
MUSK	Cashmeran	87.03	509.39		206.43			106.10							134.42			120.62
	Galaxolide	2.41	2.90	4.30	6.19	4.63	22.55	4.88	11.25	7.11	12.87	6.07	6.03	20.06		117.14	19.83	3.93
OPEs	Octicizer	2.87	0.33	2.59	0.67	2.90	9.28		63.45	1.26		1.28	0.63	0.80				10.62
	TBP H	3.64	1.31	8.77	2.36	3.15	8.80	7.46	3.24	6.19	11.87	2.47	3.30	3.25	2.04	5.87	4.00	9.38
	TCEP H						3.43											
	TDCP H			0.58	0.60	0.88	0.80			1.14				0.74			0.89	6.67
	TPhP H	0.74		7.50			24.35	0.55	1.43	0.76						13.84	2.61	1.92
	TPrP H	1.99	1.87	4.90	0.50	1.85	4.90	9.87	1.23	11.37	90.91	1.32	1.16	2.05				4.97
PHARMACEUTICALS	Lincomycin										7.33							
	Lidocaine											26.53						
	Trimethoprim											36.89						
MYCOTOXINS	Fumonisin	38.39																

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Resultados obtenidos hasta el momento (target-feed)

		FEEDS							
	COMPOUND (µg/kg)	B1.1	B1.5	PAP2	PAP3	FM2	FM3	ALT2	ALT3
PESTICIDES	Acenaphthene						1.53		
	Azaconazole				0.87				
	Carbaryl		2.58		0.36		0.56	1.06	0.48
	Carbendazim								
	Chrysene			3.43		2.44			
	DDE				0.85				
	DEET								
	Deltamethrin			8.01	4.88				
	Diphenylamine	0.28	0.31	0.62	0.46	0.37		0.32	
	Ethoxyquin		4.32						
	Ethoxyquin DIMER	13.25							
	Etofenprox				1.97				
	Fenpropimorph								
	Metalaxyl								
	Methoxychlor	57.29		2.95	7.44	0.71	0.41	3.46	0.35
	Pirimiphos methyl	2.35	9.51						
	Terbutryn	0.172							
	Thiabendazole								
PAHs	Anthracene	5.64	7.57	26.20	5.33	15.61	6.93	5.96	2.99
	Benz[a]anthracene			4.36		2.44			
	Benzo[b]fluoranthene			2.34	0.62	1.37	0.17	0.26	
	Benzo[j]fluoranthene			2.34	0.62	1.37	0.17	0.26	
	Fluoranthene	0.95		17.88	1.76	9.35	2.02	2.54	1.18
	Fluorene	1.64	2.36	6.73	1.66	4.58	2.49	2.57	1.00
	Phenanthrene	5.64	7.57	26.42	5.33	15.61	7.00	6.01	3.13
	Pyrene	0.99	2.23	12.54	1.55	6.54	2.05	2.23	1.54
UV-FILTER	EHMC			1.61	4.37		1.87		
	Octocrylene	11.57	19.16	3.68	6.23	2.81	13.12	4.67	2.45
MUSK	Cashmeran	323.40		393.76	157.25	90.18	560.17	418.10	
	Galaxolide	6.50	13.99	12.79	12.81	5.62	9.85	8.71	5.63
OPEs	Octicizer	2.07		17.65	18.30	7.56	15.64	14.18	11.72
	TBP H	8.55	4.55	3.07	11.05	1.75	2.59	2.60	1.87
	TCEP H							1.11	
	TDCP H	0.73			0.99	0.35	0.71	1.40	1.08
	TPhP H	2.61		1.41	1.73	0.38	0.90	0.65	0.73
	TPrP H			1.02	8.36	0.60	1.56	1.01	0.45
PHARMACEUTICALS	Lincomycin			6.20	6.80				
	Lidocaine	0.02							
	Trimethoprim								
MYCOTOXINS	Fumonisin								

NON-TARGET ANALYSIS (NTA)
GC-EI-Orbitrap (+ NIST Library)

Pesticides: Bensulide, Dibenzofuran, Piperonyl butoxide

UV Filters: Benzophenone

Alkyl-PAHs: 1,5-dimethyl naphtalene

Phthalates: Dimethyl phthalate, Dicyclohexyl phthalate

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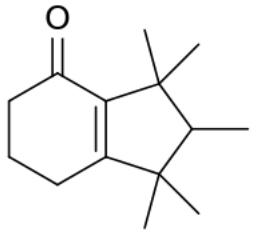
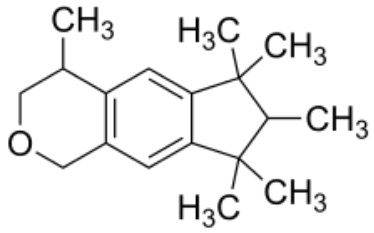
Resultados obtenidos hasta el momento (target-feed)

	THINK IN AZUL FEEDS		
Compound (µg/kg)	**FM**	**PAP**	**ALT**
Pesticides	3.02	9.48	2.83
PAHs	38.86	57.84	14.83
UV-filter	8.90	7.95	3.56
Musk	332.91	288.31	216.22
OPEs	16.02	32.30	18.40
Pharmaceuticals	Not found	6.50	Not found
Mycotoxins	Not found	Not found	Not found

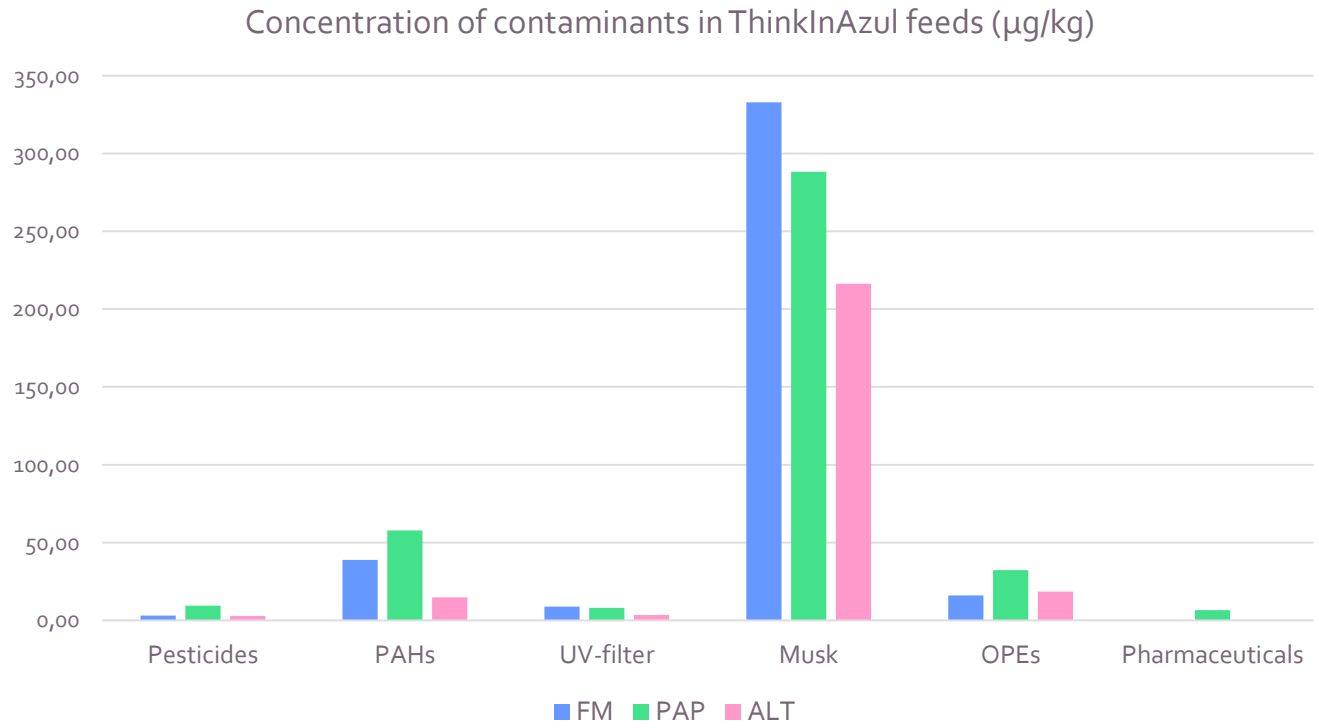
Musk fragances



Cashmeran



Galaxolide



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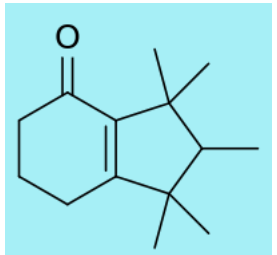
Resultados obtenidos hasta el momento (target-feed)

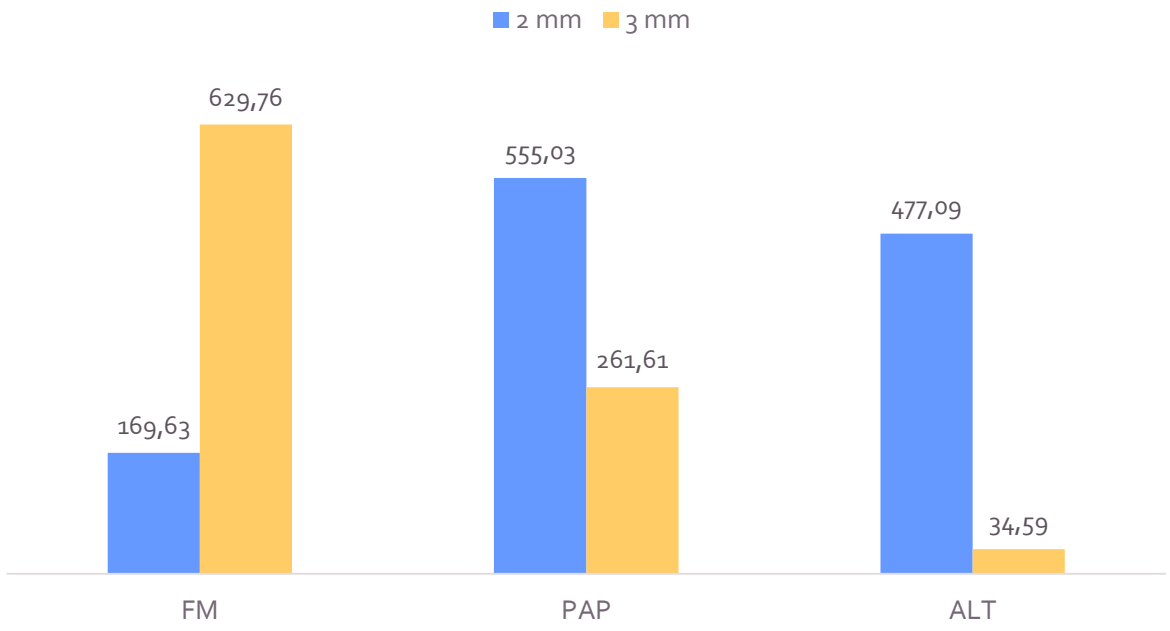
	THINK IN AZUL FEEDS		
Compound (µg/kg)	**FM**	**PAP**	**ALT**
Pesticides	3.02	9.48	2.83
PAHs	38.86	57.84	14.83
UV-filter	8.90	7.95	3.56
Musk	332.91	288.31	216.22
OPEs	16.02	32.30	18.40
Pharmaceuticals	Not found	6.50	Not found
Mycotoxins	Not found	Not found	Not found

Feed	Total concentration (µg/kg)
FM 2 mm	169.63
FM 3 mm	629.76
PAP 2 mm	555.03
PAP 3 mm	261.61
ALT 2 mm	477.09
ALT 3 mm	34.59



Cashmeran

	FEED					
COMPOUND (µg/kg)	PAP2	PAP3	FM2	FM3	ALT2	ALT3
Cashmeran	393.76	157.25	90.18	560.17	418.10	Not found



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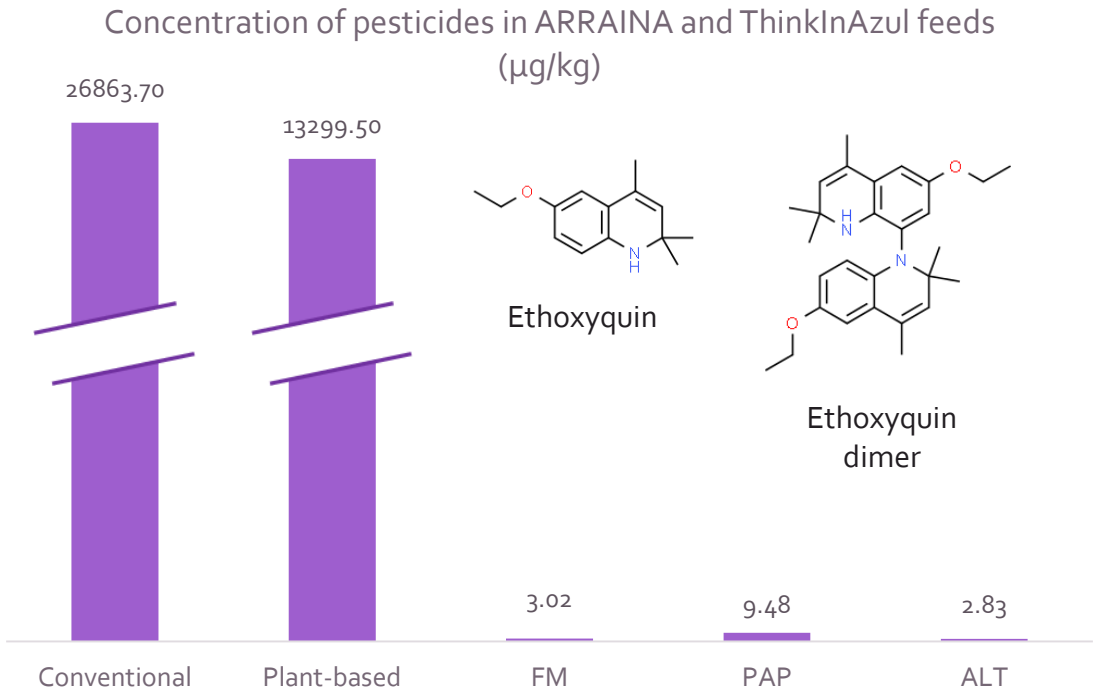
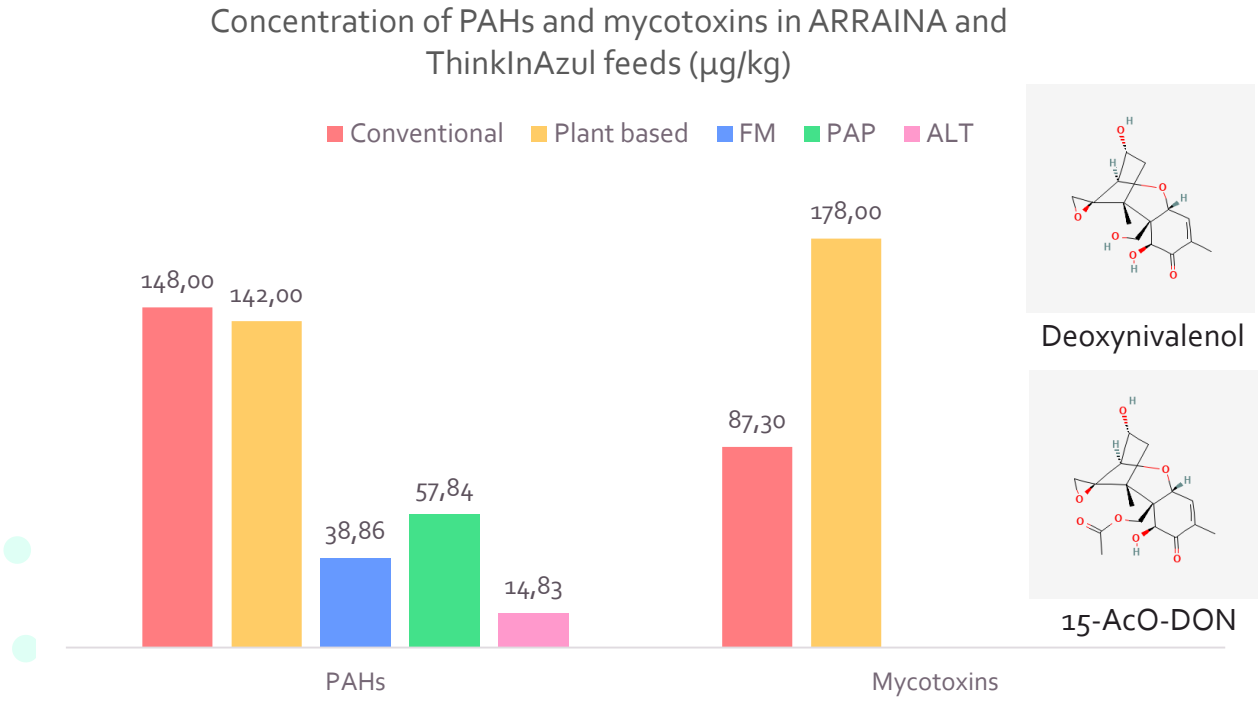
Resultados obtenidos hasta el momento (target-feed)

	ARRAINA FEEDS		THINK IN AZUL FEEDS		
Compound (µg/kg)	**Conventional**	**Plant based**	**FM**	**PAP**	**ALT**
Pesticides	26863.70	13299.50	3.02	9.48	2.83
PAHs	148.00	142.00	38.86	57.84	14.83
UV-filter	-	-	8.90	7.95	3.56
Musk	-	-	332.91	288.31	216.22
OPEs	-	-	16.02	32.30	18.40
Pharmaceuticals	-	-	Not found	6.50	Not found
Mycotoxins	87.30	178.00	Not found	Not found	Not found





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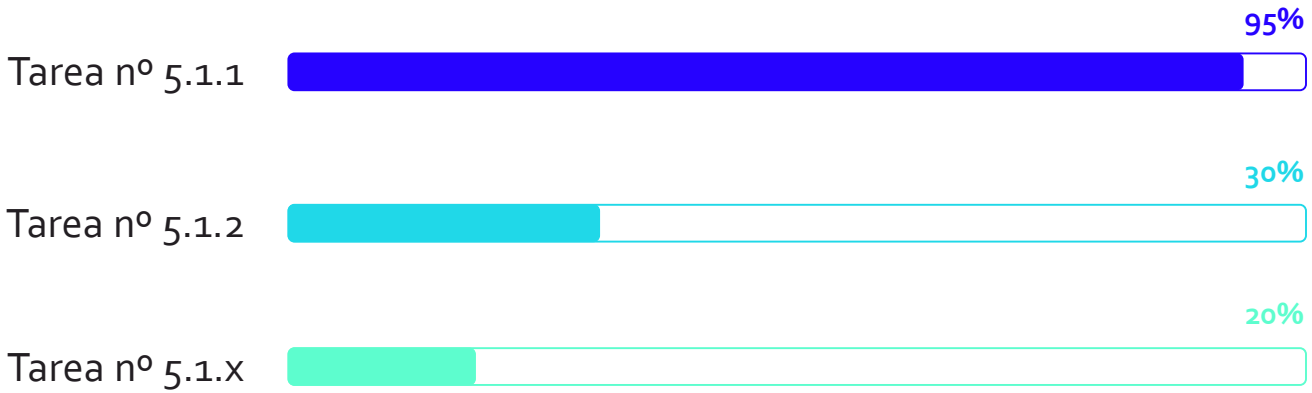
Grado de consecución de las tareas



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Desviaciones del programa inicial

- **ESTUDIO COMPARATIVO METABOLOMA PLASMÁTICO vs METABOLOMA DEL MUCUS EN DORADA**
- ¿Uso del mucus como muestra no invasiva correlacionada con cambios en el metaboloma plasmático?
- Proof-of-concept con 4 muestras de plasma y mucus de doradas dieta convencional
- Precipitación proteínas. Extracto analizado mediante UPLC-ESI-IMS-QTOFMS (RP+/RP-, HILIC+/HILIC-)

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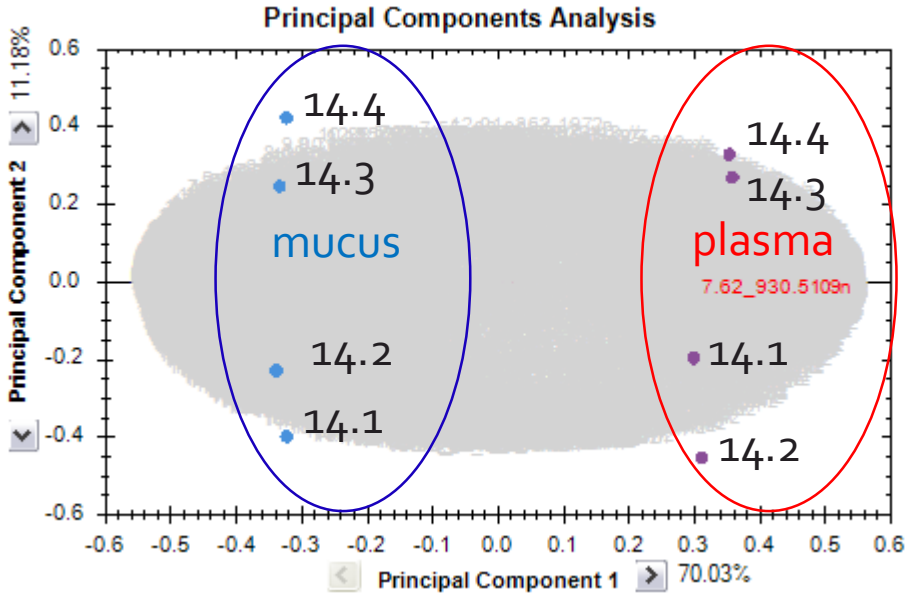
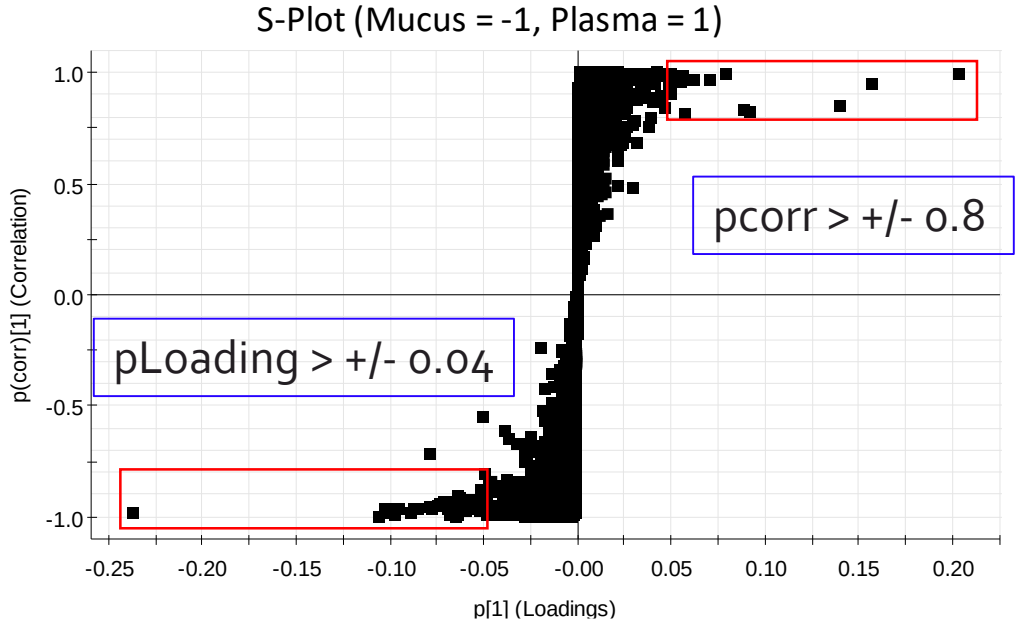
Resultados obtenidos hasta el momento (mucus metabolomics)

RP+ → 7354 features





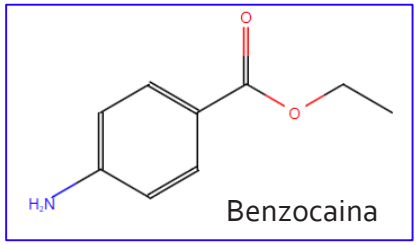
65 features

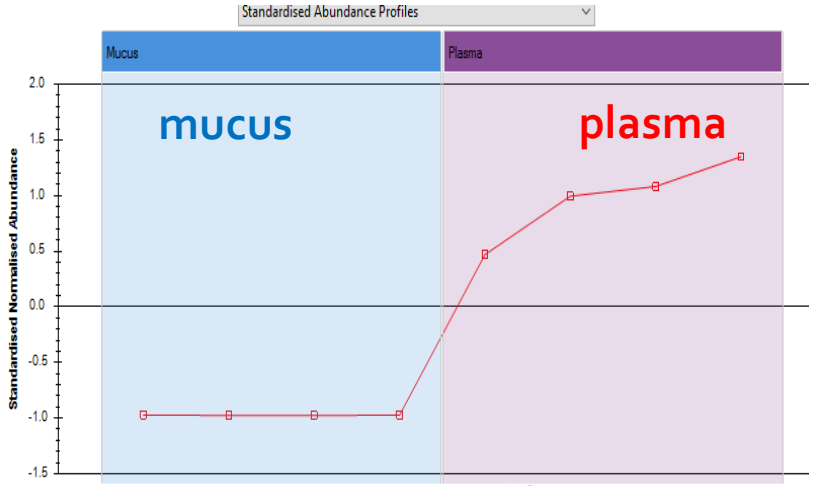
MS^E

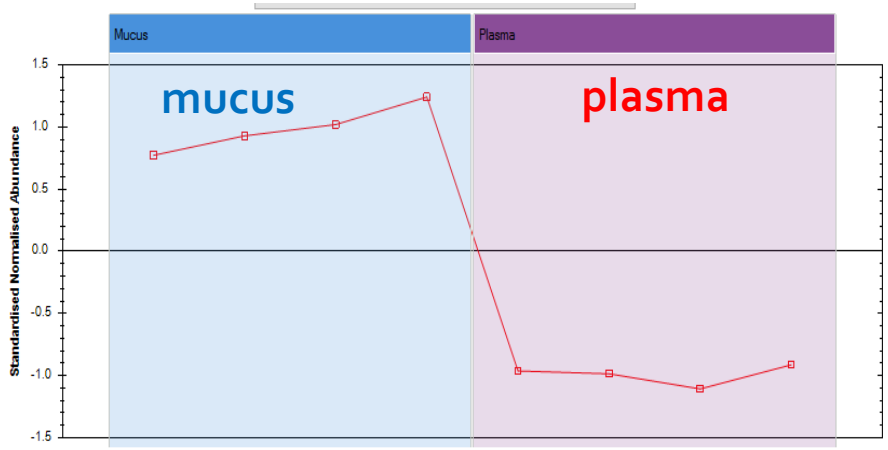
Databases
METLIN
MassBank

30 annotated

Anesthetic







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Hoja de ruta 6 próximos meses

- Tarea 5.1.1.
  - Estudio de Análisis Multivariante (MVA) entre dietas.
- Tarea 5.1.2
  - Terminar *screening* de contaminantes en filetes. Estimar transferencia. Posible metabolismo?
  - Empezar estudio lipidómica en filetes. Correlacionar con perfiles ácido grasos (UMH1)
  - Adquirir una Unidad de Desorción Térmica (TDU) para estudio de volatolómica en filetes.
- Tarea 5.1.x
  - Se han recepcionado las muestras de plasma y mucus para dietas FM, PAP y ALT (x6)
  - Analizar las muestras mediante UPLC-ESI-IMS-QTOFMS (RP+/RP-, HILIC+/HILIC-)

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We're thinking in azul

Thanks | Gràcies

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