



NEW STRATEGIES FOR THE ANALYSIS OF PESTICIDES IN AMBIENT AIR

EXPOSURE AND RISK ASSESSMENT OF AIRBORNE PESTICIDES

European Workshop on Pesticides in Ambient Air

VICENT YUSA (yusa_vic@gva.es





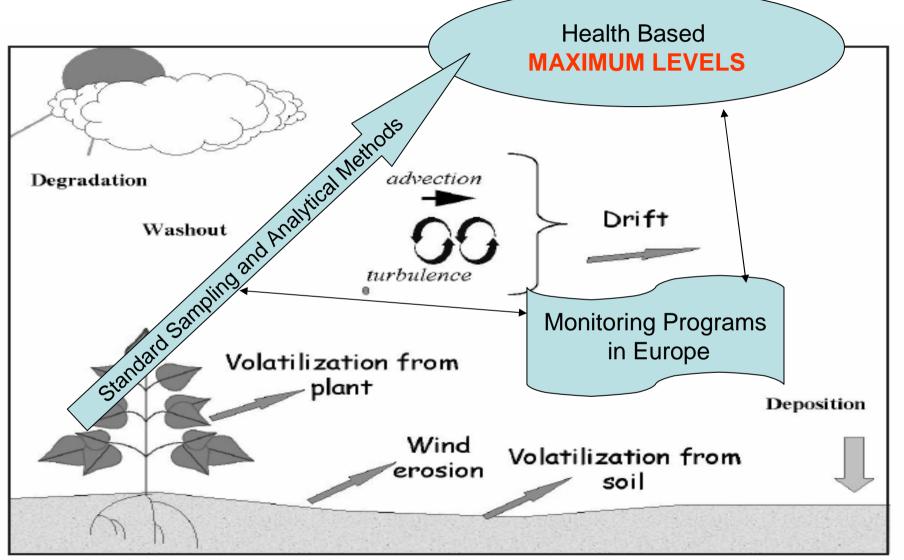


Figure 2. Processes involved in the transfer of pesticides to the atmosphere.

Carole BEDOS: Agronomie 22 (2002) 35–49





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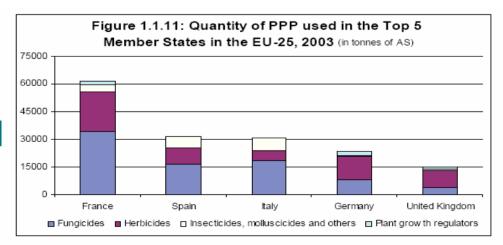
HOW MANY PESTICIDES DO WE NEED TO CONTROL IN AMBIENT AIR?

Number of pesticides authorized and a	applied in EU (2010): <u>~350</u>)
≻ <u>Herbicides: 127</u>		
≻Fungicides: 118	Recommended for use (CV)	
≻Insecticides: 38	Herbicides	12
≻ <u>Others: 67</u>	Acaricides	10
	Fungicides	60
	Inecticides	45

TOTAL

eurostat The use of plant protection prod in the European Union

Data 1992-2003







Inventory of pesticide emissions into the air in Europe

 $ER_{ijk} = D_{ijk} + E_{app,air,ijk} + E_{crop,air,ijk}$

Table S.3.5a Emissions of AS applied to vineyards (in kg/yr of AS) for 2000.

Active substances	AT	BE	DK	FI	FR	DE	GR	IE	IT	LU	NL	РТ	ES
sulphur	134542	0	0	0	6766705	722494	859849	0	3351528	0	0	3644048	4333048
glyphosate	6940	0	0	0	0	40208	30576	0	233309	0	0	147834	142650
mancozeb	0	0	0	0	482661	0	19617	0	1092042	0	0	83873	122876
propineb	0	0	0	0	0	0	18570	0	0	0	0	108518	0
amitrol	0	0	0	0	0	0	9796	0	0	0	0	0	0
copper oxychloride	0	0	0	0	0	0	0	0	117360	0	0	0	0
copper	0	0	0	0	0	0	0	0	114236	0	0	0	0
fosetyl	0	0	0	0	531511	0	0	0	0	0	0	72656	0
1,3-dichloropropene	0	0	0	0	0	0	0	0	0	0	0	0	392079
folpet	15440	0	0	0	575090	98403	0	0	0	0	0	0	30415
metiram	0	0	0	0	314409	137008	0	0	0	0	0	0	0
tolylfluanid	0	0	0	0	0	34894	0	0	0	0	0	0	0
chlorpyrifos	0	0	0	0	0	0	0	0	0	0	0	0	0
dinocap	0	0	0	0	0	0	0	0	0	0	0	0	0
myclobutanil	0	0	0	0	0	0	0	0	0	0	0	0	0
dimethoate	0	0	0	0	0	0	0	0	0	0	0	0	0
chlorothalonil	5476	0	0	0	0	0	0	0	0	0	0	0	0
dithianon	2919	0	0	0	0	0	0	0	0	0	0	0	0

AT: Austria, BE: Belgium, BG: Bulgaria, CZ: Czech Republic, DE: Germany, DK: Denmark, EE: Estonia, ES: Spain, FI: Finland, FR: France, GR: Greece, HU: Hungary

130 priority substances in five major crops (cereals., maize, oilseeds, fruit threes, vineyards)

Priority score =Hazard Factor X Kg of Use

D.A. Sarigiannis Atmospheric Environment 75 (2013) 6–14





HOW MANY METABOLITES DO WE NEED TO CONTROL IN AMBIENT AIR?

METABOLITES/DEGRADATION-TRANSFORMATION PRODUCTS/BREAKDOWN PRODUCTS

2. <u>Relevant metabolite</u>: a metabolite for which there is reason to assume that it has comparable intrinsic properties as the active substance in terms of its biological target activity, or that it has certain toxicological properties that are considered severe and unacceptable with regard to the decision-making criteria described in the text. Such a metabolite is therefore treated like the parent active substance in the assessment according to Annex VI, point C.2.5.1.2 of Directive 91/414/EEC. Where such a metabolite exceeds





DEGRADATION/TRANSFORMATION PRODUCTS

523 SOIL METABOLITES were identified from 185 CUP in UK

67 metabolites could exhibit the parent pesticidal mode of action (57 selected for further study)

Pesticide metabolite

cis-3-chloroprop-2-enoic acid trans-3-chloroprop-2-enoic acid aldicarb sulfone aldicarb sulfoxide sulfanilamide deethvlatrazine reference compound 10 2-aminobenzimidazole carbofuran carboxin sulfoxide 5-amino-4-chloropyridazin-3(2H)-one 3-carbamyl-1,2,4,5-tetrachlorobenzoic acid 3-carbamyl-2.4.5-trichlorobenzoic acid 3-cyano-6-hydroxy-2,4,5-trichlorobenzamide R417888 3-(3-chloro-p-tolyl)-1-methylurea cyanazine acid AE 0542291 5-hydroxy-XDE-570 5-trifluoromethyl-pryid-2-one FOE oxalte thiadone ethanol phosphorous acid aminomethylphosphonic acid 1-(6-chloro-pyridine-3-ylmethyl)-N-nitro guanidine AE F145740 metsulfuron-methyl 3,5-di-iodo-4-hydroxybenzamide 3,5-di-iodo-4-hydroxybenzoic acid 3-[4-(2'-hydroxy-2'-propyl)-phenyl]-methyl urea desmethylisoproturon acetaldehyde metazachlor oxalic acid

metazachlor sulfonic acid methiocarb sulfoxide ATSA demethyl metoxuron diketo metribuzin IN-D5119 IN-D5803 dimethyloxamic acid 2,6-dinitro-3,4-xylidine 4-[(1-ethylpropyl)amino]-2-methyl-3,5-dinitro benzyl alcohol 4-[(1-ethylpropyl)amino]-3,5-dinitro-o-toluic acid 4-fluoroaniline CGA 294849 BH518-2 BH518-4 deisopropylatrazine methomyl diisopropylamine 2-ethyl-7-nitro-5-(trifluoromethyl) benzimidazole





METABOLITES

	de Properties L		Univers Hertfor	dshire	
SELECT LANGUAGE	e for information about the PPDB and its condit P		PPDB 🐝		
	e	eg. CARBENDAZIM	1E		
ey metabolites:	•				
Metabolite	Formation medium		Estimated maximum occurrence fraction	91/414 relevancy	
2-aminobenzimidazole	Soil		0.08	Minor fraction, Relevant	



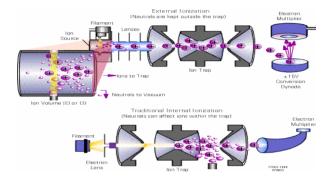
ANALYTICAL METHODS



DETERMINATION

GC-MS; GC-MS/MS





LC-MS/MS

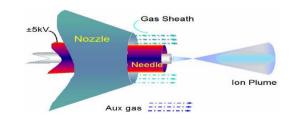
Newly introduced pesticides are:

more polar

less toxic

more degradable in ambient air

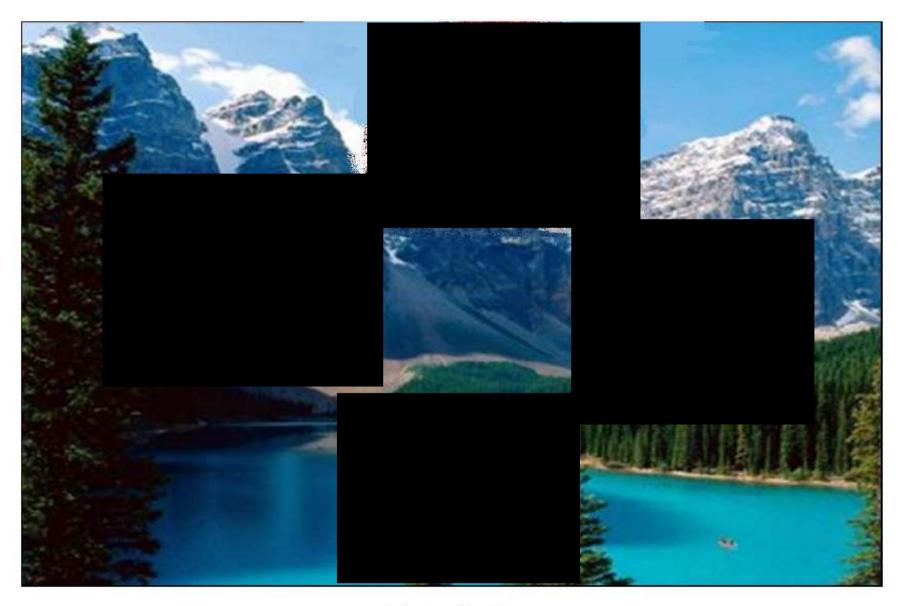






Why do we need HRMS ?



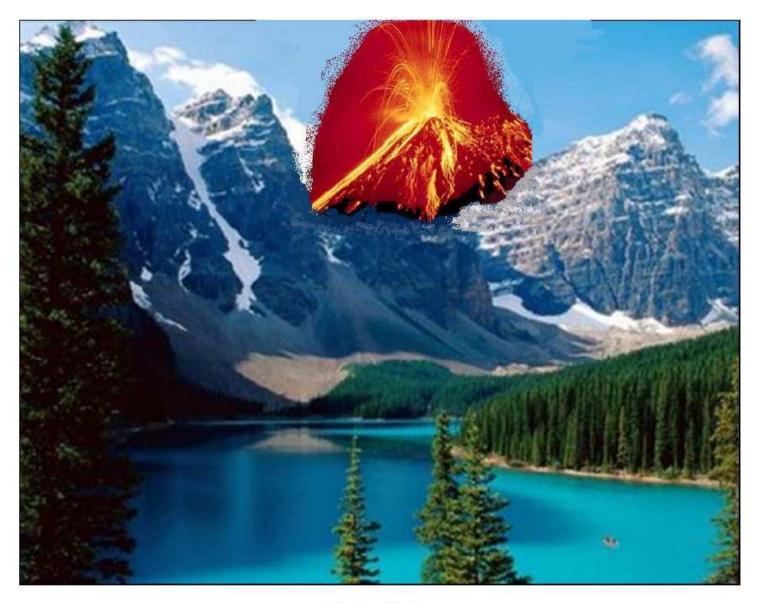


© Anton Kaufmann



Why do we need HRMS ?





© Anton Kaufmann

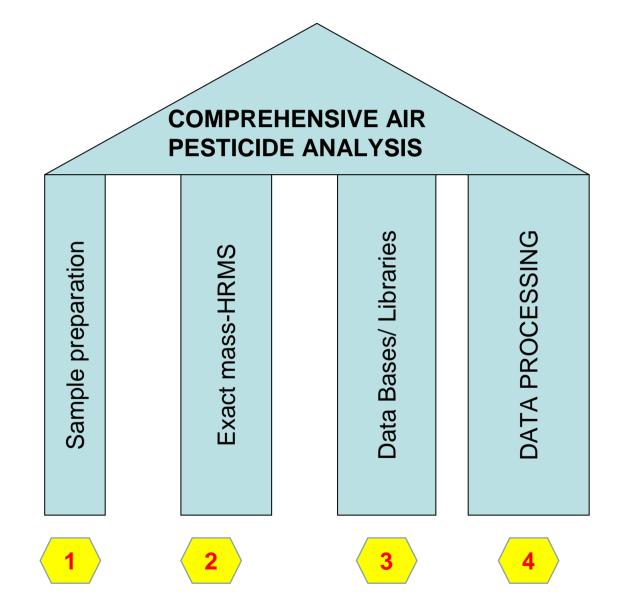




COMBINED TARGET/NON TARGET STRATEGIES FOR MASSIVE ANALYSIS OF PESTICIDES IN AIR USING LC-ACCURATE MASS- HRMS











GENERIC METHOD OF EXTRACTION

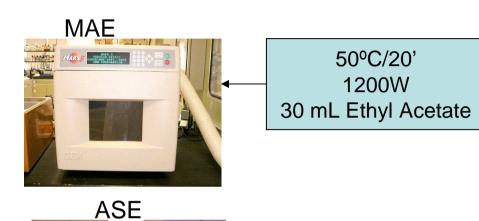
SAMPLES



filters



adsorbent



MATRIX EFFECT (ME) (%) = (B/A)*100 ;

B= sample solution; A= standard solution

High: ME= 23-59 % Moderate: ME=61-80 % Low: ME=83-90 %







Exact mass

< 1 ppm en each scan

m/z = 200 m/z= 200.1457 // 200.1455

Resolution

1000.000 max

Dinamic Range

>10⁴

Collision cell HCD

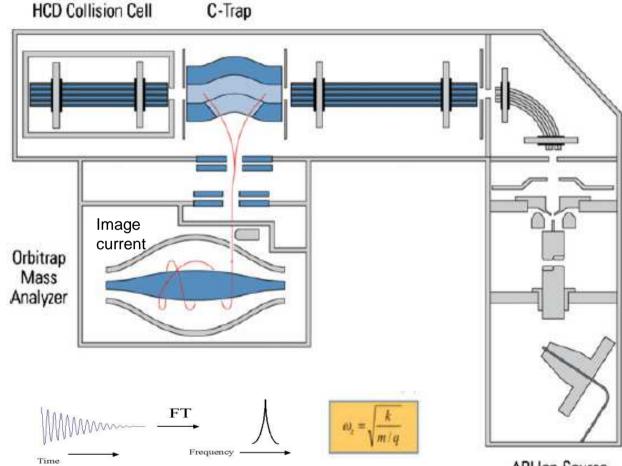
All ions fragmentation

Others

Mass range: 50-4000

Up to 10 scans/s

Polarity switching (1s)



API Ion Source

Fig. 4. Schematic layout of the Exactive[™] mass spectrometer (including an optional HCD collision cell).







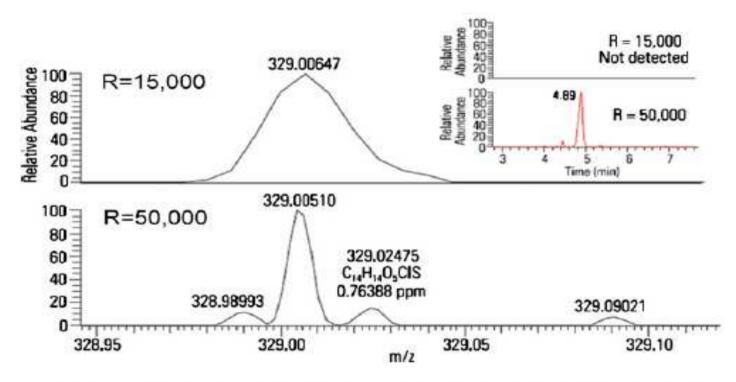


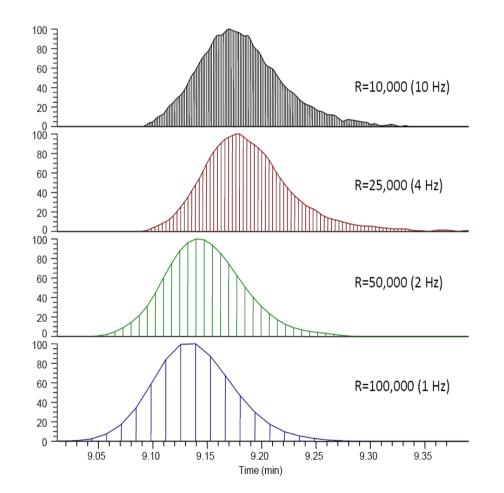
Fig. 3. High resolution prevents a false negative result. Pesticide SulcotrionTM (m/z 329.02475) was measured in a mixture with other 115 pesticides and food toxins in a horse feed matrix. The mass deviation at a resolution of 15,000 is higher than 5 ppm extraction window set by the user due to the presence of an interference (top pane) giving a false negative result (insert, top trace). Sulcotrion can be detected with mass deviation of less than 1 ppm at 50,000 resolution (bottom pane) leading to a confident identification and quantitation (insert, bottom trace). The figure courtesy of Markus Kellmann, Thermo Fisher Scientific.







HOW MUCH RESOLUTION DO I NEED?

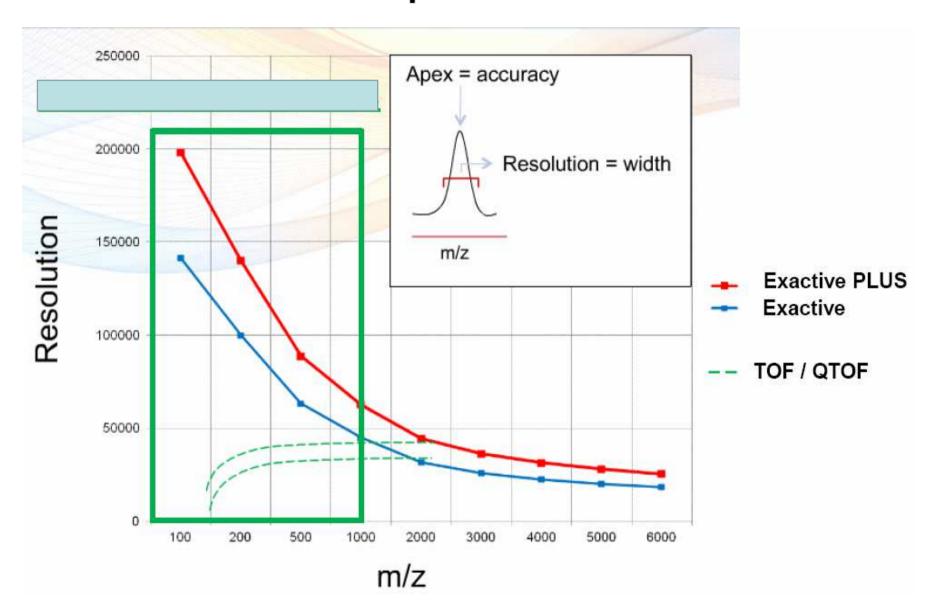


J Am Soc Mass Spectrom 2009, 20, 1464-1476



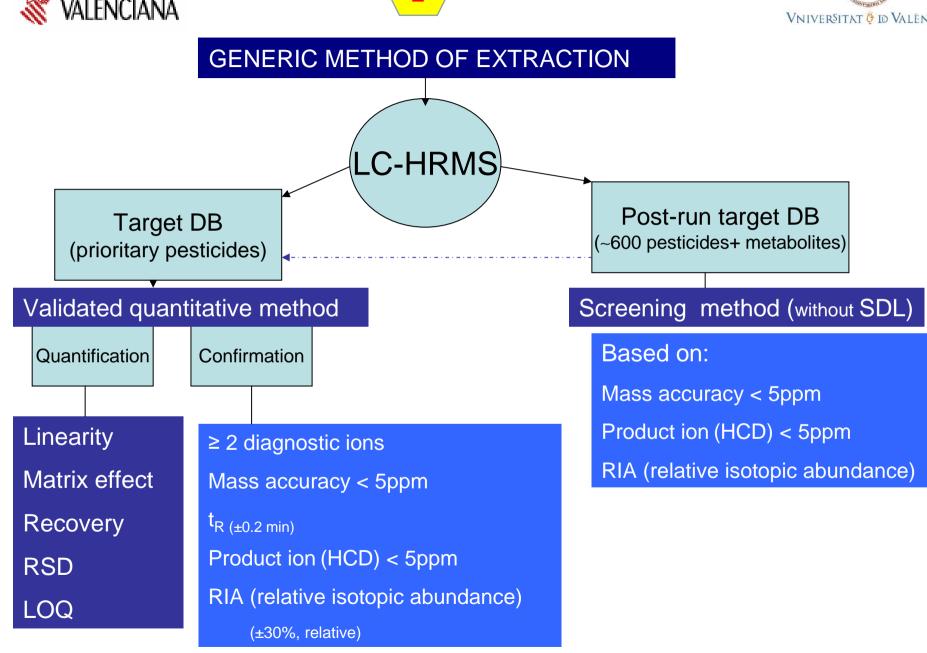












SANCO/12571/2013







DATA BASE (csv) OF PESTICIDES AND OTHER SUBSTANCES

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	A	В	С	D	E	F	G	Н		J
1	TraceFinder Compound		-		L				•	
2	Hacer macr compound			PEAK 1						
	CompoundName	ExperimentType	ChemicalFormula		ExtractedMas	Adduct	Polarity	Fragment	Fragment	Fragment
	Bupirimate	XIC	C13H24N4O3S	5000	317.16419		+	166.0975		210.1603
	Buprofezin	XIC	C16H23N3OS	5000	306,16346		+	201.1056		
	Butachlor	XIC	C17H26CINO2	5000	312.17248	M+H	+			
7	Butafenacil	XIC	C20H18CIF3N2O6	5000	475.08782		+			
8	Butamifos	XIC	C18H38NO3P	5000	348.26621	M+H	+			
9	Butocarboxim	XIC	C7H14N2O2S	5000	191.08487	M+H	+			
	Butoxycarboxim	XIC	C7H14N2O4S	5000	223.0747		+	86.06	106	166
	Butralin	XIC	C14H21N3O4	5000	296.16048		+	240.0968	222.0863	
12	Butylate	XIC	C11H23NOS	5000	218.15731	M+H	+			
	Cadusafos	XIC	C10H23O2PS2	5000	271.09498	M+H	+	158.9698	96.9508	130.9385
14	Cafenstrole	XIC	C16H22N4O3S	5000	351.14854	M+H	+			
15	Captafol	XIC	C10H9CI4NO2S	5000	347.91809	M+H	+			
	Captan	XIC	C9H8CI3NO2S	5000	299.94141	M+H	+			
	Carbaryl	XIC	C12H11NO2	5000	202.08625	M+H	+	145.0647	117.0699	155.0491
	Carbendazim	XIC	C9H9N3O2	5000	192.07675		+	160.0511		
19	Carbetamide	XIC	C12H16N2O3	5000	237.12337		+	120.0444	118.0863	100.0757
20	Carbofuran	XIC	C20H32N2O3S	5000	381.22064	M+H	+	165.091	123.0441	
21	Carbophenothion	XIC	C11H16CIO2PS3	5000	342.98113	M+H	+			
	Carbosulfan	XIC	C20H32N2O3S	5000	381.22064	M+H	+	118.0685	128.1434	
23	Carboxin	XIC	C12H13NO2S	5000	236.07398	M+H	+	143.0161		
24	Carfentrazone-ethyl	XIC	C15H14Cl2F3N3O3	5000	412.04371	M+H	+	316.0028	345.9956	
25	Carpropamide	XIC	C15H18CI3NO	5000	334.05267	M+H	+	139.0324		
26	Cartap	XIC	C13H7Br2N3O6	5000	238.06785	M+H	+			
	Carvone	XIC	C10H14O	5000	151.11175	M+H	+	109	123	
28	Chinomethionat	XIC	C10H6N2OS2	5000	234.99943	M+H	+	207.0043	163.0325	
29	Chloralose	XIC	C8H11CI3O6	5000	308.9694		+			
30	Chloramben	XIC	C7H5CI2NO2	5000	205.97701	M+H	+			
31	Chloramben *1*	XIC	C7H5CI2NO2	5000	205.97701		+			
32	Chlorantraniliprole	XIC	C18H14BrCl2N5O2	5000	481.97807	M+H	+	285.9179		
33	Chlorbenthiazone	XIC	C8H6CINOS	5000	199.99314	M+H	+			
34	Chlorbromuron	XIC	C9H10BrCIN2O2	5000	292.96869	M+H	+			
35	Chlorbromuron *1*	XIC	C9H10BrCIN2O2	5000	292.9687	M+H	+			
36	Chlorbufam	XIC	C11H10CINO2	5000	224.04728	M+H	+			
37	Chlordane	XIC	C10H6CI8	5000	406.80805	M+H	+			
38	Chlorfenapyr	XIC	C15H11BrCIF3N2O	5000	406.97681	M+H	+			
	Chlorfenprop	XIC	C9H8CI2O2	5000	218.99741	M+H	+			
40	Chlorfenvinphos	XIC	C12H14Cl3O4P	5000	358.9768	M+H	+			
41	Chlorfluazuron	XIC	C20H9CI3F5N3O3	5000	539.97024	M+H	+	158.0412	141.0146	
42	Chlorflurenol	XIC	C14H9CIO3	5000	261.0313	M+H	+			
	Chloridazon	XIC	C10H8CIN3O	5000	222.04287	M+H	+	104.0495		
44	Chlormephos	XIC	C5H12CIO2PS2	5000	234.97776	M+H	+			







DATA BASE OF PESTICIDES AND OTHER SUBSTANCES

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energinal Linuxon SCC Compound Madding Compound Madding Compound Madding Compound Compoun	Reports Screening Peak Detection Compound Database Compound Details	Lenacil Linuron Malathion Malathion dicarboxylic acid Malathion monocarboxylic acid Maleic_hydrazide MCPA MCPB	XIC XIC XIC XIC XIC XIC XIC	C9H10Cl2N2O2 C17H8Cl2F8N2O3 C10H19O6P52	-	Compound: N	1etalaxyl-M		
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Plan build Male:	Compound Database	Maleic_hydrazide MCPA MCPB	XIC	C8H15O6P52		Ionization: N	lone	Response Threshold: 5000	Neutral Mass: 279.14705803
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Compound Details Microprop Grid Microprop Mic		Mecarbam	XIC	C11H13ClO3		Target Fea	IKS		
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witchlorg/rifes-m XIC CFH/C3NO4P Witchory (VeC): 1.0.00 192.1331 Met.Chlorg/rifes-m XIC CEH20XO3S RT (min): 0.00 Met.Diazinon XIC CIH20XO4P Lens: 0.0 Met.Diazinon XIC CH120XO4P Lens: 0.0 Met.Diazinon XIC CH120XO4P Lens: 0.0 Met.Diazinon XIC CH120XO4P Lens: 0.0 Met.Fenitothion XIC CH120XO4P Lens: 0.00 Met.Fenitothion XIC CH120XO4P Energy Ramp: 0.00 Met.Fenitothion XIC CH120XO4P Energy Ramp: 0.00 Met.Fenitothion XIC CH120XO4P Energy Ramp: 0.00 Met.Foliothion XIC CH120XO4P Energy Ramp: 0.00 Met.Primiphos-methyl XIC CH120XO4P Energy Ramp: 0.00								160.11187	
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Met.Diazinon Met.Diazinon*1* Met.C C2H21N2O4P Lens: 0.0 Met.Diazinon*2* Met.Collary Energy Ramp: 0.00 Met.Penitrothion *1* Met.C CH12NO2F Energy Ramp: 0.00 Met.Penitrothion *1* Met.C CH12NO2F Energy Ramp: 0.00 Met.Penitrothion *1* Met.C CH12NO2F Energy Ramp: 0.00 Met.Primiphos-methyl Met.C CH12NO2F Energy Ramp: 0.00 Met.Primiphos-methyl*1* Met.C CH12NO2F Energy Ramp: 0.00 Met.Primiphos-methyl*1* Met.C CH12NO2F Energy Ramp: 0.00 Met.Primiphos-methyl*2* Met.C CH12NO2F Energy Ramp: 0.00 Met.Tolciofos-methyl*1** Met.C CH12NO2F Energy Ramp: 0.00 Met.Tolciofos-methyl*2* Met.C CH12NO2F Energy Ramp: 0.00 Met.Tolciofos-methyl*1** Met.C CH12NO2F Energy Ramp: 0.00 Met.Tolciofos-methyl*2* Met.C CH12NO2F Energy Ramp: 0.00 Met.Tolciofos-methyl*2* Met.C CH12NO2F Energy Ramp: 0.00 Met.Tolciofos-methyl*2* Met.C CH12NO2F Energy Ramp: 0.00 Metanitron Mct.C CH12NO2F Energy Ramp: 0.00 Metanintron Mct.C CH12NO2F Energy Ramp: </td <td></td> <td>Met.Chlorpyrifos-m **1**</td> <td>XIC</td> <td>C5H2NOCI3</td> <td></td> <td>RT (min):</td> <td>0.00</td> <td></td> <td></td>		Met.Chlorpyrifos-m **1**	XIC	C5H2NOCI3		RT (min):	0.00		
Met.Diazinon *2* XIC CoHILONG/C2H21N204P Met.Fenitrothion XIC CH12NOS Met.Fenitrothion *1* XIC CH12NOSP Met.Fenitrothion *2* XIC CH12NOSP Met.Primiphos-methyl *1* XIC CH12NOSP Met.Primiphos-methyl *1* XIC CH12NOSP Met.Primiphos-methyl *1* XIC CH12NOSP Met.Primiphos-methyl *2* XIC CH12NOSP Met.Tolclofos-methyl *1* XIC CH12NOSP Metaflumizone XIC CH12NOSP Metaflumizone XIC CH12NOSP Metaflumizone XIC CH12NOSP Metarifos XIC CH13NOSP Metharole XIC CH130SPS Metharo			XIC	C12H21N2O4P		Lens:	0.0		
Met-Fenitrothion XIC CSH12NOGP Met-Fenitrothion XIC CCH7N03 Met-Fenitrothion XIC CCH7N03 Met-Fenitrothion XIC CH12NOGP Met-Fenitrothion XIC CH12NOGP Met-Fenitrothion XIC CH12NOGP Met-Fenitrothion XIC CH12NOGP Met-Fenitrothion XIC CH15N3O4P Met-Pyrimiphos-methyl XIC CH112O4P Met-Tolicofos-methyl XIC CH112O4P Met-Tolicofos-methyl XIC CH112O4P Met-Tolicofos-methyl XIC CH112O4P Met-Tolicofos-methyl XIC CH112O4P Metaflumizone XIC CH415CNA04 Metaflumizone XIC C14415CNA04 Metazachlor XIC C14415CNB0 Methapenthizzuron XIC C14415CNB0 Methazole XIC C24H15N02 Methazole XIC C24H15N02 Methazole XIC C24H15N02 Methazole XIC C14415N02 Methazole XIC C		Met.Diazinon *1*	VIC	C9U12N2O	1N2040	Energy Ramp:	0.00		
wet.Fenitrotion "1" XIC C7H7N03 Met.Fenitrotion "2" XIC CH7N03 Met.Pyrimiphos-methyl XIC CH1H20N3O4P Met.Pyrimiphos-methyl "1" XIC C9H15N3O4 Met.Pyrimiphos-methyl "2" XIC C9H15N3O4 Met.Tolclofos-methyl "2" XIC C9H15N3O4 Met.Tolclofos-methyl "2" XIC C9H15N3O4 Met.Tolclofos-methyl "2" XIC C9H15I2O4P Met.Tolclofos-methyl "2" XIC C9H15C2O4P Met.Tolclofos-methyl "2" XIC C3H15EI2O4P Met.Tolclofos-methyl "2" XIC C3H15EI2O4P Met.Tolclofos-methyl "2" XIC C3H15EI2O4P Met.Tolclofos-methyl "2" XIC C1H110040 Met.Tolclofos-methyl "2" XIC C1H110040 Metazachlor XIC C1H110040 Metazachlor XIC C1H110040 Metazachlor XIC C1H110040 Methamidophos XIC C2H8N02PS Methamidophos XIC C2H8N02PS Methamidophos XIC C1H115N02 Methamidophos XIC C1H115N02 Methamidophos XIC C1H115N02 Methamidophos XIC C1H115N02			XIC	C9H12NO6P		-			
Met. Pyrimiphos-methyl *1* XIC C1H20N304P Met. Pyrimiphos-methyl *2* XIC C9H18N304P Met. Pyrimiphos-methyl *2* XIC C9H11C204P Met. Tolciofos-methyl *1* XIC C9H11C204P Met. Tolciofos-methyl *1* XIC C9H11C204P Met. Tolciofos-methyl *1* XIC C9H11C204P Met. Tolciofos-methyl *2* XIC C3H9C204P Met.Tolciofos-methyl *2* XIC C3H9C204P Metalaxyl-M XIC C1H420H3002 Metalaxyl-M XIC C1H1201004 Metalaxyl-M XIC C1H1101005 Metalaxyl-M XIC C1H1110005 Methanidophos XIC C1H1111005									
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wisition Met.Tolclofos-methyl *1* XIC C9Hi01204P Met.Tolclofos-methyl *1* XIC C9Hi01204P Met.Tolclofos-methyl *2* XIC C9Hi01204P Metaflumizone XIC C2Hi15F6N4022 Metamifop XIC C2Hi15F6N402 Metamifop XIC C2Hi15F6N402 Metamifop XIC C15H21N04 Methanifops XIC C14H15N03 Methanifops XIC C14H15N02 Methanifops XIC C14H15N02 Methanifophos XIC C14H15N02 Methanifophos XIC C14H15N02 Methanifophos XIC C14H15N02 Methanifophos XIC C14H15N02		Met.Pyrimiphos-methyl *1*	XIC	C9H15N3O					
Met. Tolclofos-methyl *1* XIC CPHECI20 Met. Tolclofos-methyl *2* XIC CBH9CI204P Metaflumizone XIC C24H15F6N402 Metaflumizone XIC C23H15CFN204 Metamifop XIC C19H12C1N204 Metamifop XIC C19H12FN204 Metamifop XIC C19H12C1N204 Metamifop XIC C19H12C1N204 Metamifop XIC C19H12C1N204 Metamifop XIC C19H12C1N204 Methazachlor XIC C19H12C1N30 Methazole XIC C19H1201N305 Methazole XIC C2H18002PS Methazole XIC C19H12C1N203 Methazole XIC C19H1201N302 Total Compounds: 768 XIC C14H15N02									
Metaflumizone XIC C24H15FENH02 Metamirop XIC C35H21N04 Metamirop XIC C15H21N04 Metamiron XIC C15H21N04 Metamiron XIC C10H10N40 Metacarchor XIC C14H15CN30 Methabenzthiazuron XIC C14H15CN30 Methacrifos XIC C14H1305PS Methazole XIC C2H1802PS Methazole XIC C2H1802PS Methazole XIC C2H1802PS Methazole XIC C2H1802PS Methazole XIC C2H18002PS Methazole XIC C14H15N02 Total Compounds: 768 Total Compounds: 768		Met.Tolclofos-methyl *1*	XIC	C7H6Cl2O					
Metalacyl-M XIC C15H221004 Metamifop XIC C23H18CFN204 Metamitron XIC C10H10N40 Metazachor XIC C10H10N40 Metazacole XIC C17H22CN30 Methabenzthiazuron XIC C10H11N305 Methamidophos XIC C10H11N305 Methazole XIC C2H8N02PS Methazole XIC C2H8N02PS Methazole XIC C14H15N02 Total Compounds: 768 Total Compounds: 768									
Metamitron XIC C10H100H0 Metazachior XIC C14H16CN30 Metabenzthiazuron XIC C17H22CN30 Methabenzthiazuron XIC C1H1305PS Methamidophos XIC C2H802PS Methazole XIC C3H6C12N203 Methazole XIC C3H6C12N204 Methazole XIC C3H6C12N204		Metalaxyl-M	XIC	C15H21N04					
Metazachlor XIC C14H1sCN30 Metconazole XIC C17H22CN30 Methabenzthiazuron XIC C10H1IN305 Methadophos XIC C7H1305PS Methadophos XIC C2H8N02PS Methazole XIC C3H8102PS									
Methabenzthiazuron XIC C10H11N3OS Methacrifos XIC C7H130SPS Methamidophos XIC C2H8N02PS Methazole XIC C3H8N02PS Methfuroxam XIC C14H15N02 Total Compounds: 768 Y Y		Metazachlor	XIC	C14H16CIN3O					
Methacrifos XIC C7H1305PS Methamidophos XIC C2HEN02PS Methazole XIC C9H6C12N203 Methfuroxam XIC C14H15N02 Total Compounds: 768 Total Compounds: 768									
Methazole XIC C9H6Cl2N2O3 Methfuroxam XIC C14H15NO2 Total Compounds: 768		Methacrifos	XIC	C7H13O5PS					
Methfuroxam XIC C14H15N02 uisition Total Compounds: 768			XIC	C2H8NO2P5 C9H6Cl2N2O3					
uisition Total Compounds: 768			XIC	C14H15N02	-	•			
	uisition	Total Compounds: 768							
IVSIS	lysis								







DETECTION CRITERIA post-target

Identification and Conf	irmation Settin	igs	
Pea	aks 🔽 m/z		Threshold Override 🔽 10,000
			2 S/N Ratio Threshold 5.0
Retention Til	me Identify	Confirm	Ignore if Not Defined
			Window Override (sec) 30
3 agment Io	ins 🗌 Identify	Confirm	Ignore if Not Defined
			Min. # of Fragments
4			Intensity Threshold 5,000
			Mass tolerance 5 ppm 💌
4 sotopic Patte	ern 🗌 Identify	Confirm	Fit Threshold (%) 90
		ALC: ACCURATE	Allowed Mass Deviation (ppm) 5
			Allowed Intensity Deviation (%) 10
			Use Internal Mass Calibration
Library Sea	ch 🗌 Identify	Confirm	Score Threshold (%) 80
			Use Reverse Library Searching Only







Result review

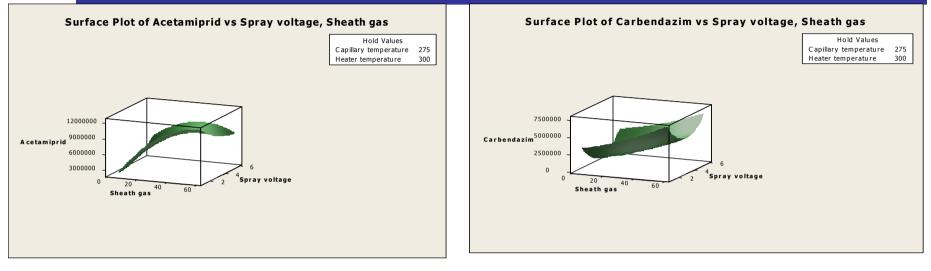
Workflow > 🛛 🗹 Meth	od Develop	privent > 🔽	Review >										
Data > 📄 Reports 1	2		_									File ?	y.
Environ and suffect according	g dagai for di	he with test samp	é.										
amples	• 5a	eening Results	8										
actfinder_test_22-05-13_155. Exa 130413_45	18 Target	t Screening Result	15										_
Exa_130413_47	12	ng	Compound Name	se painta		AT (DAMA) 44.	· water and the second second	Instant de	Non Interpret March	ad fol - Municipal Alfred	- -		- 1
		+ C L	A.	- 6	-	H			4		19 ()		
	1.1		Azoxystrobin	C22H1	7N3O5	-0.05	-1.39	0.850	4 of 4	3,9572507			
		•	Buprofezin	C16H2	3N3O5	-0.08	-1.82	0.885	SofS	2.0111507			
		•	Carbendazim	C9H9N	1302	-0.03	-1.83	0.904	4 of 4	5.3880600			-
		•	Carvone	C10H1	40	-0,05	-2.33	0.743	3 of 3	3.0192608			
		•	Gibberelline A7	C19H2	205	-0.07	-1.96	0.750	2 6/2	6.7025E04			
		•	Imazalil	C14H1	4CI2N2C	-0.08	-1.31	0,785	5 of 5	3,4095805			
		•	Imidacloprid	C9H10	CIN5O2	-0.05	-0.99	0.850	4 of 4	1.3688806			
			Iprovalicarb	C18H2	8N2O3	-0.07	-1.47	0.808	2 of 2	4.1148E05			
			Kresokim-methyl	C18H1		-0.04	-0.82		2 of 2	4,7275805			
		•	Mandipropartid		2CINO4	-0.05	-0.82		4 01 4	3.9444E05			
			Metalaxyl	C15H2	1ND4	-0.08	-1.77	0.880	2 of 3	9.1354E05			- 2
hromatogram t		-	-				Spectrum S AIF						_
130413 45 Mandpropamid NAS (1,12) + p ESI Full ms (5) 90- 90- 90- 90- 90- 90- 90- 90- 90- 90-	NL: 1.095 00-1000.01	5 m/2 412 120 AC 3944 AH 1055	39 50	e: 0.879		Atsuetus eviet	Show Jsotopic Pattern 130413 45 # 1253 This (1, 1) - 0 ESP For 412, 1307 90 80 70 80 50 40 30 		3.2653	414,2693	415 23(Ng. 5.1 Mando d	



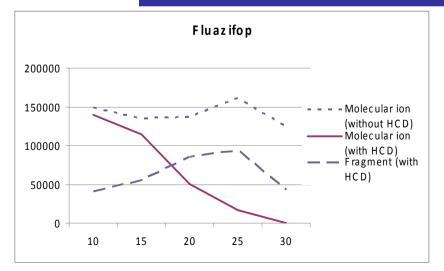
METHOD DEVELOPMENT

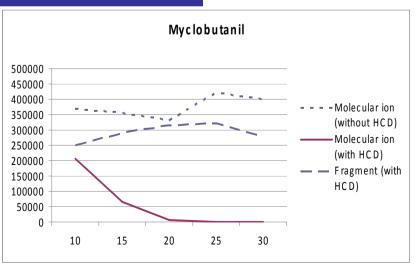


OPTIMIZATION OF ION SOURCE SETTINGS (DoE)



STUDY OF HCD FRAGMENTATION

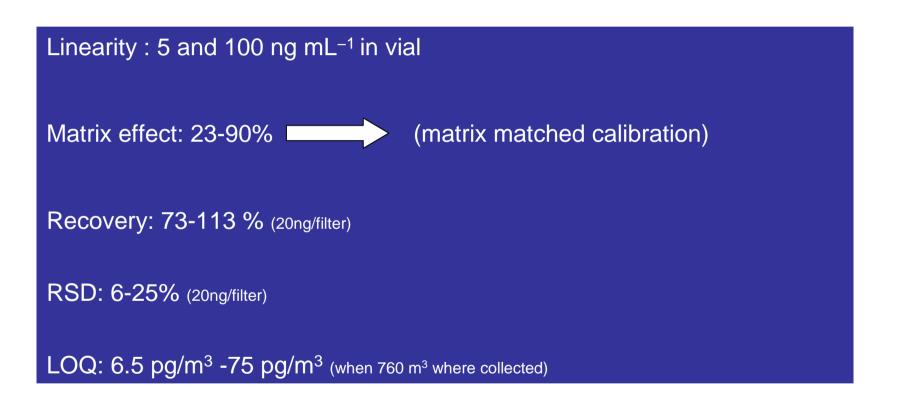


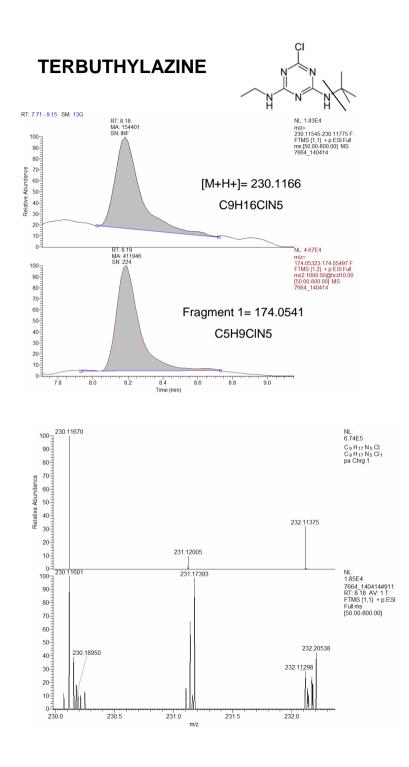






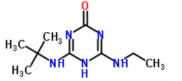
PERFORMACE OF THE QUANTITATIVE METHOD

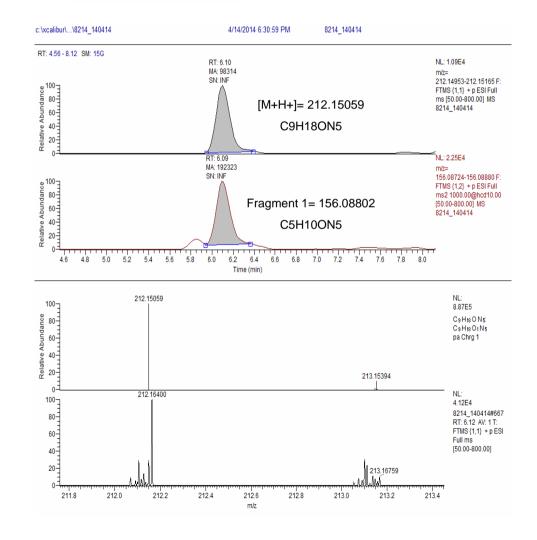


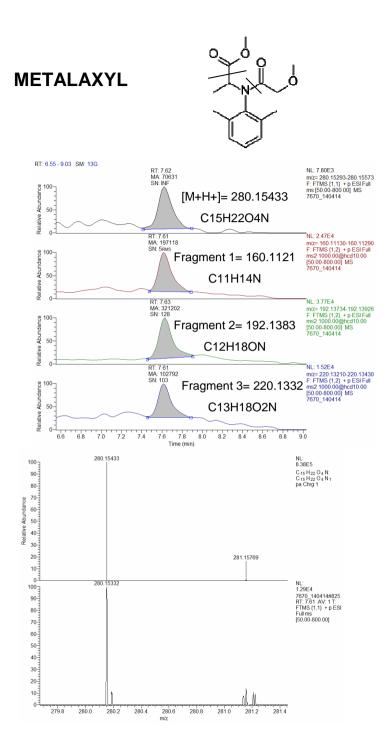


hydroxy-terbuthylazine

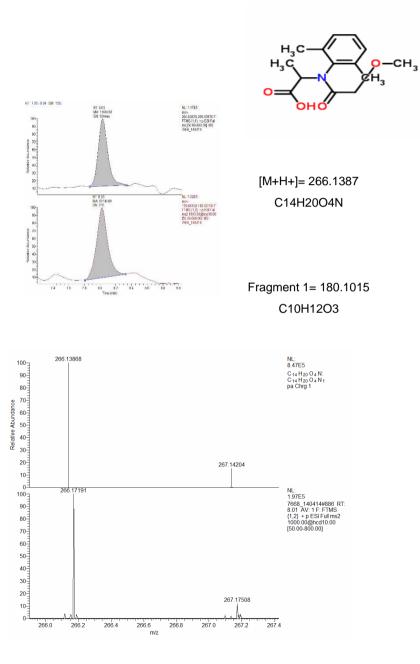
4-(tert-butylamino)-6-(ethylamino)-1,3,5-triazin-2(1H)-one

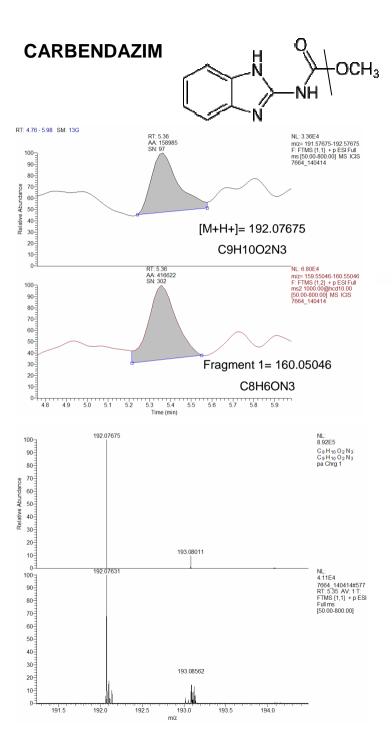






N-(2,6-dimethylphenyl)-N-(methoxyacetyl)alanine





2-AMINOBENZIMIDAZOLE

1H-Benzimidazol-2-amine

100

100 -

90-

80-

70-

60-

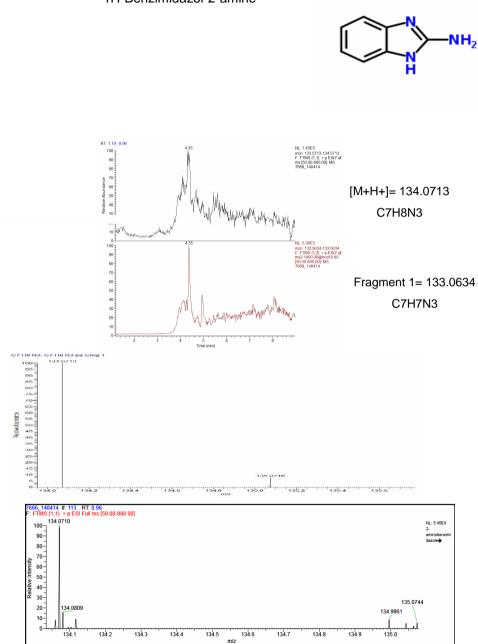
50-40-

30-

20-

10-

0.







TAKE HOME MESSAGES

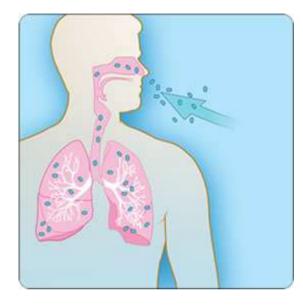
GENERIC SAMPLE PREP. SUITED FOR MANY PESTICIDES/TOXICANTS

LC-MASS ACCURACY-HRMS READY TO REPLACE MANY QqQ METHODS

COMBINE TARGET/ POST-TARGET STRATEGIES FOR MASSIVE DETECTION OF PESTICIDES AND METABOLITES IN AMBIENT AIR







EXPOSURE AND RISK ASSESSMENT

OF AIRBORNE PESTICIDES





HAZARD QUOTIENT (HQ)

$HQ = DIE_i / HBRV_i$

HBRVs: AOAEL, ADI, ARfD

Hazard Quotients (HQ) as a risk descriptor

HBRV_i is the Health Based Reference Value for i

HQ < 1 → ACCEPTABLE RISK

DAILY INHALATION EXPOSURE (DIE)

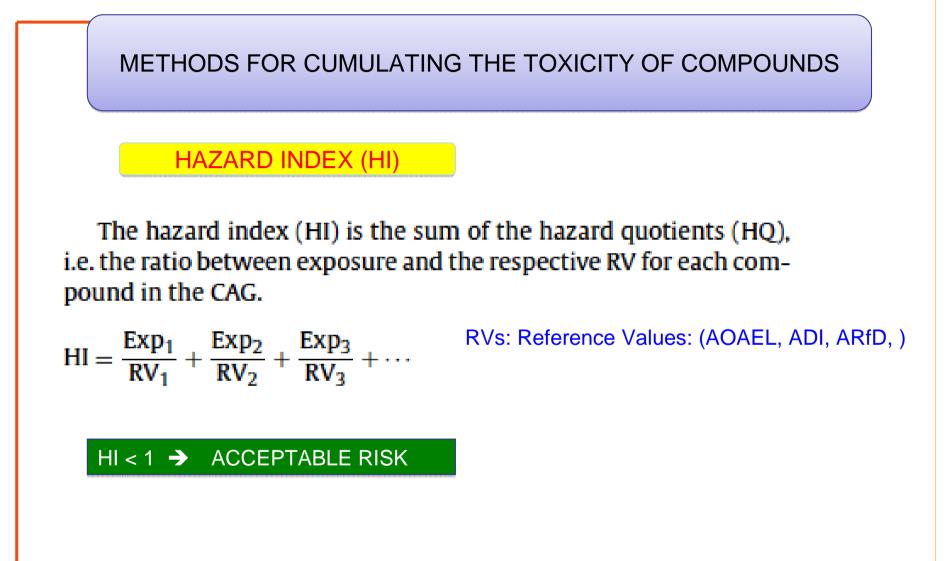
DIE (µg/kg/day) = Σ(C x IR_{inh} x ED)/ BW

C is the total (particle+ gas phases) concentration of each pesticide in the air (ngm⁻³), IR_{inh} is the inhalation rate per hour (m³/h), ED is the exposure duration (h) to air and BW is body weight of the subject (kg).

USEPA / WHO





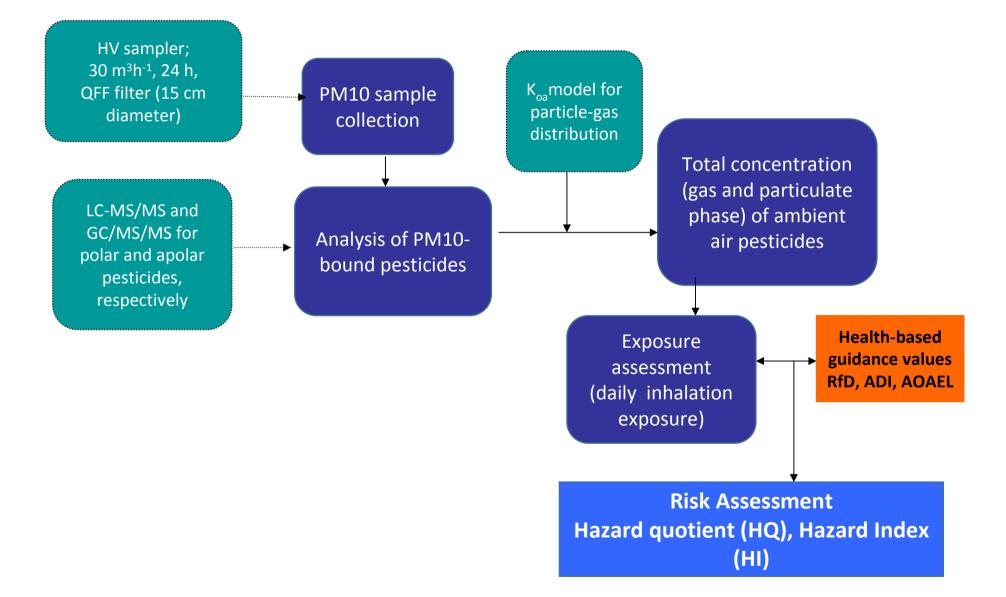


Toxicology Letters 180 (2008) 137-150



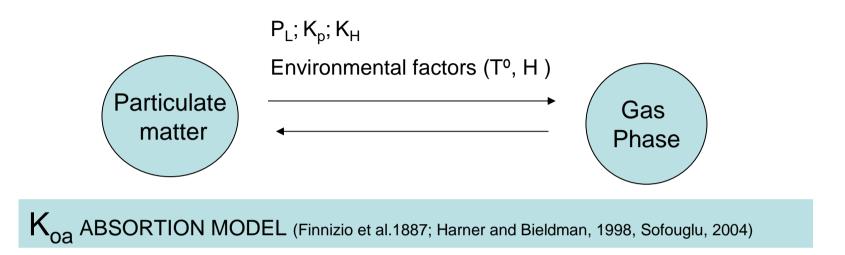


SCREENING RISK ASSESSMENT OF ATMOSPHERIC PESTICIDES









$\boldsymbol{\varnothing} = (\mathbf{K}_{p}\mathbf{C}_{TSP})/(1 + \mathbf{K}p\mathbf{C}_{TSP})$

Where ϕ is the particulate percentage (fraction of the compound in the particle phase), C_{TSP} is the concentration of total suspended particles in the air (µg m-3), and K_p is the gas/particle partition coefficient.

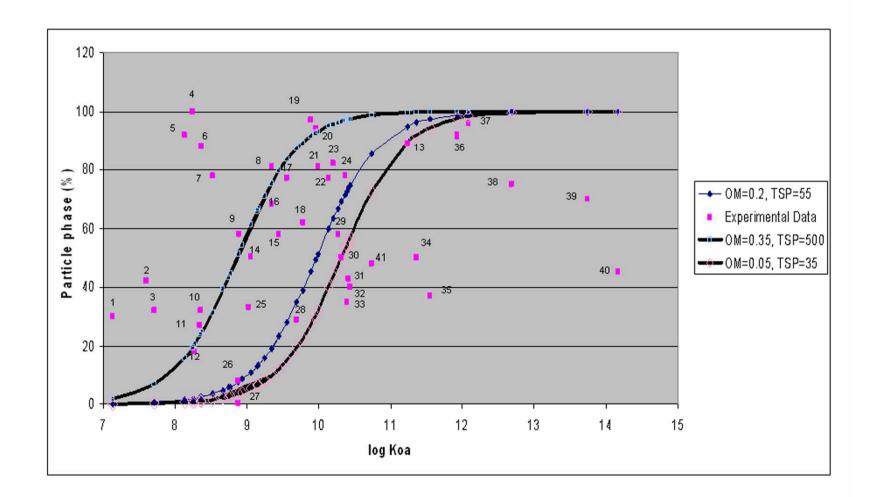
$\log K_p = \log K_{oa} + \log f_{OM} - 11.91$

Where $\log K_{oa}$ is the octanol-air partitioning coefficient, and $\log f_{OM}$ is the fraction of organic matter.





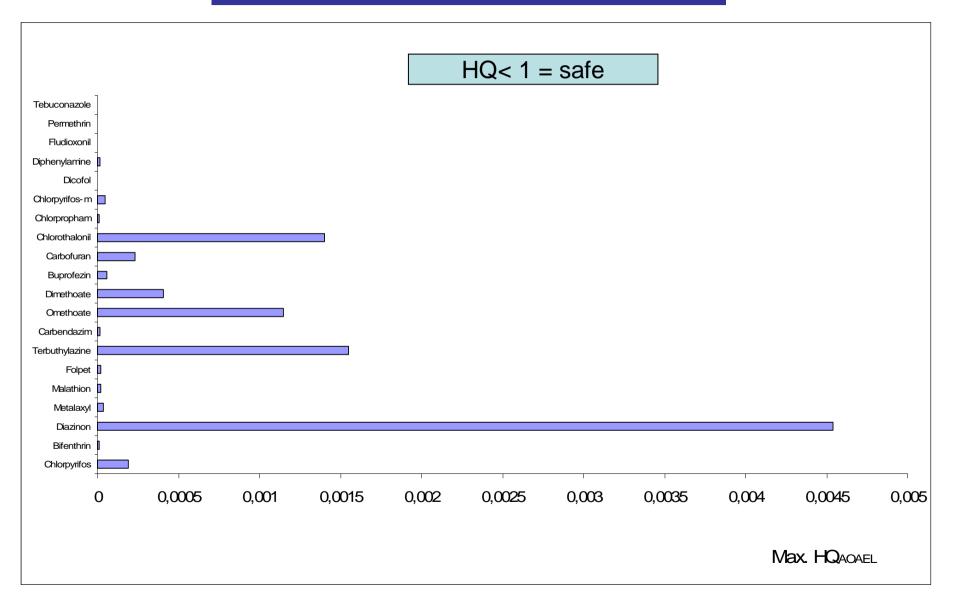
G/P PARTITIONING







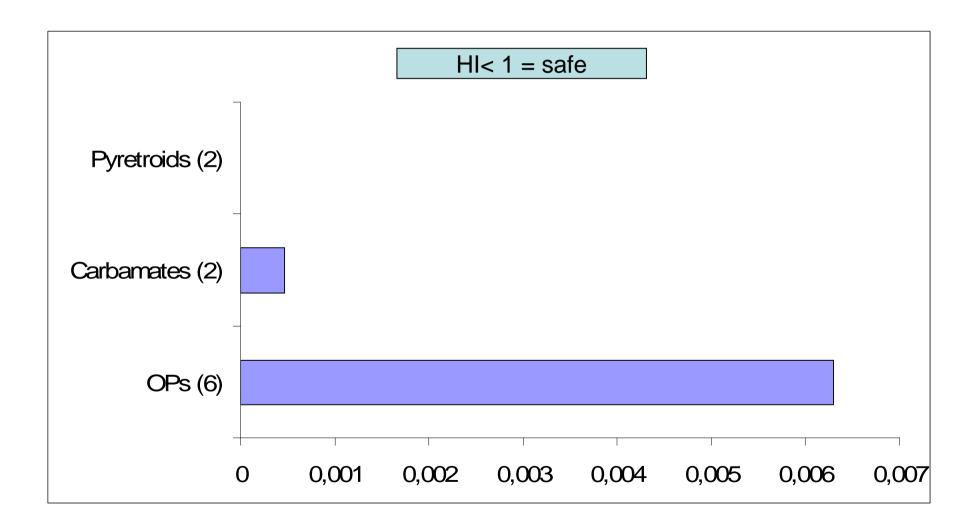
HAZARD QUOTIENT







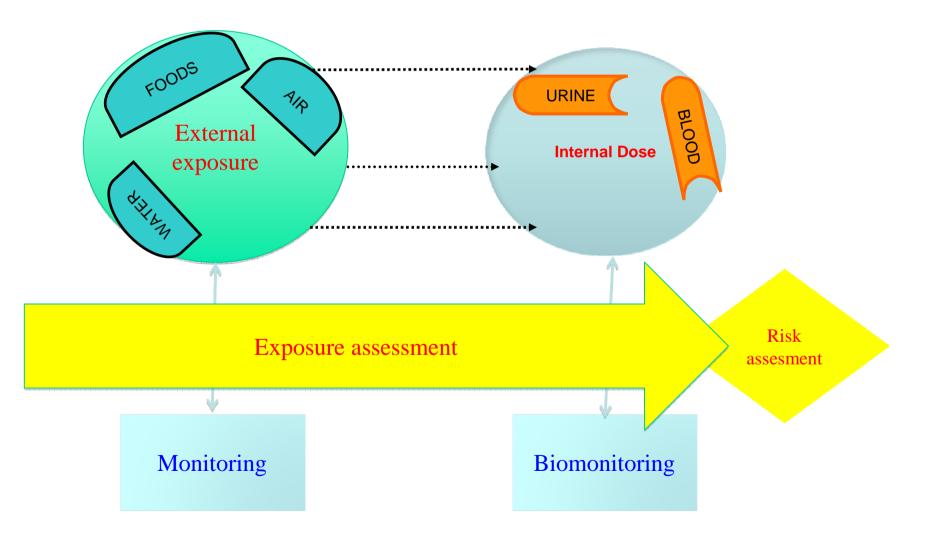
HAZARD INDEX







INTEGRATED EXPODURE







THANK YOU

Dr. Vicent Yusà (yusa vic@gva.es) // Vicent.Yusa@uv.es)