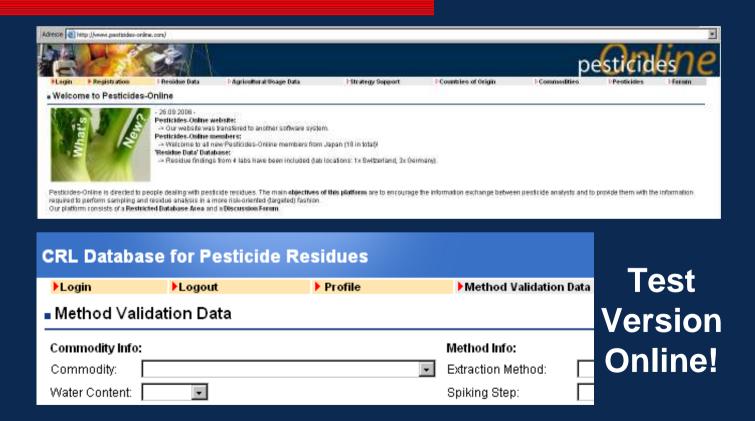
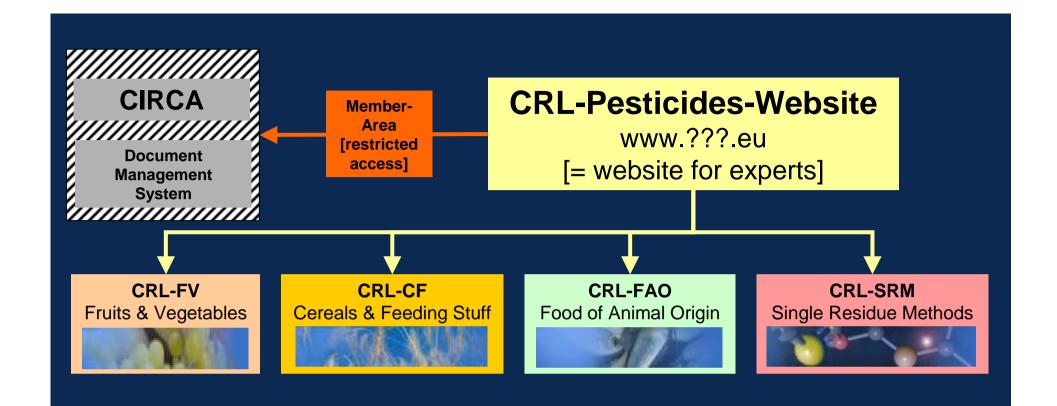
## Pesticides-Online and Method Validation Database

Two Database Modules to Access Pesticide-Related Data via the Internet



Dr. H. Zipper

Chemisches und Veterinäruntersuchungsamt Stuttgart EU-CRL for Pesticide Residues using Single Residue Methods



#### Two Database Modules to Access Pesticide-Related Data:

- → www.pesticides-online.com
- → Method Validation Database

#### **Targeted Sampling & Analysis**

High-Tech-Instrumentation & Fast Sample Preparation are Important, but...

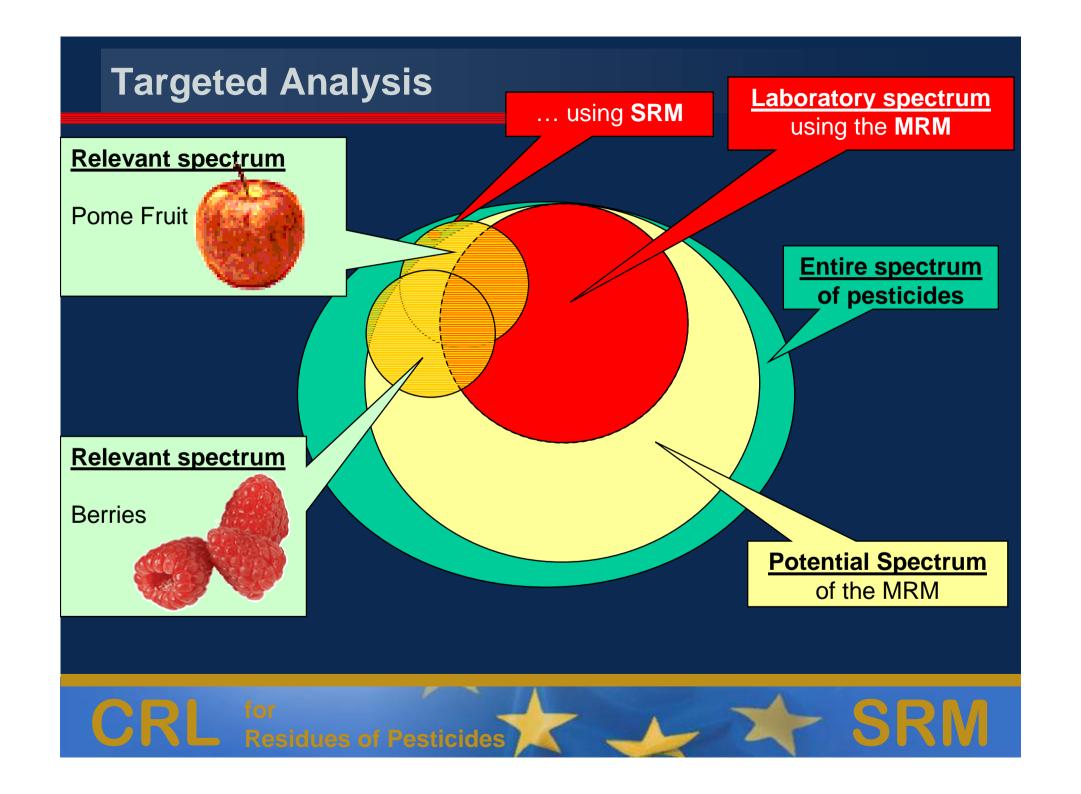
Important is not only

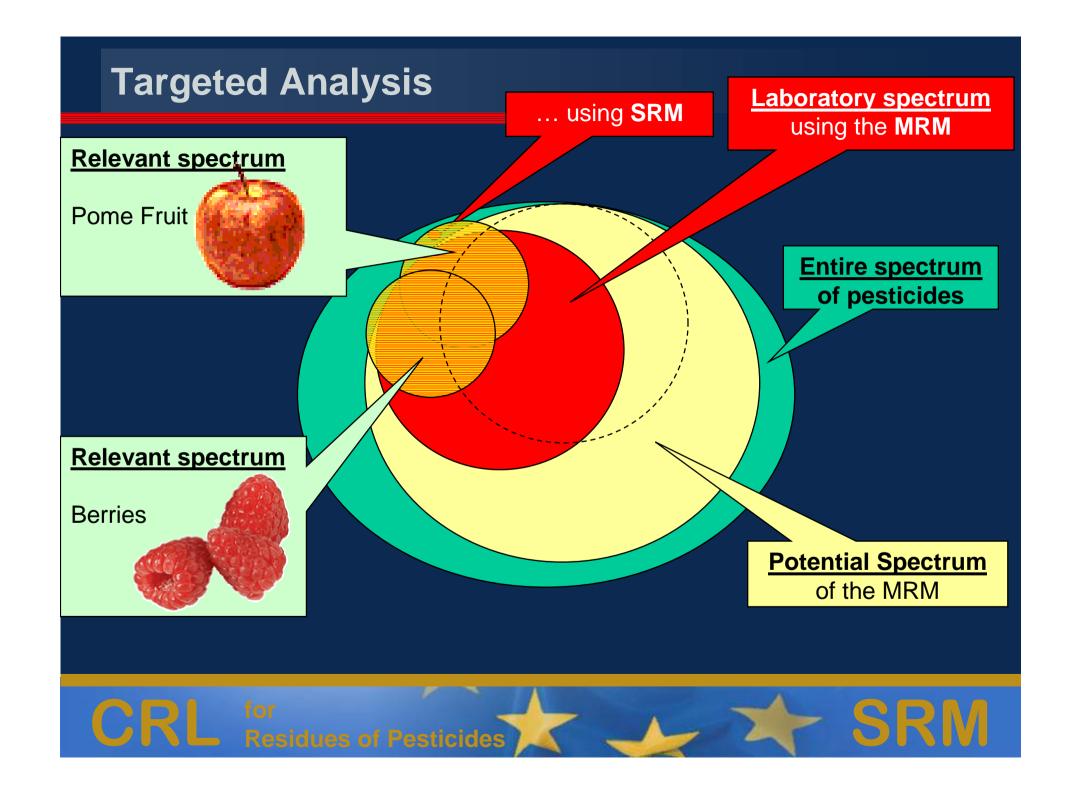
**How You Analyse** 

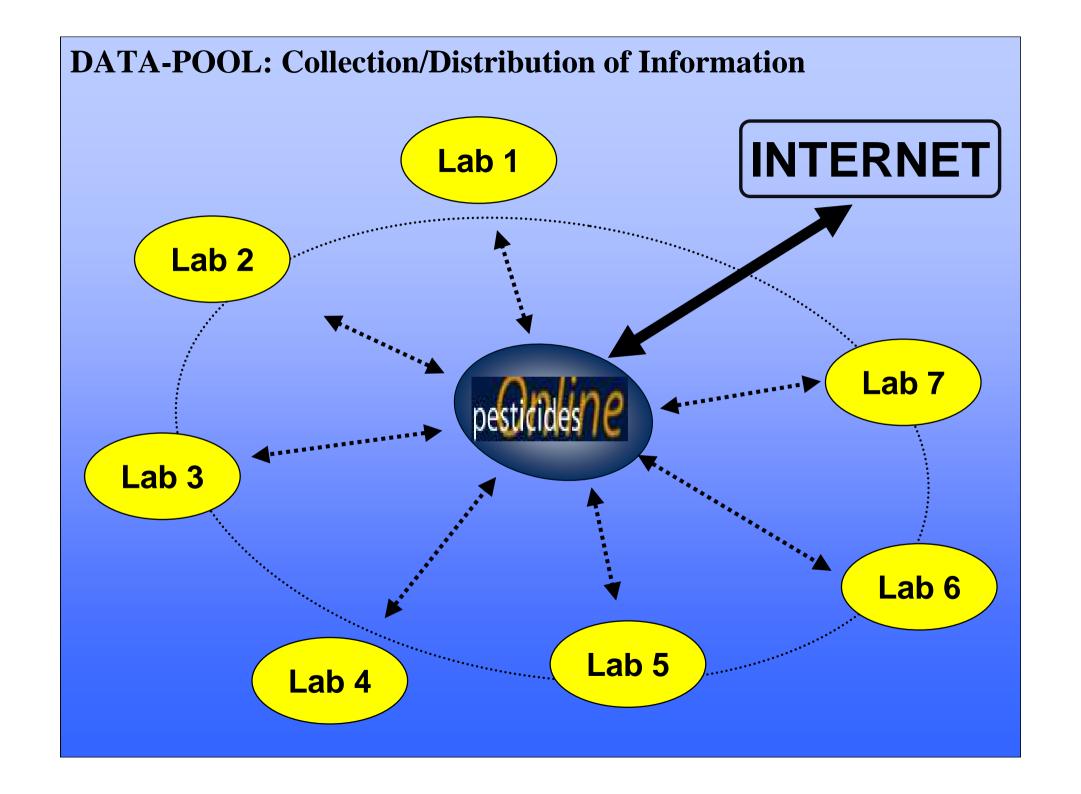
but also...

What You Analyse!

Set priorities based on information...







#### **PESTICIDES-ONLINE**

 Information Exchange between Laboratories
 Enable Targeted Pesticide-Analysis Aims:

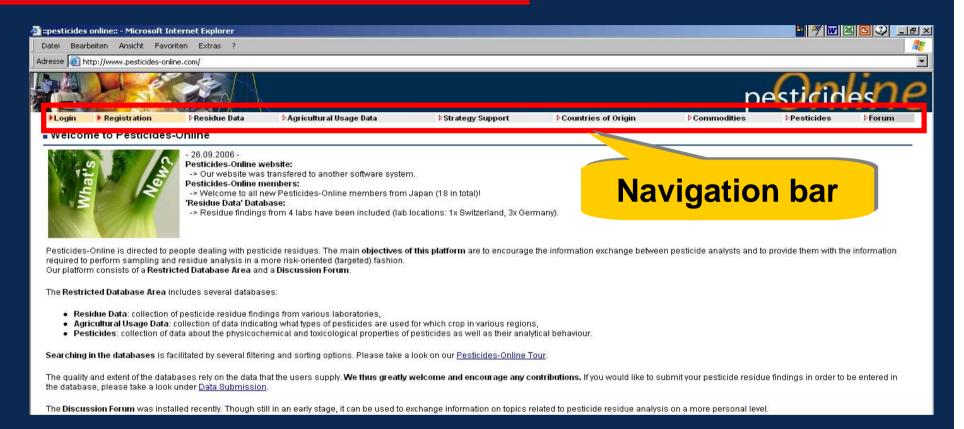
**Discussion-Forum** 

esticide-U Pesticide-Data Jsage

Data-Sheets

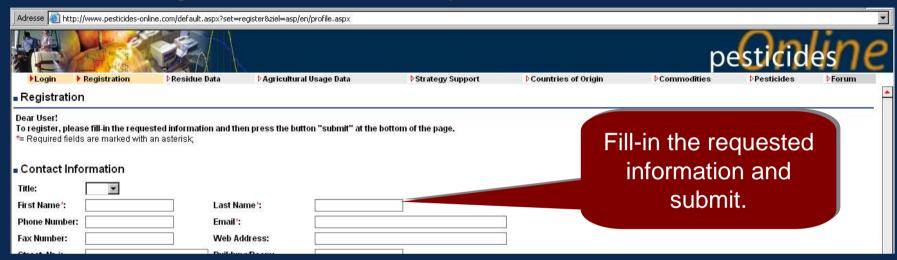
Residue Findings

### www.pesticides-online.com



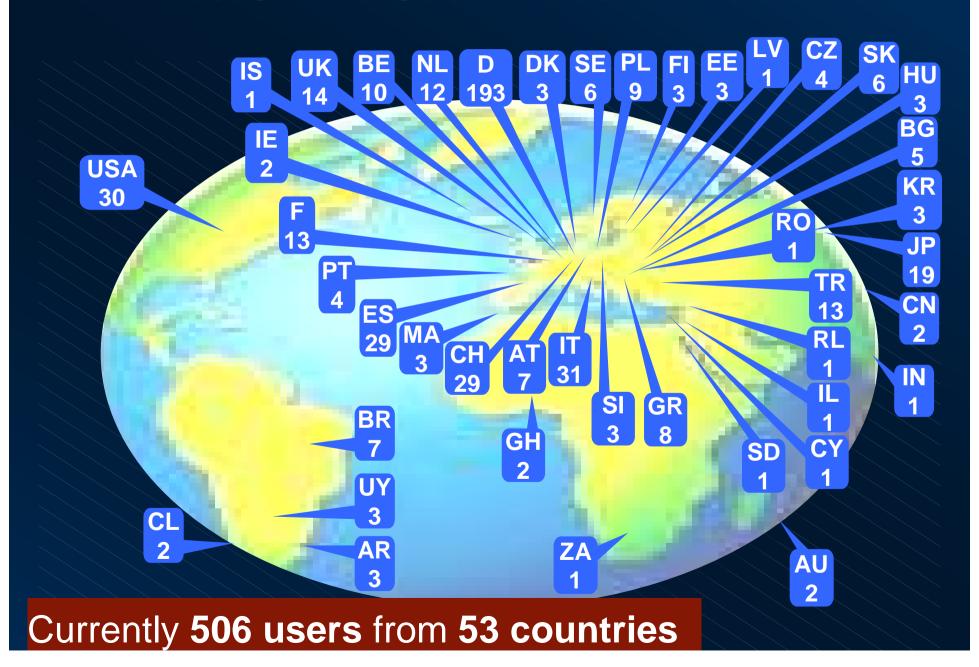
#### Registration to Pesticides-Online

Online-Registration is necessary!



- After Registration only the Forum is can be used.
   Administrator will contact you by email and give you an access!
- The access is free of charge.
- Different access rights to Pesticides-Online:
  - Full access for official labs/organisations, labs/organisation that submit data (e.g. residue findings)
  - Limited access for labs/organisations that submit no data
  - No access for NGO, journalists, private individuals, ...

#### **Pesticides-Online Users Around the World:**



esidue	Profile	Frigi	Strategy Support Coupt			Various for a ta	es	Forum 112 hi		
ars: sticide: mmodity tanisal C igin:	from 2006 to 20	06 Month:		Exclude neg. samples:  Organic:  MRL Violation:	Info Source Lab Local Sort by:		× ×		•	Sorting options for the results
Number ar Month	of Hits Compact List  Lab Location	Wide List   Clear   Frim	Commodity	Botanical Class	Organic Processing Ori	gin mg/kg Min Max	Pos. Samples S	amples Analysed	Pos(%) >	>MLR Info Source
06 1-3	Germany - Erlangen	Acetamiprid	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea	e) Tu	key 0,003	1	10	10	LAB DATA
18 48	Austria Asservance Lab 004	Andreinid	Poppore events (all colors	Calsasanana masa/Calsasana	-\\ Til	Lov 0 407	1	•	22	4 LABBATA
06 46	Germany - Erlangen	Acetamiprid	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea	e)	0,004 0,19	7	12	58	2 <u>LAB DATA</u>
J6 4-6	Germany - Erlangen	Azoxystrobin	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea	Tu	key o,	.4 2	.12	16	LAB DATA
06 46	Austria - Anonymous - Lab-001	Azoxystrobin	Peppers, sweet ~ (all colors	Solanaceous ps (solanacea	e) Tu	key 0,028	1	3	33	LAB DATA
06 1-6	Germany - Anonymous - Lab-004	Azoxystrobin	Peppers, sweet ~ (all • + -	) Solanaceous crops (Solanacea	e) Tu	key 0,01	1	1	100	LAB DATA
06 46	Germany - Stuttgart (CVUA)	Azoxystrobin	P - , a.s., sweet ~ (all colors	) Solanaceous crops (Solanacea	e) Tu	key 0,006	1	10	100	LAB DATA
06 1-3	Germany - Erlangen	Azoxystrobin	The same of the				6	10	60	LAB DATA
06 46	Germany - Erlangen	Bromopropylate	🍘 http://ww	w.pesticides-o	nline.com - ::	5i   _	X 1	5	20	LAB DATA
06 46	Germany - Stuttgart (CVUA)	Buprofezin					1	1	100	LAB DAT
06 46	Germany - Erlangen	Buprofezin	T  0,004/0,005/I	0,01/0,013/0,019	3/0,022/0,192		1	12	8	LAB DATA
06 46	Germany - Erlangen	Cadusafos, Ebufos			·		2	12	16	LAB DATA
06 46	Germany - Erlangen	Carbendazim, Carbendazol	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea	e) Tu	key <u>0,006</u> <u>0,09</u>	<u>6</u> 4	12	33	LAB DATA
06 46	Austria - Anonymous - Lab-001	Carbendazim, Carbendazol	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea	e) Tu	key 0,005	1	3	33	LAB DAT.
06 46	Germany - Stuttgart (CVUA)	Carbendazim, Carbendazol	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea	e) Tu	key 0,009	1	1	5	LAB DAT.
06 1-3	Germany - Erlangen	Carbendazim, Carbendazol	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea		ew refere	nce and	d conta	Ct-	LAB DAT.
06 1-3	Germany - Erlangen	Carbendazim (sum)		) Solanaceous crops (Solanacea	e)					2 LAB DAT.
6 46	Germany - Stuttgart (CVUA)	Carbendazim (sum)		) Solanaceous crops (Solanacea		formation	by clic	king he	ere :	LAB DAT.
6 46	Germany - Erlangen	Carbendazim (sum)	Peppers, sweet ~ (all colors	Solanaceous crops (Solanacea	e) ru	key <u>0,000</u> 0,08	20 7	14	33	LAB DAT
6 46	Germany - Erlangen	Carbofuran	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea	e) Tu	key 0,005	1	12	8	LAB DAT
6 46	Germany - Erlangen	Carbofuran (sum)	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea	e) Tu	key 0,005	1	12	8	LAB DAT
6 1-3	Germany - Erlangen	Chlorothalonil	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea	e) Tu	key 0,007	1	10	10	LAB DAT
	Germany - Erlangen	Chlorpyrifos	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea	e) Tu	key 0,002	1	110	10	LAB DAT
06 1-3		4								
	Germany - Erlangen	Chlorpyrifos	Peppers, sweet ~ (all colors	) Solanaceous crops (Solanacea	e) Tu	key 0,003	1	5	20	LAB DAT

#### Pesticides-Online - Statistics

#### **Residue Data**

>1 000 000 Entries (> 75 000 pos.)

314 Different Commodities

116 Countries of Origin

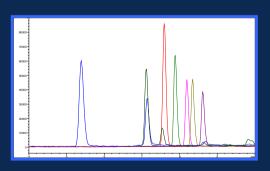
678 Compounds Sought

512 Compounds Found

91 Info Sources (35 labs)







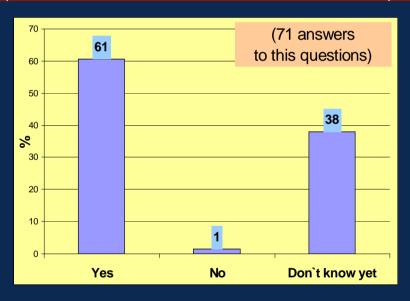


#### Results of Lab-Questionnaire 2006

Website-section of lab-questionnaire:

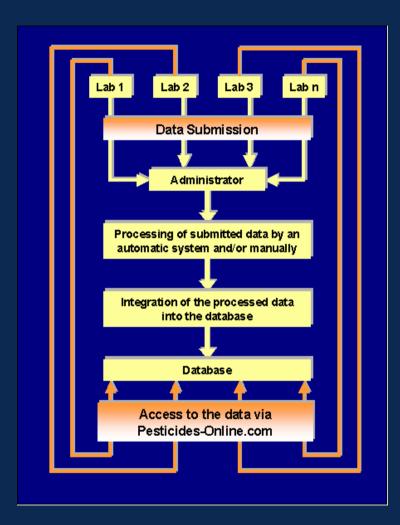
What types of data would you like to see in our common CRL website?

Would you be willing to contribute data to such a database (= RESIDUE FINDINGS Database)?

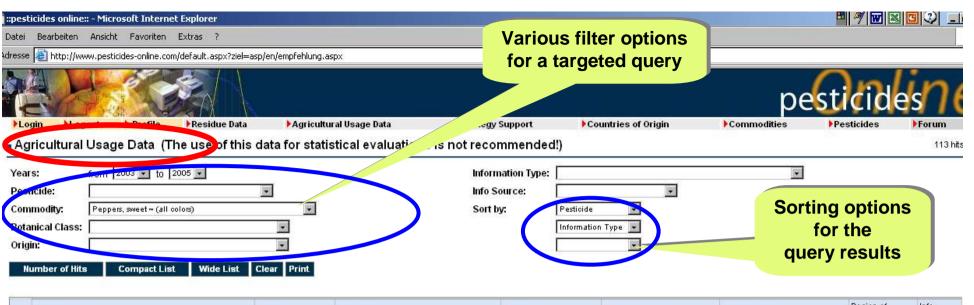




#### Data Submission to Pesticides-Online



- For more convenience, we try to use the data-formats (residue findings) that our users are already utilizing in their lab and translate them into ours.
- Thus, please send us an example of your data so that we can look at it and see what we can do.
- If you don't have a LIMS in your lab, we can also offer you a tool based on Microsoft Access to easily collect your pesticides residue data.
- Which information do we need at least?
  - Commodity (+ Processing)
  - Pesticide sought for + value (negatives also interesting!!!)
  - Year of analysis
  - Country of origin
  - (Other: organic, MRL-violation)



Year Information Type	Pesticide	Application Info	Commodity Botanical Class		Additional Info	Region of Validity	Info Source
2004 Registration for spec. applications/indications	Abamectin (sum), Avermectin	Pre-emergency	Peppers, sweet ~ (all colors)	Solanaceous crops (Solanaceae)	Expires 31.12.2013	Germany	PUBL
2004 Registration for spec. applications/indications	Acrinathrin		Peppers, sweet ~ (all colors)	Solanaceous crops (Solanaceae)		Portugal	PUBL
2003 Special permit according to §47a LMBG/§54 LFGB (Germany)	Acrinathrin	Request: 0,2 mg/kg	Peppers, sweet ~ (all colors)	Solanaceous crops (Solanaceae)	DISMISSED (no permit was issued)	Spain, Andalusia	UNDIS
2004 Registration for spec. applications/indications	Azaconazole		Peppers, sweet ~ (all colors)	(all Solanaceous crops Expires 30.06.2007 (Solanaceae) (2004/2076/EC)		Belgium	S
2003 Registration for spec. applications/indications	Azoxystrobin	Pre-emergency	Peppers, sweet ~ (all colors)			Germany	PUBL
2005 Special permit according to §18a PflSchG (Germany)	Azoxystrobin		Peppers, sweet ~ (all colors)	Solanaceous crops (Solanaceae)	Expires 31.12.2009	Germany	PUBL
2003 Recommendation for use (Official)	Bifenthrin		Peppers, sweet ~ (all colors)	Solanaceous crops (Solanaceae)		Spain, Aragon	WEB
2004 Registration for spec. applications/indications	Bifenthrin		Peppers, sweet ~ (all	Sc V			
2004 Negistration for spec. applications/indications	Differential		colors)	(s View ret	ference and con	tact-	WEB
	Bifenthrin	Request: 0,2 mg/kg	The state of the s	s View rei	terence and con tion by clicking		Same.
2004 Special permit according to §47 a LMBG/§54 LFGB (Germany)		Request: 0,2 mg/kg	colors)  Peppers, sweet ~ (all	s View rei			Same.
Special permit according to §47a LMBG/§54 LFGB (Germany)  2004 Registration for spec. applications/indications	Bifenthrin	Request: 0,2 mg/kg	colors)  Peppers, sweet ~ (all colors)  Peppers, sweet ~ (all	(S VIEW ret			UNDIS
Special permit according to §47 a LMBG/§54 LFGB (Germany)  2004 Registration for spec. applications/indications  2004 Registration for spec. applications/indications	Bifenthrin Bromucon <i>a</i> zole	Request: 0,2 mg/kg  Up to 0,5 mg/kg	colors)  Peppers, sweet ~ (all colors)  Peppers, sweet ~ (all colors)  Peppers, sweet ~ (all	(S VIEW ret (S informa  Solanaceous crops (Solanaceae)  Solanaceous crops		here Ilusia	UNDIS
Special permit according to §47 a LMBG/§54 LFGB (Germany)  2004 Registration for spec. applications/indications  2004 Registration for spec. applications/indications  2003 Special permit according to §47 a LMBG/§54 LFGB (Germany)	Bifenthrin Bromuconszole Buprofezin		colors)  Peppers, sweet ~ (all colors)	(S VIEW ret  (S informa  Solanaceous crops (Solanaceae)  Solanaceous crops (Solanaceae)  Solanaceous crops	tion by clicking	here Ilusia	UNDIS WEB PUBL
2004 Special permit according to §47 a LMBG/§54 LFGB (Germany)  2004 Registration for spec. applications/indications  2004 Registration for spec. applications/indications  2003 Special permit according to §47 a LMBG/§54 LFGB (Germany)  2004 Registration for spec. applications/indications	Bifenthrin  Bromuconazole  Buprofezin  Buprofezin		colors)  Peppers, sweet ~ (all colors)	(S VIEW ret (S informa  Solanaceous crops (Solanaceae)  Solanaceous crops (Solanaceae)  Solanaceous crops (Solanaceae)  Solanaceous crops (Solanaceous crops	Valid for entire EU Expires 30.06.2007	here Iusia	UNDIS WEB PUBL
2004 Special permit according to §47a LMBG/§54 LFGB (Germany)  2004 Registration for spec. applications/indications  2004 Registration for spec. applications/indications  2003 Special permit according to §47a LMBG/§54 LFGB (Germany)  2004 Registration for spec. applications/indications  2003 Recommendation for use (by Agr. Associations)	Bifenthrin  Bromuconazole  Buprofezin  Buprofezin  Cartap		colors)  Peppers, sweet ~ (all colors)	(S VIEW ret  Solanaceous crops (Solanaceae)	Valid for entire EU Expires 30.06.2007	here Iusia Pois Spain Italy	UNDIS WEB PUBL PUBL
Special permit according to §47 a LMBG/§54 LFGB (Germany)  2004 Registration for spec. applications/indications  2004 Registration for spec. applications/indications  2003 Special permit according to §47 a LMBG/§54 LFGB	Bifenthrin  Bromuconazole  Buprofezin  Buprofezin  Cartap  Chlorpyrifos	Up to 0.5 mg/kg	colors)  Peppers, sweet ~ (all colors)	(S VIEW ret  Solanaceous crops (Solanaceae)  Solanaceous crops (Solanaceae)	Valid for entire EU Expires 30.06.2007 (2004/2076/EC)	here Iusia Poi. Spain Italy Italy	UNDIS WEB PUBL PUBL S. WEB

#### Pesticides-Online - Statistics

#### **Agricultural Usage Data**

>16 000 Entries

**194** Commodities

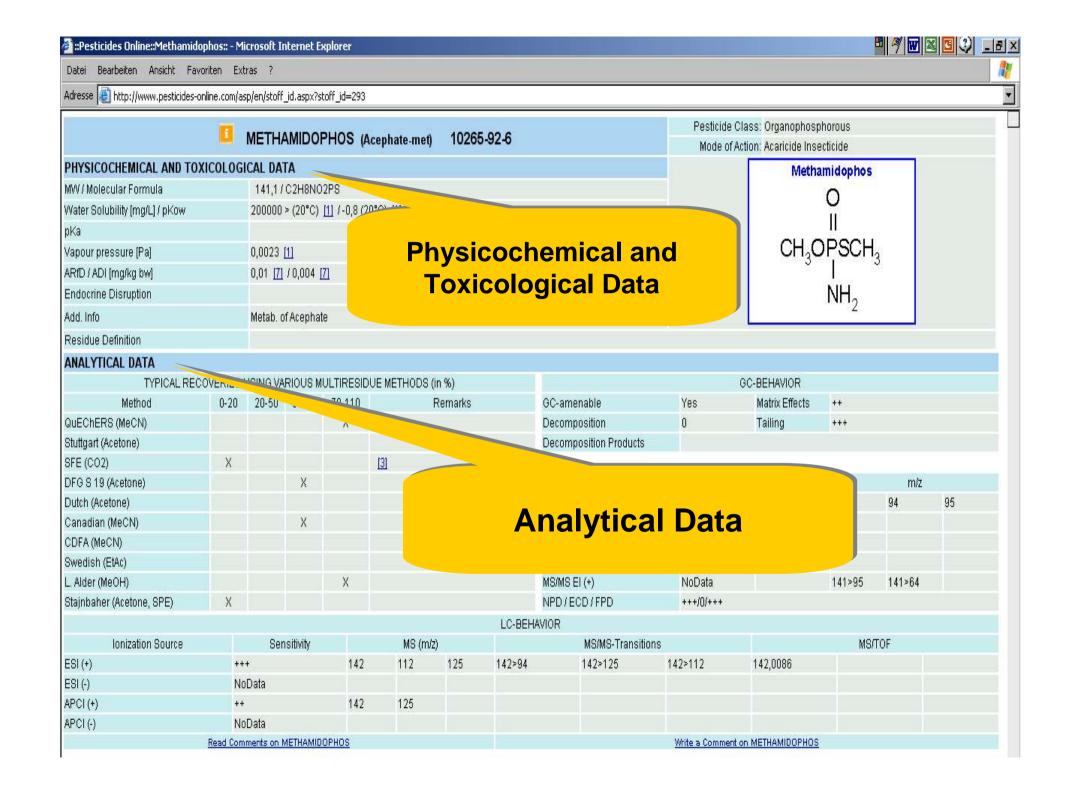
**473** Pesticides

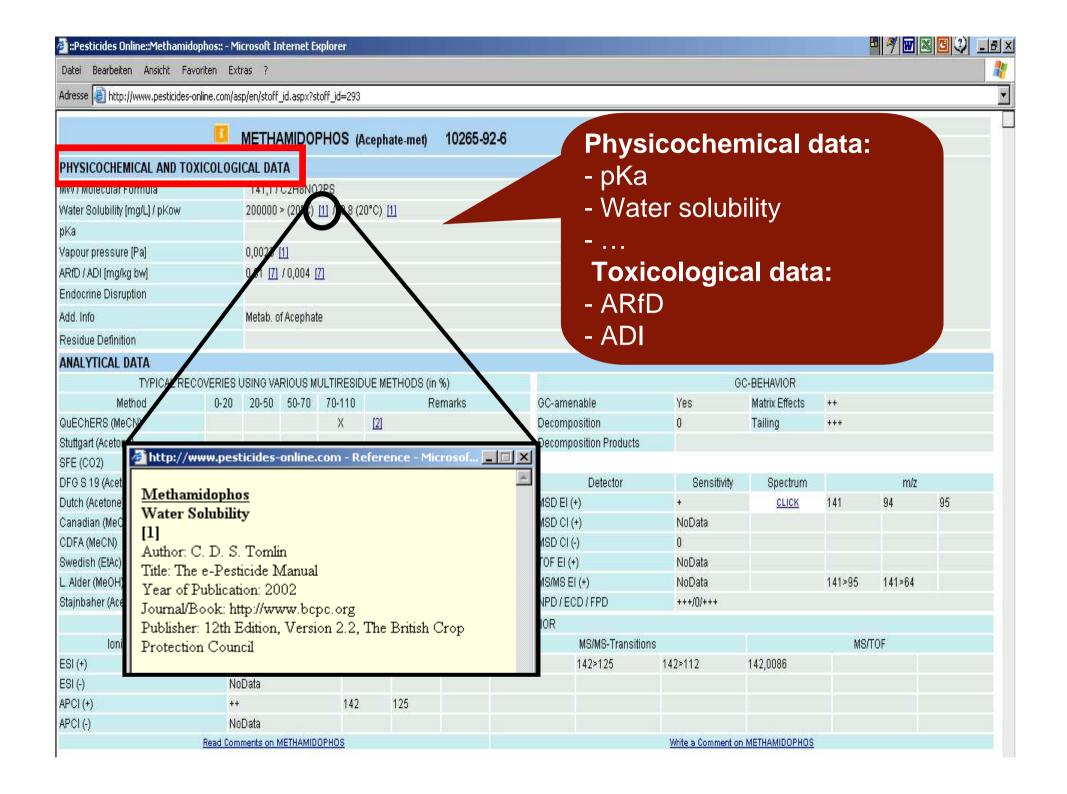
35 Countries/Regions

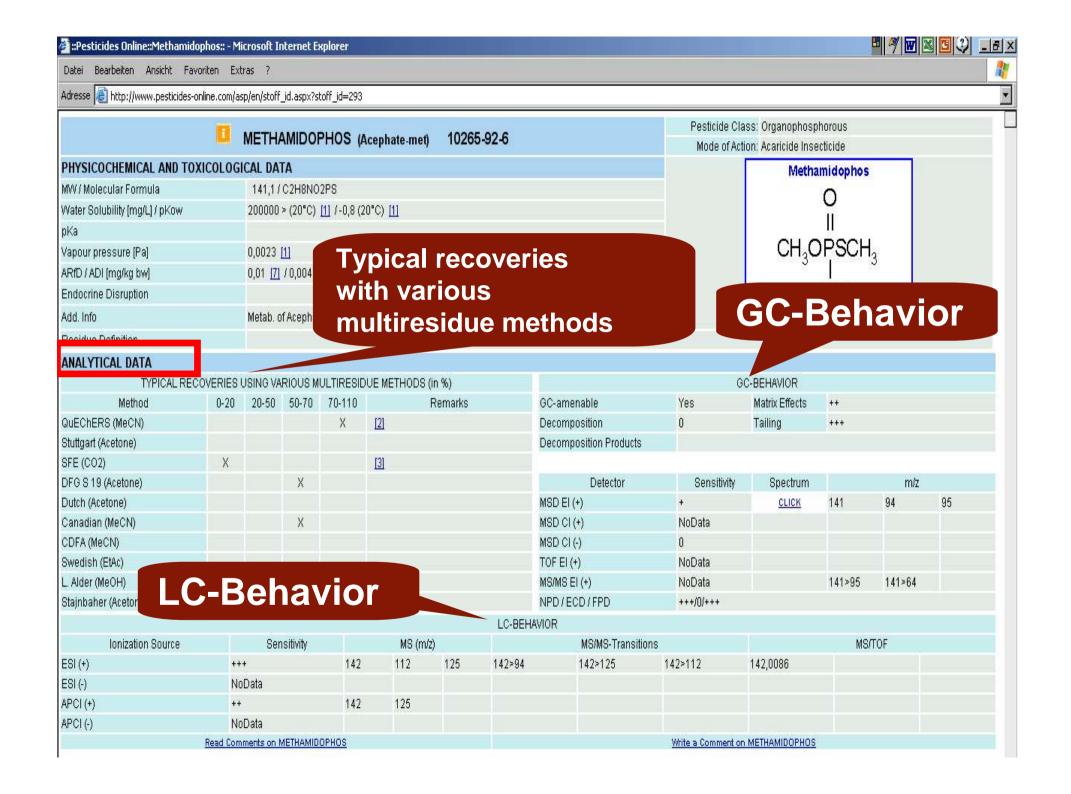


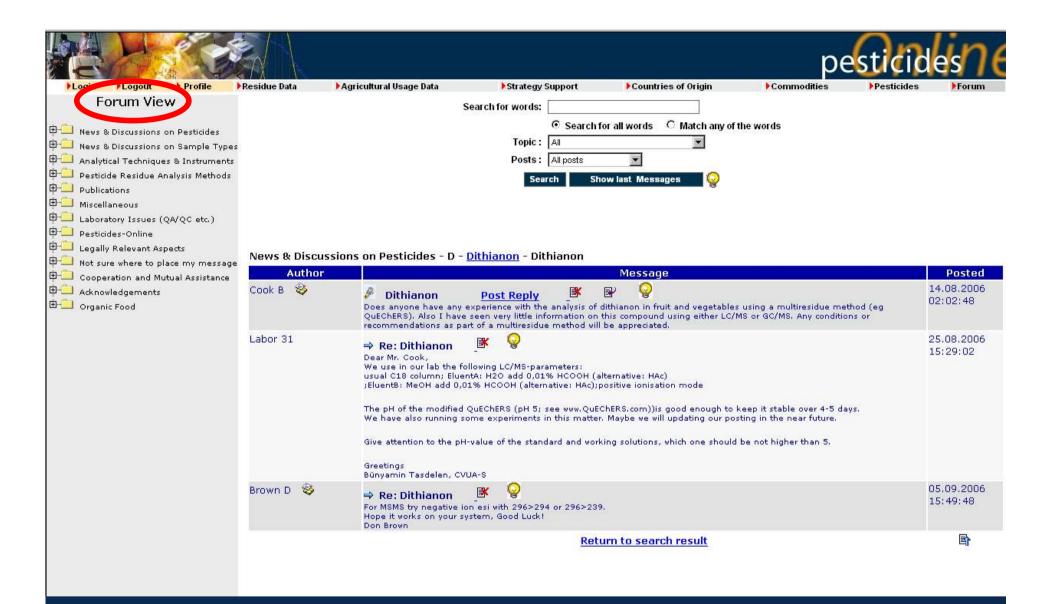


Pesticide	Pesticide Clas	s MW Water solubility [mg/L]	Log Ko	w Volatility [Pa]	GC-amenabl	e Remarks on GC-behaviour	GC-ECD	GC-NPD	GC-MSD	GC-MSD Cl po	os GC-MSD CI neg	ESI pos	ESI neg	APCI pos	s APCI ne
<u>Acrinathrin</u>	Pyrethroid	541,4 0,02	5,6	4,4E-08	Yes		+++	++	++	++	+++	NoData	++	NoData	NoData
<u>Allethrin</u>	Pyrethroid	302,4	4,96	0,00016	Yes		+++	0	++	+++	+++	NoData	NoData	NoData	NoData
<u>Alphamethrin,</u> Alpha-Cypermethrin	Pyrethroid	416,3 0,01	6,94	2,3E-05	Yes		+++	++	+++	NoData	+++	NoData	NoData	NoData	NoData
<u>Bifenthrin</u>	Pyrethroid	422,9 0,001	6	2,4E-05	Yes		+++	0	+++	+++	+++	NoData	NoData	NoData	NoData
<u>Bioallethrin,</u> d-trans-Allethrin	Pyrethroid	302,4 4,6	48-				1	THE STATE OF THE S				NoData	NoData	NoData	NoData
<u>Bioresmethrin</u>	Pyrethroid	338,4 0,3			Cli	ck here t	-0	0	s 41	00		ta	NoData	NoData	NoData
Cyfluthrin (incl. beta-)	Pyrethroid	434,3 0,002			CII	CK HEIE I		C	7 LI	IC			NoData	NoData	NoData
Cyfluthrin, beta-					Da	atiala D				-466			NoData	NoData	NoData
<u>Cyhalothrin</u>					.Pe	sticide D	ata	1 5	ne	et			NoData	NoData	NoData
Cyhalothrin, lambda-	Pyrethroid												NoData	NoData	NoData
<u>Cypermethrin</u>	Pyrethroid	416,3 0,004											NoData	NoData	NoData
<u>Deltamethrin,</u> Decamethrin	Pyrethroid	505,2 0,0002		Dhu		ah amai an I. T	Γ <u>_</u> :	I	- a:	م امم	اء ما		NoData	NoData	NoData
<u>Empenthrin</u>	Pyrethroid	274,4 0,11		Pny	SICO	chemical, 1	OXI	COI	ogi	cai a	na		NoData	NoData	NoData
<u>Fenfluthrin</u>	Pyrethroid	389,2		•	۸ .۵		. 16100	-1:-	[	<b>.</b>			NoData	NoData	NoData
<u>Fenpropathrin</u>	Pyrethroid	349,4 0,014			An	alytical Info	orma	atic	n	Or			NoData	NoData	NoData
Fenvalerate/Esfenvalerate (RR/SS)	Pyrethroid			70	E Da			<b>M</b>	4 <b>a</b> la	_1 <b>:</b> 4_			NoData	NoData	NoData
Fenvalerate/Esfenvalerate (RS/SR)	Pyrethroid			19	o Pe	sticides a	na i	vie	tap	olite	S		NoData	NoData	NoData
Fenvalerate/Esfenvalerate (sum)	Pyrethroid	419,9 0,01										a	NoData	NoData	NoData
<u>Flucythrinate</u>	Pyrethroid	451,5 0,5										oata	NoData	NoData	NoData
<u>Flumethrin</u>	Pyrethroid	510,4													
<u>Fluvalinate</u>	Pyrethroid	502,9 0,005	3,8	1,3E-05	Yes		+++	++	++	+	+++	NoData	NoData	NoData	NoData
Fluvalinate, tau-	Pyrethroid	502,9 0,001	4,28	9E-11	Yes		+++	++	+++	++	+++	NoData	NoData	NoData	NoData
<u>Permethrin</u>	Pyrethroid	391,3 0,006	6,1		Yes	2 isomers (cis and trans)	+	0	+++	NoData	+	NoData	NoData	NoData	NoData
<u>Prallethrin</u>	Pyrethroid	300,4 8	4,49	1,3E-05	Yes		+++	0	+++	NoData	+++	NoData	NoData	NoData	NoData
<u>Resmethrin</u>	Pyrethroid	338,4 0,0379	5,43	1E-05			NoData	NoData	NoData	NoData	NoData	NoData	NoData	NoData	NoData
<u>Tefluthrin</u>	Pyrethroid	418,7 0,02	6,4	0,0084	Yes		+++	0	+++	+++	+++	NoData	NoData	NoData	NoData
<u>Tetramethrin,</u> Phthalthrin	Pyrethroid	331,4 1,83	4,6	0,0021	Yes	2 peaks	+++	++	+++	++	+++	NoData	NoData	NoData	NoData
<u>Tralomethrin</u>	Pyrethroid	665 0,08	5	4,8E-09	Yes	As deltamethrin	+++	+	++	NoData	+++	NoData	NoData	NoData	NoData
															_





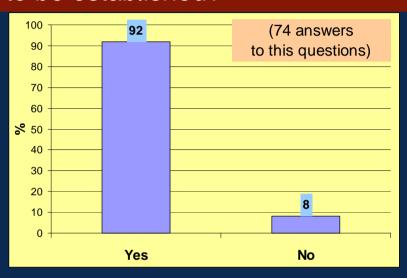




Unfortunately the Forum is not much used up to now. But ...

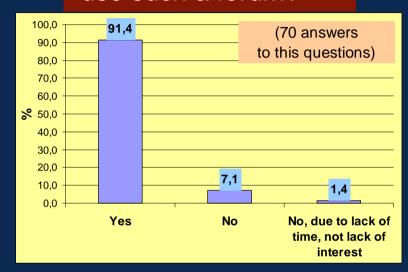
#### Results of Lab-Questionnaire 2006

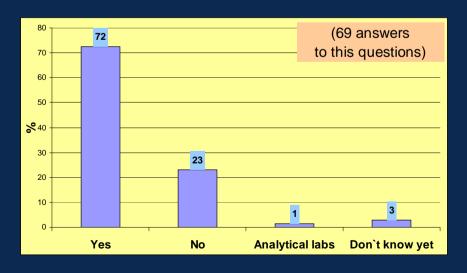
Would you like a discussion forum to be established?



Would you like the forum to be accessible also to colleagues outsite the CRL/NRL-Network (e.g. colleagues from countries outside the EU, from private labs...)?

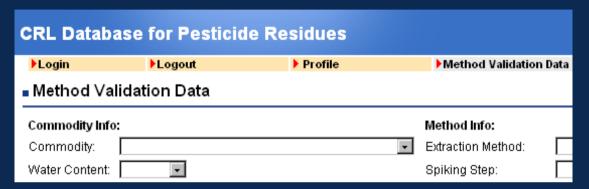
Would you be willing to use such a forum?





#### **Method Validation Database**

#### New project started this year:

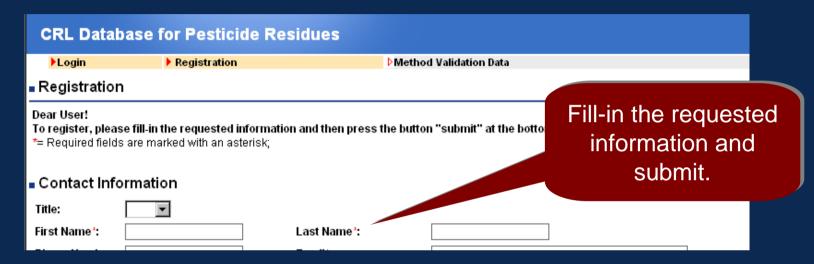


Test Version Online!

- → Database for storage of data generated within the aim of method validation experiments in various laboratories.
- ⇒ Enables the systematic collection and customized retrieval of data produced during method validation in different laboratories.

#### Registration to Method Validation Database

Online-Registration will be necessary!



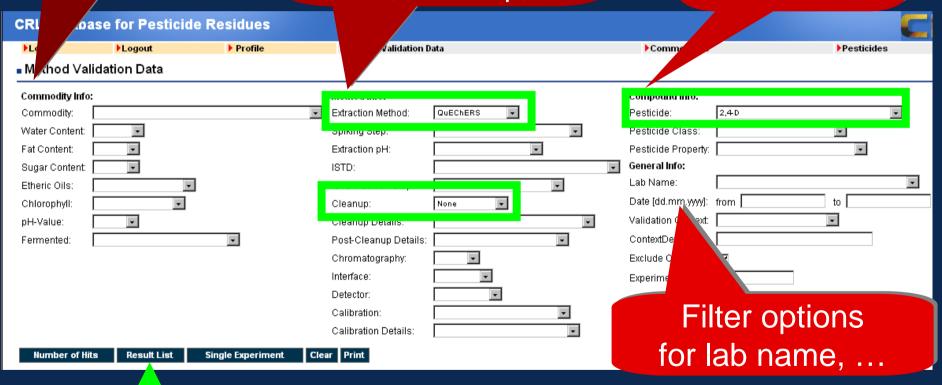


#### Query Section: Various filter options for a targeted query

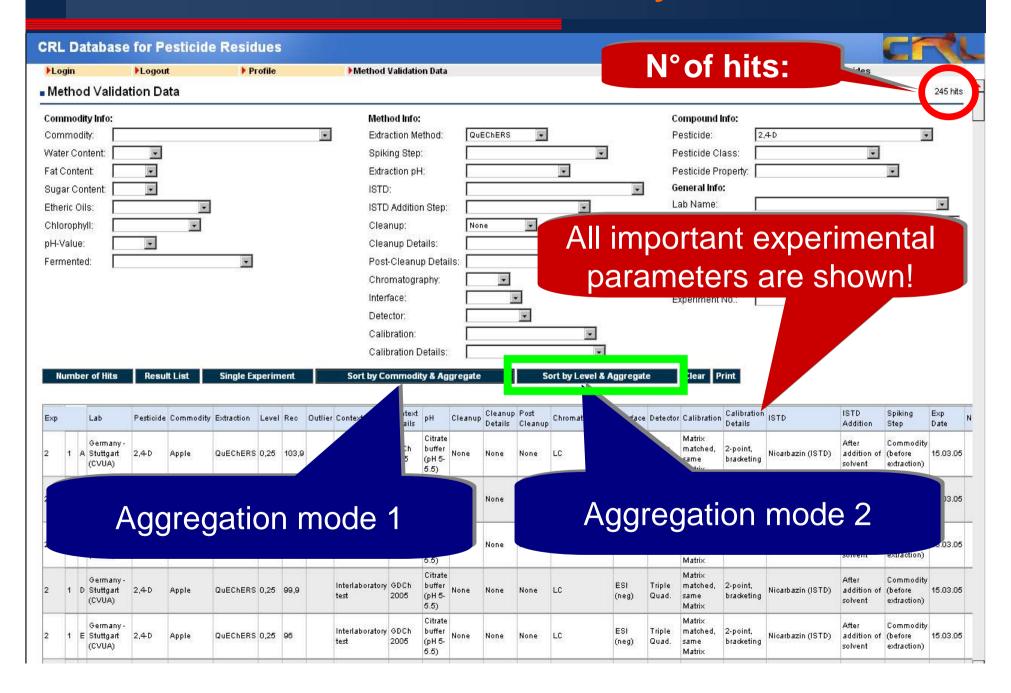
Filter options for commodity

Filter options for extraction method, ISTD, Cleanup, ...

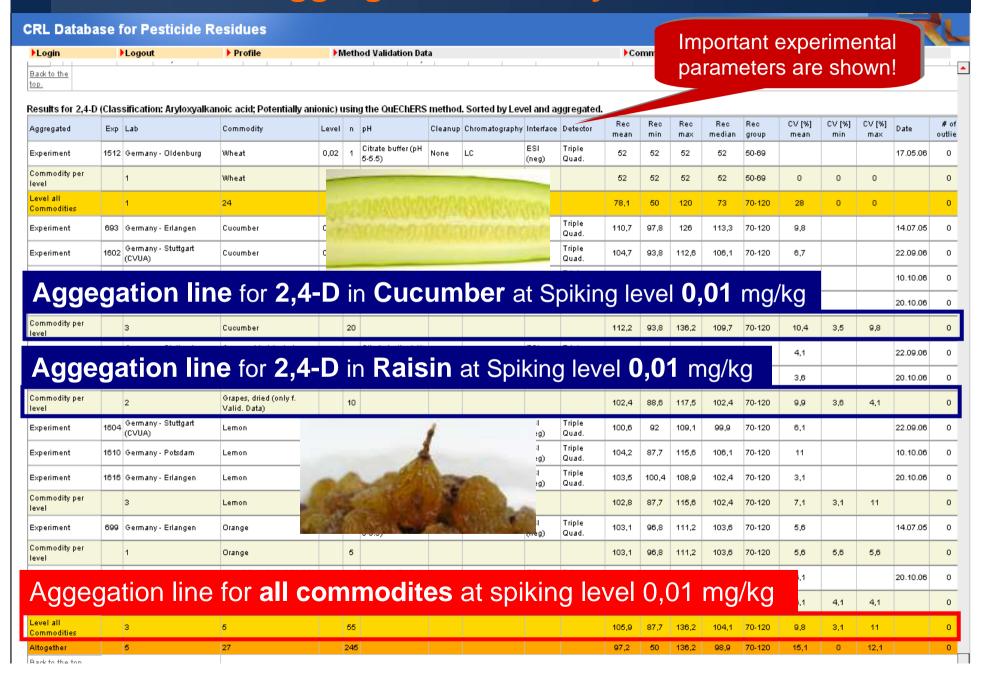
Filter options for compound



#### 1. Result list of individual recovery values



#### 2. List with aggregated recovery data



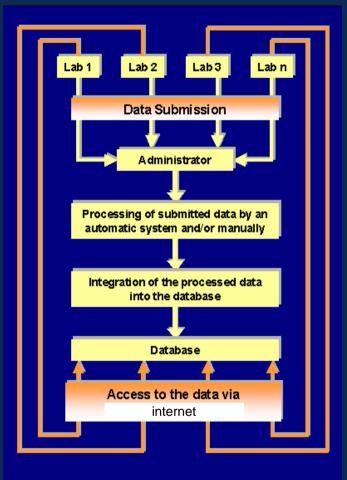
#### Method Validation Database - Statistics

- currently only data for QuEChERS-Method, but Method Validation Database is flexible to receive data from any other method!
- Recovery data for QuEChERS-Method:
  - 478 compounds
  - 44 commodities (apple, raisin, lemon, ...)
  - 17 labs data submitted
- Recovery data of S19- and ChemElute will be submitted soon from different labs.

You're welcome to submit validation data from your lab!

But how to submit?

#### Data Submission to Method Validation Database



- We offer a Data Submission-Format
   (→ Excel-file)
   If you are interested, please contact us!
- If you have huge amounts of recovery data, we will try to transform your data into our data-format.



# Thank you very much for your Attention!