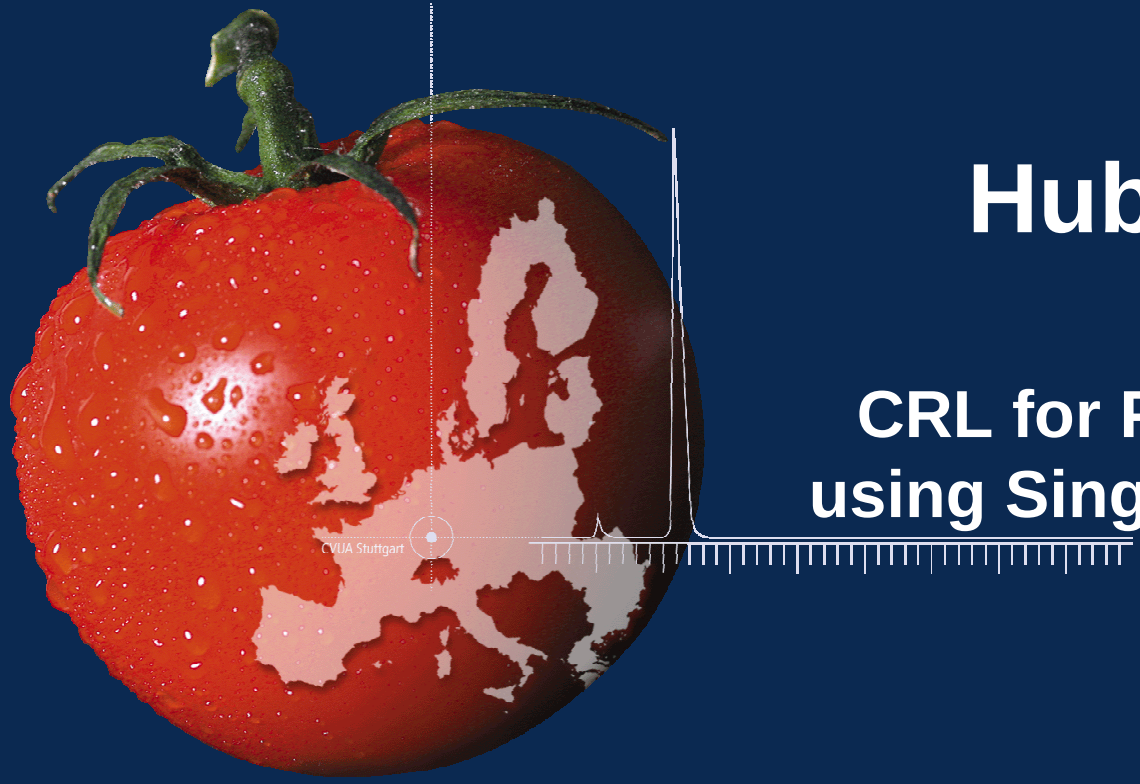
CRL-Web-Service

An Information Exchange Platform aiming at Strengthening the CRL/NRL-Network



Hubert Zipper

CRL for Pesticide Residues using Single Residue Methods

Main Tasks of the CRLs for Residues of Pesticides

Summary (among others)*:

- **To promote research, development and validation of new analytical methods**
- **To establish a network between**

  CRLs ↔ NRLs ↔ official control labs
- **To inform NRLs about new advances in methods and equipment**

→ Creation of a laboratory network

→ Coordination of information flow within it.

* See www.crl-pesticides.eu / About CRL

Principle structure of the CRL-Web-Service

CRL-Web-Service

Principle structure of the CRL-Web-Service

Interest Group in CIRCA:

Communication & Information Resource Centre Administrator

CRLs for Residues of Pesticides

CRL Data Pool

Data Pool
Community Reference Laboratories for Residues of Pesticides

www.crl-pesticides-datapool.eu

Member-Area [restricted access]

Member-Area [restricted access]

CRL-Web-Service

CRL Portal

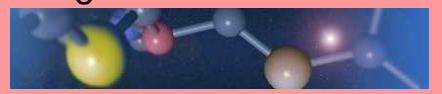
www.crl-pesticides.eu

CRL-FV
Fruits & Vegetables

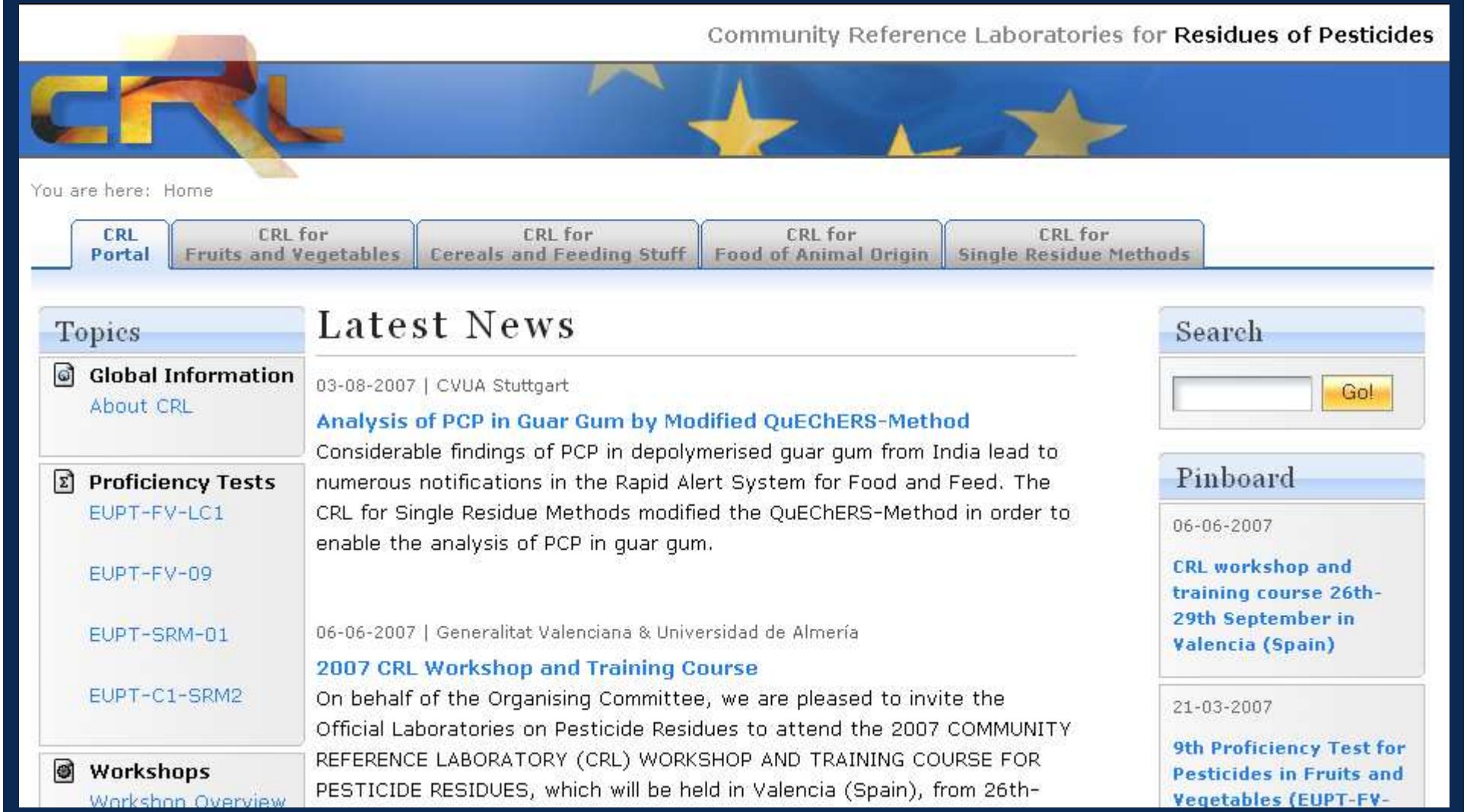
CRL-CF
Cereals & Feeding Stuff

CRL-AO
Food of Animal Origin

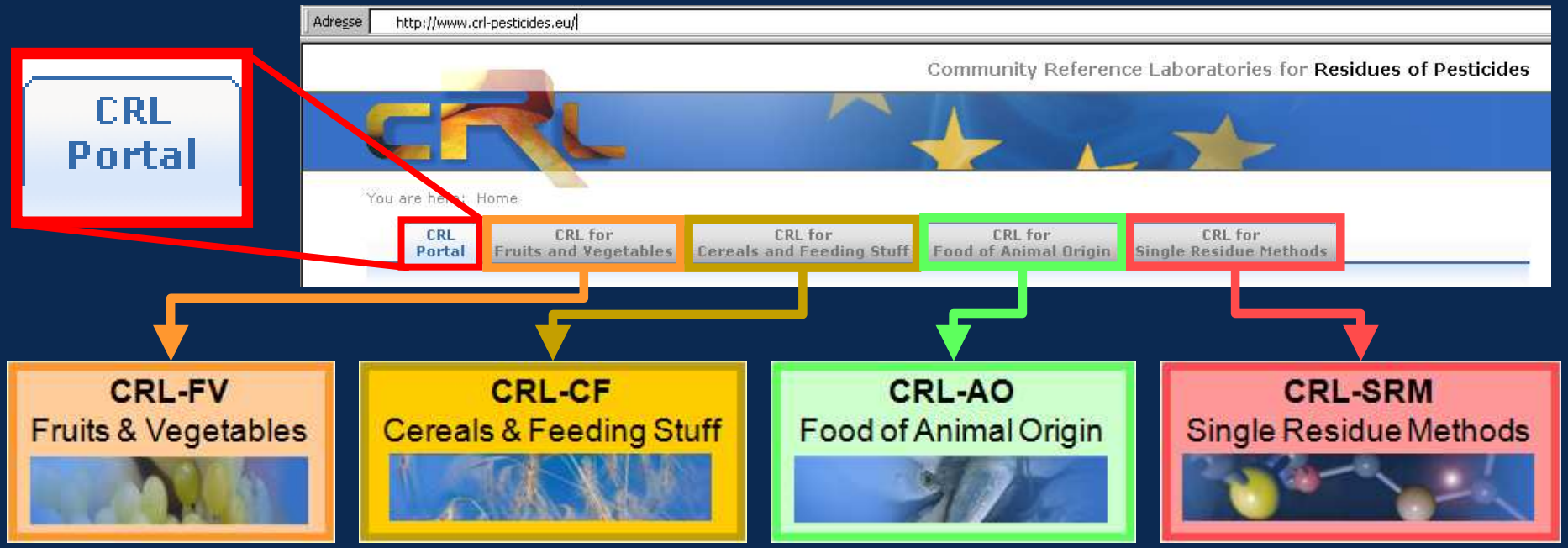
CRL-SRM
Single Residue Methods



CRL Portal - www.crl-pesticides.eu



CRL Portal - www.crl-pesticides.eu



- One common entrance-website for all four CRLs
- In a second layer, each of the four CRLs has an individual website (containing its own specific information)

⇒ A single website installed for the 4 CRLs
⇒ Easy navigation between the Central-Homepage and the 4 specific CRL-Websites.

CRL Portal - www.crl-pesticides.eu

CRL Portal is directed to experts working …

- **within the CRL/NRL/Official Labs network (primarily)**

  Result of CRL-Survey 2006:

  labs stated that it is essential, very useful or useful that the CRL Portal entails announcements about:

  a) **new pesticides and methods** 98% (45 %, 33 %, 20 %);
  b) **new legislations** 98% (43 %, 32 %, 23 %);
  c) **meetings** 98% (23 %, 38 %, 38 %).

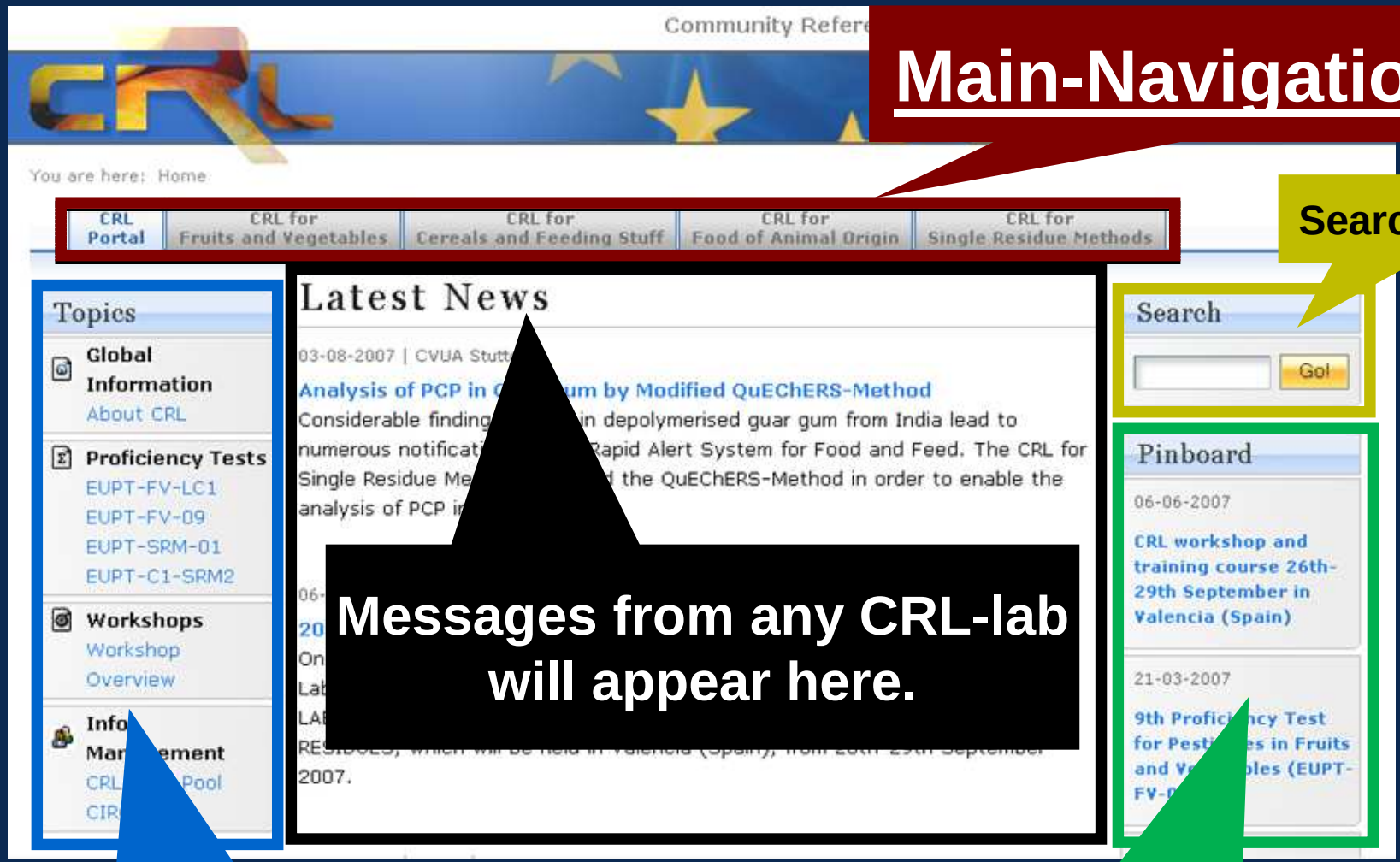
- **in the field of pesticide residues**
- **other visitors (incl. general public) are offered brief info about the CRL's mission and activities**

CRL Portal - Information offered

Content (among others):

- **basic introductory information about the CRLs**
- **news (new methods) and announcements (workshops)**
- **links to CRL-run databases (e.g. CRL Data Pool)**
- **links to hidden documents within the CIRCA platform**

CRL Portal - Principle Structure



Main-Navigation bar

Search-Button

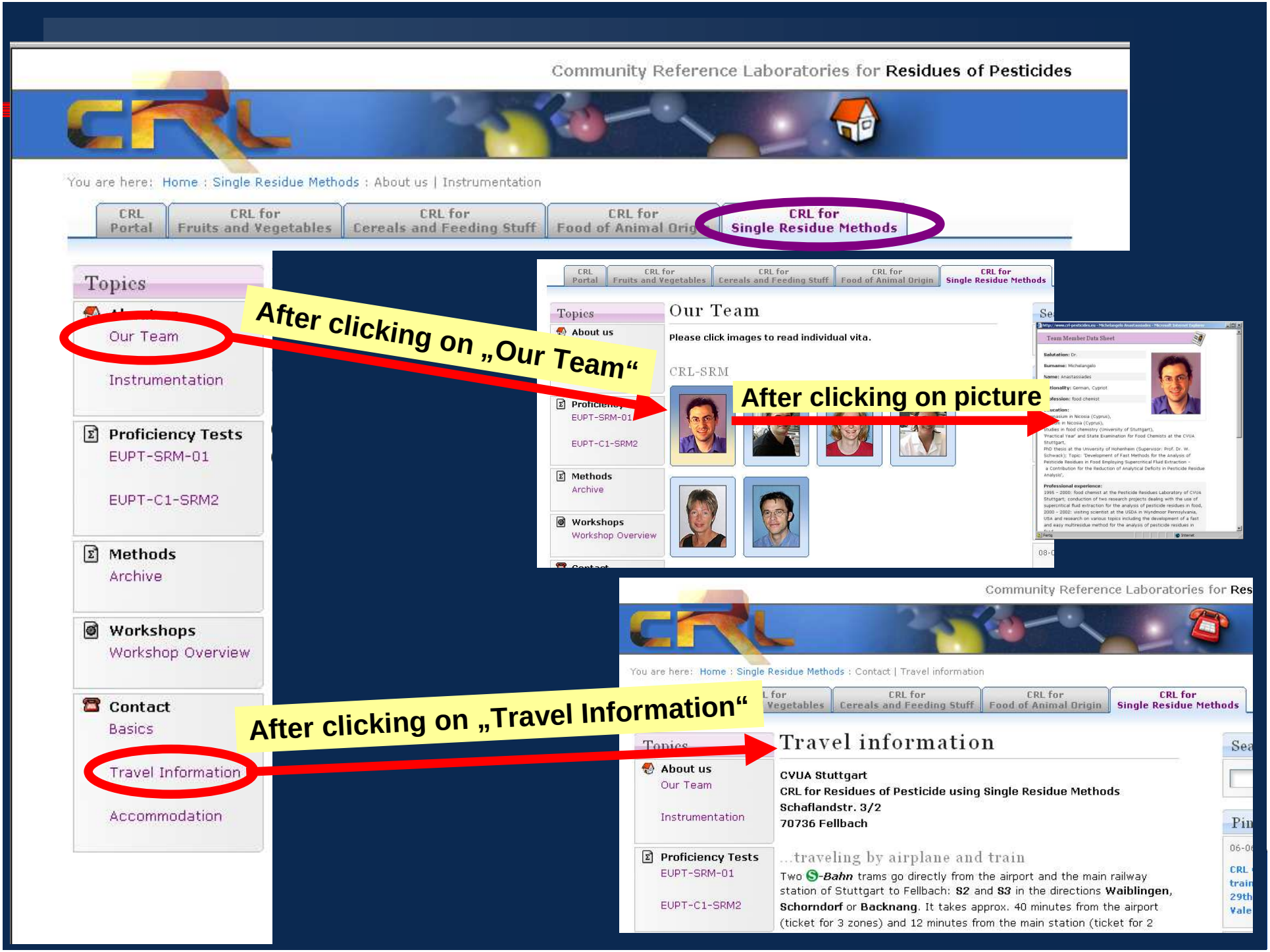
Messages from any CRL-lab will appear here.

Sub-Navigation bar

Pinboard-Area

for spec. announcements

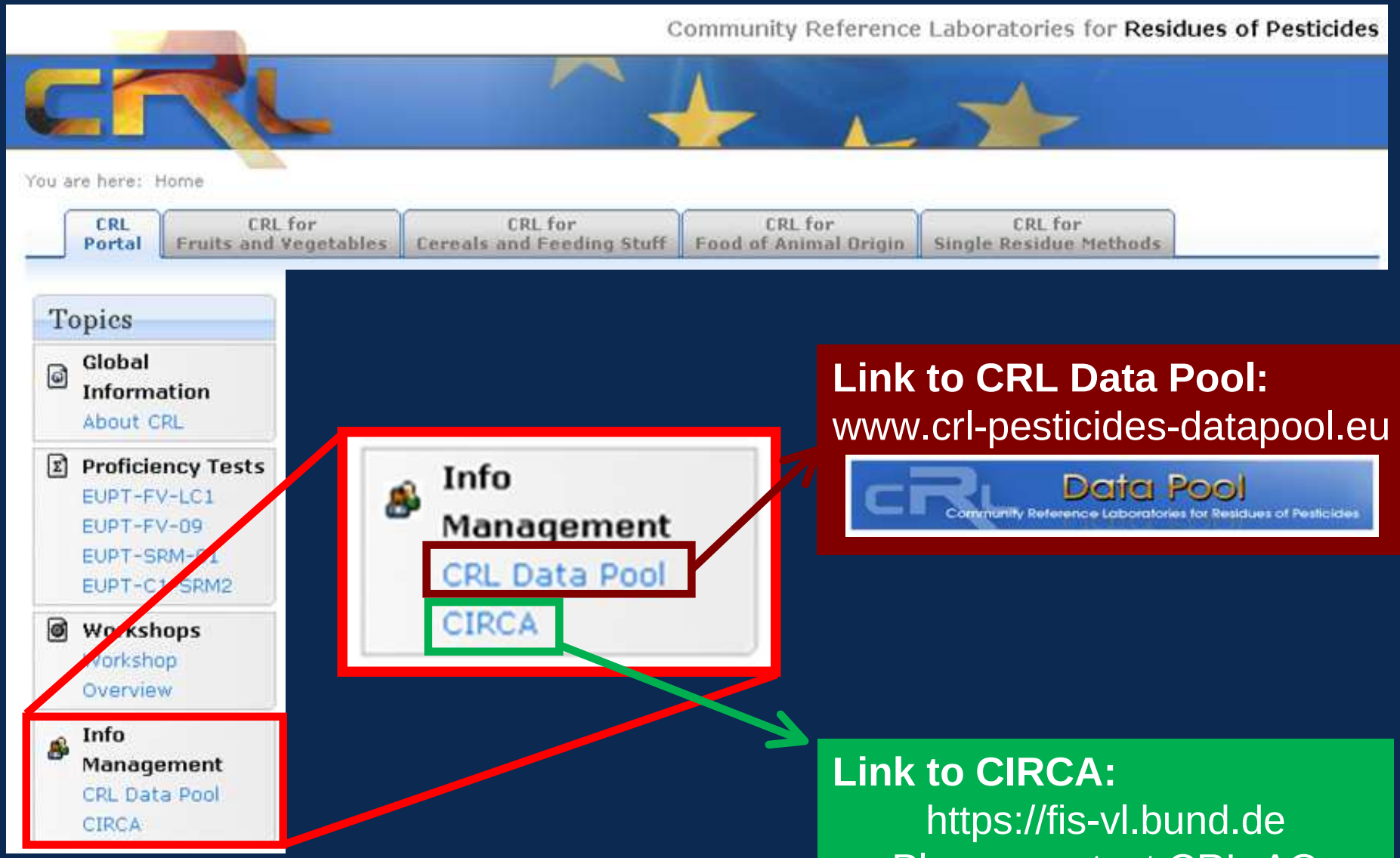
CRL Portal - Features of specific layers


Community Reference Laboratories for Residues of Pesticides
You are here: Home : Single Residue Methods : About us | Instrumentation
CRL Portal
CRL for Fruits and Vegetables
CRL for Cereals and Feeding Stuff
CRL for Food of Animal Origin
CRL for Single Residue Methods
Topics
Our Team
Instrumentation
Proficiency Tests
EUPT-SRM-01
EUPT-C1-SRM2
Methods
Archive
Workshops
Workshop Overview
Contact
Basics
Travel Information
Accommodation
After clicking on „Our Team“
Our Team
Please click images to read individual vita.
CRL-SRM
After clicking on picture
After clicking on „Travel Information“
Travel information
CVUA Stuttgart
CRL for Residues of Pesticide using Single Residue Methods
Schaflandstr. 3/2
70736 Fellbach
...traveling by airplane and train
Two S-Bahn trams go directly from the airport and the main railway station of Stuttgart to Fellbach: S2 and S3 in the directions Waiblingen, Schorndorf or Backnang. It takes approx. 40 minutes from the airport (ticket for 3 zones) and 12 minutes from the main station (ticket for 2

CRL Portal - Technical information

- Database used: **Microsoft Access 2000**
- All web-pages are **dynamically-generated**; browser language is according to XHTML 1.0
- The scripting language is "**Active Server Pages**"; server based on Windows platform with "Jet OLEDB 4.0" provider
- The CRL-website is **compatible to the different web browsers**:
  - → Mozilla Firefox (1.5 and higher)
  - → Mircosoft Internet Explorer 7.0
  - → Opera (8.54 and higher)
  - → Netscape 7.1

CRL Portal - Link to CIRCA / CRL Data Pool



CRL Data Pool: Collection/Distribution of Information

CRL Data Pool

www.crl-pesticides-datapool.eu

Aim of CRL Data Pool:

→ provide analysts with a convenient and efficient access to information needed for proper decision-making in pesticide residue analysis

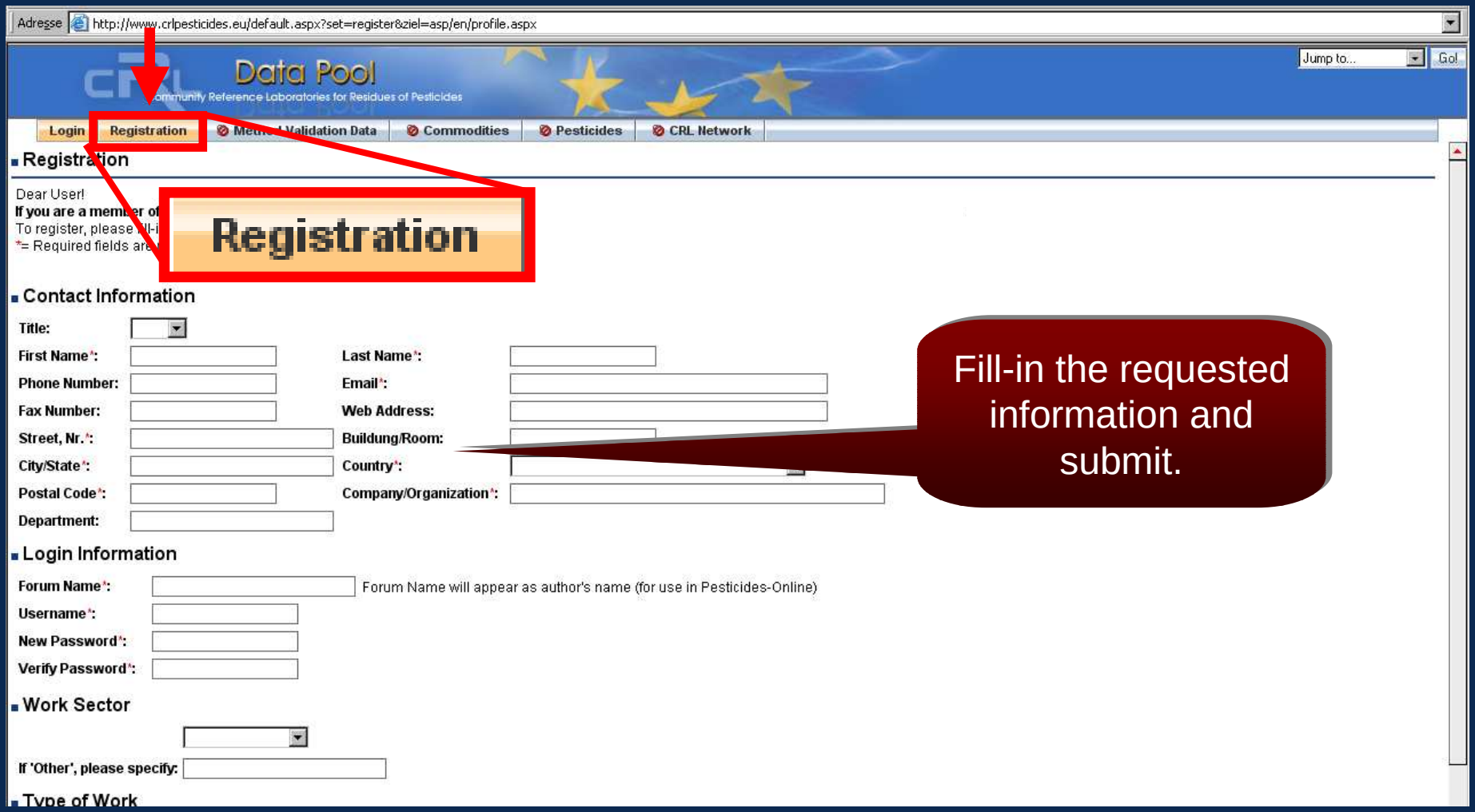
Data Pool of the CRL for Residues of Pesticides

- Website: ***www.crl-pesticides-datapool.eu***

- CRL Data Pool contains the following databases:
  - → **Method Validation Data**
  - → **Pesticides**
  - → **Commodities** (not yet installed)
  - → **CRL Network** (not yet installed)
  - → **Analytical Methods** (not yet installed; in cooperation with *ad hoc* working group on Methods of Analysis and Sampling, CCPR)

CRL Data Pool: How to use the service?

- Online-Registration to the CRL Data Pool is necessary!



→ You will be contacted by the administrator.

CRL Data Pool: Method Validation Data

- Online since April 2007
- Database for storage of data generated within the aim of method validation experiments in various laboratories.
- Enables

  → systematic collection (names of pesticides, commodities, methods of analysis, spiking levels, recovery results in %, …)

  → customized retrieval

  of data produced during method validation in different laboratories.

Method Validation Data: How to use the service?

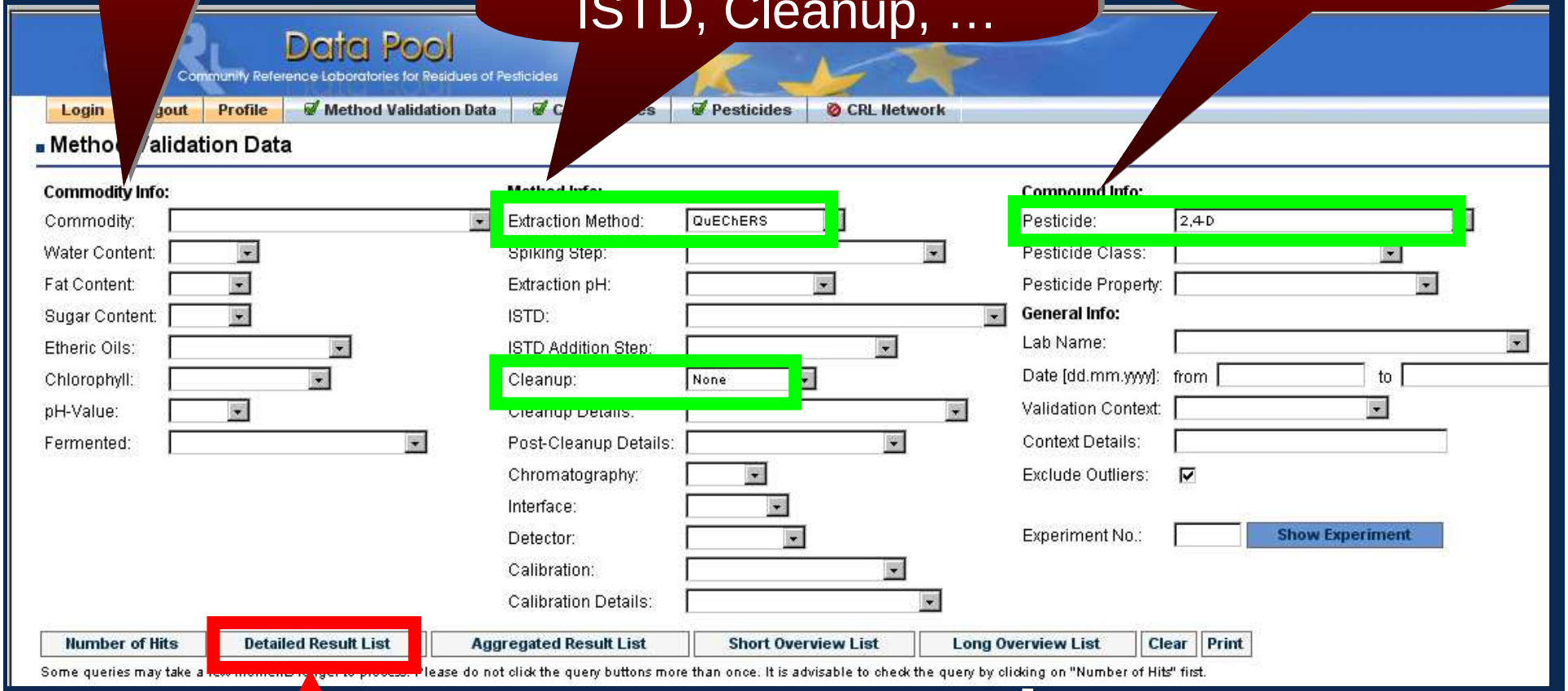
- After login, click on button „Method Validation Data“!

Method Validation Data: Query Section

Filter options for commodity

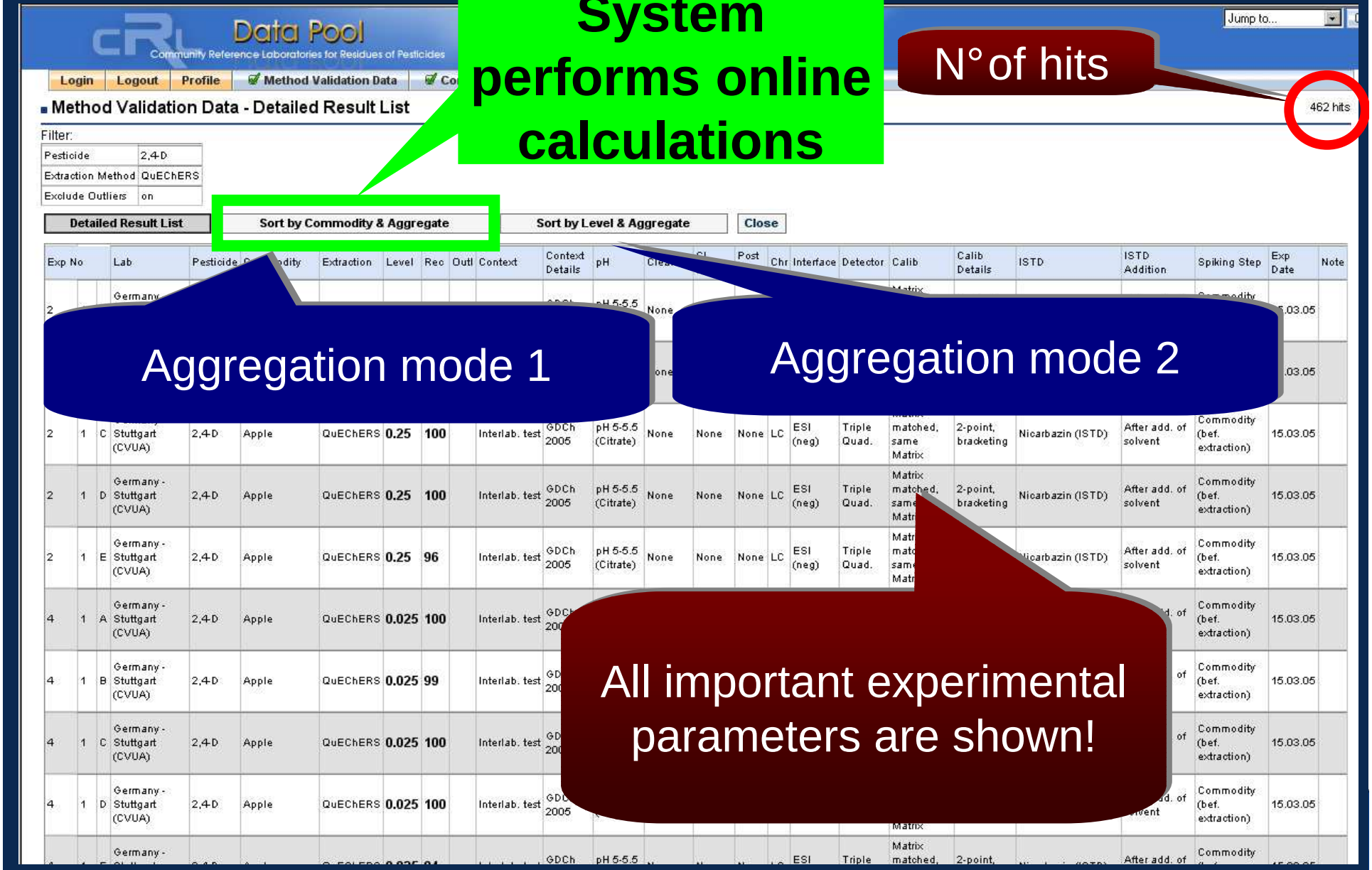
Filter options for extraction method, ISTD, Cleanup, …

Filter options for compound



Buttons allowing various aggregation steps

Method Validation Data: „Detailed Result List“



Method Validation Data: „Sort by Commodity & Aggregate“

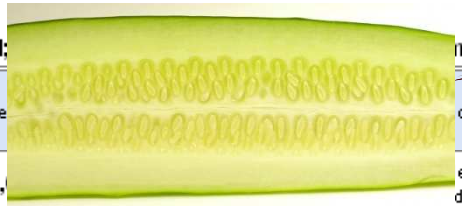
→ Database performs online calculations.

Login | Logout | Profile | Method Validation Data | Commodities | Pesticides | CRL Network

■ Method Validation Data - Detailed Result List

Result List | Sort by Commodity & Aggregate | Sort by Level & Aggregate | Close

All important experimental parameters are shown!



Results for 2,4-D (Classification: Aryloxyalkanoic acid: ... method. Sort ... by Commodity and aggregated.

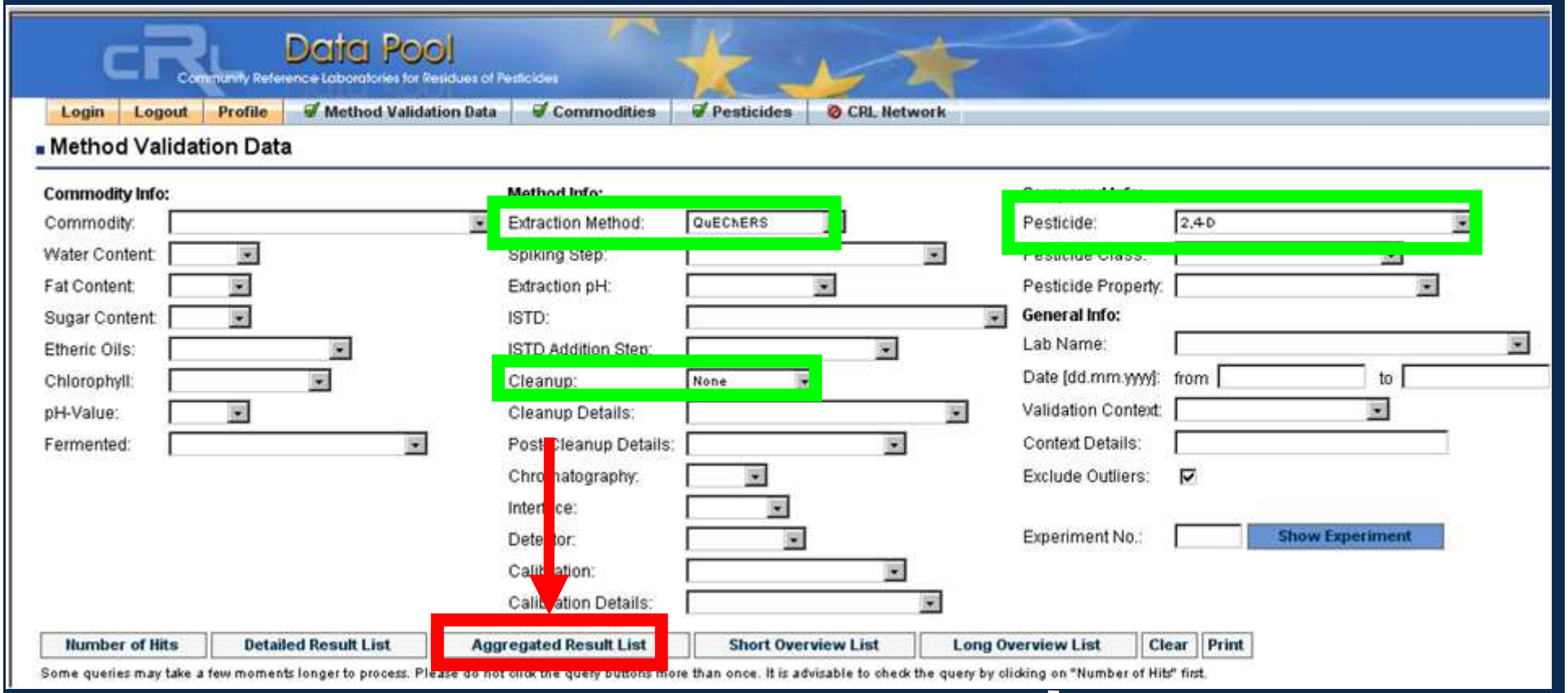
Aggregated	Exp	Lab	Commodity	Le	...	ctor	Rec mean	Rec min	Rec max	Rec median	Rec group	CV [%] mean	CV [%] min	CV [%] max	Date	# of outliers
Experiment	2020	Latvia - Riga	Cucumber	0,		e d.	108	91	126	104	70-120	15,2			01.11.06	0
															.11.06	0
One level		5		**0,01**	30		**107**	82	136	106	70-120	13,9	3,5	15,2		0
All levels		5		**3**	61		**105**	72	136	105	70-120	13,3	0	15,2		0
Experiment	2019	Germany - Hagen	Grapes, dried (only f. Valid. Data)	**0,01**	4	pH 5-5.5 (Citrate) None LC ESI (neg) Triple Quad.	**103**	86	128	99	70-120	19,7			02.11.06	0
																0
One level		4		**0,01**	19		**101**	86	128	97	70-120	11,8	3,6	19,7		0
Experiment	1615	Germany - Erlangen	Wheat flour (only Valid. Data)			riple uad.	**89**	86	92	90	70-120	3,2			20.10.06	0
One level		1					**89**	86	92	90	70-120	3,2	3,2	3,2		0
Experiment	1614	Germany - Erlangen	Wheat flour (only Valid. Data)			riple uad.	**100**	94	105	99	70-120	4,1			20.10.06	0
One level		1					**100**	94	105	99	70-120	4,1	4,1	4,1		0
																0
Altogether		7	27	**5**	284		**98**	50	136	99	70-120	14,9	0	19,7		0

Aggegation line for **2,4-D** in **Cucumber** at Spiking level **0,01** mg/kg

Aggegation line for **2,4-D** in **Raisin** at Spiking level **0,01** mg/kg

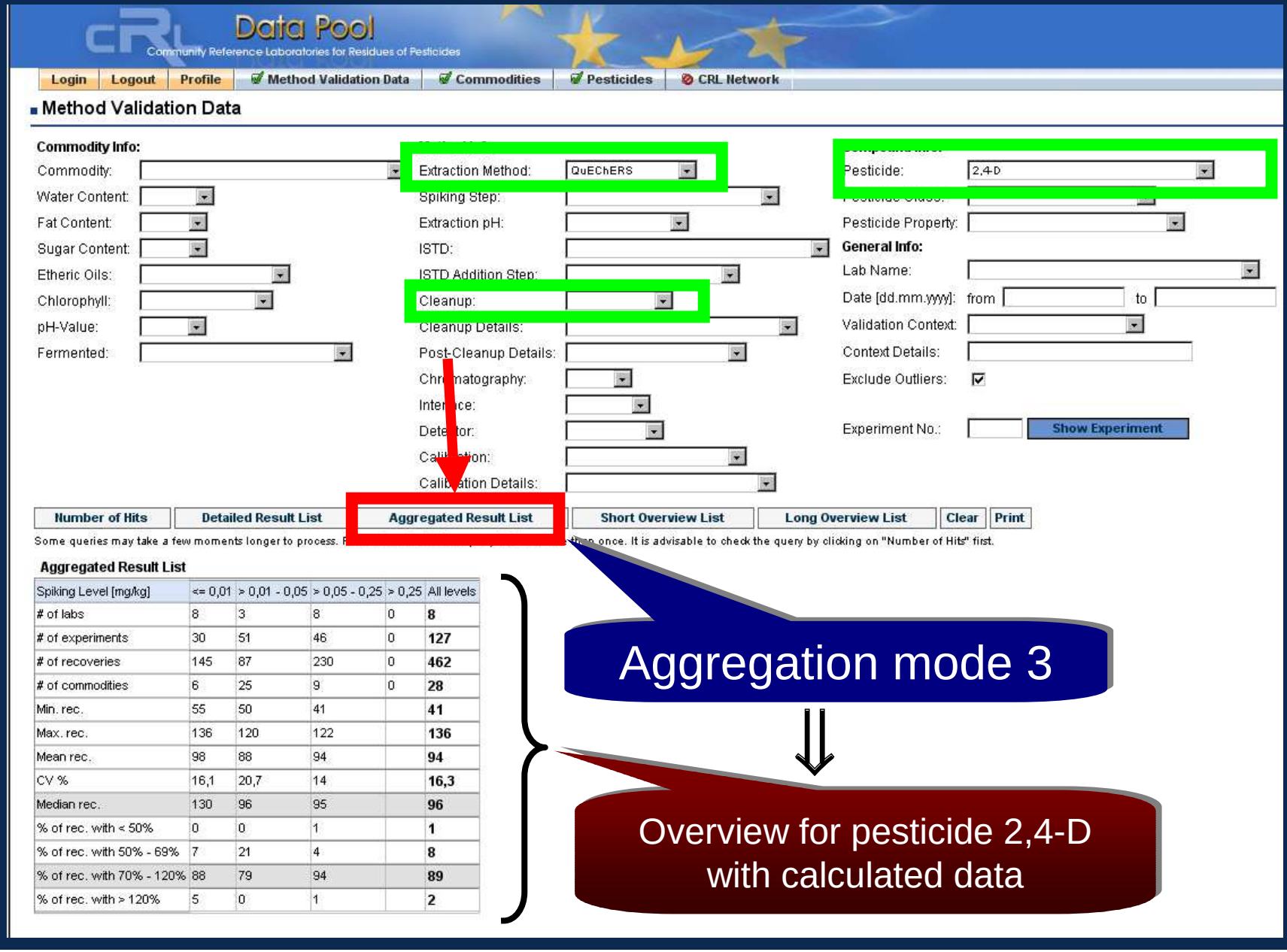
Aggegation line for **all commodites** at various spiking levels

Method Validation Data: „Aggregated Result List“



Buttons allowing various aggregation steps

Method Validation Data: „Aggregated Result List“



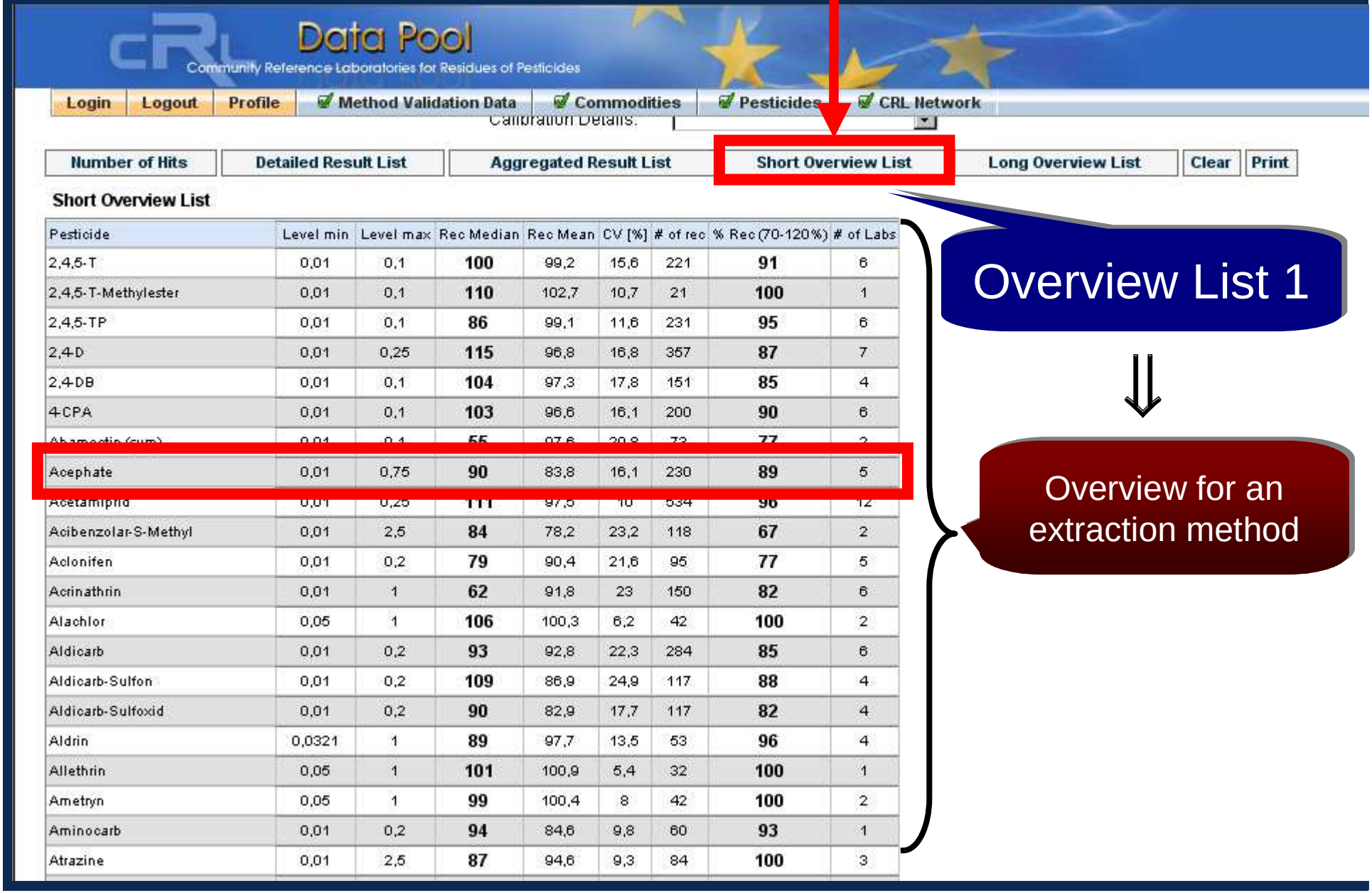
Spiking Level [mg/kg]	<= 0,01	> 0,01 - 0,05	> 0,05 - 0,25	> 0,25	All levels
# of labs	8	3	8	0	**8**
# of experiments	30	51	46	0	**127**
# of recoveries	145	87	230	0	**462**
# of commodities	6	25	9	0	**28**
Min. rec.	55	50	41		**41**
Max. rec.	136	120	122		**136**
Mean rec.	98	88	94		**94**
CV %	16,1	20,7	14		**16,3**
Median rec.	130	96	95		**96**
% of rec. with < 50%	0	0	1		**1**
% of rec. with 50% - 69%	7	21	4		**8**
% of rec. with 70% - 120%	88	79	94		**89**
% of rec. with > 120%	5	0	1		**2**

Aggregation mode 3

⇓

Overview for pesticide 2,4-D with calculated data

Method Validation Data: „Short Overview List“



Short Overview List

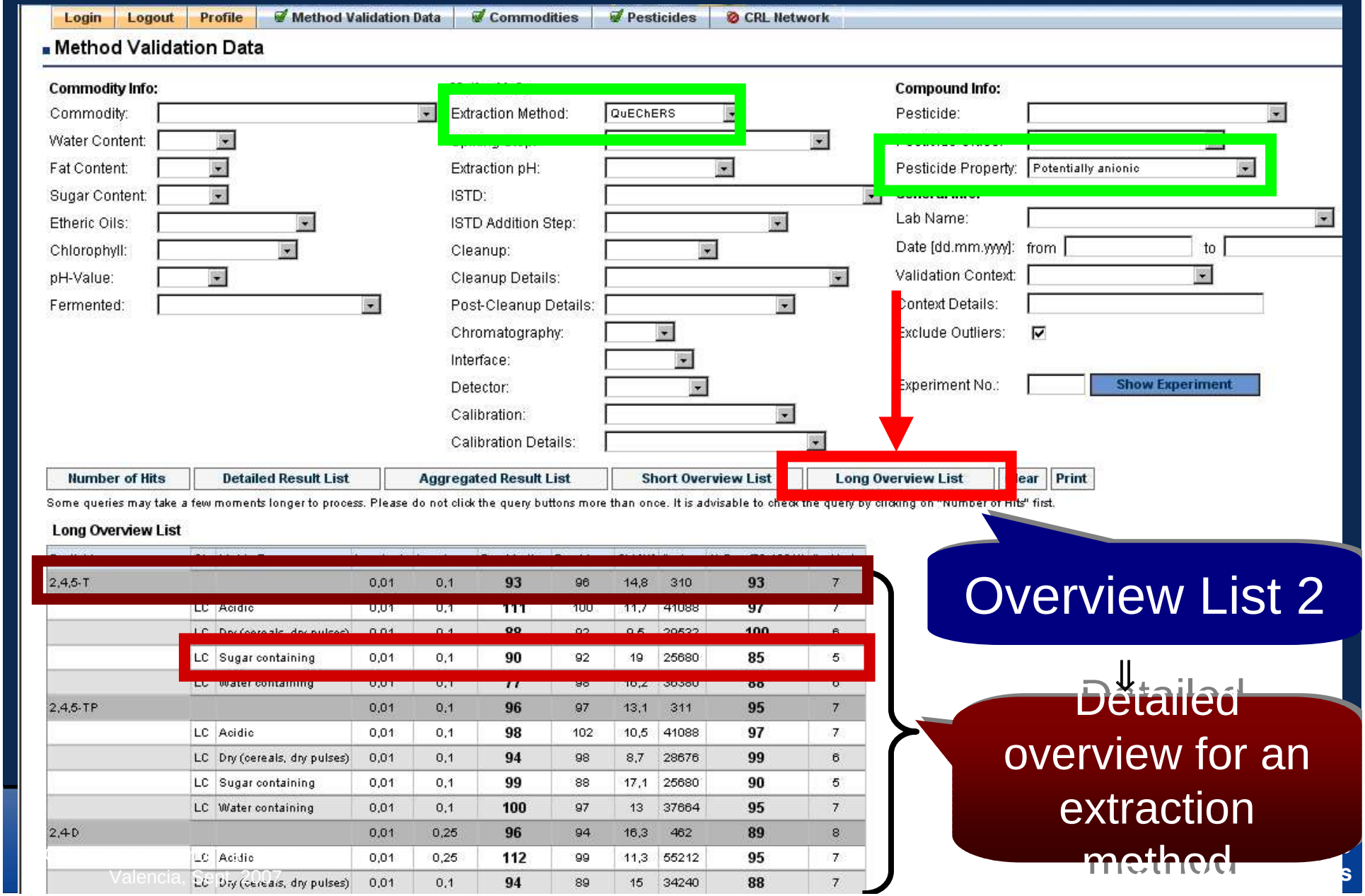
Pesticide	Level min	Level max	Rec Median	Rec Mean	CV [%]	# of rec	% Rec (70-120%)	# of Labs
2,4,5-T	0,01	0,1	**100**	99,2	15,6	221	**91**	6
2,4,5-T-Methylester	0,01	0,1	**110**	102,7	10,7	21	**100**	1
2,4,5-TP	0,01	0,1	**86**	99,1	11,6	231	**95**	6
2,4-D	0,01	0,25	**115**	96,8	16,8	357	**87**	7
2,4-DB	0,01	0,1	**104**	97,3	17,8	151	**85**	4
4-CPA	0,01	0,1	**103**	96,6	16,1	200	**90**	6
Abamectin (sum)	0,01	0,1	**55**	97,6	20,8	73	**77**	2
Acephate	0,01	0,75	**90**	83,8	16,1	230	**89**	5
Acetamiprid	0,01	0,25	**111**	97,5	10	534	**96**	12
Acibenzolar-S-Methyl	0,01	2,5	**84**	78,2	23,2	118	**67**	2
Aclonifen	0,01	0,2	**79**	90,4	21,6	95	**77**	5
Acrinathrin	0,01	1	**62**	91,8	23	150	**82**	6
Alachlor	0,05	1	**106**	100,3	6,2	42	**100**	2
Aldicarb	0,01	0,2	**93**	92,8	22,3	284	**85**	6
Aldicarb-Sulfon	0,01	0,2	**109**	86,9	24,9	117	**88**	4
Aldicarb-Sulfoxid	0,01	0,2	**90**	82,9	17,7	117	**82**	4
Aldrin	0,0321	1	**89**	97,7	13,5	53	**96**	4
Allethrin	0,05	1	**101**	100,9	5,4	32	**100**	1
Ametryn	0,05	1	**99**	100,4	8	42	**100**	2
Aminocarb	0,01	0,2	**94**	84,6	9,8	60	**93**	1
Atrazine	0,01	2,5	**87**	94,6	9,3	84	**100**	3

Overview List 1

⇓

Overview for an extraction method

Method Validation Data: „Long Overview List“



2,4,5-T			0,01	0,1	93	96	14,8	310	93	7
	LC	Acidic	0,01	0,1	111	100	11,7	41088	97	7
	LC	Sugar containing	0,01	0,1	90	92	19	25680	85	5
2,4,5-TP			0,01	0,1	96	97	13,1	311	95	7
	LC	Acidic	0,01	0,1	98	102	10,5	41088	97	7
	LC	Dry (cereals, dry pulses)	0,01	0,1	94	98	8,7	28676	99	6
	LC	Sugar containing	0,01	0,1	99	88	17,1	25680	90	5
	LC	Water containing	0,01	0,1	100	97	13	37664	95	7
2,4-D			0,01	0,25	96	94	16,3	462	89	8
	LC	Acidic	0,01	0,25	112	99	11,3	55212	95	7
	LC	Dry (cereals, dry pulses)	0,01	0,1	94	89	15	34240	88	7

Overview List 2

⇓

Detailed overview for an extraction method

Method Validation Data: Some Statistics

- currently data for QuEChERS- and ChemElut Method
  → but Method Validation Database is
  flexible to receive data from any other method!
- Recovery data for QuEChERS / ChemElut:
  - more than 80.000 / 18.000 individual recoveries
  - 532 / 246 compounds
  - 45 / 63 commodities (apple, raisin, lemon, …)
  - 18 / 8 labs data submitted
- Recovery data of **S19** will be submitted soon from different labs.

Method Validation Data: Give & Take

The quality and extent of this database also greatly relies on the contributions that the users make!

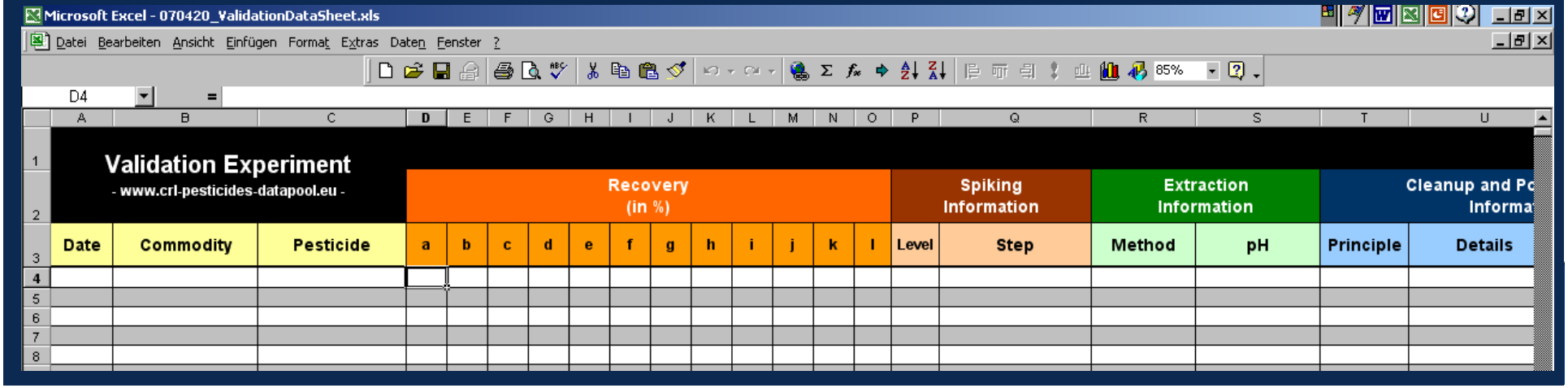
You're welcome to submit validation data from your lab!

But how to submit?

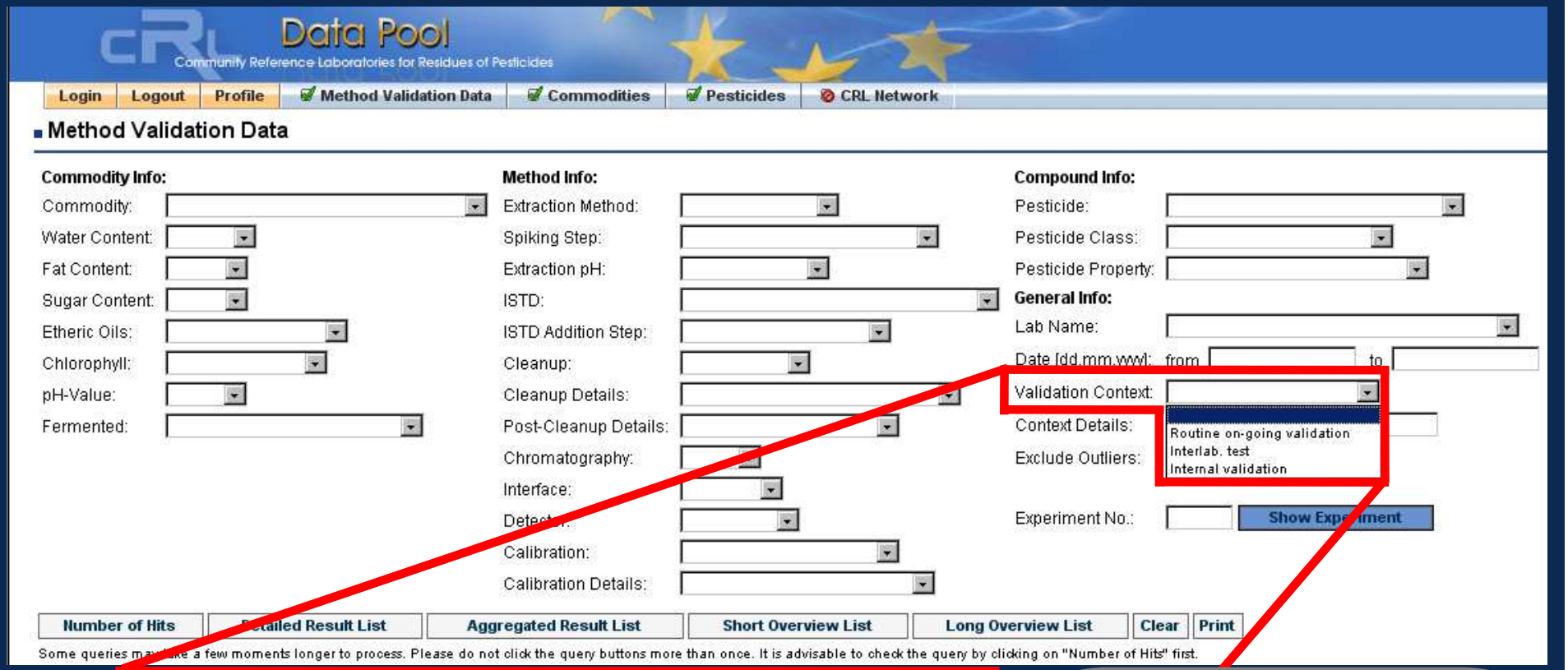
Method Validation Data: Data Submission via Excel-file

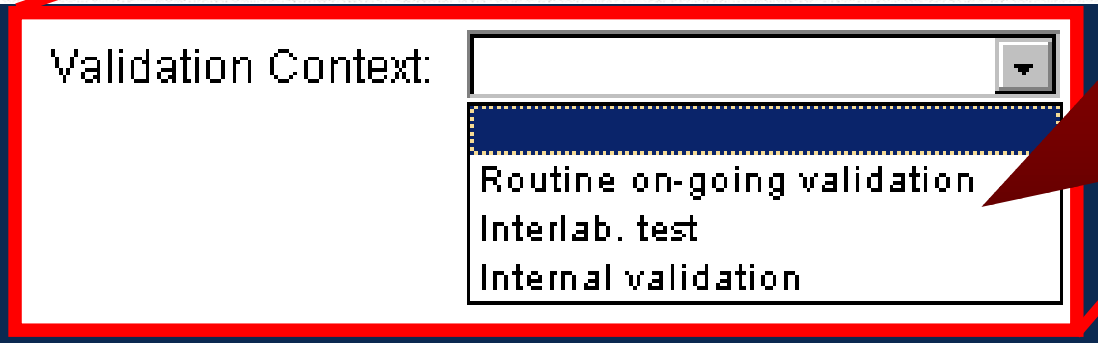
- **We offer a Data Submission-Format** (→ Excel-file)
  If you are interested, please contact us!
- If you have huge amounts of recovery data, we will try to transform your data into our data-format.
- Download Data Submission File from CRL Data Pool-Website:

- Data Submission File: = Excel-file



Method Validation Data: What kind of Validation Data?



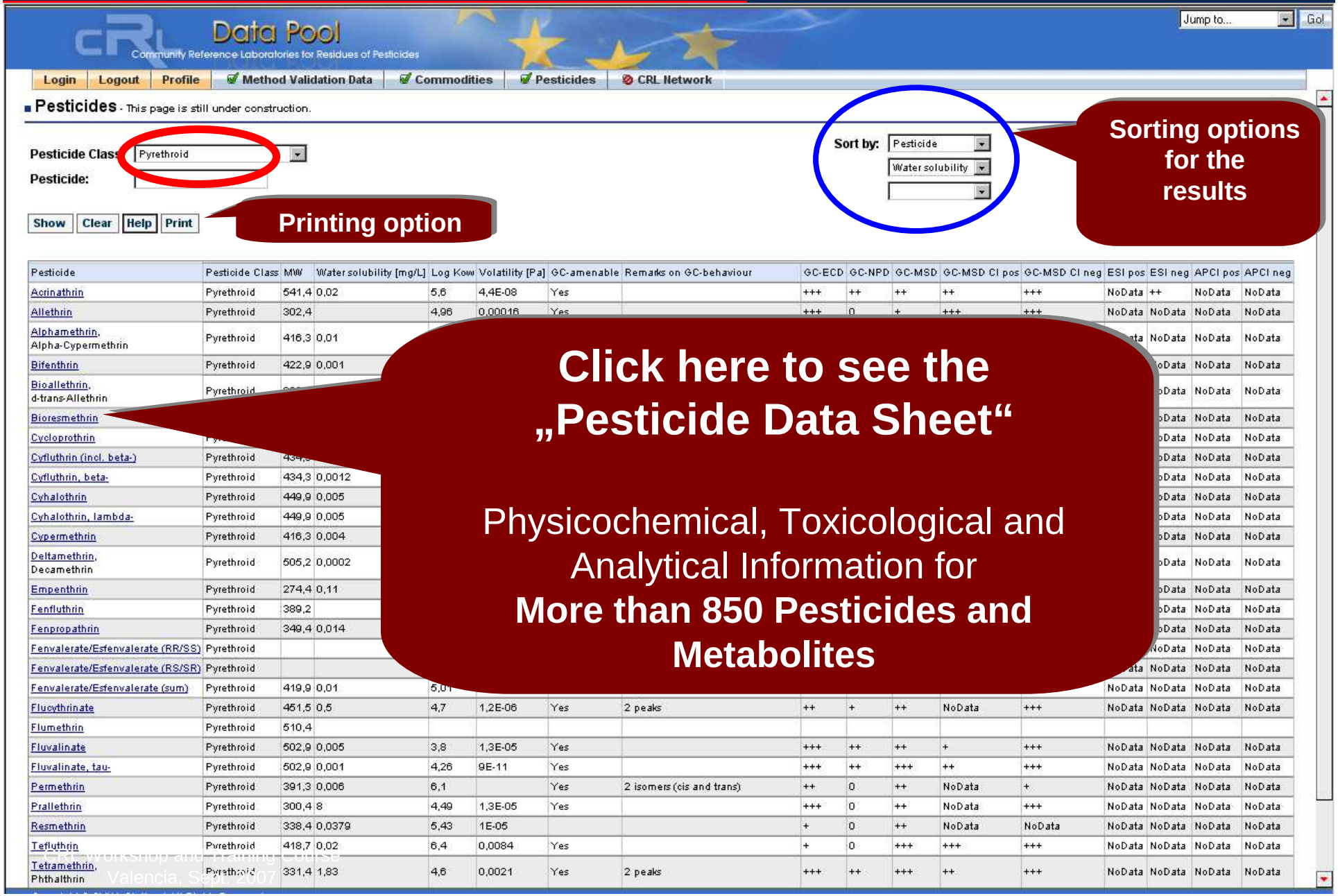


You can contribute different recovery data from your method validation experiments (**routine on-going validation**; **interlab. tests**; **internal validation**).

CRL Data Pool: Pesticides Database

- After login, click on button „Pesticides“!

CRL Data Pool: Pesticides Database



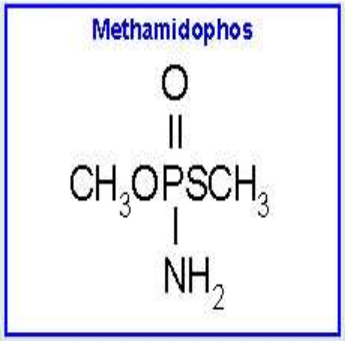
Pesticide	Pesticide Class	MW	Water solubility [mg/L]	Log Kow	Volatility [Pa]	GC-amenable	Remarks on GC-behaviour	GC-ECD	GC-NPD	GC-MSD	GC-MSD CI pos	GC-MSD CI neg	ESI pos	ESI neg	APCI pos	APCI neg
Acrinathrin	Pyrethroid	541,4	0,02	5,6	4,4E-08	Yes		+++	++	++	++	+++	NoData	++	NoData	NoData
Allethrin	Pyrethroid	302,4		4,96	0,00016	Yes		+++	0	+	+++	+++	NoData	NoData	NoData	NoData
Alphamethrin, Alpha-Cypermethrin	Pyrethroid	416,3	0,01											NoData	NoData	NoData
Bifenthrin	Pyrethroid	422,9	0,001												NoData	NoData
Bioallethrin, d-trans-Allethrin	Pyrethroid														NoData	NoData
Bioresmethrin															NoData	NoData
Cycloprothrin															NoData	NoData
Cyfluthrin (incl. beta-)	Pyrethroid														NoData	NoData
Cyfluthrin, beta-	Pyrethroid	434,3	0,0012												NoData	NoData
Cyhalothrin	Pyrethroid	449,9	0,005												NoData	NoData
Cyhalothrin, lambda-	Pyrethroid	449,9	0,005												NoData	NoData
Cypermethrin	Pyrethroid	416,3	0,004												NoData	NoData
Deltamethrin, Decamethrin	Pyrethroid	505,2	0,0002												NoData	NoData
Empenthrin	Pyrethroid	274,4	0,11												NoData	NoData
Fenfluthrin	Pyrethroid	389,2													NoData	NoData
Fenpropathrin	Pyrethroid	349,4	0,014												NoData	NoData
Fenvalerate/Esfenvalerate (RR/SS)	Pyrethroid														NoData	NoData
Fenvalerate/Esfenvalerate (RS/SR)	Pyrethroid														NoData	NoData
Fenvalerate/Esfenvalerate (sum)	Pyrethroid	419,9	0,01	5,01									NoData	NoData	NoData	NoData
Flucythrinate	Pyrethroid	451,5	0,5	4,7	1,2E-06	Yes	2 peaks	++	+	++	NoData	+++	NoData	NoData	NoData	NoData
Flumethrin	Pyrethroid	510,4														
Fluvalinate	Pyrethroid	502,9	0,005	3,8	1,3E-05	Yes		+++	++	++	+	+++	NoData	NoData	NoData	NoData
Fluvalinate, tau-	Pyrethroid	502,9	0,001	4,26	9E-11	Yes		+++	++	+++	++	+++	NoData	NoData	NoData	NoData
Permethrin	Pyrethroid	391,3	0,006	6,1		Yes	2 isomers (cis and trans)	++	0	++	NoData	+	NoData	NoData	NoData	NoData
Prallethrin	Pyrethroid	300,4	8	4,49	1,3E-05	Yes		+++	0	++	NoData	+++	NoData	NoData	NoData	NoData
Resmethrin	Pyrethroid	338,4	0,0379	5,43	1E-05			+	0	++	NoData	NoData	NoData	NoData	NoData	NoData
Tefluthrin	Pyrethroid	418,7	0,02	6,4	0,0084	Yes		+	0	+++	+++	+++	NoData	NoData	NoData	NoData
Tetramethrin, Phthalthrin	Pyrethroid	331,4	1,83	4,6	0,0021	Yes	2 peaks	+++	++	+++	++	+++	NoData	NoData	NoData	NoData

CRL Data Pool: Pesticides Database

METHAMIDOPHOS (Acephate-met) 10265-92-6

Pesticide Class: Organophosphorous

Mode of Action: Acaricide Insecticide



Physicochemical and Toxicological Data

PHYSICOCHEMICAL AND TOXICOLOGICAL DATA

MW / Molecular Formula	141,1 / C2H8NO2PS
Water Solubility [mg/L] / pKow	200000 > (20°C) [1] / -0,8 (20°C) [1]
pKa	
Vapour pressure [Pa]	0,0023 [1]
ARfD / ADI [mg/kg bw]	0,01 [7] / 0,004 [7]
Endocrine Disruption	
Add. Info	Metab. of Acephate
Residue Definition	

Analytical Data

ANALYTICAL DATA

TYPICAL RECOVERIES USING VARIOUS MULTIRESIDUE METHODS (in %)

Method	0-20	20-50	50-70	70-110	Remarks
QuEChERS (MeCN)				X	
Stuttgart (Acetone)					
SFE (CO2)	X				[3]
DFG S 19 (Acetone)			X		
Dutch (Acetone)					
Canadian (MeCN)			X		
CDFA (MeCN)					
Swedish (EtAc)					
L. Alder (MeOH)				X	
Stajnbaher (Acetone, SPE)	X				

GC-BEHAVIOR

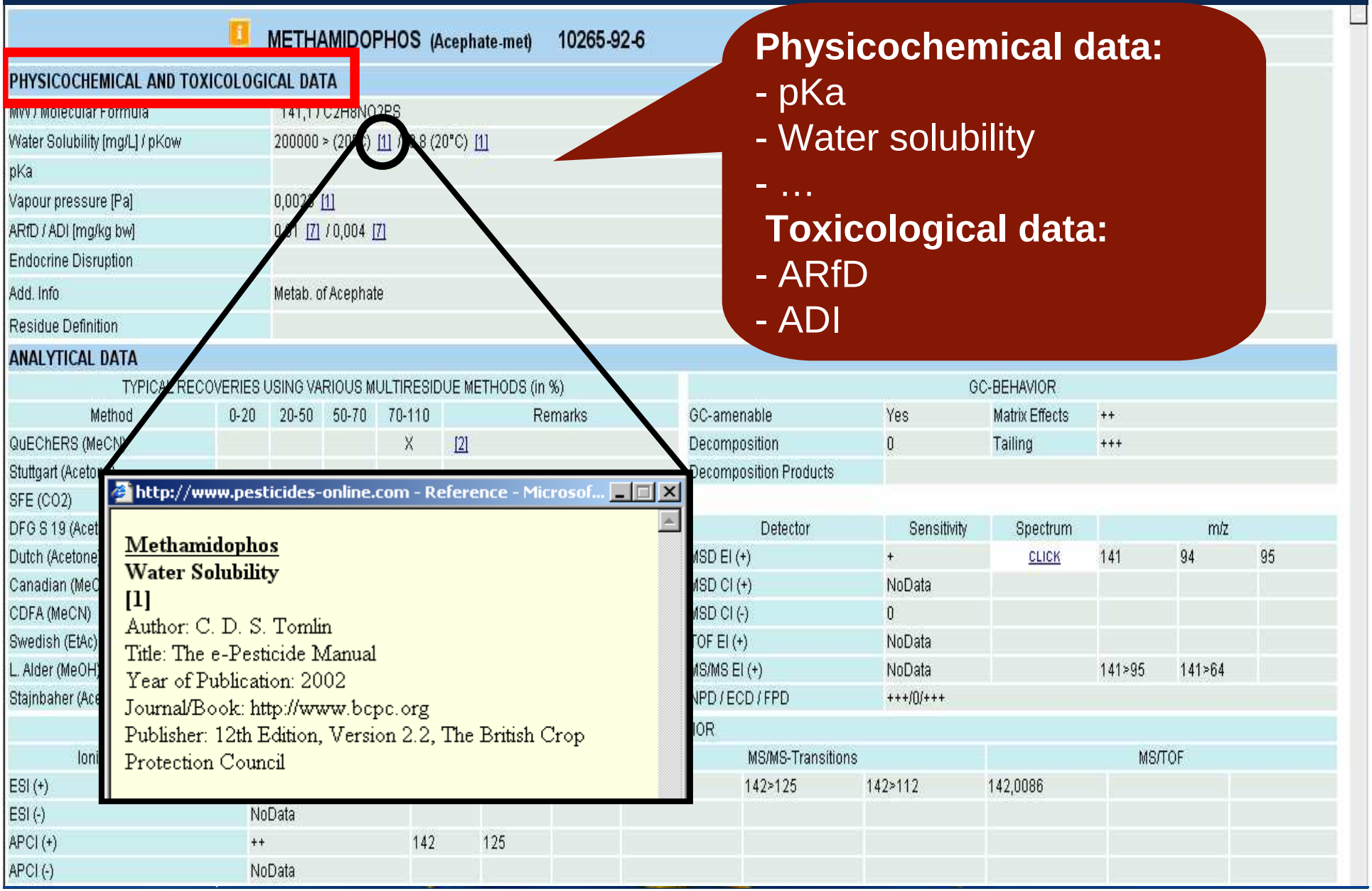
GC-amenable	Yes	Matrix Effects	++
Decomposition	0	Tailing	+++
Decomposition Products			

		m/z	
MS/MS EI (+)	NoData	141>95	141>64
NPD / ECD / FPD	+++/0/+++		

LC-BEHAVIOR

Ionization Source	Sensitivity	MS (m/z)			MS/MS-Transitions			MS/TOF		
ESI (+)	+++	142	112	125	142>94	142>125	142>112	142,0086		
ESI (-)	NoData									
APCI (+)	++	142	125							
APCI (-)	NoData									

CRL Data Pool: Pesticides Database



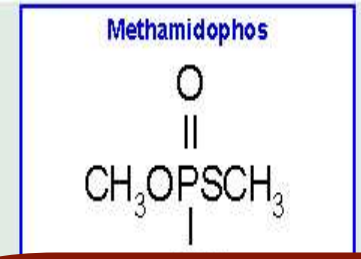
Physicochemical data:
- pKa
- Water solubility
- …

Toxicological data:
- ARfD
- ADI

CRL Data Pool: Pesticides Database

METHAMIDOPHOS (Acephate-met) 10265-92-6

Pesticide Class: Organophosphorous
Mode of Action: Acaricide Insecticide



PHYSICOCHEMICAL AND TOXICOLOGICAL DATA

MW / Molecular Formula	141,1 / C2H8NO2PS
Water Solubility [mg/L] / pKow	200000 > (20°C) [1] / -0,8 (20°C) [1]
pKa	
Vapour pressure [Pa]	0,0023 [1]
ARfD / ADI [mg/kg bw]	0,01 [7] / 0,004
Endocrine Disruption	
Add. Info	Metab. of Aceph
Residue Definition	

Typical recoveries with various multiresidue methods

GC-Behavior

ANALYTICAL DATA

TYPICAL RECOVERIES USING VARIOUS MULTIRESIDUE METHODS (in %)

Method	0-20	20-50	50-70	70-110	Remarks
QuEChERS (MeCN)				X	[2]
Stuttgart (Acetone)					
SFE (CO2)	X				[3]
DFG S 19 (Acetone)			X		
Dutch (Acetone)					
Canadian (MeCN)			X		
CDFA (MeCN)					
Swedish (EtAc)					
L. Alder (MeOH)					
Stajnbaher (Aceto					

GC-BEHAVIOR

GC-amenable	Yes	Matrix Effects	++
Decomposition	0	Tailing	+++
Decomposition Products			

Detector	Sensitivity	Spectrum	m/z		
MSD EI (+)	+	CLICK	141	94	95
MSD CI (+)	NoData				
MSD CI (-)	0				
TOF EI (+)	NoData				
MS/MS EI (+)	NoData		141>95	141>64	
NPD / ECD / FPD	+++/0/+++				

LC-Behavior

LC-BEHAVIOR

Ionization Source	Sensitivity	MS (m/z)			MS/MS-Transitions			MS/TOF		
ESI (+)	+++	142	112	125	142>94	142>125	142>112	142,0086		
ESI (-)	NoData									
APCI (+)	++	142	125							
APCI (-)	NoData									

Summary

- CRL Web Service aims to create a laboratory network and to enable an information exchange between the labs.
- CRL Portal = a single website created for the 4 CRLs
- CRL Data Pool = database system for the collection of information relevant in pesticide residue analysis & its evaluation to assist the decision-making process
- Method Validation Data enables the systematic collection + customized retrieval of method validation data for pesticides.
- Method Validation Data can perfectly help labs in identifying and selecting methods that are able to cover the analytes and commodities in question.
- A lot of features have been already installed, but the both database systems are continuously being improved to better serve the practical needs of analysts.
- You are welcome to submit data (validation data) from your lab!

Thank you very much for your Attention !

→ **CRL Portal:** http://www.crl-pesticides.eu

→ **CRL Data Pool:** http://www.crl-pesticides-datapool.eu