

A review of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in Lebanon: Environmental and human contaminants



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Jean-François Narbonne²*

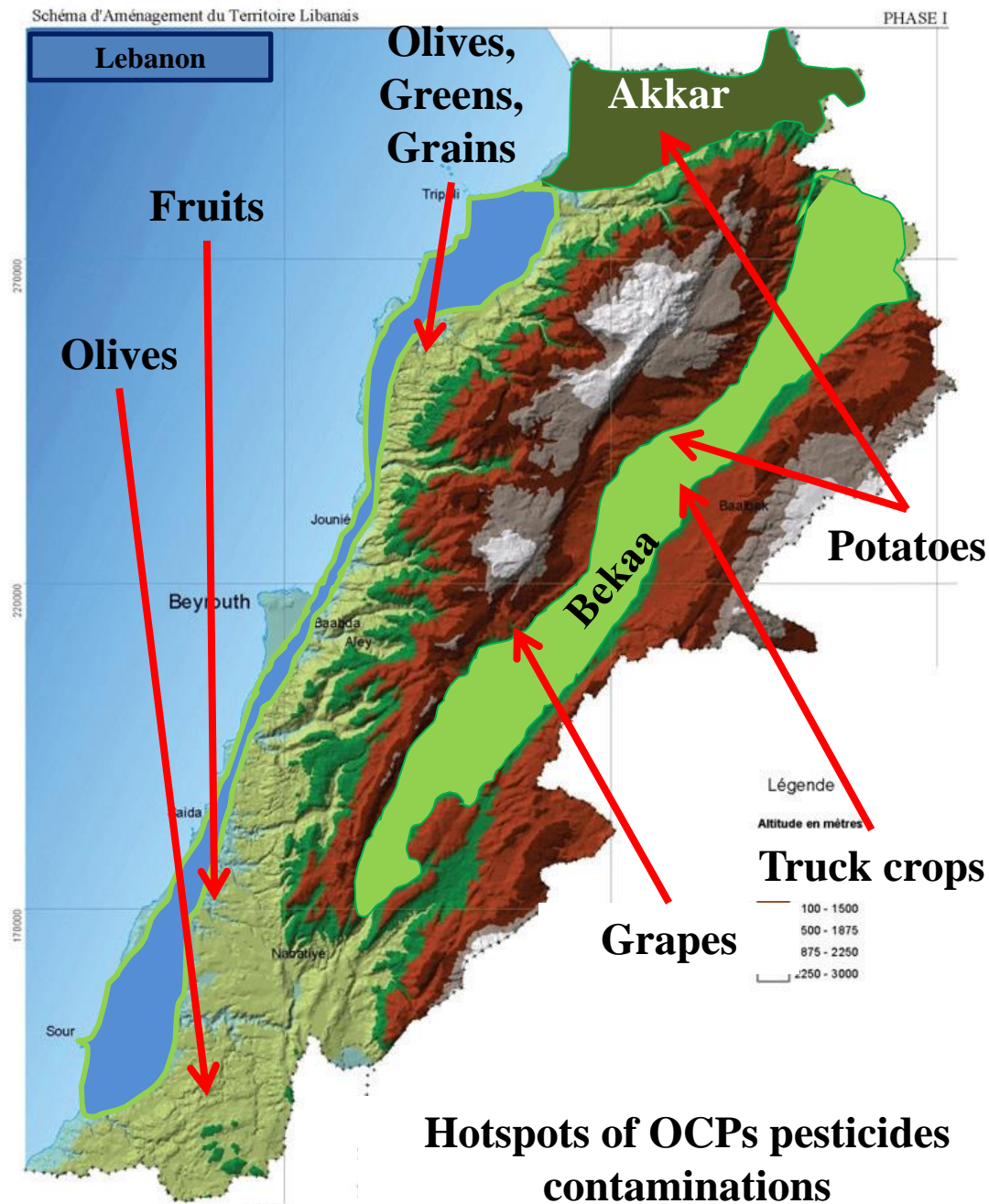
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Hotspots of organochlorine pesticides and polychlorobiphenyls in Lebanon

Hotspots of OCP contamination: Agricultural areas

- 1st: the Bekaa plain (formerly the attic of Rome)
- 2nd: Akkar
- 3rd: coastal plain



Pesticides problem

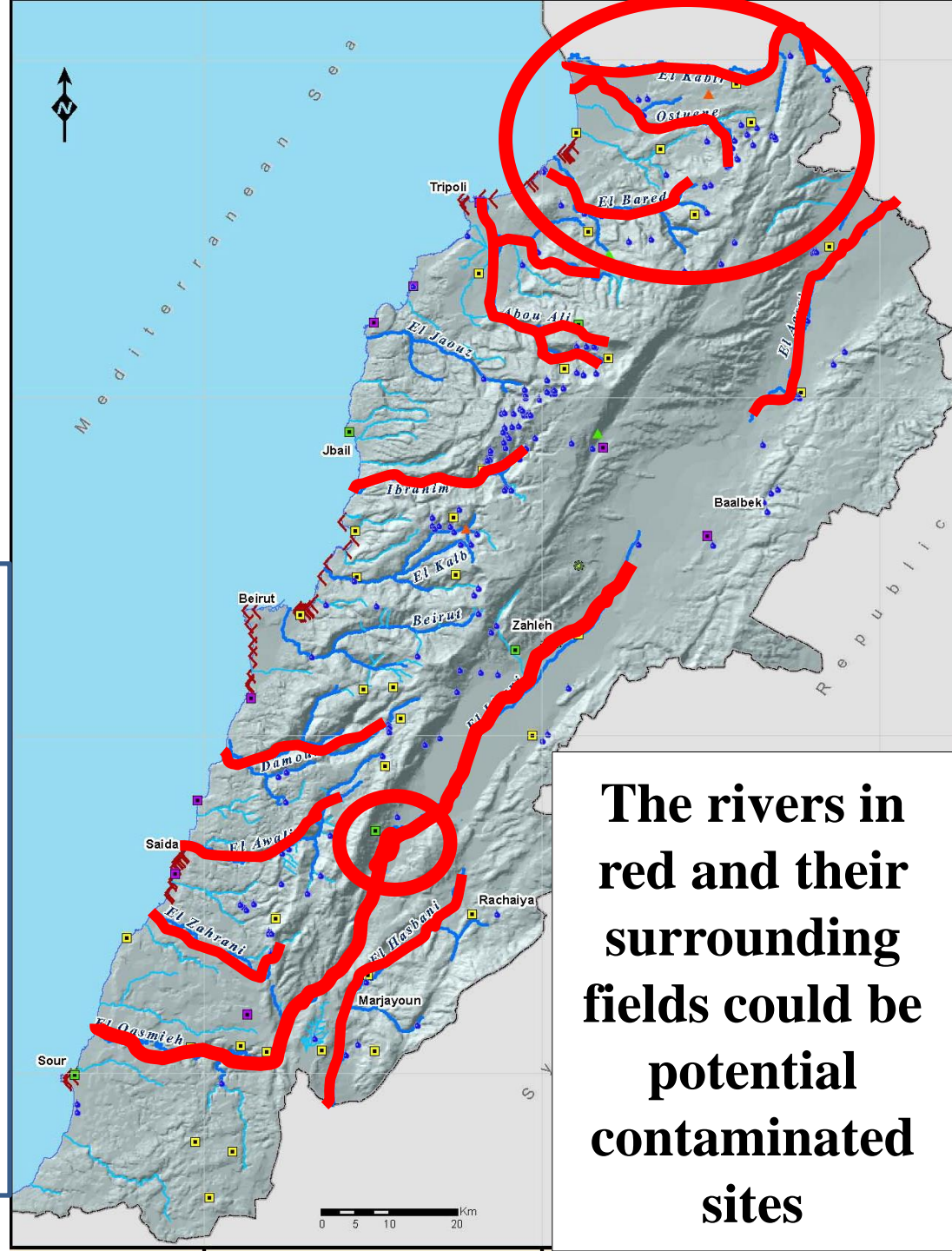
- Despite legislations, Lebanon is still incapable to control *the smuggling of OCPs, excessive usage, storage and discarding of pesticides, particularly by untrained farmers and unskilled municipal personnel*



**Example of
agricultural
room in
Akkar**

Hotspots of OCP contamination: Agricultural waters

Streams and rivers flowing into agricultural fields are potentially contaminated sites. Gravity irrigation washes OCPs out of agricultural fields and introduces them into surface water and groundwater



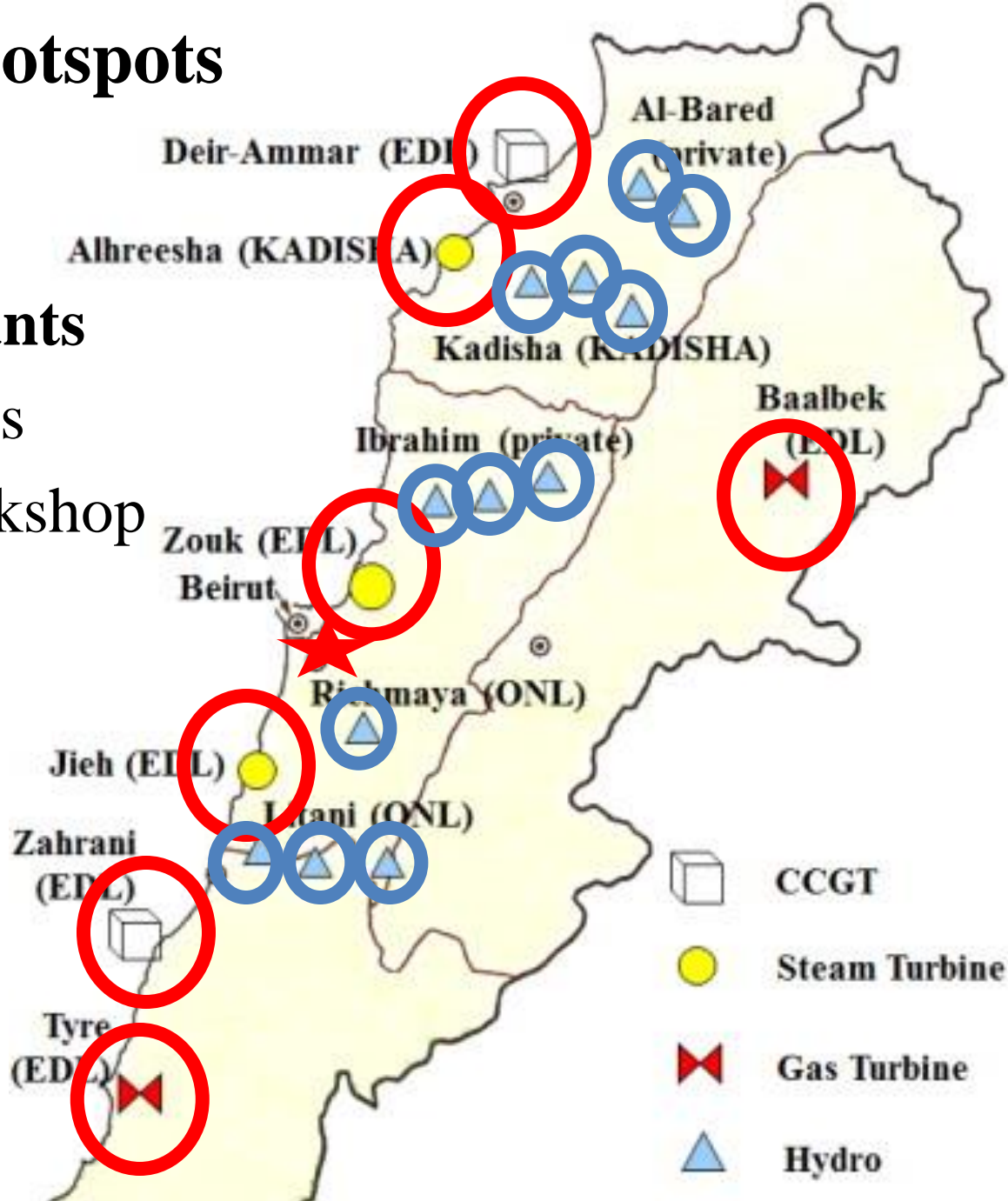
The rivers in red and their surrounding fields could be potential contaminated sites

PCB Hotspots

EDL:

- 7 thermal power plants
- 12 hydro power plants
- Baushrieh repair workshop

Insulating oils in Lebanon's Electricity Company – Electricité du Liban (EDL) are the major known sources of PCBs in Lebanon.

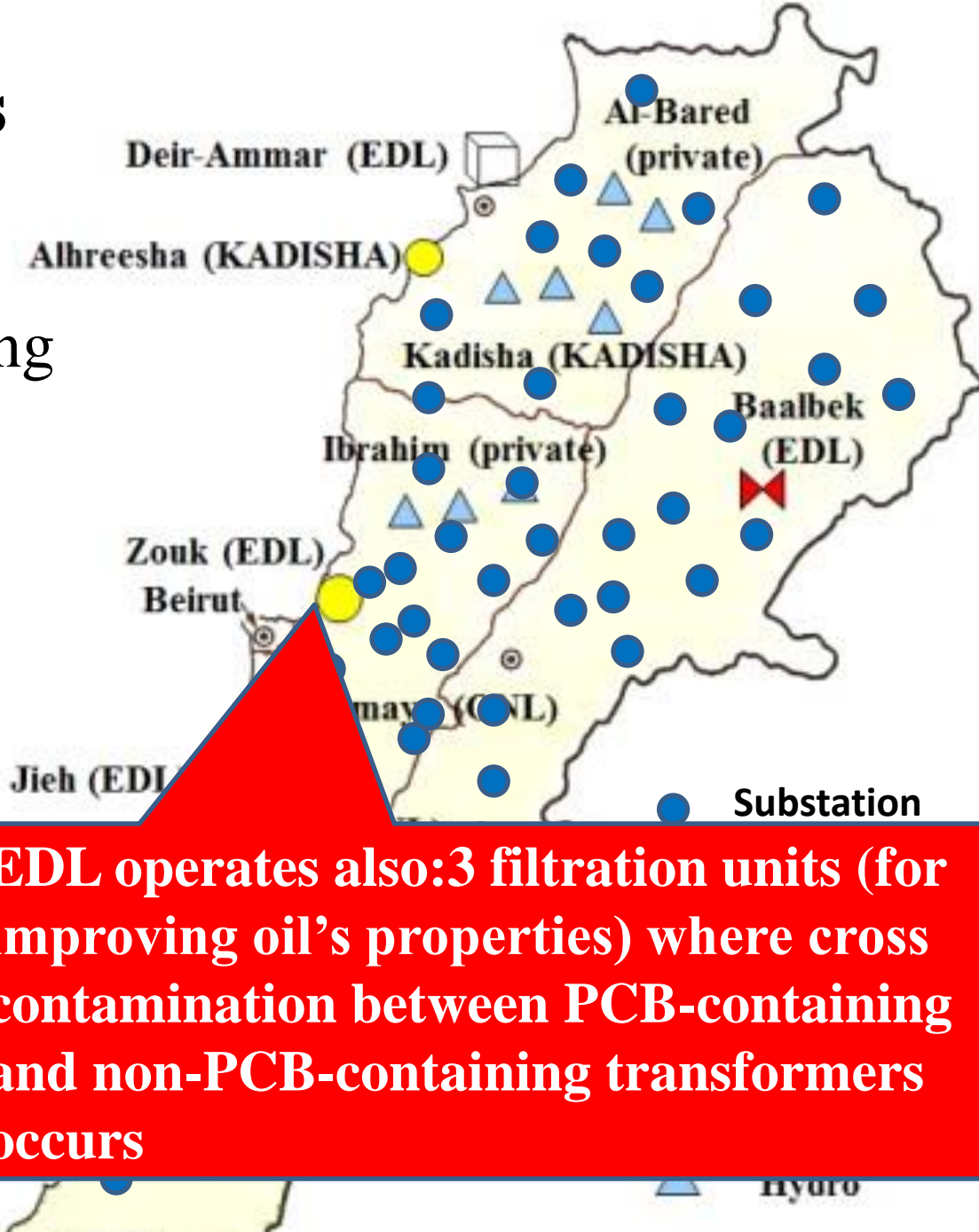


PCB Hotspots

EDL operates also:

- **58 substations** including 22,551 distribution transformers

1,130 transformers continue to reveal contamination, with PCB residues at levels exceeding 50 ppm (unpublished updated info – MoE)



EDL operates also: 3 filtration units (for improving oil's properties) where cross contamination between PCB-containing and non-PCB-containing transformers occurs

PCB Situation

Prior to 2006:

- PCB contaminated equipment of EDL used to be disposed of haphazardly or dismantled and sold as scrap.
- PCB oil used to be dumped recklessly or sold as fuel.
- No incineration kilns or dedicated landfills for PCB waste in Lebanon



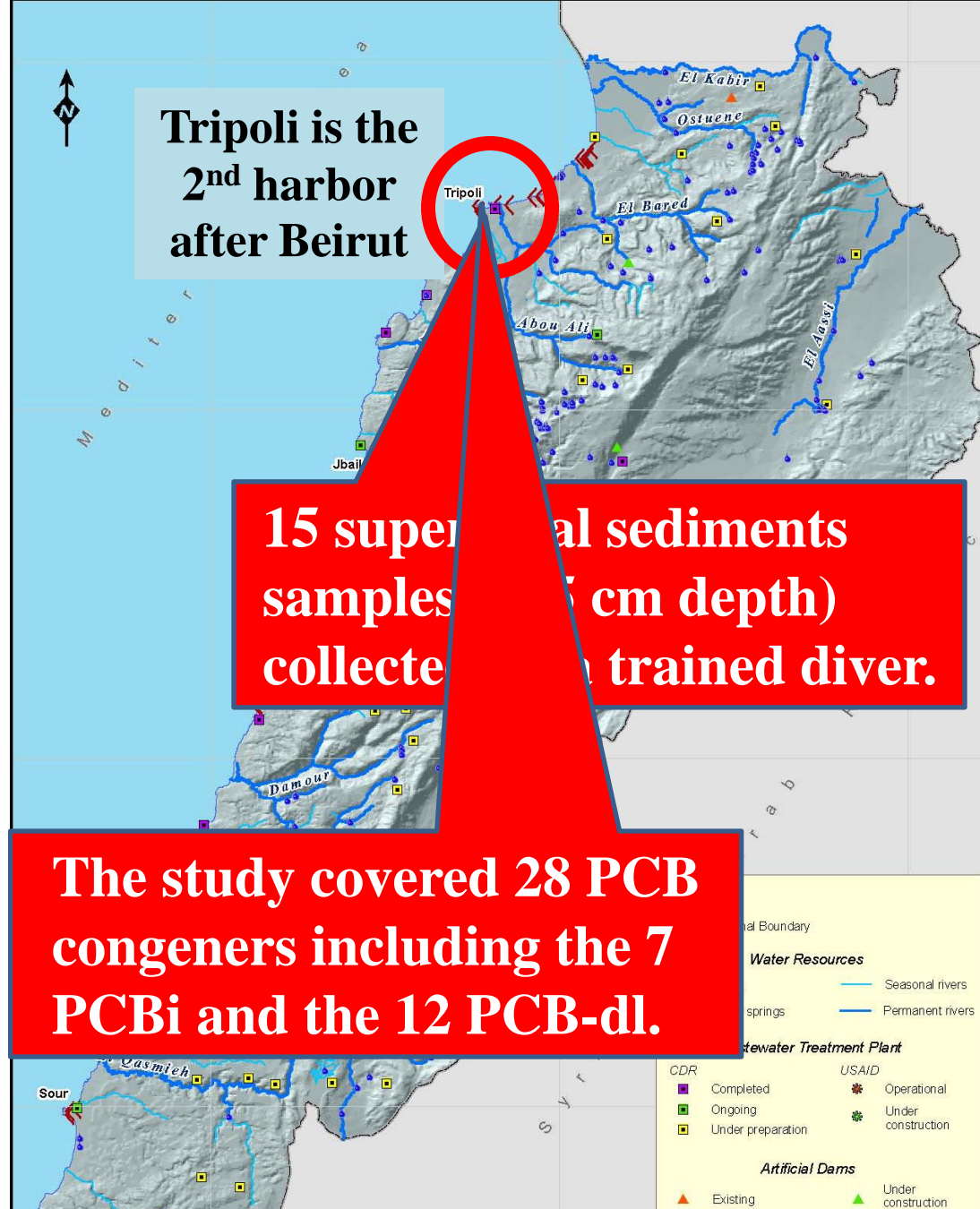
Capacitors & transformers piles: Bauchrieh

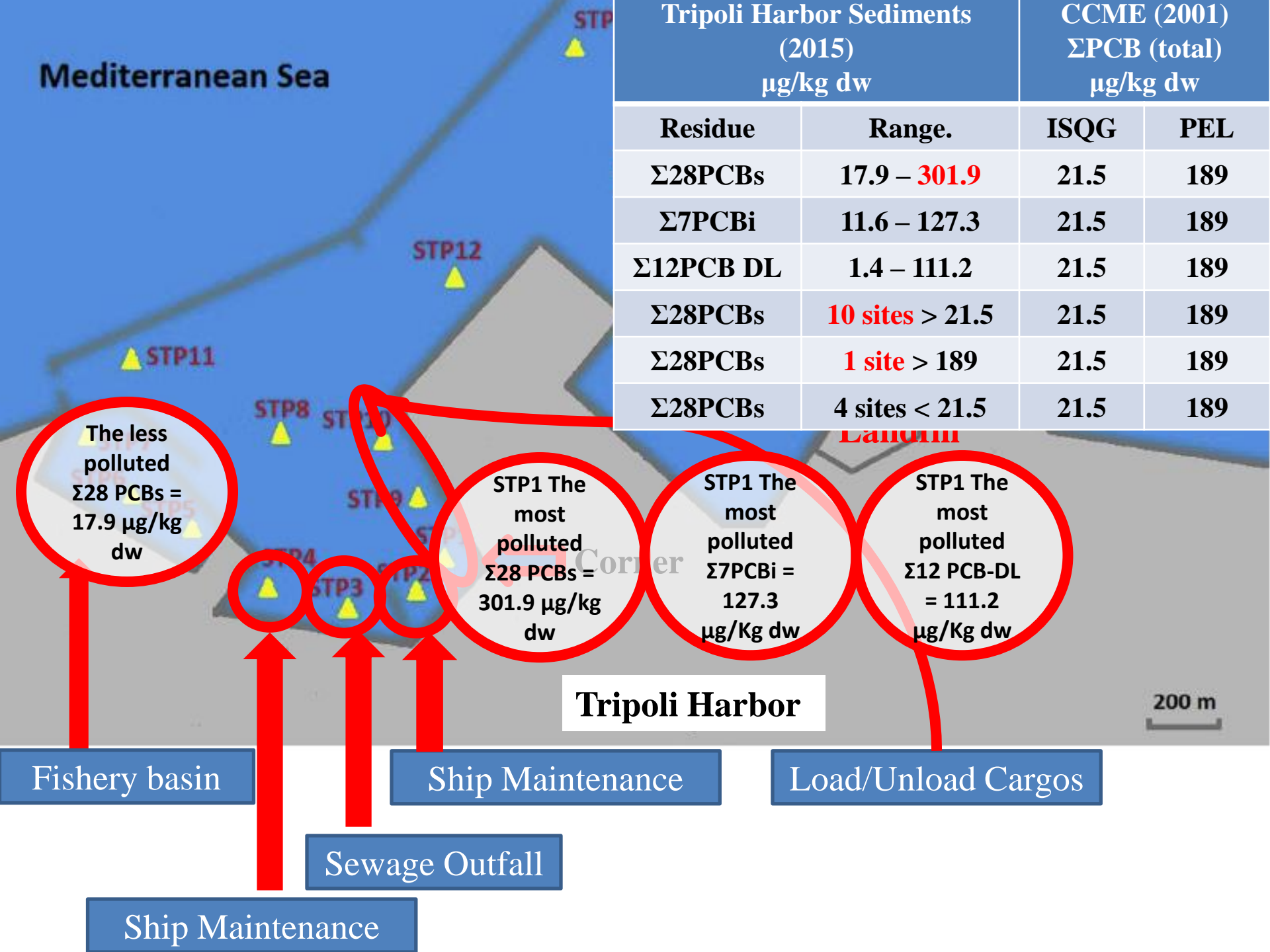


Research on OCPs and PCBs (1999 – 2017)

12 studies

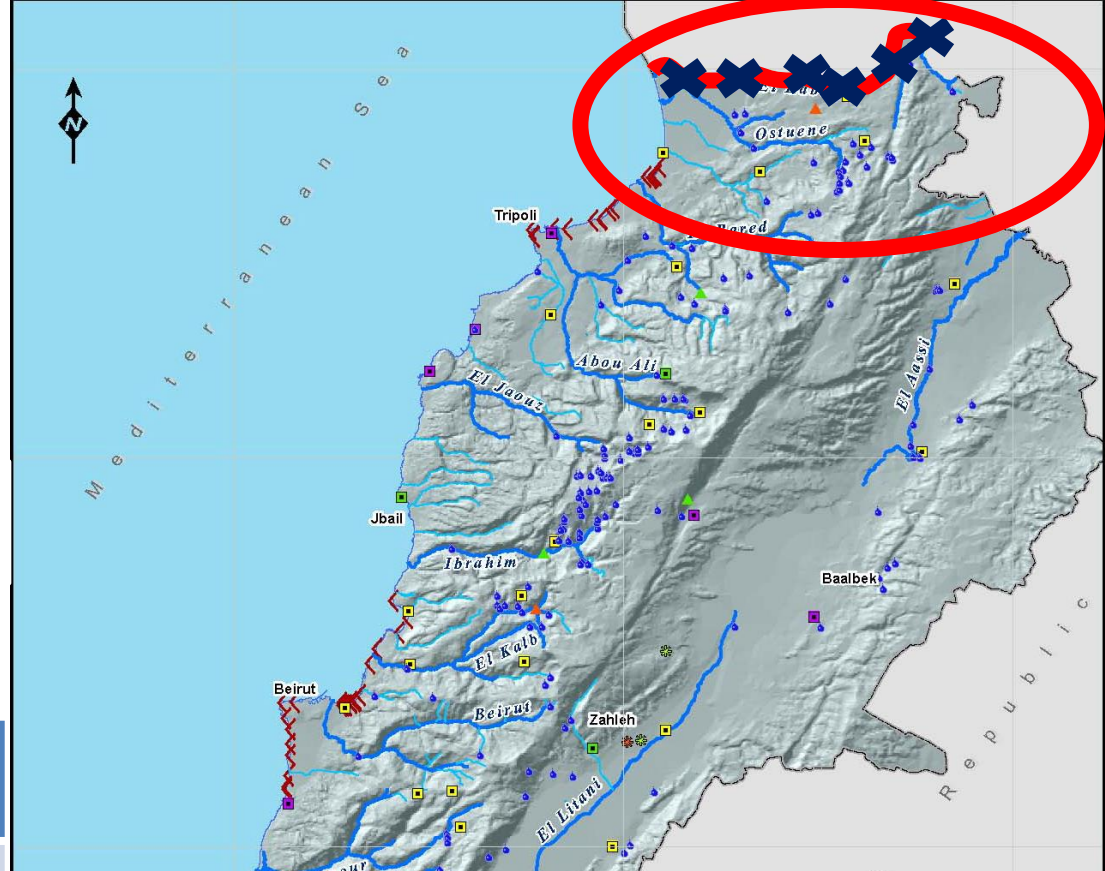
PCB in Tripoli marine sediments





OCPs in Akkar river sediments (2002)

The only study on river sediments ever done in Lebanon



Akkar River 2001 µg/kg dw		CCME (2001) µg/kg dw	
River Sediments	Conc.	ISQG	PEL
mean HCB	0.03	-	-
mean pp'-DDE	2.02	1.42	6.75
mean pp'-DDT	2.21	1.19	4.77
mean ΣDDT	3.84	-	-

- Levels of HCB were low.
- DDT mean level was higher than DDE indicating its recent use despite its ban. It was probably used in both sides of the border.
- Lindane and HCHs were not detected

OCPs in Groundwater

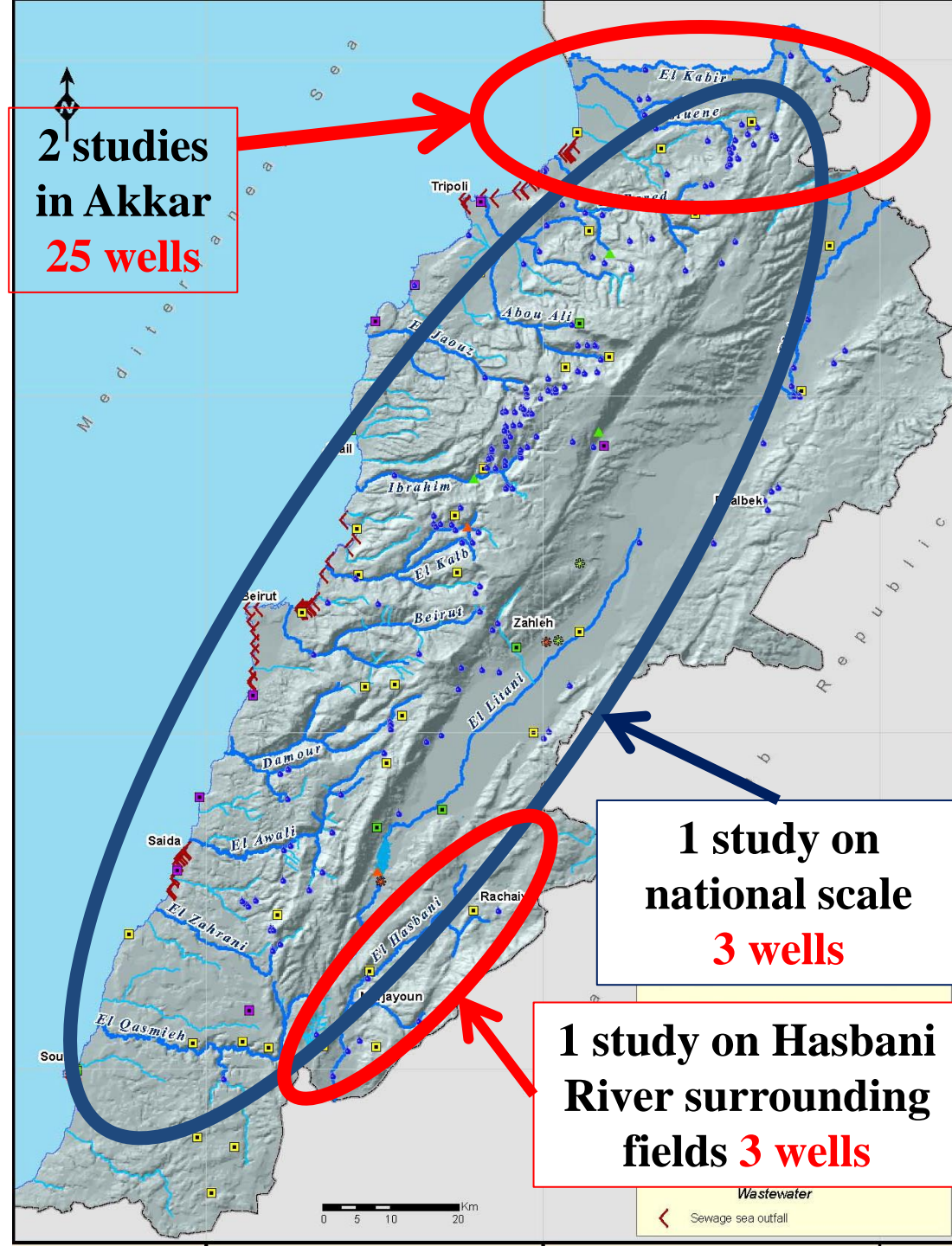
- **Four** studies carried out till now.
- Sampling by pumping in amber glass bottles (1.5 – 2.5 L)
- Analysis SPE + LGC + MS

A. Kouzayha, A. et al., Occurrence of Pesticide Residues in Lebanon's Water Resources, Bull Environ Contam Toxicol (2013) 91:503–509

El-Osmani, R., et al. *Solid Phase Extraction of Organochlorine Pesticides Residues in Groundwater (Akkar Plain, North Lebanon)*. Int. J. Environ. Res., 8(4):903-912, Autumn 2014

Lobna Youssef, et al. *Occurrence and levels of pesticides in South Lebanon water*, Chemical Speciation & Bioavailability, 2015 Vol. 27, No. 2, 62–70,

Chbib Chaza, Net Sopheak, Hamzeh Mariam, Dumoulin David, Ouddane Baghdad, Baroudi Moomen, *Assessment of pesticide contamination in Akkar groundwater, northern Lebanon*, Environ Sci Pollut Res, published online March 06, 2017



OCPs in Groundwater

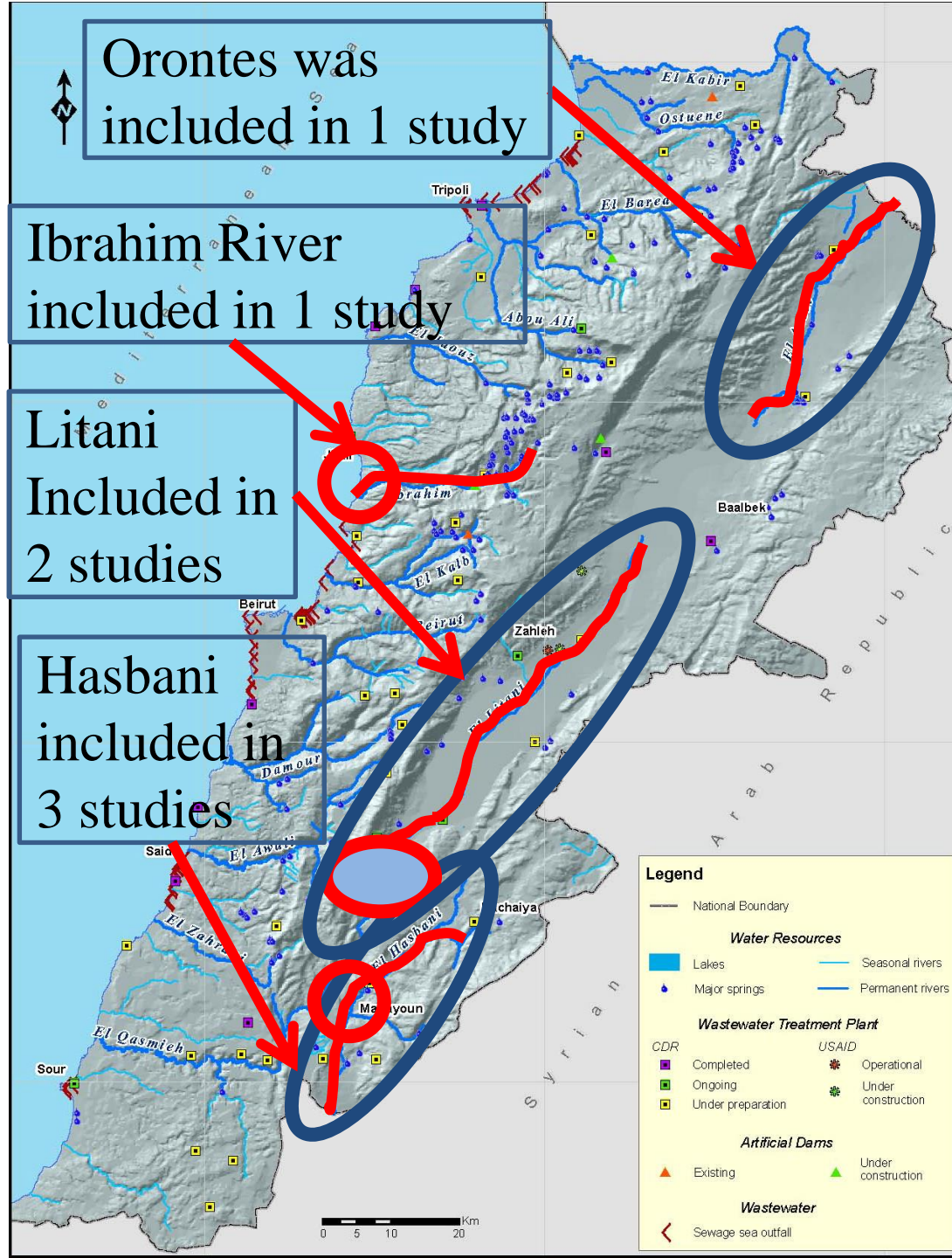
	2011–2012 ng/L		2012 ng/L		2012 ng/L		2015 ng/L		EU MRL ng/L
Authors	Kouzhaya, A. et al.		El-Osmani, R. et al.		Youssef, L. et al.		Chbib, C. et al.		
Location	Denniyeh, Terbol, Abbassieh		Akkar		Hasbani		Akkar		
N sites	3		10		3		15		
N Samples	15		30		11		30		
Samp. Method	Grab		Grab Triplicates		Grab		Grab Duplicates		
OCPs/PCBs	av	rang	av	rang	av	Rang	Av	Rang	
ΣCyclodienes							18430	1760 - 39170	-
ΣOCPs							33560	2610 - 58870	500
Aldrin	0.4	nd–0.7	280	nd–720	nq	nd–nq	2300	40–9330	30
DDD	1.6	0.9–2.2			2.80	nq–9,6	11142	90–19170	100
DDE	1.1	0.7–1.3			28.5	nq–144.8	30	nd–77	100
DDT			260	nd–690	nq	nd–nq	340	330–1290	100
ΣDDT							11840	610–19980	-
Chlorobenzilate			1111	140–6090					100
Dieldrin	0.6	nd–1.5					2721	50–9560	30
β-Endosulfan							280	20–640	100
Endosulfan sulfate			791	nd–1570			nd	nd	100
Endrin			1290	nd–2470			48	nd–80	100
Endrin Aldehyde							83.05	nd–0.19	100

OCPs in Groundwater

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Location	Dennyeh Terbol Abbassieh		Akkar		Hasbani		Akkar		
N sites	3		10		3		15		
N samples	15		30		11		30		
Samp. Method	Grab		Grab Triplicates		Grab		Grab Duplicates		
OCPs/PCBs	av	rang	av	rang	av	Rang	Av	Rang	
Endrin Ketone			240	nd–2150			592	150–1650	100
HCB	1.5	1.2–1.6			0.52	nq–1.1			100
α-HCH			1460	nd–6420			1787	20–5760	100
β-HCH			126	nd–720			160	30–360	100
γ-HCH			311	nd–770			1304	100–3160	100
δ-HCH			423	nd–1350			17	nd–70	100
ΣHCH			2420	nd–7860			3268	150–9350	-
Heptachlor Epox. A			64	nd–120					30
Heptachlor Epox. B			679	nd–1610					30
Σ Heptachlor Epox.A + B			740	nd–2050	nq	nd–nq	9005	1390 - 25120	30
Heptachlor							3375	nd–6130	30
Methoxychlor					0.88	nd–3.4	57	nd–250	100
Tetradifon	0.2	nd–0.5							NA

OCPs in Surface Waters

- **Four** studies carried out till now, each including several rivers
- Sampling by pumping in amber glass bottles (1.5 – 2.5 L)
- Analysis SPE, LGC, MS



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Al Ashi Aisha, et al, *Monitoring of 45 Pesticides in Lebanese Surface Water using Polar Organic Chemical Integrative Sampler (POCIS)*, Ocean Sci. J. (2017) 52(3):455-466

Surface water Studies

	2011–2012 ng/L			2013 ng/L		2013 ng/L	
Authors	Kouzayha, A. et al.			Badr, R. et al.		Youssef, L. et al.	
Method	SPE + GC-MS			SPE + GC-MS		SPE + GC-MS	
Location	Litani	Orontes		Hasbani – Wazzani ^a		Hasbani	
N sites	2	3		20		3	
N samples	4	6		60		15	
Samp. Method	Grab Duplicates			Grab Triplicates		Grab	
OCPs/PCBs	av	Rang	Rang	av	Rang	av	Rang
PCB ₅₂ ^e				64.75	35.43–121.61		
Aldrin						nq	nd–nq
DDD	1	nd–3.4				1.29	nq–5.6
DDE ^f	1.1	nd–2.7	< LOQ	2.03	1.12–4.99	23.25	nq–135.6
DDT						nq	nd–nq
β-Endosulfan ^g				24.46	3.26–107.39		
Endosulfan sulfate	5.3	nd–9.2					
HCB			< LOQ	1.02	0.17–2.70	0.6	nq–0.7
Heptachlor Epox. A						nq	nd–nq
Heptachlor Epox. B						nq	nd–nq
Lindane	7.8	nd–9.5					
EPA Max for PCB ₅₂ = 1.7 ng/L	1.8	nd–4.7	< LOQ				
EPA Max for DDE = 8.3 ng/L	6.6	nd–8.6	< LOQ				

CCME PEL (the level above which more than 50% adverse effects occur in marine environments) for β-Endosulfan = 3 ng/L

Surface water Studies

	2014 ng/L					
Authors	Ashi, A. et al.					
Method	SPE + LP-GC-MS/MS Triplicate samples					
Location	Ibrahim		Qaraoun		Hasbani	
N sites	1		1		1	
N samples	72		36		36	
Samp. Method	POCIS Triplicate					
OCPs/PCBs	av	Rang	av	Rang	av	Rang
DDE	23.16	nd–137.66	1.73	nd–8.63	15.43	nd–31.79

EPA Max for DDE = 8.3 ng/L

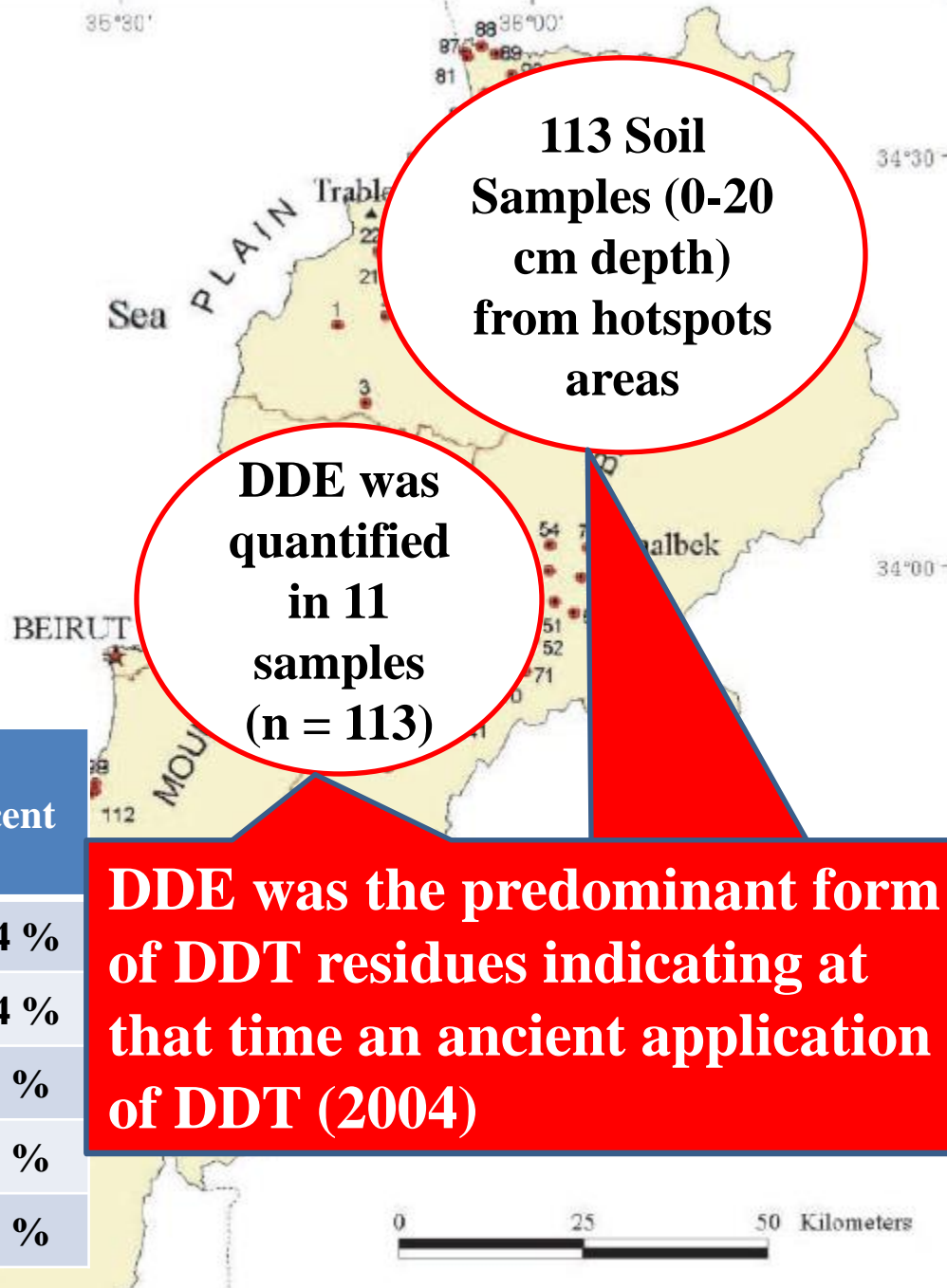
	2014 ng/g of POCIS sorbent phase					
Authors	Ashi, A. et al.					
Method	SPE + LP-GC-MS/MS Triplicate samples					
Location	Ibrahim		Qaraoun		Hasbani	
N sites	1		1		1	
N samples	72		36		36	
Samp. Method	POCIS Triplicate					
OCPs/PCBs	av	Rang	av	Rang	av	Rang
β-Endosulfan	26.67	nd–143.38	5504.90	nd–27201.42	50728.13	nd–142672.08
HCB	3.22	0.71–10.46	13.14	2.18–51.38	7.44	3.02–18.01
Heptachlor	2.72	nd–8.13	2.42	1–5.63	8.16	4–17.44

Soil Contamination (2004)

Only one study on Σ DDT (pp'DDT+pp'DDD+pp'DDE)

Detected Σ DDT range:
 $23 \leq x \leq 1190$ ng/g

Range of concentrations	Number of samples (n= 113)	Percent
n.d. ≤ 2.5 ng/g	64	56.64 %
Very Low $2.5 \leq x \leq 200$ ng/g	44	38.94 %
Low $200 \leq x \leq 500$ ng/g	3	2.65 %
Medium $500 \leq x \leq 1000$ ng/g	0	0.00 %
High $1000 \leq x \leq 2000$ ng/g	2	1.77 %



Human Biomonitoring

One study on human milk published in 1999

- N = 32 milk samples from nursing mothers in Beirut while in hospital (Milk fat extract. + SPE + GC)
- $47 \mu\text{g/l} \leq [\text{DDE}] \leq 1563 \mu\text{g/L}$
- [DDE] mean value $22+34 \mu\text{g/L}$
- No mention of LOD

OCP type	Detected n = 32	% Detection
DDT	10	31 %
DDD	6	19 %
DDE	31	97 %
α HCH	3	9 %
$\beta+\gamma$ HCH	1	3 %

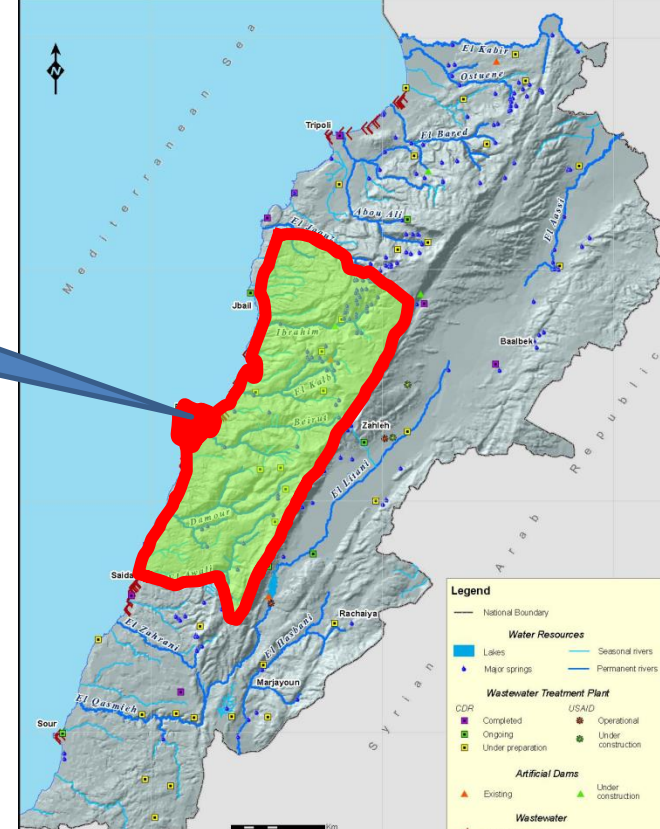
FAO/WHO (2005) stated that Σ DDT MRL for Human Milk is of $20 \mu\text{g/l}$ wm (FAO & WHO, 2005)

Positive correlation with [DDE]						
consumption of high fat meat and tuna fish	consumption of poultry products	consumption of vegetable oils	Aldrin	2	6 %	
			Endrin	1	3 %	
			Dieldrin	2	6 %	

n = 316 (133 ♂ and 181 ♀) aged 18 – 65
97.5 % of them from Beirut and Mount-Lebanon

The “ENASB - USJ” study (2014–2015)

- Samples of blood – anthropometric measures – BP – questionnaires (FFQ – 24 hrs recall – socio-demographic)
- Measured OCPs were HCB, β -HCH, DDT, and DDE
- 6 PCBi were measured (PCBs 28, 52, 101, 138, 153, 180)



**First human biomonitoring of
OCPs and PCBs in blood in
Lebanon**

Mireille Harmouche-Karaki, Joseph Matta, Khalil Helou, Yara Mahfouz, Nicole Fakhoury-Sayegh, Jean-François Narbonne, *Serum concentrations of polychlorinated biphenyls (PCBs) in a Lebanese population: ENASB study*, Environ Sci Pollut Res (2017) 24:3705–3716

Mireille Harmouche-Karaki, Joseph Matta, Khalil Helou, Yara Mahfouz, Nicole Fakhoury-Sayegh, Jean-François Narbonne, *Serum concentrations of selected organochlorine pesticides in a Lebanese population and their associations to sociodemographic, anthropometric and dietary factors: ENASB study*, Environ Sci Pollut Res Accepted: 31 May 2017

OCPs and PCBs in serum of 316 employees and students of USJ

PCB congener ng/g lipids	% > LOD (n=316)	Geom. Mean	Arithm. Mean	Min.	50 th percent.	95 th percent.	Max.
HCB ^a	50.0	7.1 ± 0.6	-	< LOD	5.8	32.0	85.1
βHCH	50.0	8.6 ± 0.6	-	< LOD	7.6	45.0	154.9
DDT ^b	49.7	2.1 ± 0.3	-	< LOD	2.0	5.0	15.8
DDE ^c	50.0	18.9 ± 0.9	-	< LOD	17.3	180.0	630.9
ΣDDE, DDT ^d	-	21	-	< LOD	-	-	646.7
PCB ₂₈	56.3	0.9	2.2	< LOD	2.2	5.6	18.2
PCB ₅₂	58.2	0.3	0.6	< LOD	0.3	1.5	17.4
PCB ₁₀₁	57.6	0.6	1.3	< LOD	0.6	3.6	17.4
PCB ₁₃₈	59.2	1.9	7.1	< LOD	8.2	16.7	50.1
PCB ₁₅₃	58.2	3.0	16.5	< LOD	16.4	45.9	87.1
PCB ₁₈₀	58.2	3.7	24.7	< LOD	24.1	66.8	170.0
Σ PCB ₁₃₈ PCB ₁₅₃ PCB ₁₈₀	-	9.0	48.3	< LOD	52.6	128.0	302.0
ΣPCBi	-	10.3	52.4	< LOD	57.9	135.0	339.0

^aBiomonitoring equivalents reference dose of non-cancer risk BERfD = 340 ng/g lipids; Biomonitoring equivalents point of departure of non-cancer risk BEPOD = 3384 ng/g lipids

^bBiomonitoring equivalents BE of 1E-05 cancer risk = 300 ng/g lipids (EPA)

^cBiomonitoring equivalents BE of 1E-05 cancer risk = 500 ng/g lipids (EPA)

^dBiomonitoring equivalents reference dose of non-cancer risk BERfD = 5000 ng/g lipids; Biomonitoring equivalents point of departure of non-cancer risk BEPOD = 16000 ng/g lipids

Human Biomonitoring

One study on PCB and OCP in human blood

The “ENASB - USJ” study (2013 – 2015)

PCB results

- PCB congeners 138, 153, and 180 predominated and accounted for 15.7, 25.2, and 34.1% of $\Sigma 6$ PCB.
- The higher contribution of PCB 180 to the detriment of PCB 153 could be due to the contamination in PCBs by transformers in the power sector
- [PCB] not age related
- The highest levels were lower than critical limits set by HBM I and II.

Comparison of PCB and OCP results between the ENASB-USJ study and the NHANES

PCBs & OCPs	LSB concentrations in serum (ng/g lipids)	LSB years	NHANES concentrations in serum (ng/g lipids)	NHANES years
PCB ₂₈	0.9	(2013-2015)	0.27	(2013-2014)
PCB ₅₂	0.3	(2013-2015)	0.3	(2007-2008)
PCB ₁₀₁	0.6	(2013-2015)	0.3	(2007-2008)
PCB ₁₅₃	3.0	(2013-2015)	0.26	(2013-2014)
PCB ₁₈₀	3.6	(2013-2015)	0.26	(2013-2014)
HCB	7.1 ± 0.6	(2013-2015)	1.3	(2013-2014)
βHCH	8.6 ± 0.6	(2013-2015)	1.3	(2013-2014)
DDT	2.1 ± 0.3	(2013-2015)	1.3	(2013-2014)
DDE	18.9 ± 0.9	(2013-2015)	1.8	(2013-2014)

Conclusions

- OCPs still are a significant problem despite legislations. Smuggling, lack of law enforcement and ignorance of the farmers are the principal cause.
- OCPs in tested groundwater and surface waters $>$ MRL, obviously non tested groundwater and surface waters in hotspots areas are contaminated too.
- Academic work increased since 2010, but still insufficient.
- Obviously PCBs in sea sediments in major ports (Beiut – Sidon – Jounieh ...) $>$ MRL

Conclusions

- No possibility to link existing data to assess human exposure (lack of data)
- Limited Human biomonitoring on serum

References

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