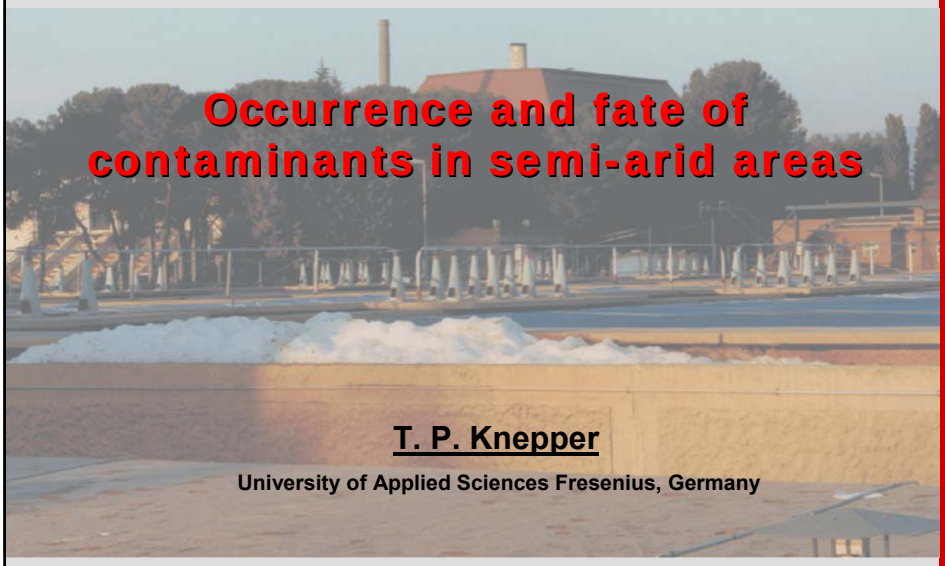

Occurrence and fate of contaminants in semi-arid areas

T. P. Knepper

University of Applied Sciences Fresenius, Germany

Outline

- An overview of the legislation in Europe
  - Water Framework Directive (WFD
  - Monitoring campaign in Hesse, Germany
- Monitoring & Fate of selected pollutants
- Analytical data of MPC and semi-arid areas
  - Turkey, Palestine, Tunesia, Egypt

European Water Framework Directive (WFD)

Strategy of monitoring (WFD):

Each ***compound***
- and also ***metabolite*** –
which could possibly appear has to be investigated.

....if an analytical method is available and the analysis not too costly

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Analytical determination of micropollutants and their metabolites

Complex matrices Low detection limits	Selective/sensitive analytical methods	Time and labour consuming procedures
Extraction clean-up →	**Separation** →	**Detection**
Filtration, solid phase extraction with various materials, derivatisation	High pressure liquid chromatograpy gas chromatography ion chromatography	electrospray ionisation mass spectrometry (ESI-MS/MS) Electron impact quadrupole and ion trap MS/MS ESI-Q-TOF-MS....QQQQQQQ

Identification of pollutants and their metabolites and degradation products via mass spectra and library searches (GC/MS)

ESI very suitable for polar and ionic compounds

Time shedule WFD:

Dec. 2000	In force
Dec. 2003	National law implementation
Dec. 2004	Characterisation and inventory
Dec. 2006	Programs for monitoring are ready for application
Dec. 2009	Program for measures and plans for management of river basin are finished
Dec. 2012	Program for measure is implemented
Dec. 2015	„good condition“ (ecological + chemical); new plans for management of river basin

Priority Substances and Other Pollutants

The Commission proposal (COM(2006)397 final) setting environmental quality standards for surface waters of 41 dangerous chemical substances includes the 33 priority substances and 8 other pollutants.

1) Priority Substances

33 substances or group of substances are on the list of priority substances including selected existing chemicals, plant protection products, biocides, metals and other groups like Polyaromatic Hydrocarbons (PAH) that are mainly incineration by-products and Polybrominated Biphenylethers (PBDE) that are used as flame retardants.

Chemical status - 33 priority compounds

Organic compounds (n = 16)

(2) Anthracene
(4) Benzene
(5) Brominated diphenylethers
(7) Chloroalkanes (C_{10} -C_{13})
(10) 1,2-Dichloroethane
(11) Dichloromethane
(12) DEHP
(15) Fluoranthene
(17) Hexachlorobutadiene
(22) Naphthalene
(24) Nonylphenols (4-para-N)
(25) Octylphenols (para-tert-O)
(26) Pentachlorobenzene
(28) PAK (Benzo-a-pyrene, Benzo-b-fluoranthene, Benzo-g,h,i-perylene, Benzo-k-fluoranthene, Indeno-1,2,3-cd-pyrene)
(31) Trichlorobenzenes (1,2,4-TB)
(32) Trichlormethane

Metals (n = 4)

(6) Cadmium
(20) Lead
(21) Mercury
(23) Nickel

Pesticides (n = 13)

(1) Alachlor
(3) Atrazine
(8) Chlorfenvinphos
(9) Chlorpyrifos
(13) Diuron
(14) Endosulfan
(16) Hexachlorobenzene
(18) HCH (Lindan)
(19) Isoproturon
(27) Pentachlorophenol
(29) Simazine
(30) TBT-cation
(33) Trifluralin

Identified as priority dangerous compounds (n = 13)

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Monitoring strategy in Hesse, Germany as case-study

HLUG

Starting 2007 the EU-member states have to conduct monitoring programs upon organic pollutants and others.

Hesse, Germany carried out a prelimary monitoring to find appropriate sampling points.

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Pesticides: Monitoring of surface waters 2004/2005 (preliminary monitoring)

- 119 sampling locations
- 95 substances
- 6 measurements 2004 or 2005

  therefrom

  4 in April - June

  2 in October -November

  → **Increased mean values during application time**
- Presetting of WFD

  For I → *12 samples/a*

  For II, III and IV → *4 samples/a*

European Water Framework Directive (WFD) – Regulation for Pesticides in surface waters

I priority pesticides

quality specifications by EU (in preparation)
e.g. IPU, Diuron, Atrazine

II river basin targeted pesticides

quality specifications by Hesse/Working Group on water issues (LAWA)

III further basin targeted pesticides

so far no regulation

IV river basin targeted pesticides

quality standard suggestion by LAWA, e.g. Terbutryn

Pesticide monitoring in 2004/2005

pesticide	quality standard [µg/L]	90-perc. [µg/L]	maximum value [µg/L]
Isoproturon	0.3 / 1.0 *	0.47	15
Mecoprop (MCPP)	0.1	0.12	11
Dichlorprop (2,4-DP)	0.1	0.11	10
n-Chloridazon	0.1	0.1	9.7
Bentazone	0.1	0.14	9
MCPA	0.1	0.16	7.7
Metazachlor	0.4	< l.d.	4.6
Diuron	0.2 / 1.8 *	0.21	4.5
Metobromuron		< l.d.	4.4
Metamitron		0.2	4.3
Ethofumesate		0.12	3.9
Terbuthylazine	0.5	0.04	2.5
Metolachlor	0.2	< l.d.	1.6
Atrazine	0.6 / 2.9 *	< l.d.	1.4
Terbutryn	0.03	0.09	1.3
Epoxiconazole		0.04	1
2,4-D	0.1	< l.d.	0.91
Propiconazole		0.07	0.8
Metribuzin		< l.d.	0.75
Fluoxypyr		0.04	0.55
Tebuconazole		0.05	0.51
Fenpropimorph		< l.d.	0.49
Terbutylazine-desethyl		< l.d.	0.47
Dichlobenil		< l.d.	0.46
Haloxyfop		< l.d.	0.46

approx. 700 samples

74 pesticides found, therefrom

25 with max. values

l.d. = limit of detection

•annual average value / maximum value

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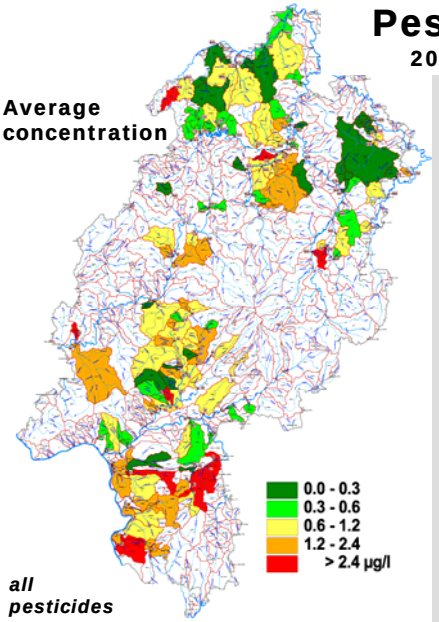
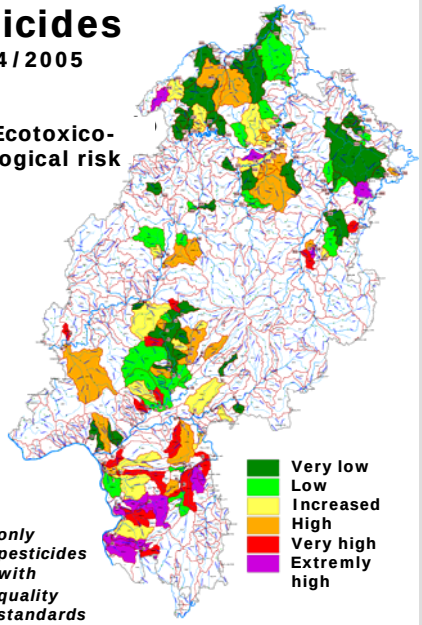
Pesticides 2004/2005

Average concentration



all pesticides

Ecotoxico-logical risk



only pesticides with quality standards

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Fate in the aquatic environment

How is the concentration in the water cycle correlated with the elimination during wastewater treatment??

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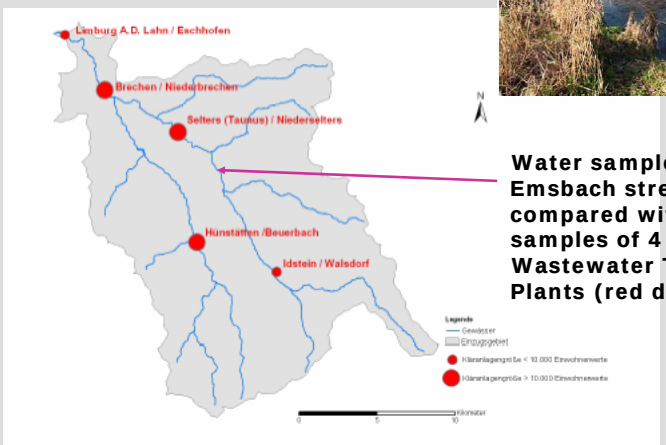
Balance of data gained for Hessian project* to fulfill requirements of WFD



Water samples of Emsbach stream compared with water samples of 4 Wastewater Treatment Plants (red dots)

*„Auswahl der kosteneffizientesten Maßnahmenkombinationen unter Berücksichtigung der Umweltziele und Ausnahmen nach Art. 4 WRRL anhand ausgewählter Wasserkörper im hessischen Teil des Bearbeitungsgebiets Mittelrhein“

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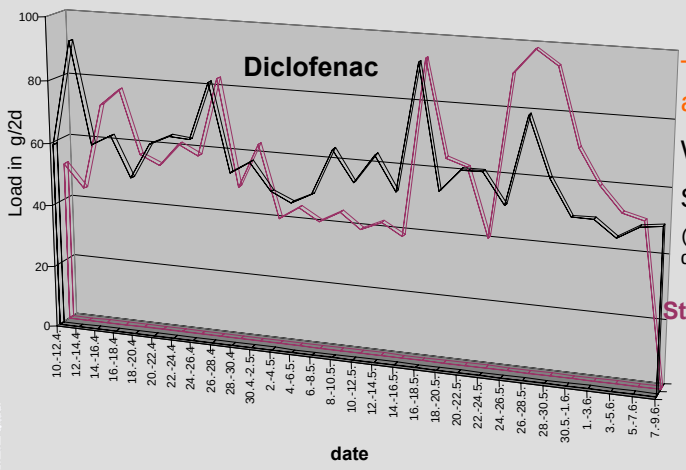
Balance of entry of emerging contaminants into the aquatic environment via WWTP:



Total for 2 month analysis (2006):

WWTP: 1.83 kg

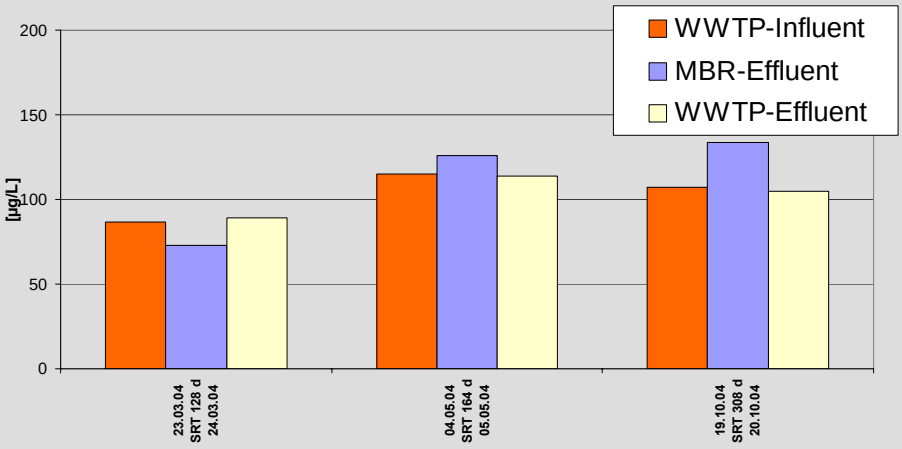
Stream: 1.77 kg

(result different for degradable compounds)

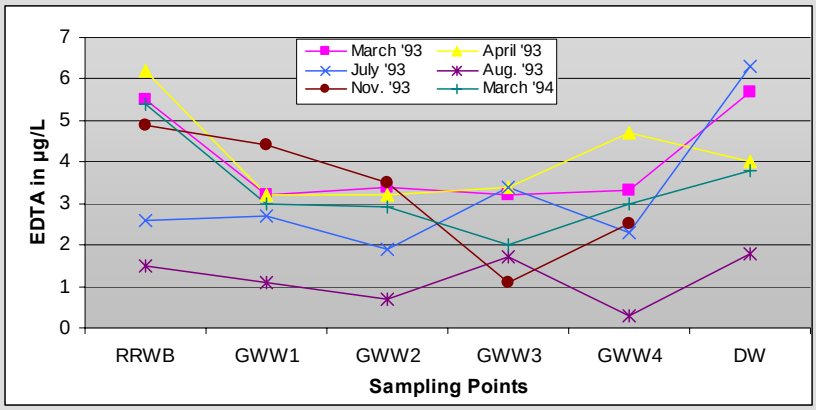
Stream

Total of 4 WWTP effluents

EDTA



Values of EDTA in ground water wells



RRWB = River Rhine Water Basin; GWW1 = Groundwater Well (1 m); GWWW2 (80 m); GWW3 (145 m); GWW4 (160 m); DW = Drinking Water

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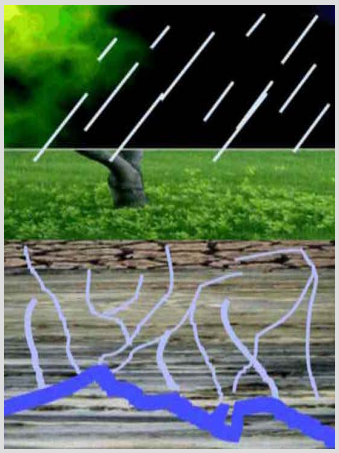
Occurrence of barbiturates in irrigated ground water (Berlin)



WW infiltration 40 y ago:

Phenobarbital: up to 1.3 µg/L

Other barbiturates:

between 0.05 and 0.08 µg/L

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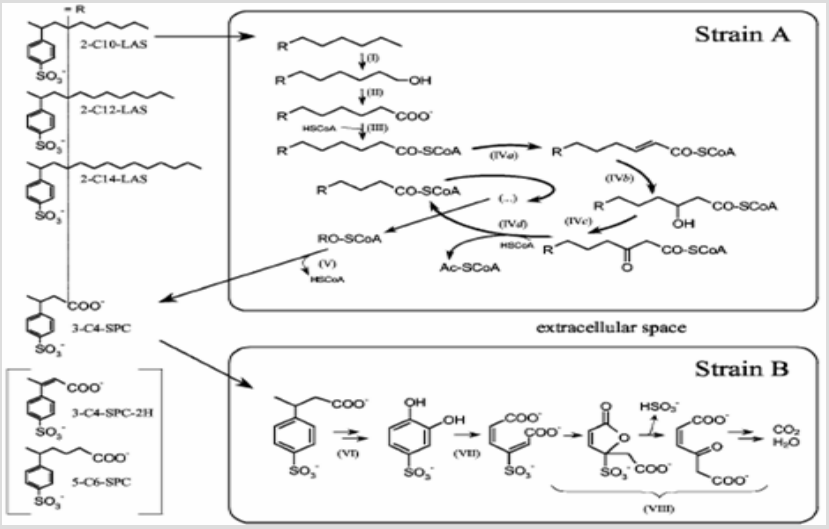
Formation of " relevant" metabolites, e.g. aerobic degradation of LAS into SPC in river systems / ground water (temperature dependent)



Schleheck, D., Knepper, T.P., Fischer, K., Cook, A.M.; *Appl. Environ. Microbiol.*, 2004.

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How to monitor in remote, semi-arid areas?

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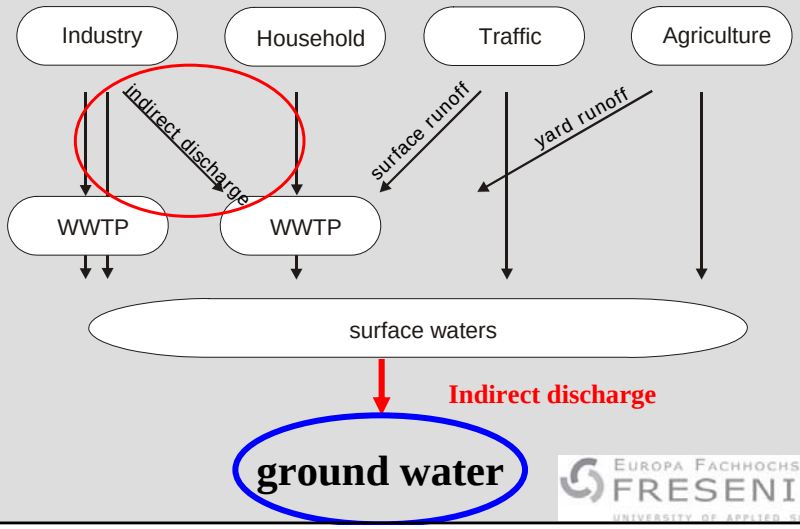
Entry of organic pollutants in the aquifer in semi-arid areas



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Literature data, for example data of Water quality of agricultural drains in Upper Egypt

Location		BOD		COD		TSS		Oil & Grease		Ammonia	
from AHD (KM)	Point Source	1998	1999	1998	1999	1998	1999	1998	1999	1998	1999
	Consent standard	30 mgO_2/l		40 mgO_2/l		30 mg/l		5 mg/l		NA	
50.000	Kom Ombo Sugar Ind.	144	760	3072	1500	58	46	1.2	9.3	0.01	0.01
63.600	Ekleet power station	1.2	4.8	2	84	28	79	1.21	2.55	0.01	0.01
119.600	Kaleh Power Station	1.4	2.0	5	40	15	32	2.26	3.09	0.01	0.10
122.450	Edfu Paper Pulp A	12	78	27	622	9	158	1.45	11.10	0.01	0.35
122.500	Edfu Paper Pulp B	13	75	19	354	9	25	0.36	2.81	0.05	0.01
123.000	Edfu Sugar Ind.	12	260		370	72	35	0.2	7.4	0.01	0.13

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Monitoring of water samples from partners of the Innova-Med project

Target analysis and non-target analysis

- **Pesticides and metabolites**
- **Pharmaceuticals**
- **Haloginated compounds**
- **Surfactants and fluorinated substances**
- **Heavy metals**

Monitoring of water samples: groundwater, surface water & waste water

Country	Samples
Turkey	5
Tunesia	10
Palestine	5
Egypt	13
Sum	33

Investigation of 13 water samples of Egypt, February 2009

	[LoQ µg/L]
Acdic compounds	
2,4 DP	0,06
2,4,5-T	0,06
2,4-D	0,06
2,4-DB	0,06
Bentazon	0,06
Dicamba	0,06
Fluazifop	0,06
Fluroxypyr	0,06
Haloxyfop	0,06
MCPA	0,06
MCPP	0,06
Triclopyr	0,06
Bezafibrat	0,06
Clofibrinsäure	0,06
Diclofenac	0,06
Ibuprofen	0,06
Ketoprofen	0,06
Naproxen	0,06

	[µg/L]
Neutral compounds	
Atrazin	0,06
Atrazin-desethyl	0,06
Epoxiconazol	0,06
Ethofumesat	0,06
Furmecyclox	0,06
Metamitron	0,06
Metazachlor	0,06
Metolachlor	0,06
n-Chloridazon	0,06
Omethoat	0,06
Propiconazol	0,06
Sebutylazin	0,06
Simazin	0,06
Tebuconazol	0,06
Terbuthylazin	0,06
Terbutryn	0,06
Chlortoluron	0,06
Diuron	0,06
Isoproturon	0,06
Linuron	0,06
Methabenzthiazuron	0,06
Metobromuron	0,06
Metoxuron	0,06
Monolinuron	0,06
Carbamazepin	0,06
Metoprolol	0,06
Phenazon	0,06
Propranolol	0,06
Sulfamethaxazol	0,06
Trimethoprim	0,06
Sum HCH	0,06

Heavy metals and others	
	[mg/L]
Fe	0,01
Pb	0,01
Zn	0,01
Cu	0,01
Na	0,01
K	0,01
Ca	0,01
Mg	0,01

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Investigation of 13 water samples from Egypt, Pharmaceuticals

Substance	LOQ	Egypt 2	Egypt 3	Egypt 4	Egypt 5	Egypt 6	Egypt 7	Egypt 8	Egypt 9	Egypt 10	Egypt 11	Egypt 12	Egypt 13	Egypt 1
		effluent VWTP	*ground water*	*ground water under land irrigated with treated WW*	*surface water from Ismailia*	*surface water at the begining of the drinking water treatment plant in Ismailia*	*mineral water*	*Tap water from Ismailia*	*Tap water from another city close to Cairo*	*surface water from Elsalam canal (WW mixed with river water to irrigate new land)*	*Tap water from Ismailia (another village)*	*Drainage water (Elmahsama drainage)*	*Drainage water (Elmahsama drainage) after mixed with treated waste water*	*influent VWTP*
	[LoQ µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]
Pharmaceutical														
Carbamazepin	0,06	**0,27**	**< LOQ**	**< LOQ**	< LOD	< LOD	< LOD	< LOD	< LOD	**0,04**	< LOD	< LOD	**0,14**	**< LOQ**
Metoprolol	0,06	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Phenazon	0,06	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Propranolol	0,06	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Sulfamethaxazol	0,06	**0,44**	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	**0,07**	< LOD	< LOD	**0,20**	**< LOQ**
Trimethoprim	0,06	**0,15**	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	**0,02**	< LOD	< LOD	**0,07**	**< LOQ**
Sum HCH	0,06	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

LOQ: 0.5 µg/L

LOD: limit of detection
LOQ: limit of quantification
n.a.: not analysed
approx.: approximately

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Samples Tunesia, February 2009

Substance	LOQ	Tunis 1	Tunis 2	Tunis 3	Tunis 4	Tunis 5	Tunis 6	Tunis 7	Tunis 8	Tunis 9	Tunis 10
	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]
Simazin	0,06	< LOQ	< LOD	0,12	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD
Carbamazepin	0,06	0,38	< LOQ	0,70	< LOD	< LOD	< LOD	< LOD	< LOD	0,28	< LOQ
Phenazon	0,06	< LOD	< LOD	0,06	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Sulfamethaxazol	0,06	0,38	< LOQ	0,26	< LOD	< LOD	< LOD	< LOD	< LOD	0,26	< LOD
		< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

No findings with LOQ of 0,6 µg/L for:

Atrazin, Atrazin-desethyl, Epoxiconazol, Ethofumesat, Furmecyclox, Metamitron, Metazachlor, Metolachlor, n-Chloridazon, Omethoat, Propiconazol, Sebutylazin, Tebuconazol, Terbuthylazin, Terbutryn, Chlortoluron, Diuron, Isoproturon, Linuron, Methabenzthiazuron, Metobromuron, Metoxuron, Monolinuron, Metoprolol, Propranolol, Trimethoprim

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Monitoring of Watersamples of Turkey, Chemical analysis

Substance	LOQ	Turkey 1	Turkey 2	Turkey 3	Turkey 4	Turkey 5
		Yesilirmak river, Anku station 1	Yesilirmak river, Anku station 2	Durucasu creek, Yesilirmak river, near Anku station 1	Ground well near Corum	Kizirmak river near Kalecik bridge Kirikkale
		27/02/09	27/02/09	February 2009	26/02/09	February 2009
	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]
Chemical analysis						
pH		7,6	7,7	n.a.	7,3	n.a.
Conductivity [µS/cm]		698	688	n.a.	888	n.a.
Salinity [%]		0,30	0,3	n.a.	0,4	n.a.
Suspended soilids [mg/L]		468	517	n.a.	n.a.	n.a.
NH3-N [mg/L]		0,36	0,39	n.a.	0,03	n.a.
PO4-P [mg/L]		0,39	0,83	n.a.	1,83	n.a.
NO3-N [mg/L]		1,4	1,6	n.a.	1,0	n.a.
COD [mg/L]		7,3	9,0	n.a.	n.a.	n.a.
NO2-N [mg/L]		0,06	0,066	n.a.	0,019	n.a.
LOD: limit of detection						
LOQ: limit of quantification						
n.a.: not analysed						
approx.: approximately						

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Monitoring of water samples from Turkey

Substance	LOQ	Turkey 1	Turkey 2	Turkey 3	Turkey 4	Turkey 5
		Yesilirmak river, Anku station 1	Yesilirmak river, Anku station 2	Durucasu creek, Yesilirmak river, near Anku station 1	Ground well near Corum	Kizirmak river near Kalecik bridge Kirikkale
		27/02/09	27/02/09	February 2009	26/02/09	February 2009
	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]
Acidic Compounds						
2,4 DP	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
2,4,5-T	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
2,4-D	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
2,4-DB	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
Bentazon	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
Dicamba	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
Fluazifop	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
Fluroxypyr	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
Haloxyfop	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
MCPA	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
MCPP	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
Triclopyr	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
Bezafibrat	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
Clofibrinsäure	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
Diclofenac	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
Ibuprofen	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
Ketoprofen	0,06	< LOD	< LOD	**0,06**	< LOQ	< LOD
Naproxen	0,06	< LOD	< LOD	< LOD	< LOD	< LOD
LOD: limit of detection						
LOQ: limit of quantification						
n.a.: not analysed						
approx.: approximately						

Neutral analytes all below LOD !!

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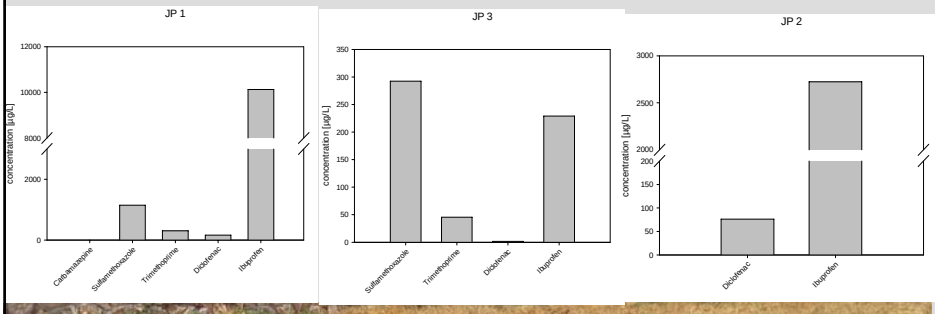
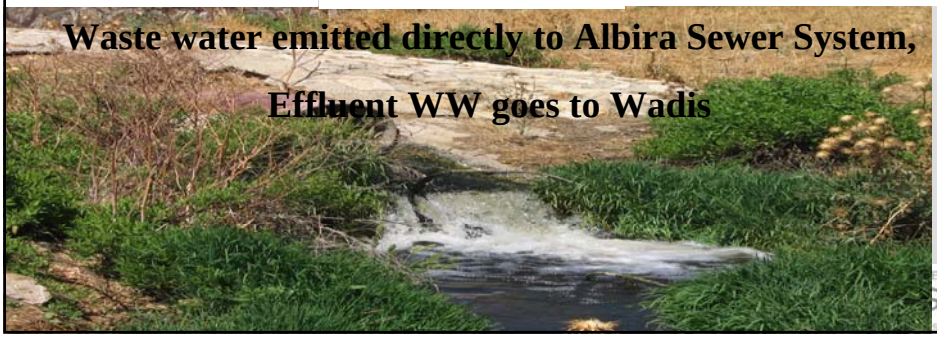
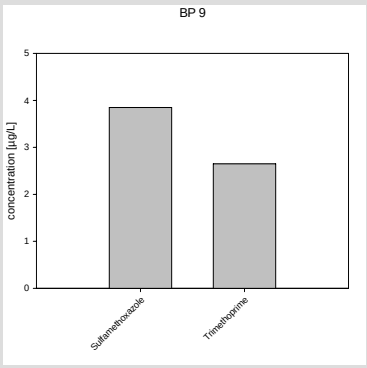
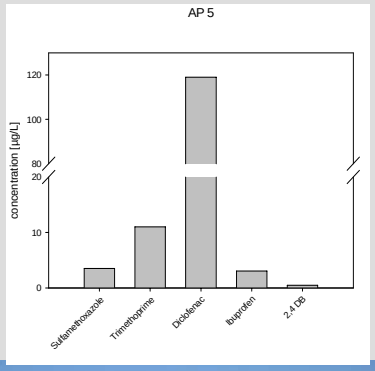
Analysed pharmaceuticals in untreated WW samples from Palestine, Jerusalem Pharmaceutical company



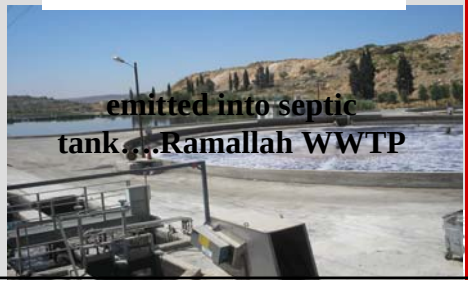


Analysed pharmaceuticals in untreated WW samples from Palestine, Birzeit and Dareshefa





emitted into septic tank….Wadis



Qualitative analysis with GC-MS

The WW samples from a pharmaceutical company and water from wells in Palestine have been additionally screened with GC-MS. Analysis was carried out in the scan mode to search for non target pollutants. The following substances have been detected with the aid of the NIST mass spectral library:

- **Chloroxylenol**
- **Croamiton**
- **4-chloro-3-methyl phenol**
- **Methylparaben**

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Water quality parameters of ground water wells in Palestine, Jenin and Tulkarem area

- Two groups have been measured with LC-MS/MS (neutral and acidic).
- With GC-MS, an additional qualitative screening analysis has been performed.
- Information obtained from the samples:
  - Well 4: T = 24.4°C; EC = 840 µS/cm; pH = 8.67;
  - Well 5: T = 24.8; EC = 1220 µS/cm; pH = 8.22
  - Well 6: T = 25.5°C; EC = 795 µS/cm, pH = 8.26;
  - Well 10, Well 9: label washed off

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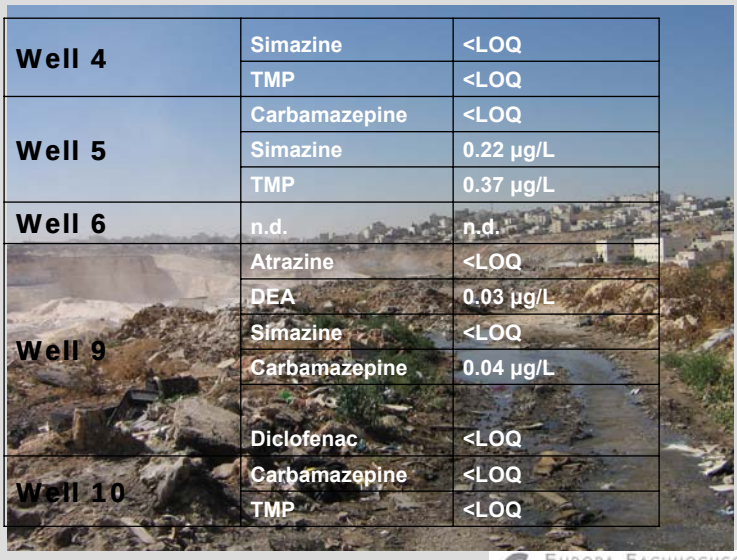
Analysed water samples from different wells in Palestine, no direct influence of pharmaceutical WW

Well 4	Simazine	<LOQ
	TMP	<LOQ
Well 5	Carbamazepine	<LOQ
	Simazine	0.22 µg/L
	TMP	0.37 µg/L
Well 6	n.d.	n.d.
Well 9	Atrazine	<LOQ
	DEA	0.03 µg/L
	Simazine	<LOQ
	Carbamazepine	0.04 µg/L
Well 10	Diclofenac	<LOQ
	Carbamazepine	<LOQ
	TMP	<LOQ



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Conclusions

- The more pollutants are analysed the more can be detected – main source for entry into the aquatic environment are WWTP.
- Monitoring campaigns need to be well thought of and organized – metabolites need to be included
- Organic pollutants are present in surface waters all over Europe at comparable concentrations (for pesticides during application time)
- Monitoring data from MPC countries are quite sparse; thus it is extremely difficult to come up with any conclusion. Further, time and spatial expanding campaigns have to be conducted (and financed) in order to get a thorough inventory!

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Acknowledgement

HSF:

Jutta Müller

Heike Weil

European Commission

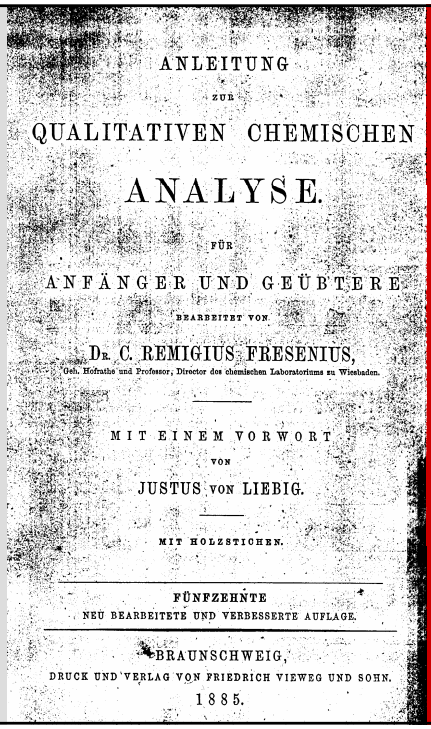
Innovamed: Damia, Mira, Mary..

Sampling: Ridvan Berber; Mohamed Tawfic, Omar Zimmo & Subhi Samhan;

Faycel Chenini; Redouane Choukr-Allah

Hessian Ministry for Environment

Peter Seel



ANLEITUNG
ZUR
QUALITATIVEN CHEMISCHEN
ANALYSE.
FÜR
ANFÄNGER UND GEÜBTERE.
BEARBEITET VON
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MIT EINEM VORWORT
VON
JUSTUS VON LIEBIG.
MIT HOLZSTICHEN.
FÜNFZEHNTE
NEU BEARBEITETE UND VERBESSERTE AUFLAGE.
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1885.