Regione Toscana
Diritti Valori Innovazione Sostenibilità

ARPAT
Agenzia regionale per la protezione ambientale della Toscana

WORKSHOP WITH ARPA TUSCANY (ARPAT)

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General Directorate of ARPAT
Via Porpora 22, Firenze

Environmental impact from pesticides, monitoring and elaboration of a pressure synthetic indicator

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The use of **pesticides** in agriculture has an impact on the quality of the **environment** and on **food safety**.

Surface water and **groundwater** are more sensitive to pollution.

Environmental Agencies play a central role in the **monitoring of water resources** for verifying the achievement of environmental quality objectives established by European standards and in **providing technical and scientific support** to the Regions in the policies of water protection.

European Union has recently promulgated the

Directive 2009/128/EC

a framework for member states for policies and actions designed to

"sustainable use of pesticides"

The main activities include

- promotion of organic farming,
- obligation of the adoption of the principles of integrated plant-health control (low pesticide-input)
- training and certification of sector's operators (vendors, users, consultants)
- information to the public about the risks of pesticide use
- proper maintenance and calibration of distribution equipment,
- prohibition on spraying by aircraft
- protection of the aquatic environment.

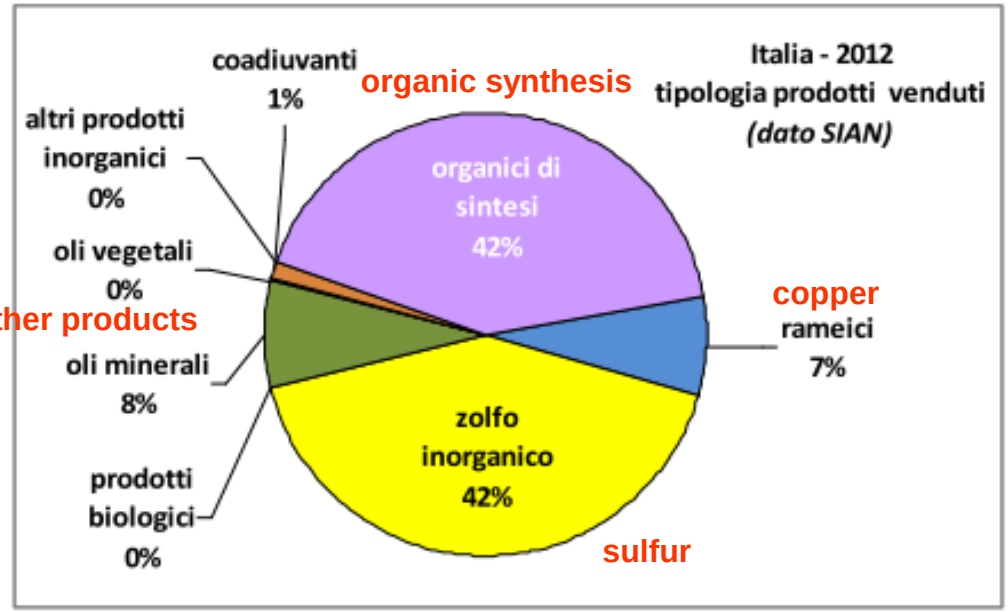
The **protection of the aquatic environment** from pollution by pesticides is carried out through various instruments

- reduction / elimination / substitution of pesticides classified as dangerous for the aquatic environment,
- use of low-dispersion distribution techniques to decrease the amount pesticide,
- specific mitigation measures to be taken in the field to reduce the phenomena of run-off or drainage or transport to surface water bodies,
- creation of respect areas for waters used for drinking purposes where prohibited / regulated the use of pesticides,
- reduction / elimination of the treatments on impermeable surface (public health use).

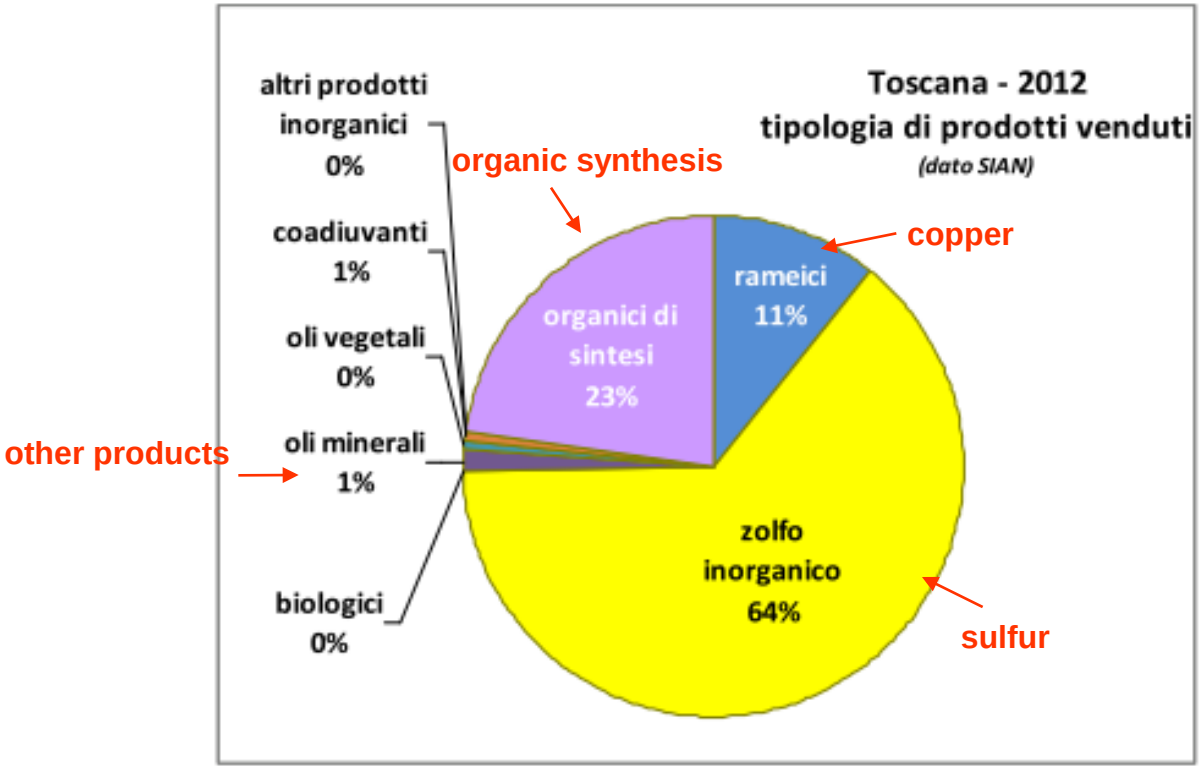
In Italy each year are currently sold around **60,000 tons of pesticides** (approximately **6 kg per hectare of agricultural area**)

- proximately 50% of the products used is represented by compounds based on **copper and sulfur** (products compatible with organic farming),
- slightly more than 40% is represented by products of **organic synthesis**,
- the remaining 10% by **other products** .

在水中农药监测



In Tuscany **75%** of the products used is based on inorganic **sulfur** and **copper** which find wide application particularly in the cultivation of the grape growing..



Synthetic organic compounds refer to more than **400 different active substances** on the market in Italy in recent years

about **10** substances represent **50%** of the total quantity sold and about **100** represent **90%**.

Some of the substances in this category may **represent a risk to the environment**, especially for their possible **impact on water resources**, as shown by the results of water monitoring in recent years.

dati di vendita elaborati dal gruppo AAAF TOSCANA 2012	
Sostanza attiva	**Kg**
ZOLFO	1277454
RAME (composti del)	213900
GLIFOSATE	104016
FOSETIL ALLUMINIO	102749
MANCOZEB	53261
OLIO DI PARAFFINA	28081
DAZOMET	15105
METIRAM	11680
FOLPET	9970
SPIROXAMINA	9848
DIMETOMORF	9270
OLIO DI COLZA	8724
CIMOXANIL	8078
PENDIMETALIN	7358
DIMETOATO	6118
CLORPIRIFOS	5800
S-METOLACLOR	5738
PROCLORAZ	5179
MCPA	4644
3,6-DIOXAEICOSILSOLFATO	4578
N-DECANOLO (1-DECANOLO)	3923
ZIRAM	3785
DITIANON	3727
IPROVALICARB	3702
METAM-SODIUM (usi essenziali fino al 31/12/2014)	3695
TEBUCONAZOLO	3450
SPINOSAD	3346
FENAMIDONE	3250

The organic products of synthesis **most sold** in Italy and in Tuscany

is the herbicide **glyphosate**

that recently the IARC *(International Agency for Research on Cancer)* has classified as probable carcinogen (class 2A).

在水中农药监测

To carry out **adequate monitoring** of residues of pesticides in **water** is required

- a **laboratory** equipped with high performance instruments and qualified operators,
- a careful design to identify both **water bodies "at risk"** of pollution
- a **list of "priority" pesticides** to be investigate in the waters,
- a system of data storage, processing and circulation to represent
  - ✓ **state** of water quality,
  - ✓ **degree of achievement** of the **objectives** set by the European Union (ecological and chemical status "good" at 2018),
  - ✓ **trend over time**.

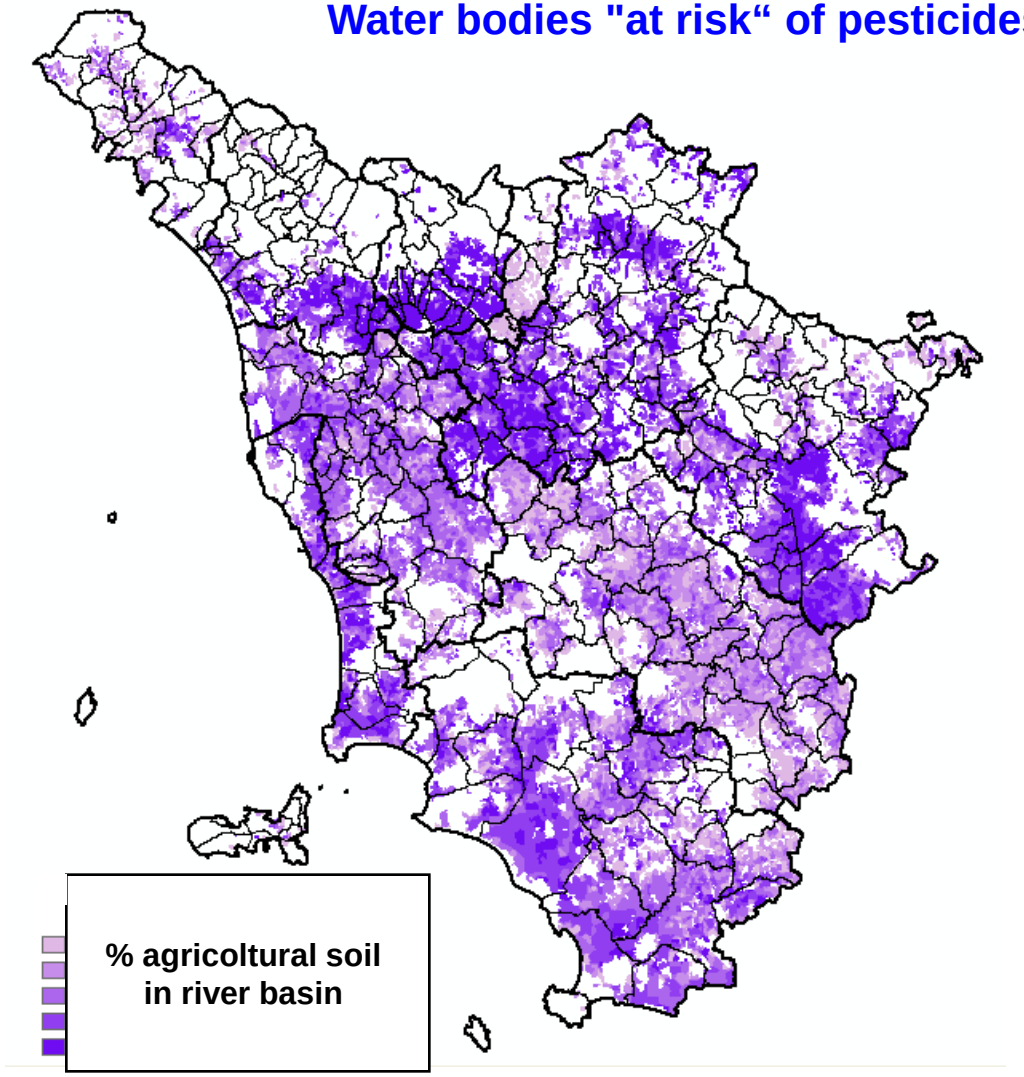
Water bodies "at risk“ of pesticides pollution

200 stations to monitor pesticides
(of about 650 monitoring stations present in Tuscany)
2/3 of these monitoring stations are water bodies for use for **drinking water** .

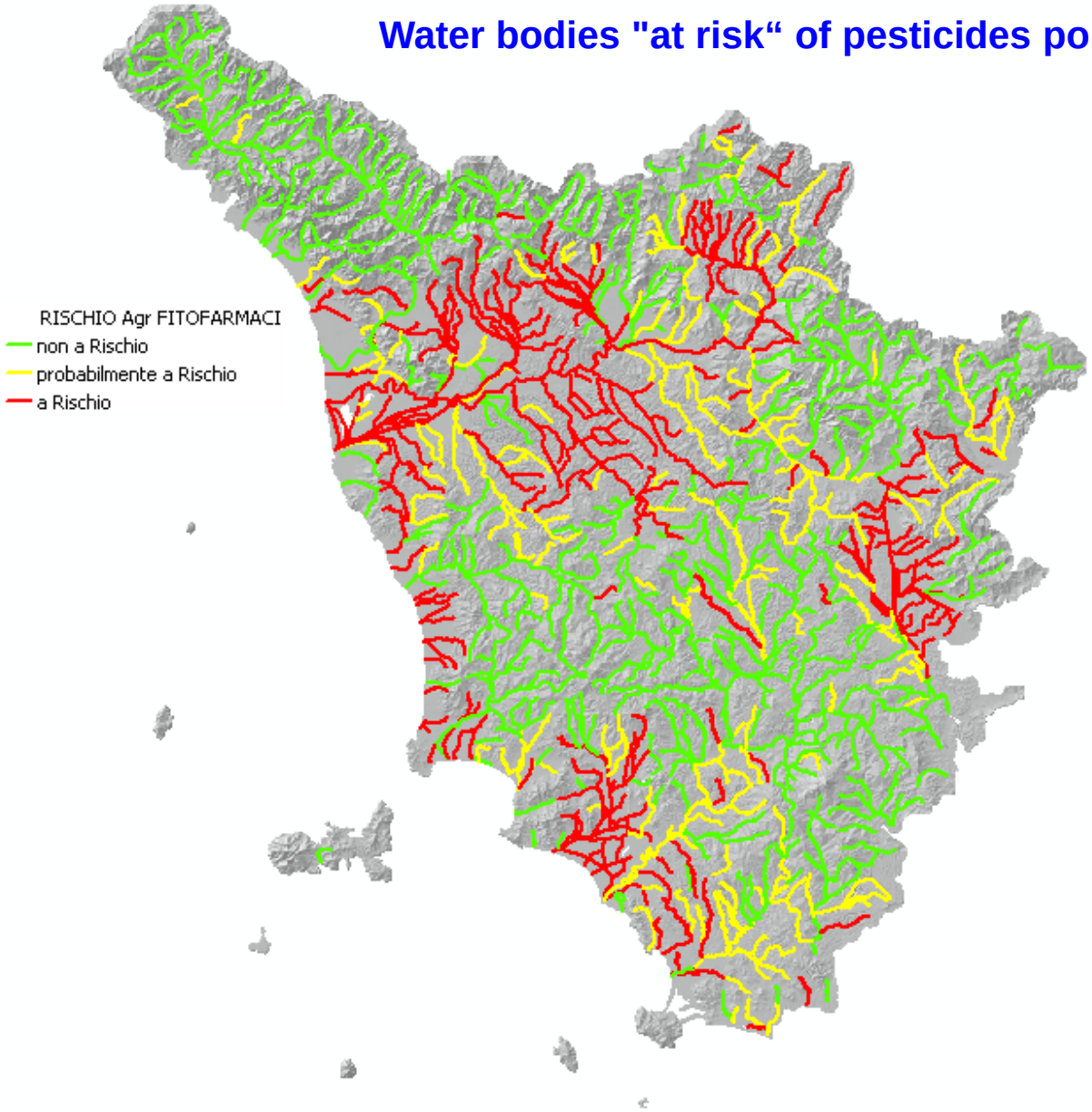
carried out
through an **analysis of pressures**
using as **pressure indicator** the **“agricultural use of the soil"**

This analysis is used to select the water bodies "at risk of pesticide pollution", those with higher extension of agricultural areas in their own recharge reservoir.

Water bodies "at risk“ of pesticides pollution



Water bodies "at risk“ of pesticides pollution



A list of "priority" pesticides

Answer to:
which pesticides to search in the waters for a
appropriate monitoring profile ?

selecting on provisional mode

from
most used pesticides in the area
(data available through the sales data)
and
physical-chemical and environmental properties
indicating a risk for the matrix water
(i.e. high solubility, persistence, mobility, ability to bio-accumulate).

A list of "priority" pesticides

Water Priority Index (GuideLine AAAF, 2011)

based on

- ✓Water solubility
- ✓Molecular weight
- ✓Vapour pressure
- ✓Kow
- ✓Koc
- ✓Degradation time in soil (DT50 soil)

WPI values from 0,4 (low risk) to 6 (high risk)

PRIORITY LIST PESTICIDES TO SEARCH IN WATER (TUSCANY - 2013-2015)							
1	ACETOCLOR	22	CLORTOLURON	43	IPROVALICARB	64	PENCONAZOLO
2	ALACLOR	23	D, 2,4-	44	ISOPROTURON	65	PENDIMETALIN
3	AMPA	24	DB, 2,4-	45	KRESOXIM-METHYL	66	PIRACLOSTROBINA
4	ATRAZINA	25	DICAMBA	46	LENACIL	67	PIRIMETANIL
5	ATRAZINA, DESETIL	26	DIMETENAMID	47	LINURON	68	PROCIMIDONE
6	ATRAZINA, DESISOPROPIL	27	DIMETOATO	48	MALATION	69	PROPAMOCARB
7	AZIMSULFURON	28	DIMETOMORF	49	MANDIPROPAMID	70	PROPICONAZOLO
8	AZOSSISTROBINA	29	DIURON	50	MCPA	71	PROPIZAMIDE
9	BENALAXIL	30	ENDOSULFAN	51	MECOPROP	72	QUIZALOFOP-ETILE-D
10	BENTAZONE	31	ENDOSULFAN, SOLFATO	52	MEPANIPYRIM	73	RIMSULFURON
11	BOSCALID	32	ETOFUMESATE	53	MESOSULFURON-METILE	74	SIMAZINA
12	CARBENDAZIM	33	FENHEXAMID	54	METALAXIL, METALAXIL,M-	75	SPIROXAMINA
13	CIMOXANIL	34	FENPROPIDIN	55	METAMIDOFOS	76	TEBUCONAZOLO
14	CIPROCONAZOLO	35	FLUFENACET	56	METAMITRON	77	TERBUTILAZINA
15	CIPRODINIL	36	FLUOPICOLIDE	57	METAZACLOR	78	TERBUTILAZINA, DESETIL
16	CLOPIRALID	37	FLUROXIPIR	58	METOLACLOR, METOLACLOR,S-	79	TOLCLOFOS-METILE
17	CLOPIRALID	38	GLIFOSATE	59	METRIBUZIN	80	TRALCOXIDIM
18	CLORIDAZON	39	GLUFOSINATE	60	NICOSULFURON	81	TRIASULFURON
19	CLORPIRIFOS	40	IMIDACLOPRID	61	OXADIAZON	82	TRIFLURALIN
20	CLORPIRIFOSMETILE	41	IODOSULFURON-METIL-SODIO	62	OXADIXIL		
21	CLORSULFURON	42	IPRODIONE	63	OXIFLUORFEN		

ARPAT
performs annually
in the water monitoring of pesticides in Tuscany
over **1000 water samples**

corresponding
200 monitoring stations of surface waters and groundwater

On each sample is performed a **"multi-residue analysis"**
able to quantify over **80 different active substances**,

for a total of approximately **80,000 determinations**

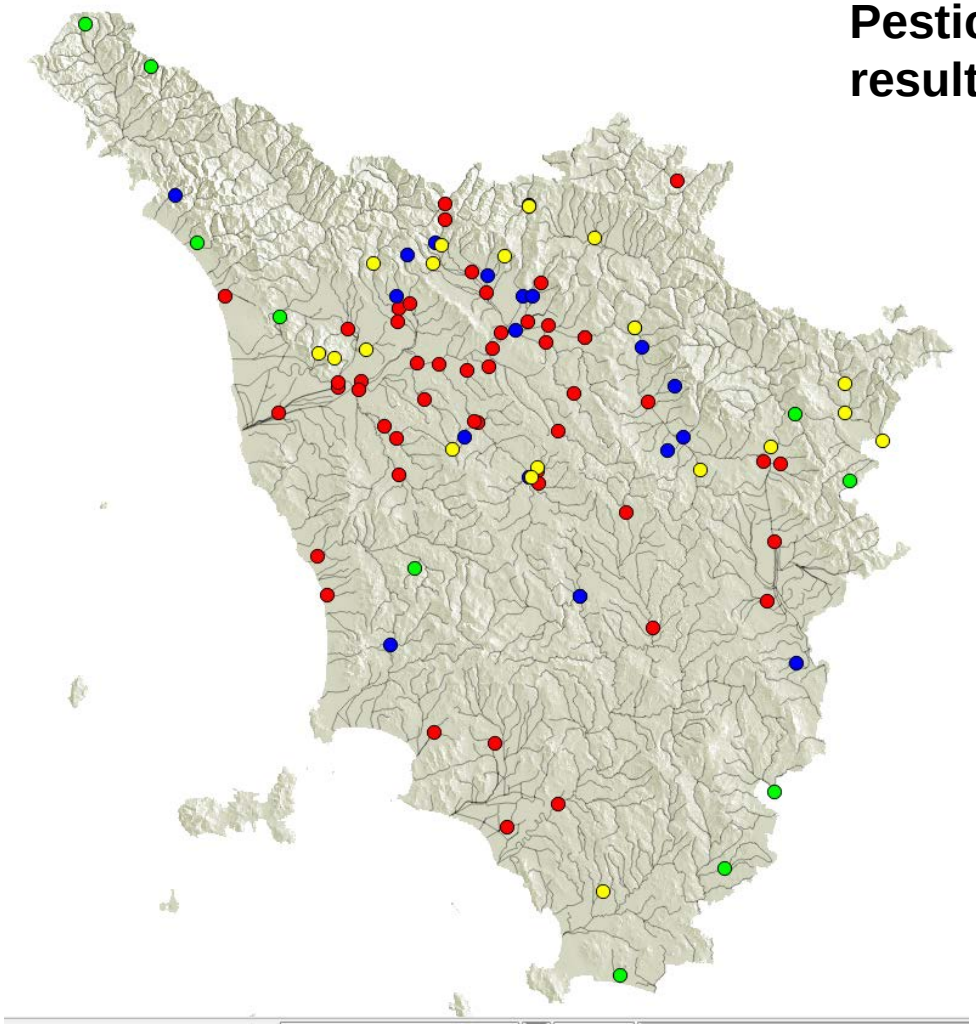
Monitoring results

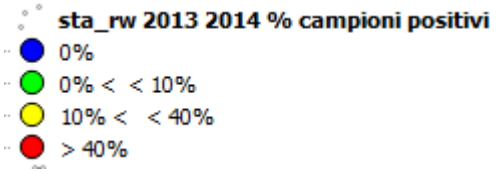
In **Tuscany**
(in line with the rest of Italy)

the **monitoring results** indicate a
widespread presence of pesticide residues in water,

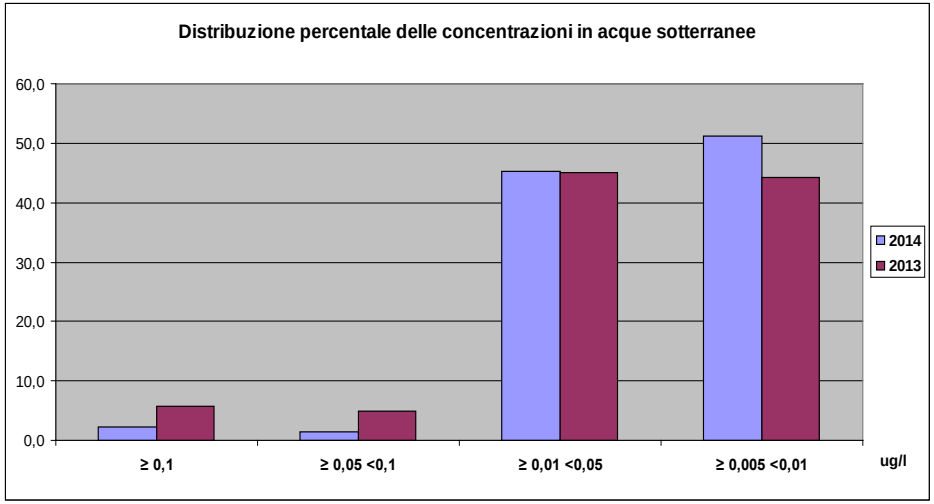
more pronounced in **surface water**
(about 50% of the samples presents detectable residues)
that in **groundwater**
(about 25% of the samples presents detectable residues).

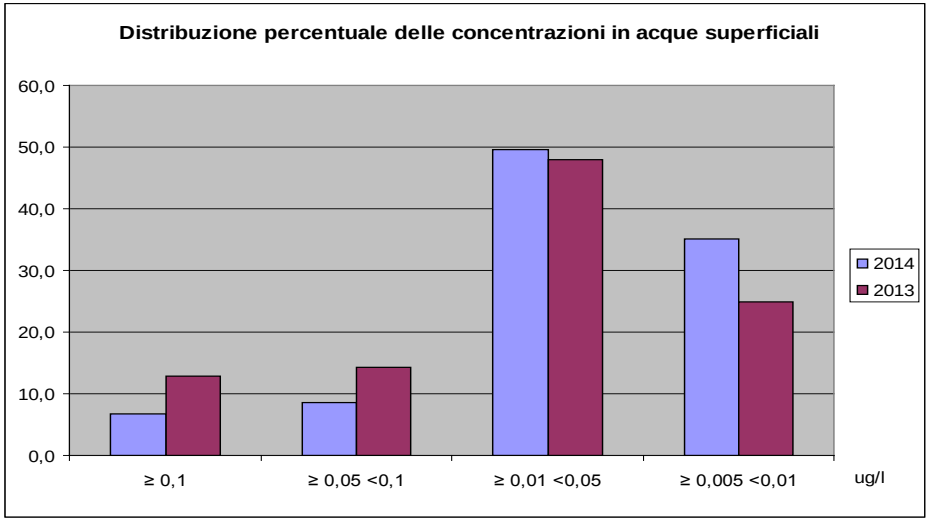
Surface water Pesticides monitoring results (2013-14)





% samples with detectable residues





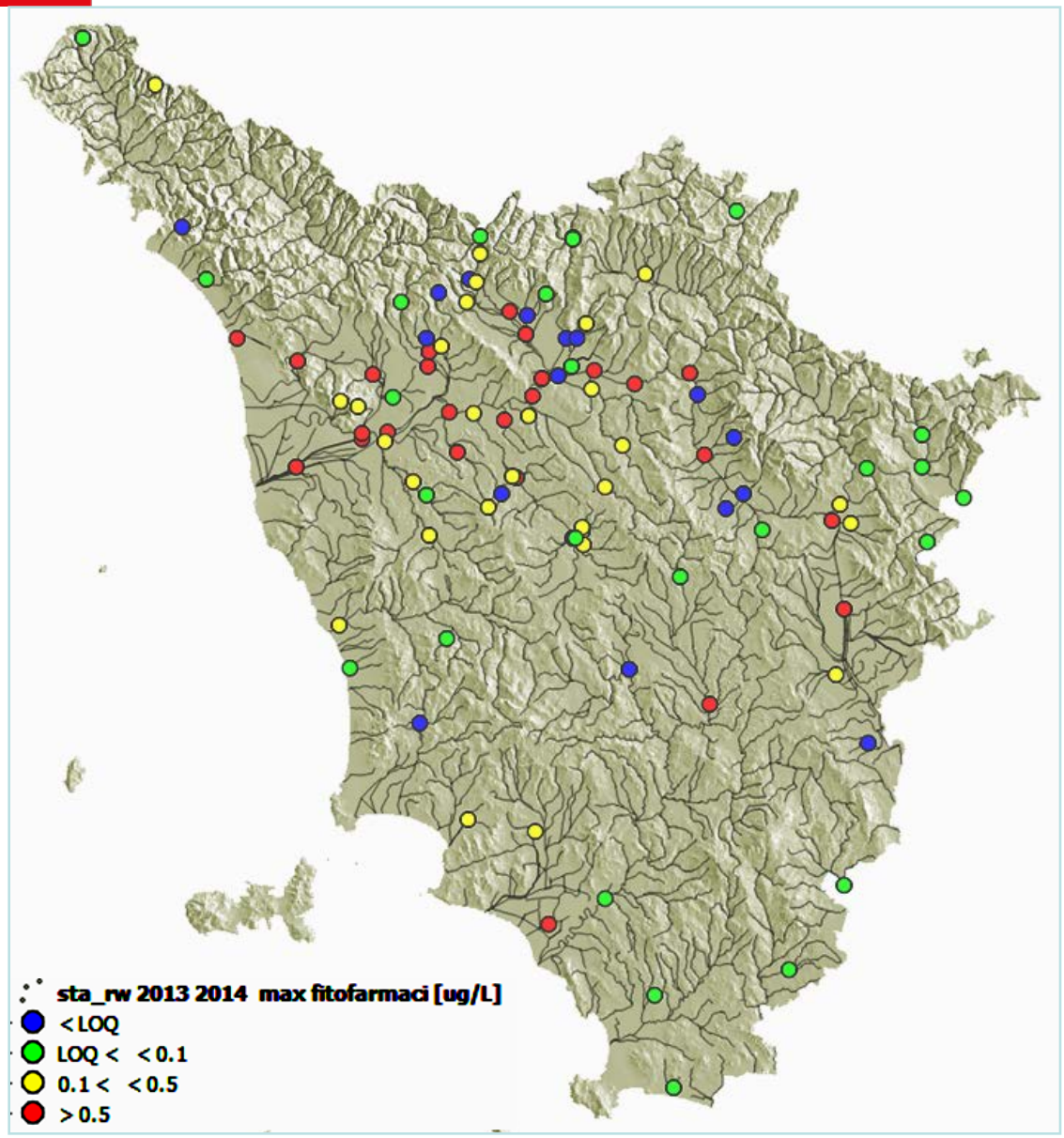
The **concentrations** are however **on average low**

only **10%** of surface water samples and **5%** of groundwater samples have concentrations of pesticides **≥ 0.1 µg / litro**
(legal limit for drinking water)

groundwater

percentage distribution of resideues concentration

surface water



Surface water
Pesticides monitoring results (2013-14)

Maximum residues level

Principal pesticide residues in surface water (Tuscany- 2014)

ELENCO DELLE SOSTANZE ATTIVE CON CONCENTRAZIONI MASSIME RILEVATE ≥ 0,1 µg/l						
	ACQUE SUPERFICIALI INTERNE	campioni positivi	Valore minimo	Valore massimo	Valore medio	Valore mediano
		n	µg/L	µg/L	µg/L	µg/L
1	AZOSSISTROBINA	23	0,005	0,254	0,030	0,009
2	BOSCALID	17	0,005	0,112	0,018	0,009
3	CARBENDAZIM	81	0,005	0,284	0,033	0,012
4	CLORTOLURON	34	0,005	0,561	0,057	0,014
5	DIMETOATO	33	0,005	0,527	0,042	0,022
6	DIMETOMORF	123	0,005	0,522	0,045	0,021
7	FENHEXAMID	8	0,007	0,273	0,071	0,020
8	FLUOPICOLIDE	111	0,005	0,235	0,028	0,016
9	GLIFOSATE	51	0,005	2,108	0,175	0,057
10	GLUFOSINATE-AMMONIO	3	0,012	0,237	0,088	0,015
11	IMIDACLOPRID	122	0,001	0,343	0,038	0,014
12	KRESOXIM-METIL	58	0,005	0,365	0,038	0,021
13	MANDIPROPAMIDE	13	0,006	0,482	0,073	0,032
14	METALAXIL-M	92	0,005	0,154	0,030	0,018
15	METOLACLOR-S	69	0,005	0,626	0,038	0,013
16	NICOSULFURON	16	0,006	0,221	0,043	0,010
17	OXADIAZON	35	0,006	0,173	0,044	0,020
18	PROPAMOCARB	21	0,007	0,863	0,086	0,020
19	TEBUCONAZOLO	96	0,005	0,101	0,022	0,015
20	TERBUTILAZINA	71	0,005	0,249	0,032	0,014

pesticide residues in groundwater (Tuscany- 2014)

	ACQUE SOTTERRANEE	campioni positivi	Valore minimo	Valore massimo	Valore medio	Valore mediano
		n	µg/L	µg/L	µg/L	µg/L
1	ATRAZINA, DESETIL-	19	0,005	0,040	0,011	0,008
2	IMIDACLOPRID	11	0,006	0,038	0,017	0,014
3	CARBENDAZIM	8	0,005	0,284	0,048	0,014
4	PENDIMETALIN	8	0,006	0,027	0,013	0,010
5	OXADIAZON	7	0,005	0,016	0,009	0,007
6	PIRACLOSTROBINA	7	0,005	0,015	0,011	0,012
7	GLIFOSATE	6	0,004	0,022	0,012	0,012
8	TERBUTILAZINA, DESETIL-	6	0,005	0,007	0,006	0,006
9	ATRAZINA, DEISOPROPIL-	5	0,006	0,015	0,011	0,010
10	BOSCALID	4	0,005	0,025	0,011	0,007
11	KRESOXIM-METIL	4	0,010	0,131	0,056	0,042
12	OXADIXIL	4	0,006	0,025	0,013	0,010
13	OXYFLUORFEN	4	0,006	0,025	0,013	0,011
14	PROPAMOCARB	4	0,005	0,009	0,007	0,007
15	TRALCOXYDIM	4	0,012	0,017	0,014	0,013
16	ATRAZINA	3	0,005	0,012	0,008	0,007
17	CLORTOLURON	3	0,007	0,022	0,015	0,017
18	DIURON	3	0,006	0,044	0,021	0,014
19	FLUOPICOLIDE	3	0,005	0,021	0,010	0,005
20	SIMAZINA	3	0,008	0,020	0,012	0,008
21	CIPRODINIL	2	0,006	0,007	0,007	0,007
22	MEPANIPYRIM	2	0,005	0,006	0,006	0,006
23	METOLACLOR-S	2	0,029	0,122	0,076	0,076
24	TEBUCONAZOLO	2	0,009	0,021	0,015	0,015
25	TERBUTILAZINA	2	0,005	0,050	0,028	0,028
26	AMPA	1	0,007	0,007	0,007	0,007
27	DIMETOATO	1	0,006	0,006	0,006	0,006
28	GLUFOSINATE-AMMONIO	1	0,015	0,015	0,015	0,015
29	LENACIL	1	0,006	0,006	0,006	0,006
30	LINURON	1	0,009	0,009	0,009	0,009
31	METAZACLOR	1	0,027	0,027	0,027	0,027
32	NICOSULFURON	1	0,017	0,017	0,017	0,017
33	PENCONAZOLO	1	0,005	0,005	0,005	0,005
34	SPIROXAMINA	1	0,006	0,006	0,006	0,006

In Tuscany the water state **is not alarming for pesticides**

but

there are however **some very critical situations** some superficial water reservoirs used for the production of **drinking water**.

National legislation provides around those points a buffer zone large 200 m where it is forbidden to use of pesticides
(that unfortunately it is not always respected)

POT-019	BACINO FALCHERETO		
PT	QUARRATA		
SOSTANZA ATTIVA	VALORE MAX (µg/l)		
	2012	2013	2014
atrazina, deisopropil		0,007	
boscalid		0,005	
carbendazim		0,086	0,006
clortoluron		0,06	
dimetoato		0,066	0,108
dimetomorf		0,322	0,076
fenhexamid		0,009	0,273
fluopicolide		0,055	0,048
glifosate			0,226
imidacloprid		0,14	
iprovalicarb	0,026	0,007	0,008
lenacil			0,019
mcpa		0,008	
metalaxil		0,172	
metalaxil-m		1,22	0,065
metolaclor-s			0,011
nicosulfuron			0,01
oxadixil		0,015	
oxyfluorfen		0,007	
pendimetalin		0,013	
simazina		0,006	
tebuconazolo		5,59	0,073
terbutilazina		0,108	
terbutilazina, desetil		0,006	

In last period ARPAT
is collaborating with the Region of Tuscany
to a **regulation** of the **protection areas** of surface and groundwater **used for drinking water production**,
by adopting **"plans for the use of pesticides"** that provide or **prohibition** or **use restrictions** for substances with **high water pollution potential**, favoring the use of substances with a lower impact.

This can be done using an **indicator proposed by ARPAT** able to represent a **"specific gravity environment" of each pesticide** calculated through the combination of **physicochemical** and **partitive properties** (solubility, degradation time, Kow octanol-water coefficient Koc adsorption of carbon-water) and some **eco-toxicological properties** (toxicity to animals and plants sensitive).

Pressure indicator is calculated combining

Indicator	Environmental, eco-tossicological, tossicological property	Potential impact threshold		
		1	2	3
		Low	Medium	high
Water solubility 20°C (mg/l)	Affinity for water	≤ 50	50-500	> 500
Koc (ml/g)	Mobility	> 500	75-500	≤ 75
DT50 soil (days)	Persistence in soil	≤ 30	30-100	>100
DT50 water - hydrolisis pH7 (days)	Persistence in water	≤ 30	30-100	>100
DT50 sed. (days)	Persistence in sediment	≤ 30	30-100	>100
GUS	Potenzial of leaching	< 1,8	1,8-2,8	> 2,8
log Kow	affinità al bioaccumulo	≤ 2,7	2,7-3	> 3
LD50 oral acute (mg/kg BW/day)	Mammalians toxicity	>2000	100-2000	<100
LD50 acute (mg/kg)	Birds toxicity	>2000	100-2000	<100
LC50 acute (96h-mg/l)	Fishes toxicity	>100	0,1-100	<0,1
EC50 acute (48h mg/l)	Aquatic Inverteb. toxicity	>100	0,1-100	<0,1
LD50 acute (48h ug/ape)	Honey bees toxicity	>100	1-100	<1
LC50 acute (14d mg/kg)	Eartworms toxicity	>1000	10-1000	<10
Endocrin destrucor	Endocrine effects	no	possible	yes
Reproduction and development	Reproductive effects	no	possible	yes
ADI (mg/kg bw)	Accettable daily intake	> 0,1	0,01-0,1	≤ 0,01

to give a "specific gravity environment“

Glyfhosate

Indicator	Environmental, eco-tossicological, tossicological property	Potential impact threshold			
			1	2	3
		No data	Low	Medium	high
Water solubility 20°C (mg/l)	Affinity for water				x
Koc (ml/g)	Mobility		x		
DT50 soil (days)	Persistence in soil		x		
DT50 water - hydrolisis pH7 (days)	Persistence in water				x
DT50 sed. (days)	Persistence in sediment			x	
GUS	Potenzial of leaching		x		
log Kow	affinità al bioaccumulo		x		
LD50 oral acute (mg/kg BW/day)	Mammalians toxicity			x	
LD50 acute (mg/kg)	Birds toxicity			x	
LC50 acute (96h-mg/l)	Fishes toxicity			x	
EC50 acute (48h mg/l)	Aquatic Inverteb. toxicity			x	
LD50 acute (48h ug/ape)	Honey bees toxicity			x	
LC50 acute (14d mg/kg)	Eartworms toxicity			x	
Endocrin destrucor	Endocrine effects	x			
Reproduction and development	Reproductive effects		x		
ADI (mg/kg bw)	Accettable daily intake			x	

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