

Occurrence of Pesticides in the Arno River and in Potable Water - A Survey of the Period 1992-1995

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The Arno river is one of the largest rivers in Italy. Its catchment area is approx. 8200 km², where pesticides are extensively used for agricultural purpose. The pesticides used can enter the river by superficial runoff (Pereira and Rostad 1990; Thurman et al. 1991) precipitation and discharge of wastewater. Because more than 90 % of the raw water used for the public water supply of Florence comes from the Arno river, public concern has increased regarding pesticide contamination of drinking water, and one of the major problems the water supply of Florence is facing is the presence of these compounds in the water. Since the maximum allowable concentration (MAC) for drinking water established by the EEC is 0.1 µg/L for individual pesticides and 0.5 µg/L for total pesticides, the water supply of Florence has intensified water quality monitoring of drinking water sources with respect to the presence of pesticides, with the aim of determining the outlines of the levels, distributions and seasonal variations, and of optimizing the treatment in drinking water plants. This paper describes the results of a long time monitoring survey of various pesticides contained in the Arno river water, as well as in finished drinking water.

MATERIALS AND METHODS

45 pesticides (32 herbicides, 11 insecticides, 1 fungicide and 1 acaricide) including triazines, organophosphate and organochlorine, carbamates, anilides, anilines and amides were analysed in this study. These compounds comprise the most commonly used and important pesticides in Italy. Pesticide standards were obtained from Supelco (Bellefonte, PA, USA) and Riedel-de-Haën (Seelze-Hannover, Germany). Standard solutions were prepared in methanol.

Water samples were collected from the river entering the drinking water treatment plant of Florence and from the finished drinking water. Water sampling was performed biweekly during winter months (February, January, November and December) and weekly in spring, summer and autumn, and as frequently as every day during storm runoff in May and June in anticipation of increased pesticide concentrations related to application timing and spring flush. Water samples were collected in 1-L baked-glass bottles in Teflon-lined caps and extracted within 4 h. Empore solid-phase extraction (SPE) disks (C₁₈-bonded silica, 47 mm diameter, containing about 500 mg of adsorbent, obtained from J. T. Baker, Phillipsburg, NJ) and an SPC DISC 6 SPE membrane workstation (Stepbio, Bologna, Italy), equipped with a Unijet II vacuum pump, were used for extraction of the analytes

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from 1-L water sample. C₁₈ SPE disks were preconditioned sequentially with 10 mL of each ethyl acetate, methanol, and reagent-grade water. Each 1-L water sample was spiked with a surrogate and internal standard. P-hexachlorobenzene (10 ng/μL in methanol, 20 μL) and passed through the preconditioned SPE disk at a flow-rate of about 50 mL/min. Analytes were eluted with 2 x 5 mL of ethyl acetate. The extract was concentrated on a Univapo 100 H concentration workstation (Stepbio, Bologna, Italy) to 0.5 mL.

Determination of pesticides was performed with a Varian 3400 gas chromatograph coupled to a Finnigan Mat ion-trap detector mass spectrometer (GC-ITDMS). A 30 m x 0.25 mm i.d. fused silica capillary column with a 0.25 μm bonded phase of DB-5 (J & W Scientific, Folsom, CA, USA) was used for GC. The injector temperature was 200°C and a splitless injection of 1 μL sample volume was performed. The column temperature was held at 50°C for 1 min and ranged at 30 °C/min to 130 °C, and then from 130 to 275 °C at 5 °C/min. Carrier gas was helium at 12 psi. The transfer line was maintained at 220 °C, and the mass spectrometer was scanned from m/z 50 to 350.

RESULTS AND DISCUSSION

The extraction efficiency of the disk SPE procedure for the pesticides analyzed in this study was determined by spiking 1-L of the Arno river water with 0.1 - 1.0 μg of each pesticide. Table 1 shows the mean recoveries obtained from six determinations. It can be observed that recoveries of 38 pesticides using C₁₈ SPE disks from 1-L water samples were higher than 75 % with a coefficient of variation less than 9 %. In the case of the C₈ disk SPE some pesticides, such as dichlorbenil, propachlor, propoxur, bendiocarb, carbofuran, terbacil, metribuzin and hexazinone, have extremely low recoveries. These compounds exhibit relatively high water solubility (Table 1), which demonstrates that the C₁₈ SPE disk is more adequate for medium polar compounds than C₈ SPE disk (Hagen et al. 1990). Identification and quantification of the pesticides studied were performed by GC-ITDMS. The most abundant ion of each analyte was used for quantification and the full mass spectrum was used for analyte confirmation. Pesticides investigated in this study had individual method detection limits (MDLs) varying from 0.005 to 0.030 μg/L (Table 1). Calibration curves constructed using the internal standard method showed good linearity from the MDL up to at least 5 μg/L for all pesticides investigated.

Table 2 shows concentrations and detection frequency of pesticides monitored in the Arno river from 1992 to 1995. In these four years, 19 pesticides (3 pesticides, 15 herbicides and 1 fungicide) were detected at or above the MDLs in at least one sample of the Arno river. Of those, the following pesticides: alachlor, atrazine, carbofuran, ethofumesate, metolachlor, simazine and terbutylazine were detected during each year of the survey period. Other pesticides in Table 2 were only occasionally detected. The pesticides, which were detected more frequently and generally at higher concentrations - in many cases > 0.1 μg/L, were metolachlor and terbutylazine. These two compounds were among the most commonly used pesticides in Italy for weed control in many crops (maize, soya, etc.) and have been frequently detected in groundwater and surfacewater throughout Italy (Gemitì 1993).

The data obtained in this study clearly show a remarkable decrease of concentration and detection frequency of triazine herbicides (simazine, atrazine and propazine) from 1992 to 1995. In 1992 for example, atrazine and simazine were detected (> 0.01 μg/L) in 59 and 67 % of the samples, respectively. whereas atrazine and simazine were detected in only 5

Table 1. Pesticides recoveries (%) from the Arno river water spiked at 1.0 - 0.1 µg/sing Empore SPE disks and GC-ITDMS analysis.

Common name	Activity ^a	Solubility (mg/L)	%Recovery ± s.d.		Quanti. ions	MDL ^b (µg/L)
			C ₁₈ SPE disk	C ₈ SPE disk		
Dichlorvos	I	10000	71 ± 11	62 ± 10	109	0.025
Dichlobenil	H	21.2	73 ± 8	44 ± 11	171,173	0.015
EPTC	H	344	91 ± 6	89 ± 5	128	0.005
Butylate	H	46	93 ± 5	95 ± 7	146	0.005
Vernolate	H	108	89 ± 5	88 ± 5	128	0.010
Pebulate	H	60	94 ± 4	98 ± 6	128	0.010
Molinate	H	970	89 ± 5	87 ± 7	126	0.005
Propachlor	H	613	94 ± 7	71 ± 9	120	0.010
Propoxur	I	1800	73 ± 8	48 ± 11	110	0.010
Ethoprop	I	750	92 ± 6	96 ± 8	158	0.020
Cycloate	H	95	86 ± 4	89 ± 7	154	0.005
Trifluralin	H	0.3	83 ± 5	85 ± 4	306	0.005
Benfluralin	H	0.1	80 ± 4	84 ± 6	292	0.005
Bendiocarb	I	40	91 ± 7	97 ± 9	151	0.010
Phorate	I	22	54 ± 5	49 ± 7	75	0.025
Carbofuran	I	351	94 ± 9	68 ± 10	164	0.010
Simazine	H	6.2	87 ± 4	83 ± 3	201	0.010
Atrazine	H	33	89 ± 6	80 ± 7	200	0.010
Propazine	H	8.6	87 ± 6	89 ± 5	214	0.010
Profluralin	H	0.1	81 ± 4	86 ± 5	318	0.005
Terbutylazine	H	8.5	92 ± 6	89 ± 7	214	0.005
Propyzamide	H	15	96 ± 9	92 ± 6	173,175	0.005
Diazinon	I	60	89 ± 5	92 ± 8	179	0.015
Terbacil	H	710	74 ± 8	46 ± 6	160,161	0.025
Propanil	H	200	82 ± 9	83 ± 11	161,163	0.020
Metribuzin	H	1220	72 ± 6	42 ± 5	198	0.020
Methyl parathion	I	60	85 ± 8	81 ± 9	263	0.015
Alachlor	H	240	84 ± 4	79 ± 6	188	0.010
Heptachlor	I	0.06	75 ± 6	86 ± 5	272,274	0.020
Ethofumesate	H	50	93 ± 4	85 ± 6	207	0.005
Linuron	H	75	91 ± 8	87 ± 9	248	0.010
Malathion	I	130	85 ± 5	91 ± 4	173	0.010
Metolachlor	H	530	92 ± 6	86 ± 6	162	0.005
Aldrin	I	0.05	58 ± 4	49 ± 6	263,265	0.015
Flurochloridone	H	28	93 ± 6	87 ± 5	311,313	0.015
Diphenamid	H	260	86 ± 7	79 ± 9	167	0.015
Isopropalin	H	0.1	78 ± 4	82 ± 5	280	0.005
Pendimethalin	H	0.275	80 ± 3	86 ± 5	252	0.010
Procymidone	F	4.5	84 ± 4	87 ± 4	96	0.005
Napropamide	H	74	90 ± 9	82 ± 11	271	0.020
Oxadiazon	H	0.7	107 ± 11	86 ± 4	258	0.010
Oxyfluorfen	H	0.1	87 ± 4	81 ± 6	252	0.015
Flamprop-methyl	H	35	79 ± 4	84 ± 6	105	0.015
Ethion	A	1.1	83 ± 3	83 ± 5	231	0.010
Hexazinone	H	33000	87 ± 7	49 ± 8	171	0.030
Diclofop-methyl	H	3	75 ± 5	81 ± 5	340	0.020

^aI, insecticide; H, herbicide; F, fungicide; A, acaricide. ^bMDL, method detection limit, calculated using a signal-to-noise (S/N) ratio of 5.

Table 2. Summary of concentrations and detection frequency of pesticides detected in the Arno river during 1992- 1995.

Compound	1992 (n=36)			1993 (n=48)			1994 (n=32)			1995 (n=51)		
	Concentration $\mu\text{g/L}$ median maxium		Detection frequency (%)	Concentration ($\mu\text{g/L}$) median maxium		Detection frequency (%)	Concentration ($\mu\text{g/L}$) median maxium		Detection frequency (%)	Concentration ($\mu\text{g/L}$) median maxium		Detection frequency (%)
Insecticides												
Carbofuran	<0.01	0.15	25	<0.01	0.03	8	<0.01	0.03	3	<0.01	0.67	31
Malathion	<0.01	<0.01	0	<0.01	0.06	6	<0.01	<0.01	0	<0.01	0.17	8
Propoxur	<0.01	<0.01	0	<0.01	0.04	6	<0.01	<0.01	0	<0.01	0.07	8
Herbicides												
Alachlor	<0.01	0.09	17	<0.01	0.44	33	<0.01	0.02	9	<0.01	0.41	37
Atrazine	0.06	0.16	67	0.05	0.13	50	<0.01	0.06	16	<0.01	0.07	4
Benfluralin	<0.005	<0.005	0	<0.005	<0.005	0	<0.005	<0.005	0	<0.005	0.05	4
Dichlorbenil	<0.015	<0.015	0	<0.015	0.05	0	<0.015	<0.015	0	<0.015	0.04	4
Diphenamid	<0.015	<0.015	0	<0.015	0.21	8	<0.015	<0.015	0	<0.015	0.07	4
Ethofumesate	<0.005	0.06	8	<0.005	0.50	35	<0.005	0.06	31	<0.005	0.06	35
Hexazinone	<0.03	0.05	3	<0.03	0.08	6	<0.03	<0.03	0	<0.03	<0.03	0
Metolachlor	0.04	0.16	63	0.13	3.68	85	0.04	0.21	66	0.13	1.56	92
Oxyfluorfen	<0.015	<0.015	0	<0.015	<0.015	0	<0.015	<0.015	0	<0.015	0.11	4
Oxadiazon	<0.01	<0.01	0	<0.01	0.11	8	<0.01	<0.01	0	<0.01	0.06	6
Profluralin	<0.005	<0.005	0	<0.005	<0.005	0	<0.005	<0.005	0	<0.005	0.02	2
Propazine	<0.01	0.07	25	<0.01	<0.01	0	<0.01	<0.01	0	<0.01	<0.01	0
Simazine	0.02	0.25	67	<0.01	0.10	46	<0.01	0.27	19	<0.01	0.30	8
Terbacil	<0.03	<0.03	0	<0.03	0.07	4	<0.03	<0.03	0	<0.03	<0.03	0
Terbutylazine	0.03	0.20	59	0.11	2.27	75	0.02	0.26	53	0.092	0.96	86
Fungicide												
Procyimdone	<0.005	<0.005	0	<0.005	0.05	0	<0.005	<0.005	0	<0.005	0.03	2

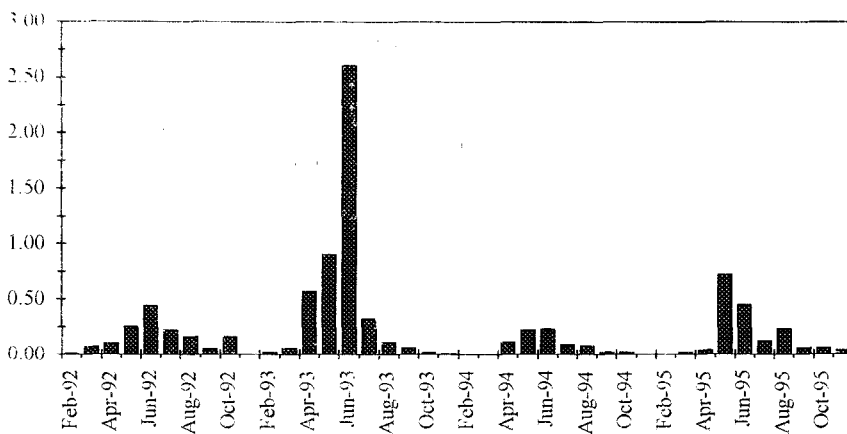


Figure 1. The monthly mean concentrations of total pesticides in the Arno river during 1992-1995.

and 8 % of the samples in 1995. It is likely that this is due to the decrease of triazine herbicides used in agriculture.

The concentration of suspended sediment in the Arno river during a storm runoff can be more than 0.6 g/L. During May and June 1993 and 1995, some water samples were filtered on 0.45- μ m PTFE filters prior to SPE extraction and analysis. The results showed that concentrations of pesticides monitored regarding the whole water sample analysis were not significantly different from those obtained from the filtered sample analysis, which means that the pesticides detected were present predominantly in the dissolved phase. These findings are consistent with other works (Squillace and Thurman 1992; Lemieux et al. 1995).

Figure 1 shows the monthly mean concentrations of the pesticides monitored in the Arno river during the period 1992-1995. The presence of pesticides in the Arno river was found to be seasonal. Maximum concentrations were observed each year in May and June. This result was in accordance with field application of pesticides in the Tuscan region, where the application period for pesticides generally lasts about 10 weeks, starting in the last week of April and lasting until the first week of July. Fall and winter applications are minimum, and this is reflected in the small concentrations and low detection frequency during fall and winter months.

Numerous studies have shown that pesticides can be flushed from croplands and transported to receiving waters as pulses during spring and early summer rainfall, and climatic and hydrological conditions seem to be the principal means of control regarding the concentrations of pesticides in surface water (Thurman et al. 1991; Fauchon et al. 1993). The same results were observed in this study. For example, the highest concentrations of metolachlor (3.68 μ g/L) and terbutylazine (2.27 μ g/L) were detected in June 1993 after an intense rainfall event; whereas lower concentrations of pesticides were observed during spring and early summer in 1994, probably due to the absence of significant rainfall in this period. Figure 2 shows the storm runoff data for metolachlor and terbutylazine during May and June (application period) in 1995. Results show that highest

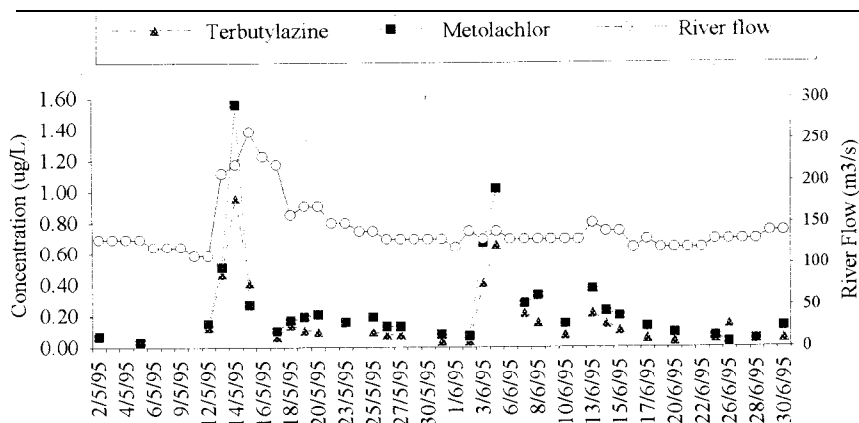


Figure 2. Metolachlor and terbutylazine concentrations in the Arno river versus river flow during May and June 1995

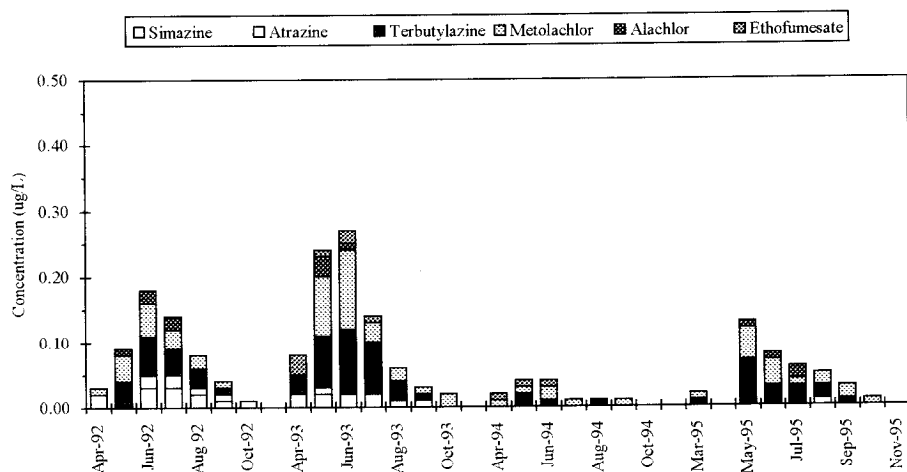


Figure 3. The monthly mean concentrations of pesticides in finished drinking water of the Anconella plant during 1992-1995

concentrations of these two pesticides occurred in the river water during the early stages of the first storm rainfall when a large part of pesticides had been applied in the river basin and the streamflow was low.

The Arno river water serves as raw water for producing the drinking water of Florence. The water treatment processes at Florence Water Supply (Anconella plant) comprise prechlorination with chlorine dioxide, followed by flocc-sedimentation (Pulsator and Dorr systems in parallel), sand filtration, ozonation and final disinfection with chlorine dioxide. Powdered activated carbon (PAC) doses of 5 to 20 mg/L were added to the raw water before sedimentation between May and June. During the four-year survey period, the concentrations of the total and individual pesticides detected in finished drinking water in the Water Supply of Florence did not exceed the levels of 0.5 $\mu\text{g/L}$ and 0.1 $\mu\text{g/L}$, respectively (Figure 3). Slightly higher concentrations than 0.1 $\mu\text{g/L}$ for terbutylazine and

Table 3. Removal of total pesticides from raw water at the Anconella plant during May, and June from 1992 to 1995.

Year ^a	Concentration in raw water (µg/L)		Concentration in finished water (µg/L)		Removal (%)	
	Range	Mean	Range	Mean	Range	Mean
1992 ^b	0.17 - 0.61	0.34	0.01 - 0.31	0.15	53.8 - 76.5	60.9
1993 ^c	0.49 - 6.45	1.71	0.18 - 0.48	0.30	51.0 - 93.3	73.8
1994 ^d	0.02 - 0.60	0.20	0.01 - 0.04	0.02	78.8 - 100	90.7
1995 ^d	0.13 - 3.79	0.65	0.01 - 0.22	0.06	69.2 - 99.2	87.5

^aOzonation (ozone dose 2.0 mg/L, contact time 10 min) was only performed during May and June 1995. ^bPAC dose 5 - 10 mg/L. ^cPAC dose 5 - 15 mg/L. ^dPAC dose 5 - 20 mg/L.

Table 4. Removal of metolachlor and terbutylazine at various stages in the Anconella plant on 13 May 1995^a.

Treatment process	Metolachlor		Terbutylazine	
	Mean concentration (µg/L)	Cumulative removal (%) from raw water	Mean concentration (µg/L)	Cumulative removal (%) from raw water
Raw water	1.36	-	0.86	-
Prechlorination	1.32	2.9	0.87	0
PAC ^b +Pulsator sedimentation	0.08	94.1	0.02	97.7
PAC ^b +Dorr sedimentation	0.58	57.4	0.30	65.1
Sand filtration	0.27	80.1	0.16	81.6
Ozonation	0.09	93.4	0.08	90.7
Postchlorination	0.08	94.1	0.08	90.7

^aBased on three determinations at each treatment process. ^bPAC dose 15 mg/L.

metolachlor were only occasionally observed in finished water from the Anconella plant in June 1993 when the heavy rains in this period did result in higher concentrations of pesticides in the Arno river water. Table 3 shows the presence of total pesticides in the raw water and percent removal from the Anconella plant during May and June from 1992 to 1995. These data show that the treatment performance at the Anconella plant was reasonably effective for removing pesticides from raw water when PAC treatment and ozonation were performed.

The amount of metolachlor and terbutylazine removed at each stage of the purification at Anconella plant was determined on 13 May 1995. The results are summarized in Table 4. Consequently, as reported by others (Miltner et al. 1989; Montiel and Welté 1992). treatment including prechlorination with chlorine dioxide, coagulation, and sand filtration was found to be ineffective for removing pesticides such as metolachlor and terbutylazine from raw water. Less than 40 % of metolachlor and terbutylazine were removed, which means that with conventional water purification systems compliance with EEC MAC of 0.1 µg/L for individual pesticides was not easy when heavy contamination of pesticides occurred in raw water during the application period of these compounds. The data in Table

4 show that removal of pesticides using PAC followed by flocc-sedimentation and sand filtration was effective. More than 60 % of metolachlor and terbutylazine, respectively, were removed by PAC and flocc-sedimentation. It is interesting to note that pesticide removal by PAC combined with Pulsator flocc-sedimentation system (4 Pulsator settling tanks, flow rate 625 L/s each, total surface 3600 m²) was significantly more efficient than PAC combined with Dorr flocc-sedimentation system (6 Dorr settling tanks, flow rate approx. 2.50 L/s each, total surface 3690 m²). For example, on 13 May PAC followed by Pulsator flocc-sedimentation system removed 37 and 32 % more metolachlor and terbutylazine, respectively, than PAC followed by Dorr flocc-sedimentation. More than 60 and 40 % of metolachlor and terbutylazine entering the ozonation system were removed by this process stage. Considering the seasonal pattern of pesticide occurrence in the Arno river, the effective treatment option for maximizing pesticide removal was found to be PAC adsorption, which allows changing the carbon dose with varying raw water quality.

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