

Removal of pesticides during the drinking water treatment process at Florence water supply, Italy

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ABSTRACT: Removal of pesticides from surface water during drinking water treatment processing was evaluated at two full-scale treatment plants that employed prechlorination with chlorine dioxide, powdered activated carbon (PAC) adsorption, flocc-sedimentation, sand filtration, ozonation, biological GAC filtration, and postchlorination. A two year-investigation showed that the conventional treatment process was ineffective in removing metolachlor and terbutylazine from the water. The effectiveness of an ozonation or biological GAC filtration process has proved to be very limited for complying with the EC drinking water standard of 0.1 µg/L for individual pesticides. The removal efficiency of the PAC treatment was dependent on the PAC dosage, as well as the type of flocc-sedimentation system employed. PAC combined with Pulsator flocc-sedimentation proved to be more effective for removing pesticides than PAC combined with Dorr flocc-sedimentation. An effective treatment option for removing the seasonal occurrence of pesticide pollution in surface water appears to be PAC adsorption followed by Pulsator flocc-sedimentation and ozonation.

INTRODUCTION

The city of Florence is located at the middle reaches of the Arno river and takes its drinking water supply from the surface water of this river. The higher reaches of the Arno river have a pleasant countryside and fertile land which is used for high-quality agriculture. In recent years, however, pollution of the Arno river by pesticides used in agriculture has been a problem of increasing concern. During a five year-survey period (1992–96), 21 pesticides were detected in water samples collected from the influents of Florence drinking water treatment plants [1]. Figure 1 shows the temporal variations in the concentration of main pesticides detected in the Arno river during 1995–96. The higher concentrations occurred in May–July, and correlated with the application period of these pesticides. Among the pesticides present in water, metolachlor and terbutylazine were the most frequently detected, and in some cases their concentrations exceeded the 1 µg/L level, whereas the EC drinking water standards for individual pesticides is 0.1 µg/L, which suggests that the treatment process will have to proceed with at least a 90% efficacy. Due to the relatively high pesticide concentrations in the raw water, public concern has increased regarding the 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 water. To meet EC drinking water standards, more efficient treatment processes, including powdered activated carbon (PAC) adsorption, granular activated carbon (GAC) filtration and ozonation, have been installed at the water works of Florence. In this study, the efficacy of various treatment processes for removing pesticides

in water was investigated in two Florence drinking water treatment plants. Based on the performance data from the water works of Florence, the capacity of various treatment processes to meet the EC drinking water standards for pesticides was evaluated.

EXPERIMENTAL METHOD

Description of water works

The Water Supply of Florence operates with two drinking water treatment plants (Fig. 2), the Anconella plant, with a daily output of 350 000 m³, and the Mantignano plant, with a daily output of 70 000 m³. The treatment processes at both plants comprise prechlorination with chlorine dioxide (1–1.5 mg/L, contact time 10 min), flocc-sedimentation (polyaluminium chloride dose 30–300 mg/L), sand filtration (sand bed thickness 1 m, filtration speed 4.6–5 m/h), ozonation (ozone dose 2 mg/L, contact time 10–12 min), and postchlorination. At the Anconella plant, after prechlorination (about 5 min), PAC (Chemisorb 410 PW and Sorbopor MV 125 A, > 325 mesh 80%) is added to the raw water before the addition of flocculant. The period between dosing PAC and dosing flocculant is about 5 min. The raw water with PAC is then split and flows into two flocc-sedimentation systems, the Pulsator system and the Dorr system. The Pulsator system consists of four Pulsator settling tanks. The Pulsator settling tank dimensions were 30 m(L) × 30 m(W) × 5 m(H) with a surface area of 900 m² and a nominal surface loading rate of 2.5 m/h. Each Pulsator tank was operated at a flow rate of 2250 m³/h with a

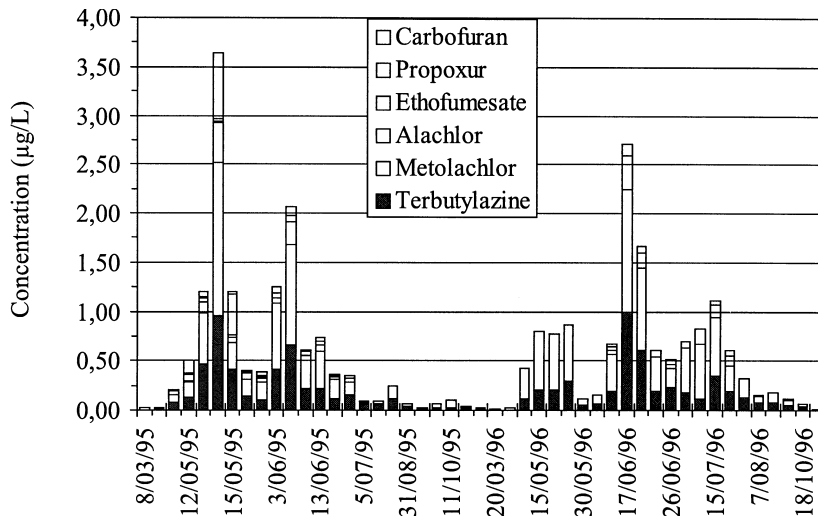


Fig. 1 Concentrations of the main pesticides detected in the Arno river during 1995–1996.

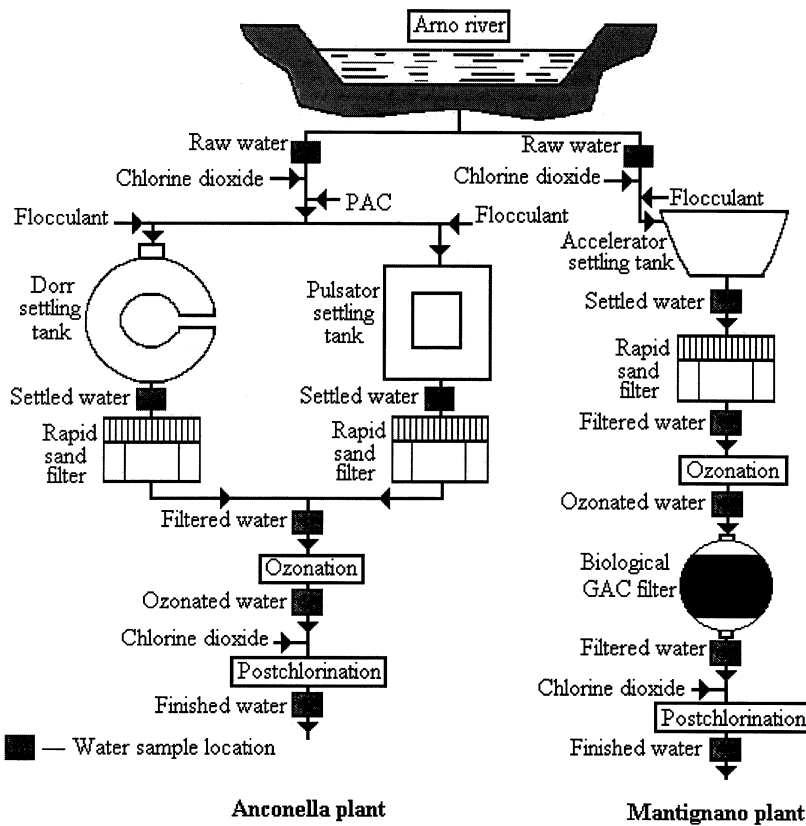


Fig. 2 Schematic of the Water Supply of Florence.

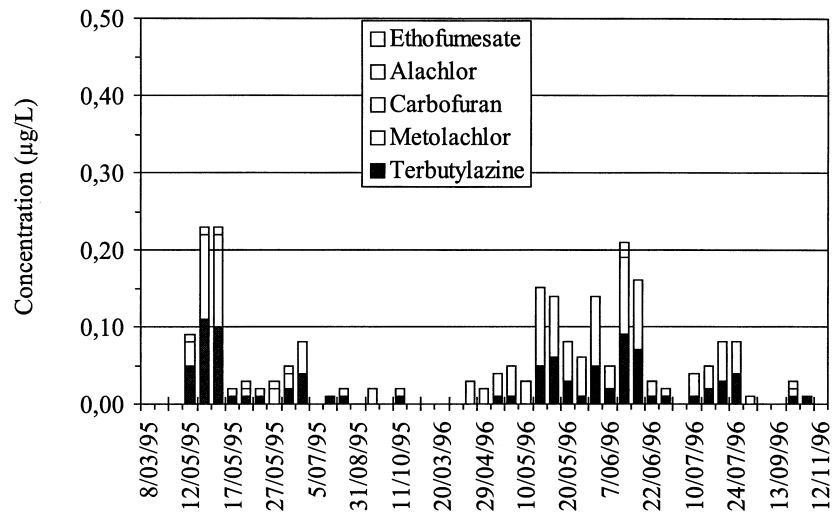
nominal hydraulic retention time of 2 h. The Dorr system consists of six Dorr settling tanks. Each Dorr settling tank (30 m i.d. × 3.8 m H, surface area 615 m²) was operated with a nominal flow rate of 900 m³/h and an average hydraulic residence time of 2.5 h. At the Mantignano plant, the ozonation process is followed by biological GAC (Chemviron F 500) filtration (GAC bed depth 1 m, empty bed contact time 9–12 min).

Water sampling and pesticide analysis

During May–July 1995 and 1996, water samples from each stage of the two plants were collected. The main water quality parameters, such as total organic carbon (TOC), turbidity and pH, as well as pesticide concentrations were measured. Table 1 presents the main water quality parameters of the raw water (Arno river water) during the study periods. Determinations of pesticides were performed by a method based on C₁₈ disk solid-

Table 1 Summary of Arno river raw water quality

Parameters	May–July 1995		May–July 1996	
	Range	Mean	Range	Mean
Temperature (°C)	18.2–29.7	24.3	17.9–30.1	25.2
pH	7.7–8.3	8.0	7.5–8.5	8.1
Turbidity (NTU)	1.2–180	15.1	2.5–501	22.8
Alkalinity (mg/L as HCO ₃ ⁻)	139–241	174	149–220	180
TOC (mg/L)	1.4–5.2	3.2	2.3–7.9	4.1
Ammonium (mg/L as NH ₄ ⁺)	0.00–0.49	0.04	0.00–0.46	0.06

**Fig. 3** Concentrations of the pesticides detected in the finished drinking water of the Anconella plant during 1995–1996.

phase extraction followed by gas chromatography coupled with an ion-trap detector mass spectrometry (GC-ITDMS) detection. The method is described in detail elsewhere [1]. The detection limits of this method were 0.01 µg/L for the pesticides investigated in this study.

RESULTS AND DISCUSSION

Removal of pesticides during the drinking water treatment process

Figure 3 shows the concentrations of pesticides detected in the finished drinking water of the Anconella plant during 1995–96. During the two-year survey period, five pesticides, including metolachlor, terbutylazine, alachlor, carbofuran and ethofumesate, were detected at or above the method detection limits in finished drinking water. The concentrations of the total pesticides detected did not exceed a level of 0.5 µg/L. Alachlor, carbofuran and ethofumesate were only occasionally detected in May and June at lower concentrations (< 0.05 µg/L), while metolachlor and terbutylazine were detected more frequently, and concentrations for these two pesticides that were slightly higher than 0.1 µg/L were occasionally observed in finished water in May and June when the heavy rains in this period

resulted in higher concentrations of these compounds in the raw water (Fig. 1). Tables 2–4 show the removal of metolachlor and terbutylazine in each treatment stage at the Anconella and Mantignano plants during May–July 1995 and 1996. Many researchers [2–4] have shown that conventional water treatment is ineffective for removing dissolved pesticides. The same result was obtained in this study. The data in Tables 2–4 show that the removal of metolachlor and terbutylazine by treatment processes including prechlorination with ClO₂, flocc-sedimentation and sand filtration was very limited. Only less than 30% of the metolachlor and terbutylazine were removed by these treatment processes. The data in Tables 2 and 3 show that the removal of metolachlor and terbutylazine using PAC followed by flocc-sedimentation was effective, but that its degree of effectiveness depended on the PAC dose and the type of flocc-sedimentation system employed. Figure 4 shows the effect of PAC dose on the removal of metolachlor and terbutylazine by PAC and flocc-sedimentation. The data clearly show that the percentage removal of these pesticides from water increases with increasing PAC doses.

As shown in Fig. 4, the removal of metolachlor and terbutylazine by PAC combined with a Pulsator system was more efficient than PAC combined with a Dorr system. For example, on 13 May 1995, PAC (PAC dose = 15 mg/L) followed by the

Table 2 Removal of metolachlor at various stages in the Anconella plant during May-July 1995 and 1996*

Date	Raw water	PAC dose	PAC + Pulsator flocc-sedimentation		PAC + Dorr flocc-sedimentation		Sand filtration		Ozonation†		Postchlorination with ClO ₂	
	Conc. (µg/L)	(mg/L)	Conc. (µg/L)	Cumulative % removal	Conc. (µg/L)	Cumulative % removal	Conc. (µg/L)	% removal	Conc. (µg/L)	% removal	Conc. (µg/L)	% removal
12 May 1995	0.15	5	0.07	53.3	0.10	33.3	0.08	46.7	0.04	73.3	0.03	80.0
13 May 1995	1.36	10	0.44	67.6	0.70	48.5	0.50	63.2	0.14	89.7	0.11	91.9
15 May 1995	0.47	5	0.17	63.8	0.29	37.8	0.23	50.9	0.10	78.7	0.10	78.7
16 May 1995	0.14	10	<0.01	>92.9	0.06	57.1	0.03	78.6	0.01	89.3	ND	nd
03 June 1995	0.67	10	0.16	76.1	0.32	52.2	ND	ND	ND	ND	ND	nd
05 June 1995	1.02	15	0.08	92.2	0.32	68.6	0.26	74.5	0.10	90.2	0.09	91.2
07 June 1995	0.28	ND	ND	ND	ND	ND	0.16	42.9	0.06	78.6	ND	nd
13 June 1995‡	0.37	10	0.12	67.6	0.18	51.4	ND	ND	ND	ND	ND	nd
14 June 1995‡	0.22	15	<0.01	>95.5	0.07	68.2	ND	ND	ND	ND	0.02	90.9
26 June 1995‡	0.13	8	0.04	69.2	0.07	46.2	0.06	53.8	ND	ND	0.04	69.2
16 May 1996‡	0.57	15	0.05	91.2	0.19	66.7	ND	ND	ND	ND	0.08	86.0
18 May 1996‡	0.53	10	0.09	83.0	0.24	54.7	ND	ND	ND	ND	0.11	79.2
20 May 1996‡	0.36	15	0.02	94.1	0.11	69.4	ND	ND	ND	ND	0.05	86.1
23 May 1996	0.56	15	ND	ND	ND	ND	0.06	89.3	0.03	94.6	0.05	91.0
17 June 1996	1.25	15	ND	ND	ND	ND	0.26	79.2	0.08	93.6	ND	nd
18 June 1996	1.02	15	0.06	94.1	0.42	58.8	0.29	71.6	0.12	88.2	0.10	90.2
20 June 1996	0.84	15	0.04	95.2	0.30	64.3	ND	ND	ND	ND	0.09	89.3
21 June 1996	0.70	15	0.05	92.9	0.31	55.7	0.19	72.9	0.05	92.9	0.04	94.3
15 July 1996	0.59	15	0.03	94.9	0.22	62.7	ND	ND	ND	ND	0.03	94.9
18 July 1996	0.46	0	0.35	23.9	0.39	15.2	0.37	19.6	0.10	73.0	0.09	80.4
22 July 1996	0.19	8	0.06	68.4	0.11	42.1	ND	ND	ND	ND	0.04	78.9

*ND, not determined. †Ozonation parameters: ozone dose, 2.0 mg/L; contact time, 10 min. ‡Ozonation was not performed.

Table 3 Removal of terbutylzine at various stages in the Anconella plant during May-July 1995 and 1996*

Date	Raw water	PAC dose	PAC + Pulsator flocc-sedimentation		PAC + Dorr flocc-sedimentation		Sand filtration		Ozonation†		Postchlorination with ClO ₂	
	Conc. (µg/L)	(mg/L)	Conc. (µg/L)	Cumulative % removal	Conc. (µg/L)	Cumulative % removal	Conc. (µg/L)	Cumulative % removal	Conc. (µg/L)	Cumulative % removal	Conc. (µg/L)	Cumulative % removal
12 May 1995	0.14	5	0.06	57.1	0.08	42.9	0.08	42.9	0.05	64.3	0.05	64.3
13 May 1995	0.86	10	0.23	73.2	0.40	53.5	0.30	65.1	0.13	84.9	0.11	87.2
15 May 1995	0.40	5	0.12	70.0	0.21	47.5	0.16	60.3	0.11	72.5	0.10	75.0
16 May 1995	0.08	10	<0.01	>98.5	0.04	50.0	0.02	75.0	0.01	87.5	ND	nd
03 June 1995	0.41	10	0.08	80.5	0.18	56.1	ND	ND	ND	ND	ND	nd
05 June 1995	0.66	15	0.01	98.5	0.21	68.2	0.14	78.8	0.09	86.4	0.10	84.8
07 June 1995	0.22	ND	ND	ND	ND	ND	0.10	54.5	0.06	72.7	ND	nd
13 June 1995‡	0.22	10	0.05	77.3	0.10	54.5	ND	ND	ND	ND	ND	nd
14 June 1995‡	0.13	15	<0.01	>92.3	0.04	69.2	ND	ND	ND	ND	0.02	84.6
26 June 1995‡	0.15	8	0.04	73.3	0.07	53.3	0.05	66.7	ND	ND	0.04	73.3
16 May 1996‡	0.31	15	0.03	90.3	0.11	64.5	ND	ND	ND	ND	0.06	80.6
18 May 1996‡	0.17	10	0.02	88.2	0.07	58.8	ND	ND	ND	ND	0.05	70.6
20 May 1996‡	0.12	15	<0.01	91.7	0.04	66.7	ND	ND	ND	ND	0.03	75.0
23 May 1996	0.30	15	ND	ND	ND	ND	0.02	93.3	0.01	96.7	0.01	96.7
17 June 1996	0.99	15	ND	ND	ND	ND	0.13	86.9	0.07	92.9	ND	nd
18 June 1996	0.67	15	0.03	95.5	0.22	67.2	0.12	82.0	0.08	88.0	0.09	86.6
20 June 1996	0.61	15	0.02	96.7	0.17	72.1	ND	ND	ND	ND	0.07	88.5
21 June 1996	0.51	15	0.03	94.1	0.19	62.7	0.12	76.5	0.04	92.2	0.04	92.2
15 July 1996	0.35	15	0.01	97.1	0.11	68.6	ND	ND	ND	ND	0.02	94.3
18 July 1996	0.26	0	0.19	26.9	0.21	19.2	0.19	26.9	0.10	61.5	0.09	65.4
22 July 1996	0.13	8	0.03	76.9	0.06	53.8	ND	ND	ND	ND	0.05	61.5

*ND, not determined. †Ozonation parameters: ozone dose, 2.0 mg/L; contact time, 10 min. ‡Ozonation was not performed.

Table 4 Removal of metolachlor and terbutylazine at various stages in the Mantignano plant during May-June 1995 and 1996*

Pesticide	Date	Raw water	Floc-sedimentation		Sand filtration		Ozonation†		GAC filtration		Postchlorination	
		Conc. (µg/L)	Conc. (µg/L)	Cumulative % removal	Conc. (µg/L)	Cumulative % removal	Conc. (µg/L)	Cumulative % removal	Conc. (µg/L)	Cumulative % removal	Conc. (µg/L)	Cumulative % removal
Metolachlor												
	13 May 1995	0.54	0.44	18.5	0.43	20.4	0.15	72.2	0.10	81.5	0.09	83.3
	15 May 1995	0.46	0.36	21.7	0.33	28.3	0.12	73.9	0.08	82.6	0.07	84.8
	03 June 1995	0.71	0.57	19.7	0.54	23.9	0.20	71.8	0.14	80.3	0.11	84.5
	09 May 1996‡	0.29	0.22	24.1	0.19	34.5	ND	ND	0.13	50.0	0.11	62.1
	18 May 1996§	0.64	0.15	76.6	0.13	79.7	ND	ND	0.09	85.9	0.08	87.5
	18 June 1996§	0.96	0.20	79.2	0.17	82.3	ND	ND	0.12	87.5	0.10	89.6
Terbutylazine												
	13 May 1995	0.50	0.36	28.0	0.32	36.0	0.16	68.0	0.09	82.0	0.10	80.0
	15 May 1995	0.39	0.26	33.3	0.24	38.5	0.13	66.7	0.09	76.9	0.08	79.5
	03 June 1995	0.36	0.27	25.0	0.27	25.0	0.14	61.1	0.10	72.2	0.09	75.0
	09 May 1996‡	0.07	0.05	28.6	0.05	28.6	ND	ND	0.04	42.9	0.04	42.9
	18 May 1996§	0.29	0.06	79.3	0.05	82.8	ND	ND	0.03	89.7	0.03	89.7
	18 June 1996§	0.62	0.12	80.6	0.10	83.9	ND	ND	0.07	88.7	0.07	88.7

*ND, not determined. †Ozonation parameters: ozone dose, 2.0–2.5 mg/L; contact time, 12 min. ‡Ozonation was not performed. §Ozonation was not performed; PAC dose of 15 mg/L was added before sedimentation.

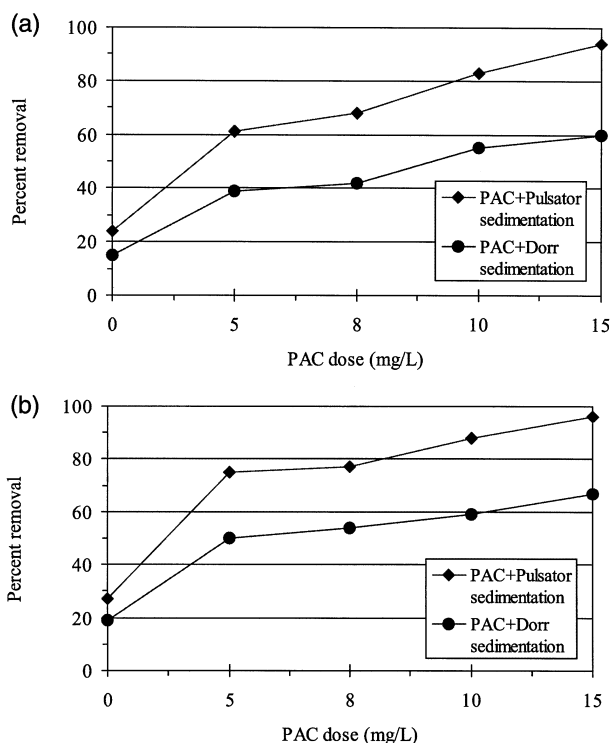


Fig. 4 Removal of (a) metolachlor and (b) terbutylazine from raw water by PAC combined with Pulsator or Dorr flocc-sedimentation system.

Pulsator system, removed 37% and 32% more metolachlor and terbutylazine, respectively, than the PAC and Dorr system; on 18 May 1996, PAC (PAC dose = 10 mg/L) and Pulsator system removed 83% of metolachlor and 88% of terbutylazine, while PAC followed by the Dorr system removed only 55% of metolachlor and 59% of terbutylazine. The results in Fig. 4 show that using the Dorr system, two to threefold greater PAC doses are necessary for a pesticide removal efficiency equal to that obtained from the Pulsator system. This implies that the adsorption process in the Dorr system is not very efficient, in

that only 30–50% of the PAC adsorption capacity is being utilised, compared to the Pulsator system.

Figure 5 compares the removal efficiencies of turbidity and TOC from raw water by Pulsator and Dorr flocc-sedimentation during May–July 1995 and 1996. As shown in Fig. 5, turbidity removal efficiencies of both flocc-sedimentation systems were found to be similar during the study period, while TOC was removed more efficiently by the PAC–Pulsator system than by the PAC–Dorr system. During the study period, the mean removal of TOC by the PAC–Pulsator system was 66% (range 48–88%), while the mean removal of TOC by the PAC–Dorr system was only 54% (range 32–77%). The higher performance of the PAC–Pulsator system compared to the PAC–Dorr system is probably due to the different operating modes of these two systems. The Dorr system is operated in a static mode, in which PAC may be easily incorporated into the floc particles thus reducing the rate of adsorption of pesticides. Incorporation of PAC into floc particles may also increase the settling rate of PAC, resulting in lower effective contact time between PAC and pesticides. On the other hand, the Pulsator system is operated in the dynamic mode, in which PAC and flocculant are maintained in suspension through pulses. Maintaining PAC in suspension through pulses could increase the effective contact time between PAC and pesticides, and subsequently result in enhanced pesticide removal. Pulsing may also reduce the interference caused by the incorporation of PAC into floc particles. This result indicates that ensuring good mixing between PAC and the water being treated is an important factor in obtaining the full utilisation of PAC adsorption capacity.

The data in Tables 2–4 show that between 48% and 75% (average 62%) of metolachlor and 31 and 67% (average 45%) of terbutylazine entering the ozonation systems at the two plants were removed by this stage. These results appear to be similar to data reported in literature [4–6]. In a pilot-plant study, Montiel & Welté [4] reported that 27.8–52.1% of terbutylazine were removed from the Marne river water by ozonation with an ozone dose of 1.0 mg/L. Bench scale experi-

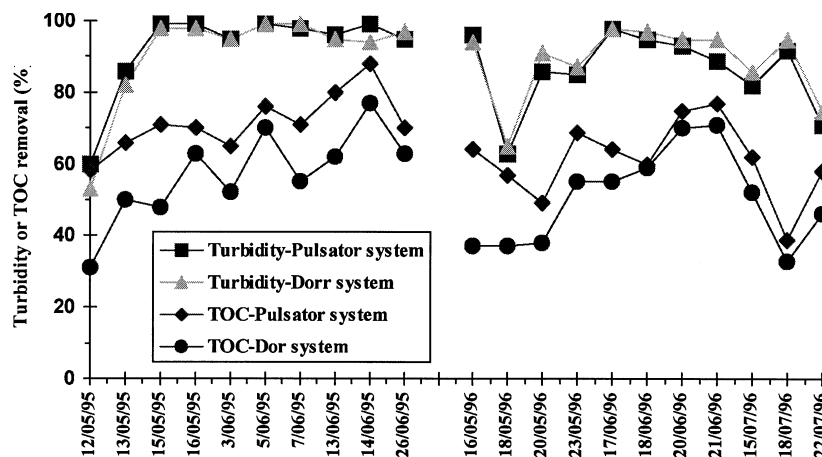


Fig. 5 Removal of turbidity and TOC from raw water by PAC combined with Pulsator or Dorr flocc-sedimentation system.

Table 5 Removal of metolachlor and terbutylazine from raw water by single or combined treatment process in the Anconella plant.

Treatment process	Percentage removal from raw water (average and range)*					
	0 mgPAC/L		5–10 mgPAC/L		15 mgPAC/L	
	Metolachlor	Terbutylazine	Metolachlor	Terbutylazine	Metolachlor	Terbutylazine
PAC + Pulsator Sed.	23.5	26.9	68.5 (53.3–83.0)	78.9 (57.1–88.2)	94.2 (92.9–95.2)	96.7 (94.1–100)
PAC + Dorr Sed.	15.2	19.2	43.6 (33.3–57.1)	52.9 (42.9–58.8)	59.8 (55.7–64.3)	67.1 (62.7–72.1)
Ozonation	62.2 (47.8–73.7)	45.4 (31.3–66.7)				
PAC + Pulsator Sed. + Ozonation	71.4 (60.0–80.0)	60.0 (50.0–75.6)	88.0 (78.3–95.5)	88.5 (79.6–96.0)	97.8 (96.3–98.7)	97.9 (96.0–99.0)
PAC + Dorr Sed. + Ozonation	67.7 (56.5–77.8)	56.5 (44.4–73.0)	78.7 (67.7–88.0)	74.4 (64.3–86.3)	84.8 (76.7–90.7)	82.1 (74.4–90.7)

*Range values in brackets.

ments performed by Meijers *et al.* [5] have shown that 83% of metolachlor can be removed from the Meuse river water by ozonation with an ozone dose of 2.2 mg/L. During this study period, TOC in sand filtered water at the two plants ranged from 0.8 to 3.3 mg/L. With an ozone dose of 2 mg/L, the range of ozone-to-TOC ratio was thus between 0.6 and 2.5 mgO₃/mgC. No significant relationship was found between pesticides removal and ozone-to-TOC ratio. This may be attributed to day-to-day variations of source water quality and the concentrations of pesticides in sand-filtered water.

At the Mantignano plant, approximately 31 and 30% of metolachlor and terbutylazine, respectively, entering the GAC filters, were removed by this stage. The GAC filters were operated for more than two years, and performed in the biological mode. The data of TOC removal show that the adsorption capacity of GAC was nearly exhausted during the study period. When ozonation was performed (during May–June 1995), TOC removal by GAC filtration ranged from 19 to 27%. When ozonation was not performed (during May–June 1996), TOC removal was less than 13%. Thus, it is presumed that the removal of pesticides on GAC filters investigated may be mainly attributed to biodegradation. These results indicate that on biological GAC filtration at a full-scale plant, the contribution of the microbiological removal of pesticides, such as metolachlor and terbutylazine, is very limited.

Treatment options for removal of pesticides

Table 5 summarises the average and range of percentage removal of metolachlor and terbutylazine from raw water by single or combined treatment process in the Anconella plant. Using these data, it was possible to make a prediction for the capacity of these treatment processes to meet the EC standard

of 0.1 µg/L for individual pesticides. The estimated concentrations of metolachlor and terbutylazine in raw water which can be reduced to 0.1 µg/L by these treatment processes are shown in Table 6. As previously described, ozonation alone or combined with flocc-sedimentation is not found to be efficient enough to comply with EC standards for these pesticides. The capacity of PAC to comply with the EC standards depends on the PAC dose and the kind of flocc-sedimentation system used. Using a PAC dose of 15 mg/L PAC combined with the Dorr system removed an average of 60% of metolachlor and 67% of terbutylazine from raw water. This implies that the levels of metolachlor and terbutylazine in the raw water must not exceed 0.25 and 0.30 µg/L, respectively: above these levels, EC standards cannot be met, while data in Fig. 1 show that in numerous samples during May–July 1995 and 1996 the concentrations of these pesticides were above these levels. On the other hand, with the same PAC dose, PAC combined with the Pulsator system removed more than 94% of metolachlor and terbutylazine from raw water, which means that all observed concentrations of these pesticides during 1995–96 can be reduced to 0.1 µg/L. This result suggests that optimisation of the PAC–flocc-sedimentation process may constitute one of the most important aspects for maximising the treatment efficiency on pesticides during drinking water processing at the Anconella plant.

The most effective treatment option for meeting the EC standard of 0.1 µg/L for metolachlor and terbutylazine was found to be PAC in combination with the Pulsator system and ozonation. Using this combined treatment process, an average of 4.57 µg/L (range 2.70–7.92 µg/L) and 4.82 µg/L (range 2.47–10.36 µg/L) of metolachlor and terbutylazine in raw water, respectively, will be reduced to 0.1 µg/L by employing a PAC dose of 15 mg/L.

Table 6 Estimated concentrations of metolachlor and terbutylazine in raw water which can be reduced to 0.1 µg/L by single or combined treatment process in the Anconella plant

Treatment process	Estimated pesticide concentrations* (µg/L) (average and range) in raw water which can be reduced to 0.1 µg/L					
	0 mgPAC/L		5–10 mgPAC/L		15 mgPAC/L	
	Metolachlor	Terbutylazine	Metolachlor	Terbutylazine	Metolachlor	Terbutylazine
PAC + Pulsator Sed.	0.13	0.14	0.32 (0.21–0.59)	0.47 (0.23–0.85)	1.72 (1.41–2.08)	2.63 (1.69–3.45)
PAC + Dorr Sed.	0.12	0.12	0.18 (0.15–0.23)	0.21 (0.18–0.24)	0.25 (0.23–0.28)	0.30 (0.30–0.36)
Ozonation	0.27 (0.19–0.38)	0.18 (0.15–0.30)				
PAC + Pulsator Sed. + Ozonation	0.35 (0.25–0.50)	0.25 (0.20–0.41)	0.84 (0.46–2.24)	0.87 (0.49–2.50)	4.57 (2.70–7.92)	4.82 (2.47–10.36)
PAC + Dorr Sed. + Ozonation	0.31 (0.23–0.45)	0.23 (0.18–0.37)	0.47 (0.31–0.84)	0.39 (0.28–0.73)	0.66 (0.43–1.07)	0.56 (0.39–1.08)

*Range values in brackets.

CONCLUSIONS

Analysis of the water supply of Florence indicates that conventional water treatment processes, including prechlorination with chlorine dioxide, flocc-sedimentation and sand filtration, can only remove less than 30% of metolachlor and terbutylazine from the raw water. The removal efficiency of PAC adsorption followed by the Pulsator flocc-sedimentation process is significantly more efficient than PAC adsorption followed by Dorr flocc-sedimentation process. Taking into consideration the seasonal pattern of pesticide pollution in the Arno river, a combination of PAC adsorption, Pulsator flocc-sedimentation and ozonation is the most effective treatment to enable compliance with the EC drinking water standards for pesticides.

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