ISSN 1001—0742
Journal of Environmental Sciences Vol. 18, No. 2, pp. 248—253, 2006
CN 11—2629/X

Article ID: 1001-0742(2006)02-00248-06 **CLC number**: X52; TU991.25 **Document code**: A

Pilot-scale study of removal effect on Chironomid larvae with chlorine dioxide

SUN Xing-bin[1], CUI Fu-yi[1,*], ZHANG Jin-song[2], GUO Zhao-hai[3], ZHAO Kai[1], LIU Li-jun[2], LV Wei-min[4]

(1. School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China. E-mail: sunxingbin1025@163.com; 2. Water Research Institute, Shenzhen Water Group, Shenzhen 518001, China; 3. State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing 100085, China; 4. Heilongjiang Province Light Industrial Science Research, Harbin 150010, China)

Abstract: Chironomid larvae propagated excessively in eutrophic water body and could not be effectively inactivated by the conventional disinfection process like chlorination due to its stronger resistance to oxidation. In this paper, a pilot-scale study of chlorine dioxide preoxidation cooperating with routine clarification process for Chironomid larvae removal was conducted in Shenzhen Waterworks in Guangdong Province, China. The experimental results were compared with that of the existing prechlorination process in several aspects, including the Chironomid larvae removal efficiencies of water samples taken from the outlets of sedimentation tank, sand filter, the security of drinking water and so on. The results showed that chlorine dioxide might be more effective to inactivate Chironomid larvae than chlorine and Chironomid larvae could be thoroughly removed from water by pre-dosing chlorine dioxide process. The GC-MS examination and Ames test further showed that the sort and amount of organic substance in the treated water by chlorine dioxide preoxidation were evidently less than that of prechlorination and the mutagenicity of drinking water treated by pre-dosing chlorine dioxide was substantially reduced compared with prechlorination.

Keywords: Chironomid larvae; chlorine dioxide; chlorine; preoxidation; water treatment

Introduction

Chironomid, from the dipteran family Chironomidae, is a non-biting midge that is widely distributed in the northern hemisphere at temperate latitudes. Chironomid larvae can be found both in lentic and lotic environments, usually in organically enriched waters. First instar larvae are predominantly planktonic, while older instars (second, third and fourth larval stages) in most species migrate to the sediment and build tubes constructed from detritus, algae and sediment particles (Charles *et al*., 2004). Chironomid larvae could excessively propagate in water source such as reservoir or fresh lake due to eutrophication(Gtirgy and Judit, 1983), which induced first instar larvae in source water to enter drinking water treatment system. There are many serious accidents of Chironomid larvae pollution in the water treatment system in the Britain, USA and China (Michael, 1997; Bay, 1993; Zhou *et al*., 2003). Although there are no indications that these organisms pose a threat to public health (WHO, 1996), their presence is not appreciated because most people associate the organisms with low hygiene.

Chironomid larvae could not be effectively inactivated by the conventional disinfection such as chlorination due to its stronger resistance to oxidation (Cui *et al*., 2004). In addition, the motility of first instar larvae made it easily penetrate sand filter into waterworks reservoir even municipal service pipe (Zhou *et al*., 2003; Cui *et al*., 2004; van Lieverloo *et al*., 2004). At present, most waterworks killed or inactivated Chironomid larvae by prechlorination and removed it thoroughly from water by subsequent water treatment process. Although with a proven removal of Chironomid larvae, prechlorination would reduce the drinking water security for increasing the halomethane content in treated water. So it was essential to explore a more effective and safe removal technique. As a powerful substitute or a supplemental disinfectant for chlorination, chlorine dioxide can eliminate bad odor and oxidize ferrous, manganous ions in underground water. Moreover, Chlorine dioxide has been reported to be effective in the inactivation of pathogenic organisms including *Cryptosporidium parvum* oocysts (Ruffell *et al*., 2000; Corona-Vasquez *et al*., 2002). Further, the oxidation of natural organic material (NOM) with chlorine dioxide does not form halogenated disinfection by-products(DBPs) such as dissolved organic halides, trihalomethanes, and haloacetic acids (Korn *et al*., 2002; Raczyk-Stanis *et al*., 2004). Previous studies on ClO_2 focused on the disinfection efficiency for harmful microorganism removal (Ruffell *et al*., 2000; Corona-Vasquez *et al*., 2002; Narkis, 1995; Huang *et al*., 1997a, b). However, information regarding chlorine dioxide inactivation Chironomid larvae is lacking in the literature.

In this paper, a pilot-scale study of chlorine dioxide preoxidation cooperating with routine clarification process for Chironomid larvae removal was conducted in Shenzhen Waterworks in Guang-

Foundation item: The National Natural Science Foundation of China(No. 503780262); the Hi-Tech Research and Development Program(863) of China (No. 2002AA601120) and the Specialized Research Fund for the Doctoral Program of Higher Education(No. 20030213036); *Corresponding author

dong Province, China. The removal efficiency of Chironomid larvae by pre-dosing chlorine dioxide in water treatment process was comprehensively compared with that of the conventional prechlorination process. The results showed that chlorine dioxide preoxidation was an excellent substitute for the conventional pre-dosing chlorine process. Hence this provided a valuable basis for the further investigation on Chironomid larvae removal from water treatment process.

1 Materials and methods

1.1 Description of the pilot plant

The pilot-scale experiments were conducted between April and September, 2004. The pilot plant is located in Shenzhen Waterworks and the raw water was taken from a eutrophic reservoir, in which the amount of Chironomid larvae has sharply increased. The pilot plant diagrammatically represented in Fig.1.

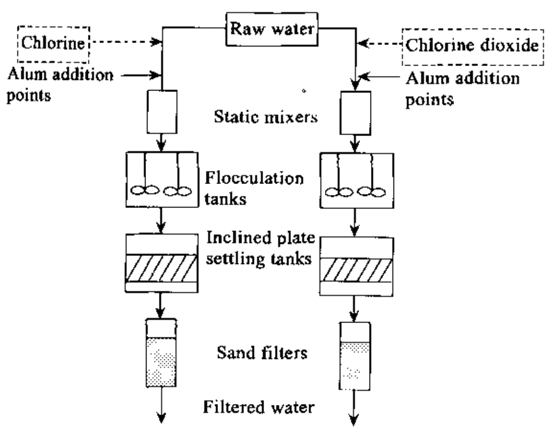

Fig.1 Flow chart of pilot-scale study of two preoxidation processes

All components of the pilot plant were constructed of inert materials, including glass, Teflon and stainless steel to be chemically inert, and to mimic the design of Shenzhen Waterworks at a scale-down factor. The raw water enters a constant head tank at a fixed elevation to ensure that gravity flow conditions are maintained throughout the pilot train. The water is then split into two identical treatment trains at a flow rate of about 50 L/min. As the raw water leaves the constant head tank, metering pumps inject aluminum sulfate. Mixing is provided by static mixers prior to entering a three-cell flocculation tank. As the water leaves the flocculators, it flows into a sedimentation tank equipped with inclined-plates, then passes to an sand filter. The filter had a hydraulic loading rate of 8.0 m/h. Chlorine and chlorine dioxide was added together with aluminum sulfate. During the study, the raw water quality characteristics are shown in Table 1.

1.2 Experimental methods

First instar larvae was determined by microscopic counting method, by which the changes of the number of first instar larvae between raw water and treated water from sedimentation tank and sand filter were investigated.

Table 1 Water quality characteristics of raw water during the experiment

Water quality parameter	Range
Temperature, ℃	23.2—25.7
TOC, mg/L	2.13—2.91
UV_{254}, cm^{-1}	0.387—0.459
Turbidity, NTU	5.9—7.7
pH	6.7—7.1

Chlorine dioxide was generated by mixing a hydrochloric acid solution(23% weight) and a sodium chlorite solution (25% weight) according to a weight ratio of 1:1, so exceeding about 300% the stoichiometric acid demand, in order to improve the efficiency and to obtain a lower Cl_2, ClO_2^- and ClO_3^- production. Componential analysis of chlorine dioxide was measured by iodimetry. A 10-ml portion from a 0.2 μm filtrate was collected to analyze ClO_2^- and ClO_3^- using ion chromatography (DIONEX, series 4500, column AS-12A, 4 mm (10—12), P/N 46034). Componential analysis of chlorine dioxide gas is listed in Table 2.

Table 2 Componential analysis of chlorine dioxide

Chemical composition	Chlorine dioxide	Chlorine	Chlorite	Chlorate
Percentage composition, %	81.7	11.6	4.8	1.9

Raw water and treated water by chlorine dioxide or chlorine preoxidation were respectively sampled 250 L. Organic substances in water samples were enriched with macroporous resin and then were eluted with about 60 ml of carbinol. The carbinol samples containing organic substances were concentrated to about 1 ml with a K-D concentrator. The concentrated samples were detected in duplicate with GC-MS test using gas chromatograph-mass spectrometer and with Ames testes using TA100 and TA98 strains without metabolic activation S9 at increasing doses of concentration (corresponding to 1, 3, 5, 7 and 9 L of equivalent volume per plate).

2 Results and discussion

2.1 Effect of chlorine dioxide dosage on Chironomid larvae

Chlorine dosage ranged from 0 to 4.0 mg/L and chlorine dioxide dosage ranged from 0 to 2.0 mg/L during the pilot-scale study. The results are shown in Figs.2 and 3. The removal effects were strengthened gradually with the increase of preoxidation dose. When 100% of removal efficiency in treated water from sand filter was obtained, the dosage of ClO_2 was 0.51 mg/L, whereas 3.97 mg/L was required for

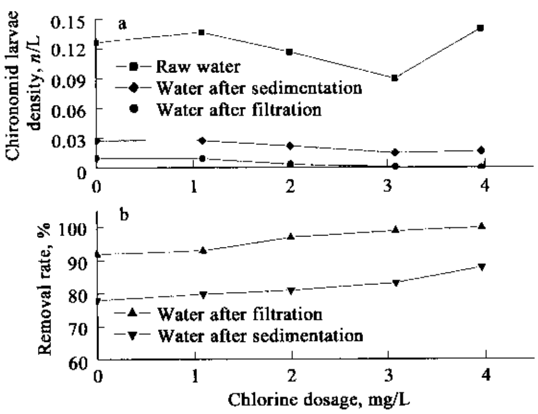

Fig.2 Effects of different chlorine dosage on Chironomid larvae density(a) and removal rate(b) of Chironomid larvae

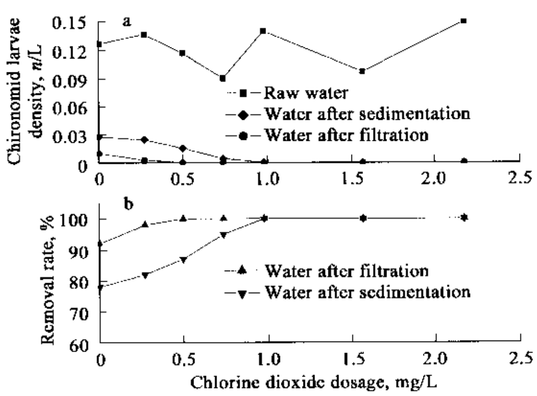

Fig.3 Effects of different chlorine dioxide dosage on Chironomid larvae density(a) and removal rate(b) of Chironomid larvae

chlorine. In addition, the removal rate in treated water by sedimentation and filtration were 78% and 92% respectively under no preoxidation dosing condition.

The removal efficiency of Chironomid larvae were separately 78% and 92% by sedimentation and filtration with no preoxidation dosing (Figs.2 and 3), which showed that Chironomid larvae could be partially removed from water by single clarification process. As motility of Chironomid larvae in raw water was found to be different, some Chironomid larvae which finished planktonic life stage may be more easily deposit together with the floc formed in flocculation process or be captured by sand filter. But the removal efficiency in single clarification process was finite because Chironomid larvae with stronger motility still might penetrate sand filter. Thus, their removal further depended on the inactivation of preoxidation process. Chironomid larvae could not be completely removed at the lower chlorine dioxide dosage (<0.51 mg/L), which showed that Chironomid larvae with stronger motility could not be effectively inactivated at lower dose of preoxidation due to its stronger resistance to oxidation. Thereby, the clarification process could not still capture this part of Chironomid larvae. It was important to inactivate or weaken stronger Chironomid larvae with adequate available chlorine dioxide in order to remove completely Chironomid larvae from water treatment system. Above all, it is necessary to cooperate chlorine dioxide inactivation and clarification process for removing Chironomid larvae completely in the viewpoint of drinking water security. Another predominance of the cooperation is to reduce the dosage of chlorine dioxide, and 100% of removal efficiency is obtained with the dosage of 0.51 mg/L.

2.2 Comparison of removal effect of two preoxidation processes

According to the above experimental results, 100% of Chironomid larvae could be removed from treated water by 0.51 mg/L of ClO_2. So during the pilot-scale study, long-term removal effect by chlorine dioxide preoxidation with 0.51 mg/L of ClO_2 was investigated in comparison with the existing prechlorination process with 2.0 mg/L of chlorine that applied in Shenzhen Waterworks (Fig.4). Long-term removal effect of chlorine dioxide preoxidation was better than that of prechlorination in treated water after sedimentation, as indicated in Fig.4, higher removal of 90% by chlorine dioxide preoxidation compared with 80% by prechlorination. Similarly, Chironomid larvae could be thoroughly removed from water body by filtration with chlorine dioxide, whereas the same efficiency was not attained by prechlorination with the conditions of dosage of 2.0 mg/L.

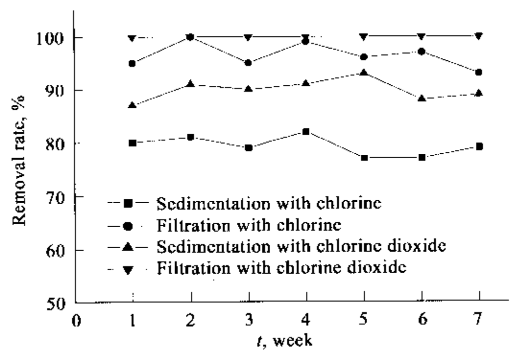

Fig.4 Long-term removal effect on Chironomid larvae in two different processes

Chironomid larvae hardly was removed from water by sedimentation unless it was effectively inactivated by oxidation with oxidant. The removal result of sedimentation tank showed that Chironomid larvae inactivation of chlorine dioxide was superior to that of chlorine. For example, 90% of removal rate in treated water after sedimentation was attained by chlorine dioxide prexidation, but for prechlorination, only 80% was attained. The distinct difference in inactivation efficiency of two preoxidation processes may be the results of the body structure of Chironomid larvae and the different performance of oxidants in oxidizing cellular tissue. Contrasted to common bacteria or virus, Chironomid larvae possesses a special surface structure such as bottom membrane, epithelium, calcific layer, and so on. The body surface provides stronger protection against oxidation for Chironomid larvae. Chironomid larvae can not be effectively inactivated unless the oxidant destroys its surface structure by oxidation or directly penetrates through it into the body as to oxidize inner protein to lose the enzyme activity and not to participate in the activities of the oxidation-reduction system. So the higher oxidizability of oxidant is key to thoroughly inactivate Chironomid larvae. For chlorine in chlorine dioxide, oxidation number is expressed as +4. According to counting, it contains 263% of available chlorine, i.e. oxidizability of chlorine dioxide is about 2.5 times as high as that of liquid chlorine (Huang *et al.*, 1997a). So the ability of chlorine dioxide to oxidize Chironomid larvae body structure is more effective than that of chlorine. In addition, after dissolving in water, 100% of ClO_2 exists in molecular state not reacting with water molecular like chlorine, which makes ClO_2 contact Chironomid larvae surface easily and permeate it through into body inner to destroy inner cellular protein as to inactivate Chironomid larvae. The above advantages of chlorine dioxide not only result in a better inactivation of Chironomid larvae but also a lower required amount of it than chlorine.

2.3 Influence of preoxidation on organic substances and mutagenicity

The GC-MS examination and Ames test with raw water sample and two treated water samples after preoxidation were carried out in order to evaluate the security of drinking water. The GC-MS examination results are shown in Table 3. The Ames test results are shown in Figs. 5 and 6.

2.3.1 GC-MS examination

Compared with that in raw water, the amount of halogenated hydrocarbon in treated water by prechlorination increased 13 species. However, the total organic substance increased only 9 species. The amount of organic substance decreased to 31 species by chlorine dioxide preoxidation, which was equal to 50% of that in raw water. Moreover, the halogenated hydrocarbon was only 2 species in treated water (Table 3).

Table 3 Analysis of GC-MS results of three water samples

Organic species	Raw water		Treated water by preoxidation			
			Chlorine		Chlorine dioxide	
	Amount	Peak area	Amount	Peak area	Amount	Peak area
Paraffin	18	48052638	16	58362012	13	31660233
Olefin	2	1602876	0	0	0	0
Halogenated hydrocarbon	1	3871012	14	60857658	2	14712049
Arene	2	5860685	3	5371070	3	5213882
Heterocyclic compound	3	6596361	2	2358607	1	734126
Nitrogen compound	8	47173412	4	10475373	1	8767319
Benzene	5	183340538	2	58419603	1	43063856
Alcohol, aldehyde, etc.	23	276046360	30	243150804	10	138458270
Total	62	572543882	71	438995127	31	242609735

The different reaction mechanism that organic substances react with chlorine dioxide and chlorine leads to the corresponding results of GC-MS test. The free radical oxidation reaction happens when chlorine dioxide reacting with organic substances and the macromolecule organic compounds are oxidized into oxocompounds and micromolecule substances, in which some volatile compounds, even CO_2 and H_2O, are formed (Benjamin *et al.*, 1986). Moreover, the stronger oxidizability of chlorine dioxide may easily oxidize organic substance to such products with low boiling point and minor molecular weight. The electrophilic substitution reaction when chlorine oxidizing organic substance results in the much more formation of more mutagenic halogenated hydrocarbon such as trichloronmethane, most of which belongs to high boiling point and macromolecule organic compounds with long retention time (Reckhow *et al.*, 1990; Langvik and Holmbom, 1994). In addition, much intermediate products such as aldehyde may be produced during chlorination due to no thoroughly oxidizing organic substances with chlorine, which results in that the total amount of organic substance by prechlorination is more than that treated by chlorine dioxide preoxidation. So it can be said that the drinking water quality by chlorine dioxide preoxidation is better than that by prechlorination.

2.3.2 The Ames test

The mutagenicity of concentrated water samples before and after preoxidation was expressed as MR value(rate of mutagenicity). The result with MR value greater than 2 was condidered as having mutagenic activity. Figs.5 and 6 showed that raw water had no mutagenic activity. However, MR value of water sample by prechlorination was higher than that of water sample by chlorine dioxide preoxidation at the same doses. Cl_2-treated (2.0 mg/L) water showed mutagenicity with TA98 strain(MR=2.34) and TA100 strains(MR=2.2) at lower doses(5 L equivalent/plate), whereas ClO_2-treated(0.51 mg/L) water had mutagenic activity detectable only at the highest doses (9 L equivalent/plate), in which the MR value with TA98 and TA100 were 2.3 and 2.17 respectively.

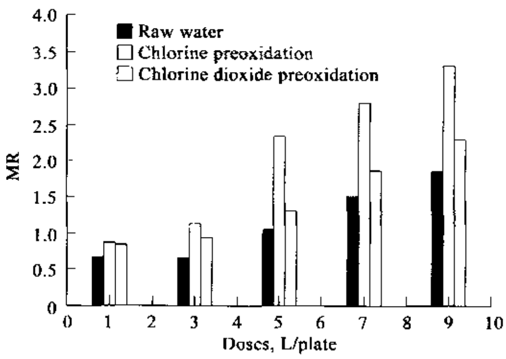

Fig.5 Changes of TA98-S9 dose-response relationship

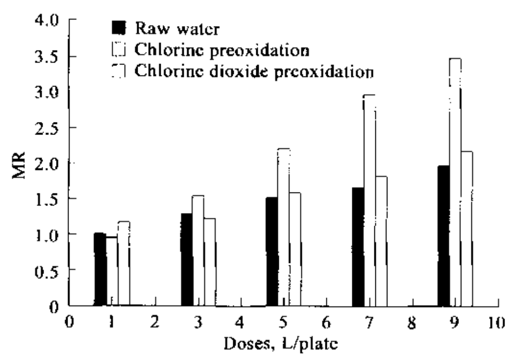

Fig.6 Changes of TA100-S9 dose-response relationship

TA98 and TA100 strain are respectively used to detect frame-shift point mutations and base pair substitution mutations. The Ames test results show that preoxidation with chlorine gives rise to the formation of more mutagenic compounds. The obvious mutagenicity of treated water by chlorine preoxidation is caused by much organic halogentated compounds (14 species) formed in chlorination due to electrophilic substitution reaction between chlorine and organic substances. The special chemical active group of halogentated compounds, halogen with stronger electrophonic effect reinforces molecule polarity as to easily react with biologic enzyme system, during which the mutagenic action is attained by a series of chemical reactions as DNA base substitution (Langvik and Holmbom, 1994). Whereas less halogentated compounds (only 2 species) are formed during chlorine dioxide preoxidation due to different reaction mechanism (oxidation-reduction reaction not electrophilic substitution reaction), so that mutagenicity of treated water is lower than that by prechlorination. In addition, the mutagenicity of ClO_2-treated water occurs at the doses of 9 L equivalent/plate, which is alien to some previous Ames test results (Huang and Li, 1998; Fiessinger, 1991). The main reason may be caused by impurities as chlorine in chlorine dioxide gas produced by generator (Table 2). The amount of chlorine accounts for 11.6% of the total chlorine dioxide content, which may result in the mutagenic activity analogous to the result of prechlorination. This can be improved by enhancing chlorine dioxide gas purity with advanced generator.

3 Conclusions

Chlorine dioxide preoxidation possesses very favorable inactivation effect on Chironomid larvae. Chironomid larvae can be effectively removed from water body by chlorine dioxide preoxidation co-operating with the conventional clarification process, i.e., flocculation, sedimentation and filtration. The existing process of prechlorination can not attain the same removal effect as chlorine dioxide.

In viewpoint of the security of drinking water it is necessary to cooperate of chlorine dioxide inactivation and clarification process for removing Chironomid larvae completely. Another predominance of the cooperation is to reduce the dosage of the oxidant, and 100% of removal efficiency is obtained with the dosage of 0.51 mg/L.

GC-MS examination and Ames test further show that the sort and amount of organic substances in treated water by chlorine dioxide preoxidation are evidently less than that of prechlorination, and the mutagenicity of drinking water is highly reduced. The advantage of Chlorine dioxide disinfection may be further improved by enhancing chlorine dioxide gas purity.

References:

Bay E C, 1993. Chironomid (Diptera: Chironomidae) larval occurrence and transport in a municipal water system [J]. Journal of the American Mosquito Control Association, 9: 275—284.

Benjamin W, Lukins J, Mark H G, 1986. Using chlorine dioxide for trihalomethane control[J]. AWWA, 78: 88—93.

Charles S, Ferreol M, Chaumot A *et al.*, 2004. Food availability effect on population dynamics of the midge *Chironomus riparius*: a leslie modeling approach [J]. Ecological Modelling, 175: 217—229.

Corona-Vasquez B, Rennecker J L, Driedge A M *et al.*, 2002. Sequential inactivation of *Cryptosporidium parvum* oocysts with chlorine dioxide followed free chlorine or monochloramine [J]. Water Research, 36: 178—188.

Cui F Y, An D, Sun X B, 2004. The reproduction rule and control of Chironomus larvae in water bodies [J]. Techniques and

Equipment for Environmental Pollution Control, 5(7): 1—4.

Fiessinger F, 1991. Advantages and disadvantages of chemical oxidation and disinfection of ozone and chlorine dioxide [J]. Science of the Total Environment, 18: 245—246.

Gtirgy D, Judit M, 1983. An attempt to trace eutrophication in a shallow lake (Balaton, Hungary) using Chironomids [J]. Hydrobiologia, 103: 169—175.

Huang J L, Wang L, Ren N Q *et al.*, 1997a. Disinfection effect of chlorine dioxide on viruses, algae and animal plankton in water [J]. Water Research, 31: 455—460.

Huang J L, Wang L, Ren N *et al.*, 1997b. Disinfection effect of chlorine dioxide on bacteria in water[J]. Water Research, 31: 607—613.

Huang J L, Li B X, 1998. Comparison of the mutagenicity of drinking water with chlorine dioxide and chlorine disinfections [J]. Environment Chemistry, 17(4): 34—38.

Korn C, Andrews R C, Escobar M, 2002. Development of chlorine dioxide related by-product models for drinking water treatment [J]. Water Research, 36: 330—342.

Langvik V, Holmbom B, 1994. Formation of mutagentic organic byproducts and AOX by chlorination of fractions of humic water [J]. Water Research, 28: 553—557.

Michael K A, 1997. New strategies for the control of the parthenogenetic Chironomed [J]. Journal of the American Mosquito Control Association, 13: 189—192.

Narkis N, 1995. Disinfection of efficient by combinations of chlorine dioxide and chlorine [J]. Water Science and Technology, 31: 1105—1147.

Raczyk-Stanis A U, Wietlik J, Browska D A *et al.*, 2004. Biodegradability of organic by-products after natural organic matter oxidation with ClO_2-case study [J]. Water Research, 38: 1044—1054.

Reckhow D A, Singer P C, Malcolm R L, 1990. Chlorination of humic materials: byproduct formation and chemical interpretations [J]. Environment Science and Technology, 24: 1655—1664.

Ruffell K M, Rennecker J L, Mari?as B J, 2000. Inactivation of *Cryptosporidium parvum* oocysts with chlorine dioxide[J]. Water Research, 34: 868—876.

van Lieverloo J H M, Bosboom D W, Bakker G L *et al.*, 2004. Sampling and quantifying invertebrates from drinking water distribution mains[J]. Water Research, 38: 1101—1112.

WHO(World Health Organization), 1996. Guidelines for drinking water quality[S]. Health criteria and other supporting information. Vol. 2. Geneva: World Health Organization. 953.

Zhou L, Zhang J S, Lei P, 2003. The research trends of preventions of Chironomid larvae pollution in drinking water treatment [J]. Water and Wastewater, 29(1): 25—28.

(Received for review June 2, 2005. Accepted July 22, 2005)