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Fate and Effects of Xanthates in Laboratory Freshwater Systems

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Xanthates (salts of the dithiocarbon acid-O-ester with a C-O-alkyl or aryl chain and C-S-metal ion) are mostly of technical significance as 'samplers' of metal sulfides in mining flotation. Alkali-metal-xanthates are stable, crystalline substances. The Na-salts are slightly hygroscopic and form dihydrates, while the K-salts crystallize free of water. More than 11 000 metric tons of Na-isopropyl (40 %), Na-ethyl-(30 %), Na-sec. butyl-(15 %) and K-isopentyl-xanthates (10 %) are consumed in flotation processes per year worldwide. Alkali-xanthates are of minor toxicity to mammals (LD_{50} for mice ranged from 400-700 mg/kg; Edelmann 1983). As Xanthates are hydrolyzed by stomach acid, poisoning is mainly caused by the hydrolysis products alcohol and carbon disulfide. Xanthates, however, are known to be strong fish poisons (Edelmann 1983; Webb et al. 1976). LD_{50} values were found between 10 and 100 mg/L water. Recently xanthates are being discussed as helpful agents in environmental protection because of their ability to remove harmful heavy metals from contaminated waters (Edelmann 1983). The present work was undertaken, to provide more information on the fate and effects on aquatic organisms of these environmental chemicals.

MATERIALS AND METHODS

To test the effects of alkali-xanthates on water plants, Lemna minor (duck weed) was used as the test organism in a laboratory culture. Ten plants of a one-leaf stage were placed in a 2-L beaker. As nutrient feed a stock solution of the following composition in deionized water, diluted to 25 % strength with the same solvent, was taken (g/L): 0.316 $Ca(NO_3)_2 \cdot 4\ H_2O$, 0.16 NH_4NO_3, 0.4 $MgSO_4 \cdot 7H_2O$, 0.02 H_3BO_3, 0.02 $NaMoO_4 \cdot 2H_2O$, 0.5924 KH_2PO_4, 0.3286 NA_2HPO_4; trace elements (chelated with EDTA-K-salt before addition): 0.00646 $FeCl_3 \cdot 6H_2O$, 0.0264 $ZnSO_4 \cdot 7H_2O$, 0.00616 $MnSO_4 \cdot 5H_2O$, 0.0076 $CoSO_4 \cdot 7H_2O$.

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L. minor were uniformly illuminated by fluorescent lamps at 110-115 μEinstein (12 h cycle of daylight and darkness). Mean room temperature was 25° C. Losses of water from the nutrient solutions were corrected daily by addition of appropriate amounts of distilled water. Test duration was 2 WK . Initial concentrations of the four xanthates tested were 10 and 20 mg/L; each test chemical was dosed in duplicates from an aqueous stock solution. The chemicals were kindly provided by the Hoechst Company (Frankfurt/Main). Toxic effects were evaluated by counting the number of leaves and measuring the length of roots in comparison with untreated controls.

Concentrations of the xanthates in water were analyzed by complexing aliquots with $NiSO_4$ in a Na-acetate/acetic acid buffer (pH 5), followed by extraction of that complex with toluene. The extinction of the organic layer was measured in a photometer (Type LP 1W, Lange Berlin) at 339 nm wavelength. The absolute amount of the xanthates was determined by calibrating the extinction vs. a concentration series.

The culture conditions for the ^{14}C-K-ethylxanthate uptake by L. minor study were as described for the toxicity test. The maximum ^{14}C-xanthate concentration, however, was limited to 50 ug/L to avoid toxic effects. Residues of ^{14}C in the plants were determined daily by combustion of aliquots to $^{14}CO_2$ in an oxidizer (Packard 306). Radioactivity in the aqueous phase was measured by liquid scintillation counting (Berthold 8000) using Hydroluma (Baker) as scintillation cocktail. The bioconcentration factor was calculated and defined as the quotient from concentration in L. minor (dpm per g wet weight) and the concentration of ^{14}C in the water (dpm per mL).

The acute toxicity of the xanthates to Cladocera was tested by the acute immobilization of Daphnia magna. These 24-h tests, determining the effective concentrations (e.g. EC_{50}), were conducted according to the OECD Guidelines No. 202 for Testing Chemicals (OECD 1984). Four groups with seven animals each were used at each test concentration and for the controls. Water temperature was 20°C, O_2-concentration was 9.8 mg/L, pH 8.4 and conductivity was 325 μS/cm. The tests were performed with animals from a cloned strain of D. magna (Straus) obtained from the Bundesgesundheitsamt Berlin.

RESULTS AND DISCUSSION

The disappearance rates of the four xanthates were determined (a) from the sterilized nutrient solution and (b) from the water in the presense of L. minor. Results are summarized in Table 1.

Table 1. Disappearance of four xanthates from water phase

Compound	Test condition	Equation of xanthates declining	$t_{1/2}$ (days)
Na-ethyl-xanthate	without Lemna	$y = 21.24\ e^{-0.18x}$	4.08
	with Lemna	$y = 19.84\ e^{-0.17x}$	3.85
Na-iso-propyl-xanthate	without Lemna	$y = 19.68\ e^{-0.2x}$	3.46
	with Lemna	$y = 4.07\ e^{-0.6x}$	1.16
Na-iso-butyl-xanthate	without Lemna	$y = 19.51\ e^{-0.23x}$	3.01
	with Lemna	$y = 20.08\ e^{-0.27x}$	2.57
K-iso-pentyl-xanthate	without Lemna	$y = 20.10\ e^{-0.28x}$	2.48
	with Lemna	$y = 20.27\ e^{-0.31x}$	2.24

The result of this residue analysis generally shows that half-lives ($t_{1/2}$)decrease with increasing length of the alkyl chain. The disappearance rates of Na-isopropyl and Na-isobutyl are significantly enhanced in the presence of the test plants. pH-values in the test beakers were 8.5 at the beginning of the test and dropped down to 6.5 after 1 WK probably due to an increases of CO_2 concentration in the water. Due to high toxicity, Na-isopropylxanthate was tested at 3.5 mg/L only. The time course of the disappearance rates are shown in Figures 1, 2 and 3.

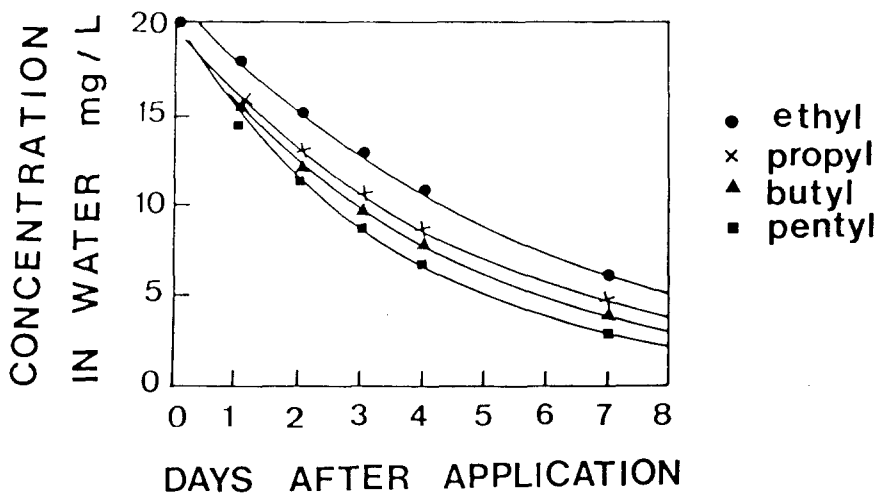

Figure 1. Disappearances of four xanthates from sterilized nutrient solution

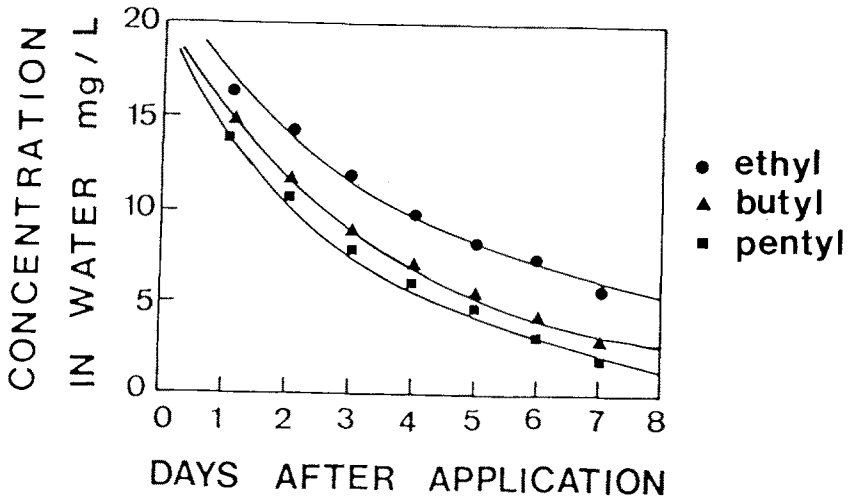

Figure 2. Disappearances of three xanthates from freshwater with L. minor

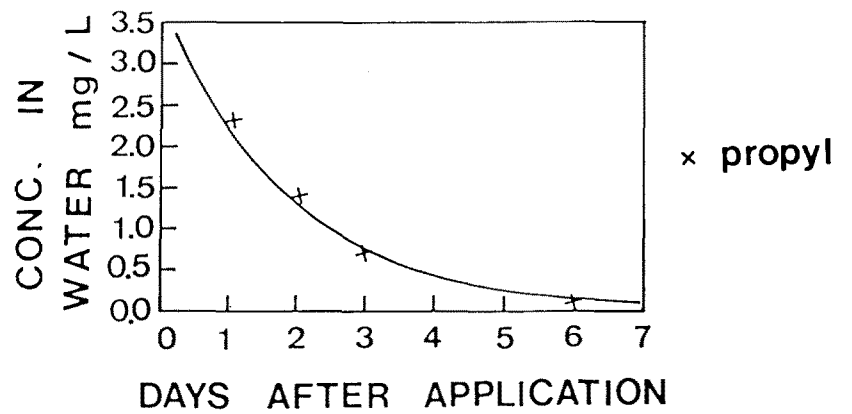

Figure 3. Disappearances of Na-isopropyl-xanthate from freshwater with L. minor

In order to analyze the amount of xanthate being concentrated in the tissues of L.minor and causing toxic effects, a total of three test cycles were performed, exposing the plants to a low concentration of the

chemical for 96 h. The results revealed that ^{14}C-labelled K-ethylxanthate was rapidly taken up from the aqueous phase by L. minor with maximum concentrations on 24 h after dosing. Bioconcentration factors (BCF) and chemical concentrations in tissues and in water are shown in Table 2.

Table 2. Uptake of ^{14}C-labelled K-ethylxanthate by L. minor

	Time of analysis (h)			
	24	48	72	96
BCF	1064	919	1070	1025
concentration in tissue (µg/g)	26.6	19.3	18.2	12.3
concentration in water (µg/ml)	0.025	0.021	0.017	0.012

These results indicate that K-ethylxanthate can lead to significant concentrations in aquatic plant tissues, being responsible for subsequent toxic effects. By using test plants with different root lengths, it was further shown that the uptake was highly dependent on the root length.

Except for Na-isopropylxanthate, which we showed to be highly toxic to L. minor in the uptake study, all xanthates were tested at 10 and 20 mg/L in duplicates to evaluate the toxicity on the test plants. Na-isopropylxanthate was tested separately at a lower concentration as it showed a 100 % lethality to L. minor above 5 mg/L concentration after 3 days testing.

The results of the toxic effects of the three other xanthates tested are summarized in Table 3 showing the growth inhibition of the plants on the examples of root length and the number of leaves (means of 2 breakers counted at the end of experiments (2 WK)).

The acute 24-h toxicity of the four xanthates to a D. magna test population was evaluated by determining the immobilization rates. The results show that Na-ethylxanthate was approximately 10 times more toxic to D. magna as compared to C_3-C_5 alkylated xanthates, which all showed a comparable toxicity range.

Table 4 presents the effective concentration (EC-values) of the xanthates tested to D. magna.

Table 3. Growth inhibition of xanthates on L. minor

Sample	Control	Na-ethyl-xanthate		Na-isobutyl-xanthate		Na-isopentyl-xanthate	
Dosage (mg/L)	0	10	20	10	20	10	20
No. of leaves	237	145	50	165	56	147	49
length of roots (mm)	25-35	10-15	< 5	10-15	< 5	10-15	< 5

Table 4. Effective concentration of xanthates causing immobilization of D. magna

Compound	Effective concentrations (mg/L) EC_{10}	EC_{50}	EC_{95}
Na-ethylxanthate	0.18	0.35	0.85
Na-isoproylxanthate	1.9	3.7	10.0
Na-isobutylxanthate	1.8	3.6	11.0
K-pentylxanthate	1.7	3.0	6.0

Summarizing the results of the fate of the xanthates tested, it was demonstrated that the chemical half-lives in water range from about 2.5 to 4 days (C_5-C_2-alkyl). K-ethylxanthate, which was also tested under outdoor conditions in an experimental pond (Rainer Lang unpublished results), showed a comparable disappearance rate to that found under laboratory conditions. The uptake rate was analyzed with the example of ^{14}C-ethylxanthate, leading to a steady-state 24 h following dosing and a mean bioconcentration factor of 1020 $\pm$ 70 (day 1-4 of experiment).

As to the toxicity of the xanthates to aquatic plants, it was shown that the isopropyl compound caused a 100 % lethality to L. minor at a concentration > 5 mg/L. C_2-, C_4- and C_5-alkylxanthates were less toxic but showed significant effects on the production of the leaves and roots of the test plants. This inhibition was relatively uniform for the three compounds as to be seen from the reduction in leaf-developments: 31-39 % at 10 mg/L and 76-79 % at 20 mg/L xanthate.

The series of toxicity tests to daphnids (D. magna) revealed nearly equal effective concentrations for C_3-C_5-

alkylxanthates causing the immobilization of the test animals, whereas ethylxanthate proved to be about 10 times more toxic. Under field conditions, using habitats in microcosms from a natural pond, ethyl- and butylxanthates caused significant reduction of the chlorophyll-contents of planktonic algae, of the oxygen concentration in water, and of the zooplankton populations between 2 and 10 mg/L xanthate (J.P.Lay, R. Lang 1986 unpublished results). On the basis of these findings and the methodology used, alkylxanthates can be classified as harmful micropollutants in aquatic systems at concentrations >2 mg/L. Unwanted intoxication can occur by high loads of xanthates in effluents entering the aquatic environment without prior waste water treatment from mining and ore-dressing plants. Xanthates are also discussed as precipitation agents for the removal of toxic heavy metals from natural waters. At higher doses possible subsequent toxic effects on the biota should therefore be taken into consideration.

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