

Evaluation of azamethiphos and dimethoate degradation using chlorine dioxide during water treatment

Marija V. Pergal,^{1*} Igor D. Kodranov,² Biljana Dojčinović,¹ Viacheslav V. Avdin,³ Dalibor M. Stanković,⁴ Branka B. Petković⁵ and Dragan D. Manojlović^{2,3}

¹Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia

²Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

³South Ural State University, Lenin prospekt 76, 454080 Chelyabinsk, Russia

⁴The Vinca Institute of Nuclear Sciences, University of Belgrade, POB 522, 11001 Belgrade, Serbia

⁵Department of Chemistry, Faculty of Natural Science and Mathematics, University of Priština, Lole Ribara 29, 38220 Kosovska Mitrovica, Serbia

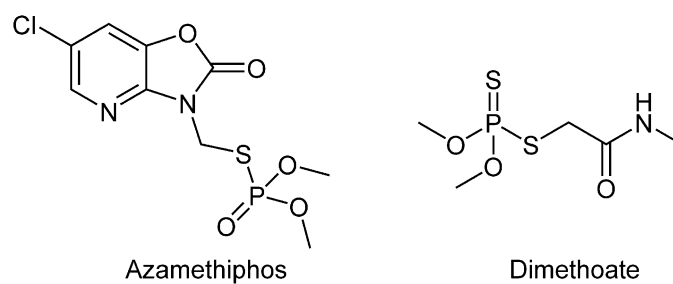


Fig. S1 Chemical structure of the organophosphorus pesticides

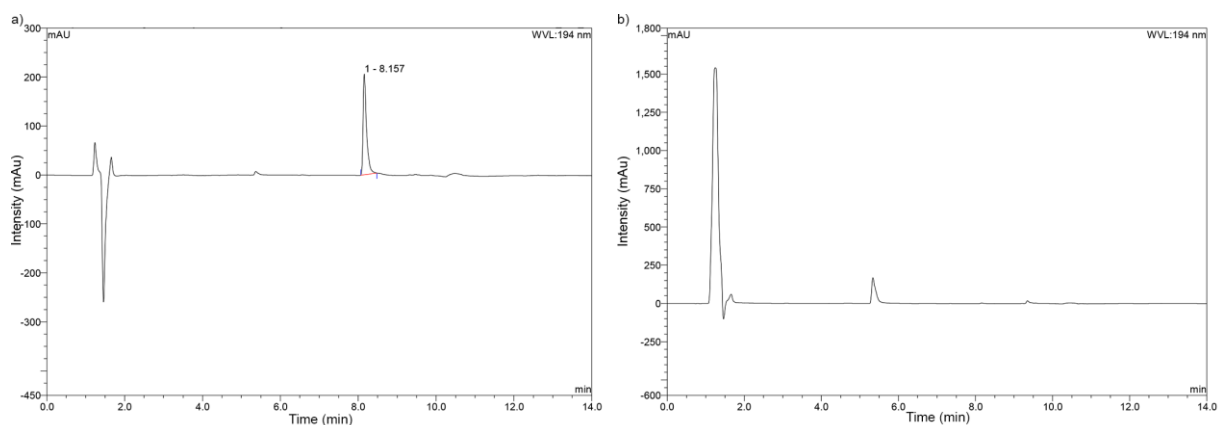


Fig. S2 HPLC chromatograms of parent azamethiphos (10 mg/L) and degradation products (with 10 mg/L ClO₂ during 1 h degradation by chlorine dioxide under light condition)

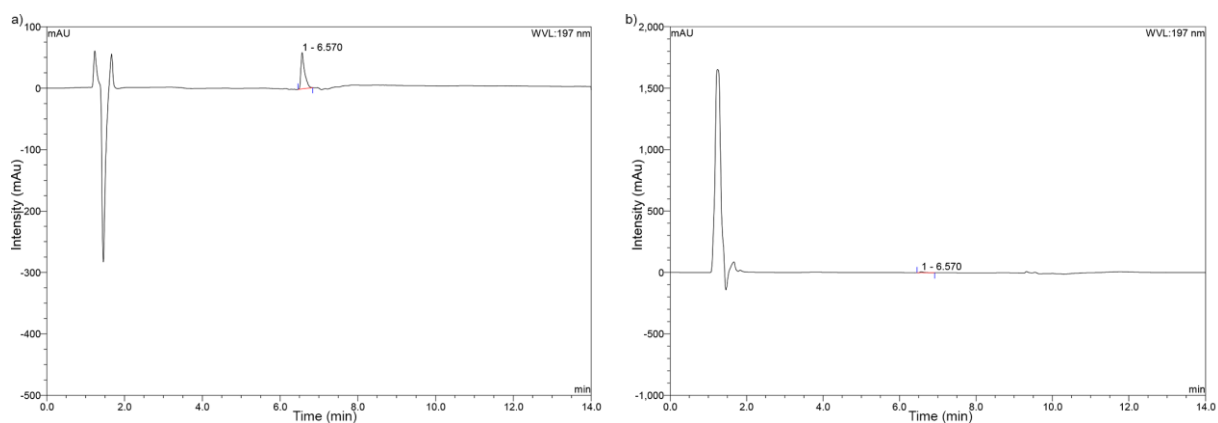


Fig. S3 HPLC chromatograms of parent dimethoate (10 mg/L) and degradation products (with 10 mg/L ClO₂ after 6 h under light condition)

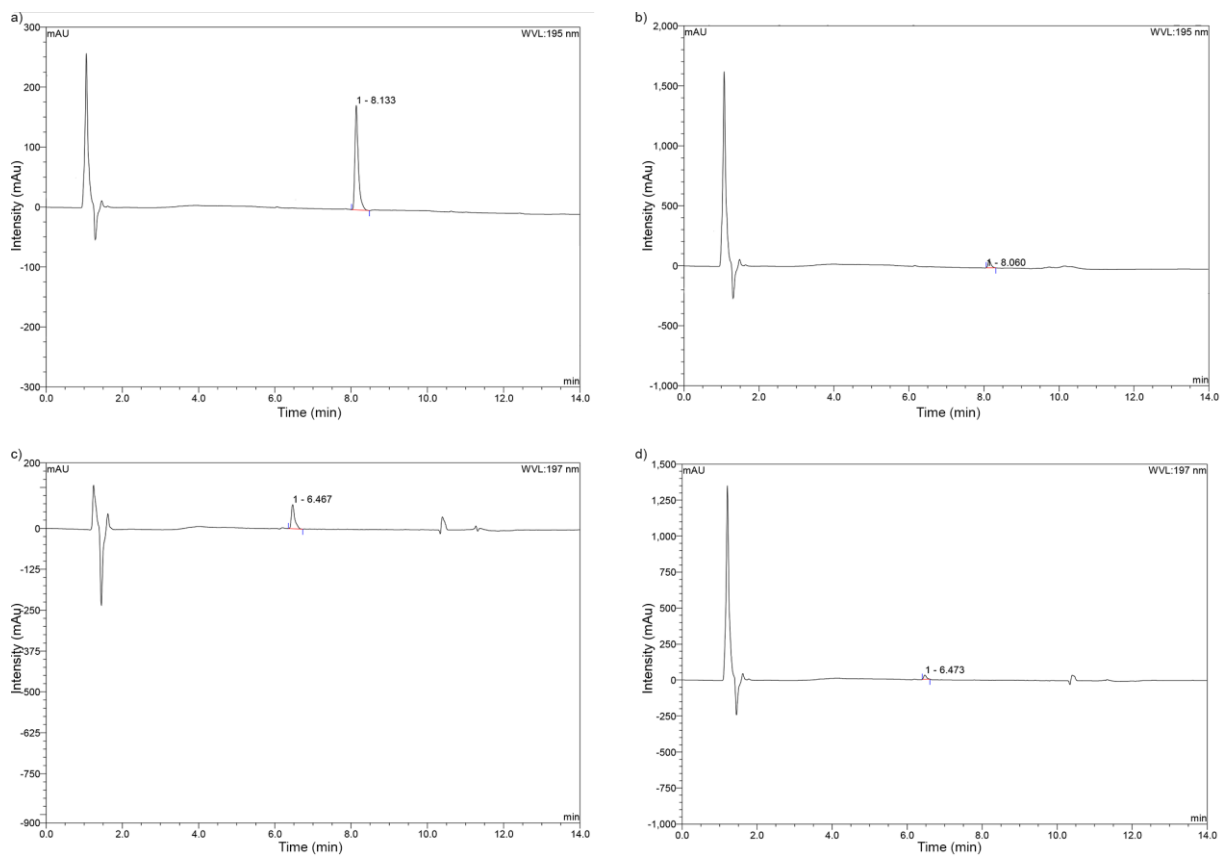


Fig. S4 HPLC chromatograms of parent azamethiphos (10 mg/L) (a) and parent dimethoate (10 mg/L) (c) and degradation products for azamethiphos (b) and for dimethoate (d) in Sava River water obtained under optimal conditions (with 10 mg/L ClO_2 after 24 h under light condition for both AZA and DM)

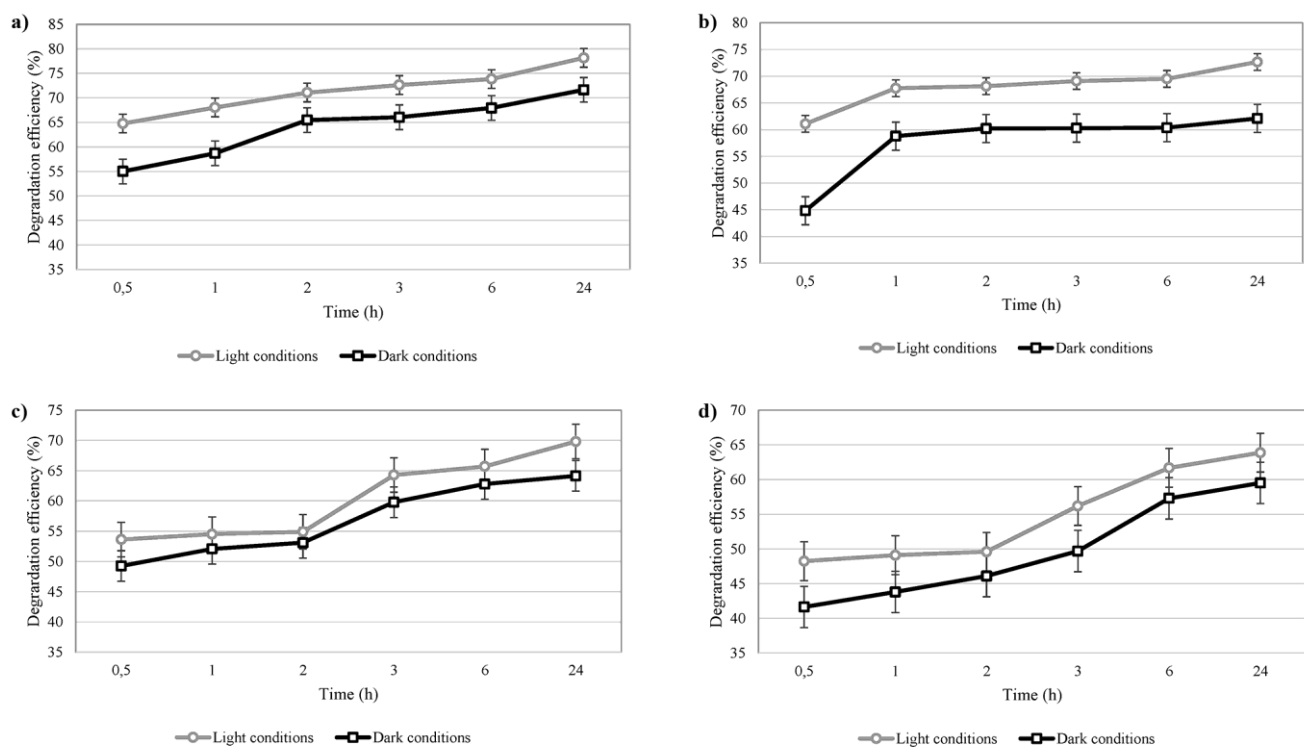


Fig. S5 Effect of humic acid concentration on degradation efficiency: a) azamethiphos with 1 mg/L of humic acid; b) azamethiphos with 5 mg/L of humic acid; c) dimethoate with 1 mg/L of humic acid; d) dimethoate with 5 mg/L of humic acid

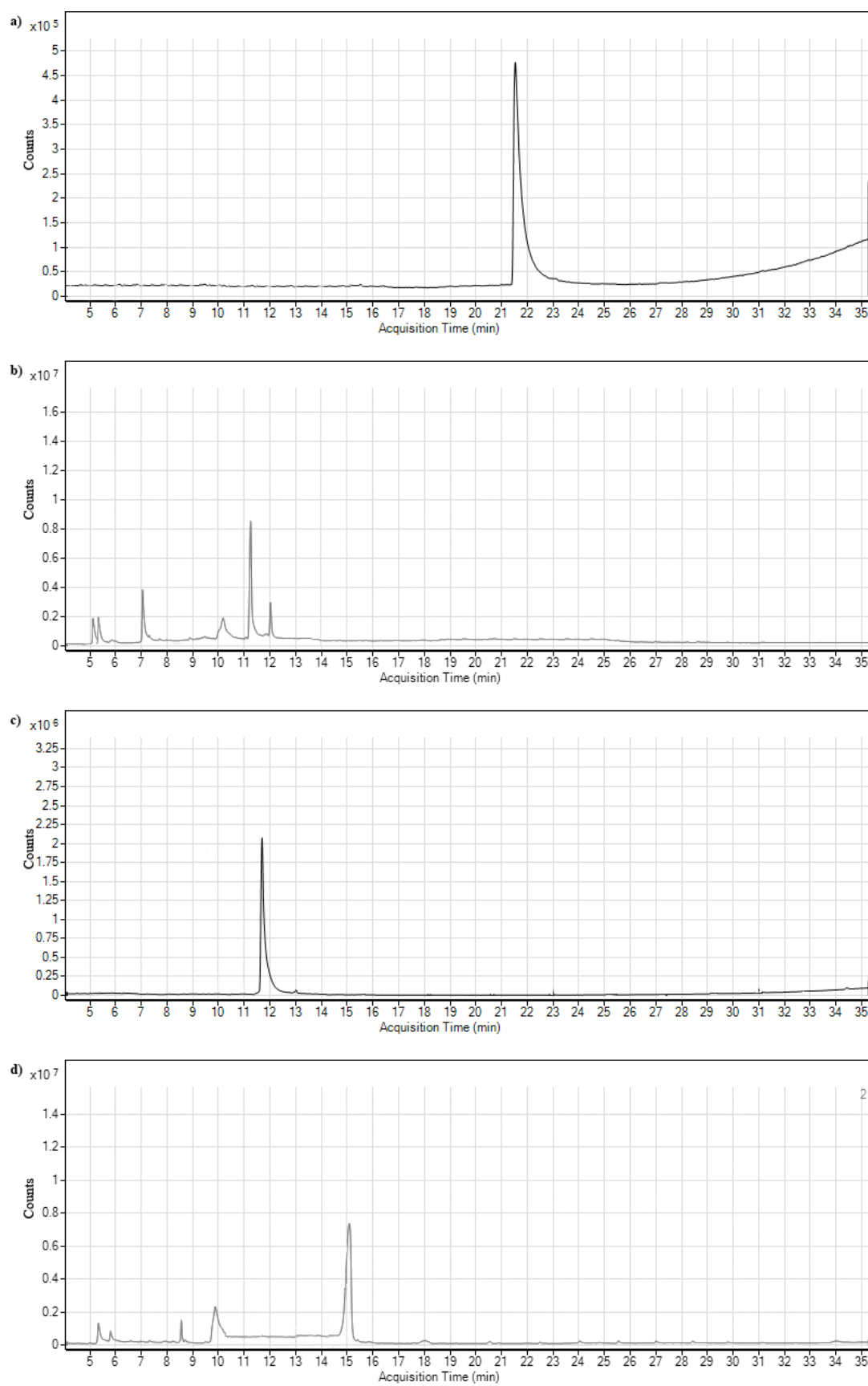


Fig. S6 GC-QQQ chromatograms for parent azamethiphos (a) and dimethoate (c) and degradation products of the organophosphorus pesticides: (b) azamethiphos and (d) dimethoate obtained under optimal conditions for both pesticides

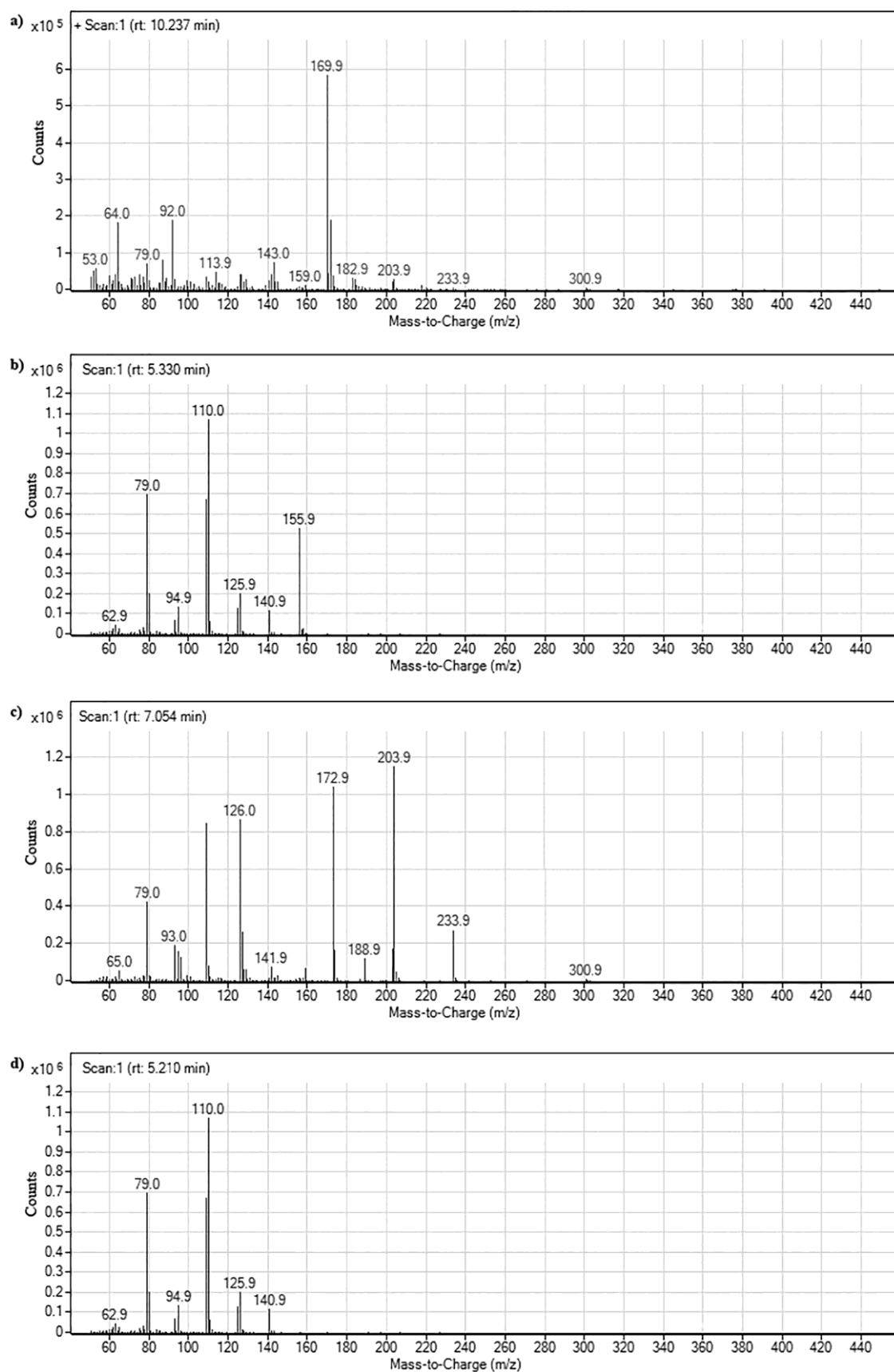


Fig. S7 Mass spectra for degradation products of azamethiphos

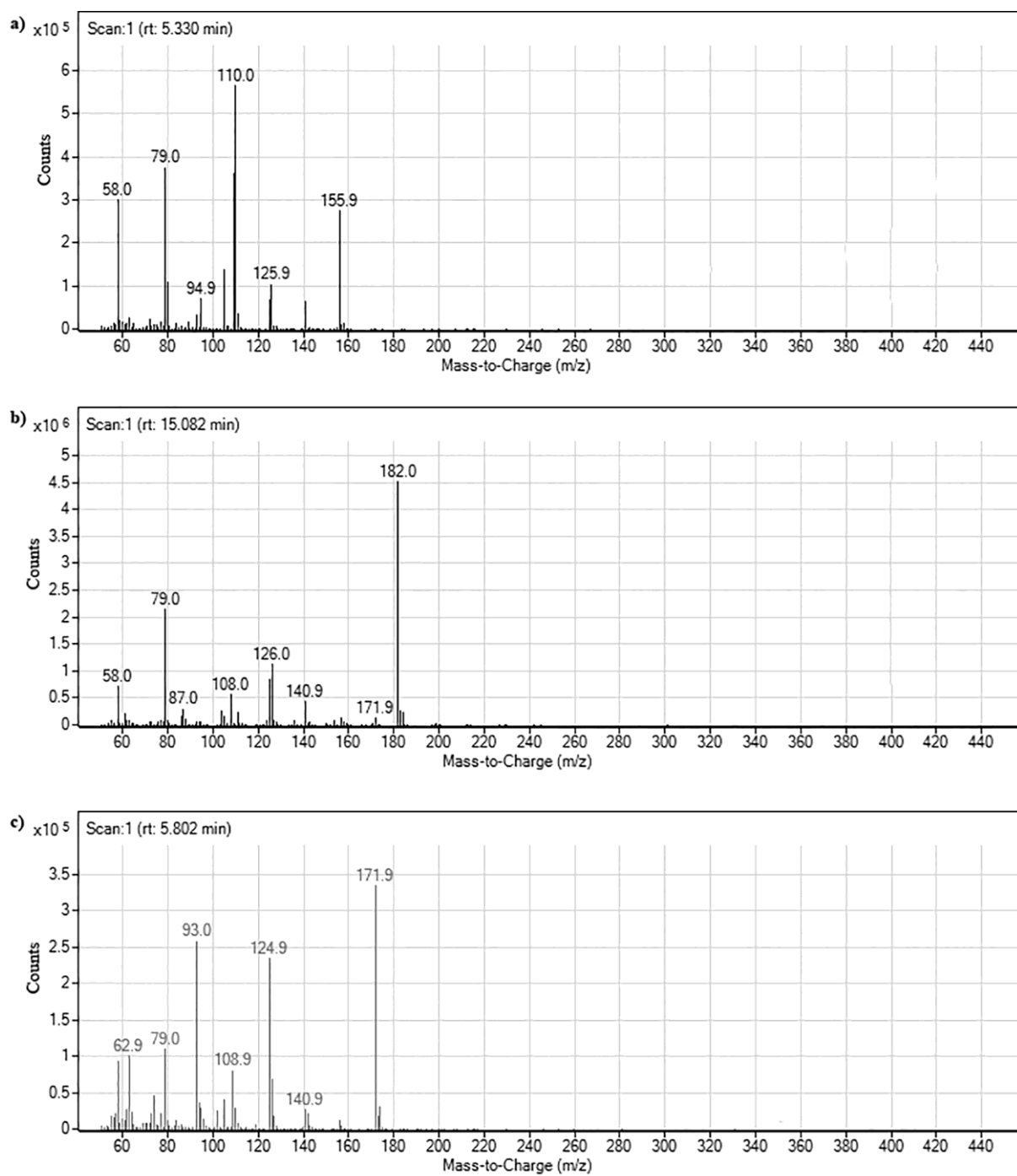


Fig. S8 Mass spectra for degradation products of dimethoate

Table S1 Full characteristics of Sava River water

| PARAMETER | UNIT | VALUE | ANALYSIS METHOD |
|-----------------------------------|-------|-------|---|
| BOD5 | mg/L | 1.10 | UP 1.34/PC 12 |
| TOC | mg/l | 2.8 | ISO 20236:2018 |
| Humic acid | mass% | 15 | APHA AWWA WEF 5510 (B) |
| Fulvic acid | mass% | 85 | Environ Sci Technol. 2007 41(19):6755-61 |
| Total Dissolved Salts | mg/L | 22 | UP 1.130/PC 12 |
| Ca ²⁺ | mg/L | 52.30 | ISO 6058:1984 |
| Mg ²⁺ | mg/L | 10.46 | |
| Fe | μg/l | 76.9 | UP 1.37/PC 12 : 2019 |
| Mn | | 26.0 | |
| Al | | 81.6 | |
| Zn | | 11.0 | |
| Cr | | 1.1 | |
| Cu | | 2.3 | |
| Pb | | 1.0 | |
| Cd | | 0.02 | |
| Ni | | 1.4 | |
| Co | | <0.5 | |
| Sb | | <0.5 | |
| As | | 1.2 | |
| B | | 95.2 | |
| SiO ₂ | | mg/l | |
| HCO ₃ ⁻ | 210 | | SRPS EN ISO 9963-1 : 2007 |
| Cl ⁻ | 21.1 | | SRPS ISO 9297:1997 |
| SO ₄ ²⁻ | 13.5 | | UP 1.101/PC 1 |
| o-PO ₄ -P | 0.041 | | UP 1.102/PC 12 |
| P total | 0.077 | | APHA AWWA WEF 4500 (A, B, E) |
| NH ₄ -N | 0.30 | | UP 1.96/PC 12 |
| NO ₂ -N | 0.004 | | UP 1.97/PC 12 |
| NO ₃ -N | 0.8 | | UP 1.98/PC 12 |
| Bisfenol A | μg/l | 0.013 | UP 1.125/PC 12 : 2019 |
| Polycyclic Aromatic Hydrocarbons* | | <LOD | UP 1.44/PC 12 : 2019 |
| Triazine-based pesticides* | | <LOD | UP 1.124/PC 12 : 2019 |
| Organochlorine pesticides* | | <LOD | UP 1.42/PC 12 : 2019 |

-all parameters (dissolved)

* for each individual

Table S2 Results of toxicity tests (after 48 h test period) and TOC analysis of parent organophosphorus pesticides and their degradation products

| Sample | LC ₅₀ (% v/v) 48h | TOC (mg/kg) |
|--|------------------------------|-------------------------|
| Azamethiphos | 2.50±0.01 ^c | 17.07±0.05 ^c |
| Degradation products for azamethiphos ^a | 61.32±0.02 ^c | 3.02±0.04 ^c |
| Dimethoate | 12.15±0.02 ^c | 11.57±0.05 ^c |
| Degradation products for dimethoate ^b | 35.36±0.02 ^c | 2.60±0.03 ^c |

^a Under optimal conditions: azamethiphos (10 mg/L); 10 mg/L ClO₂; light; 1 h.

^b Under optimal conditions: dimethoate (10 mg/L); 10 mg/L ClO₂; light; 6 h.

^c Standard deviations calculated from obtained values from four repeated measurements.

