

Monitoring water-polluting pesticides in Hungary

Erik Maloschik, András Ernst, Gyöngyvér Hegedűs, Béla Darvas, András Székács*

Plant Protection Institute, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 102, Hungary

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Abstract

A 5-year survey of pesticide active ingredients and residues in Hungarian surface water samples was carried out within the framework of a national monitoring program. Based on physicochemical and ecotoxicological properties of currently registered pesticide active ingredients, a range of analytes was selected to cover compounds that potentially contaminate surface waters due to their solubility properties or mode of use. Target analytes thus included acetochlor, atrazine, carbofuran, diazinon, fenoxycarb, metribuzin, phorate, prometryn, terbutryn, and trifluralin. During the sampling campaign these pesticides were monitored in Hungarian surface waters including streams, rivers and lakes. Samples were obtained annually in two runs: before and after pesticide sprayings in spring and early summer. Samples were prepared for analysis by solid-phase extraction and solid-phase microextraction. Target analytes were monitored by gas chromatography – mass spectrometry, using electron impact and chemical ionization techniques. Spatial distribution monitoring of the surface water pollutants indicated two heavily contaminated point sources, as well as a wide range of non-point contamination. One or more pesticide active ingredients above the detection limit of the instrumental method used were measured in 209 samples, giving the result that 59% of the samples collected during the sampling campaign contained pesticide residues.

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1. Introduction

Newly discovered ecotoxicological problems (e.g. endocrine disrupting effects [1]) related to pesticide residues, as well as the tightening of legal regulations regarding pesticide residues in drinking water (in conjunction with Hungary joining the European Union [2,3]), require analytical methods of increased sensitivity for monitoring pesticide residue levels. Organic micropollutants in surface water may present continuous subacute exposure to humans and wildlife, and consequently monitoring of existing contamination sites for persistent pollutants and newly emerging contamination is essential. Special emphasis has been given to persistent organic pollutants (POPs). In May 2001 Hungary joined the Stockholm POP Treaty, which was established as part of the UN Environmental Program. This treaty stipulates the regulation of 12 compounds and a compound group [4]. Based on Article 9 of the treaty, a

National Action Plan has to be put into place to fulfil the commitments of that particular country: national surveys are required to provide information about the incidence of POP compounds in various natural elements. Classical POPs show decade-long half-lives, and are all banned from use. However, persistent pollutants are found among currently used pesticides as well, e.g. the herbicide active ingredient atrazine [5–8]. Although the usage of POPs is prohibited in countries that have signed the Stockholm Convention, pesticides that persist in soil throughout entire vegetation periods continue to present a threat to the environment. Thus, pesticide residue analysis in environmental samples has received increasing attention in the last few decades, resulting in numerous environmental monitoring programs in various countries for a broad range of pesticides [7,9–15].

A common consequence of such persistent pollution is the contamination of surface waters with pesticide residues. This calls for urgent attention in two areas: (a) re-evaluation of environmental persistence and risks of currently registered and applied pesticides, and (b) thorough monitoring of potentially water-contaminating pesticides in surface waters and in natural water

* Corresponding author.

E-mail address: aszek@nki.hu (A. Székács).

bodies. In order to comply with such monitoring requirements, instrumental, immunoanalytical, as well as bioanalytical methods, are being developed in our environmental analytical and ecotoxicological facilities to detect and quantitatively monitor pesticide active ingredients and residues.

Pesticides are detected in aqueous samples mostly by chromatographic techniques [16–18], e.g., gas chromatography coupled with mass spectrometry (GC–MS) [7,12,19–23], electron capture or nitrogen phosphorus selective detection [16,17], high performance liquid chromatography [16,18,24] and more recently by liquid chromatography coupled with mass spectrometry (LC–MS) [11,25]. Moreover, capillary electrophoresis is also applied for the detection of pesticides [16,21]. Although high sample throughput can be achieved with thin layer chromatography (TLC) or overpressured layer chromatography (OPLC), these techniques have narrower application because of their relatively lower detection capabilities [16,26,27]. In addition bioanalytical methods, e.g., immunoassays/immunosensors [28] and immunochromatographic analyses [29] are also used for detection of pesticides. In our laboratory, the target pesticides are detected partly by GC–MS [30–33], and partly by enzyme-labelled immunosorbent assays (ELISAs) [34–37], while the aqueous toxicity of these substances is measured by the *Daphnia magna* biotest [31,38,39]. In the framework of a 5-year monitoring study, sample preparation methods and a GC–MS analytical protocol have been adapted and optimized for such monitoring purposes, and a nation-wide survey was carried out in Hungary to identify local and non-point pesticide contamination sites in surface waters and raw drinking water. This work has been carried out in close collaboration with the Plant Protection and Soil Conservation Service (PPSCS) of the Hungarian Ministry of Agriculture and Regional Development. Target analytes in GC–MS determinations included currently registered and potentially water-contaminating pesticide active ingredients in (a) herbicides such as acetochlor, atrazine, diazinon, metribuzin, prometryn and terbutryn; (b) insecticides such as carbofuran, fenoxycarb and phorate; and (c) fungicides such as trifluralin (Fig. 1). Physicochemical characteristics and GC–MS spectra of the analytes [40–44] are listed in Table 1.

2. Materials and methods

2.1. Chemicals

Chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and Sigma Chemical Co. (St. Louis, MO), unless otherwise stated. Analytical standards of the target analyte pesticides were provided by PPSCS from official standard reference materials received from the manufacturers/distributors of acetochlor, atrazine (Nitrokémia Rt., Füzögyártelep, Hungary), carbofuran (Agro-Chemie Kft., Budapest, Hungary), diazinon, fenoxycarb, prometryn (Syngenta Kft., Budapest, Hungary), metribuzin (Bayer Hungária Kft., Budapest, Hungary), phorate (BASF Hungária Kft., Budapest, Hungary), terbutryn (Agrosol Bt., Gödöllő, Hungary) and trifluralin (Budapesti Vegyiművek Rt., Budapest, Hungary). Solvents purchased from Merck KGaA (Darmstadt, Germany) were of analytical grade. CarboPrep-90 (500 mg, 6 ml) and CarboGraph (200 mg, 6 ml) columns were

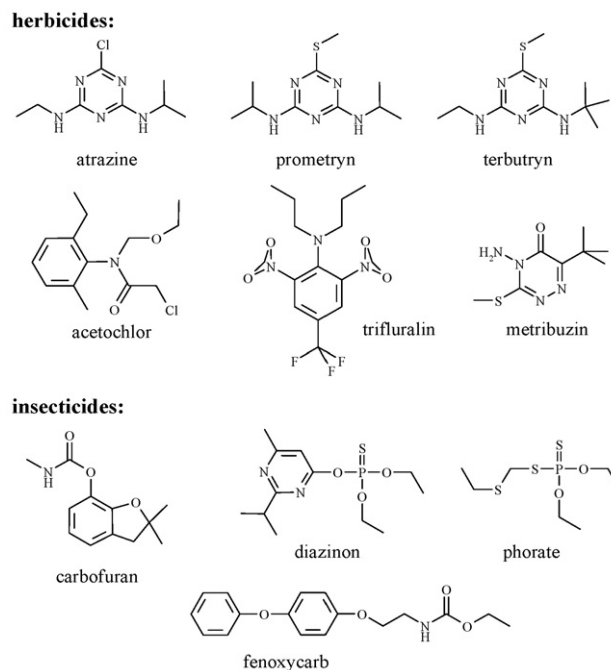


Fig. 1. Structures of the target analytes acetochlor, atrazine, diazinon, metribuzin, prometryn, terbutryn, carbofuran, fenoxycarb, phorate and trifluralin.

purchased from Restek (Bellefonte, PA, USA) and Alltech Associates, Inc. (Deerfield, IL, USA), respectively. Carbowax/divinylbenzene (CW/DVB) solid-phase microextraction fibers and holder assembly were purchased from Supelco (Bellefonte, PA, USA). HPLC grade distilled water was prepared on a MilliQ RG ion-exchanger from Millipore (Bedford, MA, USA). MN (Macherey-Nagel) 640W filter paper was obtained from Reanal Rt. (Budapest, Hungary).

2.2. Instruments

GC–MS analyses were carried out on a Saturn 2000 workstation (Varian Inc., Walnut Creek, CA, USA). It consisted of a Chrompack CP 3800 gas chromatograph and a Saturn 2000R ion-trap detector. The gas chromatograph was equipped with a Varian 1079 split/splitless injector and a CP 8200 autosampler capable of holding 48 vials.

2.3. Sample collection

Water samples for analysis included distilled water, tap water and various surface water samples (water from the River Danube and surface, lake and river water samples collected throughout Hungary). In the scope of a national monitoring program, 603 water samples were collected in total during the 5-year duration of the project: 438 samples between 2000 and 2002, and an additional 165 samples in 2003 and 2004. Surface water sampling was carried out according to the national standard ‘MSZ ISO 5667’ [45]. Water samples were collected regularly, twice a year, before and after agricultural pesticide applications, during the months of April–May and June–September. Surface water samples (from depths not exceeding 50 cm) were collected by

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