Science of the Total Environment 439 (2012) 249–259

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Use of time-of-flight mass spectrometry for large screening of organic pollutants in surface waters and soils from a rice production area in Colombia

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HIGHLIGHTS

- ► TOF MS hyphenated to LC and GC allows large screening of many organic pollutants.
- ► Surface waters and soils from a Colombian agricultural area were analyzed by TOF MS.
- ► Several pesticides and metabolites were detected and unequivocally identified.
- ► Accurate-mass full-spectrum data allowed the detection of emerging contaminants.

ARTICLE INFO

Article history:
Received 11 July 2012
Received in revised form 10 September 2012
Accepted 17 September 2012
Available online 17 October 2012

Keywords:
TOF MS
Large screening
Pesticides
Water
Soil
Rice production

ABSTRACT

The irrigate district of Usosaldaña, an important agricultural area in Colombia mainly devoted to rice crop production, is subjected to an intensive use of pesticides. Monitoring these compounds is necessary to know the impact of phytosanitary products in the different environmental compartments. In this work, surface water and soil samples from different sites of this area have been analyzed by applying an analytical methodology for large screening based on the use of time-of-flight mass spectrometry (TOF MS) hyphenated to liquid chromatography (LC) and gas chromatography (GC). Several pesticides were detected and unequivocally identified, such as the herbicides atrazine, diuron or clomazone. Some of their main metabolites and/or transformation products (TPs) like deethylatrazine (DEA), deisopropylatrazine (DIA) and 3,4-dichloroaniline were also identified in the samples. Among fungicides, carbendazim, azoxystrobin, propiconazole and epoxiconazole were the most frequently detected. Insecticides such as thiacloprid, or p,p′-DDT metabolites (p,p′-DDD and p,p′-DDE) were also found. Thanks to the accurate-mass full-spectrum acquisition in TOF MS it was feasible to widen the number of compounds to be investigated to other families of contaminants. This allowed the detection of emerging contaminants, such as the antioxidant 3,5-di-tertbutyl-4-hydroxy-toluene (BHT), its metabolite 3,5-di-tert-butyl-4-hydroxy-benzaldehyde (BHT-CHO), or the solar filter benzophenone, among others.

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1. Introduction

In the last years, there has been an increasing concern over the presence of organic contaminants in aquatic ecosystems. This has been more evident in agricultural areas due to the frequent use of pesticides. The irrigate district of Usosaldaña, Tolima (Colombia), is mainly devoted to rice production. More than 150 products are registered for use in rice production in Colombia. In addition to those pesticides applied for rice, some more pesticides are also applied for other crops existing in the area. This district uses the Saldaña River as a source of water. After irrigation, it drains to streams ending up into the Magdalena River, the most important river in Colombia. Water from the Magdalena River is finally used for human consumption; therefore, it is necessary to monitor pesticides and other potential contaminants in soils and waters of this area.

In environmental routine analysis, monitoring is generally based on multiresidue/multiclass methodologies for target substances considered as dangerous for human health or the ecosystem. Target methods are typically focused on a limited number of priority compounds, and their main objective is the accurate quantification of target analytes. Their scope rarely exceeds several tens of analytes, being quite unusual to find analytical methods for the determination of more than 100–200 organic pollutants. The techniques most widely applied in target analysis are gas chromatography (GC) (from non-polar to semi-polar, volatile compounds) and liquid chromatography (LC) (from semi-polar to

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http://dx.doi.org/10.1016/j.scitotenv.2012.09.036

polar, non-volatile compounds) coupled to mass spectrometry (MS) using different analyzers. Until recently, single quadrupole in Selected Ion Monitoring (SIM) mode has been the preferred technique. Nowadays, triple quadrupole (QqQ) and ion trap (IT) are the predominant analyzers due to their excellent sensitivity and selectivity when working under tandem MS (MS/MS) (Martínez Vidal et al., 2006; Marín et al., 2009; Pitarch et al., 2007; Petrović et al., 2005; Trtić-Petrović et al., 2010; Van Nuijs et al., 2010). Despite the strong potential of these techniques, they present a limitation in the number of compounds to be included in the scope of the method. In addition, other potentially harmful compounds might be ignored in target analysis, as only analyte-specific information is normally acquired. On the contrary, high resolution (HR) instruments, e.g. time-of-flight (TOF), offer the possibility of investigating the presence of compounds once the analysis has been performed and MS data acquired, without being dependent on the pre-selection of analytes. An advantage of the "post-target" approach is the possibility to detect a large number of contaminants in a single analysis (Hernández et al., 2005, 2011c). The sensitive full spectrum acquisition and the high mass resolution and mass accuracy provided by TOF-MS make this technique especially suited for wide-scope screening in the environment, where one can find a large number and types of organic contaminants. In addition, reliable tentative identifications can be made without using reference standards. As accurate-mass full-spectrum data remain available, a retrospective analysis is also feasible at any time to investigate the presence of other compounds without additional analysis (Hernández et al., 2011c; Ibáñez et al., 2008).

TOF MS hyphenated to both LC or GC plays a noticeable role for screening of organic contaminants, in relevant fields like environmental pollution (Hernández et al., 2011a; Ibáñez et al., 2009; Hernández et al., 2011c; Ibáñez et al., 2008; Díaz et al., 2012; Nurmi and Pellinen, 2011; Nurmi et al., 2012; Gonzáez-Mariño et al., 2012; Petrovic and Barceló, 2006; Nácher-Mestre et al., 2011; Richardson and Ternes, 2011; Richardson, 2012) or food-safety (Ibáñez et al., 2012; Díaz et al., 2012; Kaufmann et al., 2007; Cajka et al., 2008; Ferrer et al., 2011). The TOF MS post-target approach has demonstrated to be an advanced tool that allows the investigation of hundreds of compounds in the same run (Díaz et al., 2012). The complementary application of target and non-target approaches has an evident benefit in the environmental field, where many different contaminants can be present in the samples. The combined use of both approaches gives the possibility to detect non-previously selected or unexpected compounds, especially in GC methods where the availability of commercial spectral libraries simplifies this purpose (Hernández et al., 2011c; Ibáñez et al., 2008). However, despite the strong potential of these techniques, wide-scope screening of hundreds of compounds by combined use of GC–TOF and LC–TOF has been scarcely explored until now.

In this work, the complementary use of GC and LC coupled to TOF MS has been applied for rapid screening of a large number of organic contaminants and metabolites/TPs in water and soil samples from the Usosaldaña area. As far as we know, there is no previous information on the presence of pesticides or other organic contaminants in this area.

2. Experimental

2.1. Reagents and chemicals

Reference standards of pesticides, octyl/nonyl phenols, PCBs (Mix 3, 100 μg/mL in cyclohexane; Mix 41, 10 μg/mL in cyclohexane) and PAHs (Mix 9, 100 μg/mL) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). PBDE standard mixture "Lake Michigan Study", containing BDE 28, 47, 66, 85, 99, 100, 138, 153 and 154 (50 μg/mL in isooctane) and two individual standards of BDE 71 and 183 (50 μg/mL in isooctane) were purchased from Chiron (Trondheim, Norway). When the solid reference standards were available, stock solutions (around 500 μg/mL) were prepared by dissolving reference standards in acetone and stored in a freezer at −20 °C. Working solutions for GC were prepared by diluting stock solutions in acetone (quality control preparation) or in hexane (for standards injected in the chromatographic system). For LC–MS analysis, stock solutions were diluted with acetonitrile or methanol (up to 5 mg/L) and subsequently with HPLC-grade water.

Reagent-grade sodium hydroxide, and, ultra-trace quality ethyl acetate, acetone, acetonitrile, methanol (MeOH), dichloromethane (DCM) and n-hexane were provided by Scharlab. HPLC-grade water was obtained from distilled water passed through a Milli-Q water purification system (Millipore, Bedford, MA, USA). Reagent-grade formic acid (HCOOH) (>98%) was obtained from Fluka (Buchs, Switzerland). Leucine enkephalin and heptacose, used as LC–TOF and GC–TOF lock masses, respectively, were purchased from Sigma (St. Louis, MO).

500 mg Bond Elut C18 cartridges (Varian, Harbor City, CA, USA) were used for solid-phase extraction. Glass fiber filters AP40, 47 mm × 0.7 μm size pores were from Millipore.

2.2. Sampling area under study and sample collection

Thirteen surface water samples and sediments of stream waters from the irrigate district of Usosaldaña (Tolima County, Colombia) were collected in a regional survey carried out in February 2009. Additionally, nine samples of surface soils (0–10 cm) (representative of the main soil types from the same area) were collected. The monitored streams are used for recreational and fishing activities by the population living around it. Fig. 1 shows the location of sampling points. All water samples were filtered through glass fiber filters AP40 before analysis. The fresh soil samples were air-dried and ground to pass a 200 mesh sieve. Water and soil samples were maintained at −18 °C until sample preparation.

2.3. Analytical procedure

2.3.1. Water samples

200 mL water samples were pre-concentrated by solid-phase extraction (SPE), using 500 mg Bond Elut C18 cartridges previously conditioned with dichloromethane and methanol. Samples were percolated through the cartridges by gravity and vacuum dried for 15 min. Analytes were eluted using 5 mL of ethyl acetate:dichloromethane (1:1).

The final extract was divided in two 2.5 mL-aliquots, which were evaporated to dryness under a gentle nitrogen stream at 40 °C. The first aliquot was redissolved in 0.5 mL hexane and analyzed by GC–TOF MS. The second one was redissolved in 1 mL H_2O:MeOH (90:10 v/v) for UHPLC–QTOF MS analysis.

2.3.2. Soils

5 g of soil was extracted in an ultrasonic bath with 40 mL ethyl acetate for 30 min. Then, an extract-aliquot of 10 mL was taken, evaporated to dryness and redissolved in 1 mL of ethyl acetate. 0.4 mL aliquot was taken for direct GC–TOF MS analysis. The remaining soil extract (0.6 mL) was evaporated under a gentle nitrogen stream at 40 °C and redissolved in 1 mL H_2O:MeOH (90:10 v/v) for UHPLC–QTOF MS analysis.

2.4. Instrumentation

2.4.1. GC–TOF MS

An Agilent 6890N GC system (Palo Alto, CA, USA) equipped with an Agilent 7683 autosampler was coupled to a TOF MS, GCT (Waters Corporation, Milford, MA, USA), operating in electron ionization (EI) mode (70 eV). The GC separation was performed using a fused silica HP-5MS capillary column with a length of 30 m × 0.25 mm i.d. and a film thickness of 0.25 μm (J&W Scientific, Folsom, CA, USA). The oven temperature was programmed as follows: 90 °C (1 min); 5 °C/min to 300 °C (2 min). Splitless injections of 1 μL sample were carried out. Helium was used as carrier gas at 1 mL/min. The interface and source temperatures were

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