Microchemical Journal 107 (2013) 136–142

Contents lists available at SciVerse ScienceDirect

Microchemical Journal

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

Terbuthylazine and other triazines in Italian water resources

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ARTICLE INFO

Article history:
Received 29 April 2012
Received in revised form 21 June 2012
Accepted 22 June 2012
Available online 8 July 2012

Keywords:
Pesticides
Terbuthylazine
Metabolites
Desethylterbuthylazine
Water contamination

ABSTRACT

The concern on the presence of pesticides in Italian water resources historically broke out around 1980 after severe episodes of ambient, raw water and drinking water contamination due to some herbicides, atrazine (ATR), its metabolites desethylatrazine (DEA) and deisopropylatrazine (DIA), simazine, cyanazine, bentazone, molinate, which affected mainly the maize, grain and rice producing floodplains and karst areas of the northern Regions. Due to the risks of human exposure, in the early 1990 the use of atrazine was banned in Italy and was replaced by terbuthylazine (TERB). In a few years, TERB became a chemical of concern, together with its main metabolite desethylterbuthylazine (DET), because of alerting detections in surface and groundwater resources. Up to now, the risk of contamination of water resources by TERB, DET, DEA and, in some extent ATR, is of relevance in Italy due to their present and past wide employment in agriculture, the discharges or seepages in particularly vulnerable areas, their unfavorable intrinsic properties, e.g. poor sorption and high persistence, their mobility by drift, leaching and runoff in vadose zones, aquifers and surface water. So, unsurprisingly, results from national monitoring of ambient water and raw water indicate that TERB, DET, DEA and residual ATR, despite its withdrawal, are detected at remarkable frequencies and, sometimes, at levels higher than pesticide quality standards under the Italian Decrees for the protection of surface water (specifically, raw waters doomed at the drinking water abstraction), groundwater and drinking water (tap water), that is 0.1–0.5 μg/l for individual pesticides and for total pesticides, respectively, including relevant metabolites. On the other hand, in these last years, the control measures in drinking water production adopted by the waterworks Companies and the regional and central health Authorities, also in the view of the recent WHO approaches under the Water Safety Plans, ensure that levels of any pesticide residue (also involving TERB, DET, DEA, ATR) in finished tap water meet parametric values for pesticides. Therefore, in these last years, no derogation to the parametric values for drinking water has been required. The aim of this paper is to contribute to widen the knowledge on the water impact of these important water pollutants giving sound details on present usages, levels and frequencies of detection in water bodies in Italy, on their key chemiodynamic properties, e.g. soil half-lives (DT50) and soil to organic carbon partition (Koc) available in the open literature, particularly for TERB metabolites, and some details on legal provision adopted at the national level. In fact, a more effective protection of water supplies, particularly against TERB and DET, has been pursued in the late 2000s by the Italian Health Ministry through the adoption of consistent provisions aimed at mitigating emissions of TERB in routine agricultural activities, and by the Italian Ministry of the Environment through the adoption of specific Environmental Quality Standards for TERB and its metabolite DET, ATR, SIM for the protection of surface waters.

1. Introduction

Pesticides represent a wide category of inorganic (e.g. sulfur, calcium and barium polysulphides, copper sulfate and hydroxide, copper oxychloride) and organic chemicals (e. g. chloroorganics, organophosphates, pyrethroids, methylcarbamates, chloroacetanilides, chlorotriazines, phenoxycarboxylic acids, phenylureas, dithiocarbamates, triazoles, phenylamides etc.) which are intentionally applied in agricultural ecosystems with the aim to cause adverse effects on harmful animals, insects, plants, weeds, bacteria, fungi in order to limit their diffusion and inhibit their growth and survival. Pesticides are mainly used in agriculture, horticulture, vineyards, orchards, forestry, industry, public hygiene, gardening and domestic activities. They are generally spread on soil surface, in air, into deep soil, on various sections of plants (fruits, leaves, stems, roots, seeds), on livestock, on lentic water surfaces, on aquatic vegetation and pools. Besides the undeniable advantages which occurred with the adoption of pesticides in terms of high yields in intensive farming, increasing of food production, evolution of agronomic techniques and quality improvement of foodstuffs, heavy drawbacks have been observed and documented on soil and aquatic environments and on human health since the early 1960s. Serious contamination episodes affected non-target animals and plants with important consequences as the suppression of biodiversity in terrestrial

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doi:10.1016/j.microc.2012.06.011

and aquatic ecosystems, the unbalancing of food chains, the appearance of resistant species, the contamination of foods, water resources and drinking water and health impacts on the population. The awareness of the risks caused by pesticides led to the development of a number of provisions and regulations worldwide, aimed at limiting and avoiding direct and indirect exposures to pesticides via food, water and air. As an example, the fundamental, historical and high-minded efforts conducted in this half-century by the national Health Authorities and the international Organizations, as FAO and WHO, in implementing the scientific knowledge on health and environmental impact of pesticides should be considered [1–18]. With reference to water safety for consumers, the guidelines for drinking water quality of WHO have defined, since 1980s, the rationale basis to develop the risk assessment evaluation for human exposure to pesticides through drinking water and represent the pillars on which national regulations and standards are founded [19]. The worldwide consumption of pesticides is generally increasing particularly in emerging countries, both for the strong food demand and for the market pressures toward the production of biomass-derived fuels [20,21]. Statistics on pesticides sales are indirect tools to draw information on their uses. Recent data from the Unites States indicated that, in 2007, total amounts of pesticide used, expressed as active ingredients, were of 511,198 t (wood preservatives and biocides excluded) which represented the 22% of the world market uses (2,357,320 t). Herbicides, insecticides and fungicides accounted for 44%, 9% and 6%, respectively [22]. In 2003, outcomes from 25 Member States of the European Union showed that a total of 220,000 t of pesticide active principles were used (biocides excluded). The principal categories were, in decreasing order, fungicides (49%), herbicides (38%) and insecticides (10%). It is interesting to note that the 75% of total usage pertained to only 5 countries, that are France (28%), Spain and Italy (14% each), Germany (11%), United Kingdom (7%) [23]. As regards Italy, in 2009 total pesticides active principles sales amounted to 74,200 t and, among categories, fungicides accounted for 63% while herbicides and insecticides accounted for 11% each [24]. The huge inputs of pesticides from agricultural activities represent unavoidable sources of contamination in Europe [25], still the recent introduction and development, by part of the European Commission, of the Thematic Strategy on the sustainable use of pesticides (2006) has recently led to important modifications and new perspectives in the European policies addressed to the safeguard of human health, water and soil ecosystems and drinking water resources [26]. In fact, two subsequent laws, which regard risks reduction in the use of pesticides and the new revision of the authorization procedures for pesticides trading, have been issued in 2009 [27,28] and, hopefully, will produce positive results in the next years. This paper tackles some aspects regarding water contamination due to TERB and its metabolite DET which are frequently detected in surface and groundwater in Italy. The parent TERB is included among the most sold pesticides in Italy, as it is shown in Table 1 [29]. Some details on TERB environmental fate and, particularly, on the parameters which influence its persistence and mobility, as soil and water degradation and adsorption, will be presented in order to contribute to the knowledge on its relevance as water pollutant.

2. Findings in water monitoring

In Italy, the problem posed by the presence of pesticides in water bodies became a public matter in the early '80, when scientific reports and publications enhanced a diffuse presence of ATR, simazine (SIM), cyanazine, bentazone, molinate and some triazine metabolites, namely DIA and DEA, in ground and surface waters and somewhat in drinking water [30–33]. These findings implied the possibility of harmful exposures for the population living in floodplain districts of the northern Regions, which pertain to the complex watershed of the Po river or in lands where high pesticide sales, intensive agriculture and vulnerable hydrogeological settings (e.g. shallow aquifers, low thickness or absence of confining layers, permeable, alluvial and karst areas) concur.

Table 1
Trends of TERB sales of Italy in the decade 1999–2009. The numbers in the first column indicate the ranking order of TERB within the general pesticide sales list. The numbers in the second column express TERB ranking order in the general herbicide sales list. In the third column, the amounts of TERB sold per year are reported. Data have been selected from elaborations of official sales statistics [29].

Year	Ranking as pesticide (decreasing order)	Ranking as herbicide (decreasing order)	Kilograms as active ingredient
1999	33	3	360,653
2000	13	2	791,581
2001	24	2	791,282
2002	3	1	1,842,008
2003	13	2	430,502
2004	15	3	728,515
2005	16	3	421,160
2006	18	4	366,045
2007	16	4	380,059
2008	14	3	470,993
2009	14	3	451,536

Similar situations took place in other European countries and in the United States, in which extensive monitoring surveys demonstrated the widespread diffusion of pesticides and, among all, of triazines and related metabolites in water ecosystems and in drinking water at high frequencies and at levels often trespassing the national standards [5,8,9,34–41]. In Italy, the acknowledgment of the health potential risks due to exposure to triazines and to their metabolites through drinking water and, also, the objective to safeguard the quality of water resources led to the ban of uses and sales of ATR and SIM among 1990–1994 and in 2004–2005, respectively, by means of a series of legislative measures which were issued by the Health Ministry. Unfortunately, also if predictable, the atrazine substitute TERB early became a pollutant of concern in the same areas previously affected by the atrazine presence. Very recently, these compounds have been perceived as sound water pollutants at the level of mass circulation press, as it was the case of atrazine in the past. The herbicides TERB and ATR are, in fact, strictly related as for molecular structure, herbicidal properties, weeds targets (cereals, grains), intrinsic chemical properties and chemiodynamic properties, e.g. soil degradation half-lives and partition constants. Both compounds may result mobile and quite persistent under certain environmental conditions, in spite of their moderate to low solubility, as a consequence of massive uses, high application doses and timing (mostly in pre-emergence). ATR and TERB may transform into more soluble, persistent and bioactive byproducts, as the common intermediate DIA, DEA (from ATR), DET (from TERB). In Fig. 1, the Regions whose water bodies are involved in considerable pollution by TERB and DET and some residual ATR are illustrated. The highest frequencies of detections of TERB and DET are found in five Regions (Piemonte, Lombardia, Emilia Romagna, Veneto, Friuli VG), which are the principal maize producers (over 90% of the national yields) and pertain to the wide Po river watershed. Other TERB findings involve some areas of other 3 Regions (Toscana Umbria, Sicilia) which are consistent vine, grain, and citrus producers [42–44]. In Table 1, a summary of TERB sales in Italy, which refers to the decade 1999–2009, clearly indicates that this herbicide is almost at the top positions in the sales lists [29]. In Table 2, TERB sales data for some of the above mentioned Regions indicate that almost the whole Italian consumption is condensed in those areas. Also, the extension of water contamination of ambient surface and groundwater due to TERB and DET is well documented [42,44]. Some examples are given in Tables 3 and 4 which display selected results from official monitoring activities in surface and groundwater referred to triazines (ATR, SIM, TERB, DEA DET, DIA) (Table 3) and, particularity, to TERB and DET in the Regions reported above (Table 4) [44]. Data show remarkable frequencies of detection of triazines, included the withdrawn ones, in surface water and in wells and sound exceeding, by part of TERB and DET, of law limits for single pesticides and metabolites, e.g. 0.1 μg/l stated for the protection of