Distribution of triazine-type herbicides in the surface waters of the southern Baltic*

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Ksenia Pazdro
Institute of Oceanology,
Polish Academy of Sciences,
Powstańców Warszawy 55, 81–712 Sopot, Poland; e-mail: pazdro@iopan.gda.pl

Jacek Tronczyński
IFREMER,
P.O. Box 1049, Centre de Nantes, France

Janusz Pempkowiak
Institute of Oceanology,
Polish Academy of Sciences,
Powstańców Warszawy 55, 81–712 Sopot, Poland

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Abstract

Triazine-type herbicides (atrazine, simazine, terbuthylazine, DEA – deethylatrazine) were analysed in the surface waters of the Baltic Sea off Poland in September 1995 and April 1997. Total concentrations varied from 14.7 to 30.0 ng dm^{-3} in 1995 and from 8.5 to 12.7 ng dm^{-3} in 1997. Concentrations in offshore samples were much smaller than in inshore ones (15.6 ± 2.2 *vs* 23.5 ± 4.8) in 1995, while no differences were found in 1997 (9.2 ± 1.8 *vs* 10.1 ± 2.3). This was attributed to the increased input of triazines to the Baltic Sea with river run-off following the summer application of these substances in agriculture.

The ratios of concentrations of individual compounds indicate that terbuthylazine is present in similar proportions in the Pomeranian Bay and the Gulf of Gdańsk (21% *vs* 20%), despite the ban on the use of atrazine and simazine in Germany imposed in the early 1990s. Similar DEA-to-atrazine indices in both the Pomeranian Bay and the Gulf of Gdańsk (1.20 ± 0.22 *vs* 1.31 ± 0.25) support

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the inference that the run-off from the rivers Vistula and Odra contributes to the distribution of triazines in the surface waters of the southern Baltic.

1. Introduction

Several hundred different pesticides of varying chemical nature and biological properties are currently used in agriculture. Of the total tonnage used, some 50% consists of triazine type pesticides (Hock *et al.* 1995). The major triazines used in Europe are atrazine, simazine and terbuthylazine (Zhou Jun *et al.* 1996). Owing to relatively rapid biodegradation, several decomposition products of these triazines can be found in the environment (Bester & Hühnerfuss 1996), of which deethylatrazine (DEA) is the most common one (Bester & Hühnerfuss 1996, Tronczyński *et al.* 1993).

Total triazine contents per litre of seawater vary from several tenths of a nanogram in the open sea to tens of nanograms in coastal areas and hundreds of nanograms in estuarine waters (Readman *et al.* 1993, Wu 1981). Non-conservative behaviour in the mixing zone of fresh and saline waters was reported (Wu 1981) in earlier studies; however, more recent data point to conservative behaviour (Readman *et al.* 1993, Tronczyński *et al.* 1993). The apparent non-conservative behaviour was attributed both to time-restricted application on agricultural land and to random wash-out from soils to rivers following heavy rainfall (Tronczyński *et al.* 1993).

Few data can be found in the literature regarding triazine concentrations in the Baltic, apart from two publications dealing with these compounds in the western Baltic. Bester & Hühnerfuss (1993) measured concentrations of total triazines from 5 to 8 ng dm^{-3} in the Arkona Deep and from 5 to 15 ng dm^{-3} in the Bay of Mecklenburg and inshore Pomeranian Bay waters. In their study atrazine, simazine and terbuthylazine were measured. In the Arkona Deep atrazine and simazine concentrations lay within the same range of a few ng dm^{-3}, while terbuthylazine concentrations were below the limit of detection. In the coastal waters simazine exceeded atrazine by a factor of two. In a recent study Graeve & Wodarg (1996) reported triazine concentrations ranging from 6 to 60 ng dm^{-3} in the Pomeranian Bay, smaller concentrations being measured in samples collected in the centre of the Bay and the largest ones close to the eastern shore of Uznam island. However, no information is available on triazine concentrations in the Baltic Sea east of the island of Bornholm.

The purpose of the present study was to investigate distributions of atrazine, simazine, terbuthylazine and DEA in the Baltic off the coast of Poland. Samples were collected in September 1995 and April 1997 from the Gdańsk Basin, the Bornholm Basin and the Pomeranian Bay in order to assess the spatial and temporal variations of triazine herbicides concentrations.

2. Experimental

Surface water samples of total volume 40–200 dm^3 were collected using an all-teflon pumping system during the Głębie'95 and Głębie'97 cruises of r/v 'Oceania'. The distribution of sampling stations is shown in Fig. 1. Water was passed through an in-line filtering system with precombusted (450°C, 4 h) glass-fibre filters (Whatman GF/F, 293 mm diameter). Immediately after filtering, internal standards (pretilachlor and cyprazine) were added and water was pumped at a rate of 50–80 $cm^3\,min^{-1}$ through teflon columns (ϕ 2×25 cm) filled with precleaned Amberlite XAD–2 resin. After the passage of water, the resin was dried and the adsorbed organics were eluted with methylene chloride. Traces of water were removed with anhydrous Na_2SO_4, while methylene chloride was replaced with iso-octane.

Identification and quantification of the triazines were carried out in a Varian 3400 gas chromatograph equipped with an NPD detector and a DB5 30 m × 0.32 mm capillary column. The following analytical conditions were used throughout the study: helium as carrier gas, injection port temperature of 50°C held for 1 min, followed by a 15°C min^{-1} increase to 150°C, and that in turn by a 3°C min^{-1} increase to 250°C. Identification was confirmed in a GC–MS system consisting of a Hewlett-Packard HP 5890A gas-chromatograph equipped with a 5989A mass spectrometer detector and an HP Ultra 2 fused silica capillary column. Separation was carried out in the following temperature regime: injection port 80°C held for 1 min, followed by a 15°C min^{-1} increase to 140°C, followed by a 3°C min^{-1} increase to 270°C. Other details of the identification and quantification procedures can be found in Tronczyński *et al.* (1993). The detection limit of individual compounds was 0.03–0.10 ng dm^{-3}, while the precision of analyses as determined from a parallel analysis of a water sample (n = 3) yielded the following results (average ± standard deviation): atrazine 11.1 ± 0.6 (ng dm^{-3}), simazine 7.0 ± 0.2 (ng dm^{-3}), DEA 8.0 ± 0.4 (ng dm^{-3}), terbuthylazine 5.0 ± 0.9 (ng dm^{-3}).

3. Results and discussion

The concentrations of the individual triazine herbicides detected are set out in Table 1. Fig. 1 shows the concentrations of total s-triazines.

Total concentrations in September 1995 ranged from 14 ng dm^{-3} in the open sea to 30 ng dm^{-3} in the Pomeranian Bay. The respective concentration ranges of individual compounds were: atrazine – 3.1 to 9.0 ng dm^{-3}, simazine – 3.1 to 7.3 ng dm^{-3}, terbuthylazine – 1.0 to 6.4 ng dm^{-3} and deethylatrazine – 2.4 to 7.9 ng dm^{-3} for the open sea (lower limits) and coastal waters (higher limits). In April 1997 total concentrations were from 7.9 to

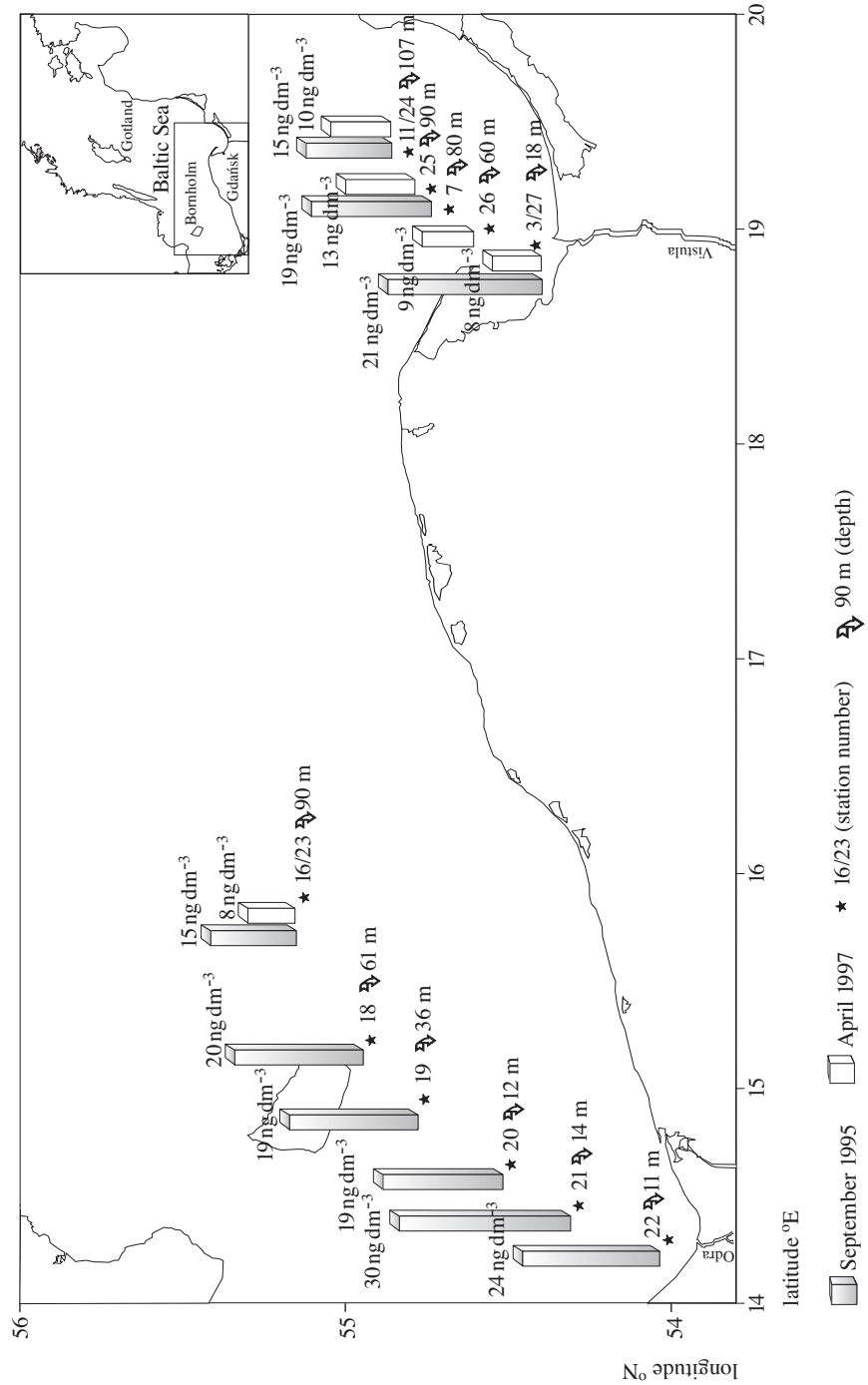

Fig. 1. Distribution of sampling stations and total concentrations of triazines in the surface waters of the southern Baltic

Table 1. Concentrations of dissolved triazines in surface waters of the southern Baltic

Sampling site[1]	Sampling area	Sampling date	Recovery %	Concentration [ng dm^{-3}] DEA	atrazine	simazine	terbuthylazine	total[2]
3/95	Gulf of Gdańsk	September 1995	57	*	7.2	7.3	6.8	21.3
7/95	Gulf of Gdańsk	September 1995	83	4.9	5.1	5.6	3.3	18.9
11/95	Gdańsk Deep	September 1995	96	3.4	4.6	4.9	1.8	14.7
16/95	Bornholm Deep	September 1995	87	3.4	4.0	4.9	2.0	14.3
18/95	Bornholm Deep	September 1995	75	5.4	4.0	6.1	4.3	19.8
19/95	Pomeranian Bay	September 1995	76	5.4	4.6	5.9	3.4	19.3
20/95	Pomeranian Bay	September 1995	74	5.3	5.0	5.7	3.0	19.0
21/95	Pomeranian Bay	September 1995	64	7.9	9.0	6.7	6.4	30.0
22/95	Pomeranian Bay	September 1995	86	5.1	7.6	5.5	5.4	23.6
(16) 23/97	Bornholm Deep	April 1997	68	1.8	2.5	3.6	*	7.9
(11) 24/97	Gdańsk Deep	April 1997	91	2.5	3.5	4.2	0.4	10.5
25/97	Gulf of Gdańsk	April 1997	69	3.6	3.9	5.0	0.1	12.7
26/97	Gulf of Gdańsk	April 1997	66	2.6	2.8	3.6	0.2	9.0
(3) 27/97	Gulf of Gdańsk	April 1997	64	2.7	2.6	3.2	*	8.5

$*$ – below detection limit (0.05 ng dm^{-3}),
[1] see Fig. 1 for distribution of sampling sites,
[2] $\sum$ (DEA, atrazine, simazine, terbuthylazine).

12.6 ng dm^{-3} without any significant spatial trend. Individual herbicide concentrations ranged from 2.5 to 3.9 ng dm^{-3} (atrazine), 3.1 to 5.0 ng dm^{-3} (simazine), <0.1 to 0.4 ng dm^{-3} (terbuthylazine) and 1.8 to 3.6 ng dm^{-3} (deethylatrazine). Two features of the distribution of triazines are evident. Firstly, average concentrations in September 1995 were much larger than in April 1997. Secondly, the inshore concentrations of triazines were larger than the offshore ones in September 1995, whereas no such pattern was observed in April 1997. Both features can be explained if one keeps in mind the fact that for the most part, triazines enter the marine environment with river run-off. Their temporal variations in the marine environment, reported in several studies (Brambilla *et al.* 1993, Zhou Jun *et al.* 1996), are therefore attributed to the increased loads discharged into the sea following the late-spring agricultural application of triazines (Tronczyński *et al.* 1993, Readman *et al.* 1993) and to their short residence times in seawater. Atmospheric transport of triazines is only of minor importance (Bester *et al.* 1995, Dörfler & Scheuner 1997). The distribution of triazines in September 1995 appears to reflect their peak load discharged into the Baltic with the Vistula and the Odra river run-offs in summer 1995 prior to sampling.

Autumn-to-early-spring concentrations of triazines in river run-off decrease as compared to summer concentrations (Brambilla *et al.* 1993, Tronczyński *et al.* 1993). Moreover, triazines in seawater are subjected to a variety of processes decreasing their concentrations (Hühnerfuss *et al.* 1997, Zhou Jun *et al.* 1996, Brambilla *et al.* 1993). Therefore, concentrations of triazines in seawater in April 1997 reflect their distribution prior to the summer increase. Rather large concentrations are conspicuous (Table 1). Much smaller triazine concentrations than in the Baltic were reported in the open waters of the North Sea – 1.2 ng dm^{-3} (Zhou Jun *et al.* 1996) and the Mediterranean – 1.5 ng dm^{-3} (Tronczyński *et al.* 1993). In both cases, however, concentrations in estuarine and near-shore areas were in excess of those in the Baltic Sea. The reason for this could be the limited exchange of water between the Baltic Sea and the ocean, exacerbated by a river run-off which is extremely large in comparison with the total volume of water in the Baltic (Voipio 1981).

Ratios of concentrations of individual triazines are listed in Table 2. They provide additional insight into the reasons for the distribution of triazine herbicides found. The average ratio of terbuthylazine (T) to simazine (S) concentrations was 0.67 ± 0.23 in September 1995. This is much larger than the ratio of 0.04 ± 0.03 in April 1997, indicating either faster removal rates of the former from seawater, or else a continuing supply of the latter in winter (although with smaller loads than in summer). The former

Table 2. Ratios of individual dissolved triazines in the surface waters of the southern Baltic

Sampling site	Sampling area	Sampling date	Ratios				
			DEA/A	S/A	T/S	T/A	T/A+S+DEA
3/95	Gulf of Gdańsk	September 1995	< 0.01	1.01	0.94	0.94	0.47
7/95	Gulf of Gdańsk	September 1995	0.96	1.10	0.59	0.65	0.21
11/95	Gdańsk Deep	September 1995	0.74	1.06	0.37	0.39	0.14
16/95	Bornholm Deep	September 1995	0.85	1.23	0.41	0.50	0.16
18/95	Bornholm Deep	September 1995	1.35	1.52	0.70	1.07	0.28
19/95	Pomeranian Bay	September 1995	1.17	1.28	0.58	0.74	0.21
20/95	Pomeranian Bay	September 1995	1.06	1.14	0.53	0.60	0.19
21/95	Pomeranian Bay	September 1995	0.88	0.74	0.95	0.71	0.27
22/95	Pomeranian Bay	September 1995	0.67	0.72	0.98	0.71	0.30
(16) 23/97	Bornholm Deep	April 1997	0.73	1.44	< 0.03	< 0.04	< 0.01
(11) 24/97	Gdańsk Deep	April 1997	0.71	1.21	0.10	0.12	0.04
25/97	Gulf of Gdańsk	April 1997	0.93	1.38	0.01	0.02	< 0.01
26/97	Gulf of Gdańsk	April 1997	0.96	1.29	0.05	0.07	0.02
(3) 27/97	Gulf of Gdańsk	April 1997	1.03	1.20	< 0.03	< 0.04	< 0.01

DEA – deethylatrazine, A – atrazine, S – simazine, T – terbuthylazine

conclusion is supported by the rather large T/S ratios, accompanied by large concentrations of terbuthylazine, measured in coastal seawater samples collected in September 1995 as compared to other locations (0.96 ± 0.02 *vs* 0.59 ± 0.19). In the case of terbuthylazine this suggests rapid removal rates and short residence times, possibly in the range of weeks. There is no indication that the ban on the use of atrazine and simazine, introduced in Germany in 1991–1992 (Graeve & Wodarg 1996, Bester & Hühnerfuss 1996) but without any restrictions on the application of terbuthylazine, has influenced the triazine composition in the Pomeranian Bay. This could well be because the river Odra/Świna, which supplies the bay with organic pollutants, carries water from Poland. On the other hand, Graeve & Wodarg (1996) have suggested that old supplies of both atrazine and simazine in eastern Germany have not yet been used up. In Poland some twenty triazines are in use, including both atrazine and simazine.

Increasing deethylatrazine-to-atrazine (DEA/A) ratios in the coast–open sea transect in the Pomeranian Bay (Table 2) could be indicative of advancing decomposition of atrazine at locations far from the Odra mouth or of faster removal rates of the former from seawater. The DEA/A index has been used to follow biodegradation of the herbicide (Pereira & Rastad 1990). Increasing simazine-to-atrazine ratios (S/A – Table 2) in the same transect could mean that the former is more resistant to biodegradation in the marine environment. This conclusion is supported by findings of Tronczyński *et al.* (1993), who measured larger simazine-to-deethylsimazine ratios (deethylsimazine is a product of simazine degradation) as compared to the ratios of atrazine to deethylatrazine in the Rhône run-off.

Concentrations of triazines measured in this study fall within the same range, as reported earlier. Bester & Hühnerfuss (1993) measured total concentrations of triazines of 5–8 ng dm^{-3} in the Arkona Deep (west of Bornholm) and of 12–18 ng dm^{-3} along the coast of the Bay of Mecklenburg in May 1991. One reason for the rather small concentrations reported in that study are the large recovery rates of triazines from water (0.94–0.89) which these authors assumed. In the present study, recovery rates, assessed individually in each sample using an internal standard, ranged from 0.57 to 0.96 (average 0.75 ± 0.11).

Recently Graeve & Wodarg (1996) investigated triazines in the western part of the Pomeranian Bay in summer 1995. They reported total concentrations from 12 to 16 ng dm^{-3} in the centre of the bay and in the 25–60 ng dm^{-3} range along the western coast of the bay. However, they were unable to prove any influence of the river Odra on the distribution of triazines. They also reported much larger concentrations of simazine than of atrazine

(S/A index = 3.5). The S/A index found in the present study in the Pomeranian Bay is 0.97 ± 0.28.

4. Conclusions

The distribution of triazines in the southern Baltic is subject to the strong influence of both the Odra and the Vistula. Increased loads of herbicides entering the Baltic Sea with the river run-off in summer give rise to falling coast-to-open-sea gradients and large concentrations in September as opposed to a uniform distribution and smaller concentrations in April.

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