Before the Curtain Falls: Endocrine-Active Pesticides – A German Contamination Legacy

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1 Introduction

As a result of the European Parliament approving a new EU pesticide regulation (1107/2009/EC replacing directive 91/414/EEC) and a directive on the sustainable use of pesticides (2009/128/EC), in October 2009, various active ingredients are likely to be banned for use as pesticides. The use of pesticides that are carcinogenic, mutagenic, and toxic to reproduction, or that have endocrine-disrupting properties, shall no longer be authorized for use. Active ingredients that are persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative

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D.M. Whitacre (ed.), *Reviews of Environmental Contamination and Toxicology*, Reviews of Environmental Contamination and Toxicology 213,
DOI 10.1007/978-1-4419-9860-6_5,

(vPvB) shall be phased out as well. The decision-making process for setting test criteria for endocrine-disrupting pesticides is pending and is planned to be finalized by 2013 (EU 2009a). The new regulation becomes effective in June 2011. According to directive 2009/128/EC, all member states are required to adopt National Action Plans for reducing the human health and environmental risks of pesticide use. The protection of the aquatic environment and drinking water supplies from pesticides, and the obligation to undertake corresponding control measures, was particularly highlighted.

According to the Statistical Office of the European Union, the overall pesticide consumption of all 25 EU member states was 219,771 t/a (annum) in 2003; in Germany alone, the consumption was 23,240 t/a (equating to 10.6% of the total) (Eurostat 2007). Germany's consumption in the EU is exceeded by only three countries: France with 61,753 t/a (28.1%), Spain with 31,815 t/a (14.5%), and Italy with 30,828 t/a (14.0%). Moreover, if the pesticide consumption of the United Kingdom is also considered (14,920 t/a or 6.8%), approximately 75% of the total pesticide consumption of the EU is allotted to these five member states (Eurostat 2007).

In 2003, fungicides played the most important role in the EU's total pesticide consumption (49%), followed by herbicides (38%), insecticides/molluscicides and others (10%), as well as plant growth regulators (3%) (Eurostat 2007). Mancozeb and inorganic sulfur represented the most frequently applied active ingredients among fungicides. Among herbicides, farmers most frequently used glyphosate and isoproturon, whereas pest insects mainly succumbed from use of chlorpyrifos and parathion-methyl (these have been excluded from the EU list of approved active ingredients since 2003). The highest application rates of pesticides occurred in European viniculture (average dosage used by crop 21.4 kg active ingredient/ha) and market gardening (average dosage used by crop 61.7 kg active ingredient/ha).

In 2010, roughly 1,200 pesticides were authorized under the German Plant Protection Act (BVL 2010), comprising a total of approximately 250 different active ingredients. The highest consumption rate of pesticides in Germany is allotted to cultivation of grain (12,000 t in 2003; application rates of about 2 kg active ingredient/ha). German users employ more herbicides (54%) than fungicides (34%), compared to the European average. In 2003, isoproturon, metazachlor, mancozeb, and inorganic sulfur (chemical most commonly used to protect grapes against powdery mildew) represented Germany's most frequently used pesticides. Among field crops, the German application rate of pesticides in potato cultivation (6 kg active ingredient/ha) is comparatively high but is exceeded by application rates in the fruit- (about 20 kg active ingredient/ha) and wine-growing (30 kg active ingredient/ha) sectors (Eurostat 2007).

2 Endocrine-Active Pesticide Ingredients

In recent years, several authors and expert panels have attempted to evaluate the endocrine-disrupting properties of pesticides. For this review, we have evaluated the metadata from nine pertinent lists and databanks to determine which of the

250 active ingredients currently used in Germany are suspected to have endocrine-disrupting properties (BKH Consulting Engineers & TNO Nutrition and Food Research 2000; BMELV 2009; DHI Water & Environment 2007; FOOTPRINT 2010; Kemikalieinspektionen 2008; McKinlay et al. 2008; Neumeister and Reuter 2008; Pesticides Safety Directorate 2008; RPS-BKH Consulting Engineers et al. 2002). The result is that 41 chemicals (16.9% of all substances used in Germany) appear in at least one of the lists or databanks evaluated. Ioxynil, mancozeb, and maneb were cited most frequently and were included on seven of the nine lists or databases. Bifenthrin (status on Annex I – approved pesticides under directive 91/414/EEC– is pending but has been resubmitted), deltamethrin, iprodione, metiram, and metribuzin were indicated as endocrine disrupters in five lists and the following active ingredients were included on up to four of the nine lists: 2,4-D, carbendazim, dimethoate, epoxiconazole, metconazole, picloram, prochloraz, tebuconazole, thiram, and triadimenol. The remaining 23 chemicals were referred to on these lists only once or twice. In summary, the azoles (triazoles and imidazoles; 13 substances or 31.7%), the dithiocarbamates/carbamates (five substances or 12.2%), and the pyrethroids (five substances or 12.2%) were rated remarkably often as having endocrine-disrupting properties.

However, we emphasize that, in this review, we do not intend to challenge or affirm whether or not the classification of a substance as an endocrine disrupter is reasonable. We are distinctly aware that a substance classification scheme will not be conclusive until the European Commission decides on corresponding test criteria (see above). Therefore, in this chapter, our intent is to give an account of the current state of the discussion regarding contamination of the environment by potentially endocrine-disrupting components of pesticides.

3 Routes of Pesticide Emission into the Environment

In Germany, approximately 80% of all pesticides are employed in agriculture and the remaining 20% are used for bib-agricultural applications to public areas (e.g., roadsides and parkways), shopping malls, and residential areas (Bavarian Environment Agency 2008). Active ingredients are known to be emitted via diffuse (spray drift, evaporation, runoff, leaching, erosion, and drainage) or point source discharges (courtyard drains, industrial discharge, municipal sewage plant discharge, etc.) into the environment.

In 1993 and 1994, the Federal Environment Agency modeled the distribution of such discharges into German surface waters of the 42 pesticide-active ingredients most frequently used in agriculture (UBA 2000). The total emission was calculated to be 30 t/a, which is equivalent to 0.1% of the total amount of pesticides used during that period (margin of uncertainty 10–70 t/a). The most important losses among diffuse discharges (∼15 t/a or 50% of the total; margin of uncertainty 2–40 t/a) were runoff (9 t/a; 30%), spray drift (3.5 t/a; 12%), and drainage (1.5 t/a; 5%). Additionally, courtyard drains contributed 10 t/a (33%; margin of uncertainty

7–22 t/a) to water pollution by pesticides. Isolated releases of direct industrial discharges (only river Rhine area) were calculated to be less than 4 t/a (13%). Discharges from municipal wastewater treatment plants were not considered.

3.1 Spray Drift

Up to 10% of the active ingredient concentrations measured in treated crops can be detected in adjacent untreated plants (Bavarian Environment Agency 2008). During spring spraying applications to fruit crops, more than 10% of the applied pesticides are lost by spray drift, whereas this value in grain and vegetable crops is only 1% (Bavarian Environment Agency 2008). Carter (2000) evaluated field monitoring data and calculated spray-drift deposition levels for arable crop treatments, and reported depositions of between 0.3 and 3.5% at a 1-m distance from the handling area. Bach et al. (2005) used DRIPS (*d*rainage, *r*unoff, and spray-drift *i*nput of *p*esticides in *s*urface waters) modeling to calculate a total loss of 38 kg of active ingredient via spray drift, following arable crop treatments in Germany. This equates to approximately 0.0003% of the total amount of applied active ingredients or to 14,053 t of the cumulative value of 59 active chemicals applied to arable cropland in 2000. Spray-drift losses from vineyard and fruit-growing areas have been reported to be 120 and 3,100 kg/a, respectively (Huber et al. 2000; Bach et al. 2001).

3.2 Runoff

The capacity for soil to absorb water or retain pesticides depends on the characteristics of the soil to which the pesticides are applied. Some soils retain little water or pesticides, whereas others may retain considerable amounts. Therefore, in addition to runoff, soluble pesticides and those bound to particulates may be horizontally translocated across the application areas (surface runoff). Neumann et al. (2002) observed measurable field runoff when precipitation exceeded 10 mm/day. Torrential rain events excluded, Carter (2000) indicated that the pesticide loss rate originating from farmland was generally less than 0.05%. Bach et al. (2005), however, estimated the runoff rates of 59 active ingredients for field crop treatment to be 14.9 t/a, which equates to 0.11% of the total amount (14,053 t) of these 59 substances applied in Germany during the year 2000.

According to Neumann et al. (2002), the application rate and octanol/water partition coefficients (P_{OW}) of active ingredients determine the level of measurable pesticide load by which different routes of entry (surface runoff, courtyard drains, storm water sewers, emergency overflows, or final effluents) contribute to the contamination of small bodies of running water. Generally P_{OW} values are negatively correlated with measured pesticide loads. This finding is traced back to the tendency of lipophilic substances to bind to particulate matter. However, for the different routes of entry analyzed by these authors, the P_{OW} as a determinant for pesticide load was confirmed only for surface runoff.

3.3 Volatilization

On the basis of a literature review comprising 28 European studies from 10 EU countries, Dubus et al. (2000) reported that 50% of 99 chemically analyzed pesticide-active ingredients (including isomers and metabolites) were found in rainwater. Measured concentrations were generally below 100 ng/L. Occasionally, maximum concentrations in the low microgram per liter range were detected. According to Carter (2000), the loss of pesticides via evaporation for most products did not exceed 20% of the amount applied. However, for extremely volatile substances, up to 90% of the applied amount may evaporate. In contrast, Huber (1998) indicated volatilization loss of pesticides in Germany to be only 50 kg/a (equivalent to approximately 0.0002% of the total German pesticide consumption). Carter (2000) concluded that, compared to the total unwanted contamination of the environment from agricultural pesticides, contamination from atmospheric deposition originating from rain, snow, and fog is marginal.

3.4 Leaching and Drainage

Leaching is the main process by which pesticides reach groundwater. Substance loss through lateral and vertical infiltration into groundwater typically constitutes less than an average of 1% of the amounts applied, and in more exceptional cases up to 5% (Carter 2000). Based on drainage water measurements, Bach et al. (2005) calculated a loss of 185 kg of pesticides resulting from 2003 field crop treatments in Germany. This corresponds to 0.0013% of 14,053 t of active ingredients used for arable crop production (based on the sales volume for the top 59 active ingredients used in agriculture in Germany in the year 2000). Carter (2000) uses a value that is 760-fold higher as a basis and predicts pesticide loss from field drainage to be up to 1% (equivalent to 140 t used in German field crop protection).

3.5 Point Sources

Direct discharges may account for up to 90% of a water body's pesticide load (Bavarian Environment Agency 2008). Direct discharges include those from industrial sources, from courtyards or other hard-surfaced areas (railroad tracks, sealed private, and public grounds), from which pesticides reach water bodies either directly or via sewage treatment plant (STP) effluents. Several authors (Bach 1999; Seel et al. 1996; Fischer et al. 1998; Müller et al. 2002) have assumed that municipal STP may contribute between 65 and 95% of the pesticide load that reaches small bodies of running water. Bach et al. (2005) determined that, depending on the substance, up to 100% of a single chemical contamination incident can be traced back to point source emissions for river catchments. Over a 3-year period, Altmayer et al. (2003) investigated 24-h mixed samples of two STPs that received multiple discharges from vineyards contaminated by pesticides commonly used in viniculture. Occasionally, active ingredient daily loads of up to 100 g were detected.

Bach et al. (2001) reported that in Germany, agricultural point sources can contribute up to 18 t/a to the total pesticide contamination of the aquatic environment. In other studies, it has been determined that single farms released between 5 and 80 g/year of active ingredients, during the periods measured (Bach et al. 2005). Neumann et al. (2002) investigated the catchment basins of two small creeks (Nette and Pletschbach) in the lower Rhine area. They focused on direct and indirect discharges originating from courtyard drains (3 of 25 adjacent farmsteads); one effluent stream included an emergency overflow and one a storm sewer that drained surface runoff from a farmed area (7 of 20 adjacent fields). Analyses were made of two insecticides, five fungicides, and thirteen herbicides during the main pesticide application period between April and mid-July 1998. The aqueous phase of the surface runoff samples contained 19 of 20 analyzed active ingredients, adding up to a total chemical load of 66.2 g, within the sampling period. Courtyard water samples contained 17 of 20 ingredients and an average amount of 24 g of all measured substances. The total substance load was 604 g, within the sampling period. Rainwater samples had residues of 20 analyzed chemicals. The estimated total substance load for rainwater was 18.5 g. No fungicides or insecticides were detected, but 11 and 12 herbicides were present in the emergency overflow and final sewer samples, respectively. The total active ingredient load measured in the final sewer effluent was 3,070 g, and the emergency overflow load was 925 g.

4 Ground and Drinking Water Contamination

According to BMG (German Federal Ministry of Health) and UBA (German Federal Environment Agency) (2006, 2008), German drinking water is of good to very good quality. Both reports refer to communications made by the 16 German states regarding 2,706 (in 2006) and 2,624 (in 2008) drinking water analyses provided by water supply companies. Only drinking water suppliers that attained an average daily flow rate of more than 1,000 m^3 or those serving more than 5,000 people were considered. An amount equal to 74% of the raw waters investigated, during the reporting period 2005–2007, originated from groundwater (76.1% during 2002–2004), 15.5% from surface water (13.3% during 2002–2004), and 10% from other sources (10.5% during 2002–2004), such as bank filtration and artificially enriched groundwater. During the reporting period 2002–2004, the EU reference values of 0.1 μg/L for a single active ingredient, and 0.5 μg/L for the sum of measured substances (EU drinking water directive 98/83/EC), were exceeded only in 1–2% of all samples taken (during 2005–2007, this value was <1%). From these analyses, local health authorities did observe long-term deviations from allowed maximum concentrations for pesticides and their metabolites in drinking water, predominantly for atrazine, bromacil, desethylatrazine (atrazine metabolite), 2,6-dichlorobenzamide (dichlobenil metabolite), and *N*,*N*-dimethylsulfamide (DMS, tolyfluanide metabolite).

In 2006, Sturm et al. (2007) carried out a study on the pesticide contamination of ground- and surface waters. The authors consulted surveys of 477 members from the German Technical and Scientific Association for Gas and Water (DVGW), excerpts of the groundwater data bank from Baden-Wuerttemberg and results of a federal state monitoring program for groundwater by the LAWA (Working group of Federal States on Water issues). Results were that 182 participating DVGW member waterworks (38% of all waterworks considered) reported positive findings of active ingredients or their metabolites that exceeded the limit of detection. However, these values did not necessarily exceed the EU drinking water reference value of 0.1 μg/L (for a single substance). Of all findings, 65% referred to groundwater, 31.0% to surface water, 4% to bank-filtered water, or artificially enriched groundwater, and 0.2% to other water sources. The number of analyzed parameters and frequency of sampling varied among the sampled waterworks, which is why identifying representative analyses (even those calculated from single-substance average concentrations) was impossible. In total, positive findings of 100 different substances were reported. Of these, 43% were approved substances (according to EU directive 91/414/EEC), 50% were prohibited, and 7% represented metabolites. The drinking water reference value of 0.1 μg/L was exceeded for 82% of all positive findings. Active ingredients found most often (listed more than 120 times) were atrazine and desethylatrazine, followed by diuron, simazine, isoproturon, and 2,6-dichlorobenzamide (number of times mentioned, 40–60). The number of times that bentazone, mecoprop, deisopropylatrazine, and terbuthylazine was mentioned ranged from 20 to 40. Hexazinone, propazine, metaxon (MCPA), chlortolurone, desethylbutylazine, and metazachlor were reported as having been detected 10–20 times by the waterworks. Five to ten positive findings occurred for the following metabolites and active ingredients: AMPA (metabolite of glyphosate), dichlorprop, glyphosate, metolachlor, ethidimuron, 1,2-dichloropropane, 2,4-D, bromoxynil, flufenacet, lenacil, metalaxyl, methabenzthiazuron, terbutryn (banned since 2003 as an active ingredient in herbicides but still approved in biocides), and ethofumesate.

Waterworks reported a total of 60 positive findings for active ingredients in groundwater. At the time of inquiry (2006), 10% of these substances were metabolites, 44% approved, and 47% no longer approved by EU pesticide regulators. For 41 substances or their metabolites (68% of all active ingredients and 6.8% of all positive findings), concentrations exceeding 0.1 μg/L (drinking water reference value) were detected. In some groundwater samples, maximum concentrations exceeded 1 μg/L (Sturm and Kiefer 2009).

A nationwide comparison of groundwater monitoring data was performed by LAWA for the periods 1990–1996 (LAWA 1998) and 1996–2000 (LAWA 2004). The studies made clear that, over the course of the preceding decade, pesticide contamination of groundwater remained unchanged. The comparison also indicated that regulatory inspections were largely consistent across the German Länder and confirmed the above-mentioned results of the waterworks. This nationwide data evaluation also demonstrated that atrazine and its metabolites, as well as bentazone, bromacil, diuron, and simazine, were most frequently detected in groundwater.

Kiefer and Sturm (2008) used their results as an opportunity to compile a list of pesticide-active ingredients and their metabolites that have "very high" relevance for water pollution control measures (Table 1). Eleven of 43 substances have been indicated as potential endocrine disrupters. Of these, only bromoxynil and metribuzin are still approved, according to the EU pesticide directive (Table 1).

5 Surface Water Contamination

During the main annual pesticide application period, waters from the rivers Danube, Main, Regnitz, and Altmühl in Bavaria, as well as small streaming waters, are frequently analyzed for residues of 100–150 active ingredients. According to Wagener and Schuster (2007), in small Bavarian streams, both the number and concentrations of pesticide-active ingredients are higher than those found in large watercourses.

Atrazine and its metabolites, terbutryn and metolachlor, were the endocrine-disrupting pesticides most often detected (Wagener and Schuster 2007) in both small and large streams. An average metolachlor maximum concentration of 0.29 μg/L (average value from 22 sampling stations spanning eight analytical studies) was detected in small streams. The LAWA environmental quality standard (EQS) requires the protection of aquatic biocoenosis at values of <0.2 μg metolachlor/L. The average maximum concentration of atrazine measured in small Bavarian watercourses met the LAWA and ICPR (International Commission for the Protection of the Rhine) target of 0.1 μg atrazine/L (drinking water and biocoenosis protection) and EU EQS of 0.6 μg atrazine/L (surface waters). In large Bavarian rivers, values were even lower. Details on the 90 percentile concentrations have not yet been provided but will become available. For terbutryn, an EQS was not defined by LAWA or any other responsible commission.

In 2002, the most important findings that concerned residues of pesticides with potentially endocrine-disrupting properties in the rivers Danube, Neckar, Rhine, Enz, Jagst, Kocher, and Tauber related to substances that no longer have authorization under applicable EU pesticide regulations. Such pesticides include alachlor, atrazine, diazinon, simazine, and terbutryn. However, active ingredients that are still approved in the EU, such as diuron, penconazole, pendimethalin, and propiconazole (LUBW – Environment Agency Baden-Wuerttemberg 2004), were also detected. For atrazine, the 90 percentile reference values of LAWA, ICPR, and IKSE (International Commission for Protection of the Elbe River) were not exceeded in any of the sampled rivers during the period of investigation. Nevertheless, some authors (Moltman et al. 2007) have proposed lower atrazine and simazine reference values (0.01 μg/L), based on ecotoxicological effect data. The 90 percentile

Table 1 Plant protection products (substances and metabolites) that have been detected most frequently by water suppliers in Germany and substances with "very high relevance" for prevention of water pollution (data of Sturm and Kiefer (2007) and Kiefer and Sturm (2008) upgraded and extended)

Substance name	Approved under directive 91/414/EEC (status October 2010)	Rank (according to water supplier's positive findings)	Rank (according to positive findings in groundwater)	Rank (according to positive findings in surface water)	Detected in ground-water	Detected in surface water	Detected in drinking water	Potential endocrine disrupter (according to lists/databanks consulted)
1,2-Dichloropropane	No	n.i.	n.i.	n.i.	X	X		No
2,6-Dichlorobenzamide	Dichlobenil metabolite	6	3	18	X	X	X	n.i.
Ametryn	No	n.i.	n.i.	n.i.		X	X	No
AMPA	Glyphosate metabolite	18	21	12	X	X		n.i.
Atrazine	No	2	2	2	X	X	X	Yes
Bentazone	Yes	7	7	9	X	X	X	No
Bromacil	No	8	6	n.i.	X	X	X	No
Bromoxynil	Yes	n.i.	n.i.	n.i.	X	X	X	Yes
Carbofuran	No	n.i.	n.i.	n.i.		X	X	Yes
Chloridazon	Yes	n.i.	n.i.	n.i.	X	X	X	No
Chlorotoluron	Yes	15	15	19	X	X	X	No
Cyanazine	No	n.i.	n.i.	n.i.	X	X		Yes
Desethylatrazine	Atrazine metabolite	1	1	7	X	X	X	n.i.
Desethylterbuthylazine	Terbuthylazine metabolite	16	14	17	X	X	X	n.i.
Deisopropylatrazine	Atrazine/simazine metabolite	10	9	19	X	X	X	n.i.
Desmetryn	No	n.i.	n.i.	n.i.		X	X	No
Diphenylchloridazon	Chloridazon metabolite	n.i.	n.i.	n.i.	X	X	X	n.i.
Dichlorprop	No	20	19	16	X	X		No
Dinoterb	No	n.i.	n.i.	n.i.	X	X	X	No
Diuron	Yes	3	5	1	X	X	X	Yes

Table 1 (continued)

Substance name	Approved under directive 91/414/EEC (status October 2010)	Rank (according to water supplier's positive findings)	Rank (according to positive findings in groundwater)	Rank (according to positive findings in surface water)	Detected in ground-water	Detected in surface water	Detected in drinking water	Potential endocrine disrupter (according to lists/databanks consulted)
Ethidimuron	No	n.i.	n.i.	n.i.	X	X	X	No
Fenpropimorph	Yes	n.i.	n.i.	n.i.	X		X	No
Flufenacet	Yes	n.i.	n.i.	n.i.		X		No
Glyphosate	Yes	20	24	10	X	X		Vague
Hexazinone	No	12	11	19	X	X	X	No
Isoproturon	Yes	5	8	3	X	X	X	No
Lenacil	Yes	n.i.	n.i.	n.i.	X	X		No
Metaxon	Yes	14	24	5	X	X		No
Mecoprop	Yes	9	10	8	X	X	X	No
Metalaxyl	No	n.i.	n.i.	n.i.	X	X		No
Metazachlor	Yes	17	19	13	X	X	X	No
Methabenzthiazuron	No	n.i.	n.i.	n.i.	X	X	X	No
Metolachlor	No	19	22	11	X	X		Yes
Metribuzin	Yes	n.i.	n.i.	n.i.	X	X	X	Yes
Metsulfuron-methyl	Yes	n.i.	n.i.	n.i.	X	X	X	No
N,*N*-Dimethylsulfamide	Tolyfluanide metabolite	n.i.	n.i.	n.i.	X	X	X	n.i.
Prochloraz	No	n.i.	n.i.	n.i.		X	X	Yes
Prometryn	No	n.i.	n.i.	n.i.	X	X	X	Yes
Propazine	No	13	12	19	X	X	X	Yes
Sebuthylazine	Not listed	n.i.	n.i.	n.i.	X		X	No
Simazine	No	4	4	4	X	X	X	Yes
Terbuthylazine	No	11	13	6	X	X	X	No
Terbutryn	No	n.i.	n.i.	n.i.		X	X	Yes

Abbreviations: X, positive finding (≥ limit of detection); n.i., no information available of the range of diuron residues found in the river Kocher was 0.12 μg/L; this value was considerably higher than the EQS for aquatic organisms recommended by LAWA (0.05 μg/L) and ICPR (0.006 μg/L). The concentrations of diazinon found in the sampled water bodies exceeded the calculated EQS of 0.003 μg/L proposed by Moltmann et al. (2007). For the other detected substances, no reference values have been provided by the river commissions for waters that are near the surface. However, active ingredients have often been detected in such waters at a concentration range that exceeded the detection limit.

Between 1985 and 2003, the Environment Agency of Rhineland-Palatinate (LUWG) carried out a monitoring program on organic trace elements in running waters. In total, analyses were conducted for 144 pesticides, biocides, and 13 pesticide metabolites (LUWG 2006). From this monitoring program, a total of 48,948 measurements were made of water samples from the rivers Rhine, Moselle, Lahn, Nahe, Saar, and Selz and from water samples taken from selected smaller watercourses. Among those analytes covered were 22 fungicides, 73 herbicides, 56 insecticides, 2 nematicides, and 1 growth regulator.

In total, 157 pesticide-active ingredients were addressed in the monitoring study. Among these, 90 (57.3%) were not detectable and 67 (42.7%) had concentrations above the detection limit. A 50% quota (i.e., 50% of all measured concentrations were higher than the detection limit for at least one sampling station over a period of 1 year) existed for 29 active ingredients. Tebuconazole concentrations in the rivers Nahe, Moselle, and Selz exceeded the detection limit (0.03–0.05 μg tebuconazole/L). Water samples from the rivers Rhine, Lahn, and Saar were negative for tebuconazole residues. In 2001, the river Selz displayed annual average values of between 0.075 and 0.53 μg tebuconazole/L (maximum value 4.7 μg/L). Quality criteria for tebuconazole concentrations in surface waters are, unfortunately, currently not specified.

The pesticides that are potentially endocrine active, such as atrazine (and its metabolites), simazine (both now banned), diuron, and metazachlor, were similarly detected and had values above the 50% quota. For example, diuron (with a detection limit of <0.1 μg/L) was consistently detected in 10 of the water bodies (44% of the samples contained concentrations above the detection limit) for which analyses were performed. Annual mean values for diuron were between 0.025 and 0.326 μg/L. A maximum value of 1.5 μg/L was measured in the river Moselle more than one decade ago, in 1995. The ICPR EQS for aquatic biocoenosis of 0.006 μg diuron/L was, thus, frequently exceeded. Although application restrictions were placed on diuron, no concentration decrease was observed (LUWG 2006). Between 1988 and 2003, metazachlor (with a detection limit of 0.01–0.12 μg/L) was analyzed for in 24 watercourses and was detected in the rivers Rhine, Selz, Nahe, Moselle, and Saar and the brook Schwarzbach. The 50% quota for metazachlor was exceeded in the rivers Rhine (1988, 1992) and Selz (1997). The annual mean residue value detected for this herbicide was 0.032 μg/L. The maximum value was 0.39 μg/L and was measured in the river Selz in 1997.

Almost 70% of all atrazine residue values measured between 1988 and 2003 exceeded the limit of detection (0.01–0.55 μg/L), and these were mostly observed after the application of atrazine was banned in 1991. A failure to detect atrazine occurred only in eight of 24 water bodies, and the 50% quota was exceeded in 12 of the 24. The annual average residue values for atrazine ranged from 0.013 to 0.354 μg/L and were therefore above the EQS of 0.01 μg/L that was recommended by Moltmann et al. (2007). The highest atrazine residue detected was 2.1 μg/L and was recorded in 1995 in the river Moselle. In addition, 39% of all simazine concentrations detected exceeded the limit of detection (0.01–0.1 μg/L). This substance was present in 20 of 24 running water bodies. Annual average residue values for simazine (0.012–0.355 μg/L; maximum value 1.54 μg/L in river Selz in 1998) were comparable to those for atrazine and therefore probably exceeded the LAWA and ICPR EQS values. For some water bodies a gradual decline of the residue levels for atrazine and simazine was observed.

Among 56 insecticides analyzed, only a few potential endocrine disrupters appeared to exceed the limit of detection (parathion-methyl/-ethyl, α-endosulfan, and dimethoate). Only lindane (gamma-HCH) exceeded the detection limit of 0.001–0.02 μg/L, in approximately half (46%) of all measurements performed, in 22 streams between 1985 and 2001. At sampling stations in which the 50% quotes were exceeded, the yearly average values were in the range of 0.01–0.37 μg/L and thus were partially above the EQS of 0.066 μg/L proposed by Moltmann et al. (2007). The proposed EU Water Framework Directive (WFD) EQS of 0.02 μg/L for lindane (EU 2006), however, was not achieved at the end of the 1980s and the beginning of the 1990s in the rivers Lahn, Moselle, Saar, and Wiesbach. A maximum value of 0.12 μg lindane/L was measured in the Moselle in 1987. Although lindane was sporadically detected until 2003, the ban on lindane across all EU countries since 2001 turned out to be effective, because, in general, measured concentrations have been declining (LUWG 2006).

Until 2003, several streams were intensively monitored. Results of those pesticide-active ingredients that exceeded the 50% quota in sampled rivers were as follows:

- in the Rhine, 14 of 113 (equivalent to 12%) active ingredients;
- in the Moselle (10 of 89) and Saar (7 of 60), the total equating to ∼11%;
- in the Nahe (14 of 73), approximately 19%;
- in the Selz (18 of 91), approximately 20%; and
- in the Lahn (7 of 27), approximately 26%.

The contamination patterns among the sampled rivers differed greatly. Over a period of 4 years, there were exceedances of the 50% quota for the following pesticides: dichlorprop, 2,4-D, MCPA, diuron, isoproturon, bentazone, chloridazon, and lindane. The rivers involved and the number of exceedances were as follows: Moselle (17), Saar (14), Rhine (9), Lahn (8), Selz (6), and Nahe (4).

In 2006, the pesticide monitoring network of the federal state Brandenburg addressed a total of 23 active ingredients and metabolites, spanning 17 sampling stations at the rivers Elbe, Odra, Neisse, Havel, Spree, Dahme, Nuthe, Rhin, Dosse, Stepenitz, Odra-Spree Canal, and Schwarze Elster. Positive findings occurred for the following 15 active ingredients: atrazine, 2,4-D, DDT, DDE, DDD, dichlorprop, α/β-endosulfan, lindane isomers, MCPA, mecoprop, glyphosate, isoproturon, metolachlor, pendimethalin, and terbuthylazine. These active ingredients were detected most frequently in the river Odra (nine substances or 39%), as well as in the rivers Havel and Schwarze Elster (seven substances or 30%). In 2006, violations of quality standards for pesticide residues were observed only for the herbicides dichlorprop and mecoprop. In contrast to the results of the preceding years, no positive findings were reported for aldrin, bentazone, chloridazon, chlortolurone, ethephon, or metazachlor (MUGV – Brandenburg State Office for the Environment 2007).

For the river Elbe, annual average residue values for 2006 were compared to the EQS of the EU WFD for several pesticides (2,4-D, aldrin, ametryn, atrazine, dichlorprop, dieldrin, dimethoate, diuron, endrin, hexazinone, isoproturon, MCPA, mecoprop, metazachlor, metolachlor, parathion-methyl, prometryn, simazine, and terbuthylazine). Results showed that all sampling stations retained good water quality. Also, tailwater areas of major tributaries, such as the rivers Schwarze Elster, Mulde, Saale, and Havel, were not significantly charged with residues (results were generally less than the limit of detection). At only one site in 2007 was there an exception; a water body near Schmilka displayed a *p*,*p*'-DDT annual average residue value that was twice the EU EQS standard (ARGE Elbe 2008a, b).

Investigations into contamination of Hessian streams were carried out either between 2004 and 2005, or between 2007 and 2009 by the Hessian State Office for Environment and Geology (HLUG 2010; data available at www.hlug.de/medien/wasser/wasser_psm/index.htm). In 2004 and 2005, a total of 122 sampling stations were examined six times annually (four samplings in spring and two in autumn) for 94 active ingredients and their metabolites. In a subsequent monitoring program (2007–2009), one-third of these stations were sampled. Herein, 74 substances were investigated and results compared with the WFD standards. In summary, HLUG found that surface waters situated in areas that have a distinct agricultural utilization profile and wastewater-loaded streams are characterized by extensive pesticide contamination. The Hessian Minister for Environment, Agriculture, and Consumer Protection, Wilhelm Dietzel, compiled a list addressing maximum pesticide residue concentrations of 21 active ingredients and their metabolites measured in Hesse during the 2004/2005 sampling campaign at 25 sampling stations (Hessian State Parliament 2006). Of these, primarily bentazone, isoproturon, diuron, dichlorprop, MCPA, mecoprop, and metamitron were detected.

The development program "Rhine 2020" of the ICPR aims at improving the water quality of the river Rhine. As part of the program, a list of contaminants relevant to the river Rhine (considering the OSPAR and WFD priority substances) is kept, along with the corresponding quality standards (ICPR 2007). Measured values for the banned chemicals aldrin, azinphos-ethyl, dieldrin, DDT, endrin, α-, β-, δ-HCH, isodrin, malathion, and simazine were in line with the established quality standards. Concentrations that were either considerably higher or partially above those standards were detected for alachlor, atrazine, azinphos-methyl, chlorfenvinphos, dichlorprop, dichlorvos, endosulfan, fenitrothion, fenthion, lindane, parathion-methyl/-ethyl, and trifluralin (banned substances according to

EU legislation). Approved substances (some of them presumably endocrine active), such as bentazone, chlorpyrifos, dimethoate, diuron, and metaxon, similarly exceeded quality standards.

In 2001, 23 pesticide-active ingredients were analyzed for in the river Danube. Among the detected residues, both atrazine and desethylatrazine were found to have average concentrations of 0.05 μg/L (ICPDR 2002). Some residue levels appeared to exceed the ICPR and LAWA EQS for atrazine (0.1 μg/L) in the tributaries. A maximum atrazine value of 0.78 μg/L was measured in the Save estuary that flows into the river Danube.

Moltmann et al. (2007) evaluated 21 pesticide-active ingredients for their relevance to surface water pollution and assigned high priority to *p*,*p*'-DDT and atrazine. Low priority was declared for the still authorized substance 2,4-D and the banned substances aldrin, β-HCH, dieldrin, endosulfan, endrin, γ-HCH, malathion, methoxychlor, parathion-methyl, mirex, *p*,*p*-DDE, and trifluralin.

6 Food Contamination

The European Commission recently published a report on pesticide residues in foods of herbal origin (EU 2008). The report is based on a systematic investigation performed in 2006 and summarizes the results of periodic monitoring of 25 EU countries, including Norway, Iceland, and Liechtenstein. Within the reporting period, a total of 65,810 samples (covering fruits, vegetables, field crops, and pre-treated products, including baby food) were analyzed. In total, 8,929,360 measurements of 54,747 samples (17,535 from Germany) were performed. The number of single-substance analyses varied among member countries and spanned 45–683 chemicals. Overall, 345 pesticide-active ingredients and their metabolites were detected. In 54% of all samples (38.1% of which were from Germany), no residues were detected. Of all positive findings, 42% (56.5% in Germany) were in the range of the maximum residue levels (MRLs) defined by the EU for each substance and product and 4.4% (5.35% in Germany) exceeded the MRL. For analyses performed in single-food categories, the following percentage of samples did not show detectable pesticide residues: 96% for baby food, 76% for pre-treated food, 73% for crops, and 51% for fruits and vegetables. Furthermore, it became evident that an exceedance of EU MRLs was more frequently observed for products originating from developing countries, compared to products originating from the EU (rate, 6.4/100 vs. 2.2/100). When comparing 10-year monitoring data (1996–2006), the percentage of foodstuff showing no detectable pesticide contamination continuously decreased, starting from 64% in 1999 to 51.5% in 2006. The percentage of samples exceeding the EU MRLs increased from 3.0 to 5.5%. In considering the significance of these trends, one must also remember that during the 10-year period, in which data were collected, analytical methodologies were enhanced and detection limits were lowered. Of all analyzed samples, 27.7% were contaminated by two or more pesticide-active ingredients or their metabolites.

Member countries were requested to compile a list of 10 active ingredients that are most frequently detected in their food samples, in order of decreasing frequencies. In Germany, the fruit and vegetable category was generally contaminated by chemicals according to the following pattern: maneb group > iprodione > procymidone (all thought to be endocrine active). Crop components most commonly contained substances of the maneb group > deltamethrin (thought to be endocrine active). A violation of EU MRLs was observed for substances of the maneb group (0.31% of all samples), dimethoate (0.27% of all samples) and procymidone (0.09% of all samples).

Market basket analyses were also conducted. The market basket contained eight fruit, vegetable, and other crop products (aubergines, bananas, cauliflower, grapefruits, orange juice, peas, bell pepper, and wheat). Analytical results showed that 56.9% of all samples had no measurable pesticide residues. In addition, 40.8% of the samples contained residues below the EU MRL. Pesticide contamination exceeding the MRL was observed for only 2.3% of the commodities. Within the scope of these analyses, residues of 55 pesticides were analyzed in food samples. Active ingredients were measured with decreasing frequency in grapefruit (68%), bananas (55%), bell peppers (42%), aubergines (33%), wheat (27%), peas (21%), cauliflower (20%), and orange juice (10%). Violations of MRL values were observed for aubergines, bell pepper, grapefruit, and pea samples. Approved and potentially endocrine-disrupting active ingredients were identified in food samples at the following relative frequencies: procymidone (16.6%), iprodione (15.6%), chlorpyrifos (15.0%), chemicals of the maneb group (13.3%), pyrimethanil (11.5%), and triadimenol (6.8%) in grapefruits. Aubergines contained predominantly procymidone (7.5% of all positive samples) and substances of the maneb group (6.8% of all samples). Bananas were mainly contaminated by chlorpyrifos (9.5% of all samples), peas by procymidone, bell peppers by procymidone and substances of the maneb group (14.0 and 9.2% of all samples, respectively), and similarly cauliflower by maneb group chemicals (29.5% of all positive samples).

Assessment of the potential chronic health risks associated with consuming contaminated foodstuffs was performed using the EFSA (European Food and Safety Authority) model. This model allows evaluators to consider country-specific eating habits. For 44 of 55 measured substances, the 90th percentile was below 0.01 mg/kg (general requirement for pesticide residues in food samples when specific limits are not provided by EU regulation). For these pesticides, a negligible uptake was expected. For four actual and potentially endocrine-active ingredients (chlorpyrifos, iprodion, maneb group, and procymidone), the 90th percentile level exceeded 0.01 mg/kg. These substances were checked to ascertain whether or not the approved ADI (acceptable daily intake) values were approached. In no case were the ADI values exceeded, because the substance exposure was lower than 0.9% of the ADI.

Acute risk assessment was performed for 34 of the 55 chemicals for which the Acute Reference Doses (ARfD) were defined by either the European Commission, the EFSA or the JMPR (Joint FAO/WHO Meeting on Pesticide Residues). Because only the maximum values were considered for calculating this risk assessment, results showed that the ingestion of a pooled food sample would have resulted in an ARfD exceedance for 15 of the 34 active ingredients. The following potential endocrine disruptors were among those 15 active ingredients: aldicarb, carbaryl, endosulfan, methomyl, parathion (banned chemicals) and dimethoate, λ-cyhalothrin, substances of the maneb group, and procymidone (approved chemicals). The number of samples exceeding the ARfD was comparatively low for those containing aldicarb, endosulfan, λ-cyhalothrin, parathion, dimethoate, and substances of the maneb group (1–5 samples) but was manifold higher for those contaminated with carbaryl, methomyl, and procymidone (14–20 samples). The most pronounced carbaryl ARfD violation was observed for grapefruit consumption, with values up to 464% (adults) and 956% (children) above the reference value. Distinct methomyl ARfD violations were recognized for bell pepper (up to 523 and 2,015% higher for adults and children, respectively) and grapefruit intake (adults up to 381% and children up to 786%). As a result, the EU withdrew the methomyl authorization in 2008 (re-registration in 2009). The highest ARfD exceedances for procymidone were noticed for grapefruit (up to 444% for adults and 917% for children). EU MRLs and more recent toxicological endpoints were checked by the Commission with regard to a prohibition of procymidone use (EU 2008; EFSA 2009). Actually, this substance is not approved under Annex I.

In Germany, the Federal Office of Consumer Protection and Food Safety (BVL) has carried out an independent Food Surveillance Programme since 1995. The program covers 72.5% of food samples of herbal origin (safflower and olive oil, rice, potatoes, spinach, onions, cucumber, green beans, carrots, red currant, peas, mandarins, apple juice, peppermint leaf tea, and rooibos tea) and 20% of food samples of animal origin (yoghurt, chicken meat, turkey meat, scalded sausages, salmon, cured trout filet, cured halibut, North Sea shrimp, and prawns) (BVL 2009). Ready-to-serve meals, candies (liquorice and chocolate), and baby food amounted to 7.5% of the sample size. The composition of the market basket utilized the Schroeter et al. (1999) model, in which German eating habits were considered. Of all samples in the market basket, 61% originated from Germany, 16% from EU member states, 13% from known, and 10% from unknown third countries. Samples were analyzed for residues of pesticides and other contaminants (biocides, veterinary drugs, heavy metals, etc.). In total, up to 52 pesticide-active ingredients, biocides, and metabolites were analyzed. In 2008, the monitoring program encompassed 5,093 samples.

Foods of animal origin predominantly contained persistent organic insecticide residues (e.g., *p*,*p*'-DDE, *p*,*p*'-DDD, *p*,*p*'-DDT, HCB, endosulfan sulfate, dieldrin, *cis*-/*trans*-nonachlor, *cis*-chlordane, oxychlordane, and toxaphene congener Parlar 26). Violations of MRLs were not detected. Samples characterized by having the most frequent positive findings were trout (74%), halibut (80%), and salmon (97%). Multiple pesticide residues (five active ingredients or more per sample) were particularly present in halibut (52% of all samples) and salmon (62% of all samples). Of the pesticide residues measured, 90% had residues below 0.05 mg active ingredients/kg.

Proportions equal to 27% of potatoes, spinach, onion, and apple juice retained pesticide residues. For safflower and olive oil samples, the quota of pesticide-contaminated samples was even lower and added up to 11%, although the BVL acknowledged that the samples were checked for comparatively few active ingredients (BVL 2009). Pesticide-active ingredients were more frequently found in rice, cucumbers, green beans, and carrots (59–70%). Of all rooibos tea samples 75% contained pesticide residues above the limit of detection. As in previous investigations, fruit revealed the highest incidence of positive pesticide findings (76–90% of the measurements exceeded the detection limit). Moreover, pears, red current, gooseberries, and mandarins presented the highest number of multiple pesticide residues (mean 3.3–3.9 active ingredients per sample).

Violation of MRL values was observed for 0.7–6.6% of spinach, onion, cucumber, green bean, red current, gooseberry, and mandarin samples. For rice, pears, and peppermint leaves, the exceedance quota amounted to more than 10% of the analyzed samples.

For single substances, the comparatively high MRL exploitation rates for carbendazim in rice, imazalil in mandarins, and amitraz in pears were noticeable (BVL 2009). For Turkish pears, a substantial exceedance of the amitraz (banned in EU member states) MRLs (and also ARfD values) was observed. Hence, these goods were withdrawn from sale (BVL 2009). Chemical-specific ARfD values were not affected for any other food sample of herbal origin.

No MRL exceedance was observed for olive and safflower oils, potatoes, carrots, apple juice, chocolate, or rooibos tea. MRL violations occurred in about 1.5% of home country samples, 1.8% of EU member state samples, and 17.9% of third country samples.

For 52 (9%) of all analyzed samples of German origin, the BVL assumed that pesticide-active ingredients were misused (BVL 2009). Such misused substances were mainly detected in peppermint leaves and pears. Residues that exceeded 0.01 mg/kg (lowest detection limit) were rated as indicating a non-approved application. However, BVL admits that this method did not allow them to differentiate between applications that were actually prohibited and applications of formerly approved persistent pesticides (brownfields), or seed and seedling treatments with banned foreign chemicals.

7 Conclusions

There are no generally accepted principles for what constitutes the critical avenues of pesticide loss from application or other sites. Such loss has many origins, including application technique, user expertise or experience, physicochemical properties of active ingredients applied, and local environmental conditions (precipitation quantity, soil quality, temperature, and average hours of sunshine per day). Therefore, quantifying pesticide loss via emission pathways varies considerably and depends on what monitoring data or mathematical computation models are used and the control variables that are applied (Table 2).

Although residue-free application is unrealistic, even very low residue concentrations may cause ecosystem damage as a result of multiple exposures or additive

Table 2 Pesticide release into the environment according to different routes of emission. Values originally provided in tons of emission per year (UBA 2000; Bach et al. 2005) have been converted on a percentage basis and refer to the total German pesticide consumption of approximately 30,000 t/a

Route of emission	UBA (2000)	Bach et al. (2005)	Carter (2000)
Spray drift (%)	~0.012	~0.00013	~0.3–3.5
Runoff (%)	~0.03	~0.05	~0.05
Volatilization	–	–	~20%
Drainage/leaching (%)	~0.005	~0.0006	~1
Point sources	~0.033%	~0.06%[a]	–

[a]Refers to emission into the aquatic environment only

effects, non-linear dose–response relationships, and susceptibility of organisms at sensitive life stages. Many pesticides that are suspected to have endocrine-disrupting properties have already been banned by the European Commission. Nevertheless, the realignment of the European Plant Health Legislation is not likely to solve the endocrine-disrupting properties that are associated with pesticide work, in part, because hormonal interferences may also result from mixture effects that are not addressed by the new EU legislation.

However, pesticide contamination has succeeded in attracting the attention of industry, agricultural enterprises, and authorities. Efforts have been made to reduce contamination by spray drift, e.g., by the development and implementation of advanced application techniques (low drift nozzles, air-assisted injector nozzles, etc.). Furthermore, the new EU directive 2009/128/EC (EU 2009b) binds all member states to ensure that the professional pesticide application equipment used is regularly inspected (5-year interval until 2020, thereafter 3 years). Finally, in the future, aerial spraying shall be allowed only in tightly controlled exceptional cases in all EU countries.

Directive 2009/128/EU addresses point source emissions through instructions that require training of professional users, including those who handle and store pesticides, clean equipment, or deal with remnant disposal. By December 2013, authorities are asked to establish certification systems to train professional pesticide users, distributors, and advisors (EU 2009b).

Preparation of this review chapter has suggested to the authors certain appropriate future action strategies that, if instituted, may help reduce pesticide residues in the environment. These include the following:

- Implementing a farmer advisory service independent of pesticide corporate interests;
- Fostering a broader embedding of water protection practices that will allow competence certification for agricultural pesticide users;
- Instigating an improved supra-regional information exchange on environmental pesticide contamination among (federal) regulatory authorities or other cooperating governmental or non-governmental groups;

- Developing a competitive pesticide classification system that will allow cultivators (farmers) and farm advisors to select the most eco-friendly pesticide for any specific authorized use;
- Assessing an eco-tax on pesticide products that will encourage use of minimal amounts of the proper product;
- Performing eco-audits of professional pesticide operators at regular intervals;
- Integrating a pesticide monitoring program for ground and surface waters on a nation/EU-wide basis;
- Addressing remobilization of previous pesticide contaminations via sediments and extending and harmonizing pesticide EQS values under WFD demands; and
- Utilizing data from existing monitoring programs that is submitted during the pesticide approval process.

8 Summary

The European Parliament recently approved a new EU regulation aimed at eliminating the use of pesticides that have unwanted endocrine-disrupting properties. The test criteria for these chemicals are slated to be finalized by 2013. For this reason, in this review, we have evaluated the metadata of lists and databanks that address pesticides with potentially endocrine-disrupting properties, and have checked which of the 250 active ingredients currently in use in Germany are affected. Azoles, dithiocarbamates/carbamates, and pyrethroids were most frequently rated as endocrine-active ingredients. In Germany, assessments have shown that total environmental pesticide emission is equivalent to approximately 0.1% of total pesticide use. Courtyard drainage and field runoff are regarded to constitute the most important sources of pesticide emission into the aquatic environment. In addition, in several investigations of drinking- and groundwater contamination, various pesticide-active ingredients and their metabolites were confirmed to be contaminants. Water suppliers recorded the following pesticides or their metabolites as being most frequently detected in drinking water: atrazine, desethylatrazine, diuron, simazine, isoproturon, and its dichlobenil metabolite 2,6-dichlorobenzamide. Surface water contamination results mainly from substances that are no longer approved by EU pesticide regulation. The most frequently detected pesticides in streaming waters that are still authorized were bentazone, diuron, glyphosate, isoproturon, MCPA, mecoprop, metamitron, pendimethalin, and tebuconazole.

Pesticide residues in comestible goods of herbal origin are periodically detected in all EU member countries. The European Commission recently published results showing that 54% of all monitoring samples were devoid of positive findings. Of samples showing detectable residues, 42% were below, and 4.4% exceeded the EU MRLs. Monitoring data over a 10-year period revealed that the percentage of food stuff without detectable pesticide residues has continuously decreased from 64 to 51.5%. In Germany, herbal samples mainly contained residues of maneb, iprodion, procymidone and deltamethrin. Notwithstanding these detections, chronic health risk evaluations indicated that there were no violations of ADI values. However, for carbaryl, methomyl, and procymidone, ARfDs were exceeded substantially for intake of grapefruit and bell peppers. As a result, the EU withdrew the methomyl authorization in 2008 and revised procymidone guideline values.

Acknowledgments This work was financially supported by the BMBF (Federal Ministry of Education and Research) as part of the *start*$_2$ project (http://www.start-project.de/english_2.htm). The authors are grateful to the whole project team and the external experts for sharing their thoughts and the constructive discussions. Furthermore, we would like to extend our sincere thanks to the reviewers of this chapter for their helpful comments and support.

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