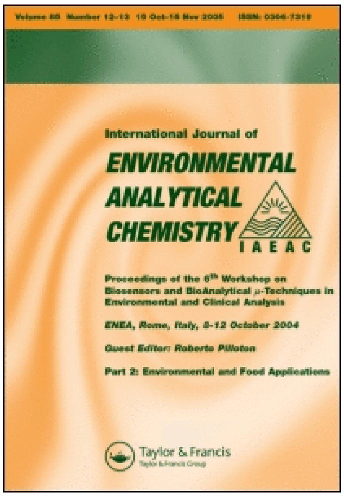

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RISK ASSESSMENT FOR PESTICIDES AND THEIR METABOLITES IN WATER

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A method based on Hasse diagram is adopted to detect priority pesticides among the 130 most used in Europe. Hasse diagrams rank pesticides in groups of potential hazard to the water environment, according to pesticide properties (water solubility, vapour pressure and persistence in soil) and usages. The procedure is applied on a territorial scale, selecting Germany, U.K. and Italy as case studies, and validated with the experimental results of monitoring programs. Most of the pesticides ranked as a first priority by the model and analyzed for in water were effectively found. The percentage of positive findings decreases from class 1 to 6 of priority in agreement with the theoretical predictions. The model suggests that each country must develop its own analytical protocol addressed to the detection of the most "probable" pesticides. Pesticide metabolities of Italian priority pesticides are appraised in detail and their risk is assessed according to their occurrence in surface and groundwater, persistence estimated from field data and ecotoxicity data. The proposed procedure can steer research efforts towards compounds that really represent a risk for human health and aquatic life.

KEY WORDS: Pesticides, pesticide metabolites, ranking model, water.

INTRODUCTION

Pesticides designed to kill target organisms can be dangerous to wildlife and human health. The global use of pesticides is expanding in scale and intensity and, although we know some environmental consequences, most potential impacts are not understood. Their widespread diffusion is related to the fact that they are applied directly to the environment and are likely to reach surface and groundwater through soil runoff and leaching. One can take advantage of this unfavourable circumstance by using the pesticide application rates in predictive models to forecast their distribution in the environmental compartments[1]. Moreover, usage data might be introduced in ranking models designed to identify priority pesticides on a territorial basis. The aim of our model[2], based on Hasse diagrams, is the protection of a target compartment (water, air, soil, biota) according to the selected pesticide properties (persistence, solubility, volatility and so on). It is a tool to set the analytical protocols in monitoring programs and to select priority pesticides to be submitted to revision or supplementary testing.

Furthermore, pesticides can metabolize into breakdown products which, in some cases, are equally or more dangerous than the parent compounds. The problem is well known since the discovery of DDT pollution: DDE and DDD, its main metabolites, had a very similar environmental fate. In this case, metabolite detection was easy to achieve because the same extraction and analytical procedure could be applied for all of them.

Unfortunately, this is not the case for most of the modern pesticides and a common feeling of the scientific community is that metabolite problem is under-evaluated for a lack of knowledge on their environmental occurrence and on their (eco)toxicological properties.

In spite of this gap, or perhaps because of this, authorities' attention is posed on pesticide metabolite problem. According to Council Directive 91/414/EEC[3], concerning the placing of plant protection products on the market, pesticide metabolic pathway and metabolite (eco)toxicological evaluation are two fundamental steps of the procedure required for registration.

In this context, "relevant metabolites" are defined as "those degradation products which are identified as having the same toxic mechanism of action as the active ingredient or as being biologically active on the basis of (eco)toxicological testing or which occur in quantities of more than 10% of the originally applied dosages"[4].

Thus, in the case of new pesticides the missing information in metabolite environmental behaviour should be fulfilled soon, but how can the problem of the hundreds of pesticides already in use be approached? Given the magnitude of the cost and the time required to study the metabolism and the biological activity of metabolites, evidently some general rules have to be employed to identify priority pesticides and priority metabolites within those already in use. A final answer cannot be given, however some procedures can be undertaken to minimize the research effort and direct it towards the most dangerous metabolites.

An application of our ranking model to pesticide metabolites could be done only if the amounts released into the environment were known and variables governing their environmental fate be determined. Otherwise, at least in the case of existing pesticides, much more useful information can be obtained by a review of the available data on pesticide metabolite occurrence and by an improvement of the analytical procedures aimed to identify them.

METHODS

Model: Hasse diagrams in environmental assessment

To identify which pesticides might be the object of field research we have used a ranking method based on Hasse diagrams; the textbooks of Harary[5], Preparate and Yeh[6], and Davey and Priestley[7] present useful background information on graphs, sets, partially ordered sets (posets) and Hasse diagrams. Hasse diagrams avoid the loss of information that occurs when data are aggregated into a ranking index. The use of an index has the disadvantage that information from each test is lost because it is aggregated. The details of the method have been published extensively in the last 10 years; Hasse diagrams have been used to rank chemicals according to environmental hazard[2,8], to compare waste disposal sites[9], to compare mathematical models[10–12], in QSAR studies[13,14], in problems of regional pollution[15,16] and in the evaluation of data sources[17].

The aim of this method is to use a formal procedure to order (or rank) pesticides according to their selected properties. Order is not a property intrinsic to a single object, it concerns comparison between pairs of objects. Hasse diagrams are multigraphs (see Figure 1, as an example). A multigraph consists of a set E of vertices (circles in Hasse diagrams). The circles are the objects, or elements, of the set E to be ranked. Hasse diagrams are oriented graphs. When Hasse diagrams are used in ranking, the circles near

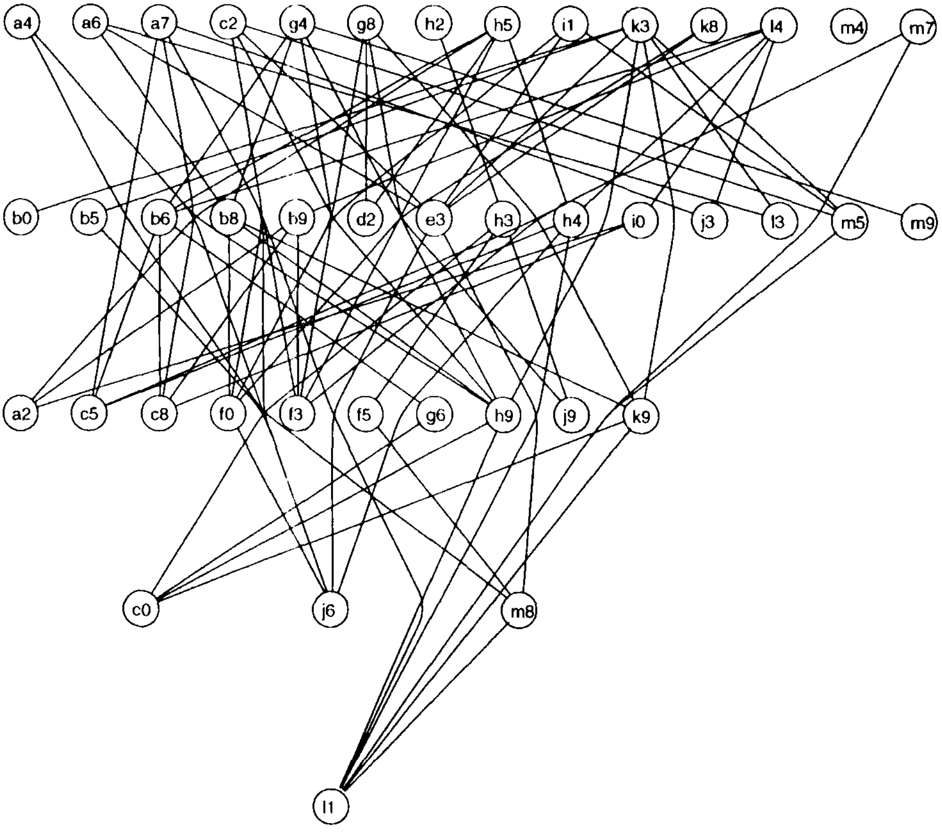

Figure 1 Hasse diagram showing the ranking of pesticides used in Germany. Table 1 identifies the chemicals.

the top of the page indicate objects that are most hazardous according to the criteria used to rank them. The objects at the top of the page have no predecessors and are called maximal. They are not "covered" by other objects[7]. Less hazardous pesticides are at the bottom of the Hasse diagram. Pesticides that are "comparable" with respect to all properties are connected by lines. In the graph, the lines should be followed in one direction only, from top to bottom. or (exclusively) from bottom to top. Lack of lines indicates that there are contradictions. The presence of a connection between two circles, either directly or indirectly through other circles, indicates that the pesticide on the superior level has ranked worse than the pesticide located in a lower level with respect to all properties. Comparable sites cannot be located on the same level because they have to be connected by a line. The number of levels in a Hasse diagram is, qualitatively, a rough measure of objects that are comparable to each other because, if the number of objects is the same, more levels mean more comparable objects.

Hasse diagrams can be constructed with raw data, as done here, as well as with scores. The use of scores diminishes uncertainty because the variation of raw data within the class defining interval do not change the score, but can generate equivalent objects. These objects are ranked exactly the same because they have the same scores. In this case only one object appears as representative in the graph and the other objects are indicated by extra lines at the bottom of the diagram.

The environmental fate of pesticides is determined by their physical-chemical properties, persistence in soil and their usage. A bibliography search has shown that a quantitative approach to evaluate which of these criteria have the greatest influence on the occurrence of pesticides in surface waters has never been tried. The criteria we use for ranking are persistence, water solubility, vapour pressure and yearly usage: mathematically these criteria are stored as vectors with four elements. We also investigate the relation between the identification of the most hazardous pesticides through ranking and through identification in the field.

Persistence and volatility are the properties that mainly influence the occurrence of a compound in soil and water. Water solubility gives indications on the mobility from soil to the surface waters. K_{OC} should be the best descriptor of the relative affinity of pesticides for soil. However, its value changes according to the organic carbon content of soil and it is unlikely to be taken into account in a general model. In this case K_{OW} should be used instead of K_{OC}, being useful in predicting soil adsorption and mobility. On the other hand both experimental and mathematical estimates for a given compound can differ by several orders of magnitude[18]. For these reasons water solubility was used to predict mobility from soil since K_{OW} and K_{OC} are strongly correlated to this parameter in the case of nonionic pesticides[8,19,20]. Ionized pesticides do not exhibit a correlation between their solubility and K_{OW}. Nevertheless soil-sorption partition coefficients for these compounds are not available or not reliable, probably because they are difficult to measure. Anyway, the use of water solubility instead of K_{OW} leads to negligible errors for environmental prediction purposes of anionic pesticides (e.g. TCA); conversely, leachability of cationic pesticides (e.g. "quats") might be overestimated because these compounds can be strongly retained by soils. These interactions were not considered in the present application of the model.

Data

Within the European Community three countries were selected from different geographical areas with different climates and presumably different agriculture practices. Also the availability of occurrence data in surface and groundwater was considered. Table 1 shows the pesticides used in three countries in amounts above 50 t/y.

Usage data refer to 1989 for Germany, 1988 for U.K., 1986–87 for Italy. They were taken from Fielding *et al.*[22] along with the occurrence data; some additional sale data for Italy were taken from the Italian National Statistics Office[23,24].

Properties are half-life in soil, water solubility and vapour pressure. Their values are taken from the Agrochemical Handbook[25] and from two databases[21,26]. Vapour pressure was handled as inverse quantity due to the improvement of the soil if the vapour pressure is high (volatilization from soil). Therefore, the vector half-life in soils, water solubility and (with a negative sign) vapour pressure describes the environmental hazard in surface waters.

Experimental

Well water samples (11) were collected at Dalmine (Bergamo, Italy) from May to July 1995. They were extracted in LiChrolut® EN (Merck) cartridges (3 ml). Elution was

Table 1 Pesticides used in amounts above 50 t/y in Germany, U.K. and Italy.

a0	alachlor	h2	mancozeb
a2	amitrole	h3	maneb
a4	atrazine	h4	MCPA
a6	benazolin	h5	mecoprop
a7	bentazone	h6	mecoprop-P
a8	bifenox	h7	metaldehyde
a9	bromoxynil	h8	metamitron
b0	bromofenoxim	h9	metazachlor
b1	butylate	i0	metham-Na
b2	captafol	i1	methabenzthiazuron
b3	captan	i4	methiocarb
b4	carbaryl	i5	methyl bromide
b5	carbendazim	i7	metolachlor
b6	carbetamide	i8	metsulfuronmethyl
b8	chloridazon	j1	molinate
b9	chlormequat	j3	oxydemetonmethyl
c0	chlorothalonil	j5	paraquat
c2	chlorotoluron	j6	parathion ethyl
c4	cyanazine	j8	pendimethalin
c5	2,4-D	j9	phenmediphan
c7	dalapon	k0	phorate
c8	dazomet	k3	prochloraz
c9	demeton-s-methyl	k6	propanil
d0	diazinon	k8	propiconazole
d2	dichlorprop(2,4-DP)ester	k9	propineb
d6	diclofop-methyl	l0	propyzamide
d8	difenzoquat	l1	pyrethrin
d9	dimethoate	l3	simazine
e1	diquat	l4	TCA
e3	diuron	l6	terbuthylazine
e5	endosulfan	l7	terbutryn
e6	EPTC	l9	thiobencarb
e9	ethirimol	m0	thiocarbazil
f0	ethofumesate	m1	thiram
f3	dichlorvos	m3	triadimefon
f4	fenpropidin	m4	triadimenol
f5	fenpropimorph	m5	triallate
f8	flampropisopropyl	m7	tridemorph
f9	fluazifop-buthyl	m8	trifluralin
g0	fluoroxypyr	m9	vinclozolin
g1	flutriafol	n0	zineb
g4	glyphosate	n1	ziram
g6	ioxynil	p0	azinphos methyl
g7	iprodione	p1	parathion methyl
g8	isoproturon	s0	dodine
h0	linuron	s1	dinocap
h1	malathion		

done with 1 ml of ethylacetate. Eluates were analyzed using a C. Erba 8000 series with a NPD selective detector. A fused silica capillary column CP-Sil 8 (50 m × 0.25 mm I.D), film thickness 25 μm, was used in the following conditions: carrier gas, helium, 1 ml/min, oven temperature 100°C, 1 min, followed by two programmed temperature steps from 100 to 180, 20°C/min and from 180 to 270°C, 1.5°C/min. The samples (1 μl) were injected with a manual on-column system. Recovery efficiency on the LiChrolut columns, tested on spiked samples, ranged between 90–100% for all the analyzed compounds.

96h acute toxicity on rainbow trout (*Oncorhynchus mykiss*) of 2,6-diethylaniline (Alltech) was determined according to OECD Guidelines[28].

RESULTS AND DISCUSSION

Case studies

Germany. This country has the most comprehensive data record on pesticide occurrence. About 170 pesticides and pesticide metabolites were monitored in ground and surface waters and 60 of them were detected. We considered as positive findings those compounds which were found in more than 1% of the samples analyzed for. Conversely, sales data are rather approximate since they indicate only usage ranges and a common upper value (> 1000 t/y) for major pesticides. In our modelling study the highest value of the range was chosen in the former case and an arbitrary value of 2000 t/y was taken in the latter case.

The Hasse diagram applied to the German data is shown in Figure 1.

United Kingdom. Occurrence data of pesticides refer to drinking water without any specification between surface water supplies and groundwater. Usage data introduced in our predictive model refer to applications in agriculture. However non agricultural uses seem to be very important: for instance atrazine, which is not employed in agriculture, is the pesticide more frequently found in groundwater at levels above 0.1 μg/l.

The Hasse diagram for the U.K. scenario is shown in Figure 2.

Italy. Occurrence data, that refer both to surface and drinking water, were taken from a literature survey and not from a systematic monitoring done by a public Authority. Usage data are derived from annual sales and represent the amount of active ingredient for all the compounds with exception of fungicides, because only data on commercial formulations are known.

The Hasse diagrams is shown in Figure 3.

Comparison of expected and detected pesticides

The validity of our ranking scheme is obtained by comparison of chemicals found in the field and those ranked as hazardous. A threshold of 0.1 μg/l was set for validating the model. This values corresponds to the present E.U. limit for pesticides in drinking waters.

Most of the pesticides ranked as a first priority by the model and analyzed for in water was effectively found. The percentage of positive findings decreases from class 1 to 6 of priority in agreement with the theoretical predictions (Table 2). This fact is in favour of a correct choice of the attributes and of the suitability of the model to rank pesticides.

Only two pesticides, TCA and prochloraz, ranked in first priority by the model in Germany and monitored in water, were never found at levels higher than 0.1 μg/l. Since both compounds were analyzed a few times (2 to 5) in comparison to other pesticides

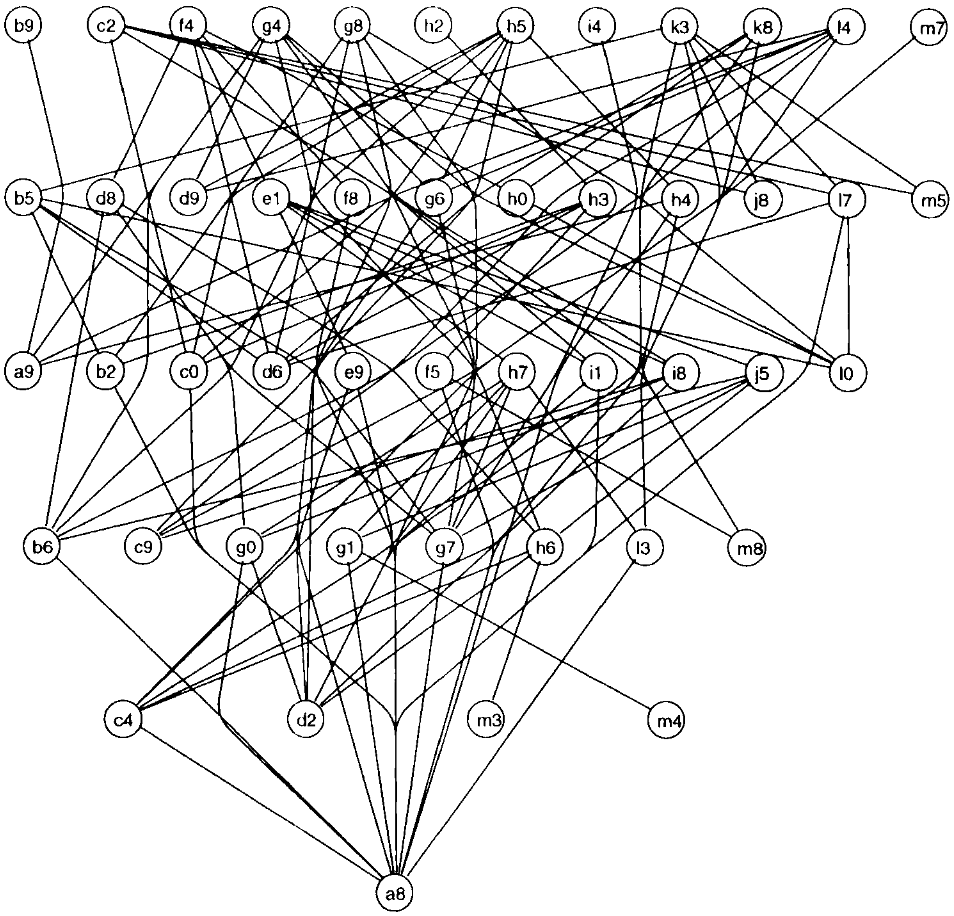

Figure 2 Hasse diagram showing the ranking of pesticides used in U.K. Table 1 identifies the chemicals.

such as triazines (3 to 4 thousands times), the monitoring effort was certainly not appropriate to detect them. In the U.K. TCA was detected in groundwater at concentration exceeding 0.1 µg/l. U.K. occurrence data do not include surface waters and no indication of the sought compounds are given. For these reasons the ratio between found and analyzed compounds was not calculated. Within the list of the Italian priority pesticides (Figure 3) there are some compounds such as "quats", methan-Na and ziram for which there is no method available that is capable of monitoring at the limit level of 0.1 µg/l. More effort should be put into developing analytical methods for these compounds and/or for the identification of their metabolities. Mancozeb poses the same analytical problems, as other dithiocarbamates, but as it is known to be transformed into ETU (ethylene bis thiourea), a very dangerous and leachable compound, thus the analytical effort should be addressed towards this metabolite more than the parent compound.

Besides ETU, also chloridazon and dalapon should be included in the monitoring programs in Italy since a suitable procedure is available.

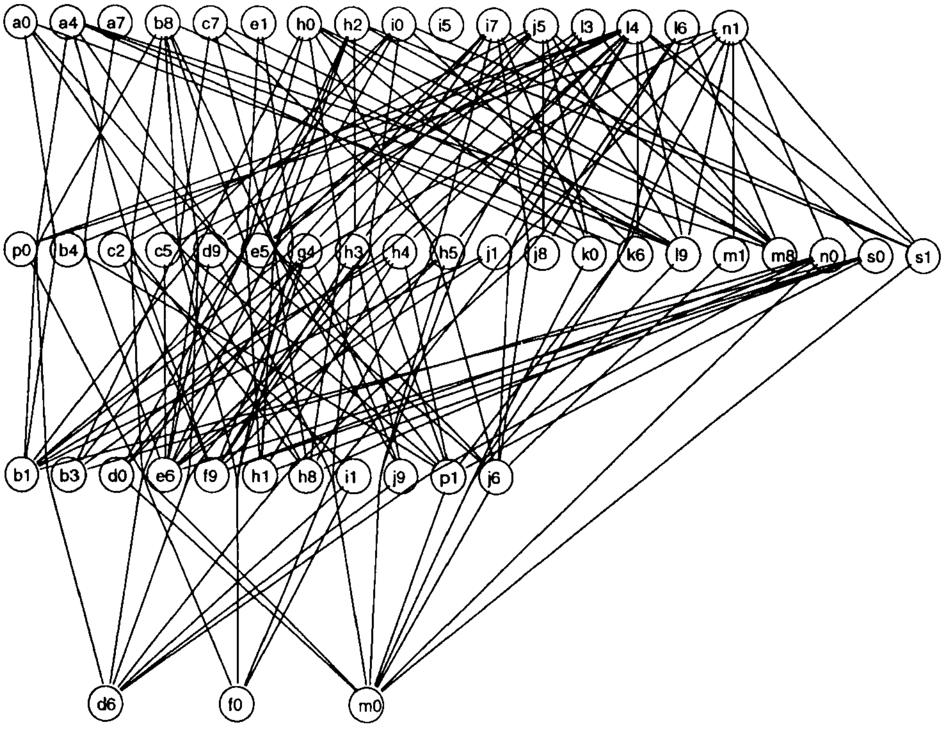

Figure 3 Hasse diagram showing the ranking of pesticides used in Italy. Table 1 identifies the chemicals.

Table 2 Proportion of pesticides sought and found in waters of the three selected countries according to the environmental hazard.

	Rank line	*1*	*2*	*3*	*4*	*5*	*6*
GERMANY	Total n. of pest. in line	14	14	10	3	1	–
	found	7	6	2	0	0	–
	analyzed for	9	8	7	2	0	–
	% found/analyzed for	78	75	29	0	–	–
U.K.	Total n. of pest. in line	12	12	11	8	4	1
	found	4	4	3	3	1	0
	analyzed for	?	?	?	?	?	?
	% found/analyzed for						
ITALY	Total n. of pest. in line	16	20	11	3	–	–
	found	7	5	1	0	–	–
	analyzed for	8	10	6	0	–	–
	% found/analyzed for	88	50	17	–	–	–

The validation of the model is obviously partial for the lack of analytical information about those priority pesticides that were never monitored in water. For these compounds it is impossible to verify whether the ranking position given by the Hasse diagram is correct. The lack of data is partially due to the unavailability of a suitable analytical procedure but it might be due also to an underestimation of the environmental threat of some pesticides. If this is the case, the Hasse diagram, our model, could be used to design a monitoring protocol that better fit with the regional situation.

A second order of problems arises from those pesticides which are actually found in water, particularly in groundwater, and not included as input data of the model as they do not appear in the EEC list[22] of compounds used in amounts above 50 t/y. Some of the pesticides found are unexpected because they are not used anymore in agriculture and have a poor tendency to leach (e.g. aldrin, endrin, dieldrin, HCB, DDT, heptachloroepoxide), but some further investigations are needed to confirm the occurrence of these pesticides. The majority of the other unexpected pesticides are probably used in amounts less than 50 t/y for specific local applications or are found in specific highly vulnerable sites. No further assumptions can be made on this subject because information on usage data is incomplete and not recorded systematically and routinely.

Comparison of the three case studies

From the comparison of first priority pesticides in Germany, Great Britain and Italy we find that only two, mancozeb and TCA, are common to all the three countries. A third compound, atrazine, prioritary in Italy and Germany, should be added because it was not included in the U.K. list due to the lack of sales data in agriculture; nevertheless atrazine is frequently found in water in this country, coming mainly from non-agricultural uses.

Germany and U.K. have ten priority pesticides in common; conversely Italy differs much more than the other two countries in the use of pesticides. A general feature of this comparison is that each country must develop its own analytical protocol addressed to the detection of the most "probable" pesticides and their transformation products.

The tremendous analytical effort done by Germany, where about 170 pesticides and metabolites were monitored, allows a better covering of the list of most hazardous pesticides given by the model. Nevertheless, at least three of 14 first priority pesticides were never monitored (glyphosate, propiconazole, tridemorph), in addition to two compounds for which no analytical method is available (mancozeb and benazolin) and TCA. As said before, only two measurements were done for TCA, which should occur in water only short after the application period, given its very high solubility. In a comparative review of pesticide survey in Germany[28] it was concluded that it exists a lack of congruence between pesticide application and pesticide monitoring.

As a general statement, it appears clear that a better water protection against pesticide pollution can be achieved with an improvement of the analytical methodology driven by predictive models that allow to identify priority pollutants.

Metabolite assessment

An interesting feature of the analysis of the occurrence data in water is that some metabolites are frequently encountered in many European countries. The most common ones are the triazine metabolites, also because they are detected by the same procedure as the parent compounds. Conversely, some metabolites such as ETU, which is a transformation product of mancozeb and related compounds, were inserted in the analytical protocols because their genotoxicity is well known.

In general the toxicity to man and environmental properties of metabolites are not known, but some transformation products can be more persistent, leachable and toxic than the parent compound. For this reason it was recommended by the EC Task Group[22] that information be gathered on the identity of transformation products of major-use pesticides as well as their environmental properties. This is not accomplished yet and so no modelling approach can be applied to rank these compounds.

Given the complexity of the problem, the lack of information and our better knowledge of the Italian situation, the evaluation of the risk associated to metabolites will be restricted here to this country, considering only first priority parent compounds. Pesticide metabolism in soils for most of the Italian first priority pesticides has been widely studied and is known to generate a number of potential pollutants to surface and groundwater. This discussion will be focused on those already detected in some real aquatic environment. Table 3 shows occurrence data in Europe.

Linuron, metolachlor and terbuthylazine were found only in surface waters in Italy. However, recent studies undertaken in the framework of the EC Project EV-5V-CT92-0061 in groundwater of an area selected because it was previously polluted by atrazine demonstrated the occurrence of metolachlor and terbuthylazine at 40 m depth (Table 4).

Table 3 Occurrence of Italian priority pesticides and their major metabolites in European waters. GW: groundwater; SW: surface water.

	Occurrence		*Major*	*Occurrence*	
	GW	*SW*	*metabolites*	*GW*	*SW*
Alachlor	0	F	Diethylaniline	N	F
Atrazine	F	F	Desethylatrazine	F	F
			Deisopropylatrazine	F	F
Bentazone	F	F	6-hydroxybentazone	N	N
			8-hydroxybentazone	N	N
Linuron	O	O	3,4-dichloroaniline	N	O
Mancozeb	N	N	ETU	O	F
Metolachlor	O	F	?	?	?
Simazine	F	F	Deisopropylatrazine	F	F
Terbuthylazine	F	F	Desethylterbuthylazine	O	N

F = frequently O = occasionally N = never

Table 4 Herbicide and metabolite concentrations (μg/l) in groundwater (Dalmine, Italy).

	May 1995	*June 1995*	*July 1995*
Alachlor	< 0.020	< 0.020	< 0.020
Atrazine	0.150	0.232	0.147
Desethylatrazine	0.030	0.045	0.031
Deisopropylatrazine	0.041	0.058	0.018
Metolachlor	0.103	0.048	nd
Simazine	0.045	0.066	0.037
Terbuthylazine	0.020	0.038	0.017

Terbuthylazine and metolachlor substituted atrazine in many agricultural applications only in recent years. Linuron is known to degrade into 3,4 dichloroaniline, a mutagenic metabolite occasionally detected in surface waters[29]. However, the source of this pollution is uncertain and not unequivocally related to the parent compound, being it also an industrial pollutant. Terbuthylazine major metabolite is desethylterbuthylazine already found in European groundwater, but not yet in Italy.

Metolachlor metabolites have been identified in soil but most of them need a confirmation. Their persistence and occurrence in water are a further task of the researches carried out in the mentioned EC Project.

Atrazine is undoubtely the most widespread herbicide and the most frequently detected in groundwater. For this reason it was banned or regulated in many European countries. In this respect it is very interesting to assess the degree of recovery of aquifers after the implementation of these measures. In the study area selected in Lombardy (Italy) for pesticide surveying, atrazine has been forbidden since 1986. At that time many wells were monitored and they were closed in the case of heavy pollution or provided with active carbon filters. One of them is still in use and a comparison can be done between present and past levels of atrazine and other herbicides. Unfortunately triazine metabolites were not analyzed in the past. Atrazine and simazine, monitored about monthly in 1987 from February to December[30], were in the range of 0.25–0.46 µg/l and 0.00–0.07 µg/l, respectively.

From the comparison between the average values of atrazine in the past and in the recent survey (Table 4), aquifer restoration appears to be very slow. A half-life in soil of two months is reported for atrazine in the literature, but its persistence in subsoils and groundwater, where bacterial activity is low or negligible, is probably much higher.

Atrazine metabolites, particularly DEA (desethylatrazine), seem to be more persistent than the parent compound even if their half-lives are unknown[31]. In Canadian studies DEA was measured at a constant concentration about one year after application[32]. In the River Po water[33] DEA was always detected together with the parent compound and the maximum level was measured in January, long after the application period and when the atrazine concentration was decreasing. The other main transformation product of atrazine dealkylation is DIP (deisopropylatrazine), which has been measured in concentrations comparable with those of DEA (Table 4). However, these metabolites can derive also from the breakdown of other triazines[31].

It can be noted that the levels of simazine in groundwater are now comparable to those detected in 1987 (0.00–0.007 µg/l), indicating a growing usage of this herbicide in this area, besides its occurrence as an impurity of atrazine formulation.

Alachlor has headed the list of herbicide sale in Italy after the banning of atrazine. At present this compound is under discussion because, in consideration of its carcinogenic activity in mammals, it was included in the list of the 90 pesticides to be revised[3]. It is moderately mobile and relatively non persistent and therefore it should be much less leachable than atrazine. In fact, extensive studies[34] performed in the USA in areas where both compounds were used in agriculture demonstrated that alachlor occurs in groundwater less frequently than atrazine. Studies on biodegradation of alachlor in soil showed that many breakdown products are formed, more polar and presumably more leachable than the parent compound[35]. Recent studies undertaken in the framework of the EC Project EV-5V-VT92-0061 showed little or negligible biodegradation in surface water. In spite of this, about 20 compounds related to alachlor were found. Some of them were in common with soil metabolites. The confirmation by synthesis is still in progress and requires a lot of time. To optimize efforts towards those metabolites that are environmentally more hazardous, we analyzed surface waters of an agricultural area to find out the metabolites actually present, confirming them by means of mass-spectra fitting. Results show that 2,6-diethylaniline is the main alachlor metabolite in surface waters. It is even more soluble than alachlor (670 mg/l)[36] and thus more mobile, increasing the risk for groundwater contamination.

2,6-diethylaniline acute toxicity is lower than that of alachlor: we measured a 96h LC50 on rainbow trout (*Oncorhynchus mykiss*) of 21 mg/l compared to 1.8 mg/l reported for alachlor[35]. Nevertheless, 2,6-diethylaniline seems to be a precursor of a mutagenic compound in mammal metabolism and its occurrence in groundwater might be a risk for human health[37].

Bentazone is used in much smaller amounts than alachlor; however it is employed mainly in rice fields, which are located exclusively in Northern Italy. Here bentazone concentrations up to 39 μg/l were found in groundwater and levels exceeding 0.1 μg/l were measured in 94 of the 131 wells analyzed in 1987[38]. This counteracts what reported in a recent review on bentazone environmental behaviour by Huber and Otto[39], who state that this herbicide poses no risk to groundwater or drinking water because it is retained by fresh organic material and roots, photodegraded and rapidly biodegraded. The same holds for the two metabolites deriving from the microbially induced degradation (6-hydroxybentazone and 8-hydroxybentazone). According to Huber and Otto[39], they should not occur in soil because both are further metabolized, more quickly than they can be produced from bentazone by hydroxylation. Nevertheless, 8-hydroxybentazone was detected in the Ebro delta (Spain), another area of rice cultivation[40]. On the other hand, Chiron *et al.*[40] are the first to set up a method enabling the detection of bentazone hydroxy derivates. To verify whether these metabolites are present also in groundwater in Italy, a SPE extraction procedure was set up employing Isolute-SAX cartridges (STEPBIO, Italy), which allow a quantitative recovery of bentazone and its two metabolites. Extracts are analyzed by HPLC-MS. A sampling campaign of wells polluted by bentazone has been undertaken in our laboratory.

CONCLUSIONS

The modelling approach is an useful tool to select priority pesticides on national scale for monitoring purposes and administrative measures. Right now it has some limitations mainly due to uncertainties of input data such as usages, physical-chemical properties and persistence. For instance, descriptors more suitable than water solubility should be selected to predict mobility from soil in the case of cationic pesticides, like diquat and paraquat, which are strongly adsorbed on soil in spite of their high solubility in water. Moreover, this tool has to be carefully applied because some pesticides intensively employed on limited areas for specific cultures can be classified at low priority level even being of concern. This is for example the case of molinate in Northern Italy that is classified at the second level of priority and posed threat for drinking water purposes, so that the limit has been raised to 0.3 μg/l. Therefore, when a country presents a variety of climates and different cultivations from a region to another, the ranking model will better fit on a regional scale[41].

Concerning metabolites, new perspectives are offered by the recent SPE preconcentration techniques that allow a better recovery of polar compounds and by HPLC-MS, suitable to analyze these compounds without the need of derivatization. Another advantage of HPLC is that, working in reverse-phase, the metabolite retention time is related to their polarity and consequently to their water solubility[42]. The exit order of peaks can give an idea of the leachability in comparison to the parent compound.

However, since it is not possible to apply ranking models to metabolites due to the lack of knowledge about properties and amounts entering the environment, some other ways to facilitate the analytical research have to be found. One of these might be the use of mass spectra obtained in metabolic studies as fingerprints for detection of relevant metabolites in the real environment. Another approach, already tested in the Po River[41], is to perform (eco)toxicological assays on water extract and address the analysis only to the most toxic ones.

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